

Durham E-Theses

The controls on transition metal stable isotope fractionation during high-temperature magmatic processes

PAGE, SOPHIE, EMILY

How to cite:

PAGE, SOPHIE, EMILY (2021) *The controls on transition metal stable isotope fractionation during high-temperature magmatic processes*, Durham theses, Durham University. Available at Durham E-Theses Online: <http://etheses.dur.ac.uk/14582/>

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a [link](#) is made to the metadata record in Durham E-Theses
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the [full Durham E-Theses policy](#) for further details.

The controls on transition metal stable isotope fractionation during high-temperature magmatic processes

Sophie Emily Page

A thesis submitted for the degree of
Doctor of Philosophy

Department of Earth Sciences
Durham University

December 2021



Abstract

Transition metal stable isotopes have the potential to trace a variety of high-temperature geological processes because they can respond to magmatic processes such as partial melting, fractional crystallisation, and changes in redox. However, since the precision required to apply transition metal isotopes to high-temperature settings has only been achieved recently, there are still significant gaps in our understanding. This thesis aims to expand our understanding of the controls on vanadium, titanium, iron, and zinc stable isotope fractionation during high-temperature magmatic processes.

Mantle xenoliths and mineral separates from the Diavik diamond mine were measured to examine the roles of oxygen fugacity, bonding environment, and metasomatism on V isotopes. This data represents the first $\delta^{51}\text{V}$ measurements on natural mineral separates. Vanadium isotopes were found to positively correlate with $f\text{O}_2$ in garnet and clinopyroxene, suggesting that $f\text{O}_2$ does influence $\delta^{51}\text{V}$. However, metasomatism and bonding environment were found to be more significant controls on $\delta^{51}\text{V}$.

IODP Expedition 352 subduction initiation fore-arc basalts (FABs) and boninites were measured for V, Ti, Fe, and Zn stable isotopes to assess the comparative contributions of magmatic versus subduction processes in the formation of arc lavas. Mantle partial melting and source depletion modelling are suggested to explain the observed $\delta^{56}\text{Fe}$ differences between FABs and boninites. Contrary to previous $\delta^{66}\text{Zn}$ work on forearc serpentinites, slab-derived inputs are unlikely to create observable $\delta^{66}\text{Zn}$ fractionation in arc lavas. Vanadium isotopes are shown to respond to differences in source depletion and potentially changes in redox during subduction initiation, and Ti isotopes suggests that the mantle may be heterogeneous in $\delta^{49}\text{Ti}$. Finally, both V and Ti isotopes correlate with fluid mobile elements in subduction-related boninites, suggesting that despite V and Ti being considered fluid immobile, halogen-rich slab-derived fluids have the potential to mobilise and fractionate $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$.

Table of Contents

Abstract	i
Table of Contents.....	ii
List of Tables	x
Statement of Copyright	xi
Acknowledgements	xii

Chapter One - Introduction

1.1. Overview	1
1.2. Stable Isotope Fractionation and Measurement.....	2
1.2.1. History of Stable Isotope Measurement	2
1.2.2. The Delta Notation.....	3
1.2.3. Theoretical Basis for Stable Isotope Fractionation	3
1.3. Applying Transition Metal Stable Isotopes to High-Temperature Geologic Systems.....	6
1.3.1. Vanadium Isotopes	8
1.3.2. Titanium Isotopes	10
1.3.3. Zinc Isotopes.....	12
1.3.4. Iron Isotopes.....	14
1.4. Thesis Outline and Aims	16
1.4.1. Chapter Two.....	16
1.4.2. Chapter Three	16
1.4.3. Chapters Four, Five, and Six.....	17
1.4.4. Chapter Seven	19
References.....	19

Chapter Two - Methods

2.1. Introduction.....	31
2.2. Sample Digestion Procedures.....	31
2.2.1. Standard Hotplate Digestion Procedure	31
2.2.2. 'Bombing' Digestion Procedure	32
2.2.2.1. Imperial College London	32
2.2.2.2. Durham University.....	32
2.3. Ion Chromatography and Mass Spectrometry Procedures	32
2.3.1. Vanadium	32
2.3.1.1. Ion Chromatography.....	33
2.3.1.2. Mass Spectrometry.....	44

2.3.2. Zinc.....	51
2.3.2.1. Ion Chromatography	51
2.3.2.2. Resolving High Zinc Blanks.....	52
2.3.2.3. Mass Spectrometry (Neptune)	54
2.3.3. Iron.....	59
2.3.3.1. Ion Chromatography	59
2.3.3.2. Mass Spectrometry (Neptune)	61
2.3.4. Titanium	67
2.3.4.1. Titanium Double Spiking.....	67
2.3.4.2. Ion Chromatography	68
2.3.4.3. Mass Spectrometry (Nu Plasma II)	70
2.3.5. Hafnium	70
2.3.5.1. Ion Chromatography	70
2.3.5.2. Mass Spectrometry (Neptune)	75
2.4. Trace Elements.....	75
2.4.1. Sample Digestion and Dilution.....	76
2.4.2. ICP-QQQ-MS Measurement.....	76
References	77

Chapter Three - The effects of oxygen fugacity and metasomatism on vanadium isotopic compositions of garnet-clinopyroxene pairs from Slave craton kimberlite-hosted mantle xenoliths

3.1. Introduction	82
3.1.1. Aims	84
3.2. Diavik Diamond Mine, Canada	85
3.2.1. Geological Setting	85
3.2.2. Petrography	86
3.2.3. Chemistry of Diavik Xenoliths	88
3.3. Methods and Results.....	90
3.3.1. Estimation of modal abundance and mineral picking.....	90
3.3.2. Trace Element Abundances	91
3.3.3. Vanadium Isotopic Composition	94
3.4. Discussion.....	97
3.4.1. Metasomatism in the Slave Craton.....	97
3.4.1.1. Previous evidence for a metasomatic influence in the Diavik samples.....	97
3.4.1.2. Trace element evidence of metasomatism	98
3.4.1.3. Fluid versus Supercritical Fluid Metasomatism	105

3.4.2. Diavik whole-rock $\delta^{51}\text{V}$ isotopic compositions	106
3.4.2.1. <i>Investigating whole-rock $\delta^{51}\text{V}$ heterogeneity</i>	107
3.4.2.2. <i>Relationship between whole-rock $\delta^{51}\text{V}$ and $f\text{O}_2$</i>	109
3.4.3. Diavik garnet and clinopyroxene $\delta^{51}\text{V}$ isotopic compositions	109
3.4.4. Isotopic mass imbalance?	112
3.4.5. Links between mantle metasomatism, $f\text{O}_2$ and $\delta^{51}\text{V}$	116
3.4.5.1. <i>The effects of metasomatism on $\delta^{51}\text{V}$</i>	118
3.5. Conclusions	126
References	126

Chapter Four - The controls on iron isotopic fractionation in IODP Expedition 352 subduction initiation lavas from the Bonin forearc

4.1. Introduction	134
4.1.1. Aims	138
4.2. Sample set and Geologic Background	139
4.2.1. Geological & Tectonic Setting of IODP Expedition 352	139
4.2.2. Expedition 352 Stratigraphy	141
4.2.3. FAB & Boninite Petrography	142
4.2.3.1. Fore-arc Basalts (FABs)	146
4.2.3.2. Boninites	146
4.2.4. FAB & Boninite Chemistry	147
4.2.4.1. Fore-arc Basalts (FABs)	147
4.2.4.2. Boninites	151
4.2.5. FAB & Boninite Petrogenesis	156
4.3. Methods & Results	159
4.3.1. Sample Selection	159
4.3.2. Trace Elements	159
4.3.3. Iron Isotopic Compositions	163
4.3.3.1. Fore-arc Basalt Fe Isotopic Compositions	165
4.3.3.2. Boninite Fe Isotopic Compositions	165
4.4. Discussion	167
4.4.1. Fore-arc Basalt Fe Isotopic Compositions	167
4.4.2. Boninite Fe Isotope Compositions	169
4.4.2.1. Comparison between Boninite and FAB Fe Isotopic Compositions	169
4.4.2.2. Cause(s) of Fe isotopic difference between FABs and boninites	169
a) <i>Processes that are unlikely to create light $\delta^{56}\text{Fe}$ signatures in boninites</i>	169
b) <i>Processes that may create light $\delta^{56}\text{Fe}$ signatures in boninites</i>	172

4.4.3. Implications for deconvolving Fe isotope fractionation in global arcs	183
4.5. Conclusions	184
References.....	184

Chapter Five - The controls on zinc isotopic fractionation in IODP Expedition 352 subduction initiation lavas from the Bonin forearc

5.1. Introduction	195
5.1.1. Aims	198
5.2. IODP Expedition 352 Samples	198
5.3. Methods & Results	199
5.3.1. Fore-arc Basalt Zn Isotopic Compositions	202
5.3.2. Boninite Zn Isotopic Compositions	202
5.4. Discussion	204
5.4.1. Lack of Zn isotope difference between FABs and boninites	204
5.4.2. Boninite Zn Isotopic Compositions	205
5.4.2.1. Origin of the isotopically light boninites	205
5.4.2.2. Cause(s) of boninite $\delta^{66}\text{Zn}$ variations without anomalously light boninites?	210
5.4.3. Fore-arc Basalt Zn Isotopic Compositions	211
5.4.3.1. Could variable fluid addition or alteration account for the FAB $\delta^{66}\text{Zn}$ variation?	213
5.4.3.2. Magmatic differentiation and source depletion as $\delta^{66}\text{Zn}$ controls in FABs	215
5.4.3.3. Could melt mixing account for the FAB $\delta^{66}\text{Zn}$ variation?	221
5.4.3.4. Origin of the Depleted FAB Sample	224
5.4.4. Implications for isolating arc lava source components.....	225
5.5. Conclusions	226
References.....	226

Chapter Six - The controls on vanadium and titanium isotopic fractionation in IODP Expedition 352 subduction initiation lavas from the Bonin forearc

6.1. Introduction	233
6.1.1. Aims	238
6.2. Methods	238
6.2.1. Vanadium Isotopes	238
6.2.2. Titanium Isotopes	238
6.2.3. Hafnium Isotopes.....	239
6.3. Results	243
6.3.1. FAB and MORB Ti and V isotopic compositions.....	243
6.3.2. FAB and boninite V and Ti Isotopic Compositions	244

6.4. Discussion	247
6.4.1. Effects of secondary alteration	248
6.4.2. Cause(s) of FAB-MORB isotopic differences	249
6.4.2.1. Contribution of Slab-derived Fluids?	249
6.4.2.2. Contribution of Slab-derived Melts?	251
6.4.2.3. Different Redox Conditions?.....	252
6.4.2.4. Fractional Crystallisation	252
6.4.2.5. Mantle Partial Melting and Source Depletion	253
6.4.2.6. Titanium Isotopic Mantle Heterogeneity	255
6.4.2.7. Current Explanations for FAB-MORB $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ differences.....	256
6.4.3. Comparison of FAB-Boninite Ti- V isotopes	257
6.4.3.1. Source Depletion and Partial Melting.....	257
6.4.3.2. Fractional Crystallisation	257
6.4.3.3. Different Redox Conditions	259
6.4.3.4. Subduction-related Processes	260
6.4.4. Implications for using V and Ti isotopes in arcs	266
6.5. Conclusions.....	268
References.....	268

Chapter Seven - Conclusions & Future Work

7.1. Chapter Three.....	276
7.2. Chapters Four, Five, and Six	277
References.....	282
Appendices.....	284

List of Figures

Chapter One

Figure 1.1: Summary comparison of $\delta^{51}\text{V}_{\text{AA}}$ literature data from high-temperature igneous studies.	10
Figure 1.2: Summary comparison of $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ literature data	12
Figure 1.3: Summary comparison of $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$ literature data.	14
Figure 1.4: Summary comparison of $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ literature data	15
Figure 1.5: Schematic diagram (not to scale) of the tectonic settings and magmatic processes that this thesis will focus on.....	16

Chapter Two

Figure 2.1: Summary of vanadium separation procedure.....	34
Figure 2.2: Adsorption of Fe(III) and V(IV).....	35
Figure 2.3: Photos taken during stage 3 of the vanadium separation procedure.....	36
Figure 2.4: Photo of one of the clean-up column stages of the vanadium separation procedure	38
Figure 2.5: Summary flow charts of the Durham University vanadium separation procedure.....	39
Figure 2.6: Photo taken during one of the titanium removal stage of the vanadium separation procedure ..	40
Figure 2.7: The sequence of matrix element elution during the stage 2 column	41
Figure 2.8: MC-ICP MS V isotope analysis measurement sequence.....	46
Figure 2.9: Long-term average for BDH solution standard.	46
Figure 2.10: Screenshot of mass scan from Neptune software during V isotope measurement.	48
Figure 2.11: Summary flow chart depicting the Fe-Zn ion chromatography stage.....	52
Figure 2.12: Screenshot of peak centre using the Neptune software for Zn isotope measurement.	56
Figure 2.13: Long-term averages for Zn solution standards	57
Figure 2.14: Example MC-ICP MS Zn isotope analysis measurement sequence	58
Figure 2.15: Zinc isotope mass dependency plot	58
Figure 2.16: Summary flow chart of the Fe ion chromatographic separation procedure	60
Figure 2.17: Screenshot of mass scan from Neptune software during Fe isotope measurement.....	63
Figure 2.18: Comparison of Ni-doping versus sample-standard bracketing correction techniques.....	63
Figure 2.19: Example MC-ICP MS Fe isotope analysis measurement sequence.....	64
Figure 2.20: Long-term average for Romil Fe solution standard.	65
Figure 2.21: Iron mass dependency plot	66
Figure 2.22: Titanium ion chromatography flow chart and photo of set-up.	69
Figure 2.23: Summary flow chart outlining the Hf ion chromatographic separation procedure.	72

Chapter Three

Figure 3.1: Chapter three location map.....	85
Figure 3.2: Thin section photos.....	87
Figure 3.3: Thin section photographs.....	88
Figure 3.4: $\Delta\log fO_2^{[FMQ]}$ versus pressure in GPa for Diavik and Panda peridotite xenoliths	89
Figure 3.5: Primitive mantle normalised REE concentrations	90
Figure 3.6: Primitive mantle normalised trace element concentrations for Diavik whole-rock xenoliths.....	92
Figure 3.7: Comparison between reconstructed whole-rock trace element concentrations and whole-rock trace element concentrations determined by ICP-QQQ MS.	98
Figure 3.8: Thin section photograph of Diavik xenolith 052.	100
Figure 3.9: Garnet Cr#.....	101
Figure 3.10: REE plot of all the Diavik garnets	101
Figure 3.11: Primitive mantle normalised REE concentrations of the eight Diavik garnets	103

Figure 3.12: Zr/Y plot	104
Figure 3.13: Experimental partition coefficients between fluid and a solid gnt-cpx residue	106
Figure 3.14: Summary of literature peridotite $\delta^{51}\text{V}$ compared to the whole-rock Diavik xenolith data.	107
Figure 3.15: Diavik lherzolite whole-rock $\delta^{51}\text{V}$ (‰) versus $\Delta\log f\text{O}_2$ relative to FMQ.	108
Figure 3.16: $\delta^{51}\text{V}$ versus $\text{Fe}^{3+}/\Sigma\text{Fe}$ and $\Delta\log f\text{O}_2[\text{FMQ}]$	111
Figure 3.17: Primitive mantle normalised REE plot of the Diavik whole-rock powders	113
Figure 3.18: $\delta^{51}\text{V}$ versus $\Delta\log f\text{O}_2[\text{FMQ}]$ (Yaxley et al. 2017) in mineral separates, whole-rock and whole-rock kimberlite	113
Figure 3.19: Reconstructed whole-rock $\delta^{51}\text{V}$ signature.....	115
Figure 3.20: Pressure- $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ profile	118
Figure 3.21: Zr/Hf versus Ti/Eu plot	122

Chapter Four

Figure 4.1: $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ (‰) versus MgO (wt%) for arc lavas, boninites, and MORB.....	135
Figure 4.2: Location map of IODP Expedition 352 to the Bonin fore-arc	140
Figure 4.3: Location map of IODP Expedition 352.....	141
Figure 4.4: Lithostratigraphy of the four drill sites from IODP Expedition 352	142
Figure 4.5: MgO Harker diagrams for IODP Expedition 352 fore-arc basalts (FABs) and MORB.	148
Figure 4.6: Ce/Yb versus Ce concentration in $\mu\text{g.g}^{-1}$ for IODP Expedition 352 fore-arc basalts (FABs).	149
Figure 4.7: Radiogenic isotopes in IODP Expedition 352 FABs and boninites	150
Figure 4.8: MgO Harker diagrams	152
Figure 4.9: Nd, Hf, Sr and Pb isotope measurements.....	157
Figure 4.10: Schematic sketch showing the conceptual model of FAB and boninite generation.....	158
Figure 4.11: Comparison and student T-test results of fore-arc basalt (FAB) and MORB $\delta^{56}\text{Fe}$	165
Figure 4.12: Comparison and student T-test results	166
Figure 4.13: Comparison and student T-test results of oceanic arc lava and boninite $\delta^{56}\text{Fe}$	167
Figure 4.14: IODP Expedition 352 FAB $\delta^{56}\text{Fe}_{\text{NRM-524}}$ (‰) versus (a) Ba concentration ($\mu\text{g.g}^{-1}$); (b) K_2O concentration (wt%); (c) loss on ignition (%); (d) MgO concentration (wt%).....	169
Figure 4.15: Expedition 352 boninite $\delta^{56}\text{Fe}_{\text{NRM-524}}$ (‰) versus slab melt indicators	171
Figure 4.16: $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ (‰) versus MgO (wt%) for Expedition 352 boninites.	172
Figure 4.17: $\delta^{56}\text{Fe}_{\text{NRM-524}}$ (‰) versus (a) Ba concentration ($\mu\text{g.g}^{-1}$); (b) Pb concentration ($\mu\text{g.g}^{-1}$); (c) Rb concentration ($\mu\text{g.g}^{-1}$); (d) Sr concentration ($\mu\text{g.g}^{-1}$)	174
Figure 4.18: Chlorine versus sulphur concentrations	175
Figure 4.19: $\delta^{56}\text{Fe}_{\text{NRM-524}}$ (‰) versus (a) spinel Cr#; (b) $\Delta\log f\text{O}_2[\text{FMQ}]$; (c) degree of serpentinisation (%) ...	177
Figure 4.20: Fe isotopic melt modelling sensitivity tests.....	179
Figure 4.21: The effects of changing Fe melt model α -values.....	180
Figure 4.22: Two-stage accumulated fractional non-modal Fe isotope melt models	182
Figure 4.23: Peridotite $\delta^{56}\text{Fe}$ data from literature	183

Chapter Five

Figure 5.1: Summary comparison of $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$ literature data	197
Figure 5.2: Location map of IODP Expedition 352 to the Bonin fore-arc	199
Figure 5.3: $\delta^{66}\text{Zn}$ comparison and student T-test results	203
Figure 5.4: Nd, Hf, and Pb isotope measurements for IODP Expedition 352 fore-arc basalts (FABs) and boninites.....	205
Figure 5.5: $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$ (‰) versus (a) MgO (wt%); (b) TiO_2 (wt%); (c) Nb ($\mu\text{g.g}^{-1}$); (d) $\epsilon\text{Hf}(\text{initial})$	206
Figure 5.6: Comparison plot of $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$ (‰) measurements for IODP Expedition 352 boninites from this study, sphalerite $\delta^{66}\text{Zn}$ literature data	208
Figure 5.7: IODP Expedition 352 boninites versus FME concentrations	209
Figure 5.8: IODP Expedition 352 boninite $\delta^{66}\text{Zn}$ versus slab melt and magmatic differentiation indicators	211
Figure 5.9: IODP Expedition 352 fore-arc basalt (FAB) $\delta^{66}\text{Zn}$ versus (a) Zn concentrations; (b) Ce/Yb; (c) TiO_2 concentrations; (d) $\text{CaO}/\text{Al}_2\text{O}_3$; (e) MgO concentrations; (f) Na_2O concentrations.....	212
Figure 5.10: FAB $\delta^{66}\text{Zn}$ versus K_2O , LOI, and Ba/Th.....	213
Figure 5.11: IODP Expedition 352 FAB $\delta^{51}\text{V}$ versus FME concentrations.....	214
Figure 5.12: H_2O versus Cl concentration.....	215
Figure 5.13: Scatter plots of IODP Expedition 352 FAB $\delta^{66}\text{Zn}$	216
Figure 5.14: Zn isotopic melt modelling.....	218
Figure 5.15: $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$ (‰) versus Eu anomaly	220
Figure 5.16: $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$ (‰) versus whole-rock Cr#	221
Figure 5.17: Zn concentration versus $\delta^{66}\text{Zn}_{\text{Lyon}}$ (‰) for IODP FABs.	222
Figure 5.18: Available peridotite $\delta^{66}\text{Zn}$ data from literature	223

Chapter Six

Figure 6.1: (a) $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ (‰) versus MgO (wt %) for literature MORB and arc lavas.	236
Figure 6.2: Comparison and student T-test results for $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$	244
Figure 6.3: Comparison and student T-test results of (a) IODP Expedition 352 fore-arc basalt (FAB) and boninite $\delta^{51}\text{V}$; (b) fore-arc basalt (FAB) and boninite $\delta^{49}\text{Ti}$	245
Figure 6.4: $\delta^{51}\text{V}_{\text{AA}}$ (‰) vs $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ (‰) for IODP FABs and boninites.....	246
Figure 6.5: Comparison and student T-test results of (a) IODP Expedition 352 high-silica boninite (HSB) and low-silica boninite (LSB) $\delta^{49}\text{Ti}$; (b) high-silica boninite (HSB) and low-silica boninite (LSB) $\delta^{51}\text{V}$	247
Figure 6.6: Chlorine versus sulphur concentrations in $\mu\text{g.g}^{-1}$	250
Figure 6.7: IODP Expedition 352 FAB $\delta^{51}\text{V}_{\text{AA}}$ and $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ versus FME concentrations.....	251
Figure 6.8: IODP Expedition 352 FAB $\delta^{51}\text{V}_{\text{AA}}$ and $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ versus Sm/Hf.	252
Figure 6.9: IODP Expedition 352 fore-arc basalt $\delta^{51}\text{V}_{\text{AA}}$ (‰) versus ϵHf_i	253
Figure 6.10: Expedition 352 FAB $\delta^{51}\text{V}_{\text{AA}}$ (‰) versus source depletion indicators.....	254
Figure 6.11: Comparison of MORB, FAB, and Cyprus basalt $\delta^{49}\text{Ti}$	256
Figure 6.12: MgO (wt%) versus $\delta^{51}\text{V}_{\text{AA}}$ (‰).....	258

Figure 6.13: MgO (wt%) versus Ti concentration ($\mu\text{g.g}^{-1}$)	259
Figure 6.14: Titanium concentration melt modelling results.	262
Figure 6.15: IODP Expedition 352 boninite Ti concentration ($\mu\text{g.g}^{-1}$) versus (a) $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ (‰) and (b) MgO (wt%).	263
Figure 6.16: IODP Expedition 352 boninite $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ (‰) versus FMEs.....	264
Figure 6.17: IODP Expedition 352 boninite $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ (‰) versus incompatible, immobile element concentrations (a-c) and slab melt indicators (d-f).	265
Figure 6.18: IODP Expedition 352 boninite $\delta^{51}\text{V}_{\text{AA}}$ (‰) versus FMEs.....	266

Chapter Seven

Figure 7.1: Schematic sketches of FAB and boninite formation.....	279
Figure 7.2: Compilation of $\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$, $\delta^{51}\text{V}$, and $\delta^{49}\text{Ti}$ versus each other.....	280

List of Tables

Chapter One

Table 1.1: Vanadium isotopic abundance data.....	8
Table 1.2: Titanium isotopic abundance data.....	11
Table 1.3: Zinc isotopic abundance data.....	12
Table 1.4: Iron isotopic abundance data.....	14

Chapter Two

Table 2.1: V concentrations in Wu et al. (2016) column cuts.....	41
Table 2.2: Compilation of V yields.....	43
Table 2.3: Results of V yield and fractionation tests.....	44
Table 2.4: Faraday cup configuration used to measure $\delta^{51}\text{V}$ on the Nu Plasma.....	45
Table 2.5: Faraday cup configuration used to measure $\delta^{51}\text{V}$ on the Neptune.....	47
Table 2.6: Comparison of running concentrations.....	48
Table 2.7: USGS reference material V isotope measurements.....	50
Table 2.8: Total procedural Zn blanks.....	52
Table 2.9: Zinc concentrations from Zn blank tests.....	54
Table 2.10: Faraday cup configuration used to measure $\delta^{64}\text{Zn}$	55
Table 2.11: USGS reference material Zn isotope measurements.....	59
Table 2.12: Total procedural Fe blanks.....	61
Table 2.13: Faraday cup configuration used to measure $\delta^{56}\text{Fe}$	62
Table 2.14: USGS reference material Fe isotope measurements.....	67

Table 2.15: $^{176}\text{Hf}/^{177}\text{Hf}$ data for USGS reference materials	74
Table 2.16: Faraday cup configuration and assigned amplifier resistivity used to measure $^{176}\text{Hf}/^{177}\text{Hf}$	75
Table 2.17: Trace element concentration data ($\mu\text{g.g}^{-1}$) for USGS reference materials	76

Chapter Three

Table 3.1: $\text{Fe}^{3+}/\Sigma\text{Fe}$, pressure, temperature and $f\text{O}_2$ estimates for the Diavik garnets	90
Table 3.2: Estimated modal abundances	91
Table 3.3: Trace element concentration data ($\mu\text{g.g}^{-1}$) for Diavik xenolith whole-rock.....	92
Table 3.4: Trace element concentration data ($\mu\text{g.g}^{-1}$) for USGS reference materials	93
Table 3.5: $\delta^{51}\text{V}$ of Diavik samples.....	95
Table 3.6: USGS reference materials analysed for $\delta^{51}\text{V}$	96
Table 3.7: The modal abundances of the four major phases found in Diavik xenolith sample 108.	116

Chapter Four

Table 4.1: Petrology summary of IODP Expedition 352 fore-arc basalts (FABs) and boninites	143
Table 4.2: Major element concentrations for IODP Expedition 352 fore-arc basalts and boninites	153
Table 4.3: Selected trace element concentrations IODP Expedition 352 fore-arc basalts and boninites.....	160
Table 4.4: Iron isotope ratios	163
Table 4.5: Fe melt model parameters	178

Chapter Five

Table 5.1: Zinc isotope ratios measured in the IODP Expedition 352 FABs and boninites.	200
Table 5.2: Zn partition coefficient and $\delta^{66}\text{Zn}$ fractionation factor	220

Chapter Six

Table 6.1: Titanium and vanadium isotope ratios	240
Table 6.2: Hafnium isotope ratios.....	241

Statement of Copyright

The copyright of this thesis rests with the author. No quotation from it should be published without the author's prior written consent and information derived from it should be acknowledged.

Acknowledgements

Thank you to my primary PhD supervisor Dr Julie Prytulak for her support and encouragement throughout the duration of my PhD and the challenges of the Covid-19 pandemic. I am grateful for all of your advice, editing, and proof-reading, that you made the transition from Imperial College London to Durham University after my first year as seamless as possible, and minimised the stress of reworking my thesis in light of the pandemic. Also thank you to my additional supervisors who joined the project when I moved to Durham, Dr Geoff Nowell and Prof Kevin Burton, who offered their expert knowledge of mass spectrometry and Fe and Zn isotope systems.

I would also like to thank Dr Marc-Alban Millet and Dr Liam Hoare who advised me on everything related to titanium isotopes. Without your help and use of your lab in Cardiff, my titanium isotope work would have been significantly harder. In a similar vein, I want to thank Dr Davide Novella and Prof Greg Yaxley for their advice while writing my Diavik mantle xenolith chapter. I would like to extend my gratitude to the MAGIC research group at Imperial College London and the entire Durham Isotope Group for their expertise and support during my data collection.

Thank you to the Natural Environment Research Council for providing the funding for my PhD, and thank you to the Science and Solutions for a Changing Planet and IAPETUS Doctoral Training Partnerships for their excellent training.

On a more personal note, I want to thank my amazing partner Calum for his patience and support over the last four years. Moving from the southeast of England to Durham was unexpected and the frequent four and half hour car journeys you made to visit kept me sane. Also thank you for reassuring me whenever I doubted myself, acting as a frequent sounding board, and teaching me VBA programming. Your support was invaluable.

CHAPTER ONE

Introduction

CHAPTER ONE TABLE OF CONTENTS

1.1. Overview	1
1.2. Stable Isotope Fractionation and Measurement	2
1.2.1. History of Stable Isotope Measurement	2
1.2.2. The Delta Notation	3
1.2.3. Theoretical Basis for Stable Isotope Fractionation	3
1.3. Applying Transition Metal Stable Isotopes to High-Temperature Geologic Systems	6
1.3.1. Vanadium Isotopes	8
1.3.2. Titanium Isotopes	10
1.3.3. Zinc Isotopes	12
1.3.4. Iron Isotopes	14
1.4. Thesis Outline and Aims	16
1.4.1. Chapter Two	16
1.4.2. Chapter Three	16
1.4.3. Chapters Four, Five, and Six	17
1.4.4. Chapter Seven	19
References	19

1.1. Overview

Transition metal stable isotopes have the potential to act as tracers for a variety of geological and cosmochemical processes. The measurement precision required to apply transition metal isotope ratios to high temperature, igneous geology has been achieved due to recent advances in multi-collector inductively coupled plasma mass spectrometry (MC-ICP MS) (e.g. Halliday *et al.* 1995; Maréchal *et al.* 1999). However, not all stable isotope systems have been investigated in detail in high temperature systems, and thus there are significant gaps in our understanding of how some transition metal isotopes behave and fractionate during magmatic processes. These gaps in understanding must be addressed to understand which igneous geology applications hold the most promise for the use of transition metal stable isotopes.

This thesis started out with the overarching aim of improving our understanding of how vanadium (V), iron (Fe), and zinc (Zn) stable isotopes fractionate during mantle melting and metasomatic

processes by detailed examination of mineral separates from a variety of mantle xenoliths from different tectonic settings. However, after work on the first suite of xenoliths from Diavik, Canada was completed, the Covid-19 pandemic required the thesis to change direction. Covid-19 resulted in closure of the laboratories at Durham University and long-term reduced laboratory capacity and access after reopening. Even with a costed extension, the reduced analytical time available necessitated a switch to material that already had a high level of characterisation, instead of continuing with lab intensive mineral separation and chemical characterisation of additional xenolith suites.

The focus of this thesis therefore shifted to examining wider magmatic processes in subduction zones and their effects on transition metal stable isotope fractionation. An extremely well characterised (e.g. major elements, trace elements, radiogenic isotopes, mineral chemistry, volatiles, thin section petrography) sample suite from International Ocean Discovery Program (IODP) Exp. 352 was available. The lavas from the expedition are those formed from the earliest stages of subduction initiation, rapidly transitioning from seafloor spreading-related ‘forearc’ basalts (FAB) to heavily subduction-influenced boninites. By examining and comparing boninites with clear subduction inputs and FAB with no subduction input, the isotope fractionation effects of different magmatic and subduction-related processes on V-Ti-Fe-Zn isotopes could be investigated, including such broad topics such as the effects of partial melting on melts and residues, redox sensitivity, and fluid-induced isotope fractionation. The investigation is the first time V-Ti-Fe-Zn isotopes have been determined on the exact same suite of lavas to directly investigate isotopic responses to magmatic processes versus the effects of subduction inputs.

1.2. Stable Isotope Fractionation and Measurement

1.2.1. History of Stable Isotope Measurement

The earliest theoretical stable isotope studies appeared before the development of mass spectrometry (e.g. Lindemann 1919; Lindemann & Aston 1919; Urey & Greiff 1935). However, the initial thinking behind the modern formula for calculating equilibrium isotope fractionation can be credited to Urey (1947) and Bigeleisen & Mayer (1947). Their work centred around “a simplified thermodynamic model of the quantum mechanics of molecular vibration and rotation”, and predicted the later observed directions, magnitudes, and temperature sensitivities of various isotope systems, and suggested the possibility of well-known modern-day geochemical fields of study, such as palaeothermometry using oxygen isotopes (Schauble 2004). Kieffer (1982) later extended Urey’s 1947 work to account for crystals. Initial stable isotope studies focussed on measurement by gas-source mass spectrometry of light element isotope systems (e.g. H, C, N, O, S)

due to the difficulty of detecting significant natural isotopic variations in heavier element isotope systems. In addition, stable isotope fractionation at high temperatures was considered to be negligible due to the inverse relationship between isotope fractionation magnitude and temperature (Urey 1947). Improvements in analytical techniques, resolutions, and precision (e.g. Halliday *et al.* 1995, 1998; Schauble 2004) have facilitated the exploration of so-called “non-traditional” stable isotopes and their applications in high-temperature geologic settings (e.g. see review in Teng *et al.* 2017).

1.2.2. The Delta Notation

The convention in the stable isotope community is to report stable isotope compositions as ratios with the heavier isotope as the numerator and the lighter isotope as the denominator (eq. 1). These ratios are reported relative to an international reference standard to allow comparisons between studies, and expressed as per mille deviations from the isotopic ratio of the reference value using the delta (δ) notation (eq. 1). Since reported stable isotope compositions are relative, with the heavy isotope as the ratio numerator, it is convention to refer to higher numerical values as “heavier”, and lower numerical values as “lighter”. All stable isotope ratios in this thesis are reported using the delta notation and the “heavy” and “light” terminology.

$$(1) \quad \delta^{51}V_{AA} = \left(\frac{{}^{51}V/{}^{50}V_{measured}}{{}^{51}V/{}^{50}V_{AA \text{ reference standard}}} - 1 \right) \times 1000$$

1.2.3. Theoretical Basis for Stable Isotope Fractionation

Theoretically, equilibrium stable isotope fractionation at high temperatures is controlled by the bond force constant, where heavier isotopes concentrate in bonds with higher vibrational frequencies. Equation 2 from Young *et al.* (2009) illustrates this, with ν_j being the first order vibrational frequency for mode j which depends on the bond force constant, $K_{f,j}$, and the reduced mass, μ .

$$(2) \quad \nu_j = \frac{1}{2\pi} \sqrt{\frac{K_{f,j}}{\mu}}$$

From equation 2, an expression of the $\delta^{51}V$ fractionation factor between two minerals (α_{a-b}) can be generated (eq. 3) (e.g. Urey 1947; Young *et al.* 2002).

$$(3) \quad \delta^{51}V_a - \delta^{51}V_b \cong 10^3 \ln \alpha_{a/b}^{51/50} = \frac{10^3}{50} \left(\frac{h}{k_B T} \right)^2 \left(\frac{1}{m_{50}} - \frac{1}{m_{51}} \right) \times \left[\sum_j \frac{K_{f,j,a}}{4\pi^2} - \sum_j \frac{K_{f,j,b}}{4\pi^2} \right]$$

Where, in this example, m_{50} and m_{51} are the atomic masses of ^{50}V and ^{51}V respectively, h is Planck's constant, k_b is Boltzmann's constant, and the summations are over bond force constants relevant to the displacements of the atoms of interest (Young *et al.* 2009). From equation 3, it can be clearly seen that the higher the bond force constant ($K_{f,j}$), the higher concentration of the heavy isotopes within that phase. The bond force constant between cations i and j is determined by equation 4 where e is the charge of an electron, ϵ_0 is the electric constant, n is the Born exponent, r is the interatomic distance, and s is the mean bond strength.

$$(4) \quad K_{f,i,j} = \frac{s_i s_j e^2 (1-n)}{4\pi\epsilon_0 r_{ij}^3}$$

The mean bond strength is defined in Pauling (1929) as equation 5, where for an ionic species i , s_i is the mean bond strength, z_i is the ion's valence, and v_i is the ion's coordination number.

$$(5) \quad \bar{s}_i = \frac{z_i}{v_i}$$

Therefore, the amount and direction of stable isotope fractionation between two phases is largely dictated by the differences in the valence and coordination of the ion in both phases. Heavier isotopes will concentrate in the phase with higher mean bond strength (higher ion valence and lower coordination), and the lighter isotopes in the phase with lower mean bond strength (lower valence and higher coordination). Ionic radius is a key control on the compatibility of different ions in different phases. As ionic radius and the size of a site in a mineral diverge, the compatibility of the ion in that site decreases. Ionic radius therefore affects the partition coefficient of an ion, the site that an ion can enter, and consequently the magnitude and direction of stable isotope fractionation. However, ionic radius is intrinsically linked to valence state and coordination. Coordination number is related to ionic radius because as the size of a cation decreases, the radius ratio between the cation and surrounding anions decreases (**Table 1.1**). Once a limiting radius ratio is reached, the coordination number decreases because the cation-anion distance is too small to maintain the bonds. In addition, as valence state increases, ionic radius decreases due to fewer electrons (**Table 1.1**). **Table 1.2** shows the preferred site coordination based on ionic radius of V, Ti, Fe, and Zn in the major mineral phases discussed throughout this thesis.

Table 1.1: The ionic radius of vanadium, iron, zinc, and titanium ions at different valence states and coordinations (Ahrens, 1952).

Ion	Valence State	Coordination	Ionic Radius (Å)
V	3+	VI	0.64
		V	0.53
	4+	VI	0.58
		VIII	0.72
		IV	0.355
	5+	V	0.46
		VI	0.54
		IV	0.63
	Fe	VI	0.78
Zn	2+	VIII	0.92
		IV	0.49
		V	0.58
		VI	0.645
	Ti	IV	0.42
		V	0.51
		VI	0.605
		VIII	0.74
		IV	0.6
	2+	V	0.68
		VI	0.74
		VIII	0.9
		IV	0.42
	4+	V	0.51
		VI	0.605
		VIII	0.74
		IV	0.6

Table 1.2: Expected coordination of preferred site of V, Ti, Fe, and Zn ions in different mineral phases based on ionic radius and site size.

Ion	Valence State	Phase	Preferred Coordination	Reference
V	3+/4+	Olivine	VI	Sossi <i>et al.</i> (2018a)
		Clinopyroxene	VI	
		Orthopyroxene	VI	
		Garnet	VI	
		Magnetite	VI	
		Silicate Melt	IV-VI	
Ti	4+	Olivine	VI	Farges <i>et al.</i> (1996)
		Clinopyroxene	VI	
		Orthopyroxene	VI	
		Fe-Ti oxides	VI	
		Silicate Melt	V	
Fe	2+	Olivine	VIII	Smyth & Bish (1988); Wilke (2005); Sossi <i>et al.</i> (2016)
	3+		VI	
	2+	Clinopyroxene	VI	
	3+		VI	
	2+	Clinopyroxene	VI	
	3+		VI	
	2+	Garnet	XII	
	3+		VI	
	2+	Spinel	VI	
	3+		IV/VI	

	2+	Silicate Melt	V-VI	
	3+			
Zn	2+	Olivine	VI	Sossi <i>et al.</i> (2018b)
		Clinopyroxene	VI	
		Orthopyroxene	VI	
		Spinel	IV	
		Silicate Melt	IV	

Ab initio studies are extremely useful for predicting isotope fractionation of non-traditional systems at high temperatures, and are efficient ways of understanding the parameters and mechanisms behind isotope fractionation (Blanchard *et al.* 2017). In particular, they have been useful for calculating vibrational frequencies which historically were of limited availability in literature for heavy mass elements such as Tl, Hg and U (Schauble 2004). However, theoretical and computational predictions of stable isotope fractionation are simplified, and require experiments and measurements of natural samples to assess their accuracy and the potential processes that cause discrepancies between calculated isotope fractionation and natural measured values (Young *et al.* 2015).

1.3. Applying Transition Metal Stable Isotopes to High-Temperature Geologic Systems

High-temperature magmatic processes such as mantle partial melting, fractional crystallisation, changing oxygen fugacity (fO_2), and metasomatism are important processes to understand and trace since they are key controls on the chemistry of high-temperature igneous rocks. Advances in high-precision MC-ICP MS analysis (e.g. Halliday *et al.* 1995; Maréchal *et al.* 1999) have allowed non-traditional, heavier isotope systems, found in lower concentrations, to be applied to high-temperature geologic settings where they can provide unique insights into magmatic processes. Compared to traditional (i.e. C, H, O, N, S) stable isotopes, non-traditional isotopes and in particular transition metal isotopes have a wider array of distinctive geochemical characteristics which make them uniquely useful. These characteristics include: (1) redox sensitivity; (2) more diverse bonding environments that are different from those of traditional systems; (3) variable concentrations in natural samples from major to trace concentrations; (4) variable volatility (e.g. see review in Teng *et al.* 2017). Such variable characteristics mean that different non-traditional isotope systems are susceptible to different isotope fractionation mechanisms, magnitudes, and directions. Transition metal stable isotopes may therefore allow a more diverse set of unique geochemical tracers to be created for a plethora of high-temperature magmatic processes. Included among these isotope systems are transition metal stable isotopes such as V, Ti, Fe, and Zn which are the focus of this thesis.

In particular, metasomatism is an important geological process that can affect mantle chemistry and is a key subject of Chapter Three. Metasomatism is classically defined as the transfer of mobile elements between different regions of an open system that can result in compositional changes (e.g. Thompson 1959, Korzhinskii 1965). However, metasomatism was originally only applied to crustal processes (e.g. Goldschmidt 1922, Korzhinski 1936). Lloyd & Bailey (1973) were the first to identify mantle-specific metasomatism, using it to explain the highly alkaline composition of amphibole-bearing peridotite xenoliths from Germany and Uganda. Mantle metasomatism is now typically split into two endmembers: modal (Harte 1983) and cryptic (Dawson 1984) metasomatism. Modal metasomatism describes the crystallisation of new minerals that are not commonly found in mantle peridotites, such as amphibole, mica, and apatite (Harte 1983). Cryptic metasomatism involves compositional changes to existing minerals without the formation of new minerals (Dawson 1984). However more recently, stealth metasomatism has been recognised as a new type of metasomatism. Stealth metasomatism involves the addition of new phases such as garnet and clinopyroxene to previously refractory protoliths such as harzburgites and dunites that are refertilised by metasomatic fluids (O'Reilly & Griffin, 2013). Since the garnet and clinopyroxene are mineralogically indistinguishable from common peridotite phases, it is not considered a variety of modal metasomatism, despite the addition of new phases (O'Reilly & Griffin, 2013).

The nature of metasomatic agents can be determined from the chemistry of fluid inclusions in minerals of metasomatic rocks, from changes in mineralogy, and changes in the chemistry of mantle minerals (O'Reilly & Griffin, 2013). However, metasomatic agents can vary considerably between silicate, kimberlitic, and carbonatitic magmas with varying amounts of dissolved volatiles and fluids such as brines, C-O-H fluids, and sulphur-rich fluids (O'Reilly & Griffin, 2013). These agents can also span fluids, melts, and supercritical fluids depending on the pressure-temperature regime. These variables make interpreting metasomatic rocks difficult. Therefore, despite recent instrumental advances that have allowed transition metal stable isotopes to be applied to high-temperature settings, there have been very few V-Ti-Fe-Zn isotopic studies related to mantle metasomatism, and no V isotope studies. This thesis therefore aims to fill some of the gaps in our understanding of the effects of mantle metasomatism on V isotope fractionation.

Overall, the controls on V-Ti-Fe-Zn isotope fractionation in high-temperature geologic settings are not yet fully understood, and there are few studies that present an approach combining several systems on the same sample material. Therefore, the detailed investigation of these systems in combination may provide key insights into the high temperature applications to which they are best applied. The next sections give basic details on the properties of V, Ti, Fe, and Zn isotope systems

and a compilation of relevant high-temperature literature data. More in depth discussions of each system are found in subsequent chapters.

1.3.1. Vanadium Isotopes

Vanadium is a refractory, moderately incompatible, transition metal that is fluid immobile, meaning it should be unaffected by alteration or weathering. Vanadium also has multiple oxidation states (V^{2+} , V^{3+} , V^{4+} , V^{5+}) which prompted research into the relationship between elemental V and oxygen fugacity (fO_2) (Canil 1997; Lee *et al.* 2003, 2005; Li & Lee 2004; Papike *et al.* 2005; Sutton *et al.* 2005; Karner *et al.* 2006; Mallmann & O'Neill 2009). However elemental V based fO_2 proxies typically have large uncertainties (Lee *et al.*, 2005), due to factors such as variable initial source concentrations, the degree of partial melting and fractionation, source mineralogy, and partitioning relationships. Vanadium isotopes have the potential to be a more robust tracer of magmatic processes than elemental V tracers, and thus measurement protocols were developed to explore the utility of the system. Vanadium has two stable isotopes, with an extreme abundance ratio (**Table 1.3**). Indeed, the vanishingly low abundance of ^{50}V was one of the factors that hindered the development of precise measurement protocols. There are a variety of other obstacles associated with V stable isotope analysis which also delayed the development of the system. Vanadium has only two relevant stable isotopes, which makes it difficult to correct for instrumental mass bias. There are other examples of systems with only two isotopes that have been successfully measured to high precision (e.g., B, Li, Tl), however, the minor isotope, ^{50}V , has two major isobaric interferences, ^{50}Ti and ^{50}Cr ; both of which occur in abundances orders of magnitude greater than ^{50}V in natural samples. This means that a chemical separation procedure must remove essentially all of the chemically similar elements Cr and Ti from a sample whilst maintaining $\sim 100\%$ V yields. Breakthroughs in both MC-ICP-MS protocols and chemical separations which overcame these obstacles and allowed for high precision V analyses have been made in the last ten years (Nielsen *et al.* 2011; Prytulak *et al.* 2011; Wu *et al.* 2016). There is no officially certified V isotope standard. However, V isotope ratios are conventionally reported as per mille deviations ($\delta^{51}V$) from Alfa Aesar (AA) (eq. 6, Nielsen *et al.* (2011)).

Table 1.3: Vanadium isotopic abundance data.

Element	Isotope	Abundance (%)
V	^{50}V	0.025
	^{51}V	99.75

$$(6) \quad \delta^{51}V_{AA} = \left(\frac{{}^{51}V/{}_{50}V_{\text{measured}}}{{}^{51}V/{}_{50}V_{\text{AA standard}}} - 1 \right) \times 1000$$

Since 2011 there has been a surge in the use of V isotopes in high-temperature igneous settings, with research focussing on both the redox tracer potential of $\delta^{51}\text{V}$ and constraining other magmatic fractionation mechanisms (e.g. Prytulak *et al.* 2013, 2017; Sossi *et al.* 2018a; Wu *et al.* 2018; Qi *et al.* 2019; Ding *et al.* 2020; Novella *et al.* 2020, **Fig. 1.1**). Wu *et al.* (2015) conducted *ab initio* calculations that emphasised the dependence of V isotope fractionation on valence, bond length and coordination. Oxide phases are a major V sink in igneous rocks, and consequently a link between $\delta^{51}\text{V}$ and the fractional crystallisation of oxides has been proposed (Prytulak *et al.* 2017; Wu *et al.* 2018; Ding *et al.* 2020), with heavier $\delta^{51}\text{V}$ being reported in more evolved rocks. Vanadium isotopes are also considered to fractionate during mantle partial melting; however, this is still not fully understood. In mafic melts V should typically be coordinated between IV- and VI-fold, whereas in major mantle minerals such as olivine, pyroxenes, and garnet, V has VI-fold coordination (Sossi *et al.* 2018a). The theory of stable isotope fractionation therefore predicts that during mantle partial melting heavier V isotopes concentrate in the lower coordination sites in the melt, and V light isotopes concentrate in the residue. Theoretical predictions are supported by the $\delta^{51}\text{V}$ of harzburgites ($\delta^{51}\text{V} = -1.20 \pm 0.18 \text{ ‰}$ 2SD (Prytulak *et al.* 2013)) being lighter than MORB ($\delta^{51}\text{V} = -0.84 \pm 0.18 \text{ ‰}$ (Prytulak *et al.* 2013; Wu *et al.* 2018)) (**Fig. 1.1**). Vanadium isotopes have been found to be insensitive to low-temperature seafloor alteration (Prytulak *et al.* 2013; Wu *et al.* 2018). However there has been no research into high-temperature alteration processes such as metasomatism. According to $\delta^{51}\text{V}$ redox studies, the relationship between $\delta^{51}\text{V}$ and $f\text{O}_2$ is complex. Whilst oxidation state is a key control on bond strength which in turn influences equilibrium stable isotope fractionation, coordination environment is also important (e.g. Sossi & O'Neill 2017). Research has suggested that whilst subtle $f\text{O}_2$ effects on $\delta^{51}\text{V}$ may be present, $\delta^{51}\text{V}$ is likely most influenced by fractionation mechanisms related to changes in bonding environment such as the fractional crystallisation of oxides and mantle partial melting (Prytulak *et al.* 2017; Sossi *et al.* 2018a; Novella *et al.* 2020). However, these studies utilise whole-rock $\delta^{51}\text{V}$ measurements or experimental mineral separates at conditions not directly applicable to the mantle. Natural mineral separate studies should allow a more direct, realistic exploration of the $\delta^{51}\text{V}$ - $f\text{O}_2$ relationship in high-temperature magmatic settings.

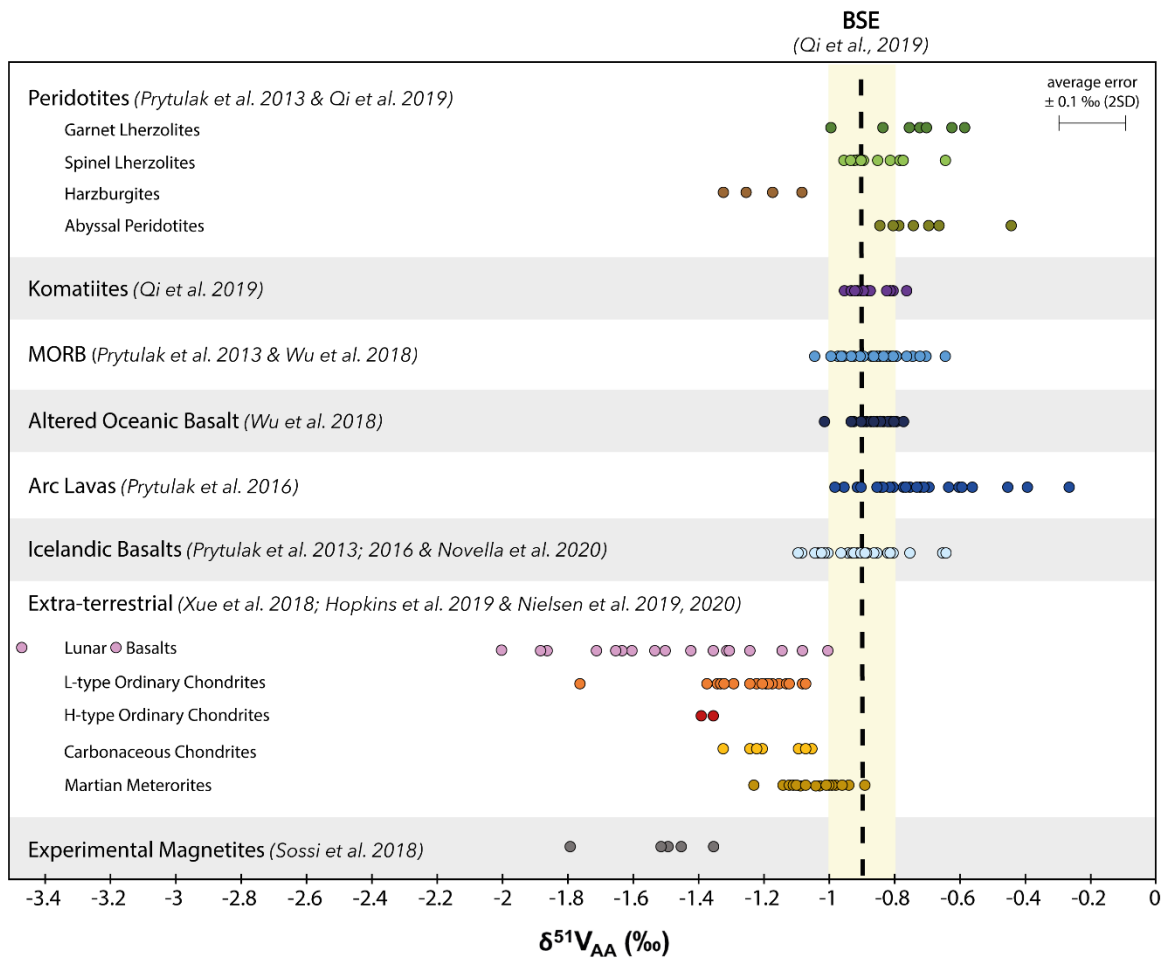


Figure 1.1: Summary comparison of $\delta^{51}V_{AA}$ literature data from high-temperature igneous studies. The data includes peridotites (Prytulak et al. 2013; Qi et al. 2019), komatiites (Qi et al. 2019), MORB (Prytulak et al. 2013; Wu et al. 2018), altered oceanic basalts (Wu et al. 2018), arc lavas (Prytulak et al. 2017), Icelandic basalts (Prytulak et al. 2013, 2017; Novella et al. 2020), extra-terrestrial samples (Xue et al. 2018; Hopkins et al. 2019; Nielsen et al. 2019, 2020), and experimental magnetite mineral separates (Sossi et al. 2018a). The average error is ± 0.10 ‰ (2SD).

1.3.2. Titanium Isotopes

Titanium is a refractory, high-field strength element that shares similar geochemical properties with elements such as Hf, Zr, Nb, and Ta. Titanium has a low mobility in aqueous fluids meaning it is relatively insensitive to post-eruptive weathering and alteration. Titanium has two valence states: Ti^{3+} and Ti^{4+} , but under terrestrial conditions it is usually present as Ti^{4+} (Millet et al. 2016). Titanium has five stable isotopes (**Table 1.4**), with its isotopic composition conventionally reported as $\delta^{49}Ti$. Similar to V, there is no officially certified international Ti isotope standard, however, most Ti isotopes studies report relative to OL-Ti (eq. 7, Millet & Dauphas 2014).

Table 1.4: Titanium isotopic abundance data.

Element	Isotope	Abundance (%)
Ti	⁴⁶ Ti	8.25
	⁴⁷ Ti	7.44
	⁴⁸ Ti	73.72
	⁴⁹ Ti	5.41
	⁵⁰ Ti	5.18

$$(7) \quad \delta^{49}\text{Ti}_{\text{OL-Ti}} = \left(\frac{{}^{49}\text{Ti}/{}^{47}\text{Ti}_{\text{measured}}}{{}^{49}\text{Ti}/{}^{47}\text{Ti}_{\text{OL-Ti standard}}} - 1 \right) \times 1000$$

The application of Ti stable isotopes to high temperature magmatic processes is relatively new (e.g. Millet *et al.* 2016; Greber *et al.* 2017; Deng *et al.* 2018, 2019; Johnson *et al.* 2019; Hoare *et al.* 2020, **Fig. 1.2**) and therefore Ti isotope literature data is limited. Current Ti isotope data suggests that negligible isotope fractionation occurs during mantle partial melting (e.g. Millet *et al.* 2016; Deng *et al.* 2018). However, similarly to V isotopes, since the Ti budget of igneous rocks is dominated by Fe-Ti oxides, the fractional crystallisation of Fe-Ti oxides exerts a major control on Ti isotope fractionation (Millet *et al.* 2016; Deng *et al.* 2019; Johnson *et al.* 2019; Hoare *et al.* 2020). The timing of oxide crystallisation is partially controlled by both $f\text{O}_2$ and H_2O concentrations (e.g. Toplis & Carroll 1995, 1996). Consequently, $\delta^{49}\text{Ti}$ has the potential to also respond to changes in redox. For example, Hoare *et al.* (2020) found that at uniform SiO_2 concentrations, more oxidised arc calc-alkaline suites are associated with heavier $\delta^{49}\text{Ti}$ than more reduced tholeiitic suites. However, since the application of Ti isotopes to high temperature igneous systems is still in its infancy, the controls on Ti isotope fractionation are not fully constrained. There are still significant gaps in existing literature data, particularly on mantle rocks, and arc lavas and OIBs with minimal differentiation that are needed to understand the causes of Ti isotope fractionation in magmatic systems.

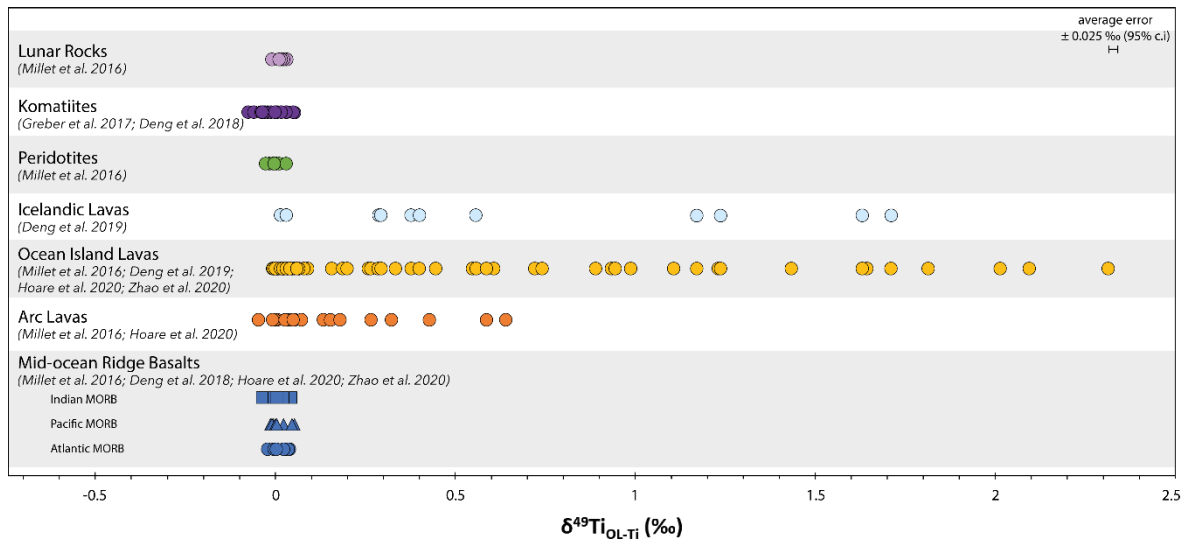


Figure 1.2: Summary comparison of $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ literature data from relevant high-temperature igneous studies. The data includes lunar rocks (Millet *et al.* 2016), komatiites (Greber *et al.* 2017; Deng *et al.* 2018), peridotites (Millet *et al.* 2016), Icelandic lavas (Deng *et al.* 2019), OIB (Millet *et al.* 2016; Deng *et al.* 2019; Hoare *et al.* 2020; Zhao *et al.* 2020), arc lavas (Millet *et al.* 2016; Hoare *et al.* 2020), and MORB (Millet *et al.* 2016; Deng *et al.* 2018; Hoare *et al.* 2020; Zhao *et al.* 2020). The average error is ± 0.025 ‰ (95 % c.i.).

1.3.3. Zinc Isotopes

Zinc is a moderately incompatible and moderately volatile element with only one oxidation state (Zn^{2+}), and five stable isotopes (**Table 1.5**). Zinc is not technically a transition metal since it has a fully occupied d electron subshell, but its properties are closer to the transition metals than other metals. Zinc has long been thought to act as a lithophile element during planetary accretion and differentiation (e.g. McDonough 2003). However recent work suggests that ~ 30 % of terrestrial Zn resides in the core, and therefore Zn is moderately siderophilic (Siebert *et al.* 2011). The Zn isotope ratio that is typically reported in literature is $^{66}/^{64}\text{Zn}$, in the delta notation relative to international reference material JMC-Lyon (Maréchal *et al.* 1999) (eq. 8). However, JMC-Lyon is no longer available and many labs, including Durham, use the Zn-ETH standard, which has been the subject of an international laboratory cross calibration effort (Archer *et al.* 2017).

Table 1.5: Zinc isotopic abundance data.

Element	Isotope	Abundance (%)
Zn	^{64}Zn	49.17
	^{66}Zn	27.73
	^{67}Zn	4.04
	^{68}Zn	18.45
	^{70}Zn	0.61

$$(8) \quad \delta^{66}\text{Zn}_{\text{JMC-Lyon}} = \left(\frac{^{66}\text{Zn}/^{64}\text{Zn}_{\text{measured}}}{^{66}\text{Zn}/^{64}\text{Zn}_{\text{JMC-Lyon standard}}} - 1 \right) \times 1000$$

Similarly, to V and Ti isotopes, only recently have Zn isotopes been able to be measured to the precisions necessary to apply them to geological settings. Zinc's high first ionisation potential (9.4 eV) means that $\delta^{66}\text{Zn}$ measurement via TIMS is difficult (Moynier *et al.* 2017). The difficulty of TIMS analysis explains the limited $\delta^{66}\text{Zn}$ work prior to the advent of high precision MC-ICP MS.

There is limited high temperature Zn isotope *ab initio* work, with most work being centred around seawater (Fujii *et al.* 2011, 2014) and organic material (e.g. Fujii & Albarède 2012). Zinc isotope measurements of natural samples have had an increasing focus on high temperature igneous applications more recently (Chen *et al.* 2013; Doucet *et al.* 2016; Inglis *et al.* 2017; Wang *et al.* 2017; Huang *et al.* 2018a, b; Sossi *et al.* 2018b; Beunon *et al.* 2020). Research has found evidence for isotopic fractionation during both mantle partial melting and fractional crystallisation. During fractional crystallisation, the liquid evolves to increasingly heavy $\delta^{66}\text{Zn}$ due to fractionation of olivine and/or Fe-Ti oxides (e.g. Chen *et al.* 2013; Wang *et al.* 2017; Sossi *et al.* 2018b). Zn^{2+} should have predominantly IV-fold coordination in mafic melts, and VI-fold coordination in olivine (Sossi *et al.* 2018b). Therefore, heavy Zn isotopes concentrate in melts as lighter Zn isotopes partition into the higher Zn coordination sites in olivine. MORB is thought to have a relatively homogenous $\delta^{66}\text{Zn}$ of $0.271\text{‰} \pm 0.055$ (2SD) (Wang *et al.* 2017; Huang *et al.* 2018b; Liao *et al.* 2020), but AOC, oceanic sediments, and subducted serpentinites are more variable in $\delta^{66}\text{Zn}$. The isotopic difference between mantle and surficial reservoirs has led to the notion that Zn isotopes may be sensitive to the addition of fluids and sediments to a mantle source and to subduction-related processes more generally. Recent research of $\delta^{66}\text{Zn}$ in serpentinitised forearc mantle peridotites suggest that Zn can be mobilised and fractionated via complexation with subducted slab dehydration fluids (e.g. Pons *et al.* 2016; Debret *et al.* 2018, 2021). However whether such fractionation has an observable effect on the $\delta^{66}\text{Zn}$ budget of the mantle wedge and resulting arc lavas is debated (e.g. Inglis *et al.* 2017; Huang *et al.* 2018b).



Figure 1.3: Summary comparison of $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$ literature data. The data includes, MORB (Wang et al. 2017; Huang et al. 2018a; Liao et al. 2020), arc lavas (Huang et al. 2018b), OIB (Herzog et al. 2009; Chen et al. 2013; Wang et al. 2017), peridotites (Doucet et al. 2016; Wang et al. 2017; Huang et al. 2018a; Sossi et al. 2018)(Doucet et al. 2016; Wang et al. 2017; Huang et al. 2018a; Sossi et al. 2018), AOC (Huang et al. 2016), serpentinites (Pons et al. 2016; Debret et al. 2018, 2021), and marine sediments (Maréchal et al. 2000; Pichat et al. 2003; Bentahila et al. 2008; Pons et al. 2011). The average error is $\pm 0.035 \text{ ‰ (2SD)}$.

1.3.4. Iron Isotopes

Unlike V, Ti and Zn, Fe is a major element in many common rock-forming minerals. Iron has two oxidation states (Fe^{2+} and Fe^{3+}) and four stable isotopes (**Table 1.6**), and for terrestrial applications is usually reported as $\delta^{56}\text{Fe}$ or $\delta^{57}\text{Fe}$ relative to the IRMM-014 reference standard in the delta notation (eq. 9).

Table 1.6: Iron isotopic abundance data.

Element	Isotope	Abundance (%)
Fe	^{54}Fe	5.84
	^{56}Fe	91.75
	^{57}Fe	2.12
	^{58}Fe	0.28

$$(9) \quad \delta^{56}\text{Fe}_{\text{IRMM-014}} = \left(\frac{{}^{56}\text{Fe}/{}^{54}\text{Fe}_{\text{measured}}}{{}^{56}\text{Fe}/{}^{54}\text{Fe}_{\text{IRMM-014 standard}}} - 1 \right) \times 1000$$

Iron was amongst the first transition metals to be investigated for high temperature isotopic fractionation (Zhu *et al.* 2000) and thus Fe isotopes are perhaps currently the best understood. Iron isotopes were originally measured via TIMS (Völkening & Papanastassiou 1989; Beard & Johnson 1999; Johnson & Beard 1999), but TIMS measurements were of low precision and reproducibility. The advent of MC-ICP MS resulted in significantly improved Fe isotope measurement precision that has contributed to the large number and variety of Fe isotope studies to date.

There has been significant work on equilibrium Fe isotope fractionation in the last two decades (e.g. Zhu *et al.* 2002; Beard & Johnson 2004; Poitrasson *et al.* 2004; Williams *et al.* 2004; Poitrasson & Freydier 2005; Weyer *et al.* 2005; Schoenberg & von Blanckenburg 2006; Teng *et al.* 2011). Due to the inverse relationship between temperature and equilibrium fractionation factors, initially all igneous rocks were thought to have homogenous $\delta^{56}\text{Fe}$, therefore acting as a baseline for comparison with sediments (Beard & Johnson 1999). However, high temperature Fe isotopic fractionation has since been linked to changing oxygen fugacity (e.g. Williams *et al.* 2004, 2005; Dauphas *et al.* 2009), magmatic differentiation (e.g. Williams *et al.* 2004, 2005; Weyer & Ionov 2007; Teng *et al.* 2008; Schuessler *et al.* 2009; Hibbert *et al.* 2012), partial melting (e.g. Weyer *et al.* 2005; Williams *et al.* 2005; Weyer & Ionov 2007; Dauphas *et al.* 2009; Teng *et al.* 2013; Williams & Bizimis 2014; Sossi *et al.* 2016), and diffusion (e.g. Teng *et al.* 2011; Weyer & Seitz 2012). **Figure 1.4** shows high-temperature $\delta^{56}\text{Fe}$ literature data that is relevant to this thesis from MORB, arc lavas, and peridotites.

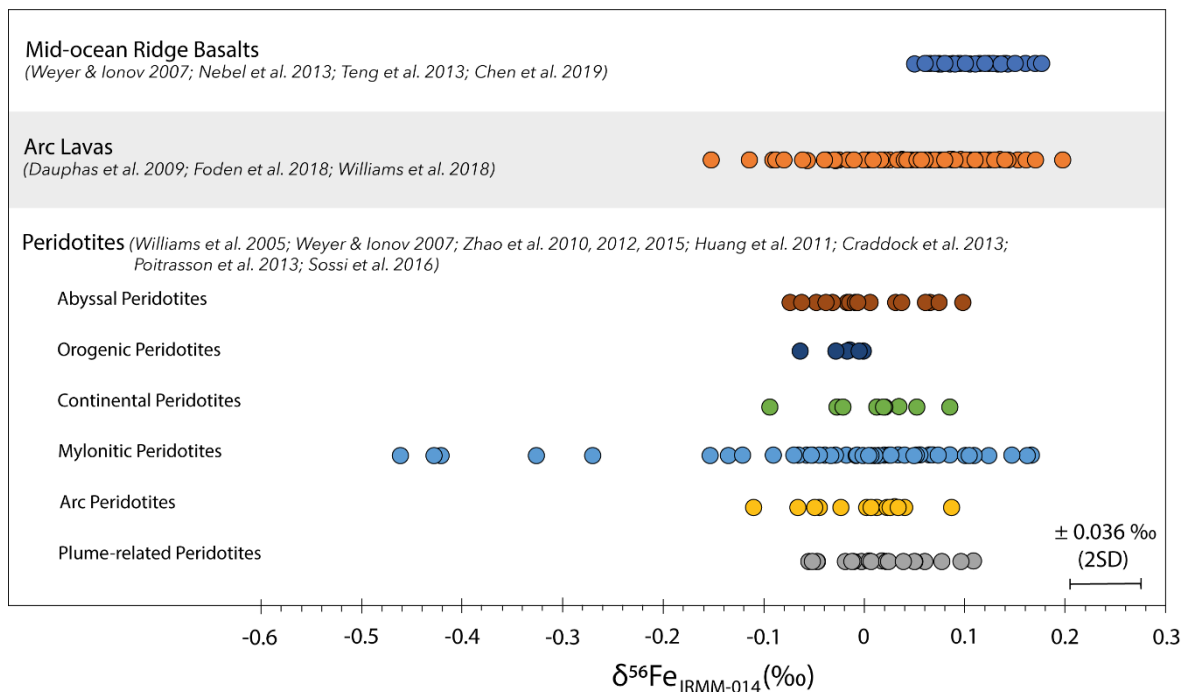


Figure 1.4: Summary comparison of $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ literature data from high-temperature igneous studies relevant to this thesis. The data includes peridotites (Williams *et al.* 2005; Weyer & Ionov 2007; Zhao *et al.*

2010, 2012, 2015; Huang et al. 2011; Craddock et al. 2013; Poitrasson et al. 2013; Sossi et al. 2016), MORB (Weyer & Ionov 2007; Nebel et al. 2013; Teng et al. 2013; Chen et al. 2019), and oceanic arc lava data (Dauphas et al. 2009; Foden et al. 2018; Williams et al. 2018). The average error on each data point is ± 0.036 ‰ (2SD).

1.4. Thesis Outline and Aims

This thesis aims to investigate the controls on V-Ti-Fe-Zn stable isotope fractionation during both mantle processes such as metasomatism and changes in redox conditions, and the wider magmatic processes associated with subduction zones (**Figure 1.5**).

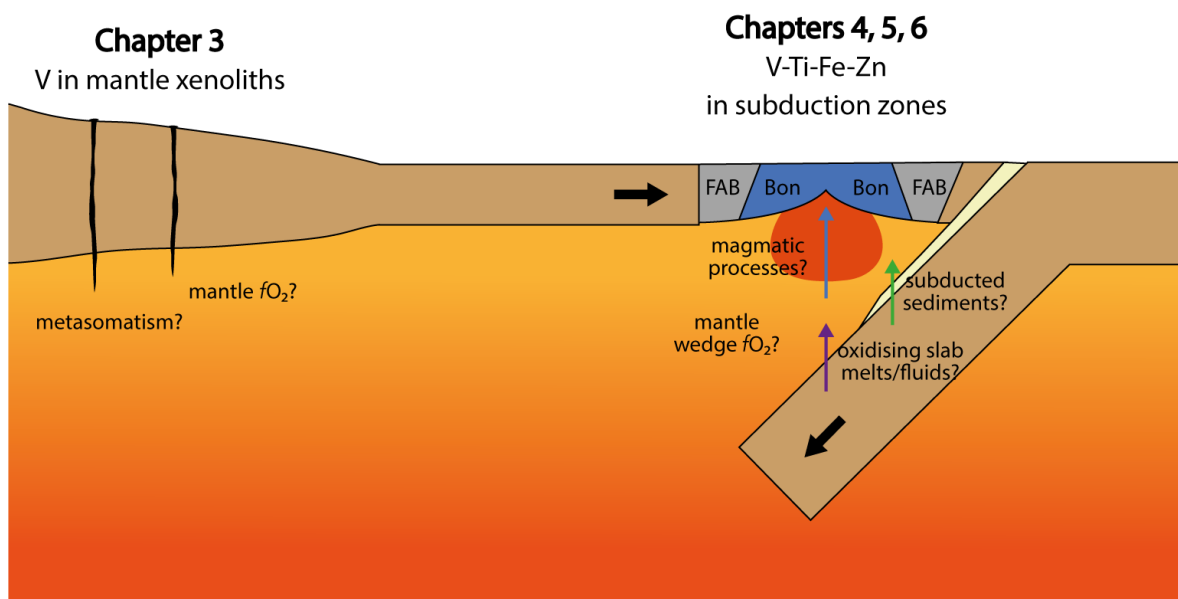


Figure 1.5: Schematic diagram (not to scale) of the tectonic settings and magmatic processes that this thesis will focus on. Chapter three takes mantle xenoliths from a kimberlite pipe in the Slave craton to study V isotopes and mantle fO_2 and metasomatism. Chapter four, five, and six measure V, Ti, Fe, and Zn isotopes in subduction initiation fore-arc basalts (FABs) and boninites to determine the controls on their fractionation and the processes involved in subduction initiation.

1.4.1. Chapter Two

Chapter two summarises the methods used throughout this PhD, and outlines detailed procedures for Fe, Zn, V, Ti, and Hf ion chromatography and MC-ICP MS measurement, plus trace element measurement via triple quadrupole- inductively coupled plasma mass spectrometry (ICP-QQQ-MS). Included are a new combined ion chromatography protocol for collecting Fe, Zn and V fractions from a single digestion, and a V isotope measurement protocol improvement that more accurately accounts for instrumental mass bias.

1.4.2. Chapter Three

One of the key draws of V isotope research at present is the potential of $\delta^{51}\text{V}$ to act as a mantle $f\text{O}_2$ tracer. However previous studies have found that processes such as the fractional crystallisation of oxide phases may swamp any observable $\delta^{51}\text{V}$ - $f\text{O}_2$ relationship. The V isotope literature distinctly lacks data from oxide-free mantle rocks from > 3 GPa or natural mineral separate data which could aid $\delta^{51}\text{V}$ - $f\text{O}_2$ investigations. Chapter three therefore examines the V isotope composition of garnet and clinopyroxene mineral separate pairs from oxide-free garnet lherzolite xenoliths from the Slave craton in Canada. The samples were specifically chosen since they are well-characterised with traditional determinations of $f\text{O}_2$, and they sample the deep upper mantle (> 5 GPa). However, kimberlite-entrained xenoliths from such depths are almost invariably metasomatic, and the effects of mantle metasomatism on $\delta^{51}\text{V}$ fractionation is not yet known. The Slave craton samples are suggested to have been metasomatised by a silicate melt, therefore chapter three also investigates the effects of metasomatism on $\delta^{51}\text{V}$ fractionation. Chapter three has the following aims:

- Determine the relationship between $\delta^{51}\text{V}$, mineral phases and $f\text{O}_2$ by comparing $\delta^{51}\text{V}$ of mantle mineral separates and whole-rock powders from lherzolites with variable $f\text{O}_2$.
- Provide the first $\delta^{51}\text{V}$ measurements of oxide-free, garnet lherzolites from pressures > 3 GPa.
- Explore how metasomatism affects V stable isotope fractionation.

1.4.3. Chapters Four, Five, and Six

Chapters four, five, and six diverge from mantle xenoliths due to the Covid-19 pandemic, and instead focus on subduction initiation which is one of the least understood cornerstones of plate tectonics. Transition metal stable isotopes have the potential to trace the source components and processes involved in the earliest stages of subduction, such as partial melting, source depletion, changes in $f\text{O}_2$, and inputs from oxidising subducted slab material, and therefore may be able to improve our understanding of subduction initiation.

The Bonin forearc represents a complete in situ record of subduction initiation. International Ocean Discovery Program (IODP) Expedition 352 travelled to the Bonin forearc in 2014 recovered two main rock types from four drill sites: fore-arc basalts (FABs) and boninites. FABs are MORB-like with no evidence of subduction-inputs, and are therefore connected to the onset of subduction (Reagan *et al.* 2015, 2017; Li *et al.* 2019; Shervais *et al.* 2019). Whereas boninites show clear chemical evidence of subduction-related inputs (Reagan *et al.* 2015, 2017; Li *et al.* 2019; Shervais *et al.* 2021). The IODP Expedition 352 rocks erupted in a seafloor spreading setting, and therefore allow the processes involved in the earliest stages of subduction to be examined without the interference of magma

transport and evolution through overlying crust. Chapters four, five, and six measure the Fe-Zn-V-Ti stable isotopic compositions of Expedition 352 FABs and boninites to investigate important questions about subduction processes.

The Fe isotopic composition of global arc lavas is consistently lighter than MORB (e.g. Dauphas *et al.* 2009; Nebel *et al.* 2015; Foden *et al.* 2018; Williams *et al.* 2018). However, there is little consensus as to whether the responsible fractionation mechanisms are related to magmatic processes such as partial melting and multiple episodes of melt extraction, or subduction-related processes such as the involvement of potentially oxidising subduction-derived fluids, melts, and sediments. Chapter four therefore measures $\delta^{56}\text{Fe}$ in IODP Expedition 352 fore-arc basalts (FABs) and boninites and ODP Leg 125 harzburgites and dunites from the Bonin forearc to determine the dominant cause of the light $\delta^{56}\text{Fe}$ of arc lavas. Chapter four aims to answer the following questions:

1. Are IODP Expedition 352 fore-arc basalt and boninite $\delta^{56}\text{Fe}$ compositions isotopically distinct, and are the boninites as isotopically light as global arc lavas?
2. Does the addition of slab melts, fluids or sediments influence the Fe isotopic composition of boninites?
3. Can magmatic processes such as prior source depletion and/or partial melting account for the full range of Fe isotopic compositions in subduction-related lavas?

Chapter five expands on Chapter four and examines whether Zn isotopes may be an effective tracer of subduction-derived melts and fluids through subduction zones and the mantle wedge. Recent $\delta^{66}\text{Zn}$ studies have suggested that Zn isotopes can be mobilised and fractionated by hypersaline, carbonate, and/or sulphate subduction-related fluids that preferentially complex with heavy Zn isotopes (e.g. Fujii *et al.* 2014; Ducher *et al.* 2016; Liu *et al.* 2016; Pons *et al.* 2016; Debret *et al.* 2018, 2021). However, there is debated as to whether the Zn budget of subduction fluids is sufficient for such mobilisation and fractionation to be observed in arc lava $\delta^{66}\text{Zn}$. Since the IODP Expedition 352 FABs show no evidence of subduction components, and the boninites do, Chapter five measures their Zn isotopic compositions to address whether subduction-related fluids are identifiable in arc lava $\delta^{66}\text{Zn}$ compositions. Chapter five therefore aims to answer the following questions:

1. Are IODP Expedition 352 fore-arc basalt and boninite $\delta^{66}\text{Zn}$ compositions isotopically distinct?
2. Does the addition of slab melts, fluids or sediments influence the Zn isotopic composition of boninites?

3. What process(es) are responsible for internal FAB and boninite $\delta^{66}\text{Zn}$ variation?

Oxygen fugacity exerts control on phase stability and element speciation and mobility. Therefore, the $f\text{O}_2$ of the mantle wedge, subduction fluids, and arc lava sources are important to understand. Since arc lavas have components of hydrous, altered oceanic crust and sediments and fluids from subducted slabs, they should be more oxidised than MORBs that form by anhydrous decompression melting. However, this is an active area of debate. Chapter six uses the Expedition 352 FABs and boninites to investigate whether V and Ti stable isotopes could be used to trace the $f\text{O}_2$ of arc sources, and aims to answer the following questions:

1. Are IODP Expedition 352 FAB and MORB $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ distinct?
2. Are IODP Expedition 352 FAB and boninite $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ distinct?
3. Can differences in source $f\text{O}_2$ between FAB and boninites influence V and Ti isotopic compositions?

1.4.4. Chapter Seven

The overall conclusions from Chapters three, four, five, and six will be summarised in Chapter seven, in addition to suggestions for future avenues of transition metal stable isotope research in high-temperature igneous settings.

References

- Ahrens, L.H. 1952. The use of ionization potentials Part 1. Ionic radii of the elements. *Geochimica et Cosmochimica Acta*, **2** (3), 155-169, [https://doi.org/10.1016/0016-7037\(52\)90004-5](https://doi.org/10.1016/0016-7037(52)90004-5).
- Archer, C., Andersen, M.B., Cloquet, C., Conway, T.M., Dong, S., Ellwood, M., Moore, R., Nelson, J., Rehkamper, M., Rouxel, O., Samanta, M., Shin, K.C., Sohrin, Y., Takano, S. & Wasylenski, L. 2017. Inter-calibration of a proposed new primary reference standard AA-ETH Zn for zinc isotopic analysis. *Journal of Analytical Atomic Spectrometry*, **32**, 415–419, <https://doi.org/10.1039/c6ja00282j>.
- Beard, B.L. & Johnson, C.M. 1999. High precision iron isotope measurements of terrestrial and lunar materials. *Geochimica et Cosmochimica Acta*, **63**, 1653–1660, [https://doi.org/10.1016/S0016-7037\(99\)00089-7](https://doi.org/10.1016/S0016-7037(99)00089-7).
- Beard, B.L. & Johnson, C.M. 2004. Inter-mineral Fe isotope variations in mantle-derived rocks and implications for the Fe geochemical cycle. *Geochimica et Cosmochimica Acta*, **68**, 4727–4743, <https://doi.org/10.1016/j.gca.2004.04.023>.
- Bentahila, Y., Othman, D. Ben & Luck, J. 2008. Strontium, lead and zinc isotopes in marine cores as tracers of sedimentary provenance: A case study around Taiwan orogen. *Chemical Geology*, **248**, 62–82, <https://doi.org/10.1016/j.chemgeo.2007.10.024>.

- Beunon, H., Mattielli, N., Doucet, L.S., Moine, B. & Debret, B. 2020. Mantle heterogeneity through Zn systematics in oceanic basalts: Evidence for a deep carbon cycling. *Earth-Science Reviews*, **205**, 103174, <https://doi.org/10.1016/j.earscirev.2020.103174>.
- Bigeleisen, J. & Mayer, G.M. 1947. Calculation of Equilibrium Constants for Isotopic Exchange Reactions. *Journal of Chemical Physics*, **15**, 261–267.
- Blanchard, M., Balan, E. & Schauble, E.A. 2017. Equilibrium fractionation of non-traditional isotopes: A molecular modeling perspective. *Non-Traditional Stable Isotopes*, **82**, 27–64, <https://doi.org/10.2138/rmg.2017.82.2>.
- Brounce, M.N., Kelley, K.A. & Cottrell, E. 2014. Variations in Fe³⁺/PFe of Mariana Arc Basalts and Mantle Wedge fO₂. *Journal of Petrology*, **55**, 2514–2536, <https://doi.org/10.1093/petrology/egu065>.
- Canil, D. 1997. Vanadium partitioning and the oxidation state of Archaean komatiite magmas. *Nature*, **389**, 842–845, <https://doi.org/10.1038/39860>.
- Chen, H., Savage, P.S., Teng, F.Z., Helz, R.T. & Moynier, F. 2013. Zinc isotope fractionation during magmatic differentiation and the isotopic composition of the bulk Earth. *Earth and Planetary Science Letters*, **369–370**, 34–42, <https://doi.org/10.1016/j.epsl.2013.02.037>.
- Chen, S., Niu, Y., Guo, P., Gong, H., Sun, P., Xue, Q., Duan, M. & Wang, X. 2019. Iron isotope fractionation during mid-ocean ridge basalt (MORB) evolution: Evidence from lavas on the East Pacific Rise at 10°30'N and its implications. *Geochimica et Cosmochimica Acta*, **267**, 227–239, <https://doi.org/10.1016/j.gca.2019.09.031>.
- Craddock, P.R., Warren, J.M. & Dauphas, N. 2013. Abyssal peridotites reveal the near-chondritic Fe isotopic composition of the Earth. *Earth and Planetary Science Letters*, **365**, 63–76, <https://doi.org/10.1016/j.epsl.2013.01.011>.
- Dauphas, N., Craddock, P.R., Asimow, P.D., Bennett, V.C., Nutman, A.P. & Ohnenstetter, D. 2009. Iron isotopes may reveal the redox conditions of mantle melting from Archean to Present. *Earth and Planetary Science Letters*, **288**, 255–267, <https://doi.org/10.1016/j.epsl.2009.09.029>.
- Dawson, J.B. 1984. Contrasting types of upper mantle metasomatism. In: Kornprobst, J. (Ed.) *Kimberlites II: the mantle and crust-mantle relationships*, Elsevier, Amsterdam, 289–294, <https://doi.org/10.1016/B978-0-444-42274-3.50030-5>.
- Debret, B., Millet, M.A., Pons, M.L., Bouilhol, P., Inglis, E. & Williams, H. 2016. Isotopic evidence for iron mobility during subduction. *Geology*, **44**, 215–218, <https://doi.org/10.1130/G37565.1>.
- Debret, B., Bouilhol, P., Pons, M.L. & Williams, H. 2018. Carbonate transfer during the onset of slab devolatilization: New insights from Fe and Zn stable isotopes. *Journal of Petrology*, **59**, 1145–1166, <https://doi.org/10.1093/petrology/egy057>.
- Debret, B., Reekie, C.D.J., Mattielli, N., Beunon, H., Ménez, B., Savov, I. & Williams, H.M. 2020. Redox transfer at subduction zones: insights from Fe isotopes in the Mariana forearc. *Geochemical Perspectives Letters*, **12**, 46–51, <https://doi.org/10.7185/geochemlet.2003>.
- Debret, B., Garrido, C.J., Pons, M.L., Bouilhol, P., Inglis, E., López Sánchez-Vizcaíno, V. & Williams, H. 2021. Iron and zinc stable isotope evidence for open-system high-pressure dehydration of antigorite serpentinite in subduction zones. *Geochimica et Cosmochimica Acta*, **296**, 210–225, <https://doi.org/10.1016/j.gca.2020.12.001>.
- Deng, Z., Moynier, F., Sossi, P.A. & Chaussidon, M. 2018. Bridging the depleted morb mantle and

- the continental crust using titanium isotopes. *Geochemical Perspectives Letters*, **9**, 11–15, <https://doi.org/10.7185/geochemlet.1831>.
- Deng, Z., Chaussidon, M., Savage, P., Robert, F., Pik, R. & Moynier, F. 2019. Titanium isotopes as a tracer for the plume or island arc affinity of felsic rocks. *Proceedings of the National Academy of Sciences of the United States of America*, **116**, 1132–1135, <https://doi.org/10.1073/pnas.1809164116>.
- Ding, X., Helz, R.T., Qi, Y. & Huang, F. 2020. Vanadium isotope fractionation during differentiation of Kilauea Iki lava lake, Hawaii. *Geochimica et Cosmochimica Acta*, **289**, 114–129, <https://doi.org/10.1016/j.gca.2020.08.023>.
- Doucet, L.S., Mattielli, N., Ionov, D.A., Debouge, W. & Golovin, A. V. 2016. Zn isotopic heterogeneity in the mantle: A melting control? *Earth and Planetary Science Letters*, **451**, 232–240, <https://doi.org/10.1016/j.epsl.2016.06.040>.
- Ducher, M., Blanchard, M. & Balan, E. 2016. Equilibrium zinc isotope fractionation in Zn-bearing minerals from first-principles calculations. *Chemical Geology*, **443**, 87–96, <https://doi.org/10.1016/j.chemgeo.2016.09.016>.
- Evans, K.A. 2012. The redox budget of subduction zones. *Earth-Science Reviews*, **113**, 11–32, <https://doi.org/10.1016/j.earscirev.2012.03.003>.
- Evans, K.A. & Tomkins, A.G. 2011. The relationship between subduction zone redox budget and arc magma fertility. *Earth and Planetary Science Letters*, **308**, 401–409, <https://doi.org/10.1016/j.epsl.2011.06.009>.
- Farges, F., Brown, G.E. & Rehr, J.J. 1996. Coordination chemistry of Ti(IV) in silicate glasses and melts: I. XAFS study of titanium coordination in oxide model compounds. *Geochimica et Cosmochimica Acta*, **60**, 3023–3038, [https://doi.org/10.1016/0016-7037\(96\)00144-5](https://doi.org/10.1016/0016-7037(96)00144-5).
- Foden, J., Sossi, P.A. & Nebel, O. 2018. Controls on the iron isotopic composition of global arc magmas. *Earth and Planetary Science Letters*, **494**, 190–201, <https://doi.org/10.1016/j.epsl.2018.04.039>.
- Fujii, T. & Albarède, F. 2012. Ab initio calculation of the Zn isotope effect in phosphates, citrates, and malates and applications to plants and soil. *PLoS ONE*, **7**, 0–4, <https://doi.org/10.1371/journal.pone.0030726>.
- Fujii, T., Moynier, F., Pons, M.L. & Albarède, F. 2011. The origin of Zn isotope fractionation in sulfides. *Geochimica et Cosmochimica Acta*, **75**, 7632–7643, <https://doi.org/10.1016/j.gca.2011.09.036>.
- Fujii, T., Moynier, F., Blichert-Toft, J. & Albarède, F. 2014. Density functional theory estimation of isotope fractionation of Fe, Ni, Cu, and Zn among species relevant to geochemical and biological environments. *Geochimica et Cosmochimica Acta*, **140**, 553–576, <https://doi.org/10.1016/j.gca.2014.05.051>.
- Goldschmidt, V.M. 1922. On the metasomatic process in silicate rocks: *Economic Geology*, **17**, 105–123.
- Greber, N.D., Dauphas, N., Puchtel, I.S., Hofmann, B.A. & Arndt, N.T. 2017. Titanium stable isotopic variations in chondrites, achondrites and lunar rocks. *Geochimica et Cosmochimica Acta*, **213**, 534–552, <https://doi.org/10.1016/j.gca.2017.06.033>.
- Halliday, A.N., Lee, D.C., Christensen, J.N., Walder, A.J., Freedman, P.A., Jones, C.E., Hall, C.M., Yi, W. & Teagle, D. 1995. Recent developments in inductively coupled plasma magnetic sector

- multiple collector mass spectrometry. *International Journal of Mass Spectrometry and Ion Processes*, **146–147**, 21–33, [https://doi.org/10.1016/0168-1176\(95\)04200-5](https://doi.org/10.1016/0168-1176(95)04200-5).
- Halliday, A.N., Lee, D.C., Christensen, J.N., Rehkamper, ., Yi, W., Luo, X., Hall, C.M., Ballentine, C.J., Pettke, T. & Stirling, C. 1998. Applications of multiple collector-ICPMS to cosmochemistry, geochemistry, and paleoceanography. *Geochimica et Cosmochimica Acta*, **62**, 919–940, [https://doi.org/10.1016/S0016-7037\(98\)00057-X](https://doi.org/10.1016/S0016-7037(98)00057-X).
- Harte, B. 1983. Mantle peridotites and processes: the kimberlite sample. In: Hawkesworth, C.J., Norry, M.J. (Eds.) *Continental basalts and their xenoliths*, Shiva, Nantwich, 46-91.
- Herzog, G.F., Moynier, F., Albarède, F. & Berezhnoy, A.A. 2009. Isotopic and elemental abundances of copper and zinc in lunar samples, Zagami, Pele's hairs, and a terrestrial basalt. *Geochimica et Cosmochimica Acta*, **73**, 5884–5904, <https://doi.org/10.1016/j.gca.2009.05.067>.
- Hibbert, K.E.J., Williams, H.M., Kerr, A.C. & Puchtel, I.S. 2012. Iron isotopes in ancient and modern komatiites: Evidence in support of an oxidised mantle from Archean to present. *Earth and Planetary Science Letters*, **321–322**, 198–207, <https://doi.org/10.1016/j.epsl.2012.01.011>.
- Hoare, L., Klaver, M., Saji, N.S., Gillies, J., Parkinson, I.J., Lissenberg, C.J. & Millet, M.A. 2020. Melt chemistry and redox conditions control titanium isotope fractionation during magmatic differentiation. *Geochimica et Cosmochimica Acta*, **282**, 38–54, <https://doi.org/10.1016/j.gca.2020.05.015>.
- Hopkins, S.S., Prytulak, J., Barling, J., Russell, S.S., Coles, B.J. & Halliday, A.N. 2019. The vanadium isotopic composition of lunar basalts. *Earth and Planetary Science Letters*, **511**, 12–24, <https://doi.org/10.1016/j.epsl.2019.01.008>.
- Huang, F., Zhang, Z., Lundstrom, C.C. & Zhi, X. 2011. Iron and magnesium isotopic compositions of peridotite xenoliths from Eastern China. *Geochimica et Cosmochimica Acta*, **75**, 3318–3334, <https://doi.org/10.1016/j.gca.2011.03.036>.
- Huang, J., Liu, S.A., Gao, Y., Xiao, Y. & Chen, S. 2016. Copper and zinc isotope systematics of altered oceanic crust at IODP Site 1256 in the eastern equatorial Pacific. *Journal of Geophysical Research: Solid Earth*, **121**, 7086–7100, <https://doi.org/10.1002/2015JB012608>.
- Huang, J., Chen, S., Zhang, X.C. & Huang, F. 2018a. Effects of Melt Percolation on Zn Isotope Heterogeneity in the Mantle: Constraints From Peridotite Massifs in Ivrea-Verbano Zone, Italian Alps. *Journal of Geophysical Research: Solid Earth*, **123**, 2706–2722, <https://doi.org/10.1002/2017JB015287>.
- Huang, J., Zhang, X.C., Chen, S., Tang, L., Wörner, G., Yu, H. & Huang, F. 2018b. Zinc isotopic systematics of Kamchatka-Aleutian arc magmas controlled by mantle melting. *Geochimica et Cosmochimica Acta*, **238**, 85–101, <https://doi.org/10.1016/j.gca.2018.07.012>.
- Inglis, E., Debret, B., Burton, K.W., Millet, M.A., Pons, M-L., Dale, C.W., Bouilhol, P., Cooper, M., Nowell, G.M., McCoy-West, A.J. & Williams, H.M. 2017. The behavior of iron and zinc stable isotopes accompanying the subduction of mafic oceanic crust: A case study from Western Alpine ophiolites. *Geochemistry Geophysics Geosystems*, **18**, 2562–2579, <https://doi.org/10.1002/2016GC006735>.
- Johnson, A.C., Aarons, S.M., Dauphas, N., Nie, N.X., Zeng, H., Helz, R.T., Romaniello, S.J. & Anbar, A.D. 2019. Titanium isotopic fractionation in Kilauea Iki lava lake driven by oxide crystallization. *Geochimica et Cosmochimica Acta*, **264**, 180–190, <https://doi.org/10.1016/j.gca.2019.08.022>.
- Johnson, C.M. & Beard, B.L. 1999. Correction of instrumentally produced mass fractionation during

- isotopic analysis of Fe by thermal ionization mass spectrometry. *International Journal of Mass Spectrometry*, **193**, 87–99, [https://doi.org/10.1016/S1387-3806\(99\)00158-X](https://doi.org/10.1016/S1387-3806(99)00158-X).
- Karner, J., Papike, J.J. & Shearer, C.K. 2006. Comparative planetary mineralogy: Pyroxene major- and minor-element chemistry and partitioning of vanadium between pyroxene and melt in planetary basalts. *American Mineralogist*, **91**, 1574–1582, <https://doi.org/10.2138/am.2006.2103>.
- Kelley, K.A. & Cottrell, E. 2009. Water and the oxidation state of subduction zone magmas. *Science*, **325**, 605–607, <https://doi.org/10.1126/science.1174156>.
- Kelley, K.A. & Cottrell, E. 2012. The influence of magmatic differentiation on the oxidation state of Fe in a basaltic arc magma. *Earth and Planetary Science Letters*, **329**, 109–121, <https://doi.org/10.1016/j.epsl.2012.02.010>.
- Kieffer, S.W. 1982. Thermodynamics and lattice vibrations of minerals: 5. Applications to phase equilibria, isotopic fractionation, and high-pressure thermodynamic properties. *Reviews of Geophysics and Space Physics*, **20**, 827–849, <https://doi.org/10.1029/RG020i004p00827>.
- Korzhinski, D.A. 1965. The theory of systems with perfectly mobile components and processes of mineral formation. *American Journal of Science*, **263**, 193–205, <https://doi.org/10.2475/ajs.263.3.193>.
- Korzhinski, D.S. 1936. Mobility and inertness of components in metasomatism: *Izv Akad Nauk SSSR Ser Geol*, **1**, 58–60.
- Lee, C.T.A., Brandon, A.D. & Norman, M. 2003. Vanadium in peridotites as a proxy for paleo-fO₂ during partial melting: Prospects, limitations, and implications. *Geochimica et Cosmochimica Acta*, **67**, 3045–3064, [https://doi.org/10.1016/S0016-7037\(00\)00268-0](https://doi.org/10.1016/S0016-7037(00)00268-0).
- Lee, C.T.A., Leeman, W.P., Canil, D. & Li, Z.X.A. 2005. Similar V/Sc systematics in MORB and arc basalts: Implications for the oxygen fugacities of their mantle source regions. *Journal of Petrology*, **46**, 2313–2336, <https://doi.org/10.1093/petrology/egi056>.
- Lee, C.T.A., Luffi, P., Le Roux, V., Dasgupta, R., Albarède, F. & Leeman, W.P. 2010. The redox state of arc mantle using Zn/Fe systematics. *Nature*, **468**, 681–685, <https://doi.org/10.1038/nature09617>.
- Li, Z.X.A. & Lee, C.T.A. 2004. The constancy of upper mantle fO₂ through time inferred from V/Sc ratios in basalts. *Earth and Planetary Science Letters*, **228**, 483–493, <https://doi.org/10.1016/j.epsl.2004.10.006>.
- Li, H.Y., Taylor, R.N., Prytulak, J., Kirchenbaur, M., Shervais, J.W., Ryan, J.G., Godard, M., Reagan, M.K. & Pearce, J.A. 2019. Radiogenic isotopes document the start of subduction in the Western Pacific. *Earth and Planetary Science Letters*, **518**, 197–210, <https://doi.org/10.1016/j.epsl.2019.04.041>.
- Liao, R., Zhu, H., Deng, J., Zhang, L., Li, H. & Li, C. 2020. Zinc isotopic systematics of the South China Sea basalts and implications for its behavior during plate subduction. **541**, <https://doi.org/10.1016/j.chemgeo.2020.119582>.
- Lindemann, F.A. 1919. Note on the Vapour Pressure and Affinity of Isotopes. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, **38**, 173–181.
- Lindemann, F.A. & Aston, F.W. 1919. The Possibility of Separating Isotopes. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, **37**, 523–534, <https://doi.org/10.1080/14786440508635912>.

- Liu, S.A., Wang, Z.Z., Li, S.G., Huang, J. & Yang, W. 2016. Zinc isotope evidence for a large-scale carbonated mantle beneath eastern China. *Earth and Planetary Science Letters*, **444**, 169–178, <https://doi.org/10.1016/j.epsl.2016.03.051>.
- Lloyd, F.E. & Bailey, D.K. 1973. Light element metasomatism of the continental mantle: the evidence and the consequences: *Physics and Chemistry of the Earth*, **9**, 389–416, <https://doi.org/10.1016/B978-0-08-018017-5.50033-X>.
- Mallmann, G. & O'Neill, H.S.C. 2009. The crystal/melt partitioning of V during mantle melting as a function of oxygen fugacity compared with some other elements (Al, P, Ca, Sc, Ti, Cr, Fe, Ga, Y, Zr and Nb). *Journal of Petrology*, **50**, 1765–1794, <https://doi.org/10.1093/petrology/egp053>.
- Maréchal, C.N., Télouk, P. & Albarède, F. 1999. Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chemical Geology*, **156**, 251–273, [https://doi.org/10.1016/S0009-2541\(98\)00191-0](https://doi.org/10.1016/S0009-2541(98)00191-0).
- Maréchal, C.N., Nicolas, E., Douchet, C. & Albare, F. 2000. Abundance of zinc isotopes as a marine biogeochemical tracer. *Geochemistry, Geophysics, Geosystems*, **1**, 1–15, <https://doi.org/10.1029/1999GC000029>.
- McDonough, W.F. 2003. Compositional Model for the Earth's Core. In: Holland, H. D. & Turekian, K. K. (eds). *Treatise on Geochemistry*, **3**, 559–577, <https://doi.org/10.1016/B978-0-08-095975-7.00215-1>.
- Millet, M.A. & Dauphas, N. 2014. Ultra-precise titanium stable isotope measurements by double-spike high resolution MC-ICP-MS. *Journal of Analytical Atomic Spectrometry*, **29**, 1444–1458, <https://doi.org/10.1039/c4ja00096j>.
- Millet, M.A., Dauphas, N., Greber, N.D., Burton, K.W., Dale, C.W., Debret, B., Macpherson, C.G., Nowell, G.M. & Williams, H.M. 2016. Titanium stable isotope investigation of magmatic processes on the Earth and Moon. *Earth and Planetary Science Letters*, **449**, 197–205, <https://doi.org/10.1016/j.epsl.2016.05.039>.
- Moynier, F., Vance, D., Fujii, T. & Savage, P. 2017. The isotope geochemistry of zinc and copper. In: Teng, F. Z., Watkins, M. & Dauphas, N. (eds) *Reviews in Mineralogy & Geochemistry*, **82**, 543–600, <https://doi.org/10.2138/rmg.2017.82.13>.
- Nebel, O., Arculus, R.J., Sossi, P.A., Jenner, F.E. & Whan, T.H.E. 2013. Iron isotopic evidence for convective resurfacing of recycled arc-front mantle beneath back-arc basins. *Geophysical Research Letters*, **40**, 5849–5853, <https://doi.org/10.1002/2013GL057976>.
- Nebel, O., Sossi, P.A., Bénard, A., Wille, M., Vroon, P.Z. & Arculus, R.J. 2015. Redox-variability and controls in subduction zones from an iron-isotope perspective. *Earth and Planetary Science Letters*, **432**, 142–151, <https://doi.org/10.1016/j.epsl.2015.09.036>.
- Nielsen, S.G., Prytulak, J. & Halliday, A.N. 2011. Determination of Precise and Accurate 51V/50V Isotope Ratios by MC-ICP-MS, Part 1: Chemical Separation of Vanadium and Mass Spectrometric Protocols. *Geostandards and Geoanalytical Research*, **35**, 293–306, <https://doi.org/10.1111/j.1751-908X.2011.00106.x>.
- Nielsen, S.G., Auro, M., Richter, K., Davis, D., Prytulak, J., Wu, F. & Owens, J.D. 2019. Nucleosynthetic vanadium isotope heterogeneity of the early solar system recorded in chondritic meteorites. *Earth and Planetary Science Letters*, **505**, 131–140, <https://doi.org/10.1016/j.epsl.2018.10.029>.

- Nielsen, S.G., Bekaert, D. V., Magna, T., Mezger, K. & Auro, M. 2020. The vanadium isotope composition of Mars: implications for planetary differentiation in the early solar system. *Geochemical Perspectives Letters*, **15**, 35–39, <https://doi.org/10.7185/geochemlet.2032>.
- Novella, D., MacLennan, J., Shorttle, O., Prytulak, J. & Murton, B.J. 2020. A multi-proxy investigation of mantle oxygen fugacity along the Reykjanes Ridge. *Earth and Planetary Science Letters*, **531**, 115973, <https://doi.org/10.1016/j.epsl.2019.115973>.
- O'Reilly, S.Y. & Griffin, W.L. 2013. Mantle metasomatism. *In: Metasomatism and the chemical transformation of rock*, Springer, Berlin, Heidelberg, 471–533.
- Papike, J.J., Karner, J.M. & Shearer, C.K. 2005. Comparative planetary mineralogy: Valence state partitioning of Cr, Fe, Ti, and V among crystallographic sites in olivine, pyroxene, and spinel from planetary basalts. *American Mineralogist*, **90**, 277–290, <https://doi.org/10.2138/am.2005.1779>.
- Pauling, L. 1929. The Principles Determining the Structure of Complex Ionic Crystals. *Journal of the American Chemical Society*, **51**, 1010–1026.
- Pearce, J.A. & Peate, D.W. 1995. Tectonic Implications of the Composition of Volcanic Arc Magmas. *Annual Review of Earth and Planetary Sciences*, **23**, 251–285.
- Pichat, S., Douchet, C. & Albare, F. 2003. Zinc isotope variations in deep-sea carbonates from the eastern equatorial Pacific over the last 175 ka. *Earth and Planetary Science Letters*, **210**, 167–178, [https://doi.org/10.1016/S0012-821X\(03\)00106-7](https://doi.org/10.1016/S0012-821X(03)00106-7).
- Poitrasson, F. & Freydier, R. 2005. Heavy iron isotope composition of granites determined by high resolution MC-ICP-MS. *Chemical Geology*, **222**, 132–147, <https://doi.org/10.1016/j.chemgeo.2005.07.005>.
- Poitrasson, F., Halliday, A.N., Lee, D.C., Levasseur, S. & Teutsch, N. 2004. Iron isotope differences between Earth, Moon, Mars and Vesta as possible records of contrasted accretion mechanisms. *Earth and Planetary Science Letters*, **223**, 253–266, <https://doi.org/10.1016/j.epsl.2004.04.032>.
- Poitrasson, F., Delpech, G. & Grégoire, M. 2013. On the iron isotope heterogeneity of lithospheric mantle xenoliths: Implications for mantle metasomatism, the origin of basalts and the iron isotope composition of the Earth. *Contributions to Mineralogy and Petrology*, **165**, 1243–1258, <https://doi.org/10.1007/s00410-013-0856-7>.
- Pons, M.-L., Debret, B., Bouilhol, P., Delacour, A. & Williams, H. 2016. Zinc isotope evidence for sulfate-rich fluid transfer across subduction zones. *Nature Communications*, **7**, 13794, <https://doi.org/10.1038/ncomms13794>.
- Pons, M., Quitté, G., Fujii, T., Rosing, M.T., Reynard, B. & Moynier, F. 2011. Early Archean serpentine mud volcanoes at Isua, Greenland, as a niche for early life. **108**, 17639–17643, <https://doi.org/10.1073/pnas.1108061108>.
- Prytulak, J., Nielsen, S.G. & Halliday, A.N. 2011. Determination of Precise and Accurate 51V/50V Isotope Ratios by Multi-Collector ICP-MS, Part 2: Isotopic Composition of Six Reference Materials plus the Allende Chondrite and Verification Tests. *Geostandards and Geoanalytical Research*, **35**, 307–318, <https://doi.org/10.1111/j.1751-908X.2011.00105.x>.
- Prytulak, J., Nielsen, S.G., Ionov, D.A., Halliday, A.N., Harvey, J., Kelley, K.A., Niu, Y.L., Peate, D.W., Shimizu, K. & Sims, K.W.W. 2013. The stable vanadium isotope composition of the mantle and mafic lavas. *Earth and Planetary Science Letters*, **365**, 177–189, <https://doi.org/10.1016/j.epsl.2013.01.010>.

- Prytulak, J., Sossi, P.A., Halliday, A.N., Plank, T., Savage, P.S. & Woodhead, J.D. 2017. Stable vanadium isotopes as a redox proxy in magmatic systems? *Geochemical Perspectives Letters*, **3**, 75–84, <https://doi.org/10.7185/geochemlet.1708>.
- Qi, Y.H., Wu, F., Ionov, D.A., Puchtel, I.S., Carlson, R.W., Nicklas, R.W., Yu, H-M., Kang, J-T., Li, C-H. & Huang, F. 2019. Vanadium isotope composition of the Bulk Silicate Earth: Constraints from peridotites and komatiites. *Geochimica et Cosmochimica Acta*, **259**, 288–301, <https://doi.org/10.1016/j.gca.2019.06.008>.
- Rapp, J.F., Klemme, S., Butler, I.B. & Harley, S.L. 2010. Extremely high solubility of rutile in chloride and fluoride-bearing metamorphic fluids: An experimental investigation. *Geology*, **38**, 323–326, <https://doi.org/10.1130/G30753.1>.
- Reagan, M.K., Pearce, J.A., Petronotis, K., Almeev, R.R., Avery, A.J., Carvallo, C., Chapman, T., Christeson, G.L., Ferre, E.C., Godard, M., Heaton, D.E., Kirchenbaur, M., Kurz, W., Kutterolf, S., Li, H., Li, Y., Michibayashi, K., Morgan, S., Nelson, W.R., Prytulak, P., Python, M., Robertson, A.H.F., Ryan, J.G., Sager, W.W., Sakuyama, T., Shervais, J.W., Shimizu, K. & Whattam, S.A. 2015e. Expedition 352 summary. *Proceedings of the International Ocean Discovery Program*, **352**, <https://doi.org/10.14379/iodp.proc.352.101.2015>.
- Reagan, M.K., Pearce, J.A., Petronotis, K., Almeev, R.R., Avery, A.J., Carvallo, C., Chapman, T., Christeson, G.L., Ferre, E.C., Godard, M., Heaton, D.E., Kirchenbaur, M., Kurz, W., Kutterolf, S., Li, H., Li, Y., Michibayashi, K., Morgan, S., Nelson, W.R., Prytulak, P., Python, M., Robertson, A.H.F., Ryan, J.G., Sager, W.W., Sakuyama, T., Shervais, J.W., Shimizu, K. & Whattam, S.A. 2017. Subduction initiation and ophiolite crust: new insights from IODP drilling. *International Geology Review*, **59**, 1439–1450, <https://doi.org/10.1080/00206814.2016.1276482>.
- Schauble, E.A. 2004. Applying Stable Isotope Fractionation Theory to New Systems. *Reviews in Mineralogy & Geochemistry*, **55**, 65–111.
- Schoenberg, R. & von Blanckenburg, F. 2006. Modes of planetary-scale Fe isotope fractionation. *Earth and Planetary Science Letters*, **252**, 342–359, <https://doi.org/10.1016/j.epsl.2006.09.045>.
- Schuessler, J.A., Schoenberg, R. & Sigmarsson, O. 2009. Iron and lithium isotope systematics of the Hekla volcano, Iceland - Evidence for Fe isotope fractionation during magma differentiation. *Chemical Geology*, **258**, 78–91, <https://doi.org/10.1016/j.chemgeo.2008.06.021>.
- Shervais, J.W., Reagan, M., Haugen, E., Almeev, R.R., Pearce, J.A., Prytulak, J., Ryan, J.G., Whattam, S.A., Godard, M., Chapman, T., Li, H., Kurz, W., Nelson, W.R., Heaton, D., Kirchenbaur, M., Shimizu, K., Sakuyama, T., Li, Y. & Vetter, S.K. 2019. Magmatic Response to Subduction Initiation: Part 1. Fore-arc Basalts of the Izu-Bonin Arc From IODP Expedition 352. *Geochemistry, Geophysics, Geosystems*, **20**, 314–338, <https://doi.org/10.1029/2018GC007731>.
- Shervais, J.W., Reagan, M.K., Godard, M. & Prytulak, J. 2021. Magmatic Response to Subduction Initiation , Part II : Boninites and Related Rocks of the Izu-Bonin Arc From IODP Expedition 352 Geochemistry , Geophysics , Geosystems. *Geochemistry, Geophysics, Geosystems*, **22**, 1–34, <https://doi.org/10.1029/2020GC009093>.
- Siebert, J., Corgne, A. & Ryerson, F.J. 2011. Systematics of metal-silicate partitioning for many siderophile elements applied to Earth's core formation. *Geochimica et Cosmochimica Acta*, **75**, 1451–1489, <https://doi.org/10.1016/j.gca.2010.12.013>.

- Smyth, J.R. & Bish, D.L. 1988. Crystal Structures and Cation Sites of the Rock-Forming Minerals. *Boston, Allen and Unwin*, pp.332, <https://doi.org/10.5860/choice.26-0936>.
- Sossi, P.A. & O'Neill, H.S.C. 2017. The effect of bonding environment on iron isotope fractionation between minerals at high temperature. *Geochimica et Cosmochimica Acta*, **196**, 121–143, <https://doi.org/10.1016/j.gca.2016.09.017>.
- Sossi, P.A., Nebel, O. & Foden, J. 2016. Iron isotope systematics in planetary reservoirs. *Earth and Planetary Science Letters*, **452**, 295–308, <https://doi.org/10.1016/j.epsl.2016.07.032>.
- Sossi, P.A., Prytulak, J. & O'Neill, H.S.C. 2018a. Experimental calibration of vanadium partitioning and stable isotope fractionation between hydrous granitic melt and magnetite at 800 °C and 0.5 GPa. *Contributions to Mineralogy and Petrology*, **173**, 1451–1458, <https://doi.org/10.1007/s00410-018-1451-8>.
- Sossi, P.A., Nebel, O., St, H., Neill, C.O. & Moynier, F. 2018b. Zinc isotope composition of the Earth and its behaviour during planetary accretion. *Chemical Geology*, **477**, 73–84, <https://doi.org/10.1016/j.chemgeo.2017.12.006>.
- Sutton, S.R., Karner, J., Papike, J., Delaney, J.S., Shearer, C., Newville, M., Eng, P., Rivers, M. & Dyar, M.D. 2005. Vanadium K edge XANES of synthetic and natural basaltic glasses and application to microscale oxygen barometry. *Geochimica et Cosmochimica Acta*, **69**, 2333–2348, <https://doi.org/10.1016/j.gca.2004.10.013>.
- Teng, F.-Z., Dauphas, N. & Watkins, J.M. 2017. Non-Traditional Stable Isotopes: Retrospective and Prospective. *Reviews in Mineralogy & Geochemistry*, **82**, 1–26, <http://dx.doi.org/10.2138/rmg.2017.82.1>.
- Teng, F., Dauphas, N. & Helz, R.T. 2008. Iron Isotope Fractionation During Magmatic Differentiation in Kilauea Iki Lava Lake. *Science*, **320**, 1620–1622, <https://doi.org/10.1126/science.1157166>.
- Teng, F.Z., Dauphas, N., Helz, R.T., Gao, S. & Huang, S. 2011. Diffusion-driven magnesium and iron isotope fractionation in Hawaiian olivine. *Earth and Planetary Science Letters*, **308**, 317–324, <https://doi.org/10.1016/j.epsl.2011.06.003>.
- Teng, F.Z., Dauphas, N., Huang, S. & Marty, B. 2013. Iron isotopic systematics of oceanic basalts. *Geochimica et Cosmochimica Acta*, **107**, 12–26, <https://doi.org/10.1016/j.gca.2012.12.027>.
- Thompson, J. B., Jr. 1959. Local equilibrium in metasomatic processes: *Researches in geochemistry: John Wiley and Sons, Inc., New York*, p. 427–457.
- Toplis, M.J. & Carroll, M.R. 1995. An experimental study of the influence of oxygen fugacity on Fe-Ti oxide stability, phase relations, and mineral-melt equilibria in ferro-basaltic systems. *Journal of Petrology*, **36**, 1137–1170, <https://doi.org/10.1093/petrology/36.5.1137>.
- Toplis, M.J. & Carroll, M.R. 1996. Differentiation of ferro-basaltic magmas under conditions open and closed to oxygen: Implications for the skaergaard intrusion and other natural systems. *Journal of Petrology*, **37**, 837–858, <https://doi.org/10.1093/petrology/37.4.837>.
- Urey, H.C. 1947. The Thermodynamic Properties of Isotopic Substances. *Journal of the Chemical Society*, 562–581.
- Urey, H.C. & Greiff, L.J. 1935. Isotopic Exchange Equilibria. *Journal of the American Chemical Society*, **57**, 321–327, <https://doi.org/10.1021/ja01305a026>.
- Völkening, J. & Papanastassiou, D.A. 1989. Iron Isotope Anomalies. *The Astrophysical Journal*, **347**, 43–46.

- Wang, Z.Z., Liu, S.A., Liu, J., Huang, J., Xiao, Y., Chu, Z.Y., Zhao, X.M. & Tang, L. 2017. Zinc isotope fractionation during mantle melting and constraints on the Zn isotope composition of Earth's upper mantle. *Geochimica et Cosmochimica Acta*, **198**, 151–167, <https://doi.org/10.1016/j.gca.2016.11.014>.
- Weyer, S. & Ionov, D.A. 2007. Partial melting and melt percolation in the mantle: The message from Fe isotopes. *Earth and Planetary Science Letters*, **259**, 119–133, <https://doi.org/10.1016/j.epsl.2007.04.033>.
- Weyer, S. & Seitz, H.M. 2012. Coupled lithium and iron isotope fractionation during magmatic differentiation. *Chemical Geology*, **294**, 42–50, <https://doi.org/10.1016/j.chemgeo.2011.11.020>.
- Weyer, S., Anbar, A.D., Brey, G.P., Münker, C., Mezger, K. & Woodland, A.B. 2005. Iron isotope fractionation during planetary differentiation. *Earth and Planetary Science Letters*, **240**, 251–264, <https://doi.org/10.1016/j.epsl.2005.09.023>.
- Wilke, M. 2005. Fe in magma - An overview. *Annals of Geophysics*, **48**, 609–617.
- Williams, H.M. & Bizimis, M. 2014. Iron isotope tracing of mantle heterogeneity within the source regions of oceanic basalts. *Earth and Planetary Science Letters*, **404**, 396–407, <https://doi.org/10.1016/j.epsl.2014.07.033>.
- Williams, H.M., McCammon, C.A., Peslier, A.H., Halliday, A.N., Teutsch, N., Levasseur, S. & Burg, J.P. 2004. Iron isotope fractionation and the oxygen fugacity of the mantle. *Science*, **304**, 1656–1659, <https://doi.org/10.1126/science.1095679>.
- Williams, H.M., Peslier, A.H., McCammon, C., Halliday, A.N., Levasseur, S., Teutsch, N. & Burg, J.P. 2005. Systematic iron isotope variations in mantle rocks and minerals: The effects of partial melting and oxygen fugacity. *Earth and Planetary Science Letters*, **235**, 435–452, <https://doi.org/10.1016/j.epsl.2005.04.020>.
- Williams, H.M., Prytulak, J., Woodhead, J.D., Kelley, K.A., Brounce, M. & Plank, T. 2018. Interplay of crystal fractionation, sulfide saturation and oxygen fugacity on the iron isotope composition of arc lavas: An example from the Marianas. *Geochimica et Cosmochimica Acta*, **226**, 224–243, <https://doi.org/10.1016/j.gca.2018.02.008>.
- Wu, F., Qin, T., Li, X., Liu, Y., Huang, J.H., Wu, Z. & Huang, F. 2015. First-principles investigation of vanadium isotope fractionation in solution and during adsorption. *Earth and Planetary Science Letters*, **426**, 216–224, <https://doi.org/10.1016/j.epsl.2015.06.048>.
- Wu, F., Qi, Y., Yu, H., Tian, S., Hou, Z. & Huang, F. 2016. Vanadium isotope measurement by MC-ICP-MS. *Chemical Geology*, **421**, 17–25, <https://doi.org/10.1016/j.chemgeo.2015.11.027>.
- Wu, F., Qi, Y., Perfit, M.R., Gao, Y., Langmuir, C.H., Wanless, V.D., Yu, H. & Huang, F. 2018. Vanadium isotope compositions of mid-ocean ridge lavas and altered oceanic crust. *Earth and Planetary Science Letters*, **493**, 128–139, <https://doi.org/10.1016/j.epsl.2018.04.009>.
- Xue, Y., Li, C. hui, Qi, Y., Zhang, C., Miao, B. & Huang, F. 2018. The vanadium isotopic composition of L ordinary chondrites. *Acta Geochimica*, **37**, 501–508, <https://doi.org/10.1007/s11631-018-0279-2>.
- Young, E.D., Galy, A. & Nagahara, H. 2002. Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance. *Geochimica et Cosmochimica Acta*, **66**, 1095–1104, [https://doi.org/10.1016/S0016-7037\(01\)00832-8](https://doi.org/10.1016/S0016-7037(01)00832-8).

- Young, E.D., Tonui, E., Manning, C.E., Schauble, E. & Macris, C.A. 2009. Spinel-olivine magnesium isotope thermometry in the mantle and implications for the Mg isotopic composition of Earth. *Earth and Planetary Science Letters*, **288**, 524–533, <https://doi.org/10.1016/j.epsl.2009.10.014>.
- Young, E.D., Manning, C.E., Schauble, E.A., Shahar, A., Macris, C.A., Lazar, C. & Jordan, M. 2015. High-temperature equilibrium isotope fractionation of non-traditional stable isotopes: Experiments, theory, and applications. *Chemical Geology*, **395**, 176–195, <https://doi.org/10.1016/j.chemgeo.2014.12.013>.
- Zhao, X., Zhang, H., Zhu, X., Tang, S. & Tang, Y. 2010. Iron isotope variations in spinel peridotite xenoliths from North China Craton: Implications for mantle metasomatism. *Contributions to Mineralogy and Petrology*, **160**, 1–14, <https://doi.org/10.1007/s00410-009-0461-y>.
- Zhao, X., Zhang, H., Zhu, X., Tang, S. & Yan, B. 2012. Iron isotope evidence for multistage melt-peridotite interactions in the lithospheric mantle of eastern China. *Chemical Geology*, **292**, 127–139, <https://doi.org/10.1016/j.chemgeo.2011.11.016>.
- Zhao, X., Tang, S., Li, J., Wang, H., Helz, R., Marsh, B., Zhu, X. & Zhang, H. 2020. Titanium isotopic fractionation during magmatic differentiation. *Contributions to Mineralogy and Petrology*, **175**, 1–16, <https://doi.org/10.1007/s00410-020-01704-1>.
- Zhao, X.M., Zhang, H.F., Zhu, X.K., Zhu, B. & Cao, H. 2015. Effects of melt percolation on iron isotopic variation in peridotites from Yangyuan, North China Craton. *Chemical Geology*, **401**, 96–110, <https://doi.org/10.1016/j.chemgeo.2015.02.031>.
- Zhu, X.K., O’Nions, R.K., Guo, Y. & Reynolds, B.C. 2000. Secular variation of iron isotopes in North Atlantic Deep Water. *Science*, **287**, 2000–2002, <https://doi.org/10.1126/science.287.5460.2000>.
- Zhu, X.K., Guo, Y., Williams, R.J.P., O’Nions, R.K., Matthews, A., Belshaw, N.S., Canters, G.W., de Waal, E.C., Weser, U., Burgess, B.K. & Salvato, B. 2002. Mass fractionation processes of transition metal isotopes. *Earth and Planetary Science Letters*, **200**, 47–62, [https://doi.org/10.1016/S0012-821X\(02\)00615-5](https://doi.org/10.1016/S0012-821X(02)00615-5).

CHAPTER TWO

Methods

CHAPTER TWO TABLE OF CONTENTS

2.1. Introduction	31
2.2. Sample Digestion Procedures	31
2.2.1. Standard Hotplate Digestion Procedure	31
2.2.2. 'Bombing' Digestion Procedure	32
2.2.2.1. Imperial College London	32
2.2.2.2. Durham University	32
2.3. Ion Chromatography and Mass Spectrometry Procedures	32
2.3.1. Vanadium	32
2.3.1.1. Ion Chromatography	33
2.3.1.2. Mass Spectrometry	44
2.3.2. Zinc	51
2.3.2.1. Ion Chromatography	51
2.3.2.2. Resolving High Zinc Blanks	52
2.3.2.3. Mass Spectrometry (Neptune)	54
2.3.3. Iron	59
2.3.3.1. Ion Chromatography	59
2.3.3.2. Mass Spectrometry (Neptune)	61
2.3.4. Titanium	67
2.3.4.1. Titanium Double Spiking	67
2.3.4.2. Ion Chromatography	68
2.3.4.3. Mass Spectrometry (Nu Plasma II)	70
2.3.5. Hafnium	70
2.3.5.1. Ion Chromatography	70
2.3.5.2. Mass Spectrometry (Neptune)	75
2.4. Trace Elements	75
2.4.1. Sample Digestion and Dilution	76
2.4.2. ICP-QQQ-MS Measurement	76
References	77

2.1. Introduction

Chapter two outlines the methods used to analyse V, Fe, Zn, Ti and Hf isotope ratios throughout this thesis. It focuses on rock digestion, ion chromatography and mass spectrometry procedures used at Imperial College London, Cardiff University and Durham University. Ion chromatography and mass spectrometry methods are described system by system. Solution standard data, USGS reference materials and total procedural blanks are also presented to demonstrate measurement accuracy and precision. In addition, trace element analysis work conducted at the Open University is briefly outlined.

The following methods were chosen to minimise error and the sample mass required for each analysis, but also to maximise yields. The V isotope method evolved throughout this study. The changes were implemented to reduce costs and maximise the number of different isotope systems that could be obtained from a single digestion.

2.2. Sample Digestion Procedures

Two approaches to digesting rock samples were used: standard hotplate digestion and bomb-assisted digestion. The ‘bombing’ procedure was only used to digest samples with high modal abundances of refractory phases such as spinel, which can be significant sources of V, Fe, Zn and Ti, but hard to digest using standard, hotplate digestion techniques. These samples included peridotites and boninites. The standard hotplate procedure was used for all other sample types (i.e. silicate mineral separates and basalts). However, the procedure used at Imperial College London was slightly different to that at Durham University. All the acids used for both sample digestion procedures were TD grade.

2.2.1. Standard Hotplate Digestion Procedure

The maximum mass of powdered sample that could be easily digested in a single 22 ml Teflon beaker by a standard hotplate digestion was about 80 mg. 1 ml of ~16M HNO₃ and 3 ml of 29M 48% HF (volume varied upon sample mass) was added to a 22 ml Teflon beaker containing the weighed, powdered sample. This was sealed, and heated at 140°C on a hotplate for 3 days. After digestion, the acid was evaporated at < 140°C to incipient dryness (white, gel-like residue). Incipient dryness was necessary to minimise the formation of insoluble fluorides. The residue was repeatedly dissolved in small volumes of ~16M HNO₃ and evaporated at 180°C until the residue turned brownish. The colour change was used as a visual indicator of the destruction of fluorides from the initial HF digestion. Once the residues turned brownish, a few drops of 6M HCl was added and

evaporated at 130°C. Finally, once dry, 4 ml of 6M HCl was added, and the solution was sealed tightly and placed on a hotplate at < 130°C for at least 24 hours, after which the solution was visually checked to see if the sample had fully dissolved. If not, the procedure was repeated.

2.2.2. 'Bombing' Digestion Procedure

The maximum mass of powdered sample that could be easily digested in a single 3 ml volume Savillex Teflon hexagonal bomb by both the following bombing digestion techniques was about 40-50 mg.

2.2.2.1. Imperial College London

0.3 ml concentrated HNO₃ and 1.5 ml 48% HF was added to a Savillex bomb containing the powdered sample. The bombs were sealed, pressurised, wrapped in aluminium foil, and placed in an oven at 140°C for 3 to 4 days. Lower volumes of acid were used for this technique compared to the hotplate digestion, to allow room for expansion under the high pressure and temperature conditions. The process after digestion was the same as in the hotplate digestion procedure, only concentrated HNO₃ was added to the residue after the white, gel-like residue had turned brownish, and the subsequent solution from all bombs of the same sample was transferred into a 22 ml beaker.

2.2.2.2. Durham University

This procedure is the same as that used at Imperial College London, but rather than the bombs being placed in an oven, they were put on a hotplate with a heating inset, and then covered with a second inset to create an "oven". The temperature was also higher at 170°C.

2.3. Ion Chromatography and Mass Spectrometry Procedures

2.3.1. Vanadium

The analysis of V isotopes was undertaken at two institutions: Imperial College London (October 2017 to August 2018) and Durham University (September 2018 to March 2021). The ion chromatography procedure for V was long and traditionally used expensive TRU Spec resin (Nielsen *et al.* 2011). The TRU Spec procedure was used at Imperial College London, but altered based on Wu *et al.* (2016) to exclude TRU Spec resin at Durham University. Both procedures are outlined below.

2.3.1.1. Ion Chromatography

To prepare the samples for analysis, V needed to be separated from the sample matrix. The main purpose of separating V was to maximise the accuracy and precision of the MC-ICP MS measurements. To obtain accurate and precise isotope data, the chemical separation procedure also needed to achieve a 100% V yield (Nielsen *et al.* 2011), since incomplete elution can cause mass fractionation (e.g. Anbar *et al.* 2005; Chapman *et al.* 2006; Sossi *et al.* 2015). The V separation procedure also removed the atomic isobaric interferences on ^{50}V (^{50}Cr and ^{50}Ti).

Imperial College London Vanadium Ion Chromatography Procedure

The V separation procedure used at Imperial College London is outlined below (**Figure 2.1**) and based upon that outlined in Nielsen *et al.* (2011). It used anion exchange resins AG 1-X8 (200-400 mesh), and TRU Spec (50-100 μm mesh). The AG 1-X8 resin was pre-cleaned by repeated shaking and rinsing in MilliQ 10 times, then with alternating 6M HCl and MilliQ 10 times.

The removal of Fe and Ti occurred in stages 1 and 2 respectively. The separation of V from Cr occurred in the third stage of the procedure, because the use of HCl and H_2O_2 required Fe and Ti to be removed before Cr, since Fe is unstable in H_2O_2 , and Ti in HCl (Nielsen *et al.* 2011). Titanium is unstable in HCl because their interaction precipitates Ti-oxides which collect at the top of the resin, where it can elute, resulting in contamination of the V fraction (Kraus *et al.* 1954; Nielsen *et al.* 2011). The addition of Fe to H_2O_2 causes the formation of large quantities of oxygen, which creates bubbles in the resin, reducing elution rates and affecting elution profiles (Nielsen *et al.* 2011). This reaction also reduces the amount of V-peroxide formed during the process that separates V from Cr in the columns that use H_2O_2 , causing V to fall through the resin, and consequent V loss (Nielsen *et al.* 2011).

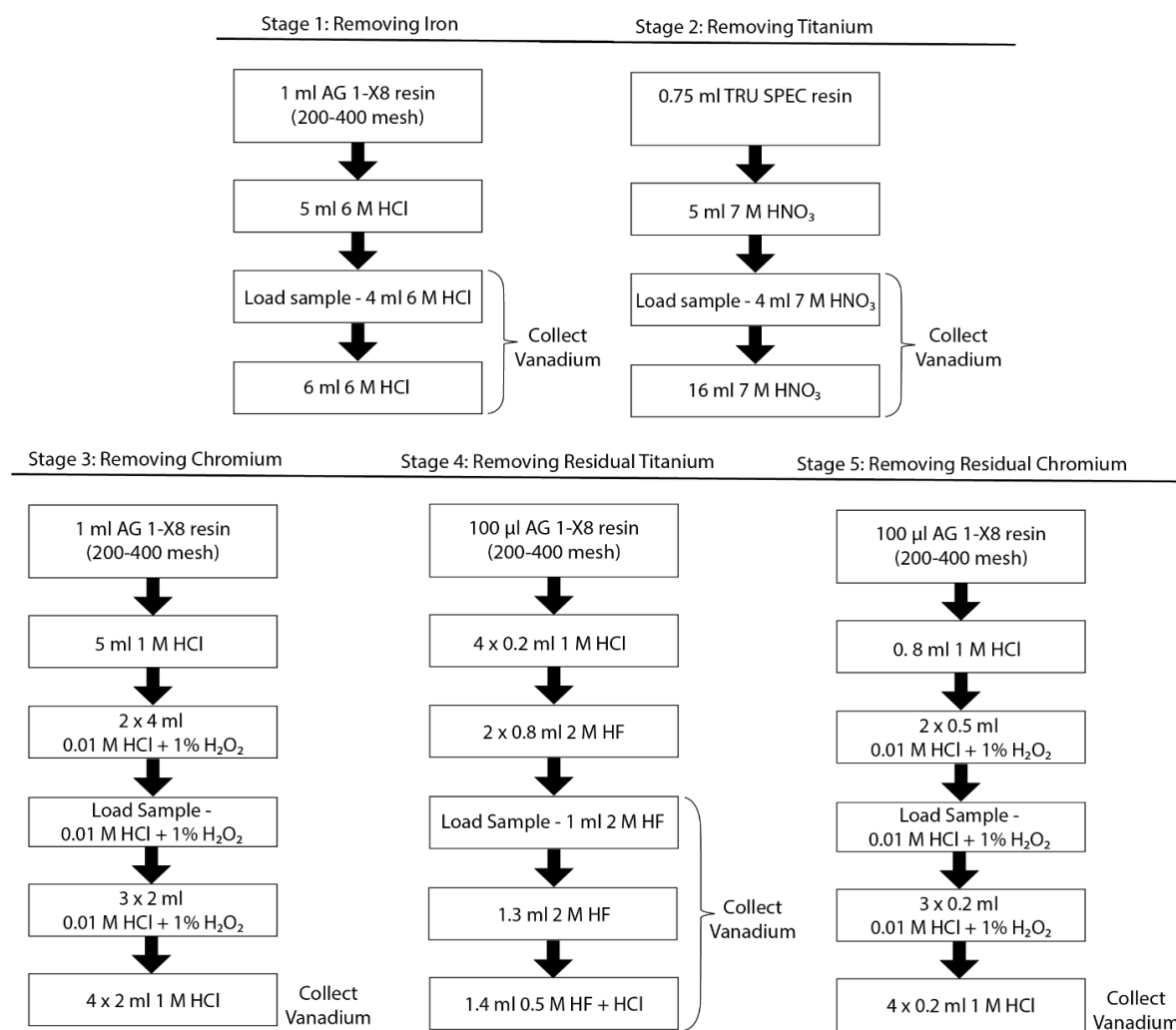


Figure 2.1: Summary of vanadium separation procedure as flow charts depicting the steps in the five different columns. Columns 1-3 use quartz columns with polyethylene frits and quartz wool. Columns 4 and 5 which are repeated once, use smaller Teflon columns with polyethylene frits. Modified from (Nielsen et al. (2011)).

Stage 1 - Removing Iron:

1 ml of AG 1-X8 200-400 mesh anion exchange resin was loaded into quartz glass columns (inner neck diameters 6-7 mm, and reservoir volumes approximately 23 cm³ or 98 cm³) with either polyethylene frits or quartz wool. The column used iron's strong partitioning onto the AG 1-X8 resin in the presence of 6M HCl (**Figure 2.2**) and V's lack of partitioning to eliminate Fe from the V cut. First, the columns were conditioned with 5 ml of 6M HCl, then the sample was loaded in 4 ml of 6M HCl, with clean 22 ml Savillex beakers beneath for immediate sample collection. Vanadium was then eluted with a further 6 ml of 6M HCl to ensure the entire sample solution had passed through the column. The collected fraction was evaporated at 130°C. ~1 ml of ~14M HNO₃ was added to remove any organics formed by partial dissolution of the resin, and evaporated at a hotplate set to

160°C. Then 4 ml 7M HNO_3 was added to the collected fraction, sealed, and placed on a hotplate set to $\sim 140^\circ\text{C}$ for at least 24 hours. This solution was then loaded onto the subsequent column.

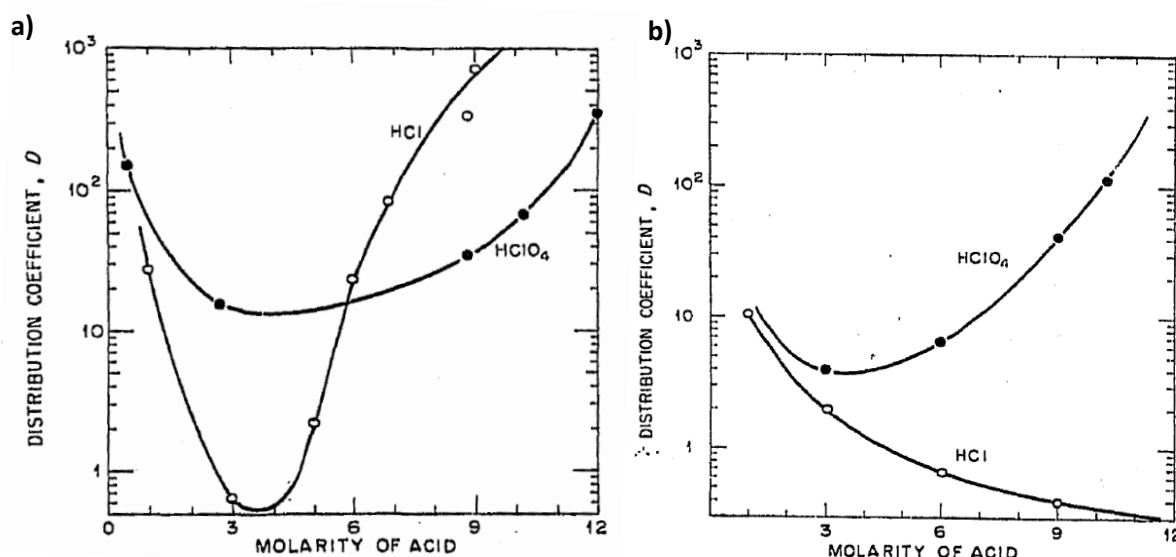


Figure 2.2: Adsorption of Fe(III) and V(IV). (a) adsorption of Fe(III) from HCl and HClO_4 solutions (Dowex 50- X_4 , 25°). (b) adsorption of V(IV) from HCl and HClO_4 solutions (Dowex 50- X_4 , 25°). From Nelson & Kraus (1979).

Stage 2 - Removing Titanium:

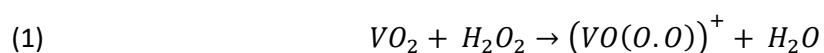
0.75 ml of Eichrom TRU Spec (50-100 μm mesh) anion exchange resin was loaded into columns of the same setup as used in the first stage. 7M HNO_3 was used throughout this stage since Ti strongly partitions onto this resin in the presence of HNO_3 , but V partitions very weakly. The column was conditioned with 5 ml of 7M HNO_3 . The 4 ml 7M HNO_3 sample solution was then loaded, and 22 ml Savillex collection beakers were placed below to collect immediately. The Ti-free V fraction was eluted in 16 ml of 7M HNO_3 and the collected solutions were evaporated on a hotplate set to $\sim 130^\circ\text{C}$, treated with concentrated HNO_3 , dried, and re-dissolved in 6M HCl.

The next separation stage required a loading solution with a pH of 2 (0.01M HCl). To reach this pH, the 6M HCl solution was evaporated, leaving the smallest volume of fluid possible in which the sample remained in solution. Water was then added to dilute the acid and the pH tested by pipetting 17 μl of sample onto pH paper.

Stage 3- Removing Chromium:

1 ml of the AG 1-X8 200-400 mesh anion exchange resin was added to the same column set up as the previous stages. The resin was conditioned with 5 ml of 1M HCl, to remove any potential V on the resin, and then with 8 ml of 0.01M HCl - 1% H_2O_2 . The H_2O_2 was stored in a dark, opaque bottle,

and refrigerated, to mitigate dissociation into water and oxygen, which is catalysed by light, heat, and transition metals. Before loading, 1% H_2O_2 was added to cool 0.01M HCl sample solutions. Vanadium complexes with H_2O_2 upon its addition, forming pale yellow diperoxy-orthovanadate ions ($VO_2(O.O)^+$) (Kakabadse & Wilson 1957), which stick to the resin, allowing all other elements to pass through, therefore isolating V. The matrix was eluted with 3 x 2 ml 0.01M HCl - 1% H_2O_2 , and then the V fraction was collected in 22 ml Savillex beakers with 4 x 2 ml 1M HCl. Depending on the concentration of V in the sample, a blood red colour change upon the addition of 1M HCl should be observed, with brighter red corresponding to higher sample V concentrations (**Figure 2.3**). Monoperoxy-pervanadyl ($VO(O.O))^+$ forms under acidic conditions, and creates the blood red colour (Kakabadse & Wilson 1957)) (eq. 1).



The collected V fraction was evaporated, and subsequently dissolved and evaporated in $\sim 14M$ HNO_3 on a hotplate set to $160^\circ C$. The residue was re-dissolved in 2M HF and evaporated, then 1 ml of 2M HF was added and the samples tightly capped and left on a hotplate set to $\sim 120^\circ C$ for at least 24 hours.

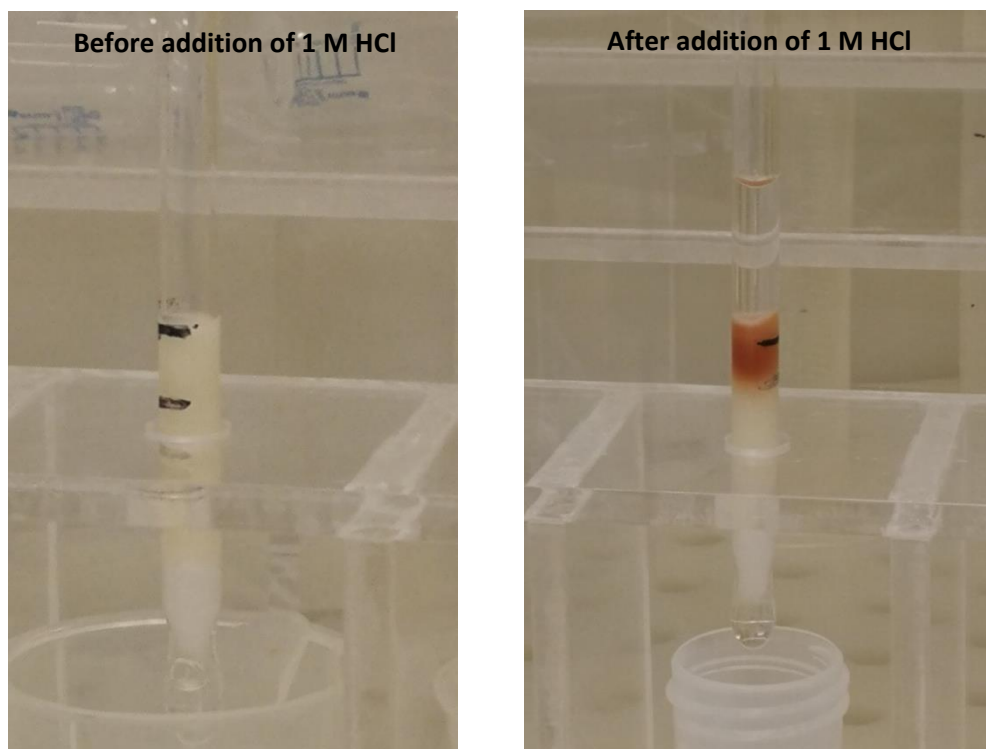


Figure 2.3: Photos taken during stage 3 of the vanadium separation procedure at Imperial College London showing the colour change to blood red that occurs upon the addition of 4 x 2 ml 1 M HCl.

Stages 4 & 5 - Removing Residual Titanium and Chromium:

Titanium and chromium have isobaric interferences on ^{50}V that require a mass resolution of ~ 21000 and ~ 44800 respectively to resolve. Since the MC-ICP-MS can only provide mass resolution up to ~ 10000 atomic interferences, Ti and Cr cannot be resolved from the analyte mass. It is therefore necessary to remove them prior to analysis and apply an algebraic correction for any residual interference. Therefore, two different “clean-up” columns were used to remove Cr and Ti as described in Nielsen *et al.* (2011). This coupled with the earlier stages achieves $^{53}\text{Cr}/^{51}\text{V}$ and $^{49}\text{Ti}/^{51}\text{V}$ ratios less than 0.00001 prior to analysis (Nielsen *et al.* 2011). Both ‘clean-up’ stages used heat-shrink Teflon columns loaded with 100 μl AG 1-X8 anion exchange resin (**Figure 2.4**). The Ti clean-up step was based on methods from Makishima *et al.* (2002) and Nielsen *et al.* (2011). It involved 2M HF and therefore could not be used for the separation of Ti from V in the second chemistry stage due to the presence of Mg and Ca that form insoluble fluorides with HF (Nielsen *et al.* 2011). The resin was conditioned with 0.8 ml of 1M HCl, and then with 1.6 ml of 2M HF. The sample was then loaded in 1 ml of 2M HF and immediately collected in 7 ml Savillex beakers. The V fraction was then eluted with 1.2 ml of 2M HF, and then with 1.4 ml of a 0.5M mixture of HF and HCl. The collected fraction was then evaporated and re-dissolved with $\sim 14\text{M}$ HNO_3 . This procedure was generally performed twice, but was performed more than twice for Ti-rich samples (e.g. oxides), and only once for Ti-poor samples (e.g. peridotites). The collected fraction was evaporated, and the residue re-dissolved with $\sim 14\text{M}$ HNO_3 and immediately evaporated on a hotplate set to $\sim 140^\circ\text{C}$. The sample was then taken up in 6M HCl, evaporated, and re-dissolved in 1 ml of 0.01M HCl, and sealed and placed on a hotplate set at 100°C for at least 24 hours.

The Cr clean-up step used the same columns, resin and resin volume as the Ti clean-up stage. The procedure was identical to the large-scale V separation using H_2O_2 , except scaled down for 100 μl of resin as described in Nielsen *et al.* (2011). Similar to the Ti clean-up, this column was performed only once for Cr-poor samples (e.g. evolved silicates), and 2-3 times for Cr-rich samples (e.g. peridotites, Cr-spinel).

Following sample purification, the solutions were evaporated and re-dissolved twice in $\sim 14\text{M}$ HNO_3 , then dissolved in 1 ml of 0.1M HNO_3 (Imperial – Nu-Plasma II) or 3% HNO_3 (Durham – Neptune) which was the loading solution for MC-ICP MS.

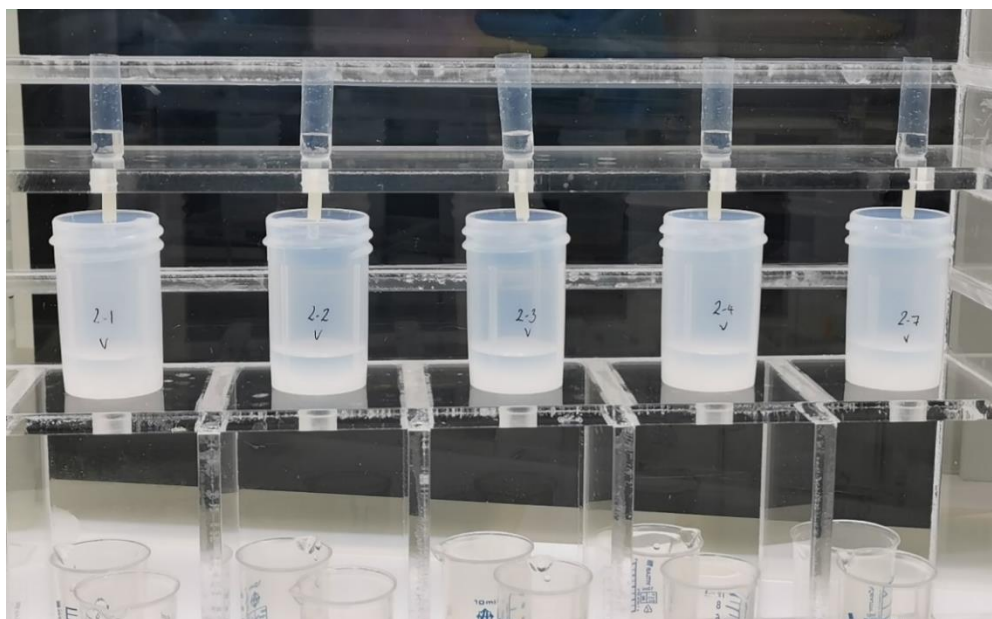


Figure 2.4: Photo of one of the clean-up column stages of the vanadium separation procedure at Durham University showing the set up. The photo was taken during collection of the V-cut.

Durham University Ion Chromatography Procedure

The V separation process used at Durham University is outlined below (**Figure 2.5**). Modifications were made to enable collection of Fe, Zn and V from the same digestion and to avoid using expensive TRU Spec resin (see below). The procedure combined methods from Sossi *et al.* (2015), Wu *et al.* (2016) and Nielsen *et al.* (2011). Excluding the first two stages, it was the same as the Imperial procedure. Stage one is outlined in the Zn section (3.2) and stage two is outlined below. It used AG 1-X8 anion exchange resin (200-400 mesh) and AG 50W-X12 cation-exchange resin (200-400 mesh).

The original V procedure of Nielsen *et al.* (2011) used TRU Spec resin which is very expensive, and the process of dissolving the sample in the loading solution for the third stage (0.01M HCl) is difficult and time consuming. The procedure outlined in Wu *et al.* (2016) replaced this column with a cation-exchange resin column. AG 50W-X12 (200-400 mesh) cation resin is cheaper than TRU Spec resin and following a column to remove Fe and Zn (see Fe and Zn sections), it is easy to dissolve the sample in 0.01M HCl. The cation column was carried out twice in Wu *et al.* (2016) to ensure all Ti was removed, and the second Ti 'clean-up' and Cr 'clean-up' columns from Nielsen *et al.* (2011) were removed. Since the Wu column takes around 7 hours compared to the Ti 'clean-up' column which takes around 3 hours, the Wu column was only done once, and one Ti 'clean-up' column and one Cr 'clean-up' column were trialled. However, the first batch of USGS standards had significant Cr and Ti concentrations well above the threshold $^{53}\text{Cr}/^{51}\text{V}$ and $^{49}\text{Ti}/^{51}\text{V}$ ratios of 0.00001 (Nielsen *et*

al. 2011). Therefore, all of the clean-up columns from the Imperial procedure were introduced to the Durham procedure.

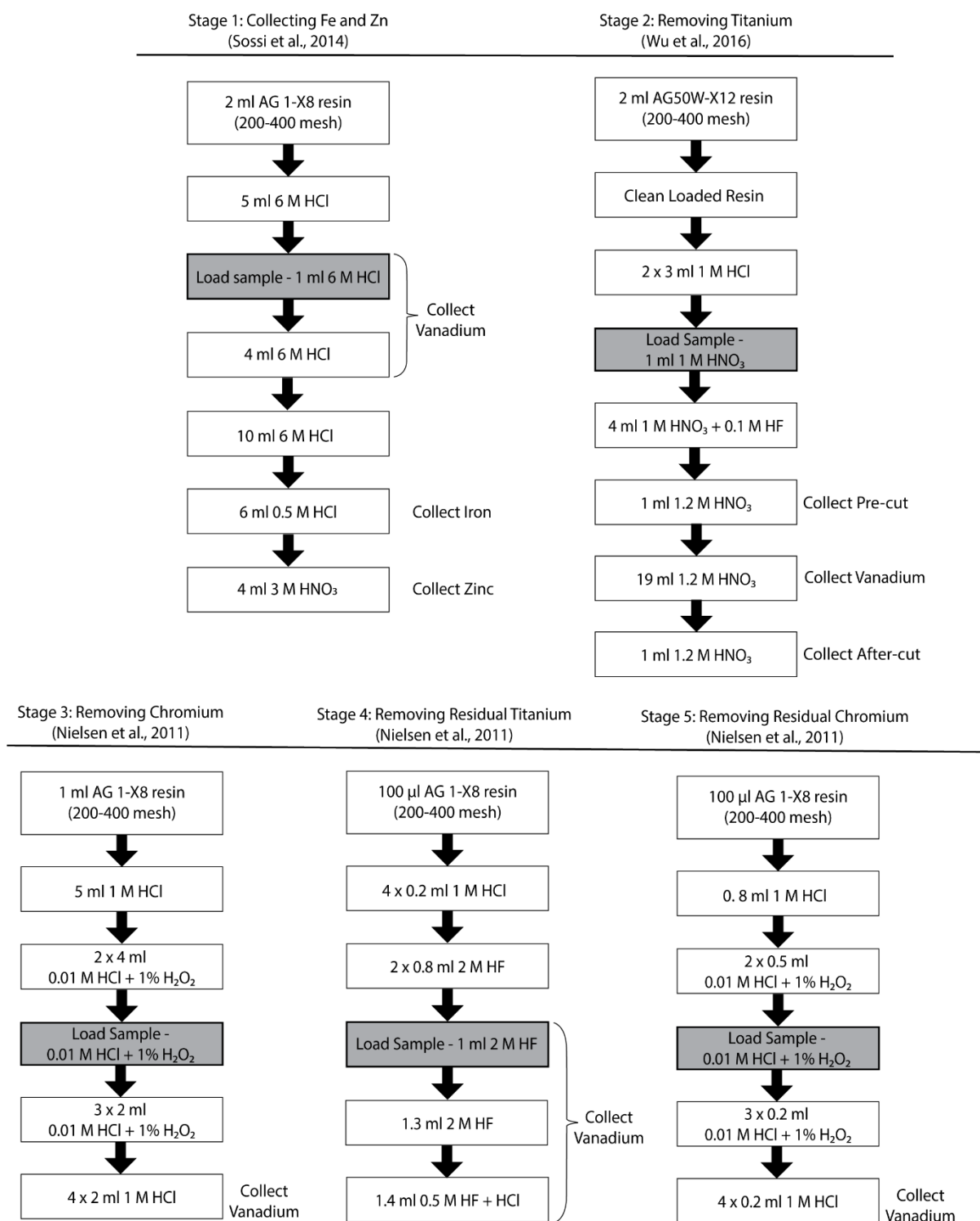


Figure 2.5: Summary flow charts of the Durham University vanadium separation procedure depicting the steps in the five different columns used. Stages 1 and 2 use Teflon columns with polyethylene frits. Stage 3 uses quartz columns with polyethylene frits and quartz wool. Stages 4 and 5 which are repeated, use smaller Teflon columns with polyethylene frits.

Stage 2: Removing Titanium (based on Wu *et al.* (2016))

The AG 50W-X12 resin was cleaned prior to the first use. The resin was cleaned by rinsing and shaking with MilliQ 10 times, then with alternating 6M HCl and MilliQ 10 times, and then alternating 1M HNO₃ and MilliQ 10 times. Savillex Teflon columns (**Figure 2.6**) with an inner diameter of 6.4 mm and a 30ml reservoir volume were used. 2 ml of AG 50W-X12 resin was added to each column, and then conditioned with 5ml of 6M HCl, 4 ml of MQ and 6 ml of 1M HNO₃ respectively. The sample was then loaded onto the resin in 1 ml of 1M HNO₃, and Ti and Al were eluted by adding 4 ml of 1M HNO₃ - 0.1M HF. Vanadium was collected by adding 19 ml of 1.2M HNO₃ (acid titrated to ensure correct molarity). Since this column uses a cation resin, the elution occurs over an elution curve (**Figure 2.7**). The aspect ratio of the columns used in this work was different to those used in Wu *et al.* (2016) and therefore a 1 ml fraction after the main V collection was taken to test for any V loss due to movement in the curve. In all cases, less than 2 ng of V was found in the after cuts from the procedure, which was less than 0.0013 % of the total V processed (**Table 2.1**).

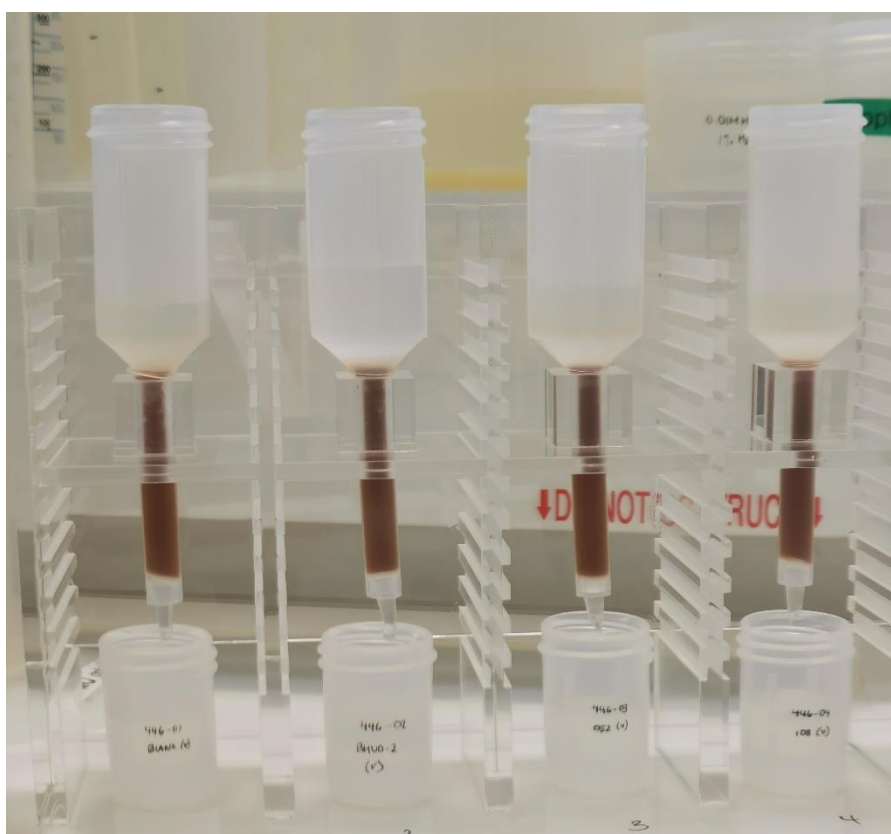


Figure 2.6: Photo taken during one of the titanium removal stage of the vanadium separation procedure (based on Wu *et al.* (2016)) at Durham University showing the set up. The photo was taken during collection of the V-cut.

The collected V fraction was evaporated, and subsequently dissolved and evaporated in $\sim 16\text{M}$ HNO_3 on a hotplate set to 160°C . The residue was re-dissolved in a small volume of 6M HCl and evaporated, followed by addition of 1 ml of 0.01M HCl before the sample beakers were tightly capped and left on a hotplate set to $\sim 120^\circ\text{C}$ for at least 24 hours. As stated in Wu *et al.* (2016), it was significantly easier to dissolve residues in 1 ml of 0.01M HCl after this column, than after the TRU Spec column in the Nielsen *et al.* (2011) procedure.

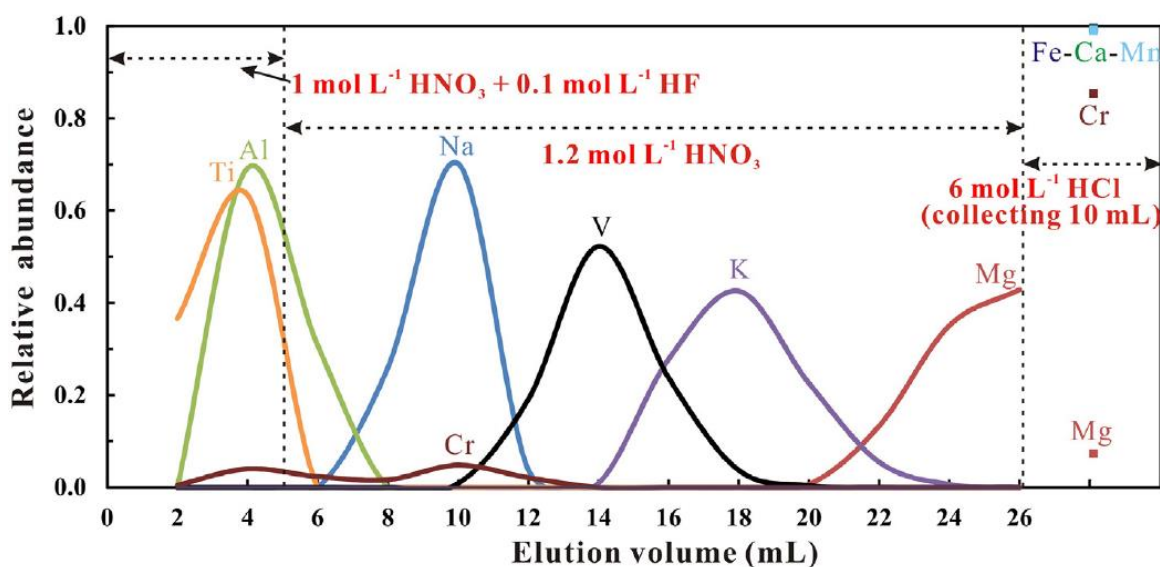


Figure 2.7: The sequence of matrix element elution during the stage 2 column using AG50W-X12 resin. The USGS standard BIR-1 was used to produce this curve. From Wu *et al.* (2016).

Table 2.1: V concentrations in Wu *et al.* (2016) column cuts. The cuts are in 1 ml either side of the main 19 ml V collection step.

Reference Material	Type	V ($\mu\text{g}\cdot\text{g}^{-1}$)	Mass (mg)	Avg $\delta^{51}\text{V}$ (‰)	2SD	n	Pre-cut V ($\text{ng}\cdot\text{g}^{-1}$)	% V loss in pre-cut	After-cut V ($\text{ng}\cdot\text{g}^{-1}$)	% V loss in after-cut
BIR-1a	Iceland basalt (USGS)	310	25.8	-1.01	0.12	2	0.162	0.00005%	0.971	0.00031%
			83.5	-0.95	0.001	2	25.434	0.00820%	0.913	0.00029%
BHVO-2	Hawaiian basalt (USGS)	317	7.9	-0.94	0.03	2	3.780	0.00119%	1.318	0.00042%
			27.6	-0.76	0.03	2	44.855	0.01415%	1.711	0.00054%
			54.7	-0.96	0.15	2	0.185	0.00006%	1.006	0.00032%
BCR-2	Columbia river basalt (USGS)	416	12.3	-0.94	0.01	2	9.249	0.00222%	1.503	0.00036%
			27.1	-0.75	0.05	2	45.665	0.01098%	1.954	0.00047%
			60.5	-0.98	0.06	2	5.318	0.00128%	2.058	0.00049%
GSP-2	Granodiorite (USGS)	52	16.8	-	-	0	0.139	0.00027%	0.566	0.00109%
			30.9	-0.77	0.15	2	0.832	0.00160%	0.671	0.00129%
			58.3	-0.71	-	1	0.289	0.00056%	0.647	0.00124%

Vanadium Yields (Durham)

After switching to the Durham V ion chromatography procedure around March 2019 V yields were unexpectedly low (**Table 2.2**) and appeared to slowly worsen with time. In stable isotope ion chromatography, it is important to ensure a 100% yield to prevent isotope fractionation on the columns. Therefore, low yields are troubling as they may indicate poor data accuracy. It was therefore important to establish where V was being lost and whether the V loss was causing synthetic isotope fractionation. Vanadium solution standards AA and BDH were passed through the first and second chromatography stages, and V yields were calculated after each. Then the solutions were passed through the entire separation procedure to test total yields. **Table 2.3** shows that AA had a 100% yield and BDH a 93% yield through the first stage, but that yields were lower for the second AG50W-X12 stage. The second stage lost up to 20% of the V loaded. Since the AG50W-X12 resin had been in the lab for almost three years, a new bottle was bought and tested for V loss to check that the slow decrease in V yields (**Table 2.2**) was not due to the AG50W-X12 resin degrading. However, there was little difference in V yield between the new and old AG50W-X12 resin (**Table 2.3**), therefore the age of the resin does not seem to be an issue. **Table 2.3** shows that V yields for the total V separation procedure are 75% or higher. A 25% loss is greater than expected, but the V isotopic composition of the solution standards after the full separation are accurate (**Table 2.3**). Therefore, it does not appear that V is fractionated on the AG1-X8 or AG50W-X12 resin during elution, and low yields do not necessarily mean poor data quality in this case.

However, a 20% V loss does not fully explain the low yields often reported for V samples since 2019. A limitation of the yield calculation became apparent during these tests. The yield calculation relies on the AA comparison solution being accurately $1 \mu\text{g}\cdot\text{g}^{-1}$. However, AA solution bottles are typically left open during measurement sessions, and evaporation increases the concentration throughout each session. This could result in artificially low sample yields. In addition, the 200 μl pipette typically used for sample dilutions was poorly calibrated, which could also result in artificially low yields since the dilutions used for yield calculations would be more than a 2% dilution. In conclusion, the unexpectedly low V yields of V samples measured from late 2019 are not an indication of poor data accuracy, and instead likely reflect inaccuracies in the yield calculation and poor pipette calibration. Therefore, the V isotope measurements can be used with confidence.

Table 2.2: Compilation of V yields estimated by comparing beam size of $\sim 1 \mu\text{g.g}^{-1}$ AA standard solution and 2% dilution of each unknown. The samples included in this list are those prepared using the new Durham ion chromatography protocol.

Batch Name	Sample Type	First Measured	Yield (%)
509-01	ODP Leg 125 Peridotites	Mar-21	57
509-03		Mar-21	58
509-05		Mar-21	49
509-09		Mar-21	53
509-11		Mar-21	71
509-13		Mar-21	58
487-04	IODP FABs and boninites	Mar-21	51
487-08		Mar-21	53
488-03		Oct-20	55
488-04		Oct-20	66
488-05		Oct-20	50
488-06		Oct-20	58
488-07		Oct-20	49
488-08		Oct-20	53
488-09		Oct-20	65
488-10		Oct-20	42
488-11		Oct-20	72
488-12		Oct-20	48
480-04/07	Diavik whole-rock peridotites and kimberlite	Sep-20	67
480-05/08		Sep-20	75
480-06/09		Sep-20	68
480-11		Sep-20	44
481-03/06		Sep-20	67
481-04/07		Sep-20	75
481-05/08		Sep-20	71
481-09/10		Sep-20	67
449-03	IODP FABs and boninites	Mar-20	80
449-04		Mar-20	52
449-05		Mar-20	74
449-06		Mar-20	93
449-07		Mar-20	83
449-08		Mar-20	58
449-09		Mar-20	82
449-11		Mar-20	78
468-02		Mar-20	78
468-03		Mar-20	75
446-03	Diavik whole-rock peridotites	Nov-19	87
446-05		Nov-19	88
446-07		Nov-19	89
446-08	Garnet & cpx mineral separates	Nov-19	80
446-09		Nov-19	89
446-10		Nov-19	95
446-11		Nov-19	91
446-12		Nov-19	94
2-1	IODP FABs and boninites	Sept-19	54
2-2		Sept-19	59
2-10		Sept-19	69
2-12		Sept-19	68
2-18		Sept-19	65
2-3		Sept-19	33
2-4		Sept-19	44
2-7		Sept-19	33
2-8		Sept-19	34
2-9		Sept-19	45
488-02	BHVO-2	Oct-20	31
480-02	BIR-1a	Sep-20	54
480-03	PCC-1	Sep-20	58
480-12	BHVO-2	Sep-20	33
446-02	BHVO-2	Nov-19	89
391-02	BIR-1a	May-19	80
391-03	BIR-1a	May-19	76
391-04	BHVO-2	May-19	81
391-05	BHVO-2	May-19	65
391-06	BHVO-2	May-19	77
391-08	GSP-2	May-19	79
391-09	GSP-2	May-19	74
391-10	BCR-2	May-19	59
391-11	BCR-2	May-19	68
391-12	BCR-2	May-19	79

Table 2.3: Results of V yield and fractionation tests conducted between May and August 2021. Vanadium isotope compositions are only included for the solution standards that passed through the full V separation procedure since organic material in the resin is present in the eluents from the first few columns which makes accurate analysis difficult. These organics are removed by the later columns.

Date of Test	Resin	Solution Standard	Initial V conc	Yield (%)	$\delta^{51}\text{V}_{\text{AA}}$ (%)	
					Measured	Expected
May 2021	AG1-X8	AA	20 μg	100		
		BDH	20 μg	93		
May 2021	Old AG50W-X12	AA	5 μg	79		
			10 μg	82		
			20 μg	86		
		BDH	5 μg	79		
			10 μg	84		
			20 μg	90		
July 2021	New AG50W-X12	AA	5 μg	89		
			10 μg	92		
			20 μg	95		
		BDH	5 μg	88		
			10 μg	92		
			20 μg	95		
	Old AG50W-X12	AA	5 μg	84		
			10 μg	92		
			20 μg	96		
		BDH	5 μg	88		
			10 μg	90		
			20 μg	94		
August 2021	Full procedure	AA	10 μg	77	0.08	0.00
			5 μg	75	-1.17	-1.19
		BDH	10 μg	76	-0.04	0.00
			10 μg	79	-1.18	-1.19

2.3.1.2. Mass Spectrometry

Imperial College London Measurement (Nu Plasma II)

All isotope measurements at Imperial College London (October 2017 to August 2018) were collected on a Nu Plasma II MC-ICP MS in the department of Earth Science and Engineering. A brief description of the protocol used is found in Hopkins *et al.* (2019).

Instrument Set-up and Parameters:

The Nu II MC-ICP MS was set up for static simultaneous collection of masses 49, 50, 51, 52, and 53 to allow both V isotopes to be measured (ie. ^{50}V , ^{51}V). ^{49}Ti and ^{53}Cr were monitored to correct for the ^{50}Ti and ^{50}Cr isobaric interferences on ^{50}V . The Faraday cup configuration and the resistors assigned to each cup are outlined in **Table 2.4**. Low intensity signals were amplified using 10^{12} resistors to allow for more accurate interference corrections. Measurements were conducted in medium resolution mode ($M/\Delta M > 5000$) to resolve polyatomic interferences (chiefly $^{40}\text{Ar}^{12}\text{C}$ from ^{52}Cr), and dry plasma mode. The average resolution across sessions was ~ 7000 . All samples were measured in dry plasma mode using a DSN-100 sample introduction system and $200\ \mu\text{L}\cdot\text{min}^{-1}$ Teflon nebulisers and a typical sensitivity of $60\ \text{V}\cdot\text{ppm}^{-1}$ on ^{51}V ($200\ \mu\text{L}\cdot\text{min}^{-1}$). An H-skimmer cone and standard sample cone unique to V were used for all measurements. The following instrumental operating conditions were used: coolant ($13.0\ \text{L}\cdot\text{min}^{-1}$), aux ($0.90\ \text{L}\cdot\text{min}^{-1}$), nebuliser (30.0 Psi), RF power (1300 W).

Table 2.4: Faraday cup configuration used to measure $\delta^{51}\text{V}$ on the Nu Plasma at Imperial College London. The table shows the assignment of analyte and interfering element masses in each cup. Monitor isotopes for the interfering element corrections are in bold.

Cup	L4	L1	H2 (C)	H5	H8
Mass	49	50	51	52	53
Analyte Isotope		V	V		
Interference Isotope	Ti	Ti Cr		Cr	Cr
Resistor	10^{12}	10^{12}	10^{11}	10^{11}	10^{12}

Prior to each measurement sequence, a plateau position was chosen that minimised polyatomic interferences. The plateau size was on average 0.01 amu. Each isotope measurement consisted of 60 s of monitoring background intensities, followed by data collection for 1 block of 70 cycles of 5 s integrations. MC-ICP MS have a bias towards heavy masses that needs to be corrected to obtain accurate measurements. Since V only has two isotopes, internal mass bias correction and double spiking techniques are not possible. Therefore, V mass bias was corrected by standard-sample bracketing. The ^{50}Ti and ^{50}Cr isobaric interferences on ^{50}V were corrected for manually at the end of each session using the measured ^{49}Ti and ^{53}Cr abundances respectively. An exponential mass fractionation factor of $\beta = -2$ was assumed for both ^{50}Ti and ^{50}Cr , and the true value of $^{50}\text{Ti}/^{49}\text{Ti}$ was taken as 0.972537, and $^{53}\text{Cr}/^{50}\text{Cr}$ as 2.18665 (Nielsen *et al.* 2011). Both corrections are believed to remain accurate to $^{49}\text{Ti}/^{51}\text{V} < 0.00001$ and $^{53}\text{Cr}/^{51}\text{V} < 0.00001$ (Nielsen *et al.* 2011).

Solution Standards:

All V isotopic ratios were reported relative to the V standard solution Alfa Aesar (AA) (eq. 2). Every sample was bracketed by two AA standard solution on each side for mass bias correction, and intermittently solution standard BDH to assess instrument stability and accuracy (**Figure 2.8**). The long-term average BDH relative to AA for all measurements at Imperial College London is $\delta^{51}\text{V}_{\text{AA}} = -1.18 \pm 0.23 \text{ ‰}$ (2SD, $n = 29$) (**Figure 2.9**) and Durham University is $\delta^{51}\text{V}_{\text{AA}} = -1.22 \pm 0.13 \text{ ‰}$ (2SD, $n = 565$) (**Figure 2.9**). Both are within error of the reported value $\delta^{51}\text{V}_{\text{AA}} = -1.19 \pm 0.12 \text{ ‰}$ (2SD, $n = 600$; (Nielsen *et al.* 2011)), but the Durham data is more precise.

$$(2) \quad \delta^{51}\text{V}_{\text{AA}} = 1000 \times \left[\left(\frac{{}^{51}\text{V}/{}^{51}\text{V}_{\text{sample}}}{{}^{51}\text{V}/{}^{51}\text{V}_{\text{AA}}} \right) - 1 \right]$$



Figure 2.8: MC-ICP MS V isotope analysis measurement sequence using standard solution-sample bracketing, based on (Nielsen *et al.*'s 2011) measurement sequence.

All solutions (AA, BDH, and samples) were run in 0.1M HNO_3 . Between every measurement, the DSN-100 sample introduction system was washed with 0.1M HNO_3 for 85 to 110 s to eliminate any cross-contamination of V between measurements. The background ${}^{51}\text{V}$ needed to reach less than 5 mV after the wash-out for the next measurement to run. All samples and standards were measured at solution concentrations of 600-800 ng.g^{-1} .

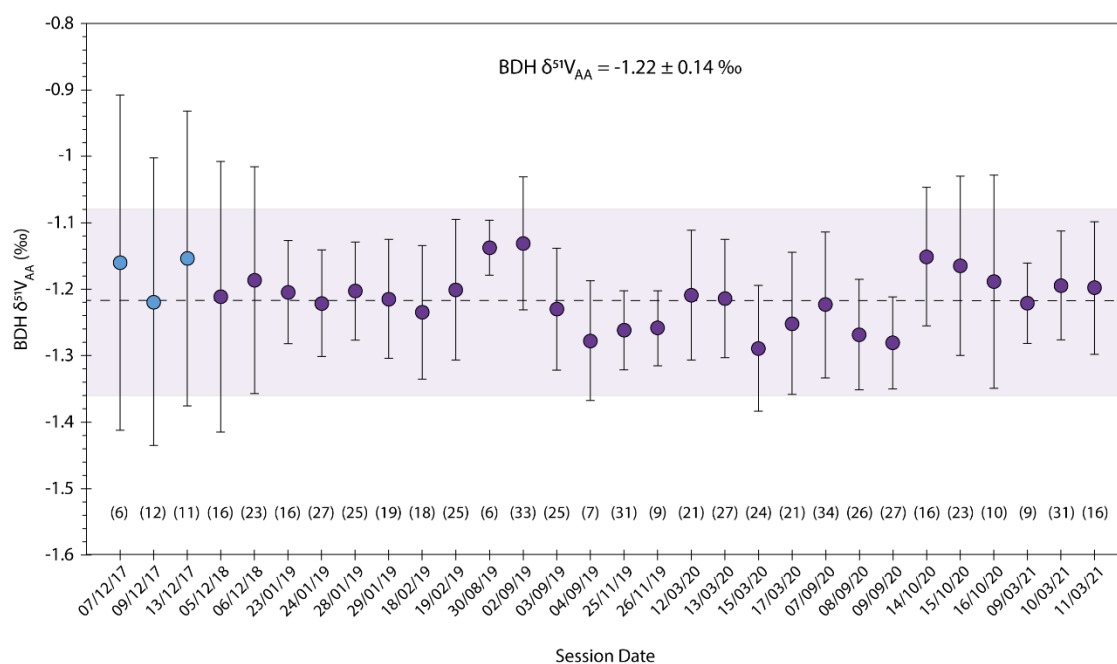


Figure 2.9: Long-term average for BDH solution standard. A BDH average was taken for each measurement day. BDH long-term average $\delta^{51}\text{V}_{\text{AA}} = -1.22 \pm 0.14 \text{ ‰}$, $n = 594$. The number in brackets beneath each point

shows the number of measurements included in the average. Error bars are shown as 2SD. The black dashed line and purple horizontal shaded area represent the average and 2SD error on the long-term standard average respectively. The blue points are Imperial College London sessions, and the purple points Durham University sessions.

Acceptance Criteria:

For measurements to be accepted, they had to meet the following criteria: (1) the solution concentrations were within 15% of the bracketing AA standard solutions. (2) the standard deviation of the bracketing AA solutions was less than 0.1%. A higher standard deviation indicated the instrument was not stable enough to gather reproducible data. (3) the bracketing BDH standards had $\delta^{51}\text{V}$ values within the long-term precision of the AA standard solution (Nielsen *et al.* 2011).

Durham University Measurement (Neptune)

All V isotope measurements at Durham University were carried out on a Thermo Scientific Neptune MC-ICP MS. The operating procedure on the surface was similar to that at Imperial College London. Both used dry plasma, medium-resolution mode, the same solution standards (AA and BDH), and the same double standard-bracketing technique. However, there were important differences.

(1) Cones and resistor set-up

Similar to the Imperial College London protocol, the Durham University protocol used a standard sample cone. However, the Durham University protocol used an X-skimmer cone which boosted the sensitivity (80 to 150 V.ppm⁻¹ on ^{51}V , 50 $\mu\text{l}.\text{min}^{-1}$) and improved precision. The resistor setup at Durham University also differed from the Imperial College London setup (**Table 2.5**). Similar to the Imperial protocol, prior to each measurement sequence, a plateau position was chosen that minimised polyatomic interferences (**Figure 2.10**). The plateau size was on average 0.01 amu and the resolution never fell below 6000.

Table 2.5: Faraday cup configuration used to measure $\delta^{51}\text{V}$ on the Neptune mass spectrometer at Durham University. The table shows the assignment of analyte and interfering element masses in each cup. Monitor isotopes for the interfering element corrections are in bold.

Cup	L4	L2	L1	C (Ax)	H1	H3
Mass	48	49	50	51	52	53
Analyte Isotope			V	V		
Interference Isotope	Ti	Ti	Ti Cr		Cr	Cr
Resistor	10 ¹¹	10 ¹¹	10 ¹¹	10 ¹⁰	10 ¹¹	10 ¹¹



Figure 2.10: Screenshot of mass scan from Neptune software during V isotope measurement. The red box shows the ideal position on the mass 51 plateau to minimise interferences when analysing V isotopes.

(2) Sensitivity and measurement set-up

Analyses were run at $1 \mu\text{g.g}^{-1}$ in the Durham protocol instead of $600\text{--}800 \text{ ng.g}^{-1}$. However, the nebuliser used in the Durham protocol was a Savillex concentric flow CF-50, which had an uptake rate of $50 \mu\text{l.min}^{-1}$ compared to the $200 \mu\text{l.min}^{-1}$ nebuliser used at Imperial. The lower uptake rate and shorter analysis time of the Durham protocol more than offset the higher running concentrations, meaning that overall, less V was consumed per analysis in the Durham protocol (**Table 2.6**). As such there was little issue with samples having sufficient V to run. The sample introduction system was an Aridus III, and measurements included 50 cycles of 4.194 s integrations. The loading and wash solution was changed to 3% HNO_3 and wash time increased to 120 s to improve the wash stage.

Table 2.6: Comparison of running concentrations, nebulisers, analysis time and total V consumed per analysis for the Imperial and Durham measurement protocols.

	Running conc	Nebuliser	Uptake rate	Analysis Time	V per analysis
Imperial	$600\text{--}800 \text{ ng.g}^{-1}$	Teflon	$200 \mu\text{l.min}^{-1}$	5.8 mins	700–930 ng
Durham	$1 \mu\text{g.g}^{-1}$	CF-50	$50 \mu\text{l.min}^{-1}$	3.5 mins	175 ng

(3) Mass bias correction

A significant difference between V isotope measurements at Imperial College London and Durham University was how instrumental mass bias and isobaric interferences were corrected. In both protocols, ^{50}Ti and ^{50}Cr isobaric interferences on ^{50}V were corrected by monitoring ^{49}Ti and ^{53}Cr , and applying the true values of $^{50}\text{Ti}/^{49}\text{Ti}$ and $^{53}\text{Cr}/^{50}\text{Cr}$. However, mass bias on the interfering isotopes was accounted for at Imperial using a fixed exponential mass fractionation factor of $\beta = -2$ for all measurement sessions. In truth the mass bias will shift between measurement sessions. Therefore, the Durham University protocol included a new method for more accurately determining the ^{50}Cr and ^{50}Ti correction β -factors in each sequence. Two BDH solutions were doped with 1 ppb Cr and 1 ppb Ti respectively. 1 ppb was a high enough concentration to exceed Ti and Cr concentrations in typical post-ion chromatography samples. The doped solutions were analysed as unknowns in every sequence at least once. The V isotope ratio of each doped BDH was calculated relative to the bracketing AA's using β -factors between -3 and -0 at intervals of 0.1. The β -factor that produced the BDH value closest to the accepted value of $\delta^{51}\text{V}_{\text{AA}} = -1.19 \pm 0.12 \text{ ‰}$ (2SD) was taken as the optimum and used for mass bias correction throughout the entire sequence. Between January 2019 and March 2021, β -factors for Cr ranged between -0.8 and -1.2 and for Ti between -0.9 and -1.4. The β -factors calculated using the above method were significantly different from the -2 assumed in the Imperial protocol. However, since ion chromatography resulted in very low $^{49}\text{Ti}/^{51}\text{V}$ and $^{53}\text{Cr}/^{51}\text{V}$ in all samples, interference corrections were small, and the β -factor changes only had minor effects on final $\delta^{51}\text{V}$ values. Note that the reference materials from Imperial and Durham are in broad agreement (see Quality Control and Assurance). Despite this, more accurately correcting for isobaric interferences was an important improvement to the V isotope measurement protocol, as it improved both data accuracy and precision.

Quality Control and Assurance

To provide extra assurance of instrument stability and ion chromatography efficacy, each batch of V samples contained at least one USGS reference material that went through the entire V separation and measurement procedure. **Table 2.7** shows the $\delta^{51}\text{V}$ ratios of all measured USGS reference materials. The literature values used for comparison in **Table 2.7** are from Wu *et al.* (2016). Wu *et al.* (2016) USGS values were chosen because they cover all the USGS reference materials measured for V in this thesis, with a high number of repeats, and Wu *et al.* (2016) used the same AG 50W-X12 resin column procedure as used in this thesis. Vanadium isotope data for some of the same reference materials is also found in Prytulak *et al.* (2011, 2013); Schuth *et al.* (2017); Sossi *et al.* (2018); Xue *et al.* (2018); Hopkins *et al.* (2019); Qi *et al.* (2019); Ding *et al.* (2020); Novella *et al.* (2020) and are also in broad agreement with Wu *et al.* (2016) and the current study.

Table 2.7: USGS reference material V isotope measurements that were used for quality control and assurance. Errors are 2SD on at least 3 repeat measurements. Where fewer than 2 measurements were obtained, the BDH 2SD from that session was taken as the error. The date listed is the date of the first analytical session the solution was measured in. Reference material solutions were often reused in later analytical sessions.

								Wu <i>et al.</i> (2016)		
Reference Material	Type	V ($\mu\text{g}\cdot\text{g}^{-1}$)	Lab	Date of 1 st analytical session	$\delta^{51}\text{V}_{\text{AA}}$ (‰)	2SD	n	$\delta^{51}\text{V}_{\text{AA}}$ (‰)	2SD	n
BCR-2	Columbia River Basalt (USGS)	416	ICL	10/12/17	-1.00	0.1	3	-0.78	0.08	36
BCR-2			DU	28/01/19	-0.74	0.14	5			
BCR-2			DU	28/01/19	-0.81	0.06	4			
BCR-2			DU	28/01/19	-0.68	0.06	5			
BCR-2			DU	21/05/19	-0.94	0.09	2			
BCR-2			DU	22/05/19	-0.98	0.09	2			
BCR-2			DU	22/05/19	-0.75	0.09	2			
BCR-2 ICL average					-1.00	0.1	3			
BCR-2 DU average					-0.78	0.21	20			
BIR-1a	Iceland basalt (USGS)	310	ICL	07/12/17	-1.20	0.22	4	-0.92	0.09	52
BIR-1a			DU	28/01/19	-0.89	0.08	4			
BIR-1a			DU	29/01/19	-0.86	0.2	3			
BIR-1a			DU	29/01/19	-0.85	0.07	2			
BIR-1a			DU	21/05/19	-0.95	0.09	2			
BIR-1a			DU	21/05/19	-1.01	0.09	2			
BIR-1a			DU	07/09/20	-1.01	0.08	10			
BIR-1a			DU	10/03/21	-0.89	0.05	7			
BIR-1a ICL average					-1.20	0.22	4			
BIR-1a DU average					-0.95	0.16	23			
BHVO-2	Hawaiian basalt (USGS)	317	DU	29/01/19	-0.87	0.07	3	-0.83	0.09	22
BHVO-2			DU	29/01/19	-0.90	0.03	4			
BHVO-2			DU	29/01/19	-0.97	0.06	3			
BHVO-2			DU	21/05/19	-0.94	0.09	2			
BHVO-2			DU	21/05/19	-0.76	0.09	2			
BHVO-2			DU	21/05/19	-0.96	0.09	2			
BHVO-2			DU	08/09/20	-0.86	0.09	4			
BHVO-2			DU	14/10/20	-0.91	0.1	2			
BHVO-2 average					-0.90	0.14	22			
GSP-2	Granodiorite (USGS)	52	DU	21/05/19	-0.77	0.09	2	-0.62	0.07	13
GSP-2			DU	21/05/19	-0.71	0.09	1			
GSP-2 average					-0.75	0.13	3			

2.3.2. Zinc

All Zn isotope analyses were undertaken at Durham University.

2.3.2.1. Ion Chromatography

The ion chromatography procedure used to isolate Zn is based the Fe-Zn-Cu column of Sossi *et al.* (2015) (**Figure 2.11**) and was combined with the Durham V chemistry procedure (**Figure 2.5**) to collect the three isotope systems from a single digestion.

The Zn separation used AG 1-X8 resin. However, due to an issue with high Zn blanks (see below), the Zn AG 1-X8 resin went through extra cleaning steps in addition to the routine shaking and rinsing method used for the V resin. For the additional cleaning step, ~20 ml of AG 1-X8 resin was loaded into a Biorad EconoPac column which was mounted on a vacuum box. The vacuum box increased the elution rate of the cleaning acids, which in turn allowed a greater volume of cleaning acid to be eluted. Three sequential additions of ~200 ml volumes each of MilliQ, 3M HNO₃, MilliQ, 3M HCl, MilliQ. The Zn separation used the same Teflon columns as the stage based on Wu *et al.* (2016) (**Figure 2.6 & Figure 2.11**). To ensure no cross contamination, between each new use of the Teflon columns, the columns were deconstructed, the frits and pipette tips discarded, and the columns were heated at < 100°C on a hotplate in weak HNO₃. The columns were reconstructed with new frits and pipette tips leached in weak HNO₃ on the morning of the separation.

2 ml of the vacuum-cleaned AG 1-X8 (200-400 mesh) resin was loaded into Teflon columns (**Figure 2.11**). The resin was conditioned with 5 ml of 6M HCl. The sample dissolved in 1 ml of 6M HCl was then loaded onto the column and V was immediately collected. An additional 4 ml of 6M HCl was eluted to wash any remaining V through the resin. The V beaker was then capped and stored for the next V ion chromatography stage, and 10 ml of 6M HCl was added to the column. 6 ml of 0.5M HCl was added to elute and collect Fe, followed by 4 ml of 3M HNO₃ to elute and collect Zn.

During development of the Zn protocol Zn fractions that passed only once through the separation often produced mass independent isotopic ratios, likely due to remaining matrix in the Zn fraction. Therefore, Zn fractions were typically passed through the separation a second time, after which isotopic data was consistently mass dependent. The Zn fraction was evaporated and re-dissolved twice in ~16M HNO₃, then dissolved in 1 ml of 3% HNO₃ which was the loading solution for Zn MC-ICP MS.

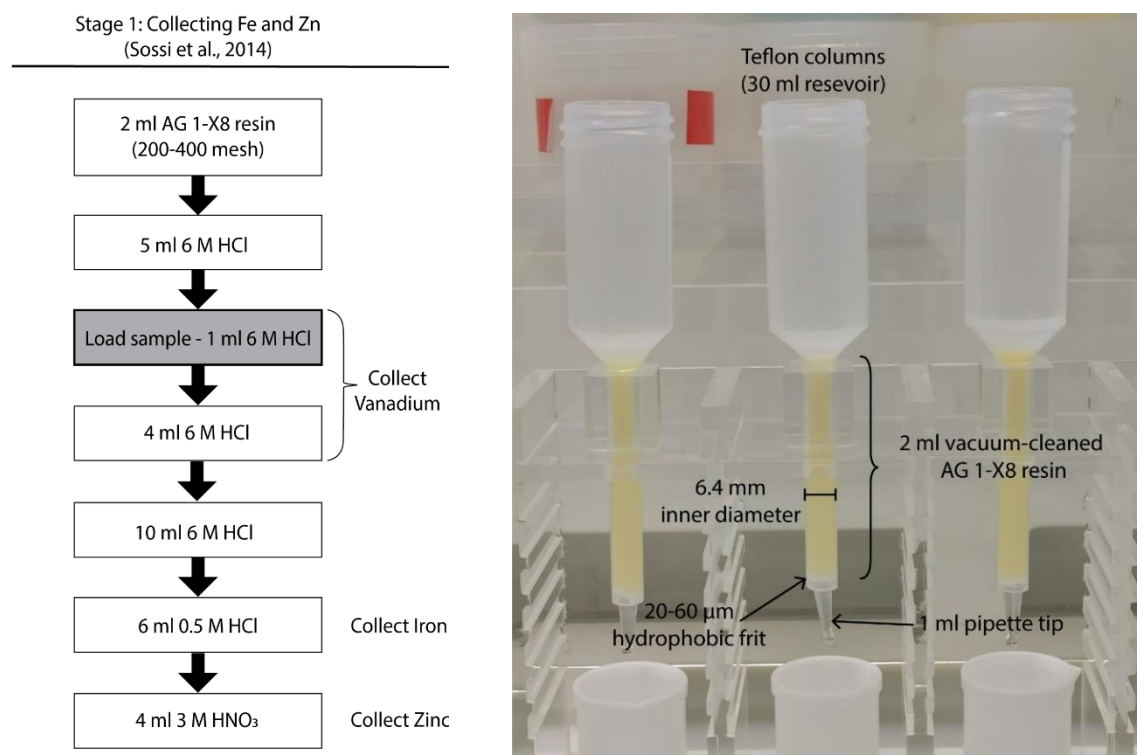


Figure 2.11: Summary flow chart depicting the Fe-Zn ion chromatography stage used at Durham University (left). The separation uses Teflon columns with 20-60 μm polyethylene frits. The annotated photo (right) shows the set-up of this stage.

2.3.2.2. Resolving High Zinc Blanks

The total procedural blanks for Zn-fractions collected from the Fe-Zn set-up were initially high and increased with progressive sample batches until plateauing in the region of 100 ng.g^{-1} (Table 2.8). The maximum acceptable total procedural Zn blank was $\sim 20 \text{ ng.g}^{-1}$. Therefore, an investigation to discover the external Zn source was undertaken. Potential sources of external Zn during ion chromatography include, the acids, resin, Teflon columns, and the frits. To determine which if any of these were the source of external Zn, a series of tests were performed that changed each of these candidates independently and in turn.

Table 2.8: Total procedural Zn blanks (ng.g^{-1}) for all Zn sample batches.

Date	Batch	Sample Types	Zn TPB (ng.g^{-1})
05-06-2019	2-x	FABs & boninites	31
21-10-2019	446	Peridotites	24
24-03-2021	487	FABs & boninites	21
22-03-2021	509	Peridotites	12
22-03-2021	511	Boninites	16
22-03-2021	512	Boninites	10
24-03-2021	515	Boninites	36
10-05-2021	517	Boninites	5

Teflon column and frit test:

Three of the Fe-Zn Teflon columns were dismantled, the frits and pipette tips discarded, and thoroughly cleaned using Sontara wipes sprayed with acetone and then MilliQ. The columns were heated on a hotplate in weak HNO_3 for two days. New frits were cut from 20-60 μm Porex hydrophobic polyethylene frit material and leached in weak, cold HNO_3 for two days along with new pipette tips. After cleaning, the columns were reassembled with new leached frits and pipette tips. Total Zn blanks from the three newly cleaned columns, and three control columns that underwent no cleaning and no frit change were obtained by conducting the Fe-Zn ion chromatography stage detailed above. The control columns and cleaned columns produced Zn blanks of similar concentrations (**Table 2.9**), and therefore dirty columns and/or frits were not the source of external Zn.

Acid test:

The three acids used during the Fe-Zn column were 3M HNO_3 , 6M HCl and 0.5M HCl. The 0.5M HCl was diluted from the 6M HCl, therefore only 6M HCl and 3M HNO_3 were tested. The total volumes of 3M HNO_3 and 6M HCl used in the Fe-Zn column were tested, 4 ml and 20 ml respectively. The specified volumes of acids were transferred to Savillex beakers, and prepped for mass spectrometry in the same way outlined for the Zn-fractions above. The acids were evaporated and re-dissolved twice in $\sim 16\text{M}$ HNO_3 , then dissolved in 1 ml of 3% HNO_3 . The Zn concentrations of these acids were measured via MC ICP-MS. The 3M HNO_3 Zn concentration was negligible and the 6M HCl had 0.61 ng.g^{-1} total Zn (**Table 2.9**). Therefore, the acids were not considered the source of external Zn.

Resin test:

Prior to all previous AG 1-X8 columns in this procedure, the resin was cleaned by repeated shaking and rinsing in MilliQ 10 times, then with alternating 6M HCl and MilliQ 10 times. 20 ml of resin was cleaned further by pulling a minimum of three rounds of MilliQ, 3M HCl, MilliQ, 3M HNO_3 , through it via a vacuum pump. The Zn concentration in this “clean” resin was tested by conducting the Fe-Zn column chemistry three times and comparing the resultant Zn concentrations to one control column that used the old “dirty” resin. The “clean” resin column blanks showed a remarkable improvement in Zn concentrations ($< 20 \text{ ng.g}^{-1}$), whereas the control resin blank contained 84 ng.g^{-1} of Zn (**Table 2.9**). The resin was therefore deemed to be the source of external Zn and responsible for the high Zn blanks.

Table 2.9: Zinc concentrations from Zn blank tests to determine the external source of Zn causing the high total procedural blanks.

Test	Type of Blank	Zn conc (ng.g ⁻¹)
Column Blank Test	Clean Column 1	111
	Clean Column 2	271
	Clean Column 3	88
	Control Column 1	90
	Control Column 2	103
	Control Column 3	109
Acid Blank Test	HCl Acid Blank	0.61
	HNO ₃ Acid Blank	Background
Resin Blank Test	Clean Resin 1	1500 (dirty beaker)
	Clean Resin 2	3.2
	Clean Resin 3	10.3
	Control Resin 1	84

Following this investigation, to maintain low Zn total procedural blanks, the resin for the Fe-Zn column always goes through the additional vacuum box cleaning steps. In addition, the frits and pipette tips were always removed from the columns after each pass of this column stage, and the Teflon columns themselves were heated in weak HNO₃ until the next use. The tips were leached in weak HNO₃ and the frits completely replaced between uses. The columns were cleaned despite the investigation showing that cleaning the columns and replacing the frits made little difference to Zn total procedural blanks. This was for peace of mind and to ensure that there was no potential long-term build-up of Zn in the columns through progressive use. All total procedural blanks from sample batches both before and after the blank investigation are displayed in **Table 2.8**. Total Zn yields for all samples ranged between 70% and 100% with an average of 82%.

2.3.2.3. Mass Spectrometry (Neptune)

All Zn isotope measurements were obtained at Durham University between 2019 and 2021 on a Neptune Plus MC-ICP MS.

Instrument Set-up and Parameters:

The Neptune Plus MC-ICP MS was set up for static simultaneous collection of masses 62, 63, 64, 65, 66, 67 and 68 to allow all significant isotopes of Zn to be measured (ie. ⁶⁴Zn, ⁶⁶Zn, ⁶⁷Zn, ⁶⁸Zn). ⁶²Ni was monitored to correct for the ⁶⁴Ni isobaric interference on ⁶⁴Zn, and ⁶³Cu and ⁶⁵Cu were monitored to allow mass bias to be corrected by external Cu doping. All Faraday cups were assigned 10¹¹ Ω resistors. The Faraday cup configuration and the resistors assigned to each cup are outlined in **Table 2.10**. Measurements were conducted in low resolution mode (M/ΔM = 400). Low

resolution was sufficient because there were no significant polyatomic interferences on Zn that require a higher resolution to resolve (e.g. $^{40}\text{Ar}^{12}\text{C}$ on ^{52}Cr during V analysis). All samples were measured in wet plasma mode using either an Elemental Scientific Incorporated (ESI) SIS or Glass Expansion “Cinnabar” cyclonic spray-chamber, a ESI 50 $\mu\text{l}.\text{min}^{-1}$ PFA nebuliser, with a sensitivity between 2 and 6.5 V.ppm $^{-1}$ on ^{64}Zn (50 $\mu\text{l}.\text{min}^{-1}$). An H-skimmer cone and standard sample cone unique to Zn were used for all measurements. The following instrumental operating conditions were used: RF power 1200 W, fore vacuum pressure 1.43×10^{-3} mbar, high vacuum 1.36×10^{-7} mbar, ion getter pressure 1.02×10^{-8} mbar.

At the start of each day of measurement, a peak centre was performed which was applied to each measurement throughout the day (**Figure 2.12**). The average plateau size was 0.08 amu. Each measurement consisted of 60 s of monitoring background intensities, followed by data collection for 1 block of 30 cycles of 4.194 second integrations. The ^{64}Ni interference on ^{64}Zn was corrected using the $^{64}/^{62}\text{Ni}$ ratio and a correction value of 0.254671. Mass bias was corrected for by Cu doping. All solutions were doped with Cu to a 2:1 ratio of Zn to Cu to boost the Cu signals, allowing it to be measured more accurately. The mass bias was corrected for by comparing the $^{65}/^{63}\text{Cu}$ ratio from each measurement to the true $^{65}/^{63}\text{Cu}$ ratio (0.44563) and the β -factor was calculated using the exponential law.

Table 2.10: Faraday cup configuration used to measure $\delta^{64}\text{Zn}$ on the Neptune mass spectrometer at Durham University. The table shows the assignment of analyte and interfering element masses in each cup. Monitor isotopes for the IECs are in bold, and isotopes for the Cu-doping mass bias correction are in italics.

Cup	L3	L2	L1	C (Ax)	H1	H2	H3
Mass	62	63	64	65	66	67	68
Analyte Isotope			Zn		Zn	Zn	Zn
Interference isotope	Ni	<i>Cu</i>	Ni	<i>Cu</i>			
Resistor	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}

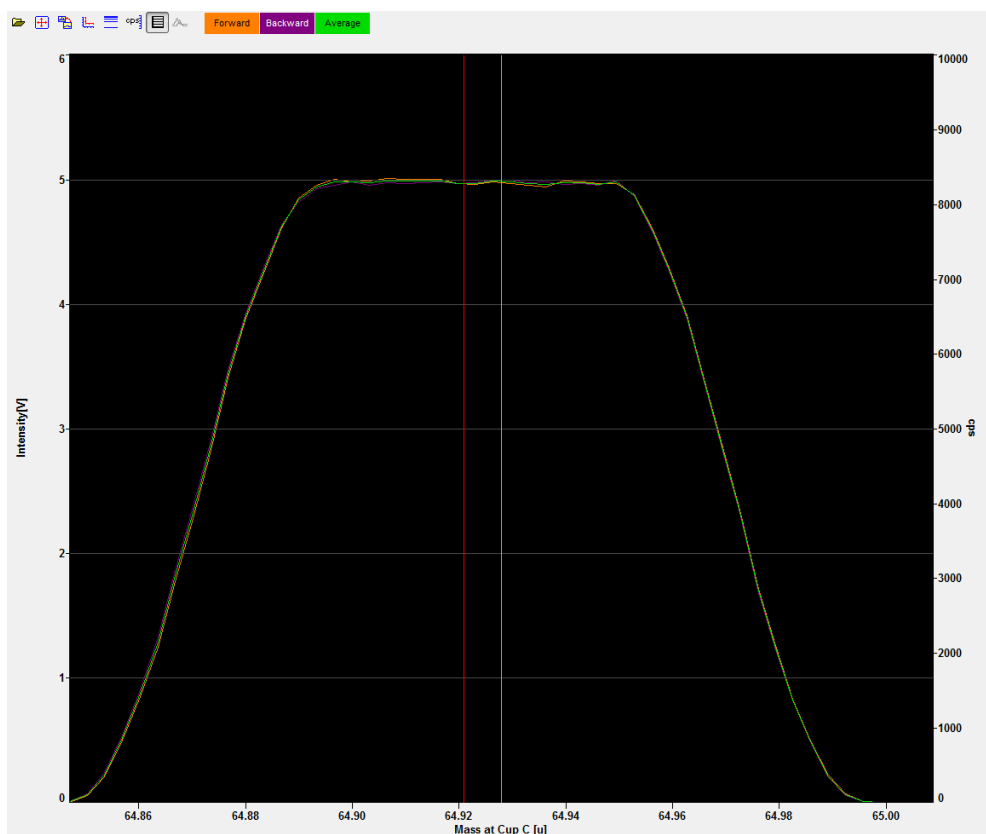


Figure 2.12: Screenshot of peak centre using the Neptune software for Zn isotope measurement. The scan was conducted on the 24th March 2021 and shows the ^{64}Zn peak and the width of the plateau (~ 0.08 amu).

Solution Standards:

The original Zn solution used to bracket samples and defined as $\delta^{66}\text{Zn} = 0$ ‰ was a Johnson Matthey Chemicals (JMC) Zn standard first analysed at the École Normale Supérieure Lyon Earth Science Laboratory and hence subsequently referred to as JMC Lyon (e.g. Maréchal *et al.* 1999). However, JMC Lyon was exhausted, and replaced by a new solution standard, ETH. The Zn isotopic composition of ETH is $\delta^{66}\text{Zn}_{\text{Lyon}} = 0.28 \pm 0.02$ ‰ (Archer *et al.* 2017). ETH was used to bracket all Zn isotope measurements throughout this thesis and was defined as 0 ‰, with reported ratios of all unknowns reported relative to ETH (eq. 3). Since ETH stocks will inevitably run out in the future, IRMM 3702 was created to replace it. IRMM 3702 is statistically identical to ETH Zn ($\delta^{66}\text{Zn}_{\text{ETH}} = 0.007 \pm 0.045$ ‰, $n = 86$, **Figure 2.13a**) and was measured intermittently relative to ETH throughout this protocol to assess instrument stability and accuracy (**Figure 2.14**), as was the in-house solution standard Romil Zn ($\delta^{66}\text{Zn}_{\text{ETH}} = -2.951 \pm 0.046$ ‰, $n = 118$, **Figure 2.13b**).

$$(3) \quad \delta^{66}\text{Zn} = 1000 \times \left[\left(\frac{{}^{66}\text{Zn}/{}^{64}\text{Zn}_{\text{sample}}}{{}^{66}\text{Zn}/{}^{64}\text{Zn}_{\text{standard}}} \right) - 1 \right]$$

All solutions (ETH, IRMM 3702, Romil Zn and samples) were run in 3% HNO₃ and measured from Teflon autosampler vials to reduce background Zn levels, since Zn is a common in plastics. The vials were cleaned using several stages of HNO₃ and MQ, and then reused in subsequent sessions. Between every measurement, the sample introduction system was washed with 3% HNO₃ for 120 s to eliminate any cross-contamination. The background ⁶⁴Zn typically reached < 3 mV after the wash-out. All samples and standards were measured at solution concentrations of 750 ng.g⁻¹.

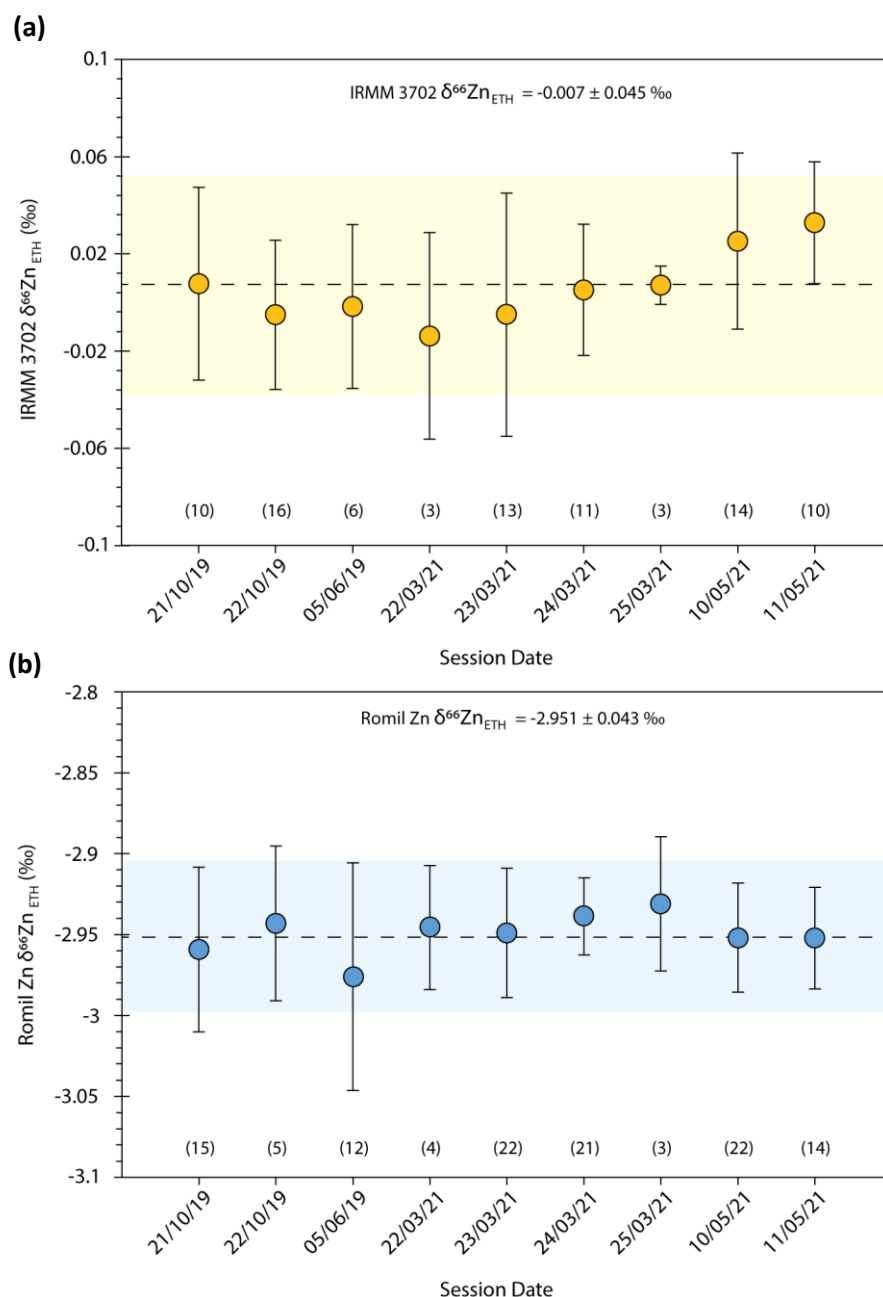


Figure 2.13: Long-term averages for Zn solution standards (a) IRMM 3702; (b) Romil Zn. An average of each solution standard was taken for each measurement day, and an average of all measurement days was taken for each standard. IRMM 3702 long-term average $\delta^{66}\text{Zn}_{\text{ETH}} = 0.007 \pm 0.045 \text{ ‰}$, $n = 86$, and Romil Zn long-term average $\delta^{66}\text{Zn}_{\text{ETH}} = -2.951 \pm 0.046 \text{ ‰}$, $n = 118$. The number in brackets beneath each point shows the

number of measurements included in the average. Error bars are shown as 2SD. The yellow and blue horizontal shaded areas represent the 2SD error on the long-term standard averages.



Figure 2.14: Example MC-ICP MS Zn isotope analysis measurement sequence using standard solution-sample bracketing.

Acceptance Criteria:

For measurements to be accepted, they had to meet the following criteria: (1) the solution concentrations were within 10% of the bracketing ETH standard, (2) the relative standard deviation of the bracketing ETH solutions was less than 0.1%, (3) the measured values were mass dependent (measured $^{66/64}\text{Zn} \times 2 = \text{measured } ^{68/64}\text{Zn} \pm 0.2$) (**Figure 2.15**), (4) the 2SD of all repeated measurements were less than 0.05 ‰.

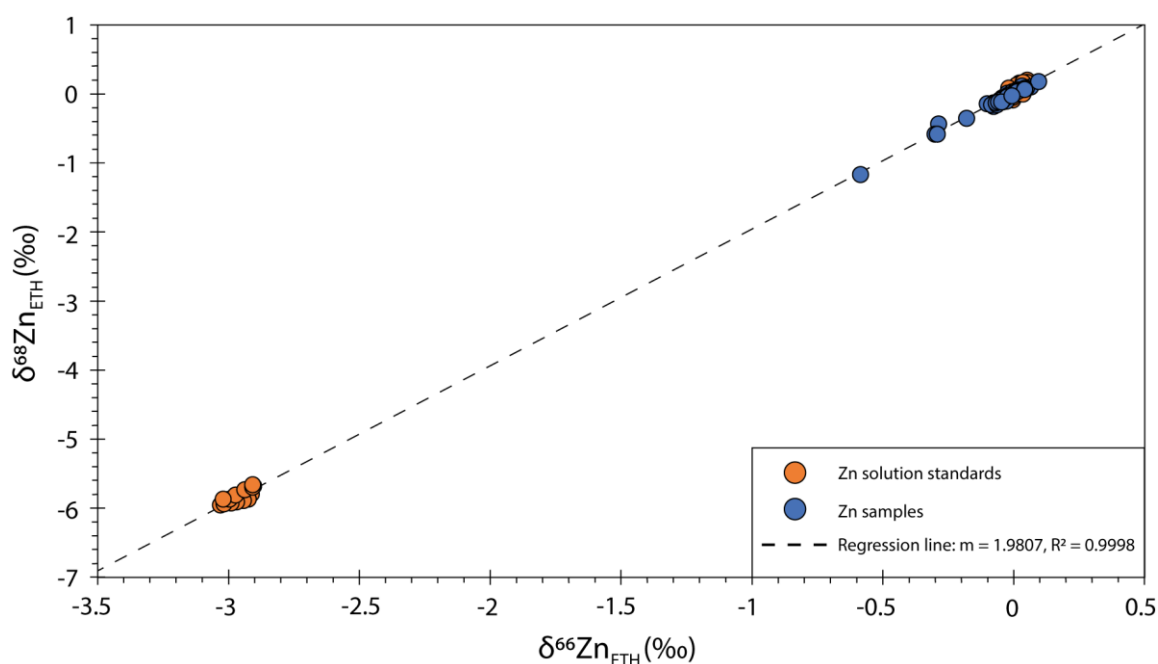


Figure 2.15: Zinc isotope mass dependency plot showing $\delta^{66}\text{Zn}$ vs $\delta^{68}\text{Zn}$ relative to Zn reference material ETH for all Zn samples and Romil Zn and IRMM3702 solution standards. The data fall on a linear regression line with a gradient of 1.9807 and an R^2 of 0.9998. All measurements are therefore assumed mass dependent since the regression gradient is in proportion with the $\delta^{66}\text{Zn}/\delta^{68}\text{Zn}$ mass dependency ratio of ~ 2 . All errors for the samples are 2SD of at least 3 repeat measurements, but are the same size or smaller than the points. All solution standard errors are internal standard errors and are all smaller than the points.

Quality Control and Assurance:

To provide extra assurance of instrument stability and ion chromatography efficacy, each batch of Zn samples contained at least one USGS reference material that went through the entire Zn separation and measurement procedure. **Table 2.11** shows the $\delta^{66}\text{Zn}$ ratios of all measured USGS reference materials. The BIR-1a, BCR-2, and BHVO-2 literature values used for comparison in **Table 2.11** are from Sossi *et al.* (2015), and the GSP-2 value is from Chen *et al.* (2016). The Sossi *et al.* (2015) values were used because the Zn ion chromatography used in this thesis was based on the Zn separation from Sossi *et al.* (2015). However, since Sossi *et al.* (2015) does not include GSP-2 data, Chen *et al.* (2016) GSP-2 data was used for comparison since it is a recent and includes a high number of repeats.

Table 2.11: USGS reference material Zn isotope measurements that were used for quality control and assurance. GSP-2 literature $\delta^{66}\text{Zn}$ came from Chen *et al.* (2016) and the rest from Sossi *et al.* (2015).

								Literature		
Reference Material	Type	Zn ($\mu\text{g}\cdot\text{g}^{-1}$)	Date of 1 st analytical session	$\delta^{66}\text{Zn}_{\text{ETH}}$ (‰)	$\delta^{66}\text{Zn}_{\text{Lyon}}$ (‰)	2SD	n	$\delta^{66}\text{Zn}_{\text{Lyon}}$ (‰)	2SD	n
BIR-1a	Iceland basalt (USGS)	70.4	05/06/19	-0.079	0.201	0.048	3	0.200	0.040	2
BIR-1a			23/03/21	-0.027	0.253	0.023	7			
BIR-1a			23/03/21	-0.042	0.238	0.024	6			
BIR-1a average				-0.042	0.238	0.047	16			
BHVO-2	Columbia river basalt (USGS)	103	05/06/19	0.036	0.316	0.061	3	0.270	0.060	18
GSP-2	Granodiorite (USGS)	120	05/06/19	0.768	1.048	0.019	3	1.070	0.060	12
BCR-2	Hawaiian basalt (USGS)	127	05/06/19	-0.016	0.264	0.020	3	0.250	0.010	3
BCR-2			23/03/21	-0.036	0.244	0.017	6			
BCR-2			10/05/21	-0.019	0.261	0.032	5			
BCR-2			11/05/21	-0.008	0.272	0.013	4			
BCR-2 average				-0.022	0.258	0.030	18			

2.3.3. Iron**2.3.3.1. Ion Chromatography**

The ion chromatography procedure used to isolate Fe is identical to the Zn method above, but Fe was collected in the 0.5M HCl collection step (**Figure 2.11 & Figure 2.16**). Since Fe, Zn and V were collected from a single digestion of each sample, to ensure adequate concentrations of V and Zn

for measurement, very high concentrations of Fe were passed through the Fe-Zn ion chromatography step. Therefore, to minimise any residual matrix and reduce any chances of mass independency or a matrix effect on the mass bias during measurement, all Fe samples were passed through an additional Fe clean-up column (**Figure 2.16**). The clean-up column utilised the quartz glass columns used in the V ion chromatography procedure (section 2.1) since unlike Zn, the mass of Fe processed through the columns is significantly larger than any column blank contribution, and the quartz glass columns benefitted from a higher flow rate. 1 ml of AG 1-X8 (200-400 mesh) resin was loaded into the columns and conditioned with 5 ml of 6M HCl. The sample was loaded in 4 ml of 6M HCl, and any matrix eluted in a further 6 ml of 6M HCl. Iron was collected in 6 ml of 0.5M HCl as in the first Fe-Zn column. The Fe fraction was then evaporated and re-dissolved once in ~16M HNO₃, then 200 µl of ~16M HNO₃ + 20 µl of 30% H₂O₂ were added and evaporated at 130°C to ensure that any residual organics were removed. The Fe fractions were then dissolved in 10 ml of 3% HNO₃, ready for MC-ICP MS measurement. All Fe total procedural blanks from all Fe sample batches are displayed in **Table 2.12**. Total Fe yields for all samples range between 78% and 100% with an average of 97% for 63 samples.

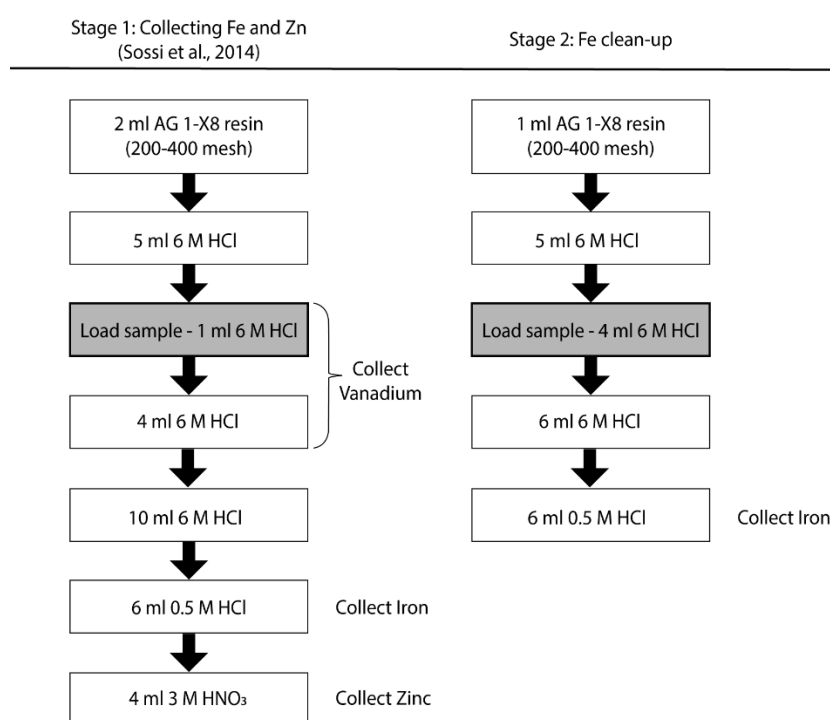


Figure 2.16: Summary flow chart of the Fe ion chromatographic separation procedure used at Durham University. The first separation uses Teflon columns with 20-60 µm polyethylene frits, and the second clean-up stage uses quartz columns with polyethylene frits and quartz wool.

Table 2.12: Total procedural Fe blanks (ng.g^{-1}) for all Fe sample

Date	Batch	Sample Type	Fe TPB (ng.g^{-1})
09-09-2019	2-x	FABs & boninites	27
09-09-2019	449	FABs & boninites	20
06-02-2020	468	FABs & boninites	42
22-02-2021	509	Peridotites	34
19-04-2021	511	Boninites	10
19-04-2021	512	Boninites	74
23-04-2021	515	Boninites	40
17-05-2021	517	Boninites	5

2.3.3.2. Mass Spectrometry (Neptune)

All Fe isotope measurements were obtained at Durham University between 2019 and 2021 on a Neptune Plus MC-ICP MS.

Instrument Set-up and Parameters:

The Neptune Plus MC-ICP MS was set up for static simultaneous collection of masses 53, 54, 56, 57, 58, 60, and 61 to allow all significant isotopes of Fe to be measured (ie. ^{54}Fe , ^{56}Fe , ^{57}Fe and ^{58}Fe). Masses ^{53}Cr and ^{61}Ni were monitored to correct for any ^{54}Cr interference on ^{54}Fe and ^{58}Ni interference on ^{58}Fe respectively. Masses ^{61}Ni and ^{60}Ni were monitored to correct for mass bias via Ni doping. All Faraday cups were assigned $10^{11} \Omega$ resistors, except cup L1 which was assigned a $10^{10} \Omega$ resistor since it collected the highest abundance Fe isotope of ^{56}Fe , and therefore needed to be able to manage a larger beam. The Faraday cup configuration and the resistors assigned to each cup are outlined in **Table 2.13**. All measurements were conducted in medium resolution mode ($M/\Delta M > 5000$) to resolve polyatomic interferences $^{40}\text{Ar}^{14}\text{N}$, $^{40}\text{Ar}^{16}\text{O}$ and $^{40}\text{Ar}^{16}\text{O}^1\text{H}$ on masses ^{54}Fe , ^{56}Fe and ^{57}Fe . The resolution across all measurement sessions never fell below 6500. All samples were measured in wet plasma mode using either an ESI SIS or GE “Cinnabar” cyclonic spray-chamber, a $50 \mu\text{l.min}^{-1}$ Savillex CF 50 nebuliser, with a sensitivity between 10 and 16 V.ppm^{-1} on ^{56}Fe ($50 \mu\text{l.min}^{-1}$). An H-skimmer cone and standard sample cone unique to Fe were used for all measurements. The following instrument operating conditions were used: RF power 1200 W, fore vacuum pressure 1.66×10^{-3} mbar, high vacuum 1.25×10^{-7} mbar, ion getter pressure 3.14×10^{-9} mbar.

Table 2.13: Faraday cup configuration used to measure $\delta^{56}\text{Fe}$ on the Neptune mass spectrometer at Durham University. The table shows the assignment of analyte and interfering element masses in each cup. The masses below were monitored to allow all significant isotopes of Fe (54, 56, 57, and 58) to be measured, plus ^{61}Ni and ^{53}Cr . Monitor isotopes for the IECs are in bold, and isotopes for the Ni-doping mass bias correction are in italics.

Cup	L4	L2	L1	C (Ax)	H1	H2	H3
Mass	53	54	56	57	58	60	61
Analyte Isotope		Fe	Fe	Fe	Fe		
Interference Isotope	Cr	Cr			Ni	<i>Ni</i>	<i>Ni</i>
Resistor	10^{11}	10^{11}	10^{10}	10^{11}	10^{11}	10^{11}	10^{11}

Prior to each measurement sequence, a plateau position was chosen that minimised polyatomic interferences (**Figure 2.17**). The plateau size was on average 0.01 amu. Each isotope measurement consisted of 60 s of monitoring background intensities, followed by data collection for 1 block of 50 cycles with 4.194 second integration per cycle. Interfering Element Corrections (IEC) were applied to the $^{56}\text{Fe}/^{54}\text{Fe}$, $^{57}\text{Fe}/^{54}\text{Fe}$, and $^{58}\text{Fe}/^{54}\text{Fe}$ ratios to correct for the presence of any residual Cr and Ni following chemistry using $^{53}\text{Cr}/^{54}\text{Cr} = 4.017677$ and $^{60}\text{Ni}/^{58}\text{Ni} = 0.385198$. Typical $^{53}\text{Cr}/^{54}\text{Fe}$ and $^{61}\text{Ni}/^{54}\text{Fe}$ ratios were 4×10^{-5} to 8×10^{-6} and 1×10^{-5} to 8×10^{-6} respectively, which is below the 1×10^{-1} threshold at which the interference correction breaks down (Dauphas *et al.* 2009b).

Initially Fe mass bias was corrected for by standard solution-sample bracketing. However, the data was often unstable and of low precision due to large mass bias shifts throughout and between sessions. Often, repeat sample measurements were not within analytical error of one another. In 2021 a different approach to mass bias correction was adopted. All solutions were doped with 8ppm total Ni to provide at least 1 V on the smallest Ni isotope ^{61}Ni . The mass bias was corrected for by comparing the measured $^{60/61}\text{Ni}$ ratio from each measurement to the true $^{60/61}\text{Ni}$ ratio of 23.004737, and the β -factor was calculated using the exponential law. Ni-doping improved solution standard accuracy and precision consistency within and across measurement sessions and obtaining consistent repeat sample measurements was more successful. All sample data previously obtained by standard-sample bracketing, was remeasured using combined standard-sample bracketing and Ni-doping. Only 50% of the samples remeasured using Ni-doping reproduced their SSB values (**Figure 2.18**), which highlights the instability observed during solution-sample bracketing, and that it was a good decision to change technique.

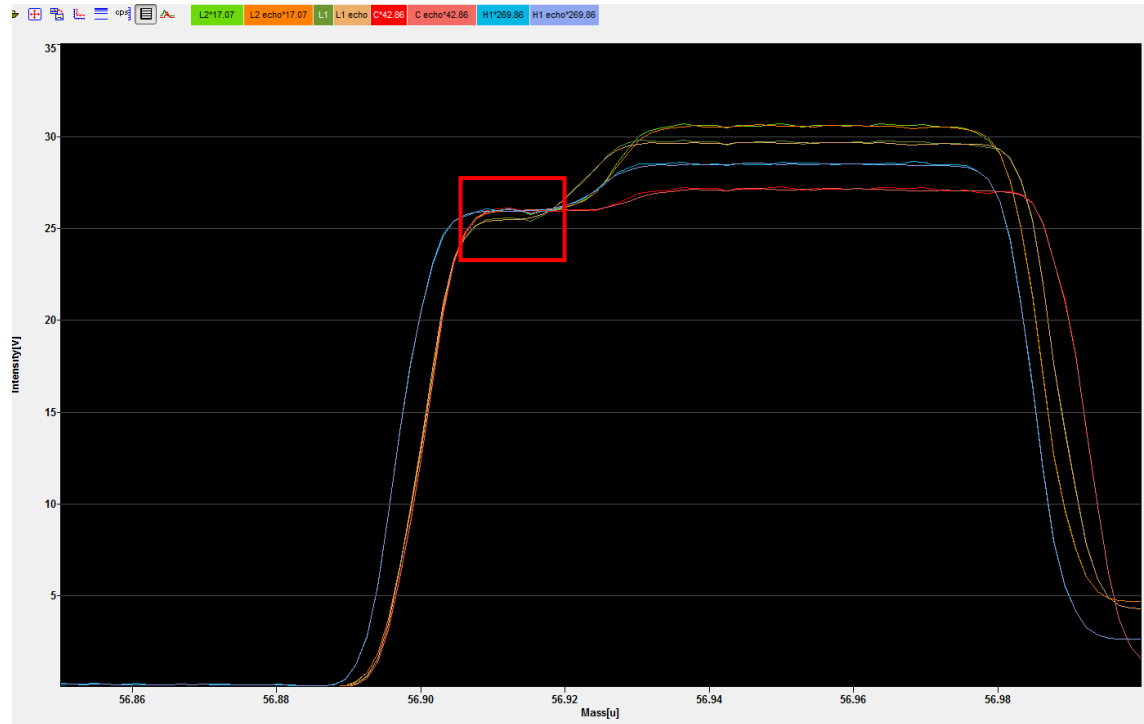


Figure 2.17: Screenshot of mass scan from Neptune software during Fe isotope measurement. The scan was conducted on the 16th April 2021. The red box shows the ideal position on the mass 57 plateau to minimise interferences when analysing Fe isotopes.

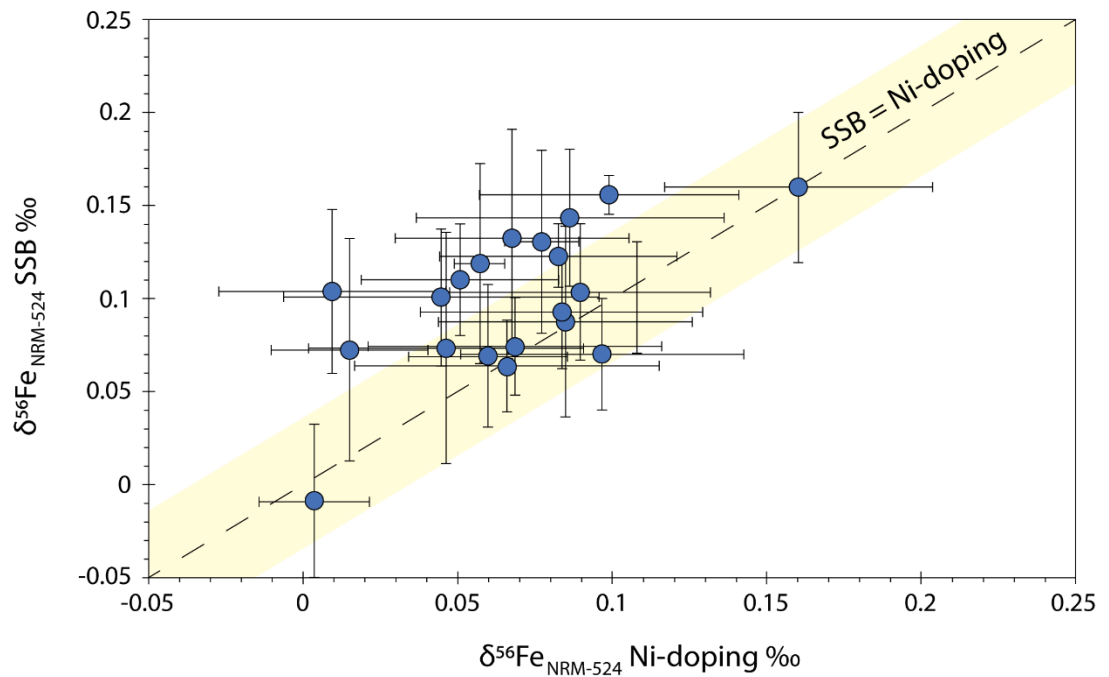


Figure 2.18: Comparison of Ni-doping versus sample-standard bracketing correction techniques. $\delta^{56}\text{Fe}_{\text{NRM-524}}$ average values are plotted for samples which were measured using both SSB and Ni-doping mass bias correction techniques. The Ni-doping $\delta^{56}\text{Fe}$ values are on the x-axis, and SSB $\delta^{56}\text{Fe}$ on the y-axis. The black dashed line represents where the two values are equal, and the yellow shaded area represents a ± 0.030 ‰

error shadow, within which measurements were assumed to be the acceptable identical. All sample error bars are 2SD on repeat measurements.

Solution Standards:

The traditional Fe solution standard used to bracket unknowns and defined as $\delta^{56}\text{Fe} = 0\text{‰}$ was IRMM-014 (eq. 4). Every measurement of an unknown was bracketed by one IRMM-014 standard solution, and intermittently an in-house solution standard called Romil Fe was measured to assess instrument stability and accuracy (**Figure 2.19**). IRMM-014 was used to bracket samples used in this thesis until October 2020 when the Durham University stock of IRMM-014 was exhausted, and purchasing more was impossible due to the Institute for Reference Materials and Measurements ceasing IRMM-014 sales. NRM-524 is an Fe solution standard with the same Fe isotopic composition as IRMM-014 since IRMM-014 was prepared from the same neutron dosimetry as NRM-524 (Craddock & Dauphas 2011). NRM-524 was purchased to replace IRMM-014 as Fe bracketing solution standard, and was used for measuring all unknowns from October 2020 onwards. The long-term average of in-house solution standard Romil Fe relative to NRM-524 was $\delta^{56}\text{Fe}_{\text{NRM-524}} = 0.177 \pm 0.061\text{‰}$, $n = 215$, **Figure 2.20**. Due to Fe having four isotopes, two isotope ratios were calculated for every measurement ($^{56/54}\text{Fe}$, $^{57/54}\text{Fe}$) but the $^{56/54}\text{Fe}$ ratio is used for interpretation due to its higher precision.

$$(4) \quad \delta^{56}\text{Fe} = 1000 \times \left[\left(\frac{^{56}\text{Fe}/^{54}\text{Fe}_{\text{sample}}}{^{56}\text{Fe}/^{54}\text{Fe}_{\text{standard}}} \right) - 1 \right]$$



Figure 2.19: Example MC-ICP MS Fe isotope analysis measurement sequence using standard solution-sample bracketing.

All solutions (NRM-524, Romil Fe, and samples) were run in 3% HNO_3 and between every measurement, the sample introduction system was washed with 3% HNO_3 for 120 s to eliminate any cross-contamination between measurements. The background ^{57}Fe decreased to $< 8\text{ mV}$ after the wash-out. All samples and standards were measured at solution concentrations of 6 to 10 $\mu\text{g}\cdot\text{g}^{-1}$.

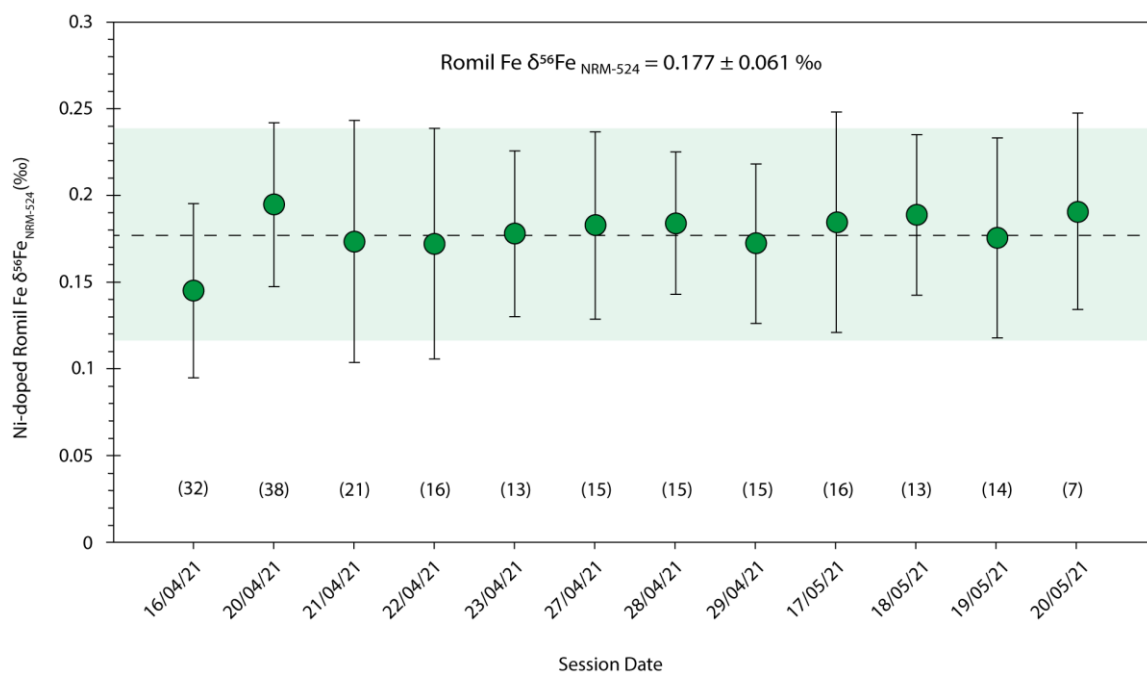


Figure 2.20: Long-term average for Romil Fe solution standard. A Romil Fe average was taken for each measurement day. Romil Fe long-term average $\delta^{56}\text{Fe}_{\text{NRM-524}} = 0.177 \pm 0.061 \text{ ‰}$, $n = 215$. The number in brackets beneath each point shows the number of measurements included in the average. Error bars are shown as 2SD. The black dashed line and green horizontal shaded area represent the average and 2SD error on the long-term standard average respectively.

Acceptance Criteria:

For measurements to be accepted, samples had to meet the following criteria: (1) the solution concentrations were within 10% of the bracketing NRM-524 standard, (2) the relative standard deviation of the bracketing IRMM solutions was less than 0.1%, (3) the measured Fe isotope ratios were mass dependent (measured $^{56}\text{Fe}/^{54}\text{Fe} \times 1.5 = \text{measured } ^{57}\text{Fe}/^{54}\text{Fe} \pm 0.2$) (**Figure 2.21**), (4) the 2SD of all repeated measurements were less than 0.05 ‰.

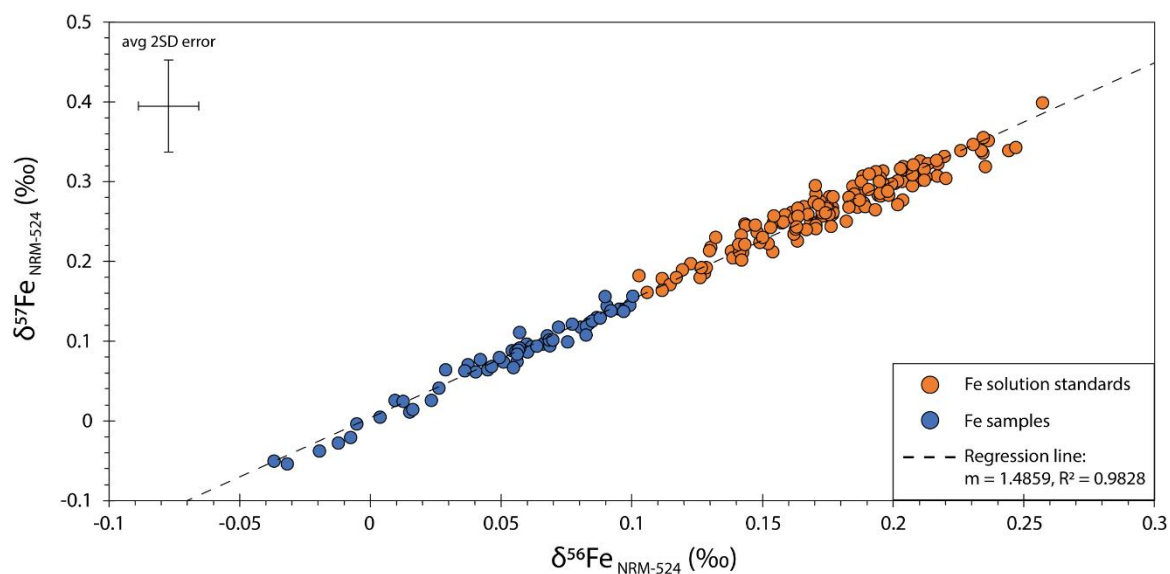


Figure 2.21: Iron mass dependency plot showing $\delta^{56}\text{Fe}$ vs $\delta^{57}\text{Fe}$ relative to Fe reference material NRM-524 for all Fe samples and Romil Fe solution standards. The data fall on a linear regression line with a gradient of 1.4859 and an R^2 of 0.9828. All measurements are therefore assumed mass dependent since the regression gradient is in proportion with the $\delta^{56}\text{Fe}/\delta^{57}\text{Fe}$ mass dependency ratio of ~ 1.5 . All errors for the samples are 2SD of at least 3 repeat measurements, and the average error bars are shown in the top left corner.

Quality Control and Assurance:

To provide extra assurance of instrument stability and ion chromatography efficacy, each batch of Fe samples contained at least one USGS reference material that went through the entire Fe separation and measurement procedure. **Table 2.14** shows the $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ ratios of all measured USGS reference materials together with indicative literature values. Gong *et al.* (2020) values are given since it is one of the most recent Fe isotopes studies that uses Ni-doping, and includes extensive USGS reference material measurements that reproduce previous literature values. However, since BIR-1a measurements are not included in Gong *et al.* (2020), BIR-1a measurements are compared to Ni-doped Fe measurements from Sossi *et al.* (2015) since the Fe separation from this work is based on the Sossi *et al.* (2015) protocol.

Table 2.14: USGS reference material Fe isotope measurements that were used for quality control and assurance. All literature $\delta^{56}\text{Fe}$ values are relative to IRMM-014 or NRM-524. BIR-1a literature $\delta^{56}\text{Fe}$ is from Sossi *et al.* (2015), and all others are from Gong *et al.* (2020).

				Iron isotope ratios vs NRM-524					Literature		
Reference Material	Type	Fe ₂ O ₃ (wt%)	Date of 1 st analytical session	δ ⁵⁶ Fe (‰)	2SD	δ ⁵⁷ Fe (‰)	2SD	n	δ ⁵⁶ Fe (‰)	2SD	n
BIR-1a	Iceland basalt (USGS)	11.3	16/04/21	0.080	0.04	0.117	0.070	10	0.06	0.01	2
BIR-1a			16/04/21	0.064	0.05	0.103	0.075	14			
BIR-1a			18/05/21	0.062	0.04	0.093	0.056	12			
BIR-1a average				0.068	0.05	0.104	0.069	36			
BHVO-2	Columbia river basalt (USGS)	12.3	28/04/21	0.124	0.04	0.193	0.055	5	0.11	0.04	81
GSP-2	Granodiorite (USGS)	4.9	11/09/19	0.160	0.03	0.229	0.039	11	0.15	0.04	40
BCR-2	Hawaiian basalt (USGS)	13.8	11/09/19	0.095	0.01	0.140	0.024	7	0.08	0.04	114
BCR-2			21/04/21	0.084	0.05	0.128	0.085	5			
BCR-2 average				0.090	0.03	0.135	0.056	12			

2.3.4. Titanium

The analysis of Ti isotopes was undertaken at Cardiff University in the Cardiff Earth Laboratory for Trace Element and Isotope Chemistry (CELTIC) with the aid of Dr. Marc-Alban Millet. The sample digestion procedure was similar to the standard hotplate procedure described in section 2, but the $\text{HNO}_3\text{:HF}$ ratio was 1:1 and 400 μl of boric acid was added to the final solution to further ensure fluoride removal and spike equilibration.

2.3.4.1. Titanium Double Spiking

Double spiking, first proposed by Dodson *et al.* (1963), is an instrumental mass bias correction method that also corrects for any sample preparation isotope fractionation. It assumes that all samples and reference standards are related by mass-dependent isotope fractionation following the exponential law, and uses an isotopically enriched “double-spike” that is added to samples before the ion chromatography stages of sample preparation (Millet & Dauphas 2014). Double spiking involves resolving equation 5 (Albarède & Beard 2004), where R_m is the measured isotope ratio, R_{std} is the isotope ratio of the standard, and R_{spike} is the isotope ratio of the spike. i_n is the

normalising isotope for the ratios, and i_x is the numerator isotope for the ratios. The proportion of normalising isotope from the spike is f , the natural fractionation factor between the sample and reference standard is α , and β is the exponential mass fractionation factor. A minimum of three isotope ratios is required to resolve the system since there are three unknowns f , α , and β . Therefore, double spiking cannot be used for stable isotope systems with less than four isotopes.

$$(5) \quad R_m = \left[\left((1 - f) \left(R_{std} \left(\frac{i_x}{i_n} \right)^\alpha \right) + f R_{spike} \right) x \left(\left(\frac{i_x}{i_n} \right)^\beta \right) \right]$$

Samples measured for Ti stable isotopes in this thesis were processed and measured using the Ti double spike method of Millet & Dauphas (2014). The method uses a ^{47}Ti - ^{49}Ti double spike mixed to an appropriate proportion based on predetermined Ti concentrations for the samples, with a 5 to 20 μg Ti aliquot of the digested sample. The spiked aliquot was dried at 130°C . Once dry, 300 μl of $\sim 14\text{M}$ HNO_3 was added, and the solution dried. This was repeated at least a further two times. 5 ml of 12M HNO_3 was then added, and the solution heated overnight. 5ml of 12M HNO_3 was the loading solution for the ion chromatography stage. After analysis, the raw data was processed using Cardiff University in-house double spike resolution codes written in Mathematica®.

2.3.4.2. Ion Chromatography

The chromatographic procedure for Ti stable isotope analysis used in this study echoes Zhang *et al.* (2011), but only utilised the first stage of separation (**Figure 2.22a**). The first separation stage used a vacuum box since the use of 12M HNO_3 + 1% H_2O_2 which bubbled, prevented the solution to elute through the resin and columns by gravity alone. The vacuum accelerated the process considerably. **Figure 2.22b** shows the set-up. The Biorad columns were connected to 2ml DN-R10-S resin cartridges (50-100 μm) and were 0.8 cm in diameter and 4 cm in length. The cartridges were connected to the vacuum box via pipette tips.

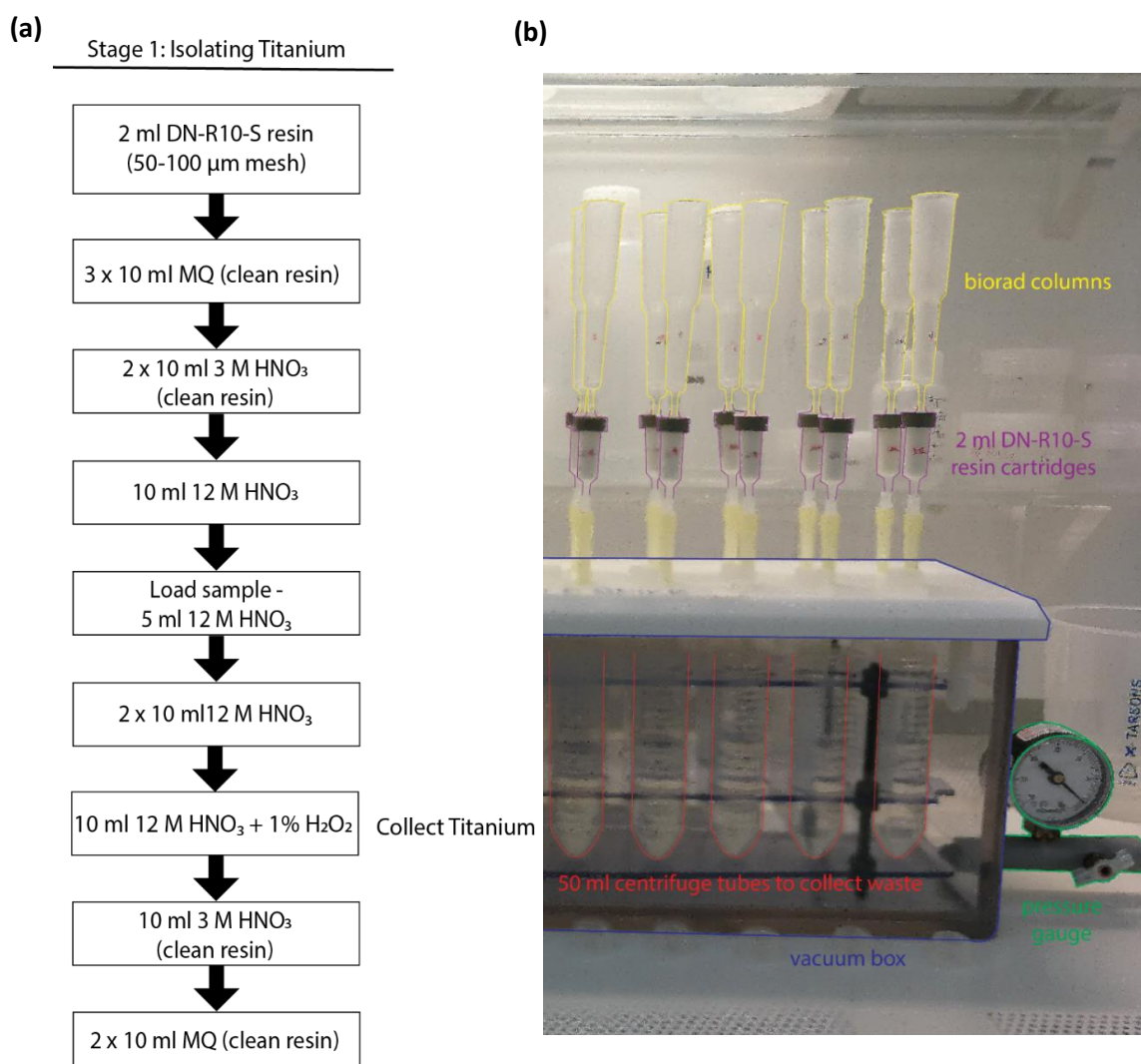


Figure 2.22: Titanium ion chromatography flow chart and photo of set-up. a) Summary flow chart outlining the procedure for the Ti ion chromatographic column setup. b) Photo of the setup used for the chromatographic separation, showing the biorad columns, resin cartridges, vacuum box, pressure gauge and centrifuge tubes used for waste collection.

The resin was first cleaned using 30 ml of MilliQ, then 20 ml of 3M HNO₃. The resin was then conditioned with 10 ml of 12M HNO₃, and the samples were loaded onto the resin in a solution of 5 ml of 12M HNO₃. A few millilitres of ~14M HNO₃ were added to the now empty beakers and heated on a hotplate until they were required for collection to remove any potentially remaining sample. After loading, the matrix was washed through the resin with 20 ml of 12M HNO₃ to Ca, which is an isobaric interference on Ti during analysis. Following this, the collection beakers were emptied, and placed beneath the columns in the vacuum box. 10 ml of 12M HNO₃ + 1 wt% H₂O₂ was added to the resin to elute the Ti for collection. The beakers were then transferred to a hotplate and evaporated overnight at 100°C. The resin was cleaned for reuse with 10 ml of 3M HNO₃, to remove the remaining matrix, and then, with 20 ml of MilliQ.

Once the beakers were dry, a small volume of $\sim 14\text{M}$ HNO_3 was added to the residues and evaporated three times. The residue was then dissolved in 2 ml of 2% HNO_3 + trace HF (5 ml of 48% HF in 2 L of 2% HNO_3) ready for analysis.

2.3.4.3. Mass Spectrometry (Nu Plasma II)

All Ti isotope measurements were measured on a Nu instruments Plasma II MC ICP-MS at Cardiff University. The exact Ti isotope measurement protocol is outlined in Hoare *et al.* (2020).

All measurements were conducted in medium resolution mode ($M/\Delta M > 5000$), and dry plasma mode using an Aridus II desolvating nebuliser. To account for minor unresolved polyatomic interferences on ^{47}Ti and ^{48}Ti , all samples were bracketed by two OL-Ti reference material measurements (Millet & Dauphas 2014). However, mass bias was corrected for by double-spiking (Millet & Dauphas 2014). All raw data was processed offline using internal double-spike deconvolution codes written in Mathematica®. All Ti data is expressed as $\delta^{49}\text{Ti}$ relative to OL-Ti which is defined as $\delta^{49}\text{Ti} = 0 \text{ ‰}$ as in equation 6. All measurement errors are reported as 95% confidence intervals.

$$(6) \quad \delta^{49}\text{Ti} = 1000 \times \left[\left(\frac{{}^{49}\text{Ti}/{}^{47}\text{Ti}_{\text{sample}}}{{}^{49}\text{Ti}/{}^{47}\text{Ti}_{\text{standard}}} \right) - 1 \right]$$

2.3.5. Hafnium

The analysis of hafnium (Hf) isotopes was undertaken at Durham University in November 2020. All samples were bomb digested as outlined in section 2 to ensure all potential sources of Hf, such as zircon inclusions, were completely dissolved. Hafnium analyses were carried out on 11 IODP FAB and boninite whole-rock powders to fill in literature data gaps. Based on the Hf concentration of the lowest concentration sample, 45 to 50 mg of each sample was digested. After digestion, the samples were transferred to 7 ml Teflon beakers and dissolved in 1 ml of 1M HCl - 0.1M HF in preparation for the first stage of Hf chromatographic separation (**Figure 2.23**).

2.3.5.1. Ion Chromatography

The chromatographic separation procedure used in this study follows closely that of Bast *et al.* (2015). Both stages of the two-stage procedure use Kynar heat-shrink columns with a 12 ml reservoir, a 10 cm column length, and a resin-bed 8.2 cm long and 5.6 mm in diameter that can hold 2 ml of resin. The polyethylene frits are 1.6 mm thick with a pore size of 35 μm . The two stage procedure is outlined in **Figure 2.23**.

Stage 1: Removing REEs

The first stage of Hf separation was a cation exchange chromatography outlined in Bast et al. (2015) that utilised 2 ml of Bio-rad AG 50W-X8 (200-400 mesh) resin. The resin could be reused up to 12 times before replacing and re-calibrating and therefore had to be extensively cleaned at the start and end of each separation. The resin was cleaned using 12 ml of 6M HCl, backflushed with MilliQ, and then further cleaned with 12 ml of 2M HF and 24 ml of 6M HCl. The resin was then conditioned with 2 x 1 ml 1M HCl – 0.1M HF. During the conditioning step the samples were transferred to microcentrifuge tubes and centrifuged for at least 5 minutes at 13500 rpm to ensure that during sample loading, no residual precipitate met the resin. The samples were then loaded on the columns and the HFSEs (including Hf) immediately collected in 5.5 ml of 1M HCl – 0.1M HF. It was possible to collect both Sr and Nd cuts from the same digestion using this procedure, however they were not needed, and to ensure the resin was clean enough for future use, the Sr and Nd steps were still undertaken. After collecting the Hf cut, Rb and the sample matrix were eluted using 26 ml of 1.5M HCl. Strontium was then eluted in 14 ml of 1.5M HCl, followed by HREEs using 8 ml of 2.5M HCl, and then the LREE fraction (including Nd) in 8 ml of 6M HCl. The resin was then cleaned with 12 ml of 2M HF and 12 ml of 6M HCl.

Stage 2: Removing Titanium and Zirconium

The HFSE aliquots were dried down overnight at around 70°C, then re-dissolved in 200 µl of 0.56M HNO₃ – 0.3M HF – 4% H₂O₂ and slowly dried at 80°C, as described by Bast et al. (2015), to oxidise any organics and aid dissolution of the sample in the loading solution for the second stage of Hf separation.

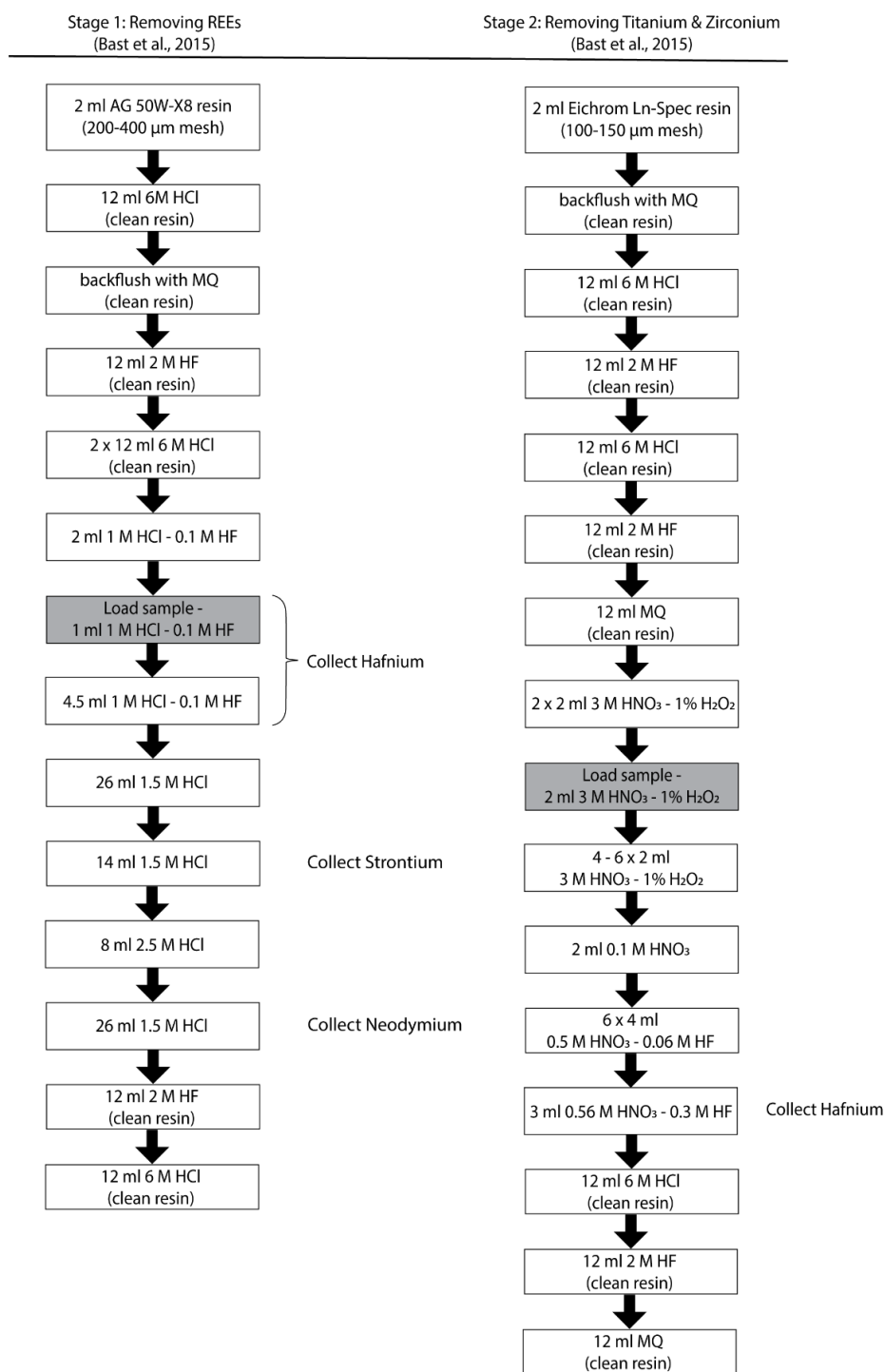


Figure 2.23: Summary flow chart outlining the Hf ion chromatographic separation procedure. The two stages are based on Bast et al. (2015) and use the same column set up.

The samples were then dissolved in 2 ml of 3M HNO₃ – 1% H₂O₂ and since heat denatures H₂O₂, the samples were placed in an ultrasonic bath for at least 30 minutes to encourage dissolution. The Ti complexed with the H₂O₂ and the solution turned yellow. This chromatographic stage used columns of the same design as in the first stage, but with 2 ml of Eichrom 100 – 150 mesh Ln-Spec resin, which could be reused up to 12 times. The resin was therefore cleaned at the start and end of each

separation. The resin was first backflushed with MilliQ, and then cleaned twice with 12 ml of 6M HCl and 12 ml of 2M HF, and then with 2 ml of MilliQ. The resin was then conditioned with 2 x 2 ml of 3M HNO₃ – 1% H₂O₂ and then the sample was loaded. There was no need to centrifuge the sample at this stage since the samples readily dissolved and fluorides were removed prior to the first column. Titanium was eluted using 3M HNO₃ – 1% H₂O₂ until the elutant turned from yellow to colourless (typically between 8 and 12 ml). Once Ti had been eluted, any remaining H₂O₂ was washed from the resin using 2 ml of 0.1 M HNO₃. Zirconium was then eluted using 6 x 4ml 0.5M HNO₃ – 0.06M HF, and the Hf was collected in 3 ml of 0.56M HNO₃ – 0.3M HF. The Hf cut was dried down, 200µl of concentrated HNO₃ was added to the residue and dried at around 160°C to oxidise any organics, and the samples were dissolved in 333µl of 0.56M HNO₃ – 0.3M HF ready for analysis. The 0.56M HNO₃ – 0.3M HF volume was kept to a minimum to maximise sample concentration and hence beam size during measurement. The HF aids Hf wash out between measurements.

Testing oxidation of organics technique and need for Zr separation:

Bast et al. (2015) explains that to ensure the Hf cut fully dissolves in the second stage loading solution, after the initial evaporation, the residue must be dissolved in 200µl of 0.56M HNO₃ – 0.3M HF – 4% H₂O₂ and dried slowly at 80°C to oxidise organics. This mix of solvents needed to be titrated and was a more complex step than that used to oxidise organics in the V-Fe-Zn separation procedure. Therefore, a single batch of 11 USGS standards were passed through this column. The batch included two digestions of AGV-1, and three digestions of BHVO-2, BCR-2, and BIR-1a each. For each of these standards, one digestion used the Bast *et al.* (2015) method for organic oxidation, and one digestion used 200µl of concentrated HNO₃ as used for the V-Fe-Zn separation. The resultant Hf isotope ratios were compared to determine if 0.56M HNO₃ – 0.3M HF – 4% H₂O₂ is required. **Table 2.15** shows that there is no analytically resolvable difference in Hf isotope ratio.

The Zr elution step in the second stage of Hf separation is long and stretches the procedure to two days. However, the elution of Zr may not be necessary. Therefore, one digestion of each USGS was split in half. One aliquot had Zr eluted and the other did not. The aliquot containing Zr moved straight from the step that washes off the H₂O₂ to collecting the Hf. **Table 2.12** again shows that there is no analytically resolvable difference in Hf isotope ratios between the Zr-containing or Zr-free aliquots and the 2SE precision of the former was the same or better than the latter. However, the Hf yield for those aliquots containing Zr was slightly lower, and this is presumably a result of missing out the 24ml Zr elution step, in which case Hf was still high up the resin bed and we missed the tail of the Hf elution peak. In the future the Hf collection step will need to be lengthened and calibrated to increase the Hf yield for small samples.

Table 2.15: $^{176}\text{Hf}/^{177}\text{Hf}$ data for USGS reference materials that went through different versions of the Hf second stage of Hf ion chromatography. Each reference material has at least 1 digestion that went through the procedure as described in Bast et al. (2015), one digestion did not have Zr eluted, and one digestion did not have the 0.56M $\text{HNO}_3 - 0.3\text{M HF} - 4\% \text{H}_2\text{O}_2$ and was instead dried down in only concentrated HNO_3 .

USGS Reference Material	Batch no.	Process	Measured				Accepted		$\Delta_{\text{measured/accepted}}$
			$^{176}\text{Hf}/^{177}\text{Hf}$ normalised	2SE	Average	2SD	$^{176}\text{Hf}/^{177}\text{Hf}$	Reference	
AGV-1	447-1A	as Bast et al. (2015)	0.282981	0.000003	0.282980	0.000003	0.282979	Weis et al. (2007)	4.6
	447-1B	$\text{HNO}_3\text{-HF-H}_2\text{O}_2$ step + no Zr elution	0.282982	0.000005					
	447-2	conc HNO_3 step + Zr elution	0.282979	0.000003					
BCR-2	447-3A	as Bast et al. (2015)	0.282867	0.000003	0.282865	0.000007	0.282870	Weis et al. (2007)	-17.2
	447-3B	$\text{HNO}_3\text{-HF-H}_2\text{O}_2$ step + no Zr elution	0.282867	0.000003					
	447-4	as Bast et al. (2015)	0.282860	0.000003					
	447-5	conc HNO_3 step + Zr elution	0.282868	0.000003					
BIR-1a	447-6A	as Bast et al. (2015)	0.283253	0.000007	0.283254	0.000011	0.283243	Fourny et al. (2016)	37.5
	447-6B	$\text{HNO}_3\text{-HF-H}_2\text{O}_2$ step + no Zr elution	0.283261	0.000009					
	447-7	as Bast et al. (2015)	0.283254	0.000005					
	447-8	conc HNO_3 step + Zr elution	0.283248	0.000006					
BHVO-2	447-9A	as Bast et al. (2015)	0.283099	0.000003	0.283098	0.000005	0.283105	Weis et al. (2007)	-26.1
	447-9B	$\text{HNO}_3\text{-HF-H}_2\text{O}_2$ step + no Zr elution	0.283094	0.000003					
	447-10	as Bast et al. (2015)	0.283100	0.000003					
	447-11	conc HNO_3 step + Zr elution	0.283099	0.000003					

2.3.5.2. Mass Spectrometry (Neptune)

Hf isotope analyses were carried out on the Thermo Scientific Neptune Plus MC-ICP MS at Durham University. The mass spectrometer was equipped with $10^{11} \Omega$ resistors on Faraday cup. The main isotopes of Hf (^{176}Hf , ^{177}Hf , ^{178}Hf , ^{179}Hf and ^{180}Hf) and one and two isotopes of the interfering elements Lu and Yb respectively (^{175}Lu , ^{173}Yb and ^{172}Yb) were measured simultaneously using the Faraday cup configuration in **Table 2.16**. An Aridus II in combination with a Cetac CF-50 nebuliser, with a measured uptake rate of $70 \mu\text{l} \cdot \text{min}^{-1}$, was used as the sample introduction system. This combination, together with an X skimmer cone and standard geometry sample cone were enhanced the sensitivity to $\sim 540 \text{ V} \cdot \text{ppm}^{-1}$ of total Hf.

A static analysis comprised of 1 block of 50 cycles with a 4.194 second integration time. An exponential mass bias correction was applied using $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$ to correct for instrumental mass bias. IECs were applied to ^{176}Hf using the monitored ^{176}Lu and ^{173}Yb monitor masses (**Table 2.16**) and the following interfering element ratios: $^{176}\text{Lu}/^{175}\text{Lu} = 0.026550$ and $^{176}\text{Yb}/^{173}\text{Yb} = 0.794447$. Periodically Hf solution standard JMC-475 was measured to assess machine accuracy and all sample values were normalised to the preferred JMC-475 $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.282160 (Nowell *et al.* 1998; Vervoort & Blichert-Toft 1999). Samples were analysed in one analytical session for which average $^{176}\text{Hf}/^{177}\text{Hf}$ of JMC-475 was 0.282147 ± 0.000006 (2SD, $n=16$). For age corrections, $\lambda^{176}\text{Lu}$ 1.867×10^{-11} was used (Scherer *et al.* 2001; Söderlund *et al.* 2004).

Table 2.16: Faraday cup configuration and assigned amplifier resistivity used to measure $^{176}\text{Hf}/^{177}\text{Hf}$ on the Neptune mass spectrometer at Durham University. The table shows the assignment of analyte and interfering element masses in each cup. Hf isotopes used for mass bias correction are in italics. Monitor isotopes for the interfering element corrections are in bold.

Cup	L4	L3	L2	L1	C (Ax)	H1	H2	H3
Mass	172	173	175	176	177	178	179	180
Analyte Isotope				Hf	<i>Hf</i>	Hf	<i>Hf</i>	Hf
Interference Isotope	Yb	Yb	Lu	Lu Yb				
Resistor	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}

2.4. Trace Elements

Whole-rock peridotite and kimberlite samples for chapter three were analysed for trace elements at the Open University in March 2019 and September 2020 by ICP-QQQ-MS.

2.4.1. Sample Digestion and Dilution

All sample digestions were undertaken at Durham University following the ‘bombing’ procedure from section 2. A maximum of 50 mg of sample powder was added to each bomb. After digestion, the samples were dissolved in 1 ml of ~16M HNO₃ and transported to the Open University. At the Open University samples were transferred to PP bottles and diluted 1000-fold relative to the original weighed sample mass using purified H₂O ready for analysis.

2.4.2. ICP-QQQ-MS Measurement

All trace element concentrations were measured at the Open University using an Agilent 8800 ICP-QQQ-MS inductively coupled plasma-mass spectrometer. The trace element measurement procedure used was identical to Brett *et al.* (2018). However, instead of two collision/reaction gas configurations, three were employed to reduce isobaric and molecular interferences in particular on the REEs: no gas in the collision cell, He gas in the collision cell, and O₂ gas in the collision cell. USGS reference materials PCC-1 and DTS-1 were run at the beginning and end of both measurement sessions to assess instrument stability and are displayed in **Table 2.17**.

Table 2.17: Trace element concentration data ($\mu\text{g.g}^{-1}$) for USGS reference materials PCC-1 and DTS-1 determined by ICP-QQQ-MS at the Open University for quality control, plus the reported literature concentrations for those materials, the percentage difference between measured and literature concentrations, and the limits of detection. Accepted concentration data for PCC-1 and DTS-1 were taken from Babechuk *et al.* (2010) and Jochum *et al.* (2016) respectively.

Trace Element	PCC-1 concentrations ($\mu\text{g.g}^{-1}$)			DTS-1 concentrations ($\mu\text{g.g}^{-1}$)			Limit of Detection ($\mu\text{g.g}^{-1}$)
	Measured	Literature	% Diff	Measured	Literature	% Diff	
Li	0.9	1	10%	1.8	2	10%	3.94×10^{-3}
Sc	7.3	9	19%	3.3	3.4	3%	3.46×10^{-3}
Ti	23.8	25.1	5%	21.1	23.5	10%	5.27×10^{-2}
V	26.6	26	-2%	9.4	10	6%	3.11×10^{-3}
Cr	2962	1913	-55%	4504	4100	-10%	1.78×10^{-2}
Mn	813	-		928	-		6.80×10^{-3}
Co	106	114	7%	140	136	-3%	1.43×10^{-3}
Ni	2090	2341	11%	2267	2298	1%	8.82×10^{-3}
Cu	5.8	7	17%	5.6	5.7	2%	6.20×10^{-3}
Zn	38.3	38.3	0%	45.1	43.8	-3%	9.36×10^{-2}
Rb	0.06	0.06	0%	0.09	0.07	-29%	5.47×10^{-3}
Sr	0.36	0.48	25%	0.31	0.3	-3%	1.04×10^{-3}
Y	0.08	0.08	0%	0.04	0.04	0%	1.02×10^{-3}
Zr	0.17	0.13	-31%	0.17	0.15	-13%	1.15×10^{-3}
Nb	0.02	0.01	-100%	0.02	0.02	0%	1.38×10^{-4}
Cs	0	0	0%	0.01	0.01	0%	1.27×10^{-3}

Ba	0.93	0.79	-18%	0.33	0.34	3%	9.53 x10 ⁻³
La	0.03	0.03	0%	0.02	0.03	33%	2.66 x10 ⁻⁴
Ce	0.05	0.05	0%	0.05	0.05	0%	1.97 x10 ⁻⁴
Pr	0.007	0.007	0%	0.007	0.006	-17%	6.63 x10 ⁻⁵
Nd	0.03	0.03	0%	0.03	0.02	-50%	4.94 x10 ⁻⁴
Sm	0.005	0.005	0%	0.004	0.004	0%	1.28 x10 ⁻⁴
Eu	0.001	0.001	0%	0.001	0.001	0%	1.32 x10 ⁻⁴
Gd	0.006	0.006	0%	0.003	0.004	25%	1.18 x10 ⁻³
Tb	0.001	0.001	0%	0.001	0.001	0%	2.06 x10 ⁻⁴
Dy	0.008	0.009	11%	0.004	0.005	20%	1.63 x10 ⁻⁴
Ho	0.003	0.003	0%	0.001	0.001	0%	6.30 x10 ⁻⁵
Ta	0.003	0.001	-200%	0.002	0.001	-100%	4.03 x10 ⁻⁴
Er	0.01	0.011	9%	0.005	0.005	0%	5.04 x10 ⁻⁴
Hf	0.005	0.004	-25%	0.005	0.005	0%	4.26 x10 ⁻⁴
Yb	0.025	0.023	-9%	0.009	0.01	10%	5.56 x10 ⁻³
Lu	0.004	0.005	20%	0.002	0.002	0%	4.42 x10 ⁻⁴
Tl	0.001	0.001	0%	0.002	0.002	0%	6.00 x10 ⁻⁴
Pb	7.6	7.6	0%	7.6	8.5	11%	5.85 x10 ⁻³
Th	0.01	0.01	0%	0.01	0.01	0%	1.78 x10 ⁻⁴
U	0.003	0.004	25%	0.003	0.003	0%	3.03 x10 ⁻⁴

References

- Albarède, F. & Beard, B.L. 2004, Analytical methods for non-traditional isotopes, *In: Johnson, C.M., Beard, B.L. and Albarède, F. (Eds.), Geochemistry of non-traditional isotopes: reviews in mineralogy and geochemistry, Mineralogical Society of America and Geochemical Society, Washington DC*, **55**, 113–152.
- Anbar, A.D., Jarzecki, A.A. & Spiro, T.G. 2005. Theoretical investigation of iron isotope fractionation between Fe(H₂O)₆³⁺ and Fe(H₂O)₆²⁺: Implications for iron stable isotope geochemistry. *Geochimica et Cosmochimica Acta*, **69**, 825–837, <https://doi.org/10.1016/j.gca.2004.06.012>.
- Archer, C., Andersen, M.B., Cloquet, C., Conway, T.M., Dong, S., Ellwood, M., Moore, R., Nelson, J., Rehkamper, M., Rouxel, O., Samanta, M., Shin, K.C., Sohrin, Y., Takano, S. & Wasylenski, L. 2017. Inter-calibration of a proposed new primary reference standard AA-ETH Zn for zinc isotopic analysis. *Journal of Analytical Atomic Spectrometry*, **32**, 415–419, <https://doi.org/10.1039/c6ja00282j>.
- Babechuk, M.G., Kamber, B.S., Greig, A., Canil, D. & Kodolányi, J. 2010. The behaviour of tungsten during mantle melting revisited with implications for planetary differentiation time scales. *Geochimica et Cosmochimica Acta*, **74**, 1448–1470, <https://doi.org/10.1016/j.gca.2009.11.018>.
- Bast, R., Scherer, E.E., Sprung, P., Fischer-Gödde, M., Stracke, A. & Mezger, K. 2015. A rapid and efficient ion-exchange chromatography for Lu-Hf, Sm-Nd, and Rb-Sr geochronology and the routine isotope analysis of sub-ng amounts of Hf by MC-ICP-MS. *Journal of Analytical Atomic Spectrometry*, **30**, 1231–1240, <https://doi.org/10.1039/C4AN00081A>.

- Spectrometry*, **30**, 2323–2333, <https://doi.org/10.1039/c5ja00283d>.
- Brett, A., Prytulak, J., Hammond, S.J. & Rehkämper, M. 2018. Thallium Mass Fraction and Stable Isotope Ratios of Sixteen Geological Reference Materials. *Geostandards and Geoanalytical Research*, **42**, 339–360, <https://doi.org/10.1111/ggr.12215>.
- Chapman, J.B., Mason, T.F.D., Weiss, D.J., Coles, B.J. & Wilkinson, J.J. 2006. Chemical Separation and Isotopic Variations of Cu and Zn From Five Geological Reference Materials. *Geostandards and Geoanalytical Research*, **30**, 5–16, <https://doi.org/10.1111/j.1751-908x.2006.tb00907.x>.
- Chen, S., Liu, Y., Hu, J., Zhang, Z., Hou, Z., Huang, F. & Yu, H. 2016. Zinc Isotopic Compositions of NIST SRM 683 and Whole-Rock Reference Materials. *Geostandards and Geoanalytical Research*, **40**, 417–432, <https://doi.org/10.1111/j.1751-908X.2015.00377.x>.
- Craddock, P.R. & Dauphas, N. 2011. Iron Isotopic Compositions of Geological Reference Materials and Chondrites. *Geostandards and Geoanalytical Research*, **35**, 101–123, <https://doi.org/10.1111/j.1751-908X.2010.00085.x>.
- Dauphas, N., Pourmand, A. & Teng, F.Z. 2009. Routine isotopic analysis of iron by HR-MC-ICPMS: How precise and how accurate? *Chemical Geology*, **267**, 175–184, <https://doi.org/10.1016/j.chemgeo.2008.12.011>.
- Ding, X., Helz, R.T., Qi, Y. & Huang, F. 2020. Vanadium isotope fractionation during differentiation of Kilauea Iki lava lake, Hawaii. *Geochimica et Cosmochimica Acta*, **289**, 114–129, <https://doi.org/10.1016/j.gca.2020.08.023>.
- Dodson, M.H. 1963. A theoretical study of the use of internal standards for precise isotopic analysis by the surface ionization technique: Part I - General first-order algebraic solutions, *Journal of Scientific Instruments*, **40**, 289–295.
- Fourny, A., Weis, D. & Scoates, J.S. 2016. Comprehensive Pb-Sr-Nd-Hf isotopic, trace element, and mineralogical characterization of mafic to ultramafic rock reference materials. *Geochemistry, Geophysics, Geosystems*, **17**, 739–773, <https://doi.org/10.1002/2015GC006181>.
- Gong, H., Guo, P., Chen, S. & Duan, M. 2020. A re-assessment of nickel-doping method in iron isotope analysis on rock samples using multi-collector inductively coupled plasma mass spectrometry. *Acta Geochimica*, **39**, 355–364, <https://doi.org/10.1007/s11631-019-00392-4>.
- Hoare, L., Klaver, M., Saji, N.S., Gillies, J., Parkinson, I.J., Lissenberg, C.J. & Millet, M.A. 2020. Melt chemistry and redox conditions control titanium isotope fractionation during magmatic differentiation. *Geochimica et Cosmochimica Acta*, **282**, 38–54, <https://doi.org/10.1016/j.gca.2020.05.015>.
- Hopkins, S.S., Prytulak, J., Barling, J., Russell, S.S., Coles, B.J. & Halliday, A.N. 2019. The vanadium isotopic composition of lunar basalts. *Earth and Planetary Science Letters*, **511**, 12–24, <https://doi.org/10.1016/j.epsl.2019.01.008>.
- Jochum, K.P., Weis, U., Schwager, B., Stoll, B., Wilson, S.A., Haug, G.H., Andreae, M.O. & Enzweiler, J. 2016. Reference Values Following ISO Guidelines for Frequently Requested Rock Reference Materials. *Geostandards and Geoanalytical Research*, **40**, 333–350, <https://doi.org/10.1111/j.1751-908X.2015.00392.x>.

- Kakabadse, G. & Wilson, H.J. 1957. Complexity of the Vanadium - Hydrogen Peroxide System. *Nature*, **180**, 861, <https://doi.org/10.1038/180861a0>.
- Kraus, K.A., Nelson, F. & Smith, G.W. 1954. Anion-exchange studies. IX. Absorbability of a number of metals in hydrochloric acid solutions. *Journal of Physical Chemistry*, **58**, 11–17, <https://doi.org/10.1021/j150511a003>.
- Makishima, A., Zhu, X.K., Belshaw, N.S. & O’Nions, R.K. 2002. Separation of titanium from silicates for isotopic ratio determination using multiple collector ICP-MS. *Journal of Analytical Atomic Spectrometry*, **17**, 1290–1294, <https://doi.org/10.1039/b204349a>.
- Maréchal, C.N., Télouk, P. & Albarède, F. 1999. Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chemical Geology*, **156**, 251–273, [https://doi.org/10.1016/S0009-2541\(98\)00191-0](https://doi.org/10.1016/S0009-2541(98)00191-0).
- Millet, M.A. & Dauphas, N. 2014. Ultra-precise titanium stable isotope measurements by double-spike high resolution MC-ICP-MS. *Journal of Analytical Atomic Spectrometry*, **29**, 1444–1458, <https://doi.org/10.1039/c4ja00096j>.
- Nelson, F. & Kraus, K.A. 1979. Ion exchange procedures: cation exchange in concentrated HCl and HClO₄ solutions. *Journal of Chromatography*, **178**, 163–181.
- Nielsen, S.G., Prytulak, J. & Halliday, A.N. 2011. Determination of Precise and Accurate 51V/50V Isotope Ratios by MC-ICP-MS, Part 1: Chemical Separation of Vanadium and Mass Spectrometric Protocols. *Geostandards and Geoanalytical Research*, **35**, 293–306, <https://doi.org/10.1111/j.1751-908X.2011.00106.x>.
- Novella, D., MacLennan, J., Shorttle, O., Prytulak, J. & Murton, B.J. 2020. A multi-proxy investigation of mantle oxygen fugacity along the Reykjanes Ridge. *Earth and Planetary Science Letters*, **531**, 115973, <https://doi.org/10.1016/j.epsl.2019.115973>.
- Nowell, G.M., Kempton, P.D., Noble, S.R., Fitton, J.G., Saunders, A.D., Mahoney, J.J. & Taylor, R.N. 1998. High precision Hf isotope measurements of MORB and OIB by thermal ionisation mass spectrometry: insights into the depleted mantle. *Chemical Geology*, **149**, 211–233, [https://doi.org/10.1016/S0009-2541\(98\)00036-9](https://doi.org/10.1016/S0009-2541(98)00036-9).
- Prytulak, J., Nielsen, S.G. & Halliday, A.N. 2011. Determination of Precise and Accurate 51V/50V Isotope Ratios by Multi-Collector ICP-MS, Part 2: Isotopic Composition of Six Reference Materials plus the Allende Chondrite and Verification Tests. *Geostandards and Geoanalytical Research*, **35**, 307–318, <https://doi.org/10.1111/j.1751-908X.2011.00105.x>.
- Prytulak, J., Nielsen, S.G., Ionov, D.A., Halliday, A.N. Harvey, J., Kelley, K.A., Niu, Y.L., Peate, D.W., Shimizu, K. & Sims, K.W.W. 2013. The stable vanadium isotope composition of the mantle and mafic lavas. *Earth and Planetary Science Letters*, **365**, 177–189, <https://doi.org/10.1016/j.epsl.2013.01.010>.
- Qi, Y.H., Wu, F., Ionov, D.A., Puchtel, I.S., Carlson, R.W., Nicklas, R.W., Yu, H-M., Kang, J-T., Li, C-H. & Huang, F. 2019. Vanadium isotope composition of the Bulk Silicate Earth: Constraints from peridotites and komatiites. *Geochimica et Cosmochimica Acta*, **259**, 288–301, <https://doi.org/10.1016/j.gca.2019.06.008>.
- Scherer, E., Münker, C. & Mezger, K. 2001. Calibration of the Lutetium-Hafnium Clock. *Science*, **293**,

683–688.

- Schuth, S., Horn, I., Brüske, A., Wolff, P.E. & Weyer, S. 2017. First vanadium isotope analyses of V-rich minerals by femtosecond laser ablation and solution-nebulization MC-ICP-MS. *Ore Geology Reviews*, **81**, 1271–1286, <https://doi.org/10.1016/j.oregeorev.2016.09.028>.
- Söderlund, U., Patchett, P.J., Vervoort, J.D. & Isachsen, C.E. 2004. The ^{176}Lu decay constant determined by Lu-Hf and U-Pb isotope systematics of Precambrian mafic intrusions. *Earth and Planetary Science Letters*, **219**, 311–324, [https://doi.org/10.1016/S0012-821X\(04\)00012-3](https://doi.org/10.1016/S0012-821X(04)00012-3).
- Sossi, P.A., Halverson, G.P., Nebel, O. & Eggins, S.M. 2015. Combined separation of Cu, Fe and Zn from rock matrices and improved analytical protocols for stable isotope determination. *Geostandards and Geoanalytical Research*, **39**, 129–149, <https://doi.org/10.1111/j.1751-908X.2014.00298.x>.
- Sossi, P.A., Prytulak, J. & O'Neill, H.S.C. 2018. Experimental calibration of vanadium partitioning and stable isotope fractionation between hydrous granitic melt and magnetite at 800 °C and 0.5 GPa. *Contributions to Mineralogy and Petrology*, **173**, 1451–1458, <https://doi.org/10.1007/s00410-018-1451-8>.
- Vervoort, J.D. & Blichert-Toft, J. 1999. Evolution of the depleted mantle: Hf isotope evidence from juvenile rocks through time. *Geochimica et Cosmochimica Acta*, **63**, 533–556.
- Weis, D., Kieffer, B., Hanano, D., Silva, I.N., Barling, J. & Pretorius, W. 2007. Hf isotope compositions of U.S. Geological Survey reference materials. *Geochemistry, Geophysics, Geosystems*, **8**, 1–15, <https://doi.org/10.1029/2006GC001473>.
- Wu, F., Qi, Y., Yu, H., Tian, S., Hou, Z. & Huang, F. 2016. Vanadium isotope measurement by MC-ICP-MS. *Chemical Geology*, **421**, 17–25, <https://doi.org/10.1016/j.chemgeo.2015.11.027>.
- Xue, Y., Li, C. hui, Qi, Y., Zhang, C., Miao, B. & Huang, F. 2018. The vanadium isotopic composition of L ordinary chondrites. *Acta Geochimica*, **37**, 501–508, <https://doi.org/10.1007/s11631-018-0279-2>.
- Zhang, J., Dauphas, N., Davis, A.M. & Pourmand, A. 2011. A new method for MC-ICPMS measurement of titanium isotopic composition: Identification of correlated isotope anomalies in meteorites. *Journal of Analytical Atomic Spectrometry*, **26**, 2197–2205, <https://doi.org/10.1039/c1ja10181a>.

CHAPTER THREE

The effects of oxygen fugacity and metasomatism on vanadium isotopic compositions of garnet-clinopyroxene pairs from Slave craton kimberlite-hosted mantle xenoliths

Abstract

Prevailing mantle oxygen fugacity (fO_2) is a hotly debated topic in Earth Sciences due to fO_2 being a highly variable, intensive physical parameter in igneous systems that is hard to constrain. The equilibrium stable isotope fractionation of multi-valent transition metals such as vanadium (V), has the potential to respond to changes in fO_2 . Vanadium could therefore offer a new way to investigate mantle fO_2 . However, valence state is not the only control on equilibrium stable isotope fractionation. Element coordination is also key. However, the novelty of V isotope studies in high temperature geologic systems, means that fractionation controls are not yet fully constrained, and further work is needed to establish whether a link exists between $\delta^{51}V$ and fO_2 . Vanadium isotope literature also lacks data from oxide-free mantle rocks (> 3 GPa). Spinel lherzolites are the basis of the current Bulk Silicate Earth (BSE), but oxides can dominate V budgets and are inferred to be isotopically light. Therefore, it is important to collect $\delta^{51}V$ from deeper oxide-free mantle rocks. However, such rocks are almost invariably metasomatised, and the effects of metasomatism on $\delta^{51}V$ are yet unknown. This chapter therefore aims to assess the effects of coordination, fO_2 , and mantle metasomatism on $\delta^{51}V$ in mantle rocks from > 3 GPa.

This chapter presents the first natural garnet and clinopyroxene mineral separate data for $\delta^{51}V$. Garnet and clinopyroxene pairs were selected from a suite of well-characterised, fO_2 constrained, metasomatic garnet-lherzolites (> 5 GPa) from the Diavik Diamond mine, Canada. We show that there is no inter-mineral $\delta^{51}V$ fractionation between garnet and clinopyroxene mineral separate pairs. However, there is a positive correlation between sample fO_2 and garnet-clinopyroxene $\delta^{51}V$. Garnet and clinopyroxene are also consistently and analytically significantly isotopically lighter than corresponding whole-rock $\delta^{51}V$ for all measured samples. The $\delta^{51}V$ offset can be reconciled by assuming metasomatism-triggered isotopic disequilibria between garnet/clinopyroxene and olivine/orthopyroxene and that olivine and orthopyroxene have BSE $\delta^{51}V$ values. This chapter therefore provides evidence that mantle metasomatism may have a strong effect on $\delta^{51}V$, and should be considered in future V isotope studies. We also suggest that in the Diavik lithospheric mantle, V isotope fractionation is primarily coordination-controlled, but fO_2 is likely a secondary

control and created the $\delta^{51}\text{V}$ variation observed between metasomatic phases from different samples.

CHAPTER THREE TABLE OF CONTENTS

3.1. Introduction	82
3.1.1. Aims	84
3.2. Diavik Diamond Mine, Canada	85
3.2.1. Geological Setting	85
3.2.2. Petrography	86
3.2.3. Chemistry of Diavik Xenoliths	88
3.3. Methods and Results	90
3.3.1. Estimation of modal abundance and mineral picking	90
3.3.2. Trace Element Abundances	91
3.3.3. Vanadium Isotopic Composition	94
3.4. Discussion	97
3.4.1. Metasomatism in the Slave Craton	97
3.4.1.1. Previous evidence for a metasomatic influence in the Diavik samples	97
3.4.1.2. Trace element evidence of metasomatism	98
3.4.1.3. Fluid versus Supercritical Fluid Metasomatism	105
3.4.2. Diavik whole-rock $\delta^{51}\text{V}$ isotopic compositions	106
3.4.2.1. <i>Investigating whole-rock $\delta^{51}\text{V}$ heterogeneity</i>	107
3.4.2.2. <i>Relationship between whole-rock $\delta^{51}\text{V}$ and $f\text{O}_2$</i>	109
3.4.3. Diavik garnet and clinopyroxene $\delta^{51}\text{V}$ isotopic compositions	109
3.4.4. Isotopic mass imbalance?	112
3.4.5. Links between mantle metasomatism, $f\text{O}_2$ and $\delta^{51}\text{V}$	116
3.4.5.1. <i>The effects of metasomatism on $\delta^{51}\text{V}$</i>	118
3.5. Conclusions	126
References	126

3.1. Introduction

Multi-valent transition metal stable isotope fractionation should respond to changes in oxygen fugacity ($f\text{O}_2$), potentially offering a new way to investigate and constrain a highly variable, intensive physical parameter. However, the oxidation state of the element of interest is not the only driving force in stable isotope fractionation. In particular, the related parameter of element coordination,

or more generally bonding environment, is also key to understanding equilibrium stable isotope fractionation. Temperature remains the first order control on stable isotope fractionation. Although, as temperature increases, the magnitude of isotopic fractionation decreases, such that at mantle conditions ($> 1000^{\circ}\text{C}$), temperature likely has a negligible influence. Before transition metal stable isotopes can be used to investigate $f\text{O}_2$, a better understanding of the causes of natural isotopic variation is needed. This chapter presents $\delta^{51}\text{V}$ data for a suite of well-characterised mantle samples, for which bonding environments and $f\text{O}_2$ are constrained, to investigate the drivers of high temperature V isotope fractionation in the mantle.

There is relatively limited previous work on V isotope fractionation in natural, terrestrial, high temperature materials (Prytulak *et al.* 2013, 2017; Schuth *et al.* 2017; Wu *et al.* 2018; Qi *et al.* 2019; Ding *et al.* 2020; Novella *et al.* 2020), and it still not understood fully how $\delta^{51}\text{V}$ is effected by partial melting. With the exception of a laser ablation study by Schuth *et al.* (2017), all previous work on natural samples reports whole-rock V isotopic compositions. Whole-rock analyses can be challenging to interpret, since they represent an averaging of the sample chemistry without strong constraint on specific phases and phase (dis)equilibria. In the only mineral separate study to date, Sossi *et al.* (2018) experimentally synthesized magnetite crystals in equilibrium with a hydrous haplogranitic melt specifically to investigate the impact of changing $f\text{O}_2$ conditions on V isotope fractionation on a mineral scale. However, these experiments were performed at low temperatures (800°C), pressures (0.5 GPa) and hydrous conditions, and compositions focussed on a single phase, magnetite. The experiments are thus not directly applicable to mantle conditions and phases. To gain a better understanding of the controls on V isotope fractionation in the mantle, natural mineral separates also need to be analysed. Careful selection of samples, minerals and the incorporation of textural evidence should yield the necessary context for more robust interpretations of V isotopic variations than whole-rock analyses alone.

Currently, all peridotite $\delta^{51}\text{V}$ measurements are on whole-rock material from pressures less than 2.3 GPa (~ 70 km depth), within the spinel stability field (Prytulak *et al.* 2013; Qi *et al.* 2019). Spinel and clinopyroxene likely hold the most vanadium in a spinel lherzolite, however a lack of mineral separate data means spinel and clinopyroxene $\delta^{51}\text{V}$ and the effects of spinel on $\delta^{51}\text{V}$ fractionation during partial melting are unknown. Indirect assessment of the V isotopic composition of spinel was first attempted by Prytulak *et al.* (2011) using two different digestion techniques on USGS reference material PCC-1 (a spinel-bearing harzburgite). High pressure bomb digestions with complete dissolution of the sample were isotopically heavier compared with standard table-top hotplate dissolutions, where spinel was visibly present and removed after digestion. Therefore, spinel in PCC-

1 was suggested to be isotopically heavy. Whilst it is not generally useful to assign meaning to mass produced reference materials, since there is no existing spinel $\delta^{51}\text{V}$ data, these experiments are the only way to speculate spinel $\delta^{51}\text{V}$.

The only mineral specific oxide $\delta^{51}\text{V}$ data available is for magnetite which is inferred to be isotopically light, with a large V isotope mineral-melt fractionation factor up to $\Delta\delta^{51}\text{V}_{\text{min-melt}} = -0.5\text{‰}$ (Prytulak *et al.* 2017; Sossi *et al.* 2018; Ding *et al.* 2020). During differentiation, the removal of isotopically light oxide phase(s) drives the residual liquid to progressively heavier values (Prytulak *et al.* 2017; Ding *et al.* 2020). Sossi *et al.* (2018) has shown experimentally that magnetite strongly fractionates $\delta^{51}\text{V}$, preferentially incorporating light V isotopes due to differences in V coordination between magnetite and coexisting melts. Magnetite is thought to incorporate V^{3+} and V^{4+} in VI-fold coordination, and melts, V^{4+} and V^{5+} in IV- and VI-fold coordination (Sossi *et al.* 2018). Furthermore, V can be strongly compatible in magnetite (e.g., $D_{\text{V}}^{\text{magnetite}} = 63.1$ at FMQ – 1; (Sossi *et al.* 2018)) and thus dominate the V budget in a sample. Regardless of the direction of isotopic fractionation in spinel, magnetite and/or ilmenite, it is clear that oxide phases not only hold significant V, but also can have a distinct V isotopic composition compared to other phases/melts.

Spinel lherzolites and komatiites are the basis of the current $\delta^{51}\text{V}$ Bulk Silicate Earth (BSE) estimate ($\delta^{51}\text{V} = -0.91 \pm 0.09\text{‰}$ 2SD $n=18$; Qi *et al.* 2019). Ideally, samples from the deeper mantle (e.g. > 3 GPa) should also be analysed and incorporated to provide a more representative estimate. Deeper garnet lherzolites lack an oxide phase, making the characterisation of V-bearing silicates such as clinopyroxene and garnet particularly important. Most mantle xenoliths recovered from depths > 3 GPa are found in stable cratonic environments and brought to the surface by explosive volcanism such as kimberlitic eruptions. However, xenoliths from these depths and tectonic setting are almost invariably affected by some degree of metasomatism. Therefore, the effects of metasomatism on $\delta^{51}\text{V}$ in the mantle must also be evaluated.

3.1.1.1. Aims

To address current gaps in our understanding of natural mantle V isotope fractionation, this chapter has the following aims:

1. Determine the relationship between $\delta^{51}\text{V}$, mineral phases and $f\text{O}_2$ by comparing $\delta^{51}\text{V}$ of mantle mineral separates (garnet and clinopyroxene) and whole-rock powders from well-characterised lherzolites with variable $f\text{O}_2$.
2. Provide the first $\delta^{51}\text{V}$ measurements of oxide-free, garnet lherzolites from pressures > 3 GPa.

3. Explore how metasomatism affects V stable isotope fractionation

3.2. Diavik Diamond Mine, Canada

3.2.1. Geological Setting

This chapter focusses on eight carefully selected, well-characterised garnet lherzolite mantle xenoliths from the 56.0 ± 0.7 Ma (Graham *et al.* 1998) A154-N diamondiferous kimberlite pipe at the Diavik Diamond mine, Lac de Gras, Northwest Territories, Canada (**Figure 3.1**). Whilst the Diavik diamond mine comprises numerous pipes, this study focusses solely on xenoliths from the A154-N pipe. The majority of xenoliths sample the deep (> 5 GPa) Archean central Slave Craton, and have been well-characterised, including mineral major and trace elements and the determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnet, which allowed for precise $f\text{O}_2$ determinations (Yaxley *et al.* 2017).

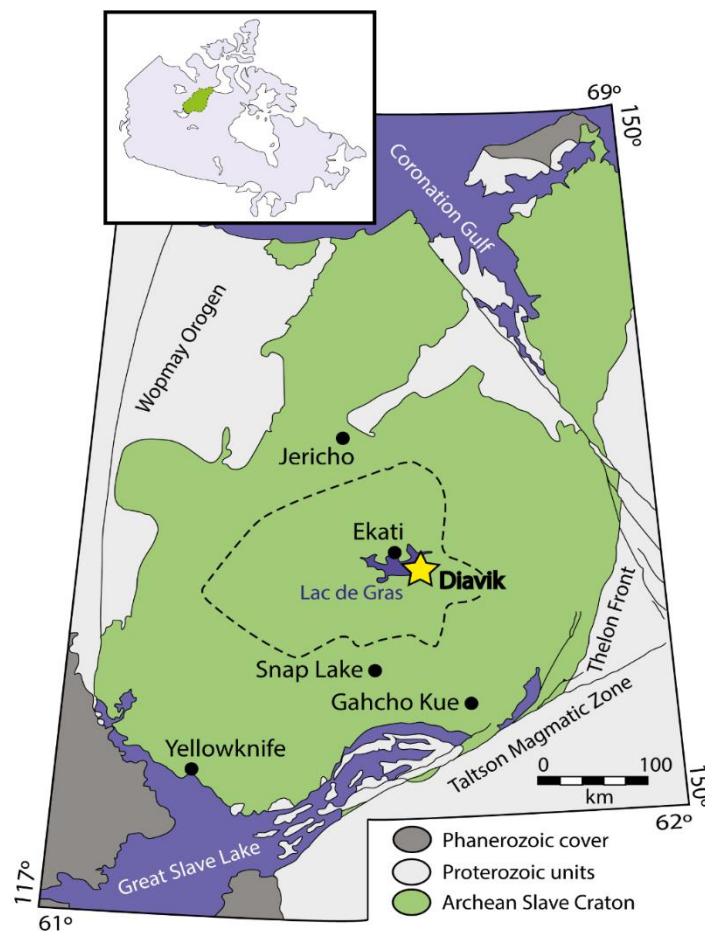


Figure 3.1: Chapter three location map adapted from Creighton *et al.* (2010) showing the location of the Diavik diamond mine where the A154-N garnet lherzolite samples were located. The mine is in the Northern Territories of Canada (inset map, top left), on an island in Lac de Gras, which is part of the Archean Slave craton, north of the Great Slave Lake and 300 km northwest of Yellowknife.

The Slave Craton is a small (600 x 400 km (Jones *et al.* 2003)) Archean province within the larger North American Craton (Griffin *et al.* 1999b). It is bound by magmatic arcs and accreted terranes, such as the Thelon Orogen (~2.2 Ga) to the east, and the Wopmay Orogen (1.9-2.1 Ga) to the west (**Figure 3.1**). To the north, the craton is bound by the overlapping of Bear Province and Arctic Platform supracrustals that are a maximum of Proterozoic in age (Griffin *et al.* 1999b). The southern boundary is a 1.8 to 2.0 Ga continental transform shear zone (the Great Slave Lake Shear Zone) that cut and offset the craton, juxtaposing Archean cratonic rocks against Churchill Province Proterozoic rocks (Griffin *et al.* 1999b).

The oldest cratonic granites and gneisses are found in the west, including the Acasta gneisses (3.6 – 4.0 Ga). The three main Archean units are as follows: (1) Greywacke-mudstone metaturbidites with abundant volcanoclastic debris components (Griffin *et al.* 1999b), (2) tonalite-quartz diorites, and (3) mica-rich granite suites (Bryan & Bonner 2003). The interbedded metaturbidites outcrop across the centre of East Island (where the Diavik mine is located) as a northwest-southeast, steeply-dipping band (Bryan & Bonner 2003), and are derived from felsic, andesitic and basaltic volcanics (Griffin *et al.* 1999b). The stabilisation of the craton is marked by the intrusion of 2.61 to 2.58 Ga tonalite-quartz diorites in the south of East Island, and 2.59 - 2.58 Ga granite suites throughout the north (Griffin *et al.* 1999b), which also host numerous kimberlites (Bryan & Bonner 2003). A154-N is hosted by granites. The Slave craton kimberlites are of several generations, and the Diavik cluster are Eocene in age.

3.2.2. Petrography

All samples in this study are garnet lherzolites. Some olivine grains boundaries show minor serpentinisation (e.g. 422; **Figure 3.2**), and a few garnets have minor kelyphitic rim development (e.g. 052 and 714; **Figure 3.2**). Otherwise, the samples lack typical metasomatic phases (e.g., amphibole, phlogopite) and abundant unaltered grains are present for all major mineral phases (olivine, clinopyroxene, orthopyroxene and garnet). Garnet grain-sizes are highly variable across the suite, varying from less than 0.5 mm (e.g. 052 and 714) to 7 mm in diameter (e.g. 1034). The samples exhibit various textures; sheared (714, 1034), porphyroclastic (052), mosaic-porphyroclastic (448, 450), and mosaic (108, 147, 422). There is no obvious petrographic evidence of host kimberlite mingling with the xenolith interiors.

One of the aims of this chapter is to analyse deep, oxide-free mantle rocks. Based upon petrographic and thermobarometric evidence, all but one of the Diavik xenoliths lie outside of the spinel stability field and are petrographically oxide-free. **Figure 3.3** shows thin sections from two different Diavik samples. Sample 448 (the only shallow garnet lherzolite in this suite) exhibits partial

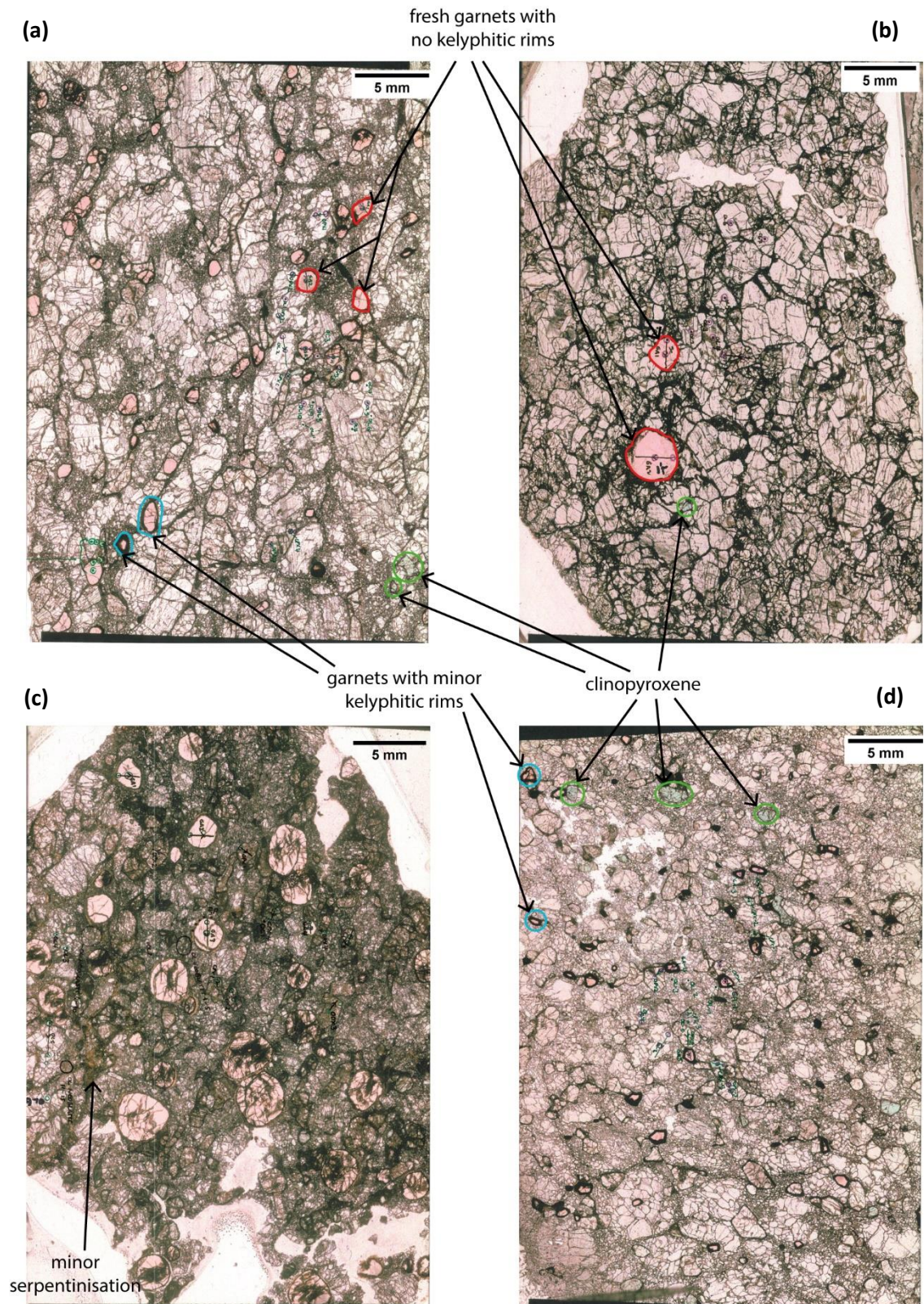


Figure 3.2: Thin section photos of the four garnet lherzolite xenoliths being analysed in this study from the Diavik A154 diamond mine. (a) 052; (b) 108; (c) 422; (d) 714.

replacement of garnet by oxides. All other samples show either no or extremely minimal replacement. The lack of oxides in all other samples is supported by thermobarometric data from

Yaxley *et al.* (2017), and all samples except 448 equilibrated at high pressures (> 5 GPa) within the garnet stability field. Sample 448 formed at much shallower conditions (2.01 GPa), which is consistent with the petrographic evidence of partial breakdown and replacement of garnet by oxides.

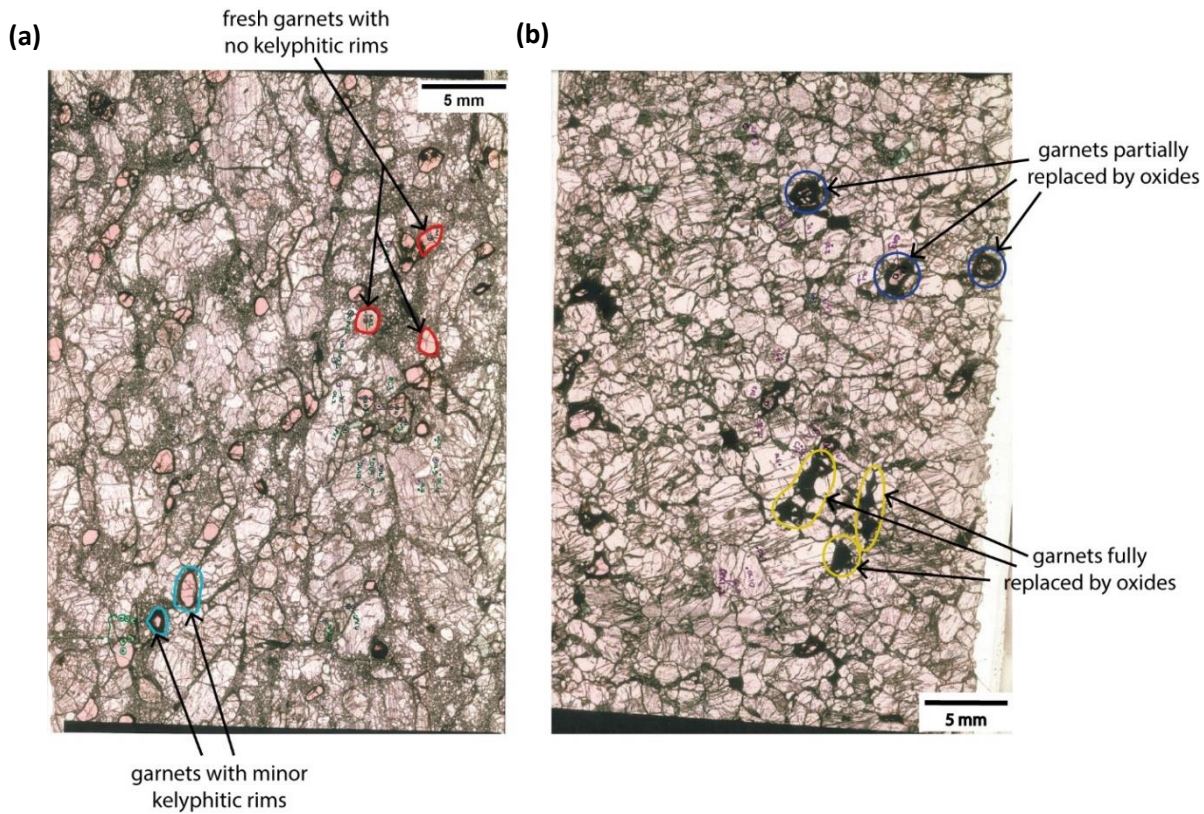


Figure 3.3: Thin section photographs of Diavik garnet lherzolite samples (a) 052 and (b) 448. Sample 448 shows considerable replacement of garnet by oxides, whereas sample 052 which is fairly representative of all other samples in this study, shows virtually no replacement.

3.2.3. Chemistry of Diavik Xenoliths

The A154-N mantle xenoliths are lherzolites, with Cr-diopside-rich clinopyroxene, and pyrope garnet. All samples contain minerals that are homogeneous on both an inter- and intra-crystalline scale, with major and trace element mineral, but not whole-rock chemistry described by Yaxley *et al.* (2017) (**Appendices A & B**).

Garnet trace element chemistry can be interpreted to reflect two distinctive lithospheric layers. At depths < 4.5 GPa (~135 km), garnets are depleted in Y, Yb, Ga and Ti. Such elements are recognised as indicators of depletion/enrichment degree in garnet peridotites (e.g. Griffin & Ryan (1995)). At pressures > 4.5 GPa, garnets are often strongly enriched in Y, Yb, Ga and Ti, and display more heterogeneous fO_2 (**Figure 3.4**). The xenoliths analysed in this chapter include one shallow, depleted sample (448) and seven deep, enriched samples.

Rare Earth element (REE) patterns can be used to investigate the petrogenesis of garnet. The garnets from this study exhibit a broad range of REE patterns. The shallow, depleted xenoliths from both Diavik and the nearby Ekati mine have primitive mantle normalised garnet REE patterns that are highly sinusoidal. Whereas the deeper, enriched xenoliths display normal, slightly sinusoidal and sinusoidal garnet patterns (**Figure 3.5**). Such REE patterns have been observed in previous work on the Slave and Kaapvaal cratons (e.g. Stachel *et al.* 1998; Griffin *et al.* 1999a; Creighton *et al.* 2010; Aulbach *et al.* 2013) and their significance is discussed later in this chapter. The enriched garnet chemistry, garnet REE patterns, and higher and more heterogeneous calculated fO_2 of this zone are used as evidence that the deep, enriched rocks are metasomatic (Yaxley *et al.* 2017).

Mössbauer spectroscopy-determined garnet $Fe^{3+}/\Sigma Fe$ and calculated pressure, temperature and fO_2 are reported in Yaxley *et al.* (2017) (**Table 3.1**). Garnet $Fe^{3+}/\Sigma Fe$ ranges from 0.020 to 0.105, and is comparable to other garnet peridotite suites from other cratons (e.g. Woodland & Koch 2003; Creighton *et al.* 2010; Hanger *et al.* 2015).

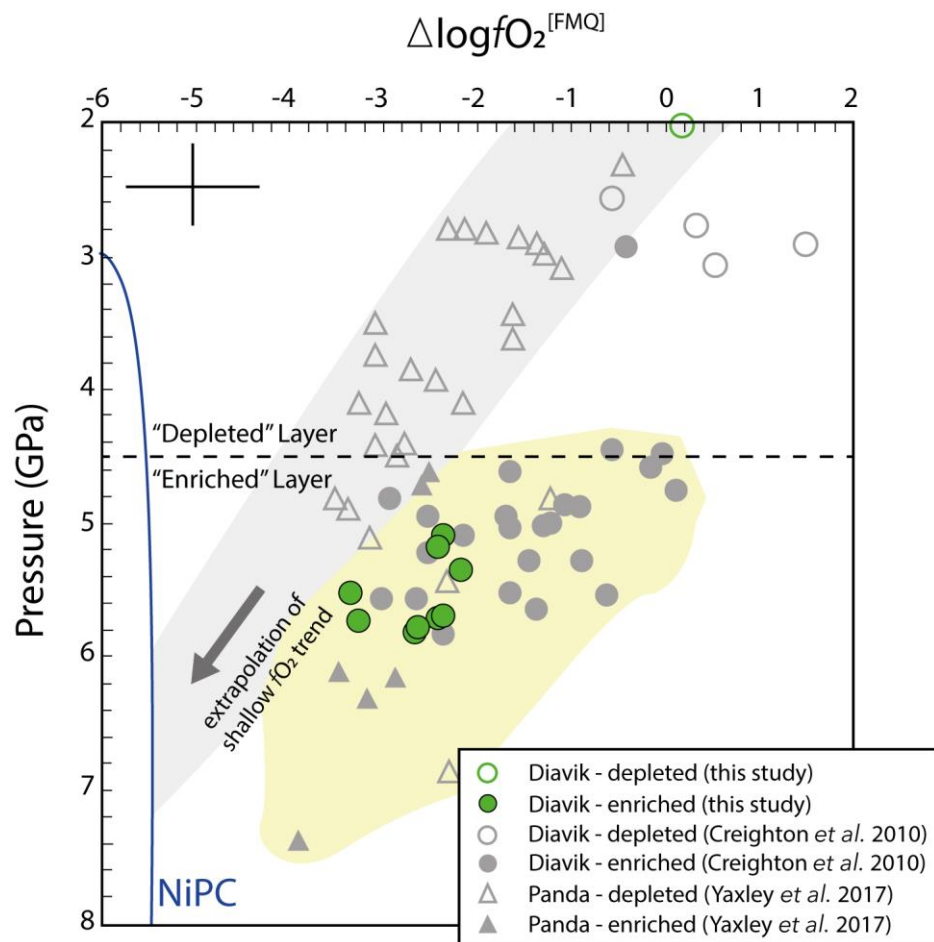


Figure 3.4: $\Delta \log fO_2^{[FMQ]}$ versus pressure in GPa for Diavik and Panda peridotite xenoliths based on garnet oxybarometry. The grey data points represent data from previous studies (Creighton *et al.* 2010; Yaxley *et al.* 2017). The green data points represent the eight Diavik xenoliths studied in this chapter. Seven samples are

deep, enriched xenoliths (green filled circles) and one is a shallow, depleted xenolith (green outlined circle). The grey field contains almost all of the depleted samples, and the yellow almost all of the enriched. NiPC is the Ni-precipitation curve. Figure adapted from Yaxley et al. (2017) and the pressure and fO_2 data for the green points is from Yaxley et al. (2017).

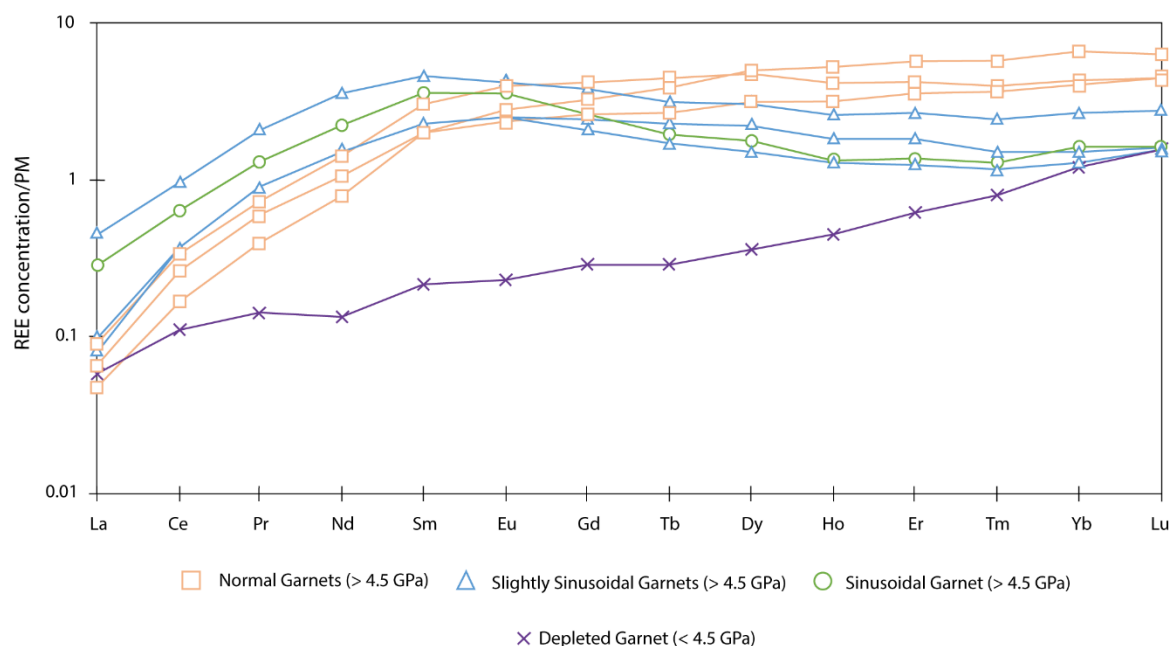


Figure 3.5: Primitive mantle normalised REE concentrations of the eight Diavik garnets analysed in this study (from Yaxley et al. (2017)). The garnets have been split into three groups based on REE pattern groupings from Creighton et al. (2010). The shallow, depleted sample 448 does not fit any of the groupings. Of the four samples with mineral separate $\delta^{51}\text{V}$ data, 422 and 714 are normal and 052 and 108 are slightly sinusoidal. Normalisation from McDonough & Sun (1995).

Table 3.1: $\text{Fe}^{3+}/\Sigma\text{Fe}$, pressure, temperature and fO_2 estimates for the Diavik garnets being analysed in this study. Data from Yaxley et al. (2017). The “G9” garnet classification is from Gurney (1984).

	Sample	Description	(Yaxley et al. 2017)				
			$\text{Fe}^{3+}/\Sigma\text{Fe}$ (Mb)	P (GPa)	T (°C)	$\Delta\log fO_2^{\text{FMQ}}$	Cr#
Garnet mineral separates	052 Gnt	G9-type garnet	0.098	5.69	1187	-2.38	23.5
	108 Gnt	G9-type garnet	0.06	5.52	1168	-3.36	20.9
	422 Gnt	G9-type garnet	0.07	5.18	1187	-2.45	5.2
	714 Gnt	G9-type garnet	0.105	5.8	1282	-2.66	18.0

3.3. Methods and Results

3.3.1. Estimation of modal abundance and mineral picking

The samples for this study were chosen due to their depth of formation, lack of oxides, abundance of unaltered grains, and their wealth of chemical characterisation. All samples were measured for

whole-rock $\delta^{51}\text{V}$ and four (052, 108, 422 and 714) were further selected for mineral (garnet and clinopyroxene) separate analysis. Modal abundances of the four major mineral phases were determined on these samples using thin section photos and area calculation software, SketchandCalc (**Table 3.2**). Samples 052, 108, 422 and 714 were hand-picked for garnet and clinopyroxene at the Australian National University in 2013 and were chosen due to their minimal garnet alteration and high abundance of garnet and clinopyroxene. At the time of picking, significantly higher concentrations of V were required for $\delta^{51}\text{V}$ measurement compared to today ($5\ \mu\text{g.g}^{-1}$ solutions (Nielsen *et al.* 2011) versus $600\ \text{ng.g}^{-1}$ to $1\ \mu\text{g.g}^{-1}$ solutions). Since the V concentration of individual phases is known (Yaxley *et al.* 2017), between 25 and 50 mg of garnet and clinopyroxene were picked for each sample. A second batch of sample 108 mineral separates was picked in 2019 at Durham University. The masses picked were smaller than in 2013, 23 mg of garnet and 7 mg of clinopyroxene due to current isotopic measurement techniques requiring lower V concentrations.

Table 3.2: Estimated modal abundances of the four major mineral phases (olivine, orthopyroxene, clinopyroxene and garnet) in the Diavik xenoliths that had mineral separates analysed for $\delta^{51}\text{V}$ in this study. The modal abundances were estimated from thin sections using area calculation software. The abundances have been rounded to the nearest whole percent except for clinopyroxene in sample 108, due to its very low abundance.

Sample	Modal Abundance (%)			
	Olivine	Orthopyroxene	Clinopyroxene	Garnet
052	81	14	1	4
108	69	30	0.1	1
422	60	26	2	12
714	87	11	1	1

3.3.2. Trace Element Abundances

The xenoliths in this study are fist sized or smaller and thus were processed by hand to minimize material loss. Samples were crushed and powdered by hand using an agate mortar and pestle at Australian National University. Whole-rock trace element data (**Figure 3.6; Table 3.3**) was measured by ICPMS-QQQ at the Open University according to the methods outlined in Chapter 2. USGS reference materials PCC-1 and DTS-1 processed and analysed with the samples as unknowns agree with accepted values to within 1% on average, and 20% for 90% of elements (**Table 3.4**).

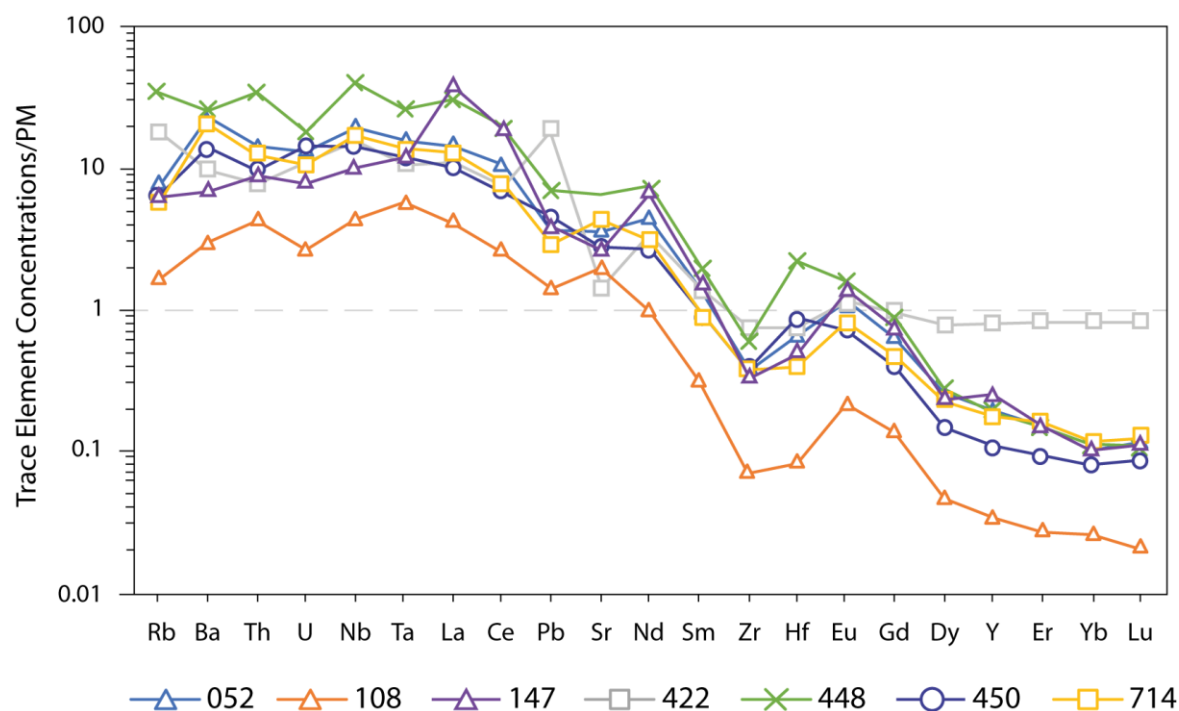


Figure 3.6: Primitive mantle normalised trace element concentrations for Diavik whole-rock xenoliths. There was insufficient sample remaining to measure trace elements in sample 1034. The square symbols relate to samples with normal garnets, the triangle symbols to slightly sinusoidal garnets, the circle symbols to sinusoidal garnets, and the cross symbols to depleted garnets. Normalisation from McDonough & Sun (1995).

Table 3.3: Trace element concentration data ($\mu\text{g.g}^{-1}$) for Diavik xenolith whole-rock powder peridotites and the host-kimberlite determined at the Open University using ICP-QQQ-MS. All concentrations except those for sample 108 represent the average from two digestions of the same sample. There was insufficient sample remaining to measure trace elements in sample 1034.

Trace Element	Diavik Whole-rock Samples' Trace Element Concentrations ($\mu\text{g.g}^{-1}$)							Kimberlite
	52	108	147	422	448	450	714	
Li	3	-	1.6	2.7	2.1	5.5	2.8	-
Sc	6.6	1.9	4.7	15.8	6.7	8.5	5.2	8.1
Ti	554	169	308	1122	756	409	598	2552
V	26	16	23	63	32	29	28	44
Cr	2218	1066	2273	2870	2760	3410	1588	1784
Mn	1699	780	1059	1004	1537	761	1738	756
Co	111	105	114	115	98	152	124	105
Ni	2460	2281	2322	2172	1932	3233	2521	1784
Cu	14	4.8	9.5	17	15	22	11	40
Zn	43	36	40	52	38	58	57	47
Rb	5.1	1	4	11	21	4	3.5	17
Sr	75	42	54	30	133	59	90	435

Table 3.3: *continued*

Trace Element	Diavik Whole-rock Samples' Trace Element Concentrations ($\mu\text{g}\cdot\text{g}^{-1}$)							
	52	108	147	422	448	450	714	Kimberlite
Y	0.88	0.16	1.1	3.5	0.82	0.5	0.81	2.7
Zr	3.9	0.79	3.62	8.3	6.6	4.2	4.2	32
Nb	14	3.1	7.2	11	29	10	12.2	75
Cs	0.09	0.02	0.04	0.12	0.19	0.16	0.07	0.43
Ba	154	21	48	61	170	97	140	1068
La	10	2.8	27	7.9	21	7.2	9	59
Ce	18	4.5	33	12	34	12	14	99
Pr	1.8	0.44	3	1.3	3.2	1.2	1.3	9.6
Nd	5.7	1.3	9	4.2	9.7	3.6	4	30
Sm	0.65	0.14	0.71	0.62	1	0.43	0.44	3.1
Eu	0.19	0.04	0.23	0.2	0.26	0.12	0.14	0.79
Gd	0.38	0.08	0.44	0.57	0.53	0.25	0.29	1.6
Tb	0.04	0.01	0.04	0.09	0.05	0.03	0.04	0.16
Dy	0.2	0.03	0.17	0.24	0.68	0.29	0.12	0.69
Ho	0.19	0.03	0.03	0.59	0.21	0.12	0.17	0.65
Ta	0.03	0.01	0.49	0.13	0.03	0.02	0.03	0.1
Er	0.08	0.01	0.07	0.4	0.07	0.05	0.08	0.24
Hf	0.06	0.01	0.15	0.4	0.06	0.05	0.06	0.18
Yb	0.01	0	0.05	0.06	0.01	0.01	0.01	0.03
Lu	0.56	0.24	0.01	0.44	0.88	0.49	0.52	3.9
Tl	0.07	0.01	0.02	0.03	0.03	0.06	0.03	0.09
Pb	0.6	0.26	0.72	3.2	1.3	0.68	0.55	3.9
Th	1.3	0.36	0.75	0.68	2.9	0.87	1.1	11
U	0.3	0.06	0.16	0.25	0.39	0.32	0.23	1.3

Table 3.4: Trace element concentration data ($\mu\text{g}\cdot\text{g}^{-1}$) for USGS reference materials PCC-1 and DTS-1, plus the reported literature concentrations for those materials and percentage difference between measured and literature concentrations. Accepted concentration data for PCC-1 and DTS-1 were taken from Babechuk et al. (2010) and Jochum et al. (2016) respectively.

Trace Element	PCC-1 concentrations ($\mu\text{g}\cdot\text{g}^{-1}$)			DTS-1 concentrations ($\mu\text{g}\cdot\text{g}^{-1}$)			Limit of Detection ($\mu\text{g}\cdot\text{g}^{-1}$)
	Measured	Literature	% Diff	Measured	Literature	% Diff	
Li	0.9	1	-10%	1.8	2	-10%	3.94×10^{-3}
Sc	7.3	9	-19%	3.3	3.4	-3%	3.46×10^{-3}
Ti	23.8	25.1	-5%	21.1	23.5	-10%	5.27×10^{-2}
V	26.6	26	2%	9.4	10	-6%	3.11×10^{-3}
Cr	2962	1913	55%	4504	4100	10%	1.78×10^{-2}
Mn	813	-		928	-		6.80×10^{-3}
Co	106	114	-7%	140	136	3%	1.43×10^{-3}
Ni	2090	2341	-11%	2267	2298	-1%	8.82×10^{-3}

Table 3.4: *continued*

Trace Element	PCC-1 concentrations ($\mu\text{g.g}^{-1}$)			DTS-1 concentrations ($\mu\text{g.g}^{-1}$)			Limit of Detection ($\mu\text{g.g}^{-1}$)
	Measured	Literature	% Diff	Measured	Literature	% Diff	
Cu	5.8	7	-17%	5.6	5.7	-2%	6.20×10^{-3}
Zn	38.3	38.3	0%	45.1	43.8	3%	9.36×10^{-2}
Rb	0.06	0.06	0%	0.09	0.07	29%	5.47×10^{-3}
Sr	0.36	0.48	-25%	0.31	0.3	3%	1.04×10^{-3}
Y	0.08	0.08	0%	0.04	0.04	0%	1.02×10^{-3}
Zr	0.17	0.13	31%	0.17	0.15	13%	1.15×10^{-3}
Nb	0.02	0.01	100%	0.02	0.02	0%	1.38×10^{-4}
Cs	0	0	0%	0.01	0.01	0%	1.27×10^{-3}
Ba	0.93	0.79	18%	0.33	0.34	-3%	9.53×10^{-3}
La	0.03	0.03	0%	0.02	0.03	-33%	2.66×10^{-4}
Ce	0.05	0.05	0%	0.05	0.05	0%	1.97×10^{-4}
Pr	0.007	0.007	0%	0.007	0.006	17%	6.63×10^{-5}
Nd	0.03	0.03	0%	0.03	0.02	50%	4.94×10^{-4}
Sm	0.005	0.005	0%	0.004	0.004	0%	1.28×10^{-4}
Eu	0.001	0.001	0%	0.001	0.001	0%	1.32×10^{-4}
Gd	0.006	0.006	0%	0.003	0.004	-25%	1.18×10^{-3}
Tb	0.001	0.001	0%	0.001	0.001	0%	2.06×10^{-4}
Dy	0.008	0.009	-11%	0.004	0.005	-20%	1.63×10^{-4}
Ho	0.003	0.003	0%	0.001	0.001	0%	6.30×10^{-5}
Ta	0.003	0.001	200%	0.002	0.001	100%	4.03×10^{-4}
Er	0.01	0.011	-9%	0.005	0.005	0%	5.04×10^{-4}
Hf	0.005	0.004	25%	0.005	0.005	0%	4.26×10^{-4}
Yb	0.025	0.023	9%	0.009	0.01	-10%	5.56×10^{-3}
Lu	0.004	0.005	-20%	0.002	0.002	0%	4.42×10^{-4}
Tl	0.001	0.001	0%	0.002	0.002	0%	6.00×10^{-4}
Pb	7.6	7.6	0%	7.6	8.5	-11%	5.85×10^{-3}
Th	0.01	0.01	0%	0.01	0.01	0%	1.78×10^{-4}
U	0.003	0.004	-25%	0.003	0.003	0%	3.03×10^{-4}

3.3.3. Vanadium Isotopic Composition

The vanadium isotopic composition of eight whole-rocks, four garnet-clinopyroxene pairs, and the host kimberlite was collected at both Imperial College London and Durham University. Full methods are outlined in Chapter 2 and all results are presented in **Table 3.5**. The V isotopic composition of reference materials processed with the samples agree with accepted values from the literature and are given in **Table 3.6**. Total procedural blanks processed with every batch of 12 samples were always < 1.2 ng of V, which is negligible compared to the total amount of V processed (~ 2-10 μg).

Table 3.5: $\delta^{51}\text{V}$ of Diavik samples. The table shows V concentration in $\mu\text{g}\cdot\text{g}^{-1}$ (derived by LA-ICP MS for mineral separates (Yaxley et al., 2017) and ICP-QQQ-MS at the Open University for whole-rock), $\delta^{51}\text{V}$ (analysed at Imperial College London and Durham University). Errors are 2SD of at least 3 repeat measurements. Where only one or two measurements were taken, the long-term solution-standard BDH 2SD from the measurement session was taken. There was insufficient sample remaining to measure trace elements in sample 1034.

	Sample	Description	V conc ($\mu\text{g}\cdot\text{g}^{-1}$)		Digestion 1			Digestion 2			Digestion 3		
					$\delta^{51}\text{V}$ (‰)	2SD	n	$\delta^{51}\text{V}$ (‰)	2SD	n	$\delta^{51}\text{V}$ (‰)	2SD	n
Garnet mineral separates	052 Gnt	slightly sinusoidal REE	Yaxley <i>et al.</i> (2017)	350	-1.25	0.07	5	-	-	-	-	-	-
	108 Gnt	slightly sinusoidal REE		325	-1.53	0.09	5	-1.46	0.14	4	-	-	-
	422 Gnt	normal REE		247	-1.54	0.17	6	-	-	-	-	-	-
	714 Gnt	normal REE		324	-1.67	0.12	6	-	-	-	-	-	-
Clinopyroxene mineral separates	052 Cpx	Clinopyroxene	Yaxley <i>et al.</i> (2017)	184	-1.34	0.10	2	-	-	-	-	-	-
	108 Cpx	Clinopyroxene		149	-1.73	0.10	1	-	-	-	-	-	-
	422 Cpx	Clinopyroxene		244	-1.48	0.14	2	-	-	-	-	-	-
	714 Cpx	Clinopyroxene		201	-1.57	0.12	4	-	-	-	-	-	-
Whole-rock	052	Enriched gnt lhz	Open University on ICP-QQQ-MS	25	-1.08	0.10	2	-1.44	0.08	5	-1.30	0.09	5
	108	Enriched gnt lhz		16	-1.22	0.02	4	-1.38	0.13	4	-1.29	0.09	4
	147	Enriched gnt lhz		22.9	-1.18	0.10	1	-0.85	0.10	2	-	-	-
	422	Enriched gnt lhz		61.0	-1.23	0.10	3	-1.13	0.12	6	-1.36	0.10	1
	448	Depleted gnt lhz		32.2	-1.47	0.10	1	-1.31	0.12	3	-1.59	0.04	5
	450	Enriched gnt lhz		27.8	-1.21	0.10	1	-1.10	0.12	2	-1.24	0.10	1
	714	Enriched gnt lhz		26.6	-1.19	0.10	1	-0.83	0.09	2	-0.95	0.10	1
	1034	Enriched gnt lhz		-	-1.01	0.10	1	-	-	-	-	-	-
Kimberlite	434-01	A154-N kimberlite	OU	44	-1.29	0.04	4	-1.25	0.06	5	-	-	-

Table 3.6: USGS reference materials analysed for $\delta^{51}\text{V}$ that were used for quality control and assurance while analysing Diavik whole-rock and mineral separate $\delta^{51}\text{V}$.

Reference Material	Type	Source	V ($\mu\text{g}\cdot\text{g}^{-1}$)	Avg $\delta^{51}\text{V}$ (‰)	2SD	n	Digestions	Reference
BCR-2	Columbia river basalt	USGS	416	-0.95	0.16	27	12	Prytulak <i>et al.</i> 2011
				-0.92	0.16	13	27	Prytulak <i>et al.</i> 2013
				-0.78	0.08	36	6	Wu <i>et al.</i> 2016
				-1.03	0.05	9	1	Schuth <i>et al.</i> 2017
				-1.11	0.04	2	1	Sossi <i>et al.</i> 2018
				-0.76	0.05	3	1	Xue <i>et al.</i> 2018
				-0.85	0.26	5	1	Hopkins <i>et al.</i> 2019
				-0.97	0.19	3	1	Novella <i>et al.</i> 2020
				-0.75	0.05	3	1	Qi <i>et al.</i> 2019
				-0.81	0.03	-	-	Ding <i>et al.</i> 2020
				-1.00	0.10	3	1	This study (ICL)
BIR-1a	Iceland basalt	USGS	310	-0.94	0.15	52	10	Prytulak <i>et al.</i> 2011
				-0.92	0.16	50	12	Prytulak <i>et al.</i> 2013
				-0.92	0.09	52	10	Wu <i>et al.</i> 2016
				-1.05	0.11	7	3	Sossi <i>et al.</i> 2018
				-0.92	0.12	3	1	Xue <i>et al.</i> 2018
				-0.89	0.23	3	1	Hopkins <i>et al.</i> 2019
				-0.89	0.21	2	1	Novella <i>et al.</i> 2020
				-0.96	0.22	3	1	Novella <i>et al.</i> 2020
				-0.90	0.09	2	1	Qi <i>et al.</i> 2019
				-1.01	0.05	-	-	Ding <i>et al.</i> 2020
				-1.20	0.22	4	1	This study (ICL)
				-1.03	0.06	5	1	This study (Durham)
BHVO-2	Hawaiian basalt	USGS	317	-0.89	0.08	9	3	Prytulak <i>et al.</i> 2011
				-0.88	0.10	14	7	Prytulak <i>et al.</i> 2013
				-0.83	0.09	22	6	Wu <i>et al.</i> 2016
				-0.91	0.08	-	-	Ding <i>et al.</i> 2020
				-0.97	0.05	2	1	This study (Durham)
GSP-2	Granodiorite	USGS	52	-0.63	0.10	6	3	Prytulak <i>et al.</i> 2011
				-0.62	0.07	26	5	Wu <i>et al.</i> 2016
				-0.61	0.15	6	1	This study (Durham)

3.4. Discussion

In this section we first discuss the geochemical evidence for metasomatism in the Diavik xenolith suite to place our new isotopic determinations into a petrogenetic context. Secondly, we examine the V isotopic composition of garnet, clinopyroxene, and whole-rocks, and their relationship with each other and with fO_2 . Finally, we discuss the implications of our findings for the effects of metasomatism on fO_2 and V isotopic compositions in the Diavik suite.

3.4.1. Metasomatism in the Slave Craton

Metasomatism is a critical, yet enigmatic geological process that can strongly influence the chemistry of magmas derived from the mantle. Classical definitions (e.g. Thompson 1959, Korzhinskii 1965) describe it as the infiltration and diffusion of mobile elements between regions of an open system. There are considered to be two end-member types of metasomatism, modal (Harte 1983) and cryptic (Dawson 1984) metasomatism. Modal metasomatism describes to crystallisation of new phases (Harte 1983) and cryptic metasomatism involves compositional changes to pre-existing minerals (Dawson 1984). The most commonly identified metasomatic agents include CO_2 -rich fluids (Andersen et al. 1984; O'Reilly & Griffin, 1988), silicate melts and fluids (Roden et al. 1984; Menzies et al. 1987; Schiano & Clocchiatti, 1994; Schiano & Bourdon, 1999) kimberlitic melts (e.g. Menzies & Wass, 1983), and carbonatitic melts (O'Reilly & Griffin, 1988; Yaxley et al. 1991; Dautria et al. 1992; Ionov et al. 1993; Rudnick et al. 1993; Griffin et al. 1996). The Diavik suite has been interpreted to have a metasomatic overprint (Yaxley *et al.* 2017) and thus original fO_2 and $\delta^{51}V$ signatures may have been affected. It is therefore important to identify the chemical and petrologic hallmarks of metasomatism in this suite.

3.4.1.1. Previous evidence for a metasomatic influence in the Diavik samples

The fO_2 profile through the Slave craton beneath the Diavik diamond mine shows that at pressures greater than 4.5 GPa, the $\Delta \log fO_2^{[FMQ]}$ calculated from garnets is 1 to 4 log units more oxidised than predicted by extrapolating the shallower fO_2 trend to higher pressures (Yaxley *et al.* 2017; **Fig. 3.4**). Yaxley *et al.* (2017) suggested that this zone experienced strongly oxidising metasomatism, and proposed two possible metasomatic agent candidates. (1) A carbonate-bearing silicate melt, potentially from the deeper, reduced asthenosphere; (2) saline, hydrous fluids from a hypothesised subducted slab beneath the base of the cratonic lithosphere. However, no consensus was reached over which of these candidates is most likely the metasomatic agent in this geological setting.

3.4.1.2. Trace element evidence of metasomatism

Further evidence for metasomatism of the Diavik xenoliths is provided by examining the new whole-rock trace element concentrations (**Table 3.3**) alongside existing laser ablation mineral trace element data (Yaxley *et al.* 2017). This data is compared with metasomatic lherzolite xenoliths from both Diavik (Creighton *et al.* 2010; Aulbach *et al.* 2013) and the Kaapvaal craton, South Africa (Stachel *et al.* 1998, 2004; Griffin *et al.* 1999b).

a) Trace element mass balance

Since metasomatism involves chemical exchange between rocks and a metasomatic agent in an open system, it causes changes in element abundances. To investigate the extent of metasomatism, a mass balance between the new measured whole-rock trace element data and a reconstructed whole-rock trace element budget using modal abundances and existing laser ablation data (Yaxley *et al.* 2017) was performed. The extent of the mismatch between the two is shown in **Figure 3.7**.

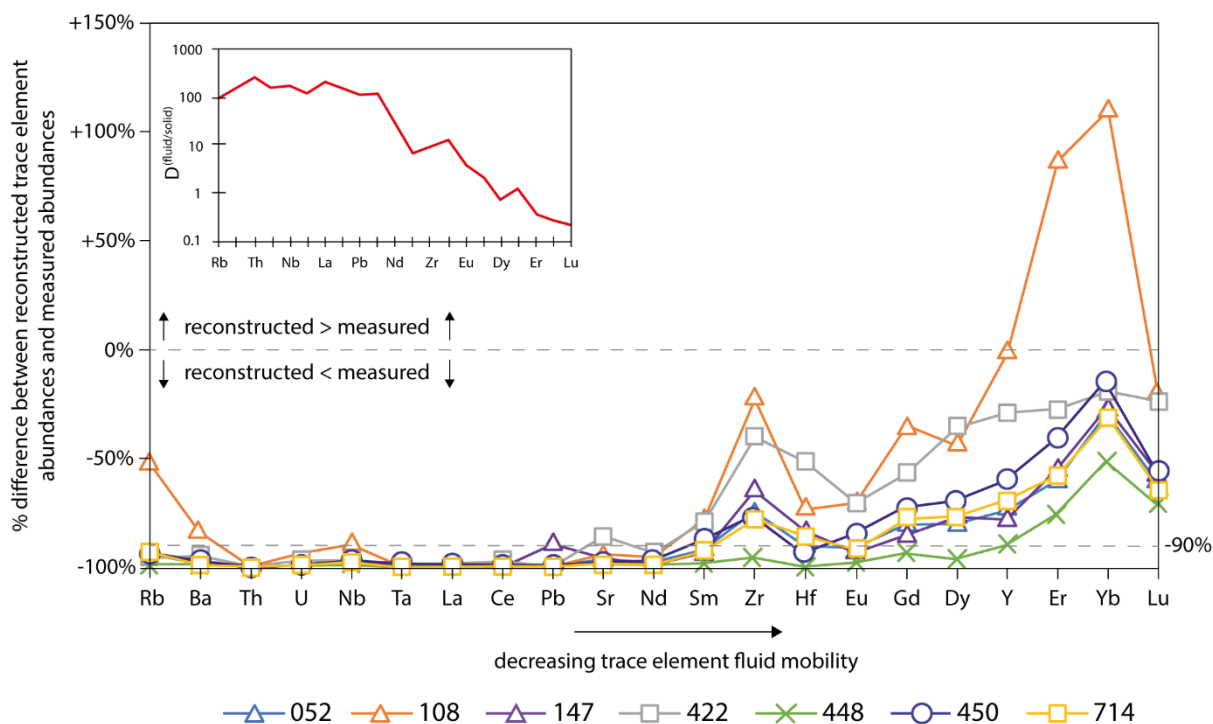


Figure 3.7: Comparison between reconstructed whole-rock trace element concentrations and whole-rock trace element concentrations determined by ICP-QQQ MS. The reconstruction used modal abundances and LA-ICP MS trace element data for major mineral phases (Yaxley *et al.* 2017). The graph shows the percentage difference between reconstructed and measured trace element abundances ((reconstructed-measured)/measured). The square symbols relate to samples with normal garnets, the triangle symbols to slightly sinusoidal garnets, the circle symbols to sinusoidal garnets, and the cross symbols to depleted garnets. The small line graph in the top left corner shows the partition coefficients between fluid and solid of eclogitic composition at 6 GPa and 1200°C (Kessel *et al.* 2005). 6 GPa and 1200 °C are comparable pressure/temperature conditions to the Diavik xenoliths. The pattern shows that the most fluid mobile

elements are those most depleted in the reconstruction compared to the measured whole-rock concentrations.

In all the Diavik xenoliths, the reconstructed and measured whole-rock concentrations could not be balanced for all trace elements. In particular, new measured whole-rock trace element abundances are always higher compared to the reconstructed concentrations for all trace elements, except for Er and Yb in sample 108 where the reconstructed concentration is higher (**Figure 3.7**). An important caveat in our approach is that it assumes that all mineral phases are accounted for in the reconstructed concentrations. An unaccounted phase could be responsible for the trace element mismatch. Oxides and/or sulphides are two possible contenders for 'missing' phases. However, petrography and pressure/temperature data (section 2.2) shows that, except for sample 448, there are no oxides present in these rocks. As for sulphides, there is no petrographic evidence. Although the samples lack S data, Cu concentrations are consistently low, ranging from 10 to 20 $\mu\text{g.g}^{-1}$. Consequently, it is unlikely that sulphides affected the whole-rock geochemistry of the samples. Given the lack of evidence for oxides/sulphides, it is difficult to account for the trace element mass imbalance via a 'missing' mineral phase.

The more likely explanation for the trace element mass imbalance is metasomatism. The high precision laser ablation data from Yaxley *et al.* (2017) used in the reconstruction are from the cores of pristine mineral phases. However, there is no data available for the interstitial material at grain boundaries. The elements depleted in the reconstructed whole-rock data could reside here. The most depleted elements in the reconstruction (> 90% depleted) are the LREEs and fluid-mobile elements (FMEs), which typically have the highest $D^{\text{(fluid/eclogite)}}$ at 6 GPa and 1200°C (Kessel *et al.* 2005) (**Figure 3.7**). The mass (im)balances may be caused by fluid/melt-metasomatism, which mobilised LREEs and FMEs, concentrating them in micro-components at grain boundaries, potentially in the form of minor accessory minerals such as Th, U, Sr, and LREE-rich apatite, and/or metasomatic fluid/melt inclusions that were avoided by LA-ICP MS analysis (e.g. Roden & Murthy, 1985; Bedini & Bodinier 1999; Garrido *et al.* 2000). Some samples (notably 052, **Figure 3.8**) petrographically show considerable interstitial grain boundary material, further supporting metasomatism. The difficulty in mass balancing trace elements, therefore, provides new evidence for metasomatic influence in these samples by infiltration of the agent(s) along grain boundaries.

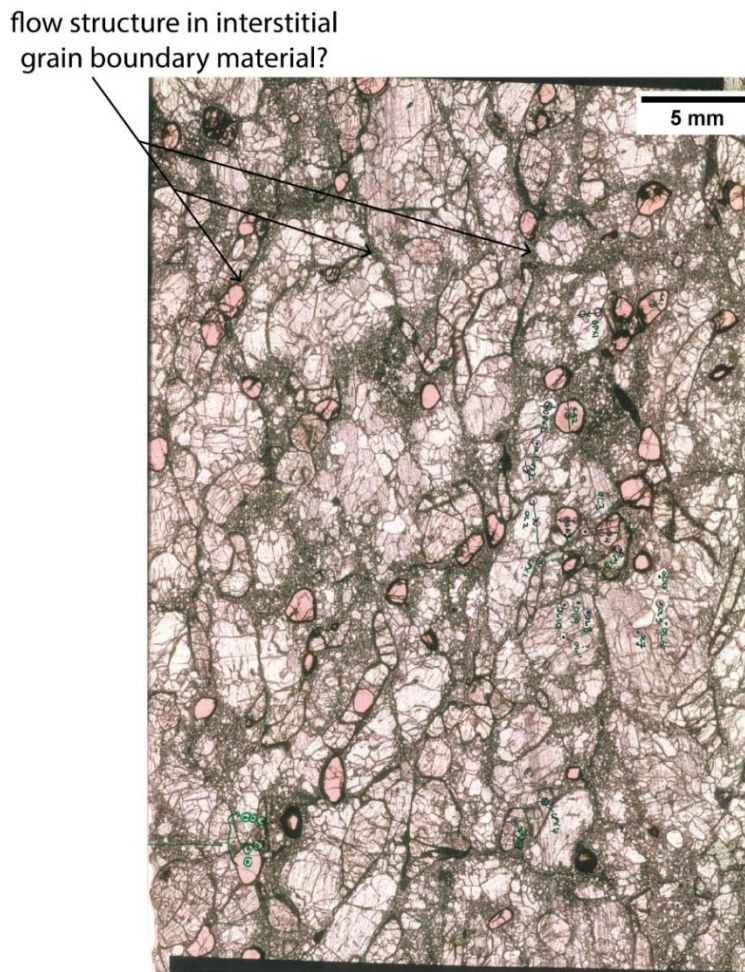


Figure 3.8: Thin section photograph of Diavik xenolith 052. This sample displays clear grain boundary interstitial material.

b) Garnet trace element chemistry

Garnets are major hosts of Cr and REEs in peridotites. Garnet Cr numbers and REE patterns can therefore be important indicators of metasomatism, enrichment and depletion processes in their host rock (Creighton *et al.* 2010). Examining the chemistry of the Diavik garnets may therefore shed light on their origins and the extent of metasomatism. Garnet Cr# ($100 \times \text{Cr} / (\text{Cr} + \text{Al})$) can be used to assess the relative depletion of the garnet protolith, and can yield information about pre-metasomatic conditions. The primitive mantle typically has garnet Cr# < 10 (e.g. Kaapvaal craton; Stachel *et al.* 1998). The Cr# of the Diavik garnets average around 20, ranging from 5.2 to 29.7, with only sample 422 overlapping with mantle Cr# at 5.2 (Yaxley *et al.* 2017; **Figure 3.9**). Stachel *et al.* (1998) argue that high Cr# garnets must result from a high Cr/Al harzburgitic protolith, depleted by extensive partial melting in the spinel stability field. The low pressure spinel stability field is the only place with Cr/Al partition coefficients high enough to create such a high Cr# ($D_{\text{Cr/Al}}^{\text{Sp/Melt}} = \sim 40$ and $D_{\text{Cr/Al}}^{\text{Opx/Melt}} = \sim 10$) (Stachel *et al.* 1998). Cr-rich garnets with positive MREE to HREE slopes (**Fig.**

3.11) may arise from extensively depleted, high Cr/Al harzburgitic residues that were brought back into the garnet stability field (Stachel *et al.* 1998; Creighton *et al.* 2010). Garnets from other Diavik xenolith studies (e.g. Creighton *et al.* 2010) have been argued to have similar origins to those from Stachel *et al.* (1998). The garnet Cr# from this study overlap with those from both previous studies (**Figure 3.9**). It therefore seems likely that the Diavik garnets are not a primary phase.

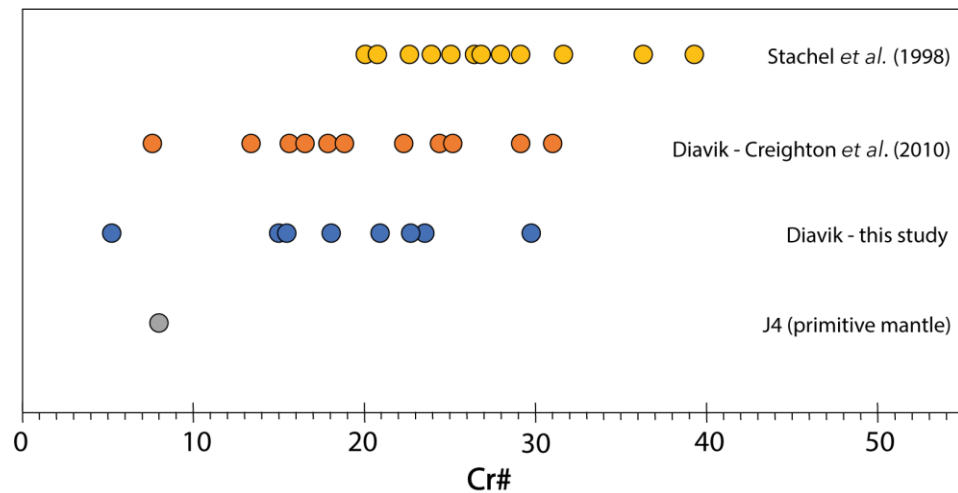


Figure 3.9: Garnet Cr# ($100 \times \text{Cr}/[\text{Cr} + \text{Al}]$) for various mantle garnet data sets. The Cr# for garnets from this study (blue) are of a comparable range to those from another study of Diavik xenoliths (orange; Creighton *et al.* (2010)). The Diavik garnet Cr# also overlaps with the African Roberts Viktor garnets (yellow) from the Stachel *et al.* (1998) paper that proposed the link between high Cr# and a depleted harzburgitic xenolith. The grey symbol represents the Cr# of primitive mantle garnet J4 from Jagersfontein (Stachel *et al.* 1998). The Cr# data for the samples in this study is from Yaxley *et al.* (2017).

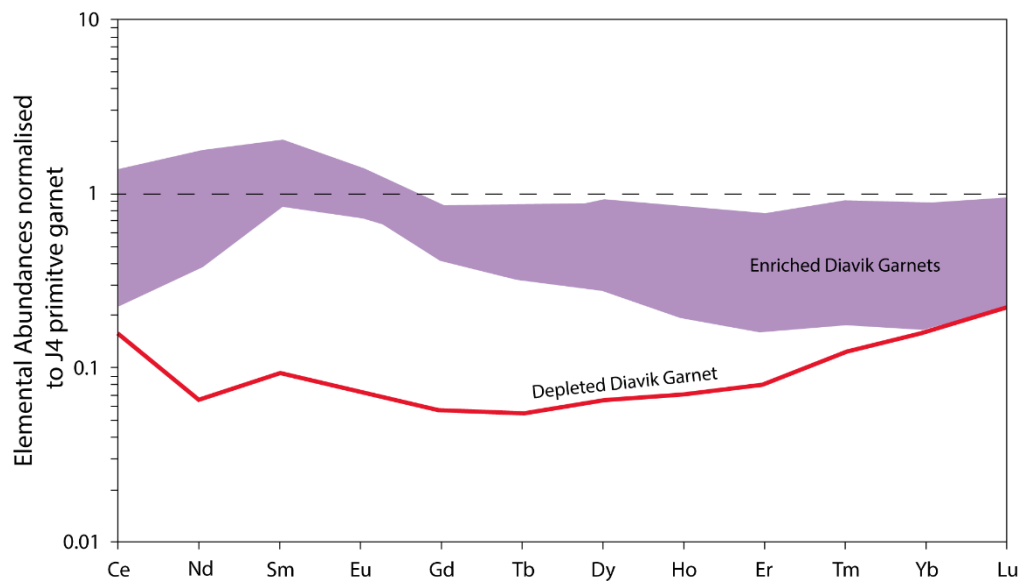


Figure 3.10: REE plot of all the Diavik garnets from this study normalised to the high-temperature sheared Iherzolite xenolith J4 from Jagersfontein (Stachel *et al.* 1998). The J4 garnet has a REE pattern close to

hypothetical garnets calculated from primitive mantle compositions using partition coefficients and mass balance considerations (Stachel et al. 1998). It is used to represent primitive garnet compositions. All garnets except those from depleted “448” (red line) vary close to 1 for all REE when normalised to J4.

Despite their inferred depleted protolith, none of the enriched Diavik garnets have REE patterns that mimic depleted garnets such as those in sample 448 (**Figure 3.10**). Instead, they exhibit a broad range of REE patterns that have been recognised in previous studies of garnets from both Kaapvaal and Diavik xenoliths (e.g. Stachel et al. 1998; Creighton et al. 2010; Aulbach et al. 2013). The REE patterns vary between U-shaped, sinusoidal, slightly sinusoidal, and normal (**Figure 3.11**). The garnets from this study all have normal and slightly sinusoidal patterns, except for sample 450 which is borderline sinusoidal, and the shallow, depleted sample 448 which does not mirror any of the patterns (**Figure 3.11e**). Given trace elements in garnets display increasing compatibility from LREEs to HREEs, later re-enrichment of REEs via metasomatism could create the variety of observed REE patterns (e.g. Stachel et al. 2004; Creighton 2010), and thus mask the evidence of depleted, harzburgitic origins. The garnet REE patterns are attributed to two different styles of metasomatic re-enrichment. The U-shaped, sinusoidal and slightly sinusoidal garnets are relatively enriched in LREEs to MREEs compared to a depleted mantle garnet such as 448 (**Figure 3.11**). This suggests that a highly fractionated fluid with a high LREE/HREE ratio variably metasomatised these xenoliths, causing re-enrichment in dominantly LREEs and MREEs (e.g. Stachel & Harris 1997; Stachel et al. 2004; Creighton 2010). Since these garnet groups span both the shallow, depleted Diavik lithosphere, and the deeper, enriched lithosphere, it is thought that the metasomatism affected both lithospheric layers. From now on, this agent will be referred to as the *LREE-rich agent*. In contrast, the normal garnets show enrichment in HREEs and LREEs, which is interpreted as evidence of another metasomatic re-enrichment by a less fractionated melt, with a lower LREE/HREE ratio and rich in HFSEs (Creighton et al. 2010). This melt is argued to have only interacted with the deep, enriched lithospheric layer, and will from now on be referred to as the *HREE-rich agent*. Since the slightly sinusoidal garnets display REE patterns that are intermediate between normal and sinusoidal, they may have also been metasomatised by the HREE-rich agent, but less strongly than the normal samples.

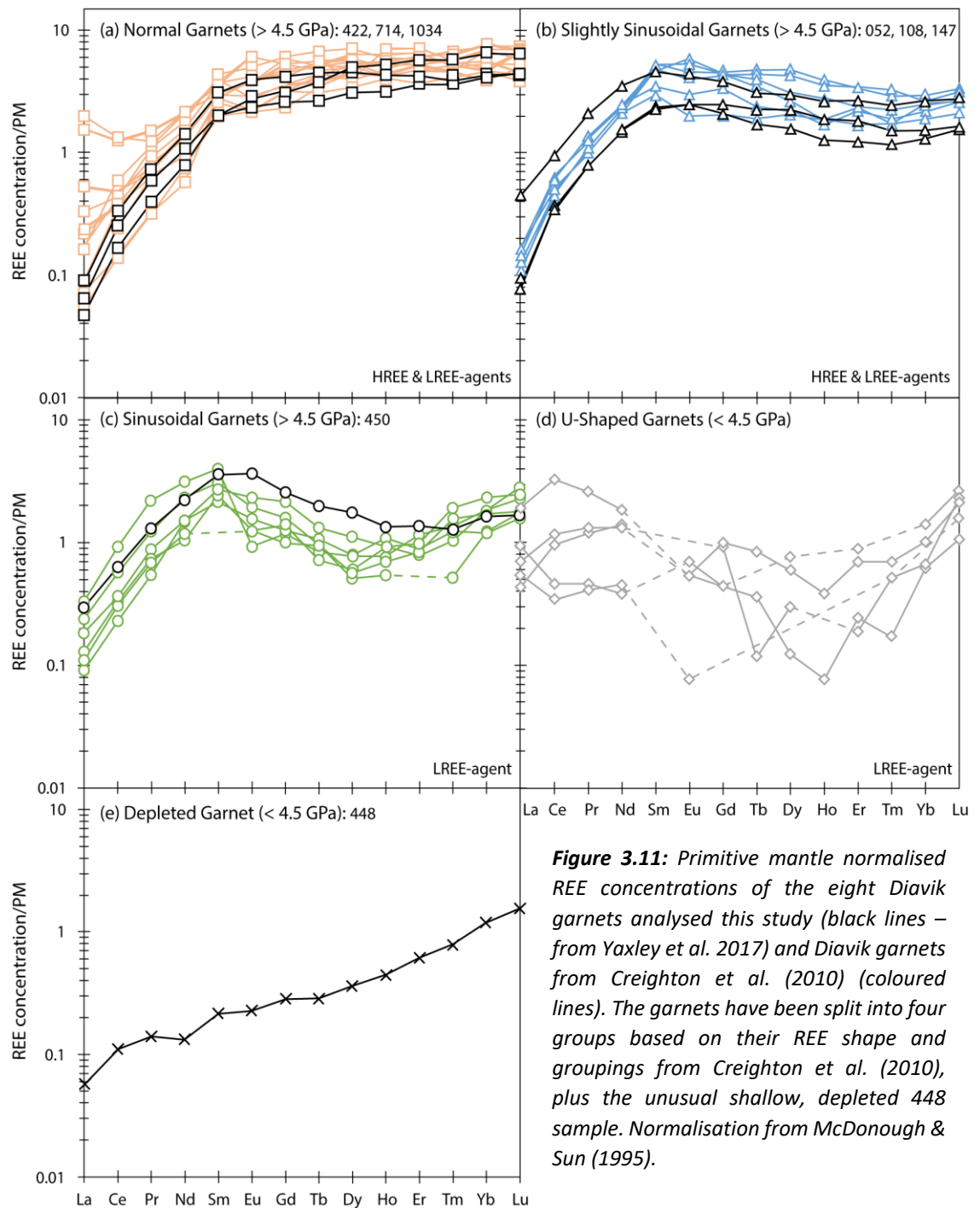


Figure 3.11: Primitive mantle normalised REE concentrations of the eight Diavik garnets analysed this study (black lines – from Yaxley *et al.* 2017) and Diavik garnets from Creighton *et al.* (2010) (coloured lines). The garnets have been split into four groups based on their REE shape and groupings from Creighton *et al.* (2010), plus the unusual shallow, depleted 448 sample. Normalisation from McDonough & Sun (1995).

The idea of two different styles of metasomatism in the Diavik mantle is supported by Zr-Y variations. Zr-Y is used to differentiate between garnets from melt and fluid metasomatised peridotites. Strongly positive Zr-Y correlations coupled with high Y concentrations are interpreted as indicative of high-T (1300°C – 1500°C) melt metasomatism (Griffin *et al.* 1999b). Alternatively, shallower positive Zr-Y correlations and lower Y concentrations are thought to indicate low-T (950 - 1100°C) fluid metasomatism (Griffin *et al.* 1999a). Diavik garnet Zr-Y data closely aligns with their

distinctive garnet REE patterns, showing two separate trends: (1) U-shaped, sinusoidal and slightly sinusoidal garnets and (2) normal garnets (**Figure 3.12**). This supports the idea proposed in Creighton *et al.* (2010) that the Diavik lithospheric mantle experienced two different metasomatic agents. It also supports the idea that the LREE-rich agent caused variable degrees of metasomatism. The U-shaped samples have the lowest Zr and Y concentrations and plot in the depleted field, and the sinusoidal and slightly sinusoidal garnets respectively display higher concentrations of both Y and Zr. Zr-Y data supports the HREE-rich agent being a melt, but it is less certain whether the LREE-rich agent is a melt or a fluid. Creighton *et al.* (2010) suggests the LREE-rich agent is a fluid, but **Figure 3.12** places it near the border between fluid and melt.

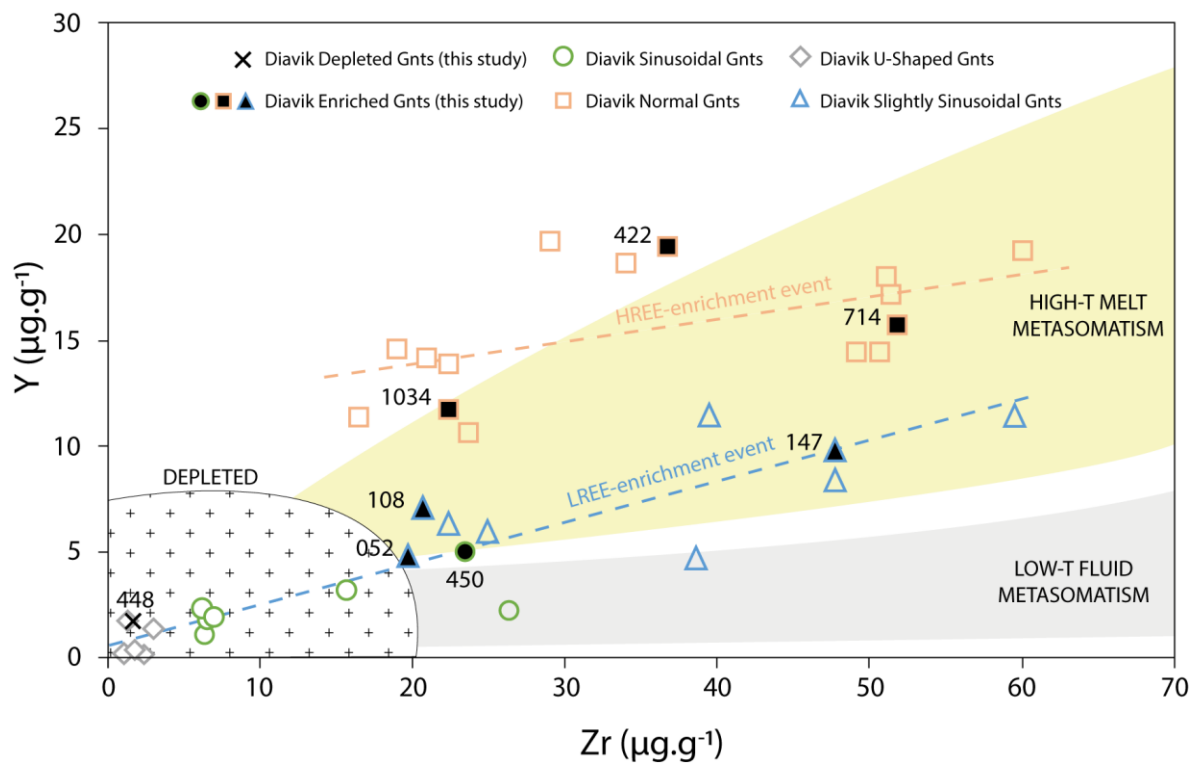


Figure 3.12: Zr/Y plot based on Griffin *et al.* (1999a) showing correlations present in the different garnet groups from Fig. 3.13. The symbols filled with white are Diavik xenoliths from Creighton *et al.* (2010) and the black filled symbols represent the eight Diavik xenoliths from this study. The data for the black filled symbols is from Yaxley *et al.* (2017). The three dashed lines are linear best fit lines for the data groups. The three fields represent different kinds of metasomatism from Griffin *et al.* (1999a). The depleted field represents no to limited metasomatism. The grey field, low-T fluid metasomatism and the yellow field, high-T melt metasomatism. The U-shaped and depleted 448 garnets appear to have little metasomatic influence. The sinusoidal garnets span the depleted and fluid metasomatism fields, suggesting a minor low-T metasomatic influence. The slightly sinusoidal and normal garnets lie within the melt metasomatism field.

The garnet chemistry of the Diavik xenoliths implies a complicated history. Garnet Cr# suggest they originated from a depleted harzburgitic protolith that crystallised garnet when subducted into the garnet stability field. Variable garnet REE patterns and Zr-Y trends are thought to suggest that two different stages of mantle metasomatism affected the Diavik mantle during garnet formation

(Creighton *et al.* 2010). A LREE-rich fluid or melt is believed to have interacted with both the shallow, depleted, and deep, enriched lithospheric layers, and created the sinusoidal, slightly sinusoidal and U-shaped garnet patterns. However, the U-shaped garnets experienced very minimal metasomatism, accounting for their low Zr and Y concentrations (Creighton *et al.* 2010). A HREE and HFSE-rich melt is suggested to have variably metasomatised the deep, enriched lithospheric layer. The HREE-rich agent is thought to have been minor and less pervasive than the LREE-enriched agent and created the normal garnet patterns causing them to mimic primitive mantle garnet REE patterns (Creighton *et al.* 2010). The HREE-rich agent may have also slightly altered the slightly sinusoidal garnets as well.

3.4.1.3. Fluid versus Supercritical Fluid Metasomatism

When discussing potential metasomatic agents, it is important to establish the differences between melts, fluids and supercritical fluids at the pressures of interest. At high pressure, the compositions of fluids and melts begin to converge along a miscibility gap which terminates in a supercritical fluid (e.g., Stalder *et al.* 2001). Experimental work by Kessel *et al.* (2005) shows that within the same pressure range as the Diavik garnets (3 to 6 GPa), the partition coefficients of trace elements between fluid and solid in aqueous and supercritical fluids are similar. They have identical downward curves from LREE to HREE, but supercritical fluids have higher partition coefficients than aqueous fluids across all REEs (**Figure 3.13**). Therefore, whether the LREE-enriched metasomatic agent is aqueous or supercritical should not impact interpretations, since it should not affect the resultant garnet REE pattern, just absolute trace element abundances. However, given that under mantle conditions, the critical point at which the miscibility gap disappears, and supercritical fluids appear is typically > 10 GPa (Stalder *et al.* 2001), the metasomatic fluid is unlikely to be supercritical.

There is strong evidence that the majority of the Diavik garnets in this study except the shallow, depleted sample 448, were affected and perhaps grown by metasomatism, and they are therefore unlikely to represent primary mantle garnets. The more variable, overall higher fO_2 in the deep, enriched lithospheric zone (**Figure 3.4**) as described by Yaxley *et al.* (2017) is thought to suggest that the metasomatism was oxidising in nature. This should mean that the fO_2 and therefore $Fe^{3+}/\Sigma Fe$ of these rocks was overprinted and may not represent the fO_2 of the xenoliths' source.

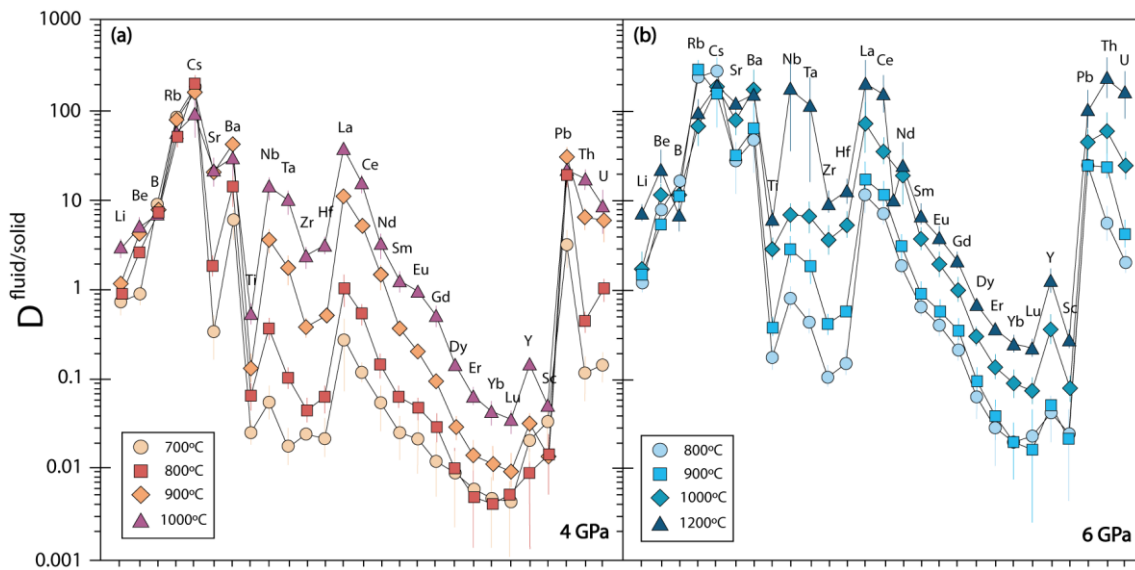


Figure 3.13: Experimental partition coefficients between fluid and a solid gnt-cpx residue for an average MORB composition. (a) Aqueous fluids (700-900°C) and hydrous melt (1000°C) and 4 GPa; (b) supercritical fluid (800-1200°C) at 6 GPa. Error bars are 1 σ . Adapted from Kessel *et al.* (2005).

3.4.2. Diavik whole-rock $\delta^{51}\text{V}$ isotopic compositions

The Diavik xenoliths experienced metasomatism which likely overprinted their $\text{Fe}^{3+}/\Sigma\text{Fe}$ and $f\text{O}_2$. Examination of the relationship between $\delta^{51}\text{V}$ and $f\text{O}_2$ in the Diavik suite may therefore help determine the potential effects of mantle metasomatism on V stable isotope fractionation. Diavik whole-rock $\delta^{51}\text{V}$ are far more variable, and generally isotopically lighter than found in previous mantle peridotite studies (**Fig. 3.14**; Prytulak *et al.* 2013; Qi *et al.* 2019). However, previous work has endeavoured to analyse pristine peridotites, mainly in pursuit of a $\delta^{51}\text{V}$ BSE estimate.

Similar increases in variability in Fe isotopes have been observed in metasomatised versus unmetasomatised suites (e.g. Beard & Johnson 2004; Weyer & Ionov 2007; Zhao *et al.* 2010; Poitrasson *et al.* 2013). The cause of variability in $\delta^{56}\text{Fe}$ is complex, and several explanations have been proposed. Beard & Johnson (2004) and Zhao *et al.* (2010) attributed the variability in $\delta^{56}\text{Fe}$ observed in mantle peridotites to kinetic isotope fractionation during metasomatism. However, Weyer & Ionov (2007) argued that whilst metasomatism could account for an increase in $\delta^{56}\text{Fe}$ variation in mantle rocks, partial melting is a more significant control. Poitrasson *et al.* (2013) found that $\delta^{56}\text{Fe}$ variation in the mantle is moderately influenced by partial melting, but metasomatism has a far stronger influence on variation. All of these studies credit kinetic fractionation via diffusion as the mechanism for $\delta^{56}\text{Fe}$ fractionation. The role of kinetic isotope fractionation in the mantle is now disputed after the effects of coordination of $\delta^{56}\text{Fe}$ were more recently documented (e.g. Dauphas *et al.* 2014).

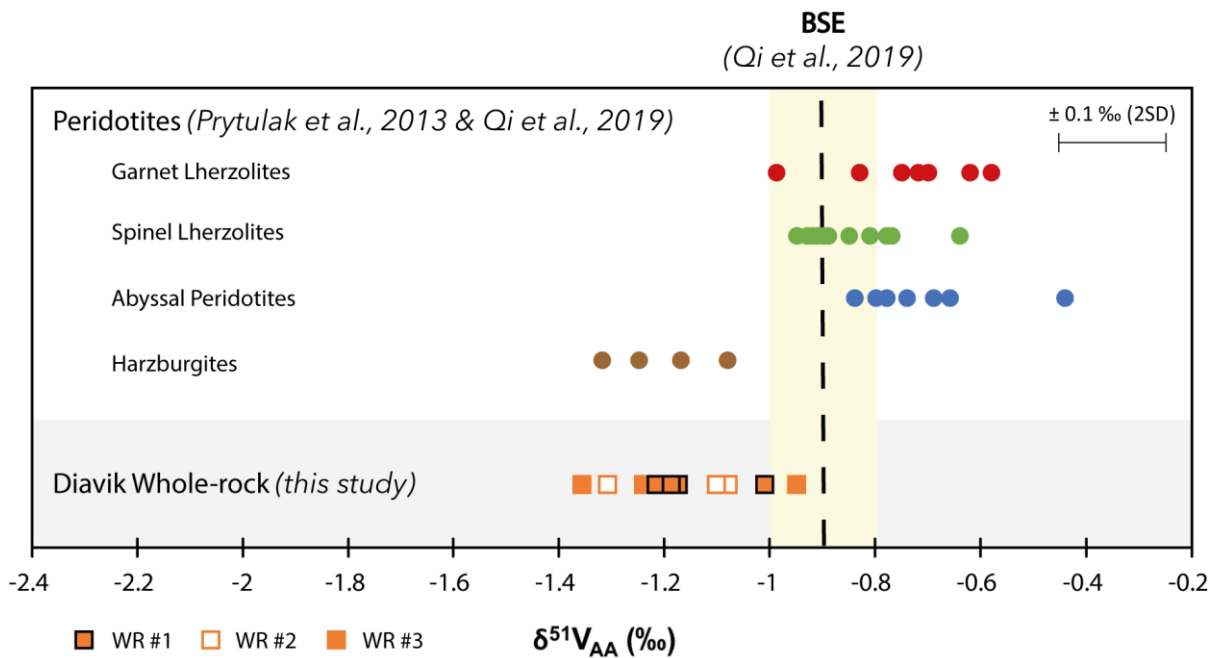


Figure 3.14: Summary of literature peridotite $\delta^{51}\text{V}$ compared to the whole-rock Diavik xenolith data. The black dashed vertical line represents the current bulk silicate earth estimate ($-0.9 \text{ ‰} \pm 0.1$; Qi et al. (2019)) and the yellow shaded area represents the 2SD on the BSE estimate. The three different symbols used for the Diavik whole-rock suite correspond to different digestions of the same whole-rock powders.

3.4.2.1. Investigating whole-rock $\delta^{51}\text{V}$ heterogeneity

During the analytical procedure for V isotopes, small masses of rock powder were digested (between 40 and 80 mg). Given the Diavik xenoliths exhibit variable crystal sizes (e.g. garnets from 0.5 mm to 7 mm diameter), and hand crushed with a mortar and pestle rather than in a ball mill to avoid sample loss, there is the potential for powder heterogeneity. If major mineral phases have distinct $\delta^{51}\text{V}$ signatures, this could create additional variability in whole-rock isotope analyses due to small differences in the modal abundances in different digestions. Consequently, most Diavik whole-rock powders were analysed three times – including full repeat digestion, V isolation, and V isotopic measurement - to assess heterogeneity outside of typical analytical error ($\sim \pm 0.1 \text{ ‰}$) and to ensure a more robust examination of any trends with $f\text{O}_2$.

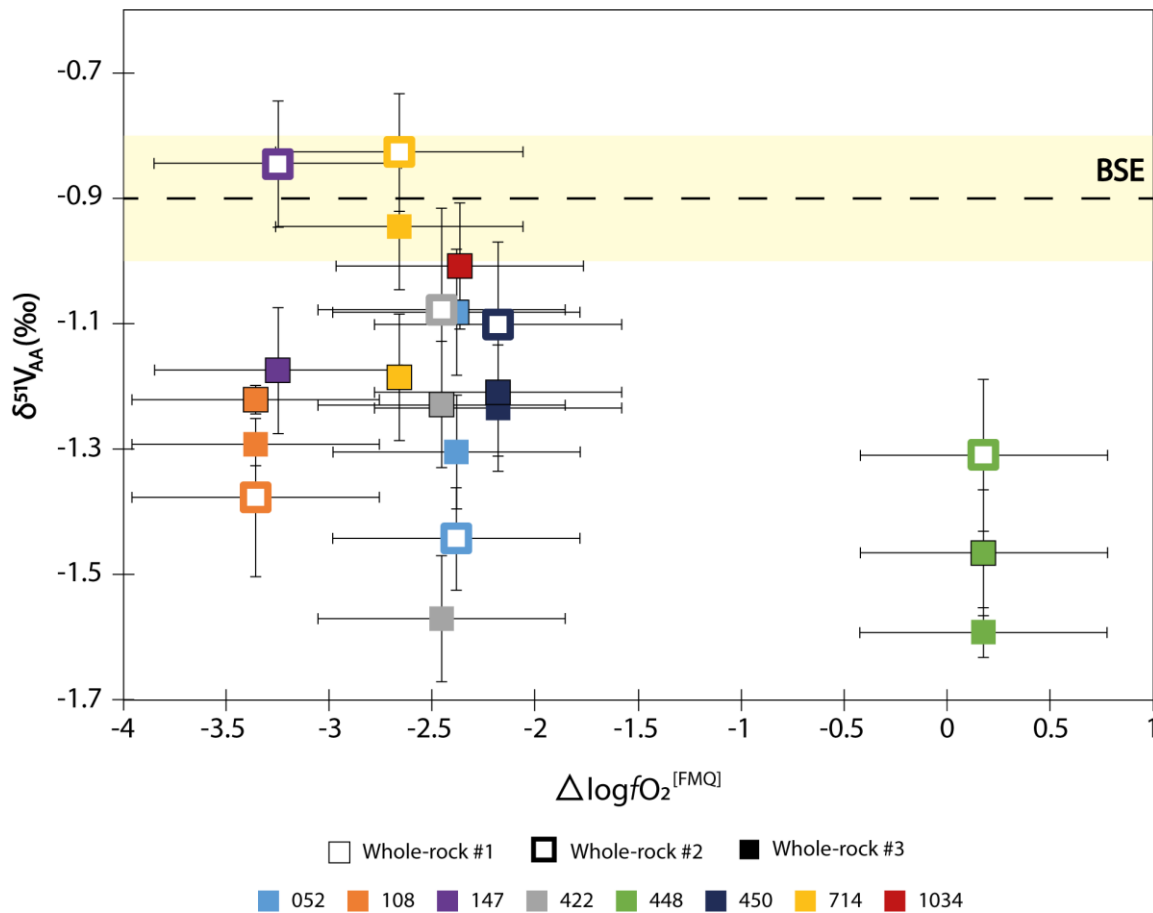


Figure 3.15: Diavik lherzolite whole-rock $\delta^{51}\text{V}$ (‰) versus $\Delta\log f\text{O}_2$ relative to FMQ. The error bars represent 2SD for $\delta^{51}\text{V}$ and 0.6 log units for $\Delta\log f\text{O}_2$. The $f\text{O}_2$ data is from Yaxley et al. (2017). The black dashed line represents the current BSE estimate (-0.9‰; Qi et al. (2019)) and the yellow box represents the error on the BSE estimate ($\pm 0.1 \text{‰}$).

Duplicate analyses of the same sample powder show variable $\delta^{51}\text{V}$, in some cases outside analytical error (**Figure 3.15**). One possible reason for this variability is analytical error, however there are several reasons that this is unlikely. The first two digestions were both performed at Imperial College London, and underwent identical ion chromatography procedures. The $\delta^{51}\text{V}$ values for both digestions were measured on the same Neptune MC-ICP MS at Durham University using identical set-ups and running conditions. Furthermore, a significant proportion of the data across both digestions was collected on the same day of the same mass spectrometry session. The V yields for all samples were 75% to 92% and do not correlate with isotopic offsets between samples. Given the yield calculations were based on concentration data obtained while concentration checking prior to $\delta^{51}\text{V}$ analysis, errors of around 20% are possible. Therefore, it is unlikely that the variability in $\delta^{51}\text{V}$ signatures is due to analytical error.

A third digestion of some of the whole-rock powders were analysed which, did not agree with one previous result over another (**Figure 3.15**), further supporting that the powders are heterogeneous. This is an important and significant issue associated with analysing only whole-rock samples. It is

therefore recommended that for coarse grained heterogeneous material, multiple digestions should be used to assess variability. Digestion heterogeneity may account for some of the increased $\delta^{51}\text{V}$ scatter observed in the Diavik xenoliths compared to previous studies. However, even when the heterogeneity is taken into account, the majority of samples have $\delta^{51}\text{V}$ significantly lighter than the BSE (**Figure 3.15**).

3.4.2.2. Relationship between whole-rock $\delta^{51}\text{V}$ and $f\text{O}_2$

Despite the whole-rock digestion heterogeneity, on first examination there appears to be a negative correlation between $\delta^{51}\text{V}$ and $\Delta\log f\text{O}_2$ (**Figure 3.15**). If $f\text{O}_2$ is directly reflected in more oxidised V in this suite, and, all else being equal, the preference for the heavy isotope of V is $\text{V}^{5+} > \text{V}^{4+} > \text{V}^{3+} > \text{V}^{2+}$, then such a relationship contradicts theoretical predictions (e.g. Bigeleisen & Mayer, 1947; Schauble 2004). However, the co-variation in **Figure 3.15** is controlled by sample 448; the only shallow, depleted lherzolite. Petrographically, 448 is the only sample examined that has considerable replacement of garnets by oxides (see section 2.2). If 448 is not considered alongside the other samples, then no obvious trends of $\delta^{51}\text{V}$ with $f\text{O}_2$ are apparent. Therefore, at the scale of $f\text{O}_2$ variation in the dataset (-3.36 to -2.38 $\Delta\log f\text{O}_2^{[\text{FMQ}]}$) whole-rock $\delta^{51}\text{V}$ does not co-vary with $\Delta\log f\text{O}_2$.

3.4.3. Diavik garnet and clinopyroxene $\delta^{51}\text{V}$ isotopic compositions

Interpretation of whole-rock $\delta^{51}\text{V}$ signatures can be challenging. There are many variables to consider, including powder heterogeneity, phase (dis)equilibrium, oxidation state and variable coordination of V in the different phases. Quantifying coordination environment is necessary to evaluate the relationship between $\delta^{51}\text{V}$ and $f\text{O}_2$. Focussing on $\delta^{51}\text{V}$ signatures of V-rich mineral separates allows coordination to be better constrained. In the case of Diavik, VI-fold coordinated V in garnet and clinopyroxene dominates the V budget of the whole-rock. Furthermore, $f\text{O}_2$ was determined by Yaxley *et al.* (2017) using measurement of garnet $\text{Fe}^{3+}/\Sigma\text{Fe}$, and it is highly likely that the garnets in the Diavik suite are metasomatic phases. Therefore, comparing garnet $\delta^{51}\text{V}$ and garnet-based $f\text{O}_2$ is a more direct comparison to assess the impacts of metasomatism on V isotope fractionation.

Similar to garnet, Diavik clinopyroxene are Cr-enriched, chemically homogeneous, and appear to be in chemical and textural equilibrium with garnet (Yaxley *et al.* 2017). There is no evidence of reaction rims, all mineral phases are chemically homogeneous in major and minor elements, and there is a general good agreement between various geothermometers in all samples except 448 (Yaxley *et al.* (unpublished)). Therefore, we consider both the garnet and clinopyroxene in the

Diavik suite to have metasomatic origins, and will examine both garnet and clinopyroxene $\delta^{51}\text{V}$ to evaluate the effects of metasomatism and the relationship between $f\text{O}_2$ and $\delta^{51}\text{V}$.

Since the coordination of V in both garnet and clinopyroxene is the same (VI-fold), the phases are in equilibrium with one another, and the suite spans a limited, high temperature range (1170 to 1280 °C) the major variable theoretically driving inter-mineral isotope fractionation should be oxidation state and therefore $f\text{O}_2$. Hence, if garnet and clinopyroxene are both metasomatic and have interacted with the same metasomatic agents, no inter-mineral fractionation factor is expected. If there is a significant relationship between $f\text{O}_2$ and $\delta^{51}\text{V}$, a positive correlation versus $f\text{O}_2$ in both garnet and clinopyroxene is predicted, with more oxidised conditions resulting in heavier $\delta^{51}\text{V}$ (e.g. Bigelsen & Mayer, 1947; Schauble 2004).

There is no correlation between $\delta^{51}\text{V}$ in garnet or clinopyroxene and $\text{Fe}^{3+}/\Sigma\text{Fe}$ (garnet) (**Figure 3.16a**) over the small range in $\text{Fe}^{3+}/\Sigma\text{Fe}$ observed in these samples. However, there is a positive trend for clinopyroxene and arguably garnet between $\delta^{51}\text{V}$ and $\Delta\log f\text{O}_2$ (**Figure 3.16b**), which is the theoretically predicted sense of variation for oxidation state driven isotopic fractionation.

Garnet and clinopyroxene $\delta^{51}\text{V}$ from the same sample are within error of each other for all samples (**Figure 3.16**). Therefore, as expected if these two phases are in equilibrium, there is no V isotope fractionation factor between garnet and clinopyroxene. However, in every sample, the garnet and clinopyroxene $\delta^{51}\text{V}$ are consistently and significantly isotopically lighter than their corresponding whole-rock $\delta^{51}\text{V}$ and the BSE (**Figure 3.16**). The coordination of V in the two other major mineral phases in these rocks (orthopyroxene and olivine) is also VI-fold. Therefore, if all the phases are in equilibrium, the whole-rock $\delta^{51}\text{V}$ signature should be within error of the mineral separates.

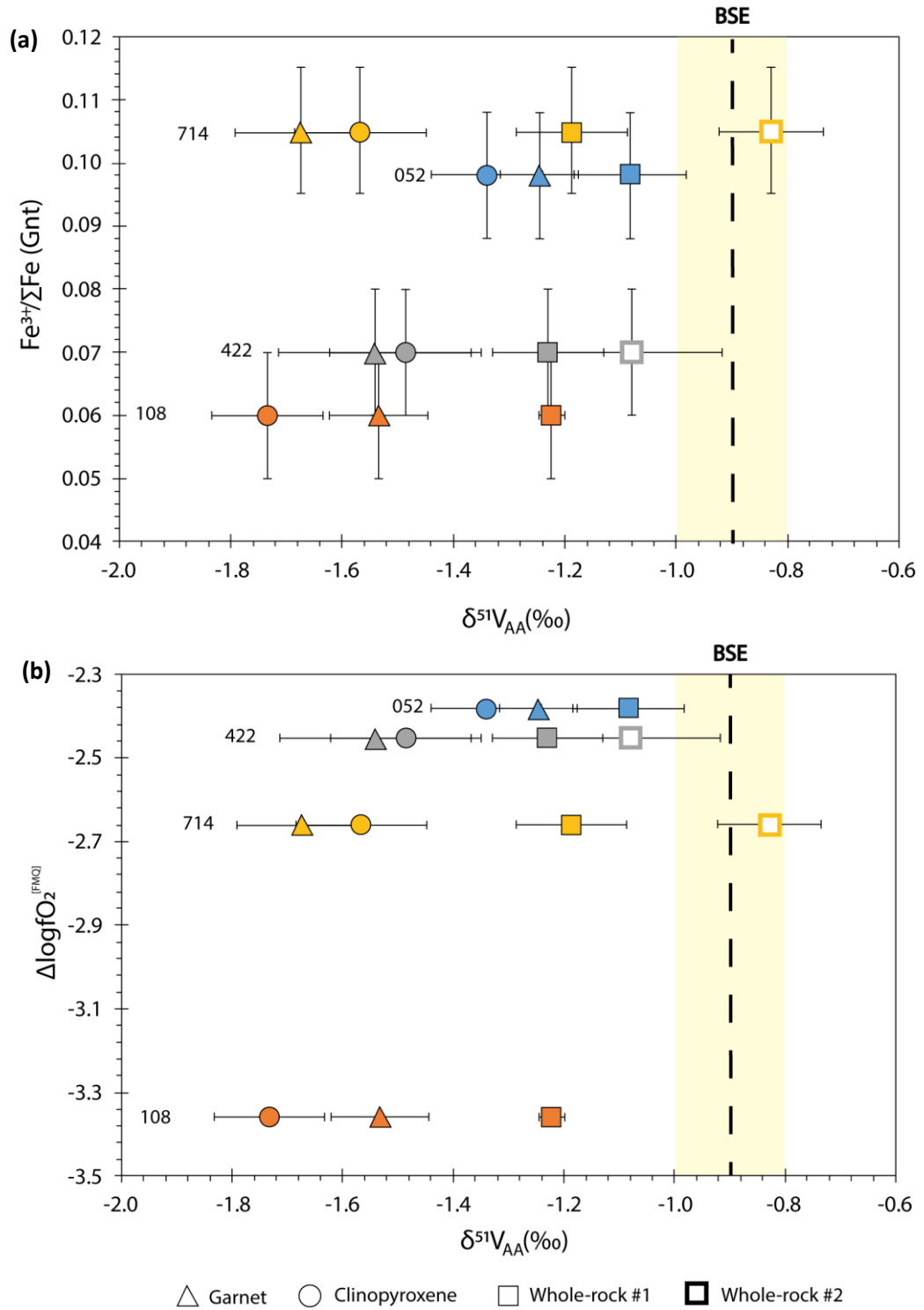


Figure 3.16: $\delta^{51}\text{V}$ versus $\text{Fe}^{3+}/\Sigma\text{Fe}$ and $\Delta\log f\text{O}_2 [\text{FMQ}]$. (a) $\delta^{51}\text{V}$ versus $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Yaxley et al. 2017) in mineral separates and whole-rock. The horizontal error bars represent 2SD and vertical error bars ± 0.01 (Yaxley et al. 2017). (b) $\delta^{51}\text{V}$ versus $\Delta\log f\text{O}_2 [\text{FMQ}]$ (Yaxley et al. 2017) in mineral separates and whole-rock. The error bars represent 2SD. Estimated errors on $\Delta\log f\text{O}_2$ are 0.6 log units (Yaxley et al. 2017). The black dashed vertical line in both graphs represents the current bulk silicate earth (BSE) estimate (-0.9 ‰ ; Qi et al. (2019)) and the yellow shaded area represents the 2SD on the BSE estimate ($\pm 0.1 \text{ ‰}$).

3.4.4. Isotopic mass imbalance?

One of the striking findings of this study is the analytically significant and consistent direction of isotopic offset between garnet and clinopyroxene $\delta^{51}\text{V}$ compared to corresponding whole-rock $\delta^{51}\text{V}$ (**Figure 3.16**). This was unexpected, given that most of the V should be hosted by garnet and clinopyroxene. Therefore, we explore possible explanations for the apparent isotopic mass imbalance.

One possibility is a V-rich, isotopically heavy phase present in the whole-rock powders, that is not accounted for. It was established in section 4.1.2a that metasomatism redistributed many elements, removing them from minerals and concentrating them at grain boundaries. Vanadium could therefore be held within the grain boundary material. If this V was isotopically heavier than that garnet and clinopyroxene, it would create an isotopic mass imbalance. However, V is only moderately incompatible during melting and has low fluid mobility. Therefore, we do not expect significant V to be hosted along grain boundaries as was found for highly incompatible elements and FMEs. Indeed, an elemental mass balance of V using the concentrations of olivine, orthopyroxene, clinopyroxene and garnet reproduces the measured whole-rock concentrations much better than the FMEs. Consequently, V-rich, isotopically heavy grain boundary material is unlikely. It is also unlikely that there is an unaccounted mineral phase. As discussed in section 4.1.2a, oxides and sulphides are the most likely contenders, and in the four samples with mineral separate data, there is no petrographic or chemical evidence for either. Therefore, an unaccounted for V-rich, isotopically heavy phase is an unlikely solution to the isotopic mass imbalance.

The Diavik suite of xenoliths were entrained during kimberlite eruptions. Therefore, although care was taken to powder only xenolith material, contamination by the host kimberlite may explain the offset in $\delta^{51}\text{V}$ between mineral separates and whole-rock. A few hand specimens have attached kimberlite, such as sample 031 (**Figure 3.17**). To investigate if kimberlite contamination is responsible for the mineral-whole-rock isotopic offset, kimberlite was removed from sample 031 using a hand-held diamond tipped drill and analysed for trace elements and $\delta^{51}\text{V}$. The primitive mantle normalised REE pattern of the kimberlite is similar in overall pattern to whole-rock garnet lherzolites, with elevated trace element abundances (**Figure 3.17**). The $\delta^{51}\text{V}$ signature of the kimberlite is $-1.27\text{‰} \pm 0.06$ (2SD) with a V concentration of $44\text{ }\mu\text{g.g}^{-1}$, which is within the same concentration range as the Diavik xenoliths (26 to $63\text{ }\mu\text{g.g}^{-1}$). Whole-rock isotopic compositions also extend to significantly heavier values than the kimberlite in 3 of the 4 samples (**Figure 3.18**). Furthermore, it is not possible to mass balance the whole-rock trace elements with any degree of kimberlite addition, and there is no petrographic evidence of pervasive kimberlite invasion into the

interior of any samples. Therefore, kimberlite contamination cannot be responsible for the offset between mineral phases and whole-rock $\delta^{51}\text{V}$.

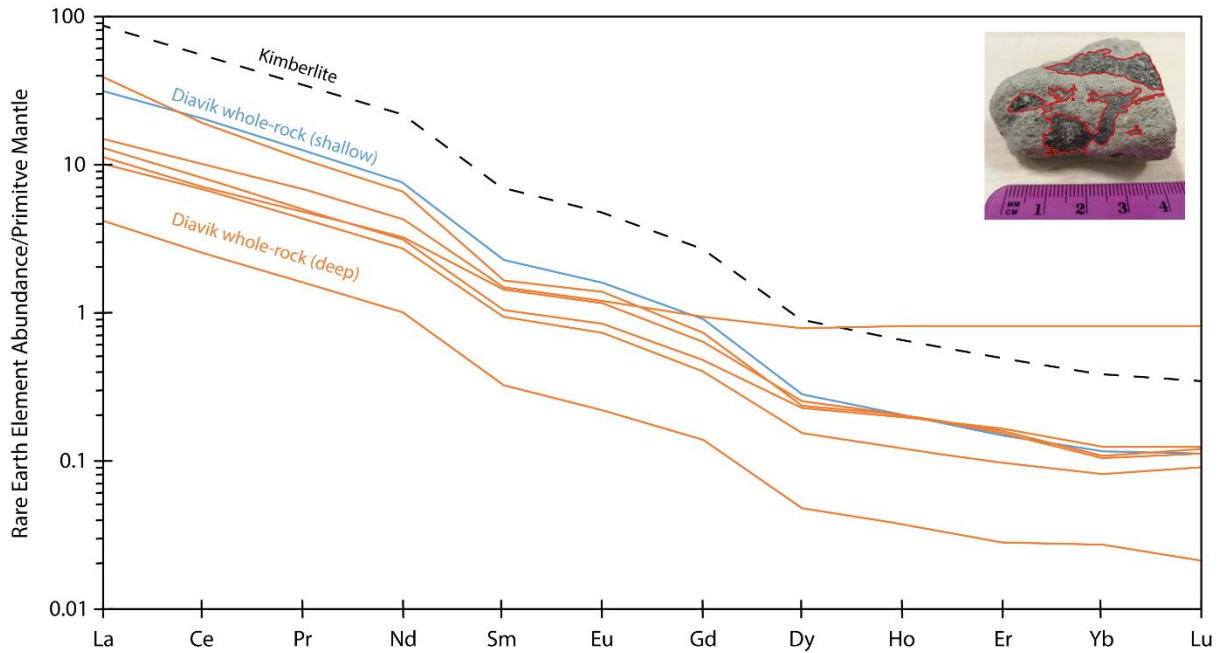


Figure 3.17: Primitive mantle normalised REE plot of the Diavik whole-rock powders and the kimberlite attached to sample 031 (photo in top right – kimberlite is outlined in red). Normalisation from McDonough & Sun (1995).

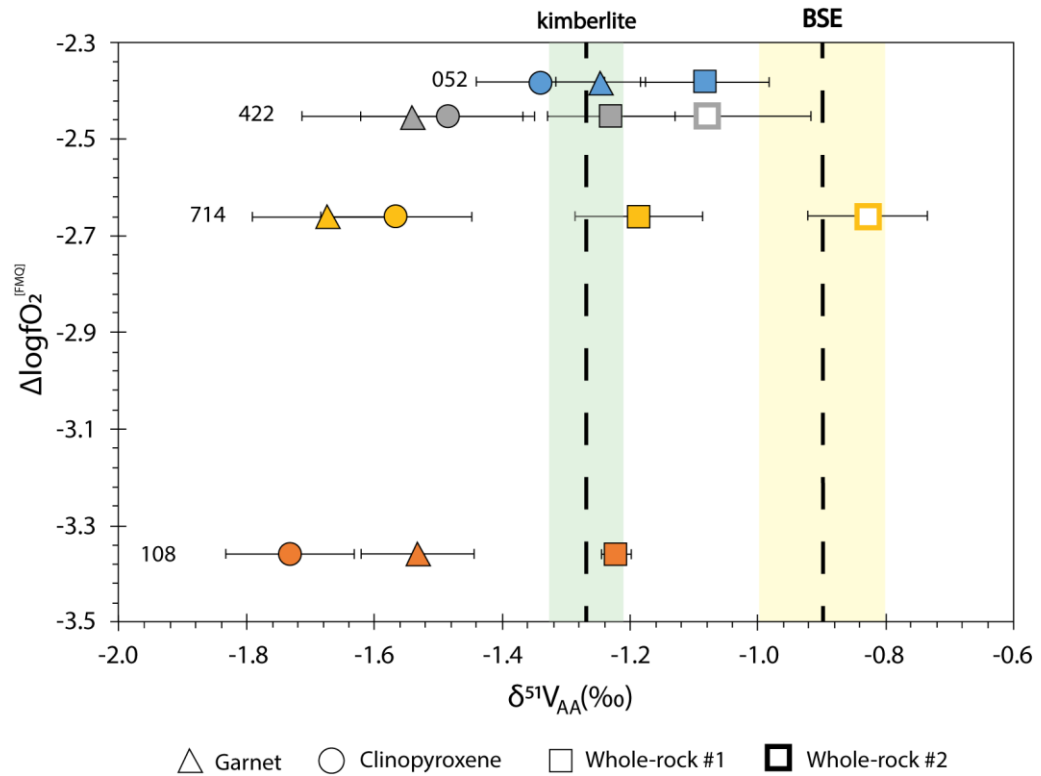


Figure 3.18: $\delta^{51}\text{V}$ versus $\Delta\log f\text{O}_2[\text{FMQ}]$ (Yaxley et al. 2017) in mineral separates, whole-rock and whole-rock kimberlite drilled off one of the Diavik samples (black dashed line with green error shadow). The error bars

represent 2SD. Estimated errors on $\Delta\log fO_2$ are 0.6 log units. The black dashed vertical line represents the current bulk silicate earth (BSE) estimate (-0.9 ‰; Qi *et al.* (2019)) and the yellow shaded area represents the 2SD on the BSE estimate (± 0.1 ‰). The black dashed line with the green halo represents the $\delta^{51}\text{V}$ signature of the host kimberlite (-1.27 ‰ ± 0.06).

A remaining explanation is potential isotopic disequilibria between garnet/clinopyroxene and olivine/orthopyroxene, both of which are present in large modal abundances in the Diavik xenoliths (**Table 3.2**). Olivine has negligible V concentrations (~ 1 to $4 \mu\text{g.g}^{-1}$ (Prytulak *et al.* 2013)), but may become influential given its very high modal abundances. Orthopyroxene V concentrations are typically around $100 \mu\text{g.g}^{-1}$ (Ionov 2004), again with significant modal abundance in the samples. Vanadium is octahedrally coordinated in both clinopyroxene and orthopyroxene, therefore they would be expected to have similar $\delta^{51}\text{V}$ if they are in equilibrium with one another. However, these rocks have metasomatic origins. Therefore, it is possible that the metasomatic garnet and clinopyroxene are in disequilibrium with the olivine and orthopyroxene. Vanadium is an immobile, refractory element, and therefore it is likely difficult to alter the isotopic composition of olivine and orthopyroxene in harzburgite through kinetic means such as diffusion. We hypothesize that olivine and orthopyroxene retain a $\delta^{51}\text{V}$ value similar to the BSE (-0.9 ‰ ± 0.1 ; Qi *et al.* 2019), and therefore are out of isotopic equilibrium with the metasomatically generated garnet and clinopyroxene phases.

To test the hypothesis that the offset between garnet-clinopyroxene and whole-rock $\delta^{51}\text{V}$ is due to inter-mineral isotopic disequilibrium, whole-rock $\delta^{51}\text{V}$ was reconstructed. The reconstruction used garnet and clinopyroxene $\delta^{51}\text{V}$ and V concentration data from LA-ICP MS (Yaxley *et al.* 2017). We assume that olivine and orthopyroxene have BSE $\delta^{51}\text{V}$ signatures (-0.9 ‰ ± 0.1 (Qi *et al.* 2019)), with typical V concentrations (e.g. Prytulak *et al.* 2013), since there is no LA-ICPMS trace element data for these phases. Whole-rock V concentration data was reconstructed using modal abundances (**Table 3.2**) and mineral V concentrations. The percentage of the whole-rock V concentration that each phase contributed was then calculated. These percentages were used to weight the $\delta^{51}\text{V}$ signatures of each phase, which were added together to produce reconstructed whole-rock $\delta^{51}\text{V}$ values. **Figure 3.19** shows that for each sample except 108, the reconstructed whole-rock $\delta^{51}\text{V}$ signature is within error of the measured whole-rock $\delta^{51}\text{V}$ signature for that sample. This strongly suggests that the offset in $\delta^{51}\text{V}$ signatures between garnet and clinopyroxene mineral separates and whole-rock powders, is due to the metasomatic history of these samples, and that the non-metasomatic phases (olivine and orthopyroxene) are not in equilibrium with the metasomatic phases (garnet and clinopyroxene).

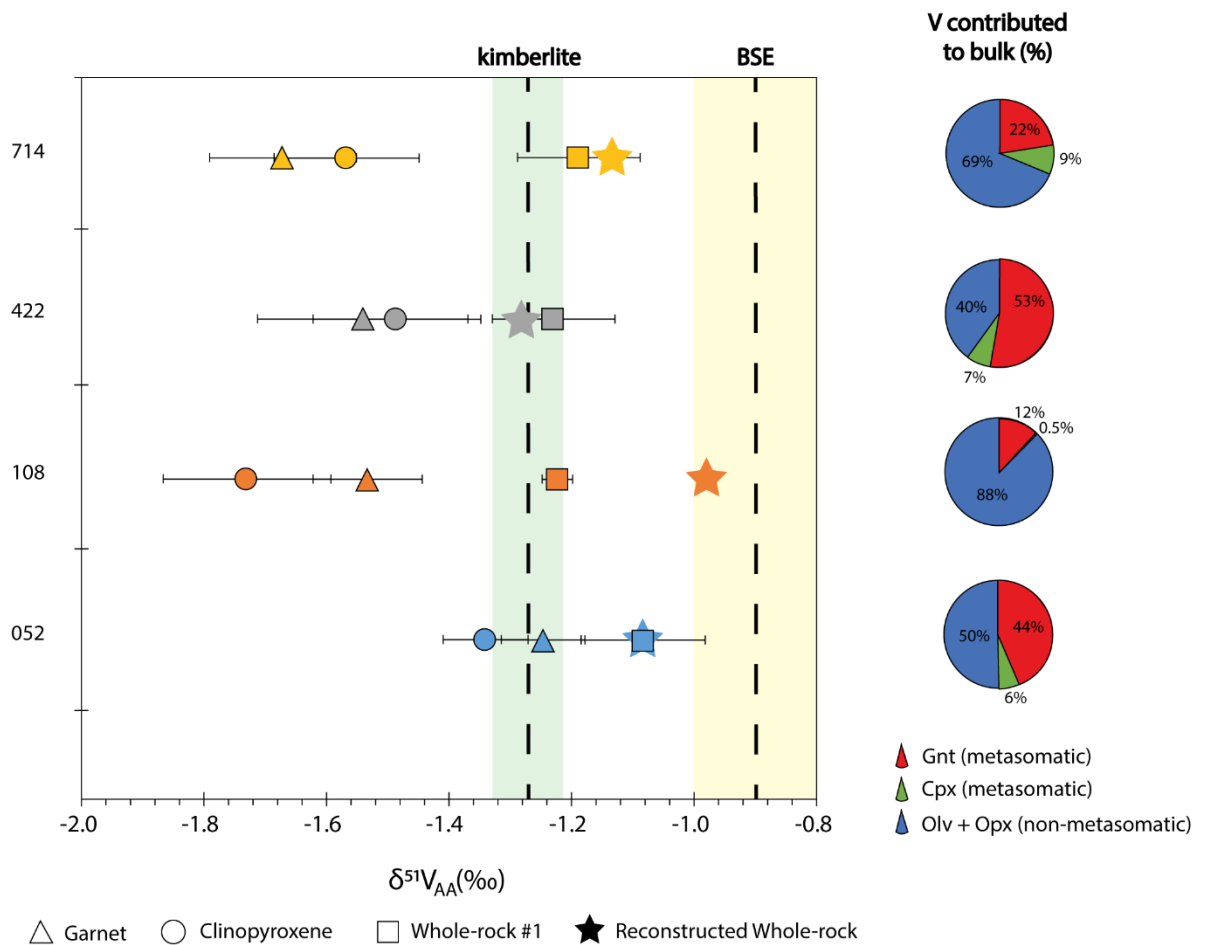


Figure 3.19: Reconstructed whole-rock $\delta^{51}\text{V}$ signature (star) for each sample with mineral separate $\delta^{51}\text{V}$ data. Olivine and orthopyroxene were assumed to be primary and non-metasomatic, with BSE $\delta^{51}\text{V}$ ($-0.9\text{‰} \pm 0.1$ (-0.9‰ ; Qi et al. (2019))). The $\delta^{51}\text{V}$ signatures of the four major mineral phases, plus the V concentrations of each phase and modal abundances were used to reconstruct the whole-rock V signature. The whole-rock V concentration for each sample was used to weight the $\delta^{51}\text{V}$ signature of each phase based on the percentage of V they contribute to the whole-rock. The pie charts to the right show the modal abundances of each of the four phases calculated from thin sections. The black dashed line with the yellow halo represents the current BSE estimate (-0.9‰ ; Qi et al. (2019)) and the black dashed line with the green halo represents the $\delta^{51}\text{V}$ signature of the host kimberlite ($-1.27\text{‰} \pm 0.06$). The halo on each dashed line represents the 2SD error.

The mismatch between $\delta^{51}\text{V}$ signatures of the reconstructed whole-rock and first digestion whole-rock for sample 108 can also be explained. Sample 108 has the lowest modal abundances of garnet and clinopyroxene of all four samples (1.3% gnt and 0.1% cpx; **Table 3.2**). This sample also has the largest garnet crystals (2 to 4 mm). Given this heterogeneous distribution, the thin section used to calculate modal abundances may not be representative of the sample as a whole. In light of this, the amount that the modal abundances would have to change by to reconcile the mismatch was calculated. Each possible combination of abundances for all four phases was tested in Excel using Visual Basic for Applications (VBA). However, to reduce the time and processing power required, the abundances were limited for each phase to a range possible within natural garnet lherzolites.

The abundance combination that reconciled the whole-rock $\delta^{51}\text{V}$ mismatch with the smallest total offset in abundances from those observed in the 108 thin section was selected. The selected modal abundances are shown in **Table 3.7**. To reconcile the isotopic mass imbalance for sample 108, the abundance of garnet would need to increase 5.4 times, and clinopyroxene 9.1 times. The calculated abundances in sample 108 are lower than those observed in the other Diavik xenolith thin sections, such as sample 422, suggesting that they are reasonable. Such modal abundance variability within sample 108 could be possible given its likely heterogeneity, and therefore the calculated abundances can be considered reasonable.

Table 3.7: The modal abundances of the four major phases found in Diavik xenolith sample 108. The modal abundances were determined using a thin section photo and the software SketchandCalc. The second row represents the combination of abundances that produces a whole-rock $\delta^{51}\text{V}$ signature that matches that measured from the first digestion of the whole-rock powder for sample 108 (-1.22 ‰). The combination of abundances was calculated using VBA in Excel, and the result included in the table is the combination of abundances with the smallest overall offset compared the abundances observed in thin section.

	Modal Abundance in Diavik sample 108 (%)			
	Garnet	Clinopyroxene	Olivine	Orthopyroxene
Observed in thin section	1.3%	0.11%	69%	30%
Closest successful combination	7%	1%	69%	23%

We suggest that garnet and clinopyroxene are not in isotopic equilibrium with olivine and orthopyroxene, and that the non-metasomatic phases likely have $\delta^{51}\text{V}$ signatures close to BSE. This could be tested in the future by measuring the $\delta^{51}\text{V}$ signature of olivine and orthopyroxene in the Diavik xenoliths. If true, the metasomatic phases may reflect the isotopic composition of the metasomatic agent. Phase disequilibrium could also explain the lack of correlation between whole-rock $\delta^{51}\text{V}$ and $f\text{O}_2$. If the determined $f\text{O}_2$ reflects $f\text{O}_2$ after metasomatism, and not the $f\text{O}_2$ of the source, the lack of a whole-rock $\delta^{51}\text{V}/f\text{O}_2$ relationship may be due to variable modal abundances of V-rich metasomatic and non-metasomatic phases.

3.4.5. Links between mantle metasomatism, $f\text{O}_2$ and $\delta^{51}\text{V}$

The Diavik metasomatic phases measured in this study belong to xenoliths with normal and slightly sinusoidal garnet REE patterns, and are isotopically light compared to whole-rock values and the $\delta^{51}\text{V}$ BSE. Such metasomatic phases are thought to have been affected by two different agents, as evidenced by garnet REE patterns and Zr-Y data (Creighton *et al.* 2010; Yaxley *et al.* 2017). A LREE-MREE-rich fluid or melt is postulated to have interacted with both the shallow, depleted, and deep,

enriched lithospheric layers. The interaction is likely responsible for the sinusoidal, slightly sinusoidal and U-shaped garnet patterns. A second, less dominant melt, rich in HREE and HFSE is argued to have variably metasomatised the deep, enriched lithospheric layer, creating the normal garnet patterns (Creighton *et al.* 2010).

The relative redox conditions of the two metasomatic agents are important to constrain. Yaxley *et al.* (2017) calculated sample fO_2 using the garnet peridotite oxybarometer from Stagno *et al.* (2013) and showed that all xenoliths from the deep (> 4.5 GPa), enriched lithospheric layer have a higher fO_2 than predicted by the trend set by the shallower samples. The fO_2 is variable, ranging over 4 log units (-1.22 to $-3.90 \Delta \log fO_2^{[FMQ]}$), and is interpreted as evidence for oxidising metasomatism (Yaxley *et al.* 2017). It is therefore tempting to assume that both metasomatic events were oxidising. However, overall oxidation could also be achieved by the minor HREE-rich agent being reducing, but largely overprinted by an oxidising, more dominant, LREE-rich agent. In support of the second proposition, Creighton *et al.* (2010) suggested that different garnet groups have different fO_2 (**Figure 3.20**). The normal garnets plot in the region of a calculated unmetasomatised garnet depth- fO_2 profile from Frost & McCammon (2008), and the other garnet groups are more oxidised (**Figure 3.20**). This could be interpreted as the normal garnets being unaffected by the metasomatism that oxidised the other samples. However, the normal garnets are likely metasomatic due to their high-Cr harzburgitic origins, Zr-Y concentrations and the $\delta^{51}V$ offset between whole-rock and garnet-clinopyroxene. It is therefore more convincing that both metasomatic agents have different redox conditions. Creighton *et al.* (2010) suggested the LREE-rich agent that spanned both the shallow, depleted, and deep, enriched lithospheric layers variably oxidised all xenoliths. Whereas the HREE-rich agent is believed to have variably interacted with the deep, enriched lithospheric layer, and mostly interacted with the normal garnet xenoliths. Since the normal garnets tend to be more reduced than the other garnet groups, and many sit close to the calculated unmetasomatised depth- fO_2 profile (**Figure 3.20**), the HREE-rich agent is suggested to have been reducing (Creighton *et al.* 2010). Although, since almost half of the normal garnets are more oxidised than the calculated unmetasomatised profile, the potentially reducing, HREE-rich agent probably varied in strength or fO_2 .

Mineral separate $\delta^{51}V$ data from this study only includes normal and slightly sinusoidal samples. Therefore, although measurements of $\delta^{51}V$ in metasomatic phases do not span all the garnet groups and degrees of metasomatic involvement, the $\delta^{51}V$ data does span samples attributed to both the LREE- and HREE-rich agents.

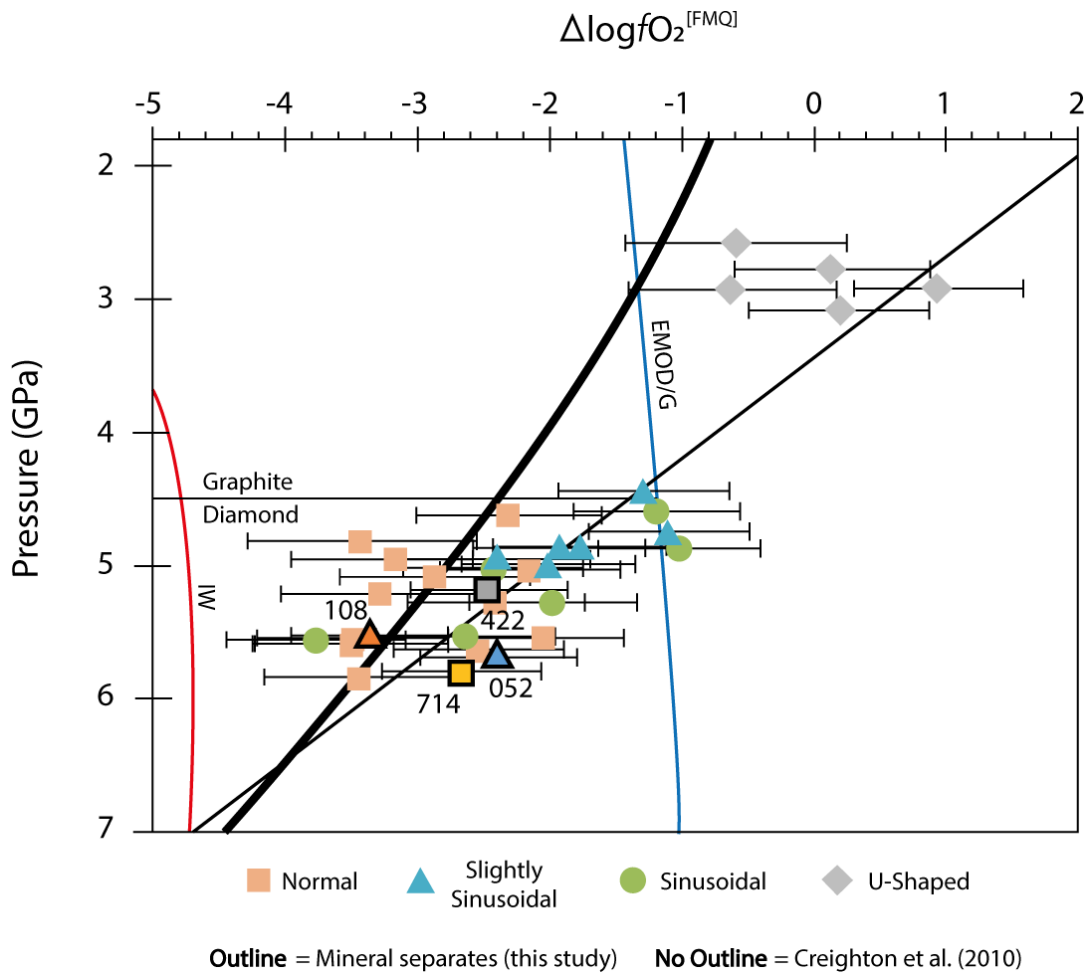


Figure 3.20: Pressure- $\Delta\log f_{O_2}^{[FMQ]}$ profile adapted from Creighton et al. (2010) and including samples from this study with mineral separate $\delta^{51}\text{V}$ data. The iron-wüstite (IW) (red line) and enstatite-magnesite-olivine-diamond/graphite (EMOD/G) (blue line) oxygen buffers are shown, as is the graphite/diamond transition. The thick black curve represents the pressure- f_{O_2} trend calculated for pre-metasomatic garnet lherzolites (Frost & McCammon 2008) and the thin black line is the linear regression through the samples Creighton et al. (2010) suggest show evidence of fluid metasomatism (U-shaped, sinusoidal and slightly sinusoidal). The colours of the points from this study correspond to the colours used in previous figures. Garnets from samples 052 and 108 are classified as slightly sinusoidal and garnets from samples 422 and 714 normal.

3.4.5.1. The effects of metasomatism on $\delta^{51}\text{V}$

To relate a metasomatic mechanism to light $\delta^{51}\text{V}$ signatures in the metasomatic garnet and clinopyroxene, we need to consider the mechanism of stable isotope fractionation. The two main methods of stable isotope fractionation are kinetic and equilibrium fractionation. Kinetic fractionation via diffusion has been previously invoked to explain metasomatic light $\delta^{56}\text{Fe}$ variations in mantle rocks (e.g. Weyer & Ionov 2007; Poitrasson et al. 2013). However, this is disputed due to the strong influence of coordination environment on isotope fractionation (e.g. Dauphas et al. 2014).

Unfortunately, since data on V diffusivity under mantle conditions is lacking, it is hard to comment on the feasibility of kinetic versus equilibrium fractionation mechanisms in the origin of light garnet-clinopyroxene $\delta^{51}\text{V}$ signatures. The Diavik garnets lack zonation, which could imply minimal V diffusion from the metasomatic agent. However, no zonation could also arise from extensive diffusion and complete overprinting. Since the coordination of V is the same in garnet-clinopyroxene-olivine-orthopyroxene, complete V overprinting by metasomatism should result in coordination-controlled $\delta^{51}\text{V}$ fractionation being uniform across those phases. Whilst V oxidation states may differ between garnet-clinopyroxene-olivine-orthopyroxene, (Prytulak *et al.* 2017; Sossi *et al.* 2018a; Novella *et al.* 2020) suggest that oxidation state effects on $\delta^{51}\text{V}$ are subtle (section 1.3.1), and Diavik whole-rock $\delta^{51}\text{V}$ measurements can only be mass balanced by assuming a large isotopic disequilibrium between garnet-clinopyroxene and olivine-orthopyroxene. It is therefore unlikely that the light isotopic signatures of the garnet and clinopyroxene were acquired via diffusion after crystallisation.

Equilibrium fractionation based on differences in oxidation state and coordination is largely agreed to be the main cause of equilibrium stable isotope fractionation in the mantle, where temperatures are uniformly high. The interplay of these two controls has been a key theme throughout this chapter. The two main scenarios for how metasomatism could affect $\delta^{51}\text{V}$ in the Diavik xenoliths are: (1) no isotope fractionation between the metasomatic agent(s) and garnet-clinopyroxene occurs, (2) isotope fractionation occurs due to different coordination of V in garnet-clinopyroxene and the metasomatic agent(s). In scenario one, with all else being equal, the garnet-clinopyroxene $\delta^{51}\text{V}$ would directly reflect that of the metasomatic agents. If the two metasomatic agents have different redox conditions, the oxidation state control on stable isotopes would dictate that the samples most affected by the more reducing agent should exhibit the lightest $\delta^{51}\text{V}$ signatures in the metasomatic phases, and vice versa. In scenario two, the $\delta^{51}\text{V}$ of garnet-clinopyroxene does not directly reflect that of the metasomatic agent(s). To fractionate garnet and clinopyroxene to lighter $\delta^{51}\text{V}$ signatures due to coordination differences, the agent would need V in a lower coordination than garnet and clinopyroxene. To determine if the Diavik lithospheric mantle experienced coordination-controlled $\delta^{51}\text{V}$ fractionation or whether garnet-clinopyroxene $\delta^{51}\text{V}$ reflects the $\delta^{51}\text{V}$ signature of the dominant metasomatic agent, ideally the coordination of V within the metasomatic agents would be constrained. However, there is limited data available on V coordination in metasomatic agents, and metasomatic agents referenced in the geological literature are extremely varied, exhibiting a wide variety of compositions. This presents a number of options to explore, including aqueous fluids, CO_2 -bearing fluids, carbonatitic melts, and silicate melts (Poitrasson *et al.*

2013). Therefore, to narrow down the metasomatic agent candidates, their nature also needs to be considered.

a) LREE-rich agent:

As discussed in section 3.2.3, the Diavik xenoliths are thought to have experienced a metasomatic enrichment that penetrated both the shallow, depleted lithospheric layer and the deep, enriched lithospheric layer. Metasomatism is thought to have created the U-shaped, sinusoidal and slightly sinusoidal garnet REE patterns which show enrichment in LREEs and MREEs relative to depleted mantle garnets. Partitioning calculations based on garnet being a metasomatic phase, require a metasomatic agent with a high LREE/HREE ratio to create sinusoidal garnet REE patterns (e.g. O'Reilly & Griffin 2013). Due to the low compatibility of LREEs in garnet, such an agent should result in only a small amount of LREEs being incorporated into garnet. Despite the higher compatibility of HREEs in garnet, their low concentrations in the agent should mean again only low concentrations in the resultant garnet structure. The highest concentrations should therefore be in the MREEs. Previously suggested agents include COH-rich fluids (e.g. Stachel *et al.* 1998; Creighton *et al.* 2010), but Zr-Y data suggests the agent could perhaps be a borderline melt.

Carbonatitic Melts:

Carbonatitic melts are one of the most commonly invoked LREE-enriched metasomatic agents. They have unique physical properties, such as very low viscosities that allow them to easily penetrate mantle grain-boundaries, and very high solubilities of elements rare in silicate melts that allow for extensive chemical exchange (Jones *et al.* 2013). Such properties make them efficient metasomatic agents.

The coordination of V in carbonatitic melts depends on their structure, which is very different to silicate melts. Unlike silica polyhedra, the dominant carbonate ionic group cannot polymerise, and therefore cannot form network structures (Genge *et al.* 1995). Instead, a randomised framework created by the bridging of carbonate groups by ionically interacting metal ions is thought to be the basis for carbonatite melt structure (Genge *et al.* 1995). Unfortunately, due to their rare occurrence, and the difficulty associated with their analysis due to technical issues and the very limited range of glasses available (Genge *et al.* 1995), there is no data on the coordination of V. However, estimations exist for the most commonly referenced metal ions in carbonatite complexation, Mg^{2+} , Ca^{2+} , Fe^{2+} , Sr^{2+} and Ba^{2+} . As can be deduced from the previous list, metal-carbonate complexation is thought to heavily favour divalent cations. Molecular dynamic studies found that most divalent cations in alkaline-earth carbonate liquids adopt similar coordinations –

VI-fold with carbonate ions, and VII to VIII-fold with oxygen (e.g. Vuilleumier *et al.* 2014). However, Mg^{2+} in MgCO_3 -bearing liquids has been found to uniquely and consistently form IV-fold coordination with both carbonate and oxygen ions and is insensitive to bulk composition (Hurt & Wolf 2020).

Under mantle conditions at FMQ – 2 to -3, V is unlikely to exhibit divalence (Sutton *et al.* 2005), and it is therefore uncertain how or if V would be incorporated into such a structure. However, V appears to be unique among other third row transition metals in that it is the only one to preferentially partition into carbonatitic over silicate melts ($D_V^{C/S} = 1.89$ to 3.46 (Guzmics *et al.* 2015) and 0.95 to 2 (Martin *et al.* 2013)). Vanadium may therefore have a unique characteristic that allows it to easily sit within the unusual carbonatite melt structure. Whether the coordination of the V site mimics that of Mg^{2+} , the other divalent cations, or has a completely different coordination is uncertain. Vanadium is closest in ionic radius to Mg of the favoured divalent cations. However, V^{3+} has a strong affinity for VI-fold coordination (Sossi *et al.* 2018) which appears to be the typical coordination of bridging ions with carbon. However, V has a significantly smaller ionic radius in VI-fold coordination than the VI-fold divalent cations (e.g. V^{3+} VI = 0.64 versus Ca^{2+} VI = 1). Unfortunately, until more work is done on the coordination of transition metals in carbonatitic melts, it is uncertain how V would be coordinated.

Carbonatitic melts are defined by their high carbonate contents (>50 wt%) and are highly LREE-enriched with high Zr/Hf and low Ti/Eu ratios (Nelson *et al.* 1988). Such characteristics are consistent with the high LREE/HREE ratio required to form sinusoidal garnets. In addition, Mg-rich carbonatite-like fluids with similar trace element patterns have been found as inclusions in coated diamonds from kimberlites in the Slave craton (e.g. Klein-BenDavid *et al.* 2007; Araújo *et al.* 2009). However, **Figure 3.21** shows that garnet Ti/Eu ratios are probably too high in most of the Diavik xenoliths to have been metasomatised by a carbonatitic melt. It could be argued that the higher Ti/Eu signatures are due to the HREE-enrichment event that caused additional metasomatism in the deep, enriched layer. In general, the U-shaped and sinusoidal garnets have the lowest Ti/Eu ratios. Since these samples are thought to have been unaffected by the HREE-rich agent, this is consistent with the above idea. In addition, the garnets with the highest Ti/Eu are mostly the normal garnets (**Figure 3.21**) which are thought to have interacted dominantly with the HREE-rich agent. It therefore seems possible that the elevated garnet Ti/Eu is due to the involvement of the second agent, and does not contradict the LREE-rich agent being a carbonatitic melt.

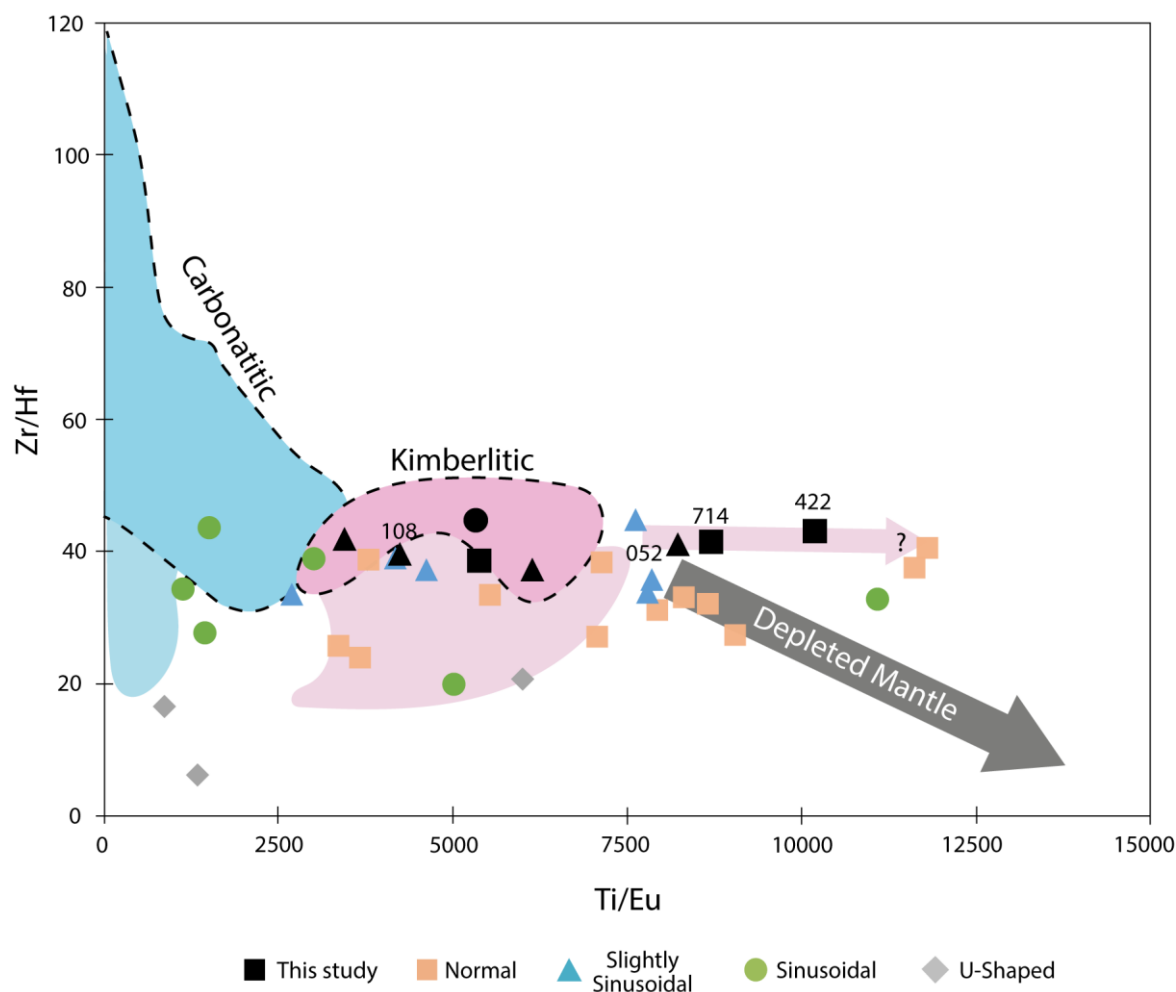


Figure 3.21: Zr/Hf versus Ti/Eu plot adapted from Shu & Brey (2015). These ratios are indicative of carbonatite (blue field) and kimberlite (pink field) metasomatism (Yaxley *et al.* 1991; Sweeney *et al.* 1992; Rudnick *et al.* 1993). The black dotted outlined areas are where samples from Shu & Brey (2015) plot, and the non-outlined fields represent peridotitic garnet diamond inclusion data from around the world (Shu & Brey 2015). Some points have higher Ti/Eu data than the extent of the kimberlite field. This field may extend to high ratios than suggested in Shu & Brey (2015).

Fluids:

Mantle fluids can be extremely variable in composition. Metasomatic mantle fluids most commonly discussed in the literature are COH-fluids whose composition and speciation is heavily controlled by fO_2 (e.g. French 1966; Matveev *et al.* 1997). Reducing conditions are more commonly associated with CH_4 - H_2 compositions and oxidising conditions with CO_2 - H_2O compositions. However, there appears to be no previous work on the coordination of V in mantle fluids. Given the relatively structureless nature of fluids compared to melts, it could be postulated that the coordination of V is high.

Stachel *et al.* (1998) and Creighton *et al.* (2010) proposed a COH-fluid as a candidate for the LREE-rich agent. However, COH-fluids cannot form grain boundary films in the uppermost mantle due to

a high wetting angle with olivine grain boundaries, unlike carbonate and silicate melts (Watson *et al.* 1990). Instead, they tend to form isolated pores at grain boundaries (Watson *et al.* 1990). It was argued in section 4.1.2a that incompatible trace element mass imbalances for LREEs and FMEs suggest metasomatism caused a concentration of LREEs and FMEs along grain boundaries in the Diavik xenoliths. Given the concentration of LREEs, it seems reasonable that the agent most responsible for this concentration was the LREE-rich agent. It therefore seems unlikely that the LREE-rich agent could be a COH-fluid that cannot form grain boundary films.

b) HREE-enrichment:

A second metasomatic agent was discussed in section 4.1.2. This agent is thought to have variably metasomatised the deep, enriched lithospheric layer, and created the normal garnet REE patterns (Creighton *et al.* 2010). Normal garnets display a convex-upwards REE pattern that typically lacks the sinuosity seen in the other patterns. Compared to depleted mantle garnets, they are still enriched in LREEs and MREEs like the sinusoidal and slightly sinusoidal garnets, but they are more strongly enriched in HREEs. However, a few of the normal garnet samples also have higher LREE concentrations than the sinusoidal and slightly sinusoidal garnets. A combination of Zr-Y data and evidence from Creighton *et al.* (2010) suggests the metasomatic agent responsible for these patterns is a high-T melt, enriched in HFSEs, that has not significantly fractionated LREEs from HREEs. Evidence from Creighton *et al.* (2010) suggests this agent only affected the normal garnets, and perhaps the slightly sinusoidal garnets. It is also thought to have been minor, but variable in its extent compared to the LREE-rich agent. We will now consider the different metasomatic melts that could have acted as this agent.

Carbonatitic Melts:

The extreme LREE-rich composition of carbonatitic melts is incompatible with the criteria for this metasomatic agent.

Silicate Melts:

Sossi *et al.* (2018) used experimental hydrous granitic melts to explore the coordination of V in silicate melts. Despite the melt composition in this study being more silicic and the experiment being conducted at lower pressures (0.5 GPa) than expected for deep, mantle-derived silicate melts, it is at present the only work that has observed the coordination of V in a silicate melt. Sossi *et al.* (2018) determined that the typical coordination of V in silicate melts is between IV and VI-fold depending on oxidation state. V^{3+} favours VI-fold coordination, V^{4+} V-fold and V^{5+} IV to V-fold. Under similar redox conditions as the Diavik xenoliths (ie. FMQ - 2 to FMQ - 3) $V^{4+} > V^{3+} > V^{5+}$

in silicate melts (Sossi *et al.* 2018). The dominant coordination of V in the melt used in Sossi *et al.* (2018) at FMQ -2 to -3 is therefore probably around V-fold. Vanadium coordination is therefore likely lower in a silicate melt-based metasomatic agent than in garnet-clinopyroxene. Therefore, metasomatism via a silicate melt could potentially cause fractionation of V isotopes to lighter $\delta^{51}\text{V}$ in garnet and clinopyroxene.

The Diavik xenoliths are associated with kimberlite pipe A154-N, and therefore a kimberlitic melt should be our first port of call when exploring potential silicate melt agents. Whole-rock analyses of kimberlites from Lac de Gras are LREE-enriched (Kjarsgaard *et al.* 2009) (**Figure 3.17**). Even though kimberlites are considered hybrid rocks that experience significant chemical changes between source and crust (e.g. Soltys *et al.* 2018), it seems unlikely that a primary kimberlitic melt would be HREE-enriched when crystallised kimberlites are the opposite. Unfortunately, no recent studies on reconstructing primary kimberlite magma compositions focus on trace elements, so it is not possible at present to know.

What is the nature of, and how is V co-ordinated in the metasomatic agents?

We have the strongest constraints on the coordination of V in the reducing, HREE-rich agent. Evidence from Zr-Y data suggests the HREE-rich agent is a melt, and the melt is thought to be silicate in composition. Since silicate melts typically have V in a lower coordination than in garnet-clinopyroxene (Sossi *et al.* 2018), it is assumed that this is also the case for the HREE-rich agent. The most likely candidate for the LREE-rich agent is a low viscosity LREE-rich carbonatitic melt. However, the coordination of V in the LREE-rich agent is uncertain due to a lack of data on transition metal coordination in carbonatitic melts.

How could metasomatism create light $\delta^{51}\text{V}$ in garnet and clinopyroxene?

To comment on how light $\delta^{51}\text{V}$ signatures were created in garnet and clinopyroxene, the metasomatic agent with the largest effect on V needs to be determined. Since the LREE-rich agent is thought to have been the primary agent in concentrating LREEs and FMEs at grain boundaries, it likely had an affinity for low compatibility and fluid mobile elements. Vanadium, however, is only moderately incompatible and immobile; **Fig. 3.13** shows that the compatibility of Sc (the closest in behaviour to V) in fluids and supercritical fluids is very low. It is therefore questionable whether the LREE-rich metasomatic agent could have an impact on garnet-clinopyroxene V contents. We will therefore assume that the $\delta^{51}\text{V}$ signatures in garnet and clinopyroxene are largely attributed to the HREE-rich metasomatic agent. Unfortunately, this study's mineral separate data only includes samples with normal and slightly sinusoidal garnets due to sample availability. Both groups are argued to have been affected by the HREE-rich agent, but the samples with sinusoidal and U-shaped

garnets are not. In the future, mineral separates from these other garnet groups should be obtained and measured for $\delta^{51}\text{V}$ since they may significantly differ from that of the normal and slightly sinusoidal garnet samples.

Based on the assumption that the measured garnet-clinopyroxene $\delta^{51}\text{V}$ signatures are predominantly attributed to the HREE-rich agent, and that that agent is a silicate melt, of the two scenarios outlined at the start of this section, scenario two is most likely. Given that scenario two is that isotope fractionation occurs due to different coordination of V in garnet-clinopyroxene and the metasomatic agent(s), garnet-clinopyroxene $\delta^{51}\text{V}$ can be largely attributed to coordination-controlled isotope fractionation. Such a process could work as follows. Garnet and clinopyroxene contain V in VI-fold coordination. If the melt had IV-fold co-ordinated V, then ^{50}V should be preferentially transferred to the garnet and clinopyroxene during metasomatism, creating light $\delta^{51}\text{V}$ signatures. However, another variable to consider is the differing compatibilities of the oxidation states of V in silicate minerals. V^{3+} is far more compatible than V^{4+} and V^{5+} in silicate minerals due to its affinity for VI-fold coordination (e.g. Nielsen *et al.* 1994; Canil 1999; Toplis & Corgne 2002; Righter *et al.* 2006; Mallmann & O'Neill 2009, 2013). This could encourage the preferential incorporation of ^{50}V into garnet-clinopyroxene, furthering fractionation to light $\delta^{51}\text{V}$.

However, the potential effects of $f\text{O}_2$ during metasomatism also need to be considered. In a scenario in which coordination and compatibility are the only controls on the isotope fractionation, and the metasomatic phases were metasomatised by a single, homogeneous metasomatic melt, the metasomatic phases should have the same $\delta^{51}\text{V}$ signature across the suite. However, section 4.3 highlights that the Diavik metasomatic phases have variable $\delta^{51}\text{V}$ signatures. There must therefore be another control on isotope fractionation that created this variation. Given the positive trends between $\delta^{51}\text{V}$ and $f\text{O}_2$ discussed in section 4.3, $f\text{O}_2$ is the most probable contender. Creighton *et al.* (2010) suggested that the HREE-rich agent was reducing, and according to stable isotope theory, under increasingly reducing conditions, ^{50}V will be increasingly incorporated into garnet-clinopyroxene over ^{51}V . This should further the fractionation to light $\delta^{51}\text{V}$ in garnet and clinopyroxene. The variation in $\delta^{51}\text{V}$ could either be related to the HREE-rich agent having variable $f\text{O}_2$, different durations of interaction with the HREE-rich agent, or a combination of both. However, it must also be noted that the xenoliths with normal and slightly sinusoidal garnets were also variably metasomatised by the LREE-rich agent. Whilst the influence of this agent on V is believed to only be minor, it could have partially contributed to the variation in $\delta^{51}\text{V}$.

The above mechanism suggests that the first order control on V isotope fractionation during metasomatism in the Diavik lithospheric mantle is coordination environment. However, the

compatibility of the different oxidation states of V and fO_2 are secondary controls. Coordination-controlled fractionation likely created the light $\delta^{51}V$ signatures in the metasomatic phases, but fO_2 probably shaped the variation in $\delta^{51}V$ observed between metasomatic phases from different samples.

3.5. Conclusions

1. Beware of using small whole-rock powder sample sizes for the isotope analysis of coarse-grained rocks, since there may be heterogeneity between different digestions of the same sample.
2. There is no equilibrium inter-mineral fractionation factor between garnet and clinopyroxene at mantle conditions for V stable isotopes.
3. Metasomatic mineral phase (garnet and clinopyroxene) $\delta^{51}V$ roughly positively varies with $\Delta \log fO_2^{[FMQ]}$, suggesting that fO_2 and V isotope fractionation may be related. A positive trend agrees with the theory of stable isotope fractionation that suggests that heavier isotopes are associated with higher oxidation states and lower coordination.
4. Metasomatism may have a strong effect on $\delta^{51}V$. The effect of metasomatism on V isotope fractionation must therefore be considered in future work.
5. Metasomatism can create light V isotope signatures relative to BSE. The Diavik xenoliths suggest that the V isotope fractionation is coordination-controlled as garnet and clinopyroxene crystallised during metasomatism. However, fO_2 is likely a secondary control and created the $\delta^{51}V$ variation observed between metasomatic phases from different samples.
6. Metasomatism means that the Diavik xenoliths likely do not represent primitive mantle, and therefore should not be used to create a more representative BSE estimate that includes deeper mantle rocks.
7. The successful reconstruction of the whole-rock $\delta^{51}V$ compositions using the current BSE estimate and assuming isotopic disequilibria between garnet/clinopyroxene and ol/orthopyroxene supports the current BSE estimate. However, work should continue to include deeper mantle rocks to review the current BSE more thoroughly.

References

- Andersen, T., O'Reilly, S.Y. & Griffin, W.L. 1984. The trapped fluid phase in upper mantle xenoliths from Victoria, Australia: implications for mantle metasomatism. *Contributions to Mineralogy and Petrology*, **88**, 72–85, <https://doi.org/10.1007/BF00371413>.
- Araújo, D.P., Griffin, W.L. & O'Reilly, S.Y. 2009. Mantle melts, metasomatism and diamond formation: Insights from melt inclusions in xenoliths from Diavik, Slave Craton. *Lithos*, **112**,

- 675–682, <https://doi.org/10.1016/j.lithos.2009.06.005>.
- Aulbach, S., Griffin, W.L., Pearson, N.J. & O'Reilly, S.Y. 2013. Nature and timing of metasomatism in the stratified mantle lithosphere beneath the central Slave craton (Canada). *Chemical Geology*, **352**, 153–169, <https://doi.org/10.1016/j.chemgeo.2013.05.037>.
- Beard, B.L. & Johnson, C.M. 2004. Inter-mineral Fe isotope variations in mantle-derived rocks and implications for the Fe geochemical cycle. *Geochimica et Cosmochimica Acta*, **68**, 4727–4743, <https://doi.org/10.1016/j.gca.2004.04.023>.
- Bigeleisen, J. & Mayer, G.M. 1947. Calculation of Equilibrium Constants for Isotopic Exchange Reactions. *Journal of Chemical Physics*, **15**, 261–267.
- Bryan, D. & Bonner, R. 2003. The Diavik Diamond Mine , Lac De Gras , Northwest Territories , Canada, In: Kjarsgaard, B.A. (ed) *VIIIth International Kimberlite Conference, Slave Province and Northern Alberta Field Trip Guidebook*, 61–65.
- Canil, D. 1999. Vanadium partitioning between orthopyroxene, spinel and silicate melt and the redox states of mantle source regions for primary magmas. *Geochimica et Cosmochimica Acta*, **63**, 557–572, [https://doi.org/10.1016/S0016-7037\(98\)00287-7](https://doi.org/10.1016/S0016-7037(98)00287-7).
- Creighton, S., Stachel, T., Eichenberg, D. & Luth, R.W. 2010. Oxidation state of the lithospheric mantle beneath Diavik diamond mine, central Slave craton, NWT, Canada. *Contributions to Mineralogy and Petrology*, **159**, 645–657, <https://doi.org/10.1007/s00410-009-0446-x>.
- Dauphas, N., Roskosz, M., Alp E., Neuville D., Hu M., Sio C., Tissot F., Zhao J., Tissandier L., Me'dard E. & Cordier C. 2014. Magma redox and structural controls on iron isotope variations in Earth's mantle and crust. *Earth and Planetary Science Letters*, **398**, 127–140, <https://doi.org/10.1016/j.epsl.2014.04.033>.
- Dautria, J.M., Dupuy, C., Takherist, D. & Dostal, J. 1992. Carbonate metasomatism in the lithospheric mantle: peridotitic xenoliths from a melilititic district of the Sahara basin. *Contributions to Mineralogy and Petrology*, **111**, 37–52, <https://doi.org/10.1007/BF00296576>.
- Dawson, J.B. 1984. Contrasting types of upper mantle metasomatism. In: Kornprobst, J. (Ed.) *Kimberlites II: the mantle and crust-mantle relationships*, Elsevier, Amsterdam, 289–294, <https://doi.org/10.1016/B978-0-444-42274-3.50030-5>.
- Ding, X., Helz, R.T., Qi, Y. & Huang, F. 2020. Vanadium isotope fractionation during differentiation of Kilauea Iki lava lake, Hawaii. *Geochimica et Cosmochimica Acta*, **289**, 114–129, <https://doi.org/10.1016/j.gca.2020.08.023>.
- French, B.M. 1966. Some geological implications of equilibrium between graphite and a C-H-O gas phase at high temperatures and pressures. *Reviews of Geophysics*, **4**, 223–253, <https://doi.org/10.1029/RG004i002p00223>.
- Frost, D.J. & McCammon, C.A. 2008. The Redox State of Earth's Mantle. *Annual Review of Earth and Planetary Sciences*, **36**, 389–420, <https://doi.org/10.1146/annurev.earth.36.031207.124322>.
- Genge, M.J., Jones, A.P. & Price, G.D. 1995. An infrared and Raman study of carbonate glasses: implications for the structure of carbonatite magmas. *Geochimica et Cosmochimica Acta*, **59**, 927–937, [https://doi.org/10.1016/0016-7037\(95\)00010-0](https://doi.org/10.1016/0016-7037(95)00010-0).
- Graham, I., Burgess, J.L., Bryan, D., Ravenscroft, P.J., Thomas, E., Doyle, B.J., Hopkins, R. & Armstrong, K.A. 1998. The Diavik kimberlites-Lac de Gras, Northwest Territories, Canada. *International Kimberlite Conference: Extended Abstracts*, **7**, 259–261.
- Griffin, W.L. & Ryan, C.G. 1995. Trace elements in indicator minerals: area selection and target

- evaluation in diamond exploration. *Journal of Geochemical Exploration*, **53**, 311–337, [https://doi.org/10.1016/0375-6742\(94\)00015-4](https://doi.org/10.1016/0375-6742(94)00015-4).
- Griffin, W.L., Smith, D., Ryan, C.G., O'Reilly, S.Y. & Win, T.T. 1996. Trace-element zoning in mantle minerals: metasomatism and thermal events in the upper mantle. *The Canadian Mineralogist*, **34**, 1179–1193.
- Griffin, W.L., Shee, S.R., Ryan, C.G., Win, T.T. & Wyatt, B.A. 1999a. Harzburgite to lherzolite and back again : metasomatic processes in ultramafic xenoliths from the Wesselton. *Contrib Mineral Petrol*, **134**, 232–250.
- Griffin, W.L., Doyle, B.J., et al. 1999b. Layered mantle lithosphere in the Lac de Gras area, Slave craton: Composition, structure and origin. *Journal of Petrology*, **40**, 705–727, <https://doi.org/10.1093/petroj/40.5.705>.
- Gurney, J.J. 1984. A correlation between garnets and diamonds. In: Glover, J.E. & Harris, P.G. (Eds.), *Kimberlite occurrence and origins: a Basis for Conceptual Models in Exploration. Geology Department and University Extension, University of Western Australia*, **8**, 143–166.
- Guzmics, T., Zajacz, Z., Mitchell, R.H., Szabó, C. & Wälle, M. 2015. The role of liquid–liquid immiscibility and crystal fractionation in the genesis of carbonatite magmas: insights from Kerimasi melt inclusions. *Contributions to Mineralogy and Petrology*, **169**, 17, <https://doi.org/10.1007/s00410-014-1093-4>.
- Hanger, B.J., Yaxley, G.M., Berry, A.J. & Kamenetsky, V.S. 2015. Relationships between oxygen fugacity and metasomatism in the Kaapvaal subcratonic mantle, represented by garnet peridotite xenoliths in the Wesselton kimberlite, South Africa. *Lithos*, **212**, 443–452, <https://doi.org/10.1016/j.lithos.2014.09.030>.
- Harte, B. 1983. Mantle peridotites and processes: the kimberlite sample. In: Hawkesworth, C.J., Norry, M.J. (Eds.) *Continental basalts and their xenoliths*, Shiva, Nantwich, 46–91.
- Hopkins, S.S., Prytulak, J., Barling, J., Russell, S.S., Coles, B.J. & Halliday, A.N. 2019. The vanadium isotopic composition of lunar basalts. *Earth and Planetary Science Letters*, **511**, 12–24, <https://doi.org/10.1016/j.epsl.2019.01.008>.
- Hurt, S.M. & Wolf, A.S. 2020. Anomalous structure of MgCO₃ liquid and the buoyancy of carbonatite melts. *Earth and Planetary Science Letters*, **531**, 115927, <https://doi.org/10.1016/j.epsl.2019.115927>.
- Ionov, D.A., Dupuy, C., O'Reilly, S.Y., Kopylova, M.G. & Genshaft, Y.S. 1993. Carbonated peridotite xenoliths from Spitsbergen: implications for trace element signature of mantle carbonate metasomatism. *Earth and Planetary Science Letters*, **119**, 283–297, [https://doi.org/10.1016/0012-821X\(93\)90139-Z](https://doi.org/10.1016/0012-821X(93)90139-Z).
- Ionov, D. 2004. Chemical Variations in Peridotite Xenoliths from Vitim, Siberia: Inferences for REE and Hf Behaviour in the Garnet-Facies Upper Mantle. *Journal of Petrology*, **45**, 343–367, <https://doi.org/10.1093/petrology/egg090>.
- Jochum, K.P., Weis, U., Schwager, B., Stoll, B., Wilson, S.A., Haug, G.H., Andreae, M.O. & Enzweiler, J. 2016. Reference Values Following ISO Guidelines for Frequently Requested Rock Reference Materials. *Geostandards and Geoanalytical Research*, **40**, 333–350, <https://doi.org/10.1111/j.1751-908X.2015.00392.x>.
- Jones, A.G., Lezaeta, P., Ferguson, I.J., Chave, A.D., Evans, R.L., Garcia, X. & Spratt, J. 2003. The electrical structure of the Slave craton. *Lithos*, **71**, 505–527, <https://doi.org/10.1016/j.lithos>.

2003.08.001.

- Jones, A.P., Genge, M. & Carmody, L. 2013. Carbonate melts and carbonatites. *Reviews in Mineralogy and Geochemistry*, **75**, 289–322, <https://doi.org/10.2138/rmg.2013.75.10>.
- Kessel, R., Schmidt, M.W., Ulmer, P. & Pettke, T. 2005. Trace element signature of subduction-zone fluids, melts and supercritical liquids at 120–180 km depth. *Nature*, **437**, 724–727, <https://doi.org/10.1038/nature03971>.
- Kjarsgaard, B.A., Pearson, D.G., Tappe, S., Nowell, G.M. & Dowall, D.P. 2009. Geochemistry of hypabyssal kimberlites from Lac de Gras, Canada: Comparisons to a global database and applications to the parent magma problem. *Lithos*, **112**, 236–248, <https://doi.org/10.1016/j.lithos.2009.06.001>.
- Klein-BenDavid, O., Izraeli, E.S., Hauri, E. & Navon, O. 2007. Fluid inclusions in diamonds from the Diavik mine, Canada and the evolution of diamond-forming fluids. *Geochimica et Cosmochimica Acta*, **71**, 723–744, <https://doi.org/10.1016/j.gca.2006.10.008>.
- Korzhinskii, D.A. 1965. The theory of systems with perfectly mobile components and processes of mineral formation. *American Journal of Science*, **263**, 193–205, <https://doi.org/10.2475/ajs.263.3.193>.
- Mallmann, G. & O'Neill, H.S.C. 2009. The crystal/melt partitioning of V during mantle melting as a function of oxygen fugacity compared with some other elements (Al, P, Ca, Sc, Ti, Cr, Fe, Ga, Y, Zr and Nb). *Journal of Petrology*, **50**, 1765–1794, <https://doi.org/10.1093/petrology/egp053>.
- Mallmann, G. & O'Neill, H.S.C. 2013. Calibration of an empirical thermometer and oxybarometer based on the partitioning of sc, Y and V between olivine and silicate melt. *Journal of Petrology*, **54**, 933–949, <https://doi.org/10.1093/petrology/egt001>.
- Martin, L.H.J., Schmidt, M.W., Mattsson, H.B. & Guenther, D. 2013. Element Partitioning between Immiscible Carbonatite and Silicate Melts for Dry and H₂O-bearing Systems at 1–3 gpa. *Journal of Petrology*, **54**, 2301–2338, <https://doi.org/10.1093/petrology/egt048>.
- Matveev, S., Ballhaus, C., Fricke, K., Truckenbrodt, J. & Ziegenbein, D. 1997. Volatiles in the Earth's mantle: I. Synthesis of CHO fluids at 1273 K and 2.4 GPa. *Geochimica et Cosmochimica Acta*, **61**, 3081–3088, [https://doi.org/10.1016/S0016-7037\(97\)00142-7](https://doi.org/10.1016/S0016-7037(97)00142-7).
- McDonough, W.F. & Sun, S. -s. 1995. The composition of the Earth. *Chemical Geology*, **120**, 223–253.
- Menzies, M.A., Rogers, N., Tindle, A. & Hawkesworth, C.J. 1987. Metasomatic and enrichment processes in lithospheric peridotites, an effect of asthenosphere-lithosphere interaction. In: Menzies, M.A. & Hawkesworth, C.J. (Eds.) *Mantle Metasomatism*. London, UK: Academic Press, pp. 313–361.
- Menzies, M.A. & Wass, S.Y. 1983. CO₂- and LREE-rich mantle below eastern Australia: a REE and isotopic study of alkaline magmas and apatite-rich mantle xenoliths from the Southern Highlands Province, Australia. *Earth and Planetary Science Letters*, **65**, 287–302, [https://doi.org/10.1016/0012-821X\(83\)90167-X](https://doi.org/10.1016/0012-821X(83)90167-X).
- Nelson, D.R., Chivas, A.R., Chappell, B.W. & McCulloch, M.T. 1988. Geochemical and isotopic systematics in carbonatites and implications for the evolution of ocean-island sources. *Geochimica et Cosmochimica Acta*, **52**, 1–17, [https://doi.org/10.1016/0016-7037\(88\)90051-8](https://doi.org/10.1016/0016-7037(88)90051-8).

- Nielsen, R.L., Forsythe, L.M., Gallahan, W.E. & Fisk, M.R. 1994. Major- and trace-element magnetite-melt equilibria. *Chemical Geology*, **117**, 167–191, [https://doi.org/10.1016/0009-2541\(94\)90127-9](https://doi.org/10.1016/0009-2541(94)90127-9).
- Nielsen, S.G., Prytulak, J. & Halliday, A.N. 2011. Determination of Precise and Accurate 51V/50V Isotope Ratios by MC-ICP-MS, Part 1: Chemical Separation of Vanadium and Mass Spectrometric Protocols. *Geostandards and Geoanalytical Research*, **35**, 293–306, <https://doi.org/10.1111/j.1751-908X.2011.00106.x>.
- Novella, D., Maclennan, J., Shorttle, O., Prytulak, J. & Murton, B.J. 2020. A multi-proxy investigation of mantle oxygen fugacity along the Reykjanes Ridge. *Earth and Planetary Science Letters*, **531**, 115973, <https://doi.org/10.1016/j.epsl.2019.115973>.
- O'Reilly, S.Y. & Griffin, W.L. 1988. Mantle metasomatism beneath western Victoria, Australia: I. Metasomatic processes in Cr-diopside lherzolites. *Geochimica et Cosmochimica Acta*, **52**, 433–447, [https://doi.org/10.1016/0016-7037\(88\)90099-3](https://doi.org/10.1016/0016-7037(88)90099-3).
- O'Reilly, S.Y. & Griffin, W.L. 2013. Mantle metasomatism. In: Metasomatism and the chemical transformation of rock, Springer, Berlin, Heidelberg, 471–533.
- Poitrasson, F., Delpech, G. & Grégoire, M. 2013. On the iron isotope heterogeneity of lithospheric mantle xenoliths: Implications for mantle metasomatism, the origin of basalts and the iron isotope composition of the Earth. *Contributions to Mineralogy and Petrology*, **165**, 1243–1258, <https://doi.org/10.1007/s00410-013-0856-7>.
- Prytulak, J., Nielsen, S.G. & Halliday, A.N. 2011. Determination of Precise and Accurate 51V/50V Isotope Ratios by Multi-Collector ICP-MS, Part 2: Isotopic Composition of Six Reference Materials plus the Allende Chondrite and Verification Tests. *Geostandards and Geoanalytical Research*, **35**, 307–318, <https://doi.org/10.1111/j.1751-908X.2011.00105.x>.
- Prytulak, J., Nielsen, S.G., Ionov, D.A., Halliday, A.N., Harvey, J., Kelley, K.A., Niu, Y.L., Peate, D.W., Shimizu, K. & Sims, K.W.W. 2013. The stable vanadium isotope composition of the mantle and mafic lavas. *Earth and Planetary Science Letters*, **365**, 177–189, <https://doi.org/10.1016/j.epsl.2013.01.010>.
- Prytulak, J., Sossi, P.A., Halliday, A.N., Plank, T., Savage, P.S. & Woodhead, J.D. 2017. Stable vanadium isotopes as a redox proxy in magmatic systems? *Geochemical Perspectives Letters*, **3**, 75–84, <https://doi.org/10.7185/geochemlet.1708>.
- Qi, Y.H., Wu, F., Ionov, D.A., Puchtel, I.S., Carlson, R.W., Nicklas, R.W., Yu, H-M., Kang, J-T., Li, C-H. & Huang, F. 2019. Vanadium isotope composition of the Bulk Silicate Earth: Constraints from peridotites and komatiites. *Geochimica et Cosmochimica Acta*, **259**, 288–301, <https://doi.org/10.1016/j.gca.2019.06.008>.
- Righter, K., Leeman, W.P. & Hervig, R.L. 2006. Partitioning of Ni, Co and V between spinel-structured oxides and silicate melts: Importance of spinel composition. *Chemical Geology*, **227**, 1–25, <https://doi.org/10.1016/j.chemgeo.2005.05.011>.
- Roden, M.F., Frey, F.A. & Francis, D.M. 1984. An example of consequent mantle metasomatism in peridotite inclusions from Nunivak Island, Alaska. *Journal of Petrology*, **25**, 546–577, <https://doi.org/10.1093/petrology/25.2.546>.
- Roden, M.F. & Murthy, V.R. 1985. Mantle Metasomatism. *Annual Review of Earth and Planetary Sciences*, **13**, 269–296.
- Rudnick, R.L., McDonough, W.F. & Chappell, B.C. 1993. Carbonatite metasomatism in the northern Tanzanian mantle. *Earth and Planetary Science Letters*, **114**, 463–475.

- Schauble, E.A. 2004. Applying Stable Isotope Fractionation Theory to New Systems. *Reviews in Mineralogy & Geochemistry*, **55**, 65–111.
- Schiano, P. & Bourdon, B. 1999. On the preservation of mantle information in ultramafic nodules: glass inclusions within minerals versus interstitial glasses. *Earth and Planetary Science Letters*, **169**, 173–188, [https://doi.org/10.1016/S0012-821X\(99\)00074-6](https://doi.org/10.1016/S0012-821X(99)00074-6).
- Schiano, P., Clocchiatti, R., Shimizu, N., Weis, D. & Mattielli, N. 1994. Cogenetic silica-rich and carbonate-rich melts trapped in mantle minerals in Kerguelen ultramafic xenoliths: Implications for metasomatism in the oceanic upper mantle. *Earth and Planetary Science Letters*, **123**, 167–178, [https://doi.org/10.1016/0012-821X\(94\)90265-8](https://doi.org/10.1016/0012-821X(94)90265-8).
- Schuth, S., Horn, I., Bröske, A., Wolff, P.E. & Weyer, S. 2017. First vanadium isotope analyses of V-rich minerals by femtosecond laser ablation and solution-nebulization MC-ICP-MS. *Ore Geology Reviews*, **81**, 1271–1286, <https://doi.org/10.1016/j.oregeorev.2016.09.028>.
- Shu, Q. & Brey, G.P. 2015. Ancient mantle metasomatism recorded in subcalcic garnet xenocrysts: Temporal links between mantle metasomatism, diamond growth and crustal tectonomagmatism. *Earth and Planetary Science Letters*, **418**, 27–39, <https://doi.org/10.1016/j.epsl.2015.02.038>.
- Soltys, A., Giuliani, A. & Phillips, D. 2018. A new approach to reconstructing the composition and evolution of kimberlite melts: A case study of the archetypal Bultfontein kimberlite (Kimberley, South Africa). *Lithos*, **304**, 1–15, <https://doi.org/10.1016/j.lithos.2018.01.027>.
- Sossi, P.A., Prytulak, J. & O'Neill, H.S.C. 2018. Experimental calibration of vanadium partitioning and stable isotope fractionation between hydrous granitic melt and magnetite at 800 °C and 0.5 GPa. *Contributions to Mineralogy and Petrology*, **173**, 1451–1458, <https://doi.org/10.1007/s00410-018-1451-8>.
- Stachel, T. & Harris, J.W. 1997. Diamond precipitation and mantle metasomatism - evidence from the trace element chemistry of silicate inclusions in diamonds from Akwatia, Ghana. *Contributions to Mineralogy and Petrology*, **129**, 143–154, <https://doi.org/10.1007/s004100050328>.
- Stachel, T., Viljoen, K.S., Brey, G. & Harris, J.W. 1998. Metasomatic processes in Iherzolitic and harzburgitic domains of diamondiferous lithospheric mantle: REE in garnets from xenoliths and inclusions in diamonds. *Earth and Planetary Science Letters*, **159**, 1–12, [https://doi.org/10.1016/S0012-821X\(98\)00064-8](https://doi.org/10.1016/S0012-821X(98)00064-8).
- Stachel, T., Aulbach, S., Brey, G.P., Harris, J.W., Leost, I., Tappert, R. & Viljoen, K.S. 2004. The trace element composition of silicate inclusions in diamonds: A review. *Lithos*, **77**, 1–19, <https://doi.org/10.1016/j.lithos.2004.03.027>.
- Stagno, V., Ojwang, D.O., McCammon, C.A. & Frost, D.J. 2013. The oxidation state of the mantle and the extraction of carbon from Earth's interior. *Nature*, **493**, 84–88, <https://doi.org/10.1038/nature11679>.
- Stalder, R., Ulmer, P., Thompson, A.B. & Günther, D. 2001. High pressure fluids in the system MgO-SiO₂-H₂O under upper mantle conditions. *Contributions to Mineralogy and Petrology*, **140**, 607–618, <https://doi.org/10.1007/s004100000212>.
- Sutton, S.R., Karner, J., Papike, J., Delaney, J.S., Shearer, C., Newville, M., Eng, P., Rivers, M. & Dyar, M.D. 2005. Vanadium K edge XANES of synthetic and natural basaltic glasses and application to microscale oxygen barometry. *Geochimica et Cosmochimica Acta*, **69**, 2333–2348, <https://doi.org/10.1016/j.gca.2004.10.013>.

- Sweeney, R.J., Green, D.H. & Sie, S.H. 1992. Trace and minor element partitioning between garnet and amphibole and carbonatitic melt. *Earth and Planetary Science Letters*, **113**, 1–14, [https://doi.org/10.1016/0012-821X\(92\)90207-C](https://doi.org/10.1016/0012-821X(92)90207-C).
- Thompson, J. B., Jr. 1959, Local equilibrium in metasomatic processes: *Researches in geochemistry: John Wiley and Sons, Inc., New York*, p. 427-457.
- Toplis, M.J. & Corgne, A. 2002. An experimental study of element partitioning between magnetite, clinopyroxene and iron-bearing silicate liquids with particular emphasis on vanadium. *Contributions to Mineralogy and Petrology*, **144**, 22–37, <https://doi.org/10.1007/s00410-002-0382-5>.
- Vuilleumier, R., Seitsonen, A., Sator, N. & Guillot, B. 2014. Structure, equation of state and transport properties of molten calcium carbonate (CaCO₃) by atomistic simulations. *Geochimica et Cosmochimica Acta*, **141**, 547–566, <https://doi.org/10.1016/j.gca.2014.06.037>.
- Watson E.B., Brenan J.M. & Baker D.R. 1990). Distribution of fluids in the continental mantle. In: Menzies M.A. (Ed) Continental mantle. *Oxford Monographs*, **16**, 111–125.
- Weyer, S. & Ionov, D.A. 2007. Partial melting and melt percolation in the mantle: The message from Fe isotopes. *Earth and Planetary Science Letters*, **259**, 119–133, <https://doi.org/10.1016/j.epsl.2007.04.033>.
- Woodland, A.B. & Koch, M. 2003. Variation in oxygen fugacity with depth in the upper mantle beneath the Kaapvaal craton, Southern Africa. *Earth and Planetary Science Letters*, **214**, 295–310, [https://doi.org/10.1016/S0012-821X\(03\)00379-0](https://doi.org/10.1016/S0012-821X(03)00379-0).
- Wu, F., Qi, Y., Yu, H., Tian, S., Hou, Z. & Huang, F. 2016. Vanadium isotope measurement by MC-ICP-MS. *Chemical Geology*, **421**, 17–25, <https://doi.org/10.1016/j.chemgeo.2015.11.027>.
- Wu, F., Qi, Y., Perfit, M.R., Gao, Y., Langmuir, C.H., Wanless, V.D., Yu, H. & Huang, F. 2018. Vanadium isotope compositions of mid-ocean ridge lavas and altered oceanic crust. *Earth and Planetary Science Letters*, **493**, 128–139, <https://doi.org/10.1016/j.epsl.2018.04.009>.
- Xue, Y., Li, C. hui, Qi, Y., Zhang, C., Miao, B. & Huang, F. 2018. The vanadium isotopic composition of L ordinary chondrites. *Acta Geochimica*, **37**, 501–508, <https://doi.org/10.1007/s11631-018-0279-2>.
- Yaxley, G.M., Crawford, A.J. & Green, D.H. 1991. Evidence for carbonatite metasomatism in spinel peridotite xenoliths from western Victoria, Australia. *Earth and Planetary Science Letters*, **107**, 305–317, [https://doi.org/10.1016/0012-821X\(91\)90078-V](https://doi.org/10.1016/0012-821X(91)90078-V).
- Yaxley, G.M., Berry, A.J., Rosenthal, A., Woodland, A.B. & Paterson, D. 2017. Redox preconditioning deep cratonic lithosphere for kimberlite genesis - Evidence from the central Slave Craton. *Scientific Reports*, **7**, 1–10, <https://doi.org/10.1038/s41598-017-00049-3>.
- Zhao, X., Zhang, H., Zhu, X., Tang, S. & Tang, Y. 2010. Iron isotope variations in spinel peridotite xenoliths from North China Craton: Implications for mantle metasomatism. *Contributions to Mineralogy and Petrology*, **160**, 1–14, <https://doi.org/10.1007/s00410-009-0461-y>.

CHAPTER FOUR

The controls on iron isotopic fractionation in IODP Expedition 352 subduction initiation lavas from the Bonin forearc

Abstract

The Fe isotopic composition of arc lavas has been found to be lighter than MORB (e.g. Dauphas *et al.* 2009; Nebel *et al.* 2015; Foden *et al.* 2018; Williams *et al.* 2018). Previous studies have invoked processes such as partial melting, historic melt extraction, and the involvement of subduction-derived fluids, melts and sediments to explain the difference (e.g. Dauphas *et al.* 2009; Nebel *et al.* 2015; Debret *et al.* 2016, 2018, 2020, 2021; Inglis *et al.* 2017; Foden *et al.* 2018; Turner *et al.* 2018; Williams *et al.* 2018). However, there is currently no consensus. This study investigated the Fe isotopic compositions of IODP Expedition 352 fore-arc basalts (FABs) and boninites from the Bonin forearc to determine whether magmatic processes or subduction inputs are more influential in creating the light $\delta^{56}\text{Fe}$ of arc lavas. Expedition 352 lithologies represent a complete *in situ* record of subduction initiation in a seafloor spreading setting. The FABs are anhydrous MORB-like rocks that show little evidence of subduction input, whereas the later boninites show clear evidence of subduction inputs (Li *et al.* 2019). Therefore, a comparison of these two different lithologies that are related in both space and time allows the effects of different early stage subduction processes on Fe isotopes to be examined in detail.

There is a statistically significant isotopic difference between Expedition 352 FAB and boninite $\delta^{56}\text{Fe}$ ($\Delta^{56}\text{Fe}_{\text{FAB-Bon}}$ average = 0.035 ‰). The boninites are isotopically lighter than the FABs and similar to global arc lavas. Different redox conditions and the addition of subducted sediments or slab melts are shown to be unlikely causes of light $\delta^{56}\text{Fe}$ of boninites and arc lavas. However, historic source depletion, fractional crystallisation and the addition of slab-derived fluids have the potential to create a FAB-boninite $\delta^{56}\text{Fe}$ difference in the observed direction, but there is limited geochemical evidence to support any of these mechanisms. Iron isotopic melt modelling has shown that source depletion creates Fe isotope fractionation in the correct direction to explain the light $\delta^{56}\text{Fe}$ of arc lavas, and that accumulated fractional non-modal melting of a source slightly isotopically lighter than DMM ($\delta^{56}\text{Fe}$ = 0 ‰ versus 0.026 ‰) can reproduce the observed FAB and boninite average $\delta^{56}\text{Fe}$. We therefore suggest that the light $\delta^{56}\text{Fe}$ of arc lavas may be explained by greater mantle source depletion compared to MORB. However, the lack of geochemical correlations between $\delta^{56}\text{Fe}$ and major, trace and isotopic data show that Fe isotopes are difficult to interpret, and pairing Fe isotope measurements with other stable isotope data may further aid interpretations.

CHAPTER FOUR TABLE OF CONTENTS

4.1. Introduction	134
4.1.1. Aims	138
4.2. Sample set and Geologic Background	139
4.2.1. Geological & Tectonic Setting of IODP Expedition 352	139
4.2.2. Expedition 352 Stratigraphy	141
4.2.3. FAB & Boninite Petrography	142
4.2.3.1. Fore-arc Basalts (FABs)	146
4.2.3.2. Boninites	146
4.2.4. FAB & Boninite Chemistry	147
4.2.4.1. Fore-arc Basalts (FABs)	147
4.2.4.2. Boninites	151
4.2.5. FAB & Boninite Petrogenesis	156
4.3. Methods & Results	159
4.3.1. Sample Selection	159
4.3.2. Trace Elements	159
4.3.3. Iron Isotopic Compositions	163
4.3.3.1. Fore-arc Basalt Fe Isotopic Compositions	165
4.3.3.2. Boninite Fe Isotopic Compositions	165
4.4. Discussion	167
4.4.1. Fore-arc Basalt Fe Isotopic Compositions	167
4.4.2. Boninite Fe Isotope Compositions	169
4.4.2.1. Comparison between Boninite and FAB Fe Isotopic Compositions	169
4.4.2.2. Cause(s) of Fe isotopic difference between FABs and boninites	169
<i>a) Processes that are unlikely to create light $\delta^{56}\text{Fe}$ signatures in boninites</i>	<i>169</i>
<i>b) Processes that may create light $\delta^{56}\text{Fe}$ signatures in boninites</i>	<i>172</i>
4.4.3. Implications for deconvolving Fe isotope fractionation in global arcs	183
4.5. Conclusions	184
References	184

4.1. Introduction

Subduction is one of the key drivers of plate tectonics, and subduction zones are the major location of chemical transfer between the Earth's surface and the mantle. Subduction systems are therefore essential to understand. The redox state of the mantle wedge is a significant unresolved question

in geochemistry. Arc lavas have higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ than MORB which is thought to come from oxidised, volatile-rich, slab-derived components interacting with the mantle wedge (e.g. Kelley & Cottrell 2009, 2012; Evans & Tomkins 2011; Evans 2012; Brounce *et al.* 2014). However, it is unclear whether measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ is truly reflective of source conditions, or acquired by secondary processes *en route* to the surface (Kelley & Cottrell 2009). Iron isotopes have been employed to investigate arc lava and mantle wedge $f\text{O}_2$ because they are considered to fractionate due to changes in Fe oxidation state and coordination (e.g. Polyakov & Mineev 2000; Shahar *et al.* 2008; Young *et al.* 2015). Isotope theory predicts that arc lavas should be isotopically heavier than MORB due to the greater oxidation state of arc lavas (Dauphas *et al.* 2009, 2014). However, arc lavas are commonly isotopically lighter than MORB (e.g. Dauphas *et al.* 2009; Nebel *et al.* 2015; Foden *et al.* 2018; Williams *et al.* 2018) (**Fig. 4.1**). If the mantle wedge is oxidised as is assumed, this is counter-intuitive, and raises questions about what process(es) create the light $\delta^{56}\text{Fe}$ of arc lavas. Previous Fe isotope studies have called upon source depletion, magmatic differentiation, and the introduction of slab-derived fluids, melts or sediments (e.g. Dauphas *et al.* 2009; Nebel *et al.* 2015; Debret *et al.* 2016, 2018, 2020, 2021; Inglis *et al.* 2017; Foden *et al.* 2018; Turner *et al.* 2018; Williams *et al.* 2018), however there is no consensus.

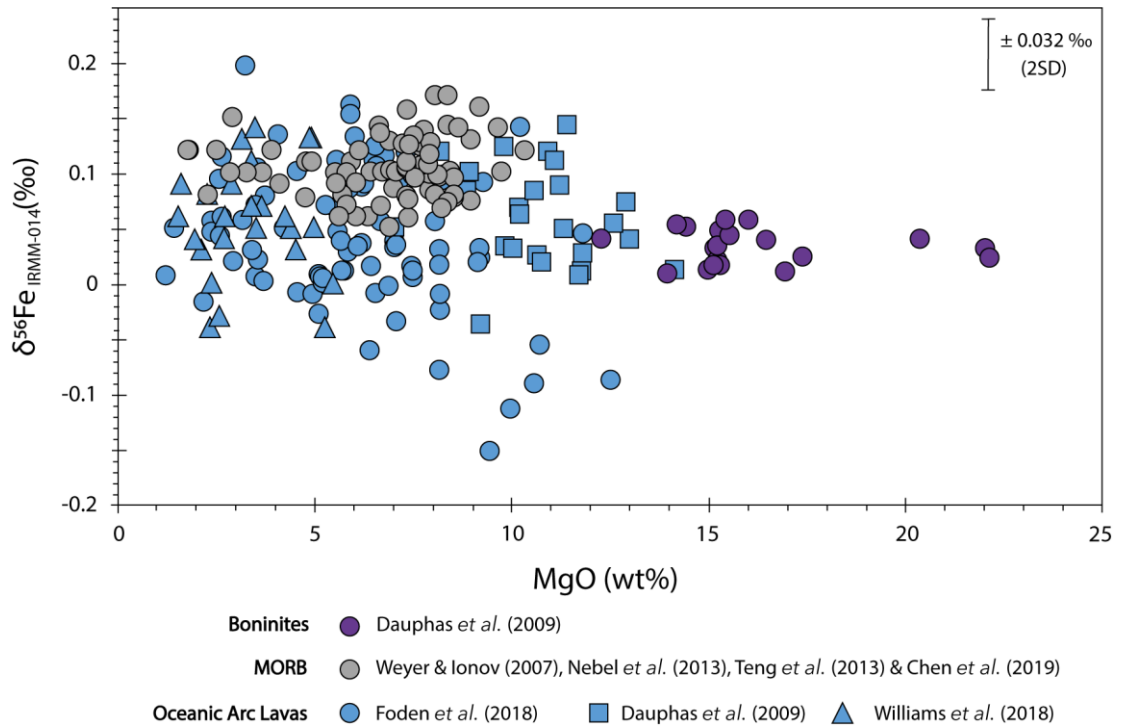


Figure 4.1: $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ (‰) versus MgO (wt%) for arc lavas, boninites, and MORB. Arc lava data is from Dauphas *et al.* (2009), Foden *et al.* (2018), Williams *et al.* (2018), the MORB data is from Weyer & Ionov (2007), Nebel *et al.* (2013), Teng *et al.* (2013), Chen *et al.* (2019), and the boninite data is from Dauphas *et al.* (2009).

During magmatic differentiation, it is assumed that Fe^{3+} is more incompatible than Fe^{2+} (Woodland & Koch 2003). Therefore, isotopically heavy Fe should be preferentially incorporated into Fe^{3+} sites, such as magnetite and silicate melts, and light Fe into Fe^{2+} sites such as olivine and pyroxenes (Polyakov & Mineev 2000; Shahar *et al.* 2008; Schuessler *et al.* 2009; Macris *et al.* 2015; Young *et al.* 2015; Sossi *et al.* 2016). Indeed, NRIXS studies show that silicate melts have Fe-O bond structures that support the preferential incorporation of heavy Fe (Dauphas *et al.* 2014; Roskosz *et al.* 2015). Therefore, if partial melting is the dominant control on $\delta^{56}\text{Fe}$ of MORB, OIB and arc lavas, their $\delta^{56}\text{Fe}$ should be isotopically heavier than their sources. MORB and OIB have been observed to be ~ 0.1 to ~ 0.2 ‰ heavier than fertile mantle peridotites (Weyer *et al.* 2005; Williams *et al.* 2005; Weyer & Ionov 2007; Teng *et al.* 2013; Williams & Bizimis 2014; Sossi *et al.* 2016) and inferred primitive mantle (Dauphas *et al.* 2009). However, observed ranges in MORB, OIB, and abyssal peridotite $\delta^{56}\text{Fe}$ are often greater than those predicted by melting models (e.g. Williams *et al.* 2005; Dauphas *et al.* 2009; Williams & Bizimis 2014), and arc lavas are lighter than MORB and OIB (e.g. Dauphas *et al.* 2009; Nebel *et al.* 2015; Foden *et al.* 2018; Williams *et al.* 2018). Iron isotopic mantle heterogeneity has been suggested as a way to reconcile such variation (e.g. Teng *et al.* 2013) and may explain the light $\delta^{56}\text{Fe}$ of arc lavas. For example, sub-arc mantle xenoliths from Kohistan and Simcoe have very light $\delta^{56}\text{Fe}$ compositions (~ -0.5 ‰, Williams *et al.* (2004), (2005)). Such Fe isotopic mantle heterogeneity would require an observable difference between the $\delta^{56}\text{Fe}$ of different mantle lithologies.

Lithologically distinct mantle components are thought to arise by the incorporation of recycled, metamorphosed remnants of subducted slabs into the convecting mantle which react with surrounding peridotites to create enriched, pyroxene-rich lithologies (Yaxley & Green 1998; Sobolev *et al.* 2007). Pyroxene-rich mantle lithologies are thought to be isotopically heavier than more peridotitic lithologies due to the stronger Fe-O bonds in pyroxene creating a heavier $\delta^{56}\text{Fe}$ signature than olivine (Sossi & O'Neill 2017). Williams & Bizimis (2014) investigated whether Fe isotopes could trace both depleted, peridotitic and enriched, pyroxenitic mantle lithologies. They measured the Fe isotopic compositions of mineral separates from enriched pyroxenitic, and depleted peridotitic Hawaiian xenoliths. They found that the peridotites were isotopically lighter than the pyroxenites, and that the lightest $\delta^{56}\text{Fe}$ were found in the depleted peridotitic rocks with the highest degrees of historic melt extraction. However, the large $\delta^{56}\text{Fe}$ variations (0.3‰) required multiple melt extraction and refertilisation events. The isotopically heavy pyroxenites were suggested to contribute to the heavy $\delta^{56}\text{Fe}$ of OIBs, and this work is supported by recent work on Samoa, Pitcairn, and the Galapagos (Konter *et al.* 2016; Nebel *et al.* 2019; Gleeson *et al.* 2020). However, Soderman *et al.* (2021) argues that heavy OIB $\delta^{56}\text{Fe}$ (Williams & Bizimis 2014; Konter *et al.* 2016; Nebel *et al.*

2019; Gleeson *et al.* 2020) cannot be achieved through heterogeneous source lithology alone, and that such compositions require a combination of heavy Fe selective processes.

Previous Fe isotope work specifically targeting arc basalts and boninites has led to varied interpretations of their light $\delta^{56}\text{Fe}$. Dauphas *et al.* (2009) measured Fe isotopes in boninites and suggested that they reflect a chondritic mantle $\delta^{56}\text{Fe}$. They suggested that light boninitic $\delta^{56}\text{Fe}$ is due to Fe fractionation being partially suppressed in arc sources compared to MORB sources due to increased degrees of partial melting and fluid involvement. However, light Banda arc and Marianas arc $\delta^{56}\text{Fe}$ measurements have been interpreted as reflecting historic source melt extraction and subsequent fluxing of the source with oxidising fluids that induced melting, but did not alter $\delta^{56}\text{Fe}$ (Nebel *et al.* 2015; Williams *et al.* 2018). Foden *et al.* (2018) suggest that a negative correlation exists between global arc lava $\delta^{57}\text{Fe}$ and the geodynamically controlled slab thermal parameter, ϕ , generally used as an indicator of slab temperature, where $\phi = \text{age of slab} \times \text{slab speed} \times \sin(\text{angle of subduction})$. The correlation was taken as evidence that the light $\delta^{56}\text{Fe}$ of the arc lavas is the result of process-driven source depletion and melting – in other words a mantle process rather than being directly linked to subduction inputs. Alternatively, a number of studies exploring Fe isotopes in ultra-high pressure terrains as a proxy for the subducted slab and serpentinised forearc mantle peridotites have suggested that Fe can be mobilised and isotopically fractionated by subduction-related fluids (e.g. Debret *et al.* 2016, 2018, 2020, 2021; Turner *et al.* 2018). Serpentinite devolatilisation-generated sulphate, carbonate and/or hypersaline fluids have been suggested to preferentially complex with isotopically light Fe ($\text{Fe(II)}\text{--SO}_x$, $\text{Fe(II)}\text{--CO}_3^{2-}$, or $\text{Fe(II)}\text{--Cl}_2$) (Debret *et al.* 2016, 2020) which could influence the Fe isotopic composition of the mantle wedge, and therefore arc lavas. However, some high pressure metamorphic veins in subducted eclogites have MORB-like $\delta^{56}\text{Fe}$ signatures, suggesting altered oceanic crustal fluids have a minimal impact on $\delta^{56}\text{Fe}$ in arc lavas and might instead just create local variations (Huang *et al.* 2020). In addition, it has been argued that the high Fe abundances of the mantle wedge and arc lavas means that significant amounts of Fe are required to alter their $\delta^{56}\text{Fe}$ compositions. Therefore mantle wedge and arc lava $\delta^{56}\text{Fe}$ has been argued to be relatively insensitive to the addition of isotopically light subduction fluids (e.g. Nebel *et al.* 2015; Williams *et al.* 2018).

Overall, there remains considerable uncertainty surrounding the cause(s) of the first order observation that most arc lavas have isotopically light Fe compared to MORB. Iron being a major element in rock-forming minerals, and the number of components and processes involved in arc lava (and MORB) formation makes it challenging to deconvolve Fe isotope fractionation mechanisms and their effects. This study utilises a carefully selected suite of rocks formed during subduction initiation to investigate whether *magmatic processes* such as partial melting and source

depletion, or *subduction inputs* such as the addition of slab melts, fluids, and sediments are more influential in creating light arc lava $\delta^{56}\text{Fe}$.

The Bonin forearc is part of the Izu-Bonin-Mariana (IBM) intraoceanic convergent plate margin and represents a complete *in situ* record of subduction initiation. It preserves a full geological record from the start of subduction to the onset of arc volcanism, consequently, early stage subduction processes can be examined in detail, including the addition of new components to the system such as slab-derived material. International Ocean Discovery Program (IODP) Expedition 352 ventured to the Bonin forearc in 2014. The Expedition drilled four sites and recovered two main rock types: anhydrous, MORB-like fore-arc basalts (FABs) associated with the onset of subduction, and hydrous boninites with known slab components (e.g. Reagan *et al.* 2015). These two starkly different lithologies erupted within 1 Myr of each other from the same mantle source (e.g. Li *et al.* 2019; Reagan *et al.* 2019). Forearc basalts do not show evidence of a subduction influence, whereas the boninites which erupted immediately after clearly record subduction input(s). Therefore, a comparison between these two lithologies provides a powerful test of the influence (or not) of subduction inputs on Fe isotopes. Furthermore, both rock types erupted in a seafloor spreading setting, negating the complicating effect of magma transport and evolution through the crust. Comparison of Fe isotopes in FABs versus boninites may therefore aid in deconvolving the competing processes that can fractionate Fe isotopes, thus allowing the evaluation of the most likely reason(s) for the light $\delta^{56}\text{Fe}$ of global arc lavas.

4.1.1. Aims

To re-examine the potential cause(s) of isotopically light Fe isotopes in arcs, this chapter aims to answer the following questions:

1. Are IODP Expedition 352 fore-arc basalt and boninite $\delta^{56}\text{Fe}$ compositions isotopically distinct, and are the boninites as isotopically light as global arc lavas?
2. Does the addition of slab melts, fluids or sediments influence the Fe isotopic composition of boninites?
3. Can magmatic processes such as prior source depletion and/or partial melting account for the full range of Fe isotopic compositions in subduction-related lavas?

4.2. Sample set and Geologic Background

The samples used in this chapter to investigate Fe isotope fractionation during subduction initiation include nine fore-arc basalts (FABs) and forty boninites from the Bonin forearc, recovered by IODP Expedition 352. In addition, six well-characterised harzburgites and dunites from the flanks of the Torishima Seamount on the Bonin forearc recovered from Ocean Drilling Program (ODP) Leg 125 were analysed. The Leg 125 mantle samples are interpreted as the closest available samples to the residues left after FAB and boninite extraction. For detailed descriptions of Leg 125 samples, see Parkinson & Pearce (1998) and Parkinson *et al.* (1998). IODP Expedition 352 FABs and boninites are the main focus of this chapter and are described below.

4.2.1. Geological & Tectonic Setting of IODP Expedition 352

IODP Expedition 352 targeted the Bonin forearc of the Izu-Bonin-Mariana (IBM) subduction system (**Fig. 4.2**) because it preserves a full record of subduction, from the start of subduction to the onset of ‘normal’ arc volcanism, and is young enough to be little disturbed by subsequent deformation or erosion (Reagan *et al.* 2015e). The IBM system is an intraoceanic convergent plate boundary between the Philippine Sea Plate and the subducting Pacific Plate which extends 2800 km from the Izu Peninsula, Japan, to Guam, USA (**Fig. 4.2**) (Stern *et al.* 2003; Wu *et al.* 2016). The Philippine Sea Plate of the northwest Pacific contains a complex array of remnant arcs, volcanic arcs, back-arc basins and oceanic plateaus that include the oldest terranes in the IBM system which are Cretaceous and found along the IBM periphery (Reagan *et al.* 2019). Such terranes include the Oki-Daito and Daito Ridges and the Amami Plateau (Hickey-Vargas 1998, 2005; Ishizuka *et al.* 2011a), the Huatung Basin (Hickey-vargas *et al.* 2008), and the Palau Basin (Taylor & Goodliffe 2004). The West Philippine Basin is the oldest back-arc basin in the IBM system, and began opening 55-52 and 30 Ma (Deschamps & Lallemand 2002; Savov *et al.* 2006; Ishizuka *et al.* 2011b, 2013).

Initiation of subduction in the IBM system occurred approximately 52 Ma (Taylor & Goodliffe 2004; Ishizuka *et al.* 2011b; Reagan *et al.* 2013) and progressed from the generation of FABs to boninites over ~1 Ma (Reagan *et al.* 2019). It is suggested that the initiation event may have extended along much of the western Pacific (Reagan *et al.* 2013) due to the recovery of FABs and boninites generated during the initiation along significant stretches of the IBM fore-arc (e.g. Reagan *et al.* 2010; Ishizuka *et al.* 2011b).

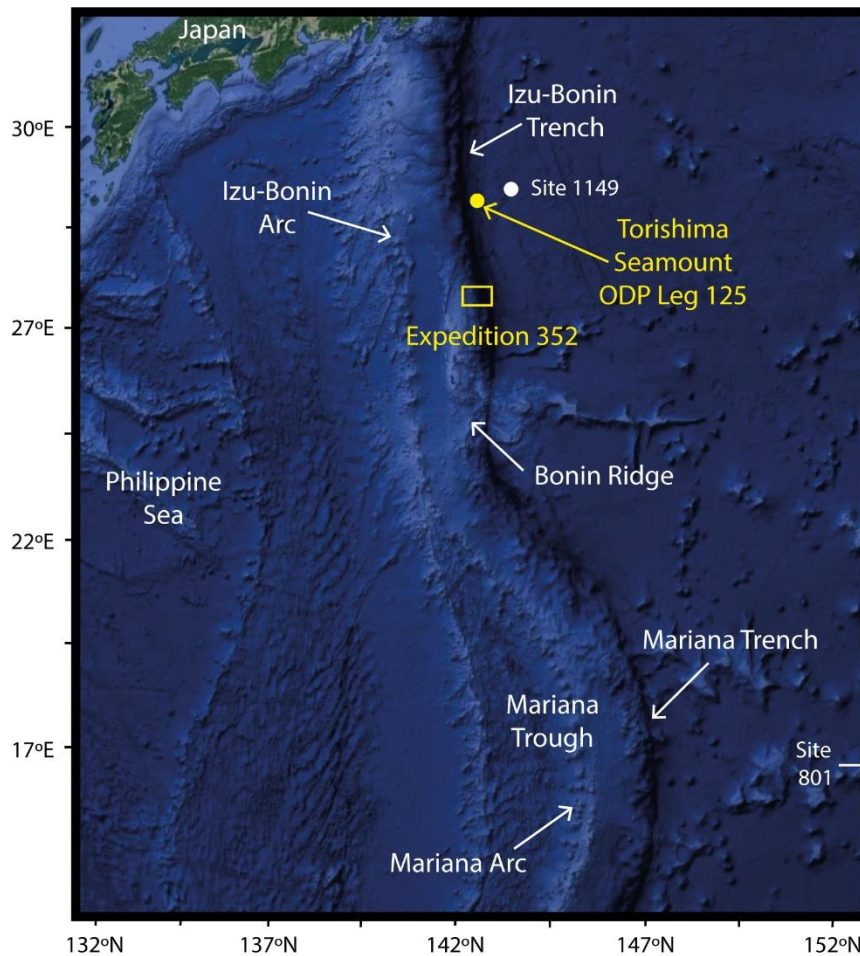


Figure 4.2: Location map of IODP Expedition 352 to the Bonin fore-arc from Chapter four. Yellow inset shows area in Fig. 4.3. Topography map and coordinates taken from Google Earth, and annotations from Reagan *et al.* (2015) and Parkinson & Pearce (1998).

Expedition 352 visited the southern Izu-Bonin forearc, and drilled the Bonin trench slope (**Fig. 4.3**) due to its exposure of early arc rocks, revealed by previous dredging and dive work (Reagan *et al.* 2010; Ishizuka *et al.* 2011a). Depleted mantle rocks are exposed the furthest downslope and are stratigraphically lowest, followed progressively upslope by gabbros, dolerites, FAB lavas, and boninites respectively (**Fig. 4.3**) (Ishizuka *et al.* 2011b). The Bonin trench therefore allowed Expedition 352 to sample the oldest rocks associated with Bonin subduction initiation, and observe how subduction zones evolve through time from earliest onset to fully established ‘typical’ calc-alkaline arc volcanism.

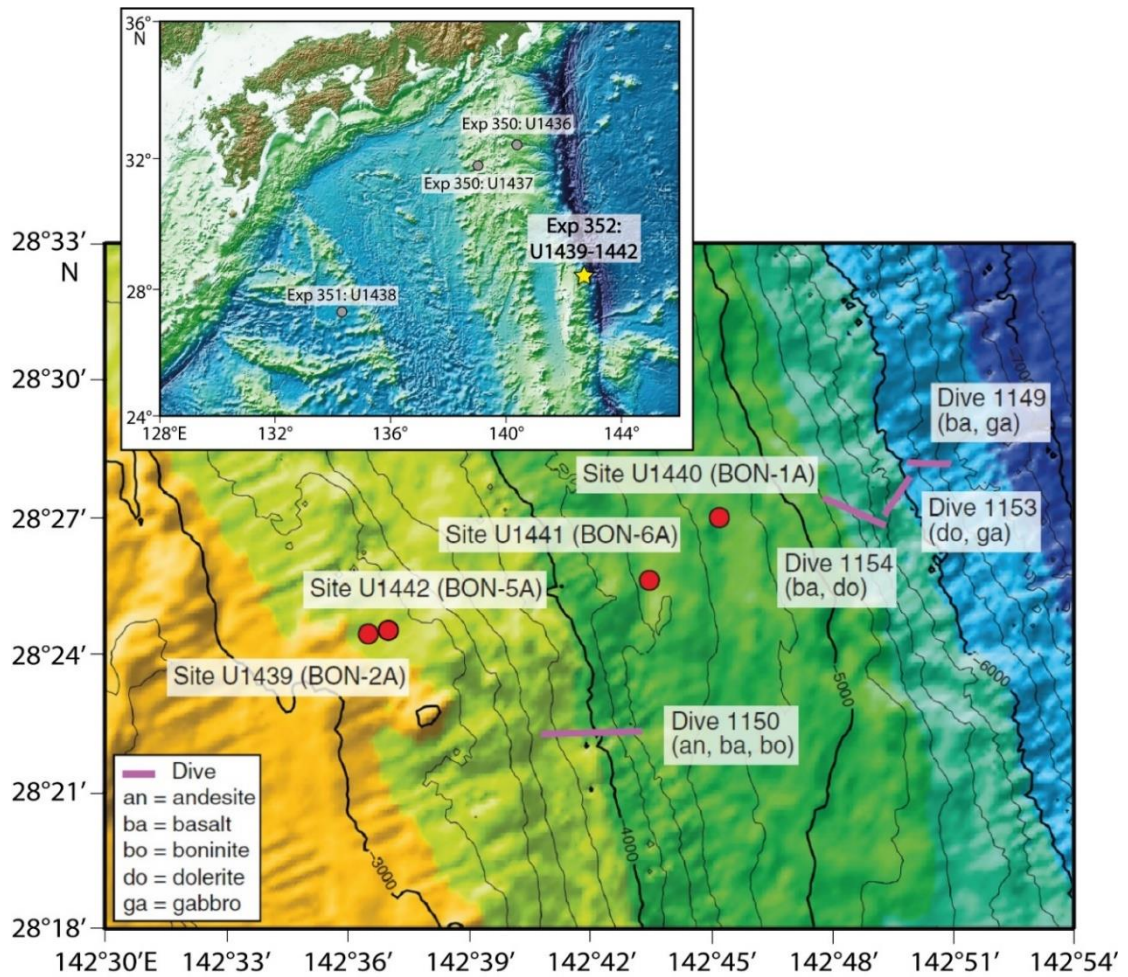


Figure 4.3: Location map of IODP Expedition 352, adapted from Reagan *et al.* (2015).

4.2.2. Expedition 352 Stratigraphy

IODP Expedition 352 drilled four sites between the Bonin trench wall and the Bonin Ridge volcanic arc (**Fig. 4.3**). Sites U1440 and U1441 mostly recovered fore-arc basalts (FABs) and sites U1439 and U1442 mostly recovered boninites. **Figure 4.4** summarises the vertical stratigraphy and rock types recovered from each of the four drill sites. Detailed stratigraphic information is available in Reagan *et al.* (2015).

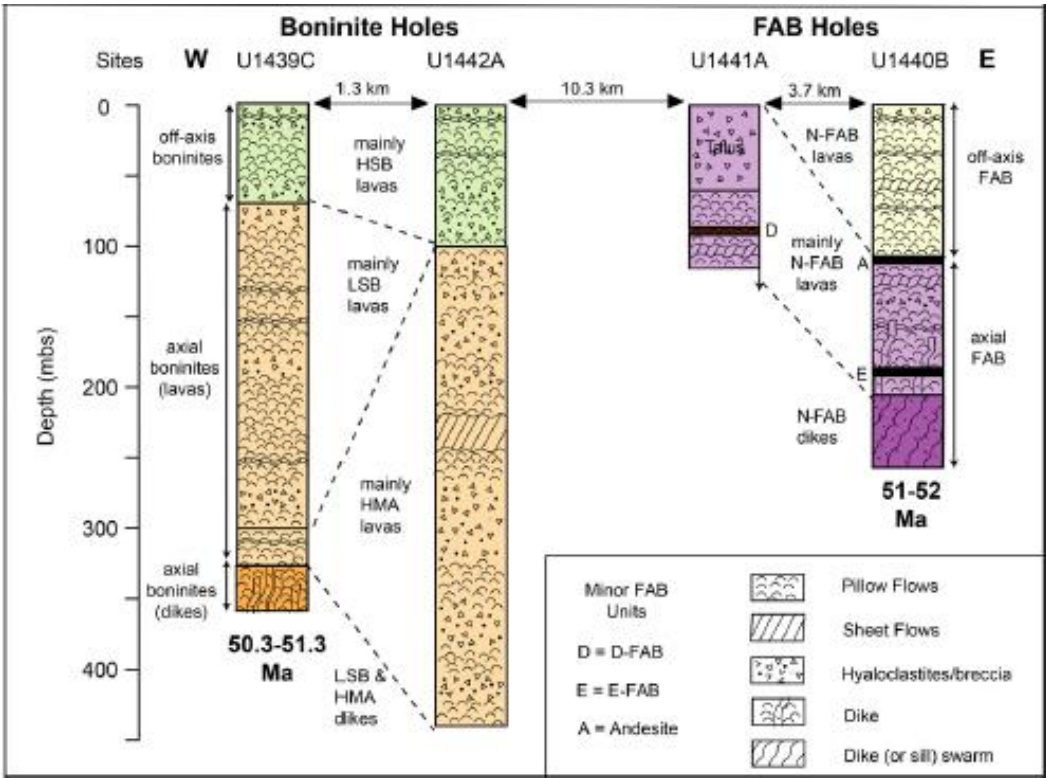


Figure 4.4: Lithostratigraphy of the four drill sites from IODP Expedition 352 (Li et al. 2019).

4.2.3. FAB & Boninite Petrography

Bonin forearc FAB and boninite petrography has been previously described in detail (Shervais et al. 2019, 2021; Whattam et al. 2020). General observations are summarised below, and **Table 4.1** details the petrology of the analysed samples.

Table 4.1: Petrology summary of IODP Expedition 352 fore-arc basalts (FABs) and boninites included in this study. Mineral modal abundances are split into phenocrysts and groundmass and measured in percent. Data is from Reagan et al. (2015a, c, b, d).

			Phenocryst Modal Abundance (%)					Groundmass Modal Abundance (%)					
Sample	Series	Type	Olv	Opx	Cpx	Oxide	Plag	Olv	Opx	Cpx	Oxide	Plag	Glass
U1439C - Boninites													
U1439C 16R1-26/30	axial	LSB	16	0	0	0.5	0	0	0	30	0	0	53.5
U1439C 22R1-89/95	axial	LSB	8	1	0	1	0	0	0	25	0	0	65
U1439C 41R1-99/106	axial	LSB	1	0	5	0	0	0	0	0	3	50	41
U1439C-29R-4-W 78/82	axial	LSB	15	0	0	0	0	0	20	20	0	10	35
U1439C-31R-5-W 12/17	axial	LSB	10	0	0	0	0	0	0	50	1	0	39
U1439C 19R4 11/17	axial	LSB	7	0	0	0.5	0	0	20	36	2	1.5	33
U1439C 40R1 33/38	axial	LSB	0	0	6	0	0	0	0	30	0	50	14
U1439C 31R1 15/20	axial	LSB	20	0	0	0	0	0	0	0	0	0	80
U1439C 26R1 132/137	axial	LSB	5	0	0	0	0	0	0	15	1	0	79
U1439C 19R3 58/62	axial	LSB	26	2	0	1	0	0	0	20	0	0	52
U1439C 11R1 124/127	axial	LSB	14	8	2	1	0	0	10	20	0	0	45
U1439C 33R2-W 23/30	axial	LSB	6	1	2	0	0	0	0	20	0	0	71
U1439C 38R1 103/106	axial	LSB	5	0	1	0	1	0	0	10	0.5	40	42.5
U1439C 27R3-W 80/87	axial	LSB	15	0	0	0	0	0	0	5	0	0	70
U1439C 23R1-W 42/48	axial	LSB	14.5	0	0	0.5	0	0	0	30	0	0	55
U1439C 28R2-W 66/71	axial	LSB	30	0	0	0	0	0	0	0	0	0	70
U1439C-10R2-W 13/19	axial	BB	2	2	0	0.5	0	0	10	15	0	0	70.5
U1439C-37R1-W 42/48	axial	HMA	0	0	1	0	0	0	0	20	0	50	29
U1439C 4R1-W 26/32	off-axis	HSB	0	5	0	0	0	0	30	20	0	0	45
U1439C 6R1 25/30	off-axis	HSB	1	3	0	0	0	0	35	5	0	0	56
U1439C 2R3-W 38/46	off-axis	HSB	5	15	0	0	0	0	40	0	0	0	40
U1439A 23X1-W 0/3	off-axis	HSB	0	8	12	0	0	0	0	0	0	0	80

Table 4.1: continued

Sample	Series	Type	Phenocryst Modal Abundance (%)					Groundmass Modal Abundance (%)					
			Olv	Opx	Cpx	Oxide	Plag	Olv	Opx	Cpx	Oxide	Plag	Glass
U1439A 21X1-W 0/7	off-axis	HSB	5	15	0	0	0	0	20	0	0	0	60
U1439C 5R1-W 92/96	off-axis	HSB	2	4	0	0	0	0	20	20	0	0	54
U1442A - Boninites													
U1442A-35R1-1-W 51/55	axial	LSB	1	0.5	0.5	0	0	0	0	25	3	40	32
U1442A 23R1 99/103	axial	LSB	5	10	0	0.1	0	0	15	5	0	0	65
U1442A 56R1 19/24	axial	LSB	0	0	0	0	0	0	0	25	0	50	25
U1442A 49R2-W 60/65	axial	LSB	1.5	0.5	0	0	1.5	0	10	15	0	0	73
U1442A 36R2-W 17/22	axial	LSB	3	0	15	0	5	0	0	10	0	40	30
U1442A 54R1-W 13/18	axial	LSB	0	2	15	0	30	0	0	0	0	0	53
U1442A 57R2-W 116/121	axial	LSB	0	0	1	0	0	0	0	20	0	45	34
U1442A 30R2-W 21/27	axial	BB	0.5	0.5	0.5	0	0	0	0	50	0	0	48.5
U1442A 20R1-104/108	off-axis	HSB	0.5	0.5	0	0	0	0	55	0	0	0	44
U1442A 22R1-122/125	off-axis	HSB	5	20	0	0	0	0	8	7	0	0	50
U1442A 47R1-W 50/55	off-axis	HSB	1	0	10	0	3	0	0	0	0	0	86
U1442A 23R2-W 30/35	off-axis	HSB	5	2	0	0	0	0	20	5	0	0	70
U1442A 28R1-W 10/14	off-axis	HSB	no thin section from this section										
U1442A 48R1-W 87/92	off-axis	HSB	0	0	0	0	0	0	0	3	0	0	97
U1442A 15R1-W 70/75	off-axis	HSB	10	10	0	0	0	0	5	20	0	0	55
U1442A 13R1-W 4/10	off-axis	HSB	0.5	0	0	0	0	0	40	20	0	0	40

Table 4.1: continued

			Phenocryst Modal Abundance (%)					Groundmass Modal Abundance (%)					
Sample	Series	Type	Olv	Opx	Cpx	Oxide	Plag	Olv	Opx	Cpx	Oxide	Plag	Glass
U1440B - Fore-arc basalts													
U1440B 17R2-23/32	axial	N-FAB	0	0	2	0	0	0	0	25	5	50	18
U1440B 26R1-64/68	axial	N-FAB	0	0	0	0	0	0	0	25	5	50	20
U1440B 28R1-31/38	axial	N-FAB	0	0	0.5	0	0.5	0	0	20	0.25	10	68.75
U1440B-8R-1-W 20/23	off-axis	N-FAB	0	0	0	0	0	0	0	15	2	25	57.8
U1440B-12R-2-W 4/8	off-axis	P-FAB	0	0	0	0	0	0	0	10	0	45	45
U1440B-17R-1-W 11/13	axial	N-FAB	0	0	0	0	0	0	0	20	3	40	37
U1440B-29R-1-W 5/8	axial	N-FAB	0	0	0	0	1	0	0	39	1	50	9
U1441A - Fore-arc basalts													
U1441A-21R-1-W 37/42	axial	N-FAB	0	0	0	0	0	0	0	20	0	50	30
U1441-A3-19R1-66/72	off-axis	D-FAB	0	0	3	0.5	2	0	0	15	0	35	20

4.2.3.1. Fore-arc Basalts (FABs)

Bonin forearc FABs are dominantly pillows and sheet flows, but also include vitrophyres and dolerites (Shervais *et al.* 2019). FABs have very low vesicularity of 0 to 5%, and are aphyric to sparsely plagioclase (0.2 - 5%) or augite (0.3 - 2%) phyric (≤ 1 mm in size), with a glassy to microcrystalline groundmass with plagioclase (10 - 53%), augite (8 - 35%), magnetite (1 - 3%), and a mesostasis of quench crystals $\pm$ glass (0 - 82%) (Shervais *et al.* 2019; Whattam *et al.* 2020). The groundmass glass is commonly devitrified (Whattam *et al.* 2020). FAB vitrophyres are sparsely microphyric with $\sim 0.5\%$ glomerocrysts of augite and plagioclase surrounded by glass (Shervais *et al.* 2019).

Doleritic FABs were only recovered in unit 15 of hole U1440B (**Fig. 4.4**) and have fine to medium grained (0.3 - 2 mm) seriate textures (Shervais *et al.* 2019). Subhedral plagioclase with rare sieve textures is the dominant phase ($\sim 50\%$) (Shervais *et al.* 2019). Doleritic FAB mineralogy also includes subhedral, blocky-to-prismatic augite (30 - 40%), that is commonly ophimottled, and equant interstitial Fe-Ti oxides (1 - 2%; 0.1 - 0.3 mm). Doleritic FAB interstitial material comprises altered glass with chlorite and quartz (Shervais *et al.* 2019).

4.2.3.2. Boninites

Boninites are highly vesicular and porphyritic (typically 8 - 15% phenocrysts, but can reach 20 - 40%), and most contain phenocrysts of olivine, clinopyroxene and orthopyroxene that are strongly zoned (Shervais *et al.* 2021; Whattam *et al.* 2020). The Bonin forearc boninites are subdivided into high-silica boninites (HSBs) and low-silica boninites (LSBs) based on Pearce & Reagan (2019). LSBs with lower than typical SiO_2 (ie. < 52 wt % SiO_2) are classified as basaltic boninites (BB) (Reagan *et al.* 2017) of which this chapter includes two samples. The boninite samples analysed in this chapter also include a single high-Mg andesite (HMA) which is likely related to the boninites by crystal fractionation.

HSBs contain abundant phenocrysts of orthopyroxene (0 - 15%; 0.7 - 0.9 mm), olivine (0 - 10%; 0.5 - 0.9 mm) $\pm$ augite (0 - 0.5%; 0.3 mm) with Cr-spinel (0 - 0.1%; < 1 mm) (Shervais *et al.* 2021; Whattam *et al.* 2020). Plagioclase is not present as phenocrysts or groundmass. The groundmass comprises a glassy matrix with pyroxene microliths (Reagan *et al.* 2017). Textures are typically vitrophyric where the glass contains acicular pyroxenes (Shervais *et al.* 2021).

LSBs comprise phenocrysts of olivine (0 - 30%; 0.7 - 0.9 mm), clinopyroxene (0 - 6%; 0.4 - 0.6 mm), Cr-spinel (0 - 1%; commonly as olivine inclusions) $\pm$ orthopyroxene (0 - 2%; 0.7 mm) and rare, small plagioclase (≤ 0.5 mm) in a glassy ($\sim 70\%$ glass) or microcrystalline groundmass of clinopyroxene $\pm$

plagioclase microliths and rare chromite (Reagan *et al.* 2017; Shervais *et al.* 2021; Whattam *et al.* 2020).

BBs typically contain phenocrysts of euhedral, prismatic olivine (1 - 14%; up to 7 mm), orthopyroxene (2 - 8%), clinopyroxene (1 - 5%; as discrete phenocrysts or overgrowths of low-Ca pyroxene) and Cr-spinel (1 - 4%; < 1 mm) (Shervais *et al.* 2021; Whattam *et al.* 2020). The groundmass is typically glassy (30 - 50% glass) or microcrystalline with augite, low-Ca pyroxene and plagioclase (Shervais *et al.* 2021; Whattam *et al.* 2020).

HMAs generally are sparsely porphyritic with phenocrysts (0.5 - 0.8 mm) of augite (0 - 15%) ± orthopyroxene (0 - 1%) ± plagioclase (0 - 5%) and rare olivine (0 - 3%) in a fine-grained to microcrystalline groundmass of quench clinopyroxene and plagioclase (Shervais *et al.* 2021; Whattam *et al.* 2020). Trachytic textures are common (Shervais *et al.* 2021). The HMA included in this chapter has prismatic clinopyroxene phenocrysts (1%, 0.3 mm), and a groundmass of plagioclase (50%, 0.2 mm), clinopyroxene (20%, 0.1 mm) and mesostasis (29%) with intersertal and trachytic textures and magma mingling microstructures.

4.2.4. FAB & Boninite Chemistry

4.2.4.1. Fore-arc Basalts (FABs)

Fore-arc basalts (FABs) from Expedition 352 are tholeiitic, and MORB-like in terms of major elements with 5 to 9 wt % MgO, and similar Al₂O₃ and CaO, but lower TiO₂ and P₂O₅ and higher CaO/Al₂O₃ ratios (**Table 4.2, Fig. 4.5**). Trace elements are also similar to MORB (**Appendix C, Fig. 4.5**), but FABs are more depleted in high-field strength elements (HFSEs), light rare earth elements (LREEs), and Ti and P, reflecting a more depleted source (Reagan *et al.* 2010; Shervais *et al.* 2019). Heavy rare earth elements (HREEs) and Y overlap with low MORB compositions.

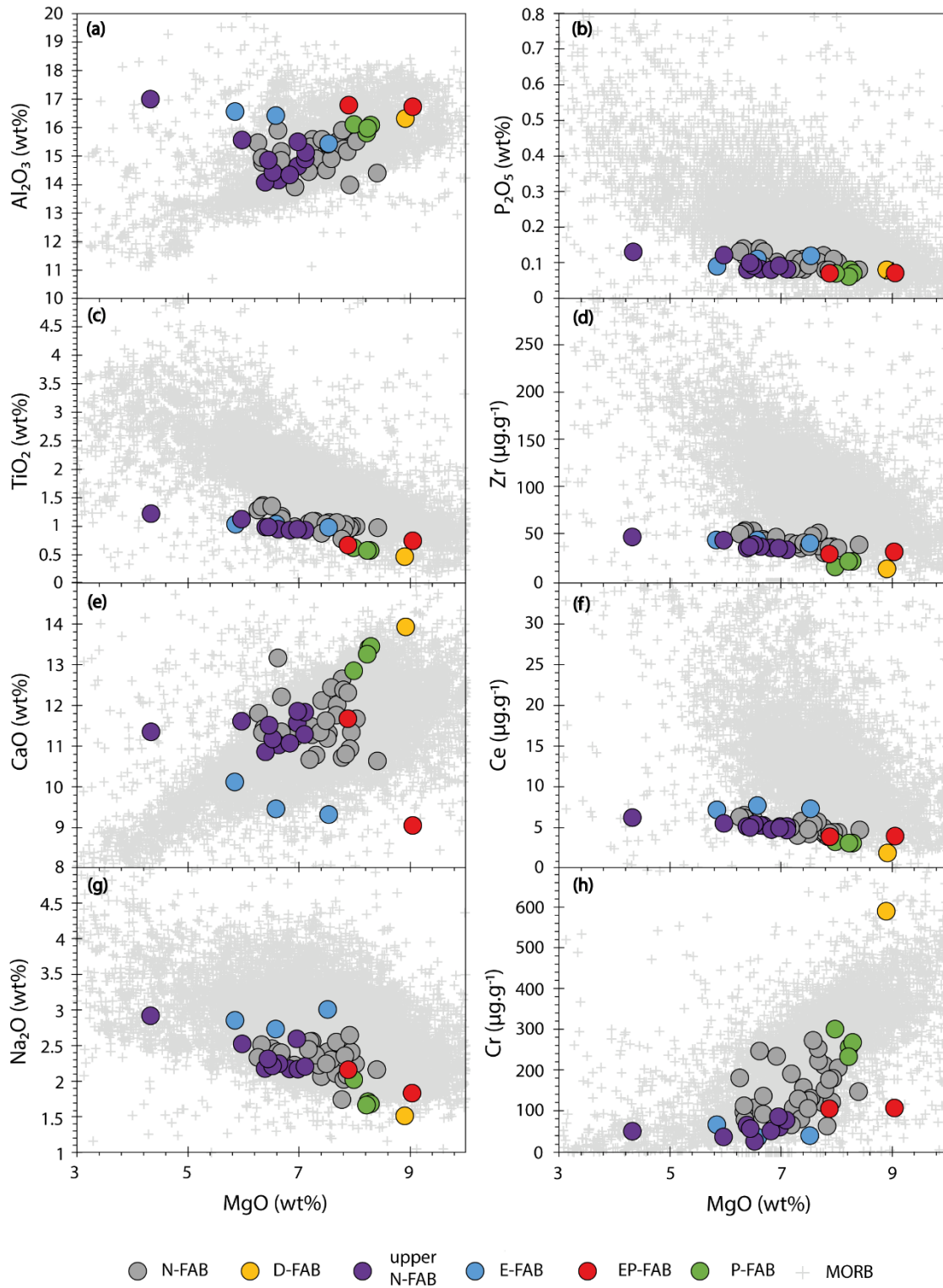


Figure 4.5: MgO Harker diagrams for IODP Expedition 352 fore-arc basalts (FABs) and MORB. The FABs are split into chemically defined subgroups that are outlined in Shervais et al. (2019) and Fig. 4.6. The FAB data is from Shervais et al. (2019), and the grey crosses are MORB data from the PETDB geochemical database. Graphs are modified from Shervais et al. (2019).

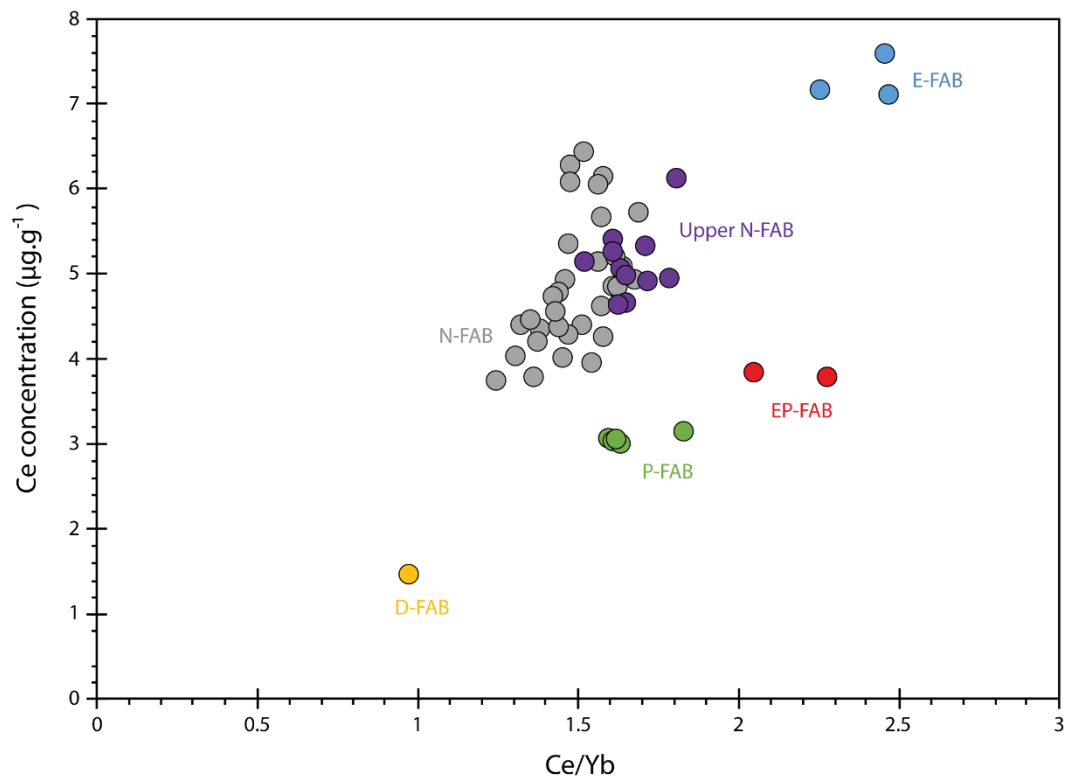


Figure 4.6: Ce/Yb versus Ce concentration in $\mu\text{g.g}^{-1}$ for IODP Expedition 352 fore-arc basalts (FABs). The data is from Shervais *et al.* (2019) and the plot is modified from Shervais *et al.* (2019).

The FABs are chemically diverse. Shervais *et al.* (2019) split FABs into multiple subgroups based on REE compositions and plots such as **Fig. 4.6**; normal-FAB (N-FAB), enriched-FAB (E-FAB), primitive-FAB (P-FAB), depleted-FAB (D-FAB) and enriched/primitive-FAB (EP-FAB). N-FABs dominate the Expedition 352 FAB cores. N-FABs comprise all dolerites and most lavas. P-FABs are exclusive to U1440B Unit 3, display similar REEs patterns to N-FABs, but have lower concentrations of all REEs. P-FABs are also very high in MgO and Cr and low in TiO_2 (**Fig. 4.5**). D-FABs are exclusively from U1441A Unit 3 and are the most depleted of all FABs in all REEs. D-FABs also have higher CaO and lower TiO_2 and Na_2O than both MORB and all other FABs (**Fig. 4.5**). E-FABs are found in U1440B Unit 13 are closer to MORB REE concentrations than N-FAB, reflecting less depleted origins. EP-FABs have REE patterns similar to E-FABs but are more depleted in REEs.

Melt modelling from Shervais *et al.* (2019) accounted for the REE diversity of the FAB subgroups using two-stages of melting from the garnet and spinel-stability fields, and variable degrees of melting. N-FAB REE patterns were best reproduced by 2 - 3% garnet-field melt extraction, followed by 7 - 10% spinel-field melting. The P-FABs are associated with 1% garnet-field extraction, and then 20% spinel-field melting. E-FABs are thought to have experienced 2% garnet-field extraction, followed by 3 - 5% spinel-field melting, and D-FAB, 2% garnet-field extraction, followed by 23% spinel-field melting.

Radiogenic isotope analyses of Sr, Nd, Hf and Pb provide a second way of grouping FABs. FABs interpreted to have erupted on-axis and off-axis have distinct Nd, Hf and Pb isotope ratios (Li *et al.* 2019). Off-axis FABs have higher ϵHf_i and $^{206}\text{Pb}/^{204}\text{Pb}$, and lower ϵNd_i than axial FABs (**Fig. 4.7**). In addition, the lower, axial FABs display upwards chemostratigraphic fractionation trends towards lower MgO, and higher FeO, TiO_2 and P_2O_5 which contributed to their interpretation as products of an axial magma system (Shervais *et al.* 2019). The transition to upper, off-axis FABs is marked by an abrupt reversal to more primitive compositions (Shervais *et al.* 2019). The lowermost upper FAB unit comprises P-FABs which are some of the most primitive compositions, and lower MgO, TiO_2 and high Sr/Zr (Shervais *et al.* 2019). The lower, axial FABs are therefore interpreted to indicate the introduction of a new batch of primitive magma distinct from the lower FAB source, that did not interact with the axial magma chamber due to the transition of off-axis magmatism (Shervais *et al.* 2019).

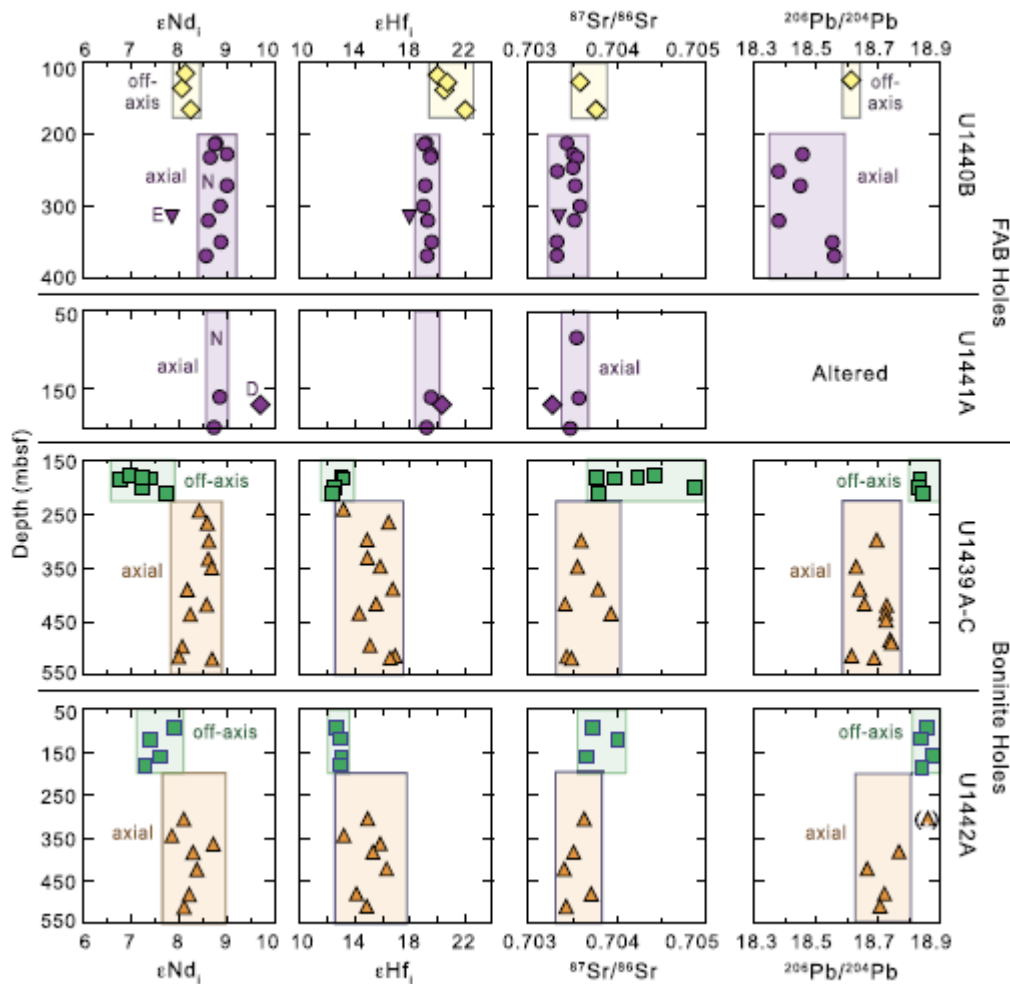


Figure 4.7: Radiogenic isotopes in IODP Expedition 352 FABs and boninites from Li *et al.* (2019).

4.2.4.2. Boninites

Expedition 352 boninites are chemically distinct from FABs. They are hydrous, with higher SiO_2 (52 - 63 wt%), lower $\text{TiO}_2 < 0.5$ wt%, and high $\text{MgO} > 8$ wt% (**Fig. 4.8**) in agreement with the IUGS classification of boninites (Le Bas 2000). Furthermore, recent re-examination of boninite classification was based largely on the Exp. 352 boninites (Pearce & Reagan 2019). Expedition 352 boninites are very similar to boninites from the geographically proximal boninite type locality of Chichijima, Bonin Island, (Peterson, 1891; Umino, 1986; Dobson *et al.* 2006). Unlike FABs, MORB and island arc tholeiites, Expedition 352 boninite TiO_2 and SiO_2 increase with increasing MgO , and follow similar iron-depletion trends to calc-alkaline suites (Shervais *et al.* 2021). Boninites have high alkali concentrations with $\text{Na}_2\text{O} < 3.0\%$ and $\text{K}_2\text{O} < 1.0\%$, and CaO is lowest in the HSB but increases progressively from LSB to BB as SiO_2 decreases (Shervais *et al.* 2021, **Fig. 4.8**). HSB have similar compositions to boninites recovered from DSDP site 458 (e.g. Meijer *et al.*, 1982). Whereas LSBs are akin to low-Ca boninites chemically, and typically have the higher TiO_2 concentrations than HSB (Shervais *et al.* 2021, **Fig. 4.8**). HMA of which there is one in this study, typically have high SiO_2 and low TiO_2 similar to boninites, but higher MgO than normal calc-alkaline andesite and dacite, but less than 8 wt% (Shervais *et al.* 2021, **Fig. 4.8**).

Expedition 352 Boninites typically have lower HFSE concentrations than FABs or MORB, and show little enrichment with increasing MgO (Shervais *et al.* 2021). Whereas fluid mobile elements such as Sr, Ba and Pb are enriched in boninites relative to FABs, and compatible elements Cr, Ni and Co all decrease with decreasing MgO (Shervais *et al.* 2021). Boninite Ti/V ratios are very low and significantly lower than FAB Ti/V ratios, largely due to FABs having considerably higher V concentrations ($> 250 \mu\text{g.g}^{-1}$); FAB Ti/V = 10 - 20, LSB/BB/HMA Ti/V = 10 - 14, and HSB Ti/V = ≤ 10 (Shervais *et al.* 2021). Boninites also have exceptionally high Zr/Sm ratios compared to FABs and MORB, showing increasing Zr/Sm (25 - 70) at relatively and consistently low Sm concentrations ($< 1.5 \mu\text{g.g}^{-1}$). Boninites have smooth chondrite-normalised REE patterns (Shervais *et al.* 2021), with high LREE and low HREE concentrations. Similarly to most arc lavas, the Expedition 352 boninites are enriched in Sr and Pb relative to other surrounding REEs, but have unusual positive Hf anomalies (Li *et al.* 2019). Trace elemental differences between axial and off-axis boninites are more subtle than the differences between axial and off-axis FABs (Li *et al.* 2019). Instead of the LREE-depletion seen in axial LSB, off-axis HSB are LREE-enriched, with lower, more variable HREE patterns, and have higher Hf, Pb, and Sr concentrations (Li *et al.* 2019). Boninites have lower ϵHf_i and $^{208}\text{Pb}/^{204}\text{Pb}$ than the FABs, and HSB have lower ϵNd_i & lower or similar ϵHf_i to LSB, but higher or similar Sr and Pb isotope ratios (**Fig. 4.7**) (Li *et al.* 2019).

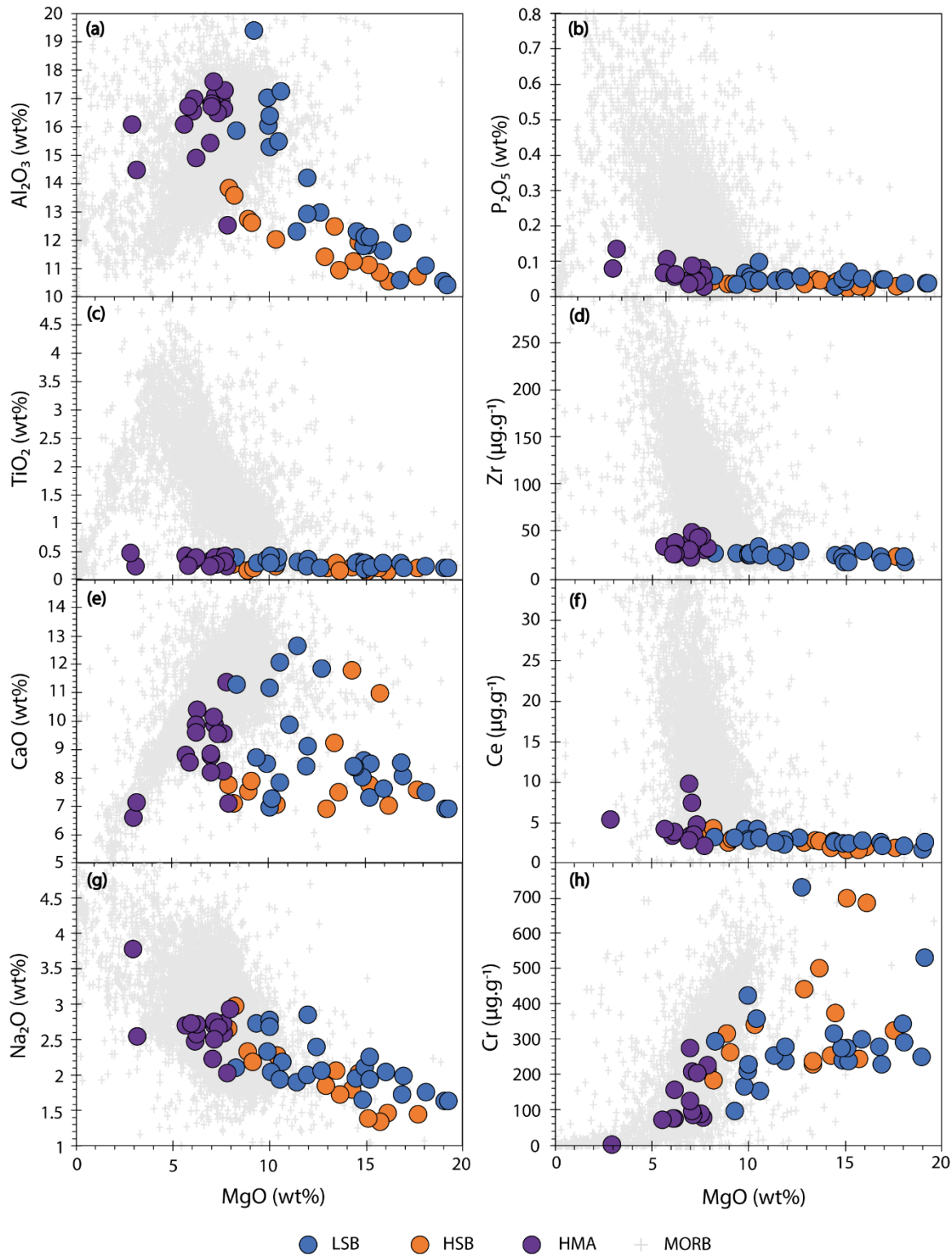


Figure 4.8: MgO Harker diagrams for IODP Expedition 352 low-silica boninites (LSBs), high-silica boninites (HSBs), high-magnesian andesites (HMA), and MORB. The boninite data is from Shervais et al. (2019) which includes no fresh basaltic boninites, and the grey crosses are MORB data from the PETDB geochemical database. Graphs are modified from Shervais et al. (2019).

Table 4.2: Major element concentrations for IODP Expedition 352 fore-arc basalts and boninites used in this study. Data is from Reagan et al. (2017). Rock type abbreviations are as such: N-FAB (normal fore-arc basalt), P-FAB (primitive fore-arc basalt), D-FAB (depleted fore-arc basalt), LSB (low-Si boninite), HSB (high-Si boninite), BB (basaltic boninite), HMA (high-magnesian andesite).

				Major Element Concentrations (wt%)											
Sample	Series	Type	Depth (mbsl)	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Sum
U1439 - Boninites															
U1439C 16R1-26/30	axial	LSB	299.76	53.92	0.29	11.91	8.19	0.13	14.62	7.44	2.05	0.56	0.05	5.36	99.34
U1439C 22R1-89/95	axial	LSB	349.19	52.48	0.31	11.55	8.66	0.13	14.85	8.22	2.02	0.71	0.05	7.07	99.17
U1439C 41R1-99/106	axial	LSB	515.09	51.22	0.44	14.58	7.00	0.13	10.93	11.54	2.02	0.13	0.06	3.72	98.22
U1439C-29R-4-W 78/82	axial	LSB	421.29	50.26	0.22	10.62	8.91	0.22	20.51	6.75	1.36	0.18	0.05	12.38	99.36
U1439C-31R-5-W 12/17	axial	LSB	441.80	51.40	0.29	11.15	9.51	0.14	12.61	10.70	1.99	0.60	0.07	7.77	98.64
U1439C 40R1 33/38	axial	LSB	509.43	54.10	0.37	16.37	8.10	0.15	10.48	6.94	2.59	1.47	0.07	8.62	101.31
U1439C 31R1 15/20	axial	LSB	436.25	53.79	0.23	11.32	7.88	0.14	16.74	8.03	1.86	0.42	0.06	8.80	100.67
U1439C 26R1 132/137	axial	LSB	388.62	52.98	0.30	10.91	9.42	0.13	16.31	7.98	2.01	0.38	0.07	11.82	99.54
U1439C 19R3 58/62	axial	LSB	332.22	54.27	0.32	12.40	8.41	0.13	14.29	7.84	2.21	0.71	0.06	7.74	101.72
U1439C 11R1 124/127	axial	LSB	266.64	51.30	0.32	11.41	9.31	0.25	18.28	7.59	1.82	0.40	0.05	10.48	99.65
U1439C 33R2-W 23/30	axial	LSB	457.17	53.90	0.25	12.79	7.73	0.12	15.01	8.52	2.04	0.14	0.05	11.50	100.63
U1439C 38R1 103/106	axial	LSB	495.63	54.18	0.33	16.23	8.07	0.13	9.26	9.77	2.39	0.24	0.03	5.43	100.61
U1439C 27R3-W 80/87	axial	LSB	400.47	54.05	0.24	11.95	8.00	0.13	16.09	7.64	1.89	0.38	0.05	11.53	101.58
U1439C 23R1-W 42/48	axial	LSB	358.52	53.60	0.36	13.31	9.28	0.13	12.37	8.13	2.56	1.03	0.05	11.41	100.41
U1439C 28R2-W 66/71	axial	LSB	408.91	53.51	0.24	11.97	8.25	0.13	17.64	6.40	1.94	0.38	0.06	13.62	101.71
U1439C 19R4 11/17	axial	LSB	333.16	53.06	0.34	13.46	8.86	0.16	13.23	8.95	2.04	0.36	0.08	8.92	100.00
U1439C-10R2-W 13/19	axial	BB	262.03	50.60	0.38	13.24	9.57	0.14	12.49	9.41	2.24	0.90	0.13	8.42	99.29
U1439C-37R1-W 42/48	axial	HMA	485.22	56.24	0.36	17.10	6.59	0.06	7.14	9.18	2.72	0.42	0.07	2.49	99.94
U1439C 4R1-W 26/32	off-axis	HSB	201.86	56.32	0.20	11.52	8.21	0.14	12.02	7.28	1.90	0.83	0.05	4.14	98.62
U1439C 6R1 25/30	off-axis	HSB	221.45	60.24	0.19	12.64	8.01	0.13	9.25	7.36	2.23	0.58	0.05	3.99	99.37
U1439C 2R3-W 38/46	off-axis	HSB	185.13	55.81	0.16	10.32	8.64	0.15	16.84	6.76	1.38	0.57	0.04	2.99	99.81

Table 4.2: continued

				Major Element Concentrations (wt%)											
Sample	Series	Type	Depth (mbsl)	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Sum
U1439 - Boninites															
U1439A 23X1-W 0/3	off-axis	HSB	196.20	55.99	0.16	9.90	8.82	0.15	17.26	6.42	1.29	0.70	0.00	2.82	98.57
U1439A 21X1-W 0/7	off-axis	HSB	182.50	56.00	0.15	10.30	8.78	0.15	16.63	6.76	1.29	0.63	0.04	3.36	101.24
U1442 - Boninites															
U1442A 23R1 99/103	axial	LSB	189.69	53.62	0.17	12.49	9.46	0.15	13.91	7.79	2.01	0.95	0.07	6.98	100.98
U1442A 56R1 19/24	axial	LSB	510.49	53.86	0.31	16.89	7.50	0.06	10.27	9.15	2.51	0.09	0.06	4.29	99.69
U1442A-35R-1-W 51/55	axial	LSB	306.01	56.31	0.34	15.35	7.47	0.13	7.02	9.97	2.67	0.46	0.07	2.90	99.85
U1442A 49R2-W 60/65	axial	LSB	443.85	53.81	0.38	16.59	8.08	0.06	10.14	8.79	2.58	0.15	0.07	6.17	98.70
U1442A 36R2-W 17/22	axial	LSB	316.50	54.77	0.37	15.54	8.17	0.13	8.64	10.81	2.02	0.14	0.07	4.17	100.95
U1442A 54R1-W 13/18	axial	LSB	490.93	55.42	0.30	16.56	7.55	0.05	9.68	8.59	2.35	0.12	0.06	4.55	99.69
U1442A 57R2-W 116/121	axial	LSB	522.63	53.68	0.28	14.49	8.24	0.08	13.05	8.48	2.45	0.09	0.05	4.94	101.58
U1442A 30R2-W 21/27	axial	BB	258.44	56.03	0.30	13.56	8.05	0.16	9.42	10.21	2.15	0.52	0.05	11.59	100.98
U1442A 20R1-104/108	off-axis	HSB	160.64	58.68	0.22	11.96	7.86	0.14	10.62	6.76	2.23	0.57	0.05	4.88	99.21
U1442A 22R1-122/125	off-axis	HSB	180.22	54.00	0.13	9.76	8.92	0.15	17.39	7.13	1.07	0.28	0.04	1.34	99.08
U1442A 47R1-W 50/55	off-axis	HSB	423.10	57.60	0.36	15.47	8.09	0.12	8.13	8.45	2.17	0.38	0.06	7.41	98.62
U1442A 23R2-W 30/35	off-axis	HSB	190.46	57.21	0.22	12.62	8.70	0.18	11.92	6.54	2.14	1.17	0.04	10.86	101.02
U1442A 28R1-W 10/14	off-axis	HSB	237.50	57.54	0.19	11.24	8.56	0.15	13.85	6.87	1.72	0.63	0.04	4.12	100.01
U1442A 48R1-W 87/92	off-axis	HSB	433.17	57.28	0.36	15.55	8.06	0.12	8.52	8.05	2.20	0.51	0.06	5.92	99.56
U1442A 15R1-W 70/75	off-axis	HSB	119.40	55.50	0.16	11.04	8.70	0.17	15.85	7.42	1.30	0.42	0.04	3.38	98.35
U1442A 13R1-W 4/10	off-axis	HSB	110.94	60.08	0.18	11.82	9.07	0.15	10.26	6.79	1.95	0.81	0.05	4.37	100.94
U1439C 5R1-W 92/96	off-axis	HSB	212.32	60.34	0.19	12.75	8.09	0.13	9.01	7.31	2.24	0.61	0.05	3.54	100.75

Table 4.2: continued

				Major Element Concentrations (wt%)											
Sample	Series	Type	Depth (mbsl)	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Sum
U1440 - Fore-arc Basalts (FABs)															
U1440B 17R2-23/32	axial	N-FAB	213.80	50.29	1.21	15.28	12.86	0.19	7.03	11.39	2.36	0.38	0.11	1.70	101.22
U1440B 26R1-64/68	axial	N-FAB	271.14	50.93	1.05	14.90	11.45	0.17	7.63	12.40	2.19	0.26	0.11	0.70	101.19
U1440B 28R1-31/38	axial	N-FAB	290.31	50.80	1.10	14.11	13.35	0.21	7.18	11.46	2.11	0.11	0.09	1.30	100.62
U1440B-8R-1-W 20/23	off-axis	N-FAB	136.54	50.71	0.99	14.40	13.56	0.20	6.66	11.47	2.21	0.32	0.09	0.56	100.70
U1440B-12R-2-W 4/8	off-axis	P-FAB	165.14	50.41	0.59	15.61	10.03	0.17	8.22	13.18	1.61	0.44	0.07	1.26	100.41
U1440B-17R-1-W 11/13	axial	N-FAB	212.31	49.81	1.49	14.35	15.22	0.21	5.74	10.96	2.51	0.44	0.16	0.58	100.96
U1440B-29R-1-W 5/8	axial	N-FAB	299.75	50.26	1.09	13.89	14.25	0.20	7.42	11.24	2.10	0.28	0.09	2.19	100.89
U1441 - Fore-arc Basalts (FABs)															
U1441A-21R-1-W 37/42	axial	N-FAB	190.27	50.43	1.01	14.93	11.55	0.17	8.12	11.69	2.04	0.52	0.10	2.13	100.65
U1441-A3-19R1-66/72	off-axis	D-FAB	171.16	49.33	0.49	15.50	9.92	0.15	9.01	13.72	1.37	0.52	0.08	2.26	100.22

4.2.5. FAB & Boninite Petrogenesis

Radiogenic Hf-Nd-Pb isotope data clearly shows that all of the Expedition 352 FABs have a mantle source of 'Indian' provenance (**Fig. 4.9**) (Li *et al.* 2019), with a long depletion history in which a significant extraction event occurred 400-500 Ma (Yogodzinski *et al.* 2018). Melt models suggest that the Indian mantle source experienced at least two distinct melting events during FAB genesis (Shervais *et al.* 2019). The first melting event involved 1 - 3% anhydrous decompression melting in the garnet-stability field, leaving a depleted mantle source relative to the DMM. The melt was extracted from the source prior to the second melting stage and is possibly similar to the Yogodzinski *et al.* (2018) proposed depletion event (Li *et al.* 2019). The second stage of decompression melting produced the FAB chemistry observed in the IODP cores. 7-15% melting in the spinel-stability field was required to create the N-FABs, 20% melting to create P-FABs, and 23% melting to create D-FABs. There is no evidence of subduction fluid or sediment input into FABs. Th/Yb shows no enrichment relative to Nb/Yb when compared to MORB (Shervais *et al.* 2019) and Sm-Nd-Hf-Pb isotope data shows no evidence of fluid or sediment input (Li *et al.* 2019). The lack of a subduction component in Expedition 352 FABs, suggests that FABs either formed immediately before subduction initiated, or immediately after, before the Pacific plate had subducted sufficiently to release components to the overlying wedge. Regional-scale sampling via dredging showed that FABs exist on a spectrum that extends from subduction-free FAB to FAB with subduction enrichment (Reagan *et al.* 2010). Li *et al.* (2019) therefore concluded that FAB genesis most likely began immediately after subduction initiation, with melting invoked by sea-floor spreading due to slab-roll back, where rapid mantle upwelling minimised the subduction component input where Expedition 352 sampled (**Fig. 4.10**).

Expedition 352 boninites first appeared ~ 1 Ma after the FABs (Reagan *et al.* 2019). Low concentrations of incompatible elements such as TiO₂ and HREE relative to FABs suggest that boninites have mantle sources even more depleted than FABs (Li *et al.* 2019). Radiogenic Sm-Nd-Hf-Pb data from Li *et al.* (2019) shows that the most likely boninite source was the depleted FAB mantle. The lower ϵ_{Hf_i} and $^{208}\text{Pb}/^{204}\text{Pb}$ of boninites relative to FABs is interpreted as involvement from a melt with 'Pacific' provenance (**Fig. 4.9**) from the newly-subducting slab that was not seen during FAB genesis (Li *et al.* 2019). Low boninite Sm/Hf and Sm/Zr suggests that the slab component was an amphibolite-facies slab melt (Li *et al.* 2019). Amphibole in the slab retained Sm, but slab temperatures were sufficient to dissolve significant zircon and release Hf into the melt (Pearce 1992; Tollstrup *et al.* 2010; Li *et al.* 2013). The LREE-depletion of axial LSBs versus the LREE-enrichment of off-axis HSBs, plus HSBs having lower ϵ_{Nd_i} and lower or similar ϵ_{Hf_i} to LSBs, is interpreted as evidence of a LREE-enriched subduction component in HSBs from Pacific Pelagic

Sediment (PPS) (Li *et al.* 2019). The PPS were initially accreted rather than subducted and therefore not present in LSBs (Li *et al.* 2019; Maunder *et al.* 2020). Li *et al.* (2019) proposed that the transition from accreted to subducted PPS was triggered by increased subduction rate and slab dip. Melting models from Shervais *et al.* (2021) show that the LSB compositions could be reproduced with $\sim 15 - 20\%$ spinel-facies melting of the residual FAB source, with no more than 2 - 3% total slab melt flux to the mantle wedge. HSB compositions could be matched by either: (1) fluxing the residual FAB source with 1 - 2% slab melt and 1% subducted sediment-derived melt, followed by $\sim 10\%$ spinel-facies melting, or (2) 1 - 1.5% slab melt, 0.5 - 1% sediment melt, followed by $\sim 10 - 15\%$ spinel-facies melting of LSB residue after 15% melt extraction and 1% of melt is retained (Shervais *et al.* 2021). These two scenarios were interpreted as end members and that the actual HSB source was likely a mixture of both FAB and LSB residues. In addition, a flux of some kind of aqueous fluid is required to reach observed FME concentrations (Shervais *et al.* 2021).

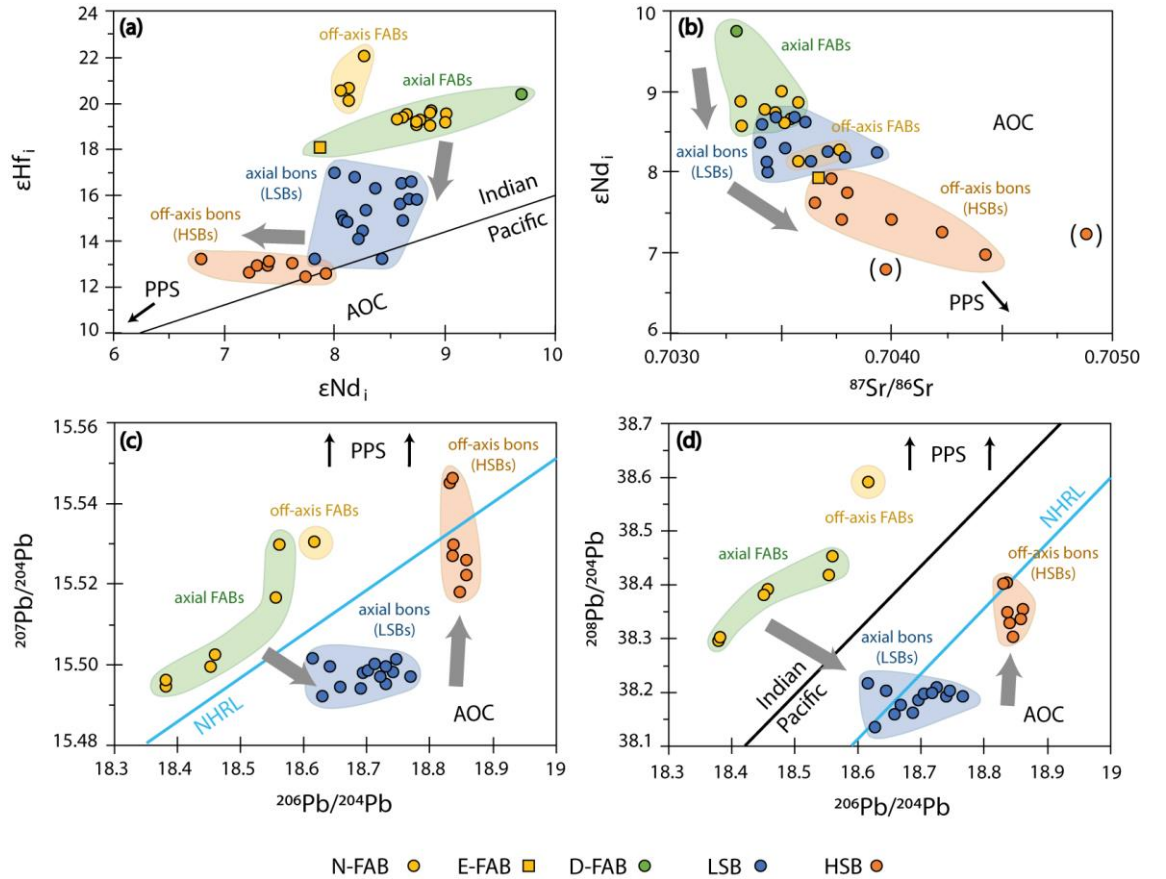
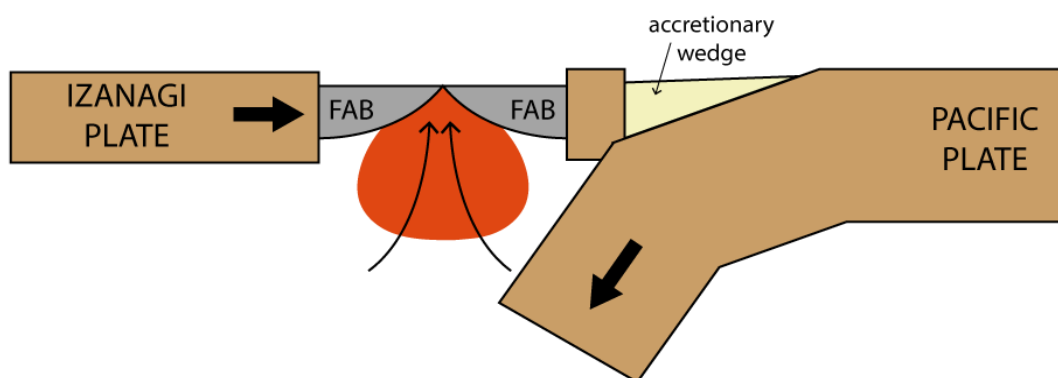


Figure 4.9: Nd, Hf, Sr and Pb isotope measurements for IODP Expedition 352 fore-arc basalts (FABs) and boninites, showing the evolution of magmatism throughout the early stages of subduction. Figure is adapted from Li *et al.* (2019).

(a) Schematic sketch of fore-arc basalt (FAB) formation:



(b) Schematic sketch of high-Si boninite (HSB) and low-Si boninite (LSB) formation:

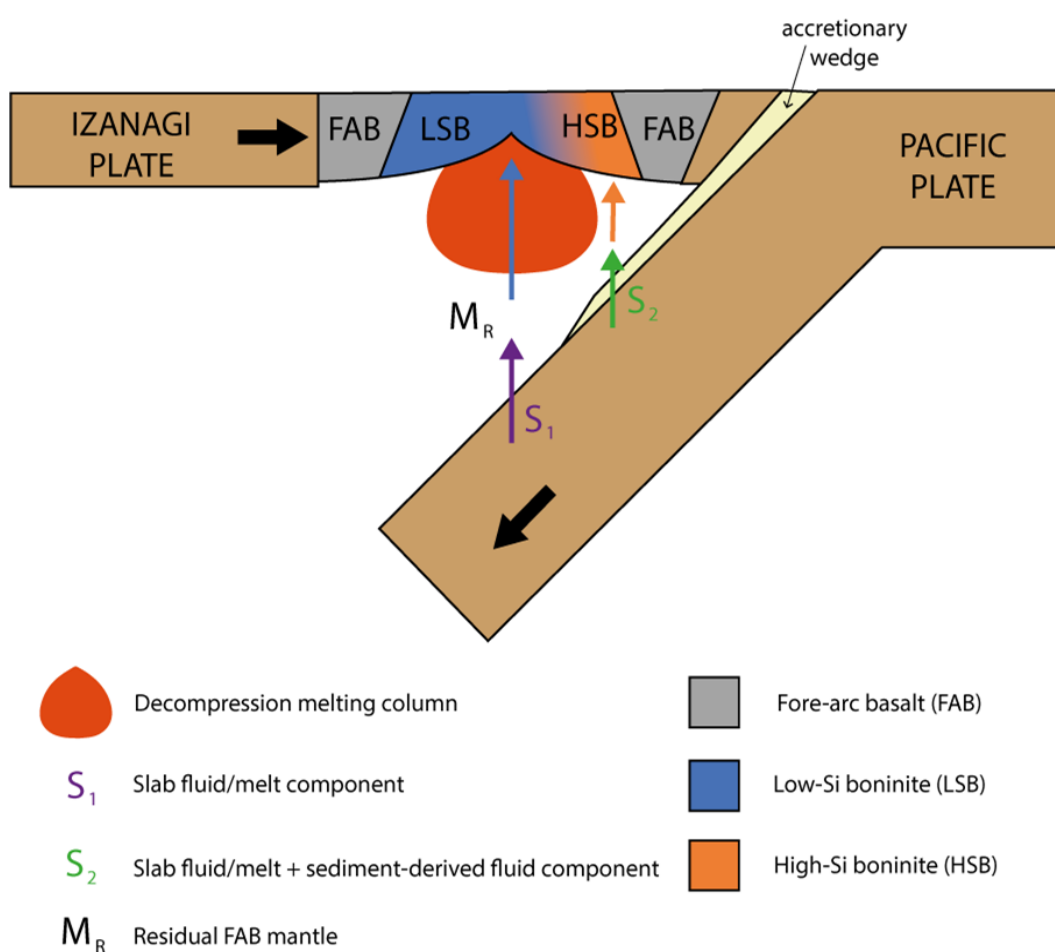


Figure 4.10: Schematic sketch showing the conceptual model of FAB and boninite generation during the early stages of subduction at the site of IODP Expedition 352. The model is based on Li et al. (2019). **(a)** the generation of FABs by anhydrous decompression melting due to slab rollback. **(b)** the generation of boninites when the slab has subducted sufficient to introduce slab fluid/melts and sediments to the depleted FAB residue in the mantle wedge.

4.3. Methods & Results

4.3.1. Sample Selection

The nine FABs and forty boninites selected for Fe isotope measurement in this study were chosen because they belong to a set of fresh, well-characterised Expedition 352 POOL samples. The POOL samples were chosen during shipboard Expedition 352 sampling to encompass the full chemical variation exposed by the four drill cores. The goal of the POOL samples was to create a cross-calibrated and self-consistent database of major, trace, and isotope data on the same set of homogenous whole-rock powders. The samples were chosen in aid of on-board pXRF data (Ryan *et al.* 2017), and log and petrological descriptions (Reagan *et al.* 2015) to ensure that they were the most representative and the freest from alteration. The POOL samples have been measured for major, trace and radiogenic Sr-Nd-Pb-Hf isotope data by previously published studies (Li *et al.* 2019) and under preparation for publication studies (Godard *et al.* in prep). The samples included in this study were chosen to encompass the freshest POOL samples that covered a wide range of chemical variation.

The six ODP Leg 125 Torishima harzburgites and dunites included in this study were chosen because they are interpreted as the residues of 20% to 25% fractional mantle melting in a suprasubduction zone environment and are in close proximity to the Expedition 352 site (Parkinson & Pearce 1998). They can therefore potentially be used as an analogue for the FAB and boninite source after melt extraction.

4.3.2. Trace Elements

Selected pre-existing, but at present unpublished trace element data can be found in **Table 4.3**, with the full dataset in **Appendix C**. Most POOL sample trace element analyses were conducted by Expedition 352 cruise participants at the Open University using an ICP-QQQ MS by methods similar to those described in Chapter 2. A few additional samples were measured as part of an interlaboratory comparison of POOL sample trace element data, co-ordinated by Margo Godard at the University of Montpellier. Data for those samples has been cross calibrated, and the full IODP POOL trace element dataset is under preparation for publication (Godard *et al.* in prep).

Table 4.3: Selected trace element concentrations ($\mu\text{g.g}^{-1}$) IODP Expedition 352 fore-arc basalts and boninites. Rock type abbreviations are as such: N-FAB (normal fore-arc basalt), P-FAB (primitive fore-arc basalt), D-FAB (depleted fore-arc basalt), LSB (low-Si boninite), HSB (high-Si boninite), BB (basaltic boninite), HMA (high-magnesian andesite). All data is awaiting publication in Godard et al. (in prep).

					Trace Element Concentrations (μg.g ⁻¹)													
Sample	Series	Type	Depth (mbsl)	Source	V	Zn	Rb	Sr	Zr	Nb	Ba	La	Ce	Nd	Sm	Yb	Hf	Pb
U1439 - Boninites																		
U1439C 16R1-26/30	axial	LSB	299.76	OU	137	43.7	8.51	114	29.5	0.48	17.8	0.83	2.51	2.20	0.75	0.74	0.79	0.95
U1439C 22R1-89/95	axial	LSB	349.19	OU	136	45.6	8.78	106	29.2	0.45	12.5	0.84	2.62	2.40	0.83	0.77	0.78	0.69
U1439C 41R1-99/106	axial	LSB	515.09	OU	186	45.1	0.87	116	31.3	0.49	6.6	0.98	3.21	3.29	1.19	1.23	0.88	0.33
U1439C-29R-4-W 78/82	axial	LSB	421.29	OU	125	47.8	2.10	65	21.9	0.37	2.9	0.57	1.65	1.51	0.52	0.55	0.57	0.60
U1439C-31R-5-W 12/17	axial	LSB	441.80	OU	149	54.0	8.08	103	24.2	0.50	13.6	0.74	2.18	2.14	0.76	0.80	0.67	0.44
U1439C 19R4 11/17	axial	LSB	333.16	OU	142	59.3	4.21	123	29.6	0.48	4.3	0.95	2.62	2.40	0.82	0.92	0.80	0.80
U1439C 40R1 33/38	axial	LSB	509.43	OU	164	66.8	13.51	146	28.7	0.61	78.2	1.18	3.21	2.82	0.93	0.97	0.77	0.91
U1439C 31R1 15/20	axial	LSB	436.25	OU	132	48.1	7.13	100	21.8	0.46	15.0	0.65	1.60	1.38	0.46	0.56	0.60	0.66
U1439C 26R1 132/137	axial	LSB	388.62	OU	133	54.0	5.57	102	26.8	0.46	3.5	0.87	2.46	2.21	0.73	0.65	0.71	0.65
U1439C 19R3 58/62	axial	LSB	332.22	OU	131	79.7	9.99	117	29.6	0.52	16.6	0.82	2.54	2.25	0.77	0.78	0.79	0.82
U1439C 11R1 124/127	axial	LSB	266.64	OU	137	58.8	6.12	64	24.1	0.45	4.3	0.53	1.90	1.89	0.70	0.65	0.68	0.48
U1439C 33R2-W 23/30	axial	LSB	457.17	Lab A	129	46.2	2.07	102	23.8	0.40	11.6	0.64	1.75	1.56	0.51	0.55	0.76	0.66
U1439C 38R1 103/106	axial	LSB	495.63	Lab E	177	51.4	1.78	162	35.6	0.58	7.4	0.95	2.92	2.47	0.85	0.87	0.95	1.21
U1439C 27R3-W 80/87	axial	LSB	400.47	Lab A	126	48.1	5.00	109	20.5	0.40	9.5	0.78	1.95	1.69	0.53	0.58	0.58	0.71
U1439C 23R1-W 42/48	axial	LSB	358.52	Lab A	162	61.5	13.70	76	31.8	0.57	17.1	0.70	2.66	2.16	0.79	0.84	0.84	0.77
U1439C 28R2-W 66/71	axial	LSB	408.91	Lab C	98	39.6	6.06	108	23.1		6.8	0.78	2.06	1.79	0.58	0.59	0.63	1.24
U1439C-10R2-W 13/19	axial	BB	262.03	OU	180	60.3	9.25	100	29.8	0.54	10.7	0.99	2.94	2.83	0.97	0.87	0.83	0.64
U1439C-37R1-W 42/48	axial	HMA	485.22	OU	185	36.5	2.50	175	33.6	0.58	16.8	1.30	3.63	3.07	1.01	0.90	0.93	0.66
U1439C 4R1-W 26/32	off-axis	HSB	201.86	OU	145	49.2	17.84	123	32.1	0.56	25.6	1.01	2.42	1.81	0.55	0.63	0.85	1.23
U1439C 6R1 25/30	off-axis	HSB	221.45	OU	156	61.5	17.06	125	33.8	0.65	28.2	1.12	2.64	1.92	0.56	0.63	0.90	1.43
U1439C 2R3-W 38/46	off-axis	HSB	185.13	Lab A	155	54.4	11.79	77	21.3		20.5	0.82	1.79	1.32	0.41	0.51	0.69	1.02

Table 4.3: continued

Sample	Series	Type	Depth (mbsl)	Source	Trace Element Concentrations ($\mu\text{g}\cdot\text{g}^{-1}$)													
					V	Zn	Rb	Sr	Zr	Nb	Ba	La	Ce	Nd	Sm	Yb	Hf	Pb
U1439A 23X1-W 0/3	off-axis	HSB	196.20	Lab A	155	112.5	12.44	74	17.8	0.52	18.1	0.77	1.63	1.17	0.35	0.47	0.53	0.97
U1439A 21X1-W 0/7	off-axis	HSB	182.50	Lab A	159	75.2	13.24	78	19.0	0.52	19.0	0.78	1.68	1.21	0.35	0.48	0.57	1.06
U1439C 5R1-W 92/96	off-axis	HSB	212.32	Lab A	167	58.6	15.04	119	33.5	0.72	29.1	1.12	2.76	1.76	0.53	0.63	0.90	1.40
U1442 - Boninites																		
U1442A-35R-1-W 51/55	axial	LSB	306.01	OU	171	198.0	8.52	168	37.3	0.60	17.7	1.33	3.64	3.08	1.01	0.95	1.01	1.01
U1442A 23R1 99/103	axial	LSB	189.69	OU	147	67.6	25.79	83	21.1	0.47	17.4	1.83	2.23	2.19	0.56	0.61	0.54	0.92
U1442A 56R1 19/24	axial	LSB	510.49	OU	189	53.5	1.17	188	31.9	0.60	4.1	1.26	3.11	2.54	0.82	0.78	0.84	0.87
U1442A 49R2-W 60/65	axial	LSB	443.85	Lab D	201		0.87	169	30.8	0.56	5.2	1.63	4.27	3.34	1.09	1.07	0.93	
U1442A 36R2-W 17/22	axial	LSB	316.50	Lab A	219	80.6	2.50	117	26.9	0.57	7.2	1.01	2.73	2.53	0.84	0.97	0.79	0.64
U1442A 54R1-W 13/18	axial	LSB	490.93	Lab D	183		1.40	172	27.3	0.44	5.2	1.36	3.66	2.78	0.89	0.82	0.79	
U1442A 57R2-W 116/121	axial	LSB	522.63	Lab A	190	60.0	1.36	121	25.7	0.52	2.8	0.95	2.60	2.14	0.73	0.88	0.72	0.75
U1442A 30R2-W 21/27	axial	BB	258.44	Lab C	152	42.5	6.04	109	23.9	0.45	8.7	0.81	2.13	2.02	0.70	0.82	0.67	1.10
U1442A 20R1-104/108	off-axis	HSB	160.64	OU	134	46.9	13.45	136	34.6	0.68	22.4	1.21	3.04	2.25	0.69	0.65	0.97	1.11
U1442A 22R1-122/125	off-axis	HSB	180.22	OU	129	49.6	9.58	63	17.2	0.35	15.8	0.60	1.40	1.05	0.32	0.46	0.46	0.80
U1442A 47R1-W 50/55	off-axis	HSB	423.10	Lab A	171	51.7	5.88	121	27.5	0.54	12.1	0.89	2.50	1.93	0.64	0.77	0.73	0.64
U1442A 23R2-W 30/35	off-axis	HSB	190.46	Lab A	151	59.1	14.05	101	34.1	0.63	22.1	0.85	2.53	1.90	0.67	0.74	0.94	1.27
U1442A 28R1-W 10/14	off-axis	HSB	237.50	Lab D	151		13.31	93	29.0	0.51	20.4	0.94	2.36	1.57	0.48	0.58	0.85	0.27
U1442A 48R1-W 87/92	off-axis	HSB	433.17	Lab D	166		8.28	124	25.9	0.46	12.3	1.00	2.78	2.22	0.74	0.90	0.78	1.88
U1442A 15R1-W 70/75	off-axis	HSB	119.40	Lab A	165	53.5	11.12	62	18.6	0.41	17.3	0.60	1.28	0.98	0.30	0.47	0.60	0.94
U1442A 13R1-W 4/10	off-axis	HSB	110.94	Lab A	172	59.0	19.25	94	31.0	0.75	30.7	1.15	2.65	1.64	0.47	0.57	0.81	1.54

Table 4.3: continued

					Trace Element Concentrations (μg.g ⁻¹)													
Sample	Series	Type	Depth (mbsl)	Source	V	Zn	Rb	Sr	Zr	Nb	Ba	La	Ce	Nd	Sm	Yb	Hf	Pb
U1440 - Fore-arc Basalts (FABs)																		
U1440B 17R2-23/32	axial	N-FAB	213.80	OU	461	137.9	7.18	61	47.0	1.06	9.9	1.37	4.58	5.11	2.08	2.74	1.48	0.41
U1440B 26R1-64/68	axial	N-FAB	271.14	OU	342	87.3	4.87	57	51.7	1.03	3.9	1.38	4.71	5.56	2.29	3.14	1.61	0.29
U1440B 28R1-31/38	axial	N-FAB	290.31	OU	412	104.2	0.92	57	44.2	1.03	10.6	1.26	4.23	4.82	1.97	2.88	1.40	0.19
U1440B-8R-1-W 20/23	off-axis	N-FAB	136.54	OU	393	103.5	5.93	63	40.3	1.05	8.0	1.54	4.59	5.04	2.02	2.87	1.27	0.28
U1440B-12R-2-W 4/8	off-axis	P-FAB	165.14	OU	274	69.1	6.28	52	23.4	0.62	5.5	0.90	2.83	3.01	1.22	1.80	0.73	0.24
U1440B-17R-1-W 11/13	axial	N-FAB	212.31	OU	509	124.8	8.00	69	61.0	1.35	15.2	1.92	6.17	6.85	2.78	3.89	1.99	0.35
U1440B-29R-1-W 5/8	axial	N-FAB	299.75	OU	399	98.0	11.96	58	43.4	1.04	6.6	1.28	4.37	4.91	2.02	2.79	1.39	0.23
U1441 - Fore-arc Basalts (FABs)																		
U1441A-21R-1-W 37/42	axial	N-FAB	190.27	OU	339	85.3	7.50	55	39.5	0.80	4.4	1.21	4.07	4.80	2.00	2.93	1.24	0.20
U1441-A3-19R1-66/72	off-axis	D-FAB	171.16	OU	252	64.1	6.29	41	15.1	0.29	7.4	0.42	1.48	1.89	0.85	1.51	0.52	0.07

4.3.3. Iron Isotopic Compositions

All Fe isotope data was collected at Durham University in the Arthur Holmes Isotope labs. Full methods are outlined in Chapter 2 and all results are presented in **Table 4.4**. The Fe isotopic compositions of reference materials processed with the samples agree with accepted literature values, and are presented in Chapter 2. Total procedural blanks processed with every batch of 12 samples are detailed in Chapter 2 and were always $< 74 \text{ ng.g}^{-1} \text{ Fe}$, which is negligible relative to the total amount of Fe processed (3000-11,000 μg).

Table 4.4: Iron isotope ratios measured in the IODP Expedition 352 FABs and boninites and ODP Leg 125 Torishima harzburgites and dunites reported as $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ (‰) relative to reference standard NRM-524. Rock type abbreviations are as such: N-FAB (normal fore-arc basalt), P-FAB (primitive fore-arc basalt), D-FAB (depleted fore-arc basalt), LSB (low-silica boninite), HSB (high-silica boninite), BB (basaltic boninite), HMA (high-magnesian andesite). All isotope measurements were conducted on Neptune MC-ICP MS.

				Iron Isotopes				
Sample	Series	Type	Depth (mbsl)	$\delta^{56}\text{Fe}_{\text{NRM-524}}$ (‰)	error (2SD)	$\delta^{57}\text{Fe}_{\text{NRM-524}}$ (‰)	error (2SD)	n
U1439C - Boninites								
U1439C 16R1-26/30	axial	LSB	299.76	0.098	0.046	0.156	0.074	8
U1439C 22R1-89/95	axial	LSB	349.19	0.060	0.026	0.086	0.039	3
U1439C 41R1-99/106	axial	LSB	515.09	0.046	0.045	0.068	0.063	6
U1439C-29R-4-W 78/82	axial	LSB	421.29	0.051	0.032	0.074	0.031	6
U1439C-31R-5-W 12/17	axial	LSB	441.8	0.045	0.051	0.065	0.075	8
U1439C 19R4 11/17	axial	LSB	333.16	0.120	0.026	0.178	0.026	4
U1439C 40R1 33/38	axial	LSB	509.43	0.072	0.028	0.118	0.037	5
U1439C 31R1 15/20	axial	LSB	436.25	0.061	0.036	0.087	0.034	4
U1439C 26R1 132/137	axial	LSB	388.62	0.068	0.039	0.101	0.069	4
U1439C 19R3 58/62	axial	LSB	332.22	0.056	0.036	0.085	0.065	4
U1439C 11R1 124/127	axial	LSB	266.64	-0.032	0.021	-0.054	0.038	4
U1439C 33R2-W 23/30	axial	LSB	457.17	0.016	0.047	0.014	0.054	4
U1439C 38R1 103/106	axial	LSB	495.63	-0.012	0.030	-0.028	0.046	3
U1439C 27R3-W 80/87	axial	LSB	400.47	-0.008	0.052	-0.021	0.076	9
U1439C 23R1-W 42/48	axial	LSB	358.52	0.036	0.037	0.063	0.048	4
U1439C 28R2-W 66/71	axial	LSB	408.91	0.049	0.041	0.079	0.038	3
U1439C-10R2-W 13/19	axial	BB	262.03	0.004	0.018	0.005	0.028	5
U1439C-37R1-W 42/48	axial	HMA	485.22	0.068	0.038	0.107	0.056	5
U1439C 4R1-W 26/32	off-axis	HSB	201.86	0.057	0.008	0.091	0.033	3
U1439C 6R1 25/30	off-axis	HSB	221.45	0.049	0.037	0.077	0.047	3
U1439C 2R3-W 38/46	off-axis	HSB	185.13	0.040	0.049	0.062	0.057	6
U1439A 23X1-W 0/3	off-axis	HSB	196.2	0.056	0.018	0.083	0.021	3
U1439A 21X1-W 0/7	off-axis	HSB	182.5	0.064	0.042	0.094	0.059	3
U1439C 5R1-W 92/96	off-axis	HSB	212.32	0.013	0.035	0.025	0.038	6

Table 4.4: continued

				Iron Isotopes				
Sample	Series	Type	Depth (mbsl)	$\delta^{56}\text{Fe}_{\text{NRM-524}} (\text{‰})$	error (2SD)	$\delta^{57}\text{Fe}_{\text{NRM-524}} (\text{‰})$	error (2SD)	n
U1442A - Boninites								
U1442A-35R-1-W 51/55	axial	LSB	306.01	0.085	0.041	0.125	0.059	3
U1442A 23R1 99/103	axial	LSB	189.69	0.037	0.026	0.070	0.056	3
U1442A 56R1 19/24	axial	LSB	510.49	0.054	0.019	0.088	0.046	4
U1442A 49R2-W 60/65	axial	LSB	443.85	0.052	0.033	0.099	0.084	4
U1442A 36R2-W 17/22	axial	LSB	316.495	0.092	0.048	0.138	0.053	8
U1442A 54R1-W 13/18	axial	LSB	490.93	0.056	0.044	0.089	0.079	7
U1442A 57R2-W 116/121	axial	LSB	522.63	0.088	0.032	0.130	0.043	4
U1442A 30R2-W 21/27	axial	BB	258.435	0.075	0.043	0.099	0.084	5
U1442A 20R1-104/108	off-axis	HSB	160.64	0.009	0.037	0.026	0.058	3
U1442A 22R1-122/125	off-axis	HSB	180.22	0.069	0.047	0.095	0.064	5
U1442A 47R1-W 50/55	off-axis	HSB	423.1	0.057	0.050	0.111	0.071	3
U1442A 23R2-W 30/35	off-axis	HSB	190.46	0.023	0.039	0.025	0.075	4
U1442A 28R1-W 10/14	off-axis	HSB	237.5	0.082	0.048	0.108	0.069	4
U1442A 48R1-W 87/92	off-axis	HSB	433.17	0.056	0.029	0.074	0.067	5
U1442A 15R1-W 70/75	off-axis	HSB	119.4	0.055	0.043	0.066	0.055	3
U1442A 13R1-W 4/10	off-axis	HSB	110.94	0.029	0.041	0.064	0.055	5
U1440B - Fore-arc basalts								
U1440B 17R2-23/32	axial	N-FAB	213.8	0.099	0.042	0.144	0.059	3
U1440B 26R1-64/68	axial	N-FAB	271.14	0.083	0.038	0.119	0.078	3
U1440B 28R1-31/38	axial	N-FAB	290.31	0.160	0.043	0.239	0.079	9
U1440B-8R-1-W 20/23	off-axis	N-FAB	136.54	0.015	0.025	0.011	0.039	3
U1440B-12R-2-W 4/8	off-axis	P-FAB	165.14	0.097	0.046	0.137	0.065	6
U1440B-17R-1-W 11/13	axial	N-FAB	212.31	0.086	0.050	0.129	0.070	8
U1440B-29R-1-W 5/8	axial	N-FAB	299.75	0.084	0.046	0.122	0.099	3
U1441A - Fore-arc basalts								
U1441A-21R-1-W 37/42	axial	N-FAB	190.27	0.077	0.012	0.121	0.014	3
U1441-A3-19R1-66/72	off-axis	D-FAB	171.16	0.066	0.049	0.096	0.073	7
ODP Leg 125 - Torishima Peridotites								
783A-18R1-064/071	Torishima Forearc Seamount	Harz		-0.005	0.043	-0.004	0.059	3
784A-38R2-072/077		Dunite		0.100	0.042	0.157	0.089	4
784A-40R2-070/075		Dunite		-0.020	0.049	-0.038	0.043	3
784A-45R2-33/38		Harz		-0.037	0.048	-0.051	0.086	9
784A-45R-CC-7/10		Harz		0.026	0.043	0.041	0.054	8
783A-18R1-119-124		Harz		0.070	0.029	0.102	0.062	3

4.3.3.1. Fore-arc Basalt Fe Isotopic Compositions

The Expedition 352 FABs have a $\delta^{56}\text{Fe}$ range of 0.145 ‰ and a mean of 0.085 ± 0.075 ‰ (**Fig. 4.11**). FAB $\delta^{56}\text{Fe}$ does not correlate with any major or trace element concentrations or radiogenic isotopic ratios. The D-FAB is not isotopically distinct from the N-FABs (**Fig. 4.11**). FAB and MORB $\delta^{56}\text{Fe}$ ranges are similar (0.145 ‰ vs 0.126 ‰), but on average FABs are slightly isotopically lighter than MORB (FAB average $\delta^{56}\text{Fe} = 0.085 \pm 0.075$ ‰ and MORB average $\delta^{56}\text{Fe} = 0.104 \pm 0.055$ ‰) (**Fig. 4.11**). However, student T-tests that test for a statistically significant difference between the means of two sample populations, produced a p-value of 0.171, showing that at a 95% confidence interval, there is not enough evidence for FAB and MORB $\delta^{56}\text{Fe}$ to be distinguished. However, there is the caveat that many more MORB ($n = 81$) were analysed compared to FAB ($n = 9$).

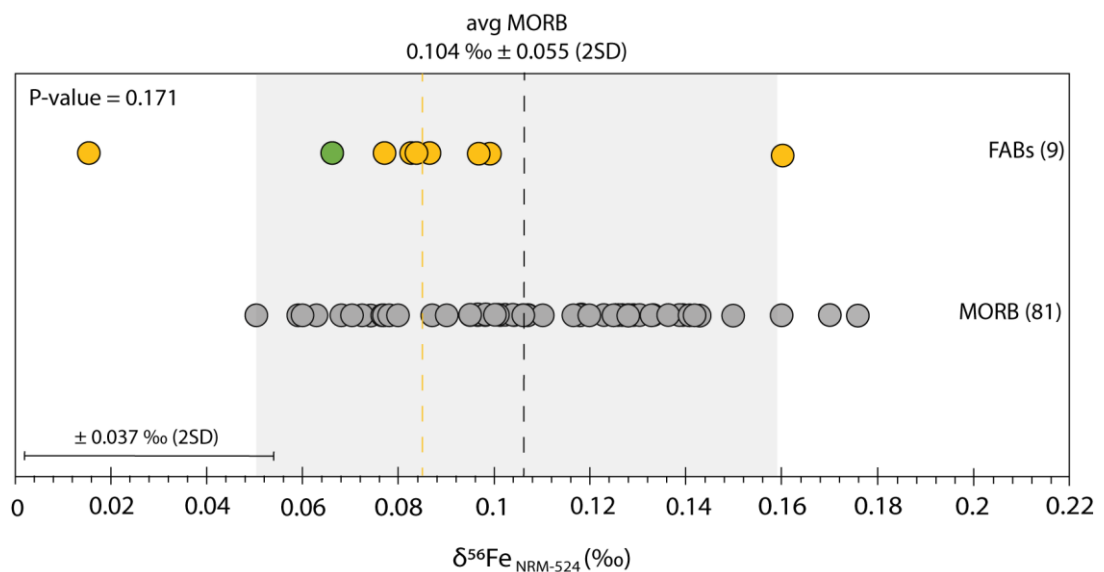


Figure 4.11: Comparison and student T-test results of fore-arc basalt (FAB) and MORB $\delta^{56}\text{Fe}$. The FAB data is from this study, and the MORB data is from Weyer & Ionov (2007), Nebel et al. (2013), Teng et al. (2013) and Chen et al. (2019). The vertical dashed lines represent the averages for each population that were compared in the student T-tests, and are colour coded to match the data point colours. The MORB average $\delta^{56}\text{Fe}$ is 0.104 ± 0.055 (2SD) and the FAB $\delta^{56}\text{Fe}$ average is 0.085 ± 0.075 . The average error on each data point is ± 0.037 ‰ (2SD). The p-value is from a student T-test. A p-value of less than 0.05 dictates that there is enough evidence for the population means to be distinguished at a 95% confidence interval.

4.3.3.2. Boninite Fe Isotopic Compositions

The Expedition 352 boninites have a $\delta^{56}\text{Fe}$ range of 0.152 ‰ and an average $\delta^{56}\text{Fe}$ composition of 0.050 ± 0.062 ‰. There are no clear correlations between the boninite $\delta^{56}\text{Fe}$ and any major or trace element concentrations or radiogenic isotopic compositions. The boninite range is slightly larger than the FAB $\delta^{56}\text{Fe}$ range (0.152 ‰ vs 0.145 ‰) and on average the boninites are isotopically lighter than the FABs ($\delta^{56}\text{Fe} = 0.050 \pm 0.062$ ‰ and 0.085 ± 0.075 ‰ respectively) (**Figure 4.12**). A student T-test comparing the FAB and boninite $\delta^{56}\text{Fe}$ means supports the boninites being on average isotopically

lighter than the FABs, despite both populations having large 2SD errors that overlap. The test returned a p-value of 0.005, showing that at a 95% confidence interval the FAB and boninite means can be considered statistically distinct (**Figure 4.12**). Boninites being isotopically lighter than FABs agrees with global arc lavas being isotopically lighter than MORB. Indeed, **Figure 4.13** shows that boninite and global arc lava $\delta^{56}\text{Fe}$ means cannot be distinguished to a 95% confidence interval.

The HSBs have a smaller $\delta^{56}\text{Fe}$ range than the LSBs (0.152 ‰ vs 0.073 ‰) but they have similar means (HSB $\delta^{56}\text{Fe} = 0.047 \pm 0.043$ ‰ and LSB $\delta^{56}\text{Fe} = 0.052 \pm 0.072$ ‰) (**Figure 4.12**). A student T-test comparing the HSB and LSB $\delta^{56}\text{Fe}$ produced a p-value of 0.610 showing that at a 95% confidence interval HSB and LSB means cannot be distinguished (**Figure 4.12**).

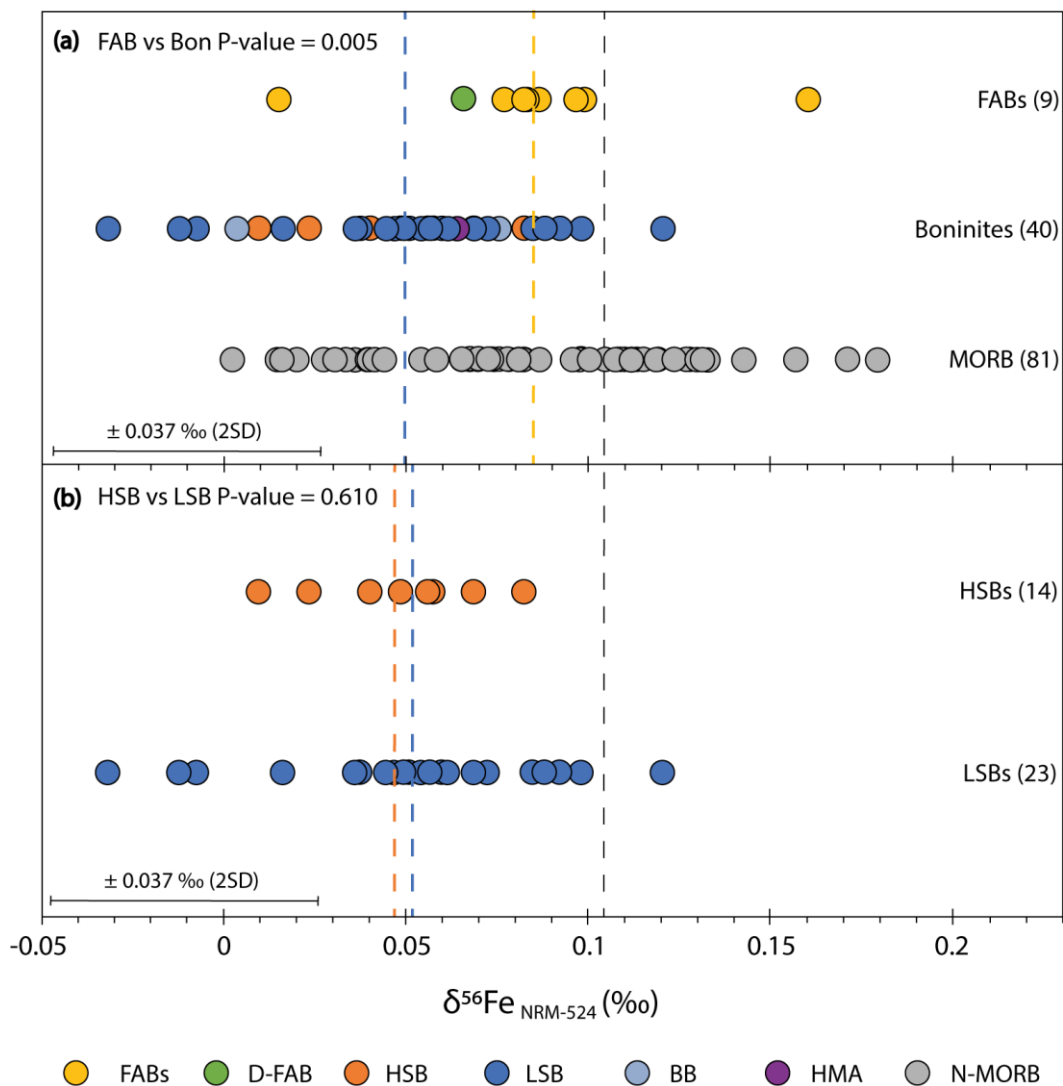


Figure 4.12: Comparison and student *T*-test results of **(a)** fore-arc basalt (FAB) and boninite $\delta^{56}\text{Fe}$ compositions, with MORB data for reference; **(b)** high-silica boninite (HSB) and low-silica boninite (LSB) $\delta^{56}\text{Fe}$ compositions. The FAB and boninite data is from this study, and the MORB data is from Weyer & Ionov (2007), Nebel et al. (2013), Teng et al. (2013) and Chen et al. (2019). The vertical dashed lines represent the averages for each population that were compared in the student *T*-tests, and are colour coded to match the data point colours. The MORB average $\delta^{56}\text{Fe}$ is $0.104 \text{ ‰} \pm 0.037$ (2SD), the FAB $\delta^{56}\text{Fe}$ average is $0.085 \text{ ‰} \pm 0.075$, the

boninite average is $0.050\text{‰} \pm 0.062$, the HSB average is $0.047\text{‰} \pm 0.043$, and the LSB average is $0.052\text{‰} \pm 0.072$. The average error on each data point is $\pm 0.037\text{‰}$ (2SD). The p -values represent the p -values from student T -tests. A p -value of less than 0.05 dictates that there is enough evidence for the population means to be distinguished at a 95% confidence interval.

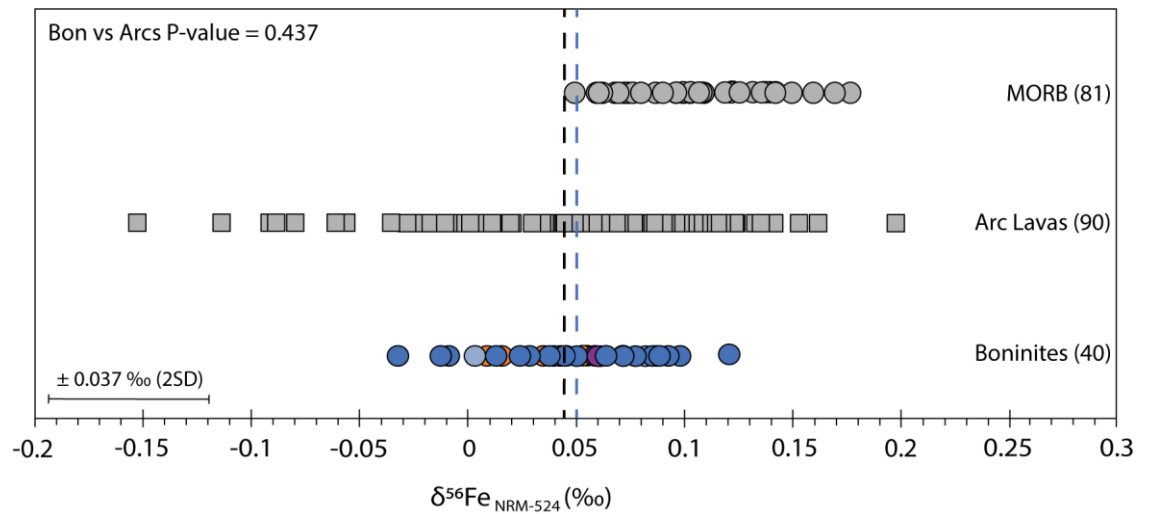


Figure 4.13: Comparison and student T -test results of oceanic arc lava and boninite $\delta^{56}\text{Fe}$. The boninite data is from this study, and the arc data is from Dauphas et al. (2009), Foden et al. (2018) and Williams et al. (2018). The MORB data is from Weyer & Ionov (2007), Nebel et al. (2013), Teng et al. (2013) and Chen et al. (2019). The vertical dashed lines represent the averages for each population that were compared in the student T -tests, and are colour coded to match the data point colours. The arc average $\delta^{56}\text{Fe}$ is $0.043\text{‰} \pm 0.124$ (2SD), and the boninite average is $0.050\text{‰} \pm 0.062$ (2SD). The average error on each data point is $\pm 0.037\text{‰}$ (2SD). The p -values represent the p -values from student T -tests. A p -value of less than 0.05 dictates that there is enough evidence for the population means to be distinguished at a 95% confidence interval.

4.4. Discussion

To re-examine the potential cause(s) of isotopically light Fe isotopes in arcs compared to MORB, this section will discuss the new FAB and boninite Fe isotope measurements. Recall that the specific power of this suite is that they are derived from the same mantle source and are close in space and time. FABs have a tectonic setting akin to MORB, without any evidence for subduction inputs. Whereas the boninites which erupted immediately after FAB generation, have clear and distinct subduction inputs including slab melts, fluids, and sediments. The potential cause(s) of isotopic variation(s) will be examined, weighing contributions from mantle versus subduction processes, and the implications of this work on deconvolving the origin of isotopically light arc lavas and subduction settings on a wider scale will be reviewed.

4.4.1. Fore-arc Basalt Fe Isotopic Compositions

The $\delta^{56}\text{Fe}$ similarity between FABs and MORB (**Figure 4.11**) may be explained by their similar petrogenetic origins; both form by anhydrous decompression melting during seafloor spreading.

However, the depletion of HFSEs, LREEs, Ti and P in FABs versus MORB implies FABs have a more depleted source. Trace element melt modelling also implies that N-FAB span spinel-facies melt degrees similar to MORB, but the D-FAB experienced higher melt degrees of 23% (Shervais *et al.* 2019). Previous work has suggested that Fe isotopes are sensitive to historic melt extraction (e.g. Nebel *et al.* 2015; Williams *et al.* 2018). The greater source depletion but similar partial melting extents of N-FABs compared to MORB suggests that if source depletion is a significant Fe isotope fractionation mechanism, FABs should have lighter $\delta^{56}\text{Fe}$ than MORB. However, the T-test result and the D-FAB not being isotopically distinct from the other FABs despite its greater inferred depletion (**Fig. 4.11**), do not support a melt extraction control on FAB $\delta^{56}\text{Fe}$. However, if Fe isotopes are fractionated during partial melting, the higher the degree of melt, the more closely the lava approximates its source (e.g. Sossi *et al.* 2016). Therefore, the higher degree of melt inferred for D-FAB makes direct comparison with N-FABs of smaller melt degrees challenging by obscuring $\delta^{56}\text{Fe}$ differences that may have been imparted by variable existing source depletion.

The two peripheral FABs in **Fig. 4.11** are conspicuous and isotopically different from the rest of the FABs. Both samples are N-FABs, and have no obvious petrographic or chemical differences from the other FABs. Since the FAB $\delta^{56}\text{Fe}$ range is comparable to the MORB $\delta^{56}\text{Fe}$, perhaps the two peripheral FABs only appear extreme due to the small number of FABs measured, and more FAB $\delta^{56}\text{Fe}$ data may fill in the gaps, and/or extend the range. However, they could also be truly extreme values. Therefore, the potential cause(s) for their isotopic differences will be examined.

Since Fe is fluid mobile, an obvious candidate is secondary alteration. However, these two FABs are not outliers in LOI or Ba concentrations (**Fig. 4.14**). K_2O concentrations are used in Coulthard *et al.* (2021) to suggest that FAB whole-rocks experienced secondary alteration and enrichment in K. The isotopically heaviest FAB has the lowest K_2O concentration of the FABs, suggesting a low degree of alteration. However, Fe isotope studies of altered oceanic crust (e.g. Rouxel *et al.* 2003) suggest that alteration preferentially removes light Fe from the crustal minerals. Therefore, the isotopically heaviest FAB should have the highest K_2O concentration if its Fe isotopic composition is largely alteration controlled. Therefore, alteration is not a likely candidate for the cause(s) of the $\delta^{56}\text{Fe}$ of either of the peripheral FABs. Magmatic differentiation is an unlikely candidate as well since there is no correlation between FAB $\delta^{56}\text{Fe}$ and MgO , and the two peripheral FABs are not anomalous in MgO concentrations (**Fig. 4.14**). Since neither of these FABs have unusually high phenocryst abundances (**Table 4.1**), accumulation is also an unlikely candidate. There is therefore no clear reason as to why the two peripheral FABs have Fe isotopic compositions that are more extreme than the other FABs. In which case they will not be considered anomalous.

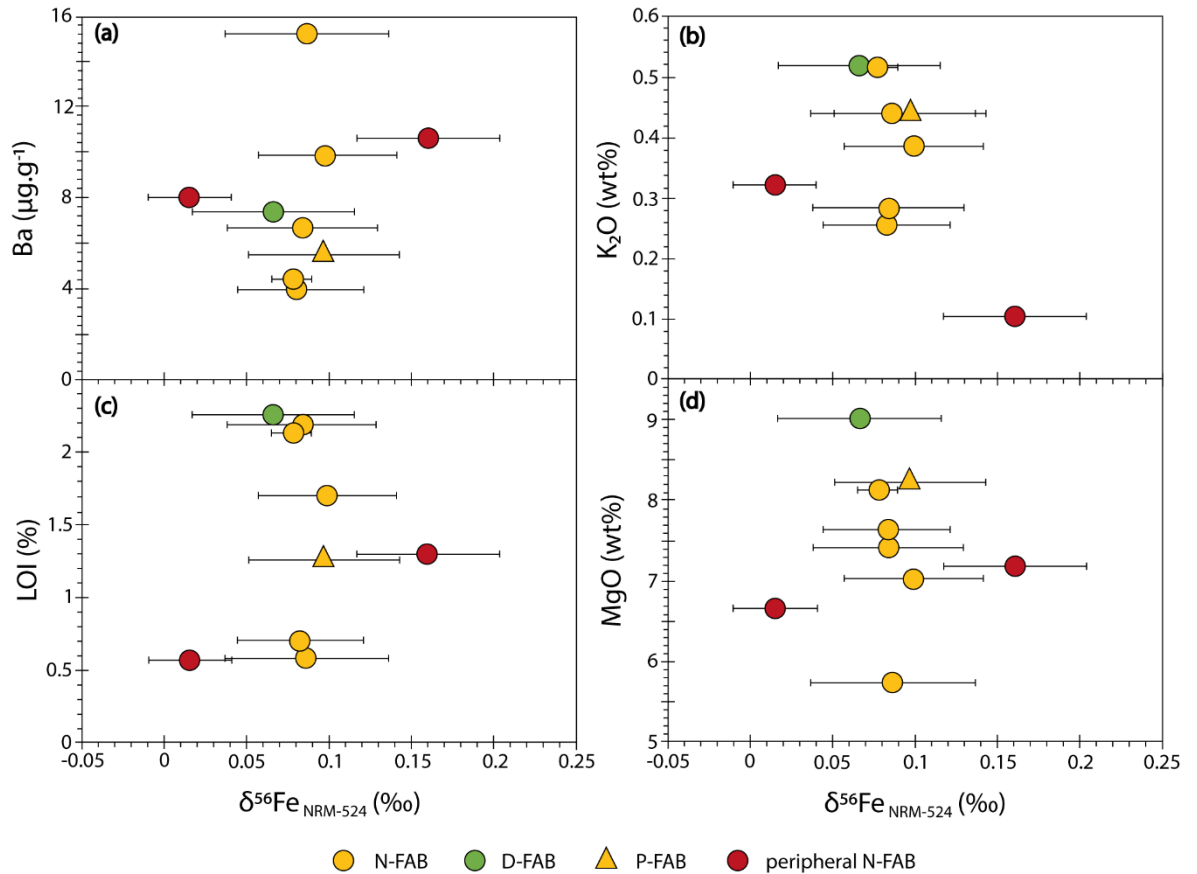


Figure 4.14: IODP Expedition 352 FAB $\delta^{56}\text{Fe}_{\text{NRM-524}}$ (‰) versus **(a)** Ba concentration ($\mu\text{g.g}^{-1}$); **(b)** K_2O concentration (wt%); **(c)** loss on ignition (%); **(d)** MgO concentration (wt%). The horizontal error bars represent 2SD based on at least three repeat measurements. The red symbols represent the two N-FABs with peripheral Fe isotopic compositions in Fig. 4.11.

4.4.2. Boninite Fe Isotope Compositions

4.4.2.1. Comparison between Boninite and FAB Fe Isotopic Compositions

The key petrogenetic differences between FABs and boninites are the degree of source depletion, and the presence of subduction inputs. The isotopic difference between the FABs and boninites established in **Fig. 4.12** therefore may suggest that mantle processes and/or differences in subduction inputs may cause Fe isotopic fractionation, and may therefore be responsible for the isotopic differences between global arc lavas and MORB. However, the statistical similarity between HSB and LSB $\delta^{56}\text{Fe}$ (**Fig. 4.12**) suggests that the process(es) or component(s) responsible for the FAB-boninite $\delta^{56}\text{Fe}$ difference are common to all boninite types. The potential causes of Fe isotopic differences between the FABs and boninites will be discussed in turn.

4.4.2.2. Cause(s) of Fe isotopic difference between FABs and boninites

a) Processes that are unlikely to create light $\delta^{56}\text{Fe}$ signatures in boninites

Contribution of Subducted Sediments?

Previous Expedition 352 trace element and radiogenic isotope data suggests that only the HSBs incorporated subducted sediments (Li *et al.* 2019; Ishizuka *et al.* 2020; Shervais *et al.* 2021). Therefore, the contribution of subducted sediment is unlikely to be responsible for the overall lighter $\delta^{56}\text{Fe}$ in boninites versus FAB because HSBs and LSBs are not statistically distinct in their $\delta^{56}\text{Fe}$ (**Fig. 4.13**). In addition, measurements of arc lavas with ~10% subducted sediment inputs from Banda arc, Indonesia found no evidence of a sediment control on arc lava $\delta^{57}\text{Fe}$ signatures (Nebel *et al.* 2015). Mass balance calculations showed that even with the most extreme sediment $\delta^{57}\text{Fe}$, low Fe concentrations mean that sediment contributions to the mantle wedge would need to exceed 20% to significantly alter its $\delta^{57}\text{Fe}$ (Nebel *et al.* 2015). The Expedition 352 HSB sediment contribution is estimated between 0.5 and 1% (Shervais *et al.* 2021). In addition, Fe isotope measurements of arc lavas from the established Marianas arc found no evidence that $\delta^{57}\text{Fe}$ is sensitive to sediment input (Williams *et al.* 2018). It is therefore unlikely that the Bonin forearc sediment input had sufficient Fe to alter mantle wedge $\delta^{56}\text{Fe}$ during boninite formation, and therefore alter boninite $\delta^{56}\text{Fe}$.

Contribution of a Slab Melt Component?

The positive Hf anomalies of Expedition 352 boninites have been interpreted as evidence of an amphibolite facies slab melt component (Li *et al.* 2019). Since a slab melt component could be present in all boninites, it could account for the boninites' light $\delta^{56}\text{Fe}$ compared to FAB. The main Fe-bearing mineral of interest for an amphibolite facies slab melt is amphibole. Unfortunately, there is limited mineral specific amphibole data. The only amphibole $\delta^{56}\text{Fe}$ fractionation factor available at present is from Ye *et al.* (2020) who used a metamorphosed iron formation to determine an amphibole-garnet $\delta^{56}\text{Fe}$ fractionation factor ($\Delta^{56}\text{Fe}_{\text{Amp-Gt}} = 0.34 \pm 0.15 \text{ ‰}$). Whilst there is unlikely to be garnet present at the depths of the amphibolite facies slab, the fractionation factor shows that on average amphibole is isotopically heavier than garnet. Since Fe^{2+} has XII-fold coordination, and Fe^{3+} VI-fold coordination in garnet (Smyth & Bish 1988), and mafic melts coordinate Fe between V and VI, and IV to V in rhyolitic melts (Wilke 2005), garnet-melt fractionation should create heavy melts. Therefore, if amphibole is isotopically heavier than garnet, $\Delta^{56}\text{Fe}_{\text{Amp-Melt}}$ should be smaller than $\Delta^{56}\text{Fe}_{\text{Gt-Melt}}$, and create only slightly heavy $\delta^{56}\text{Fe}$ melt signatures. Amphibolite-facies slab melts do not therefore provide an obvious mechanism to explain isotopically light boninites. In addition, during amphibolite-facies slab melting, Sm should be retained by amphibole in the slab due to its high partition coefficient, while the slab temperature should be sufficient to melt zircon and release Hf and Zr (e.g. Pearce 1992; Tollstrup *et al.* 2010; Li *et al.* 2013). Therefore, if variable contributions of an amphibolite facies slab melt is responsible for the FAB-boninite $\delta^{56}\text{Fe}$ difference, then boninite

$\delta^{56}\text{Fe}$ might be expected to correlate with Sm/Hf and Zr/Sm, and possibly ϵHf_i , which is not the case (Fig. 4.15).

Both the inferred $\delta^{56}\text{Fe}$ composition of amphibole and the lack of $\delta^{56}\text{Fe}$ correlations with slab melt chemical indicators suggest that the interaction between boninitic melts and amphibolite-facies slab melts is unlikely to have contributed to the FAB-boninite $\delta^{56}\text{Fe}$ difference.

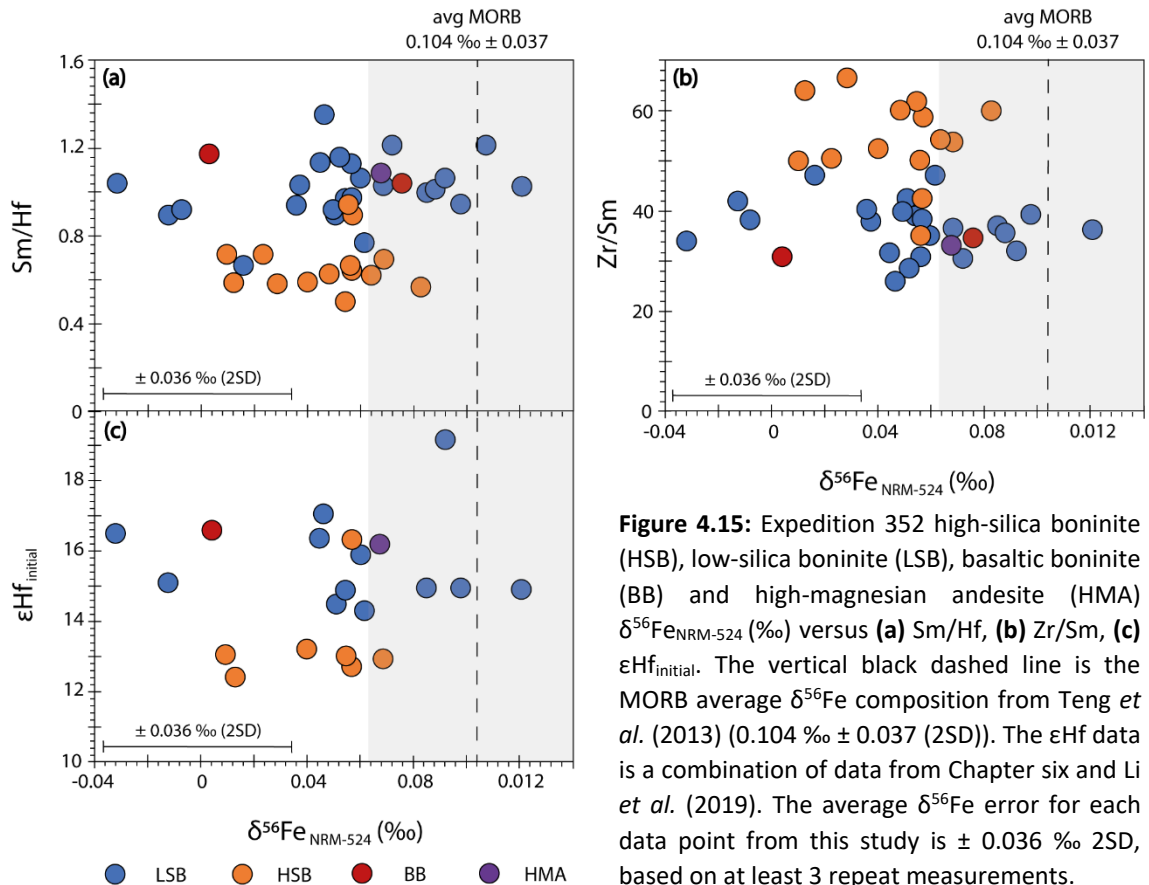


Figure 4.15: Expedition 352 high-silica boninite (HSB), low-silica boninite (LSB), basaltic boninite (BB) and high-magnesian andesite (HMA) $\delta^{56}\text{Fe}_{\text{NRM-524}} (\text{‰})$ versus (a) Sm/Hf, (b) Zr/Sm, (c) $\epsilon\text{Hf}_{\text{initial}}$. The vertical black dashed line is the MORB average $\delta^{56}\text{Fe}$ composition from Teng *et al.* (2013) (0.104 ‰ ± 0.037 (2SD)). The ϵHf data is a combination of data from Chapter six and Li *et al.* (2019). The average $\delta^{56}\text{Fe}$ error for each data point from this study is $\pm 0.036 \text{ ‰ 2SD}$, based on at least 3 repeat measurements.

Redox Conditions?

Previous studies have described the potential of Fe isotopes to respond to changes in redox due to the multiple oxidation states of Fe during partitioning between liquids and crystalline solid residues (e.g. Polyakov & Mineev 2000; Williams *et al.* 2004; Shahar *et al.* 2008; Young *et al.* 2015). Differences in $f\text{O}_2$ between FABs and boninites could therefore potentially explain why boninites have lighter $\delta^{56}\text{Fe}$ than FAB. Stable isotope theory predicts that heavier isotopes are associated with stiffer bonds, and with all else being equal, stiffer bonds are associated with higher oxidation states

and lower coordination (e.g. Urey 1947; Schauble 2004). Brounce *et al.* (2021) showed that Expedition 352 boninites are more oxidised than FABs ($\text{Fe}^{3+}/\Sigma\text{Fe} = 0.181 - 0.225$ and $0.136 - 0.177$ respectively). Therefore, if Fe isotopic composition was a direct reflection of redox state, we would predict that boninites should have *heavier* $\delta^{56}\text{Fe}$ than FABs, which is not the case (**Fig. 4.11**). Therefore, changes in $f\text{O}_2$ are unlikely to have directly caused the $\delta^{56}\text{Fe}$ difference between FABs and boninites during subduction initiation.

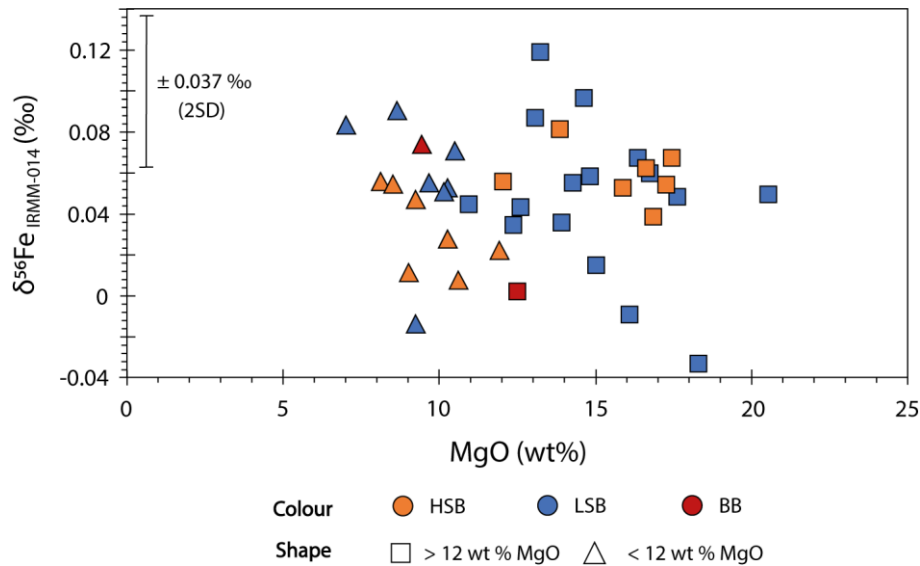


Figure 4.16: $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ (‰) versus MgO (wt%) for Expedition 352 boninites. The squares represent boninites with more than 12 wt % MgO and the triangles boninites with less than 12 wt% MgO. The average y-axis error is ± 0.037 ‰ (2SD) based on at least 3 repeat measurements.

b) Processes that may create light $\delta^{56}\text{Fe}$ signatures in boninites

Fractional Crystallisation?

The effects of fractional crystallisation on Fe isotope fractionation has been discussed in detail by many previous studies (e.g. Teng *et al.* 2008; Schuessler *et al.* 2009; Sossi *et al.* 2012; Foden *et al.* 2015; Wawryk & Foden 2017). More evolved material such as granites and rhyolites have been shown to be isotopically heavier than basalts, and some modelling studies (e.g. Dauphas *et al.* 2014; Foden *et al.* 2015) argue that fractional crystallisation can explain silicic rock isotopic variations with no need for additional processes. However, $\delta^{56}\text{Fe}$ only changes significantly once the system has reached at least 65% SiO_2 , perhaps due to the change in the Fe^{2+} force constant between mafic and silicic melts (Dauphas *et al.* 2014), or due to the removal of fractionating phases such as magnetite that preferentially incorporate isotopically heavy Fe (e.g. Williams *et al.* 2018; Stow *et al.* in revision).

The boninites in this study were chosen to minimise the effects of fractional crystallisation. Samples with MgO less than 12 wt% are assumed to have undergone net fractional crystallisation (Shervais *et al.* 2021), which only encompasses 40 % of the forty boninites in this study. Also, given that the lowest MgO boninite has 7.02 wt% MgO, the low MgO boninites likely only experienced minor fractional crystallisation. The co-precipitation of magnetite and silicate minerals such as olivine and pyroxenes in subduction magmas suggests that the early stages of fractional crystallisation should create slightly isotopically heavier melts (e.g. Foden *et al.* 2018). The FABs and boninites are not part of a cogenetic fractional crystallisation sequence, consequently the $\delta^{56}\text{Fe}$ difference between FABs and boninites cannot be directly attributed to progression through a fractional crystallisation sequence. However, if the boninites experienced less fractional crystallisation than the FABs, with all else being equal the boninites should be isotopically lighter than the FABs. However, MgO and $\delta^{56}\text{Fe}$ do not correlate in the boninites with < 12 wt% MgO, and they are not isotopically lighter than the other boninites (**Fig. 4.16**). Also previous studies have suggested that fractional crystallisation is not a key contributor to the light or diverse $\delta^{56}\text{Fe}$ of arc lavas (e.g. Foden *et al.* 2018). Therefore, although fractional crystallisation (or accumulation) of isotopically distinct Fe-rich phase(s) may account for some of the scatter in the dataset, it is unlikely to be significant when considering the first order FAB-boninite $\delta^{56}\text{Fe}$ difference.

Devolatilisation of the Subducting Slab?

A key difference between Expedition 352 FABs and boninites is that the boninites show clear geochemical evidence of a subduction fluid/melt component, whereas FABs do not. Previous studies have suggested that the sulphate, carbonate, and/or hypersaline fluids released during devolatilisation of subducted serpentinites, can preferentially complex with isotopically light Fe ($\text{Fe(II)}\text{--SO}_x$, $\text{Fe(II)}\text{--CO}_3^{2-}$, or $\text{Fe(II)}\text{--Cl}_2$), causing isotope fractionation (Debret *et al.* 2016, 2018, 2020, 2021; Turner *et al.* 2018). Since the Expedition 352 boninites have lighter $\delta^{56}\text{Fe}$ than the FABs, and have a known slab component, slab devolatilisation may explain the FAB-boninite $\delta^{56}\text{Fe}$ difference.

If light-Fe rich subduction-fluids interacted with the boninite source or melts to impart a light Fe boninite signatures, then $\delta^{56}\text{Fe}$ should correlate with various FME concentrations. However, there are no such correlations in the boninites (**Fig 4.17**). Furthermore, the complexation mechanism of Fe with Cl, SO_x , and/or CO_x ions (Debret *et al.* 2016, 2020) should create a $\delta^{56}\text{Fe}$ signature associated with elevated boninitic Cl, S or C compared to anhydrous rocks such as MORB and FABs. However, **Figure 4.18** shows that S is lower in boninites than FABs and MORB, and Cl is at similar concentrations to FABs. The lack of evidence for a slab fluid Fe fractionation mechanism in the boninites supports mass balance calculations that suggest Fe contribution from slab fluids is too

minor to significantly alter arc lava $\delta^{56}\text{Fe}$ (e.g. Inglis *et al.* 2017; Williams *et al.* 2018). The involvement of subducted slab devolatilisation fluids in boninite formation is therefore not likely to be the primary cause of the FAB-boninite $\delta^{56}\text{Fe}$ difference.

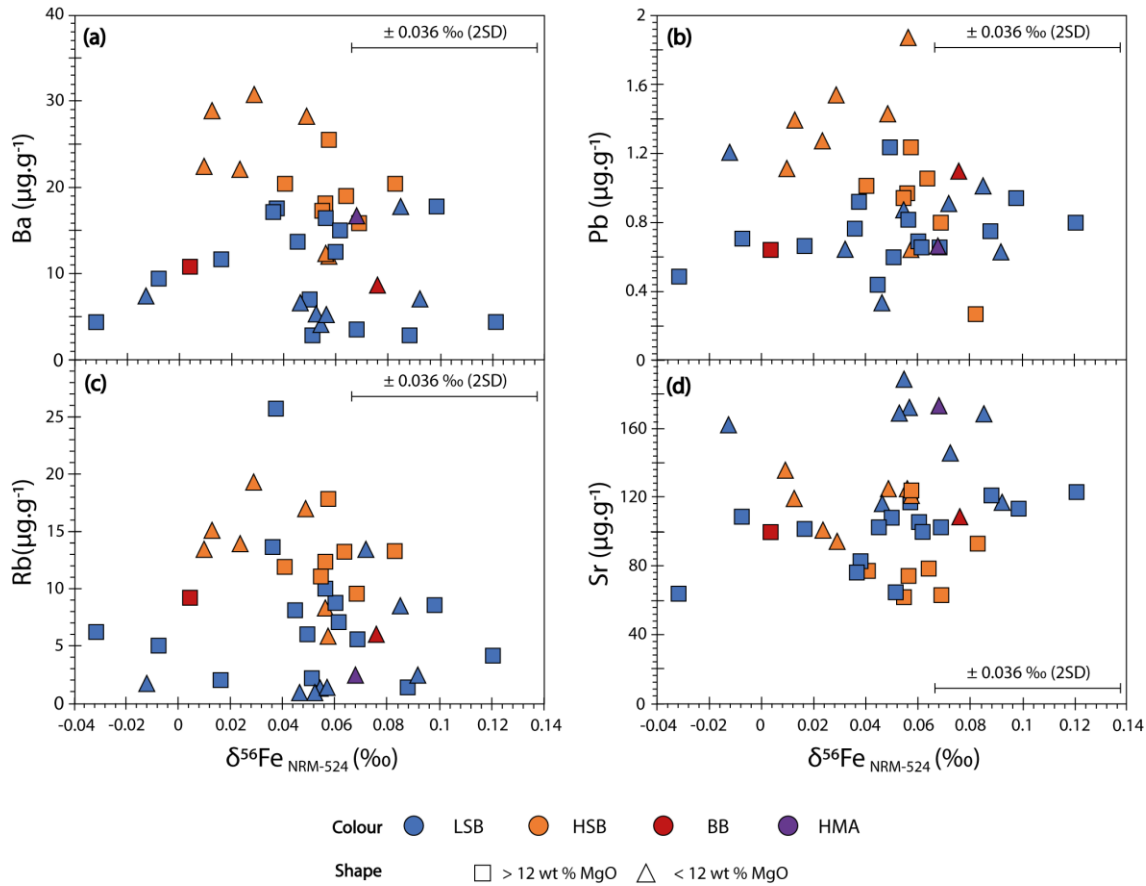


Figure 4.17: $\delta^{56}\text{Fe}_{\text{NRM-524}}$ (‰) versus (a) Ba concentration ($\mu\text{g.g}^{-1}$); (b) Pb concentration ($\mu\text{g.g}^{-1}$); (c) Rb concentration ($\mu\text{g.g}^{-1}$); (d) Sr concentration ($\mu\text{g.g}^{-1}$) for low-silica boninites (LSBs), high-silica boninites (HSB), basaltic boninites (BB) and high-magnesian andesite (HMA). The average horizontal error is ± 0.036 ‰ which represents the average 2SD based on at least three repeats from all samples.

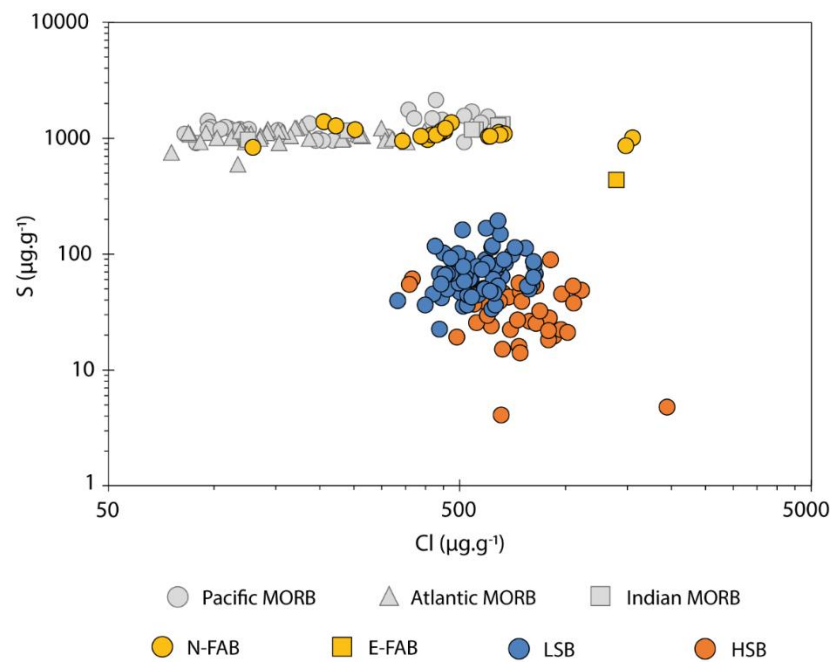


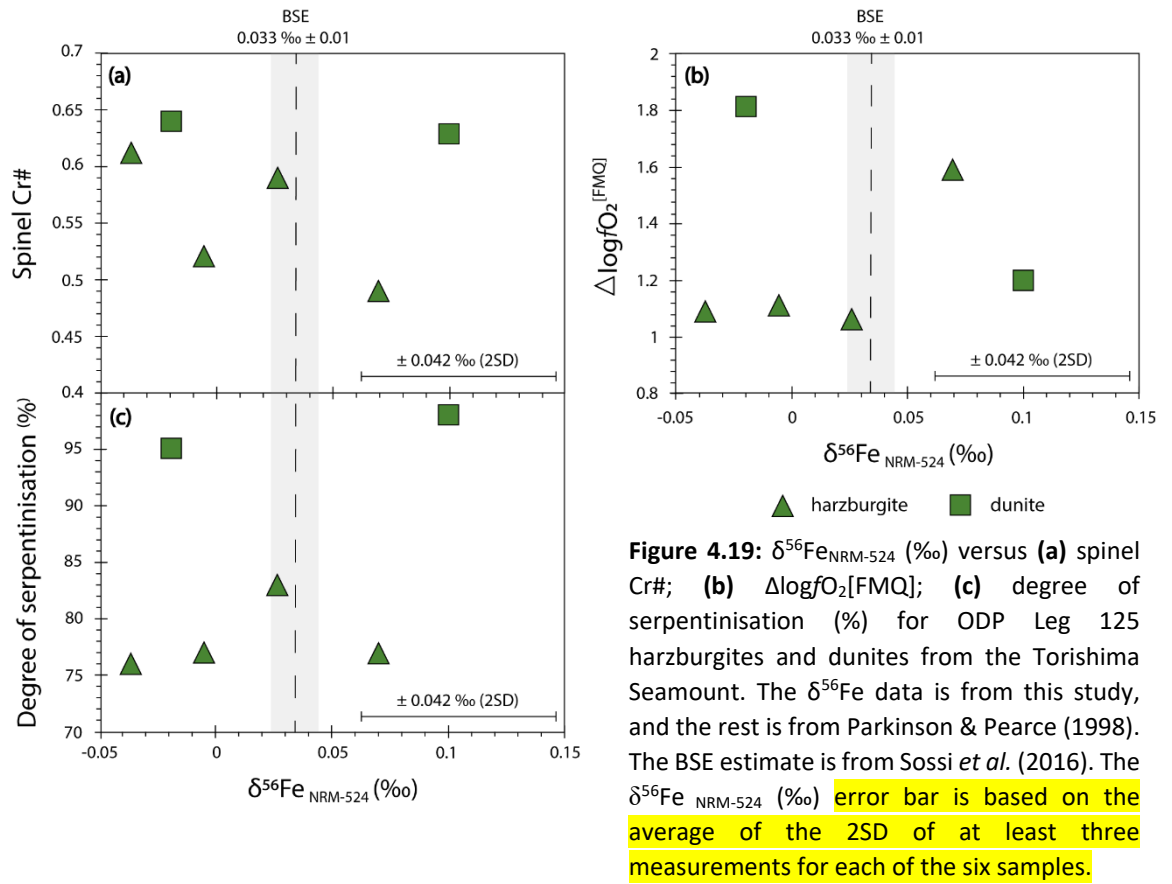
Figure 4.18: Chlorine versus sulphur concentrations in IODP Expedition 352 FABs and boninites, and Pacific, Atlantic and Indian MORB. The FAB and boninite glass data is from Coulthard *et al.* (2021) and the MORB data is from Jenner & O'Neill (2012) and Shimizu *et al.* (2019).

Source Depletion and Partial Melting?

The Expedition 352 boninites formed by melting of the depleted FAB residue, and therefore have a more depleted source than the FABs. Mantle partial melting should concentrate heavy Fe in melts, leaving an isotopically lighter residue (e.g. Williams *et al.* 2005). Previous arc lava studies have called upon historic source melt extraction event(s) to explain the light $\delta^{56}\text{Fe}$ of Banda and Marianas arc lavas (Nebel *et al.* 2015; Williams *et al.* 2018). Modelling of melt extraction with a Depleted MORB Mantle (DMM) starting composition ($\delta^{57}\text{Fe} = 0.04\text{‰}$ (Craddock *et al.* 2013)) has been shown to approach similar $\delta^{57}\text{Fe}$ to the Banda arc sources after 25 to 30% fractional melt extraction (Nebel *et al.* 2015), and such melt extraction degrees are in agreement with those recorded by some arc mantle xenoliths (e.g. Ionov *et al.* 2010). The difference in source depletion between FABs and boninites due to extraction of the FAB melts may therefore explain the $\delta^{56}\text{Fe}$ FAB-boninite difference and the light $\delta^{56}\text{Fe}$ of global arc lavas. However, there are some key concerns. Firstly, such a mechanism would require $\sim 30\%$ source melt extraction for all arcs globally, which seems unlikely. For example, trace element modelling of the Expedition 352 FABs and boninites (Shervais *et al.* 2019, 2021) suggests that boninite sources experienced only 15-20% prior melt extraction. Secondly, since partial melting creates isotopically heavier melts (Williams *et al.* 2005), the partial melting of the FAB residue required to create boninitic melts may overprint any source depletion related, light $\delta^{56}\text{Fe}$ signatures in the boninites. For source depletion to be a major contributor to light boninite $\delta^{56}\text{Fe}$, the partial melting induced $\delta^{56}\text{Fe}$ fractionation needs to be small enough to not

bring boninite $\delta^{56}\text{Fe}$ back towards heavier FAB values, and not offset the source depletion effects. Finally, if historic melt extraction is the dominant control on $\delta^{56}\text{Fe}$ fractionation in arc systems, why are FABs not isotopically lighter than MORB? Lower HFSEs, LREEs, Ti and P concentrations in FABs suggest that FABs have a more depleted source than MORB (Shervais *et al.* 2019). There is a slight offset between MORB and FAB $\delta^{56}\text{Fe}$ averages when visually examining the data, but it is not statistically significant (**Fig. 4.11**).

Ocean Discovery Program (ODP) Leg 125 dunites and harzburgites, recovered from the flanks of Torishima seamount on the Bonin forearc may also provide useful information about the FAB-boninite mantle source. The harzburgites and dunites are interpreted as the residues of 20 to 25% fractional melt extraction in a suprasubduction zone environment (Parkinson & Pearce 1998). However, these samples are extremely depleted, and therefore, their chemistry could have been easily altered by melt/fluid interaction. Since their current chemistry may not be primary, and therefore not only reflect melt extraction, care is needed. The ODP Leg 125 dunites and harzburgites are on average isotopically lighter than the boninites ($\delta^{56}\text{Fe} = 0.022 \pm 0.107 \text{ ‰}$) which supports a source depletion $\delta^{56}\text{Fe}$ control, but they also have a large variance from 0.100 ‰ to -0.037 ‰. There is a sense of a negative trend between Leg 125 harzburgite $\delta^{56}\text{Fe}$ with spinel Cr# (**Fig. 4.19a**) suggesting that a higher Cr#, and therefore inferred greater melt extraction, is associated with lighter $\delta^{56}\text{Fe}$. There are also no correlations between $\delta^{56}\text{Fe}$ and degree of serpentinisation or calculated $f\text{O}_2$ (**Fig. 4.19**) which highlights that the Leg 125 sample $\delta^{56}\text{Fe}$ variation is unlikely to be related to secondary alteration or directly to redox. Variable extents of melt extraction may therefore account for the large variance in the Leg 125 samples, and support source depletion as a contributing factor to the $\delta^{56}\text{Fe}$ difference between FABs and boninites.



To test whether partial melting and source melt extraction alone can create the observed $\delta^{56}\text{Fe}$ difference between the Expedition 352 FABs and boninites, two-stage melting models were employed. All models are based on formulations from Sossi & O'Neill (2017) which account for the different compatibilities of ferrous and ferric Fe, and all parameters are given in **Table 4.5**. All modelling assumed an initial FAB source of DMM composition ($\delta^{56}\text{Fe} = 0.026 \text{ ‰}$ (Craddock *et al.* 2013)) and that the boninites formed by melting the FAB residue left behind after FAB melt extraction (maximum 23-25% melting for D-FAB). The FAB residue $\delta^{56}\text{Fe}$ after 23-25% FAB melt extraction was used as the source for the boninite melting stage. Before FAB and boninite $\delta^{56}\text{Fe}$ modelling was attempted, the sensitivity of $\Delta^{56}\text{Fe}_{\text{FAB-Bon}}$ to different parameters was tested, and the ideal parameters to maximise $\Delta^{56}\text{Fe}_{\text{FAB-Bon}}$ were chosen.

Table 4.5: Fe melt model parameters used in this study. Partition coefficients are from Mallmann & O'Neill (2009), and $D(\text{Fe}_T)$ was calculated from weighting $D(\text{Fe}^{2+})$ and $D(\text{Fe}^{3+})$ according to typical $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. DMM modes and FeO_T are from Workman & Hart (2005). The melt reaction is from Walter (1998) $0.4 \text{ Opx} + 0.82 \text{ Cpx} + 0.15 \text{ Spl} \rightarrow 0.38 \text{ Ol} + 0.62 \text{ Melt}$. The force constants are from Sossi & O'Neill (2017).

Phase	Partition Coefficient (min/melt)			DMM (Workman & Hart 2005)		Melt Reaction (Walter 1998)	Force Constant (N/m)
	$D(\text{Fe}^{2+})$	$D(\text{Fe}^{3+})$	$D(\text{Fe}_T)$	Modes	FeO_T (wt%)		
Olivine	1.080	0.063	0.927	0.57	10.16	-0.38	185
Orthopyroxene	0.680	0.201	0.608	0.28	6.27	0.4	185
Clinopyroxene	0.287	0.453	0.312	0.13	2.94	0.82	185
Cr-spinel	1.930	2.880	2.044	0.02	12.56	0.15	145

There are three types of melt equations that are traditionally used for melt modelling, batch modal, batch non-modal, and accumulated fractional non-modal (Shaw 1970), each of which produce a different $\Delta^{56}\text{Fe}_{\text{liq-solid}}$ (**Fig. 4.20a**). The accumulated fractional non-modal equation is likely the most appropriate approach for replicating the large $\delta^{56}\text{Fe}$ difference between FABs and boninites through melting alone, because accumulated fractional melting creates the largest $\Delta^{56}\text{Fe}_{\text{liq-solid}}$ (**Fig. 4.20a**) and is likely the closest to what happens in nature. The accumulated fractional approach also accounts for melting stoichiometry by incorporating a melting reaction. The melting reaction used in this case is $0.4 \text{ Opx} + 0.82 \text{ Cpx} + 0.15 \text{ Spl} \rightarrow 0.38 \text{ Ol} + 0.62 \text{ Melt}$ (Walter 1998), and the melting reaction coefficients in **Table 4.5** are based on the stoichiometry of this equation. A second key modelling parameter is mineral partition coefficients. Partition coefficients are a limitation of this modelling because there is no self-consistent dataset available of total Fe partition coefficients ($D(\text{Fe}_T)$) for all phases of interest. Instead, to create a self-consistent $D(\text{Fe}_T)$ dataset, ferric and ferrous Fe partition coefficients (Mallmann & O'Neill 2009) were weighted according to typical mantle $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. Typical upper mantle $\text{Fe}^{3+}/\Sigma\text{Fe}$ range between about 0.15 and 0.35 (Wood & Virgo 1989), and 0.15 was used in this study. Varying the absolute $\text{Fe}^{3+}/\Sigma\text{Fe}$ used to calculate $D(\text{Fe}_T)$ caused negligible changes to $\Delta^{56}\text{Fe}_{\text{(liquid-solid)}}$ (**Fig. 4.20b**), and therefore the $\text{Fe}^{3+}/\Sigma\text{Fe}$ used for $D(\text{Fe}_T)$ calculation was not critical.

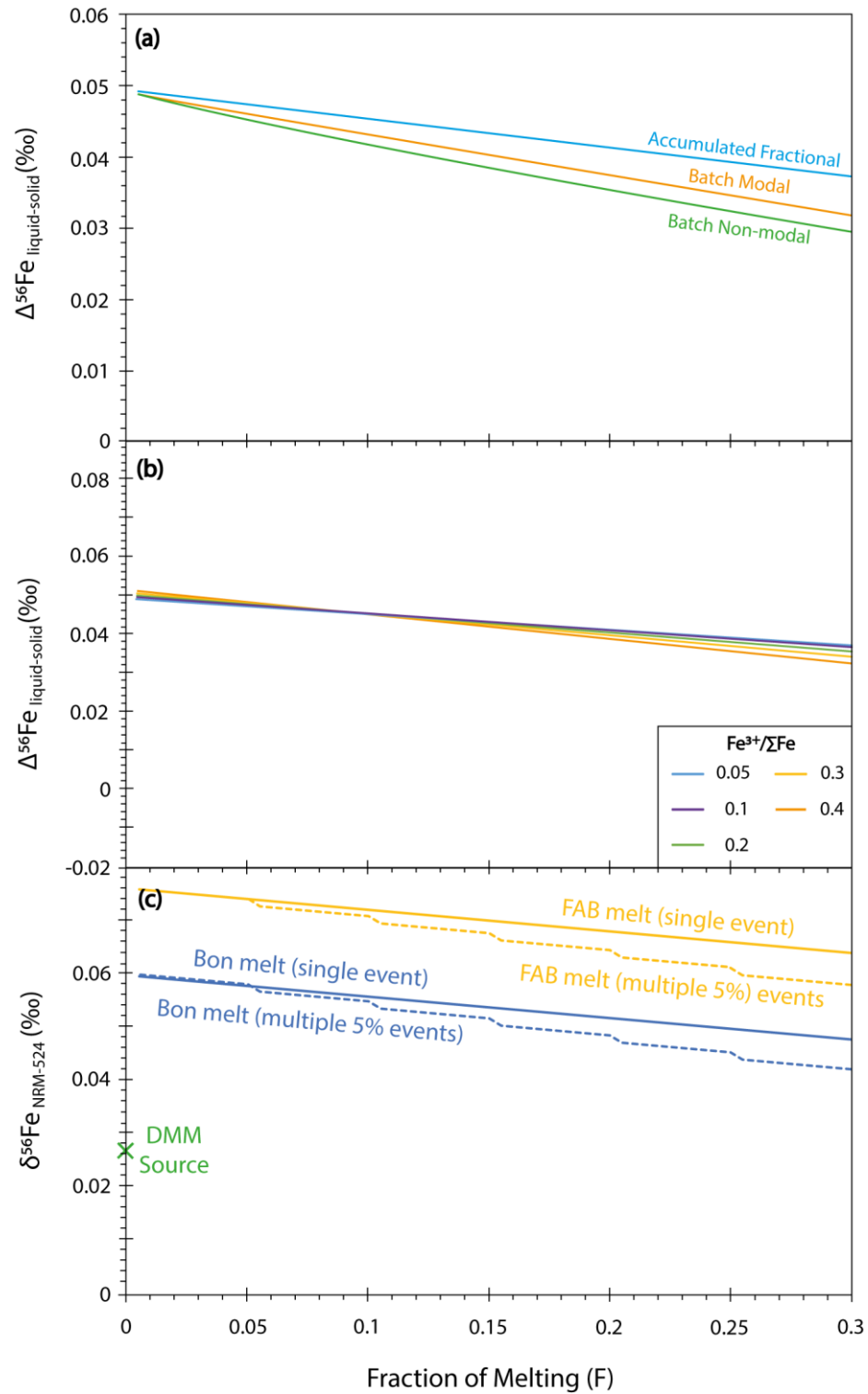


Figure 4.20: Fe isotopic melt modelling sensitivity tests. **(a)** Comparison of $\Delta^{56}\text{Fe}_{\text{liq-solid}}$ versus fraction of melting for the three different melt equations from Shaw (1970). **(b)** The effects of varying $\text{Fe}^{3+}/\Sigma\text{Fe}$ which was used to calculate total Fe partition coefficients from ferric and ferrous Fe partition coefficients on $\Delta^{56}\text{Fe}_{\text{liq-solid}}$. **(c)** The effects of melting in a single fractional melting event versus multiple 5% events. All models used a DMM source ($\delta^{56}\text{Fe} = 0.026 \text{ ‰}$ (Craddock et al. 2013)), and **(b)** and **(c)** both used accumulated fractional non-modal melt equations.

Another potential parameter that may influence FAB and boninite melt $\delta^{56}\text{Fe}$ is the number of melt extraction events. A series of multiple melt extraction events such as five 5% fractional melting events instead of one single 23-25% FAB fractional melting event is likely more realistic. However, events of equal melting extent are still simplistic. **Figure 4.20c** shows that a two-stage melt model where FABs and boninites are produced from multiple fractional melting events, results in FAB and boninite melt $\delta^{56}\text{Fe}$ that are lighter than those produced by single fractional melting events. However, the overall $\Delta^{56}\text{Fe}_{\text{FAB-Bon}}$ is unchanged. Since multiple extraction events are likely more realistic, multiple extraction models will be favoured. The final modelling parameter tested was mineral ^{56}Fe fractionation factors (α) which are derived from mineral and melt force constants taken from Sossi & O'Neill (2017) (**Table 4.5**). **Figure 4.21** shows that α has a strong influence on $\Delta^{56}\text{Fe}_{\text{FAB-Bon}}$. A model that uses α 's derived from **Table 4.5** force constants creates a $\Delta^{56}\text{Fe}_{\text{FAB-Bon}}$ of 0.016 ‰, significantly lower than the observed average $\Delta^{56}\text{Fe}_{\text{FAB-Bon}}$ of 0.035 ‰. However, an α change for all mineral phases of -0.00005 creates a $\Delta^{56}\text{Fe}_{\text{FAB-Bon}}$ of 0.034 ‰. Whilst there are no quoted errors on the specific force constants used in this model, other force constants from Sossi & O'Neill (2017) have an average error of $\sim \pm 17\%$. The maximum α change achievable with a 17% error is 0.000082 for olivine, clinopyroxene and orthopyroxene, and 0.000074 for spinel. Therefore, a -0.00005 α change constitutes a force constant change that is within the 17% error average, and therefore considered acceptable.

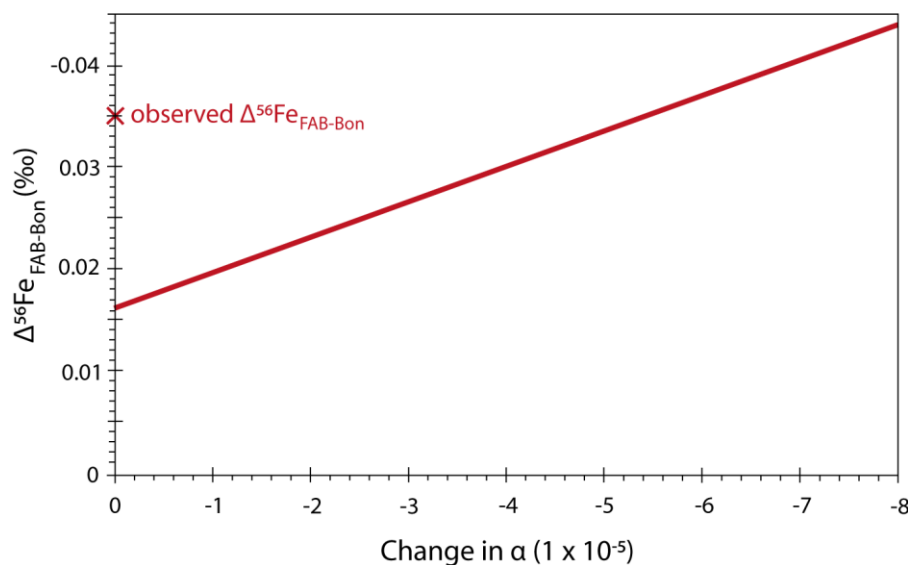


Figure 4.21: The effects of changing Fe melt model α -values for olivine, orthopyroxene, clinopyroxene and spinel on FAB and boninite melt $\delta^{56}\text{Fe}$. The observed average FAB-boninite $\delta^{56}\text{Fe}$ difference from this study is reached with an α change of ~ 0.00005 .

Two-stage accumulated fractional non-modal Fe melt modelling using multiple 5% melting events for both FABs and boninites and $\alpha - 0.00005$ produced a $\Delta^{56}\text{Fe}_{\text{FAB-Bon}}$ of 0.034 ‰ (**Fig. 4.22a**) which

is close to the measured $\Delta^{56}\text{Fe}_{\text{FAB-Bon}}$ of 0.035 ‰. When modelled FAB and boninite melt $\delta^{56}\text{Fe}$ from the median estimated melt degree (11% and 15% respectively) are compared, $\Delta^{56}\text{Fe}_{\text{FAB-Bon}}$ is 0.035 ‰ (FAB $\delta^{56}\text{Fe}$ at 11% melting = 0.112 ‰ and boninite $\delta^{56}\text{Fe}$ at 15% melting = 0.077 ‰). However, the absolute Fe isotopic compositions of the FAB and boninite melts are isotopically heavier than measured averages. This suggests that the DMM source used may be too isotopically heavy. Since the FAB source is thought to be more depleted than MORB sources (Li *et al.* 2019; Shervais *et al.* 2019), and during source depletion light Fe is concentrated in residues, the FAB source may indeed be isotopically lighter than DMM. For the modelled FAB and boninite melts to reach the observed average $\delta^{56}\text{Fe}$ at appropriate melt degrees, the FAB source needs to be ~ 0 ‰ (**Fig. 4.22b**). This value is not unreasonable since there are numerous peridotite $\delta^{56}\text{Fe}$ of 0 ‰ or lighter (e.g. Weyer & Ionov 2007; Zhao *et al.* 2010; Huang *et al.* 2011; Craddock *et al.* 2013, **Fig. 4.23**).

Iron melt modelling with minor adaptations has shown that source depletion and partial melting alone can create the observed FAB-boninite $\delta^{56}\text{Fe}$ difference and that observed FAB and boninite average $\delta^{56}\text{Fe}$ can be reproduced by melt degrees consistent with previous estimations from Shervais *et al.* (2019, 2021). We therefore favour source depletion and partial melting as the dominant cause(s) for boninite and therefore arc lavas having isotopically light $\delta^{56}\text{Fe}$.

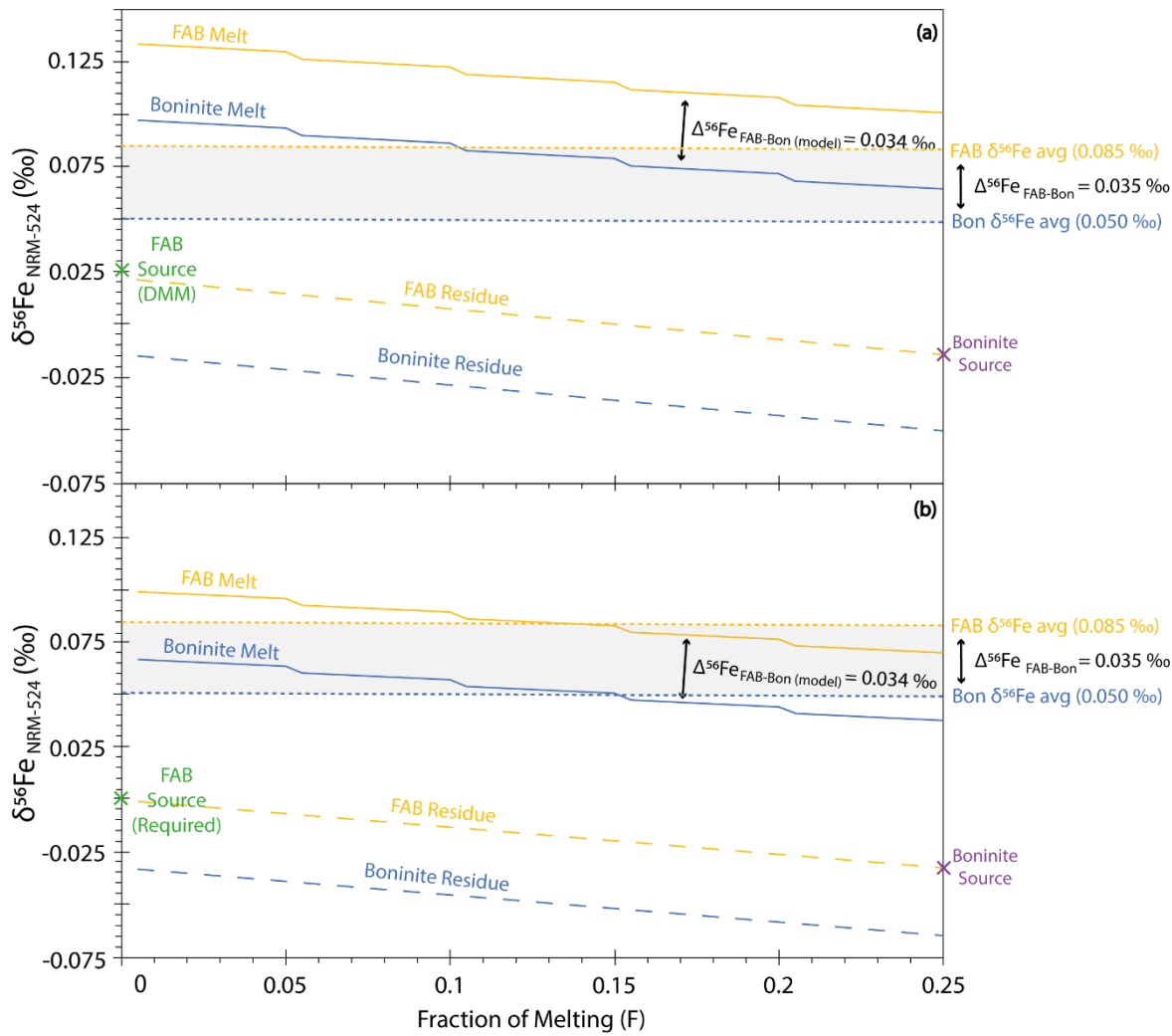


Figure 4.22: Two-stage accumulated fractional non-modal Fe isotope melt models of IODP Expedition 352 FABs and boninites. Both models were based on modelling from Sossi & O'Neill (2017) and assumed that the boninites formed after the FABs from the depleted FAB residue after ~ 23-25 & melting that is the suggested melt degree of the D-FAB (Shervais et al. 2019). Both models also assumed multiple 5% melt extraction events instead of one event, and used parameters from Table 4.5. For both models the mineral fractionation factors were altered by -0.00005 (within force constant error) to increase the $\Delta^{56}\text{Fe}_{\text{FAB-Bon}}$. Panel a used a DMM source composition ($\delta^{56}\text{Fe} = 0.026$ ‰ (Craddock et al. 2013)), but FAB and boninite melt $\delta^{56}\text{Fe}$ was isotopically heavier than measured. Panel b used the FAB source $\delta^{56}\text{Fe}$ necessary to reproduce the FAB and boninite $\delta^{56}\text{Fe}$ measured at appropriate melt degrees ($\delta^{56}\text{Fe} = 0$ ‰).

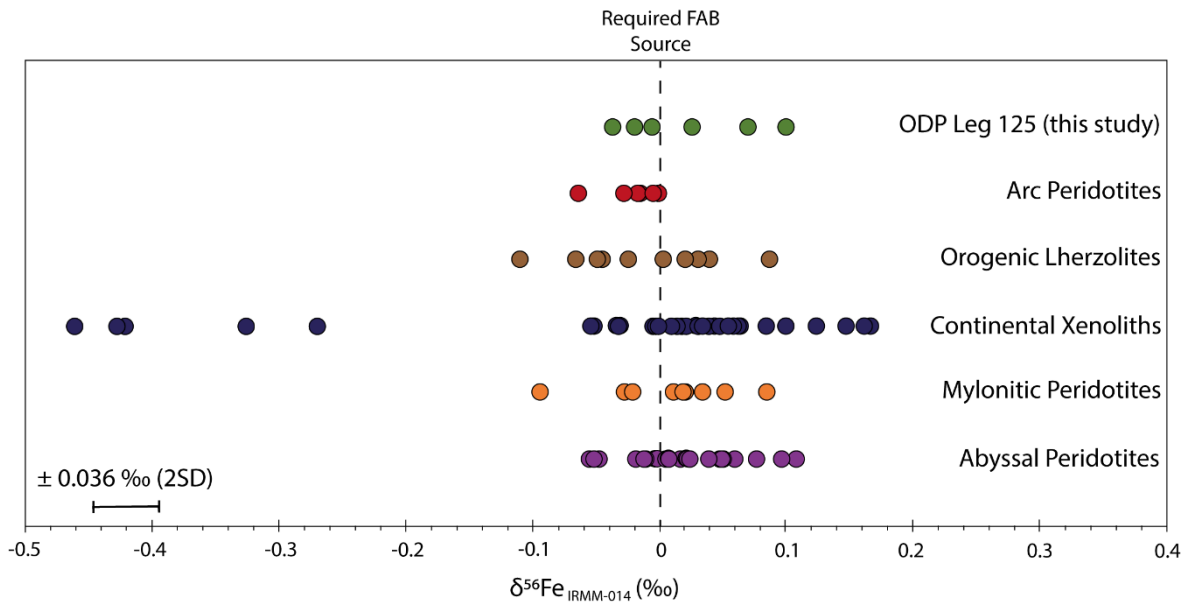


Figure 4.23: Peridotite $\delta^{56}\text{Fe}$ data from literature and the ODP Leg 125 peridotite $\delta^{56}\text{Fe}$ data from this study. The abyssal peridotite and mylonitic peridotite data are from Craddock et al. (2013). The continental xenolith data is from Williams et al. (2005), Weyer & Ionov (2007), Zhao et al. (2010, 2012, 2015), Huang et al. (2011) and Poitrasson et al. (2013). The orogenic lherzolite data is from Weyer & Ionov (2007) and Sossi et al. (2016). The arc peridotite data is from Weyer & Ionov (2007). The average $\delta^{56}\text{Fe}$ error is $\pm 0.036 \text{ ‰}$.

4.4.3. Implications for deconvolving Fe isotope fractionation in global arcs

The limited geochemical evidence for any of the proposed $\delta^{56}\text{Fe}$ fractionation mechanisms, and minimal correlations between FAB or boninite $\delta^{56}\text{Fe}$ with major, trace or radiogenic geochemical tracers makes accurately deconvolving the effects of different fractionation processes difficult. Despite a lack of geochemical correlations with $\delta^{56}\text{Fe}$, modelling of Fe isotopic fractionation during partial melting shows that source depletion and partial melting alone can recreate the observed FAB and boninite Fe isotopic compositions if a source slightly isotopically lighter than DMM is used ($\delta^{56}\text{Fe} = 0 \text{ ‰}$ versus 0.026 ‰). Previous Fe isotope work has measured non-metasomatic mantle rocks of similar Fe isotopic compositions, so 0 ‰ is reasonable. Therefore, this study has shown that historic source depletion and partial melting may explain the light $\delta^{56}\text{Fe}$ of arc lavas, and that slab-derived fluids, melts and sediments do not have significant influence over the Fe budget of arc lavas.

The lack of geochemical covariations between FAB and boninite $\delta^{56}\text{Fe}$ and major and trace element data highlights how difficult it can be to interpret Fe isotope data from high temperature igneous settings. Since Fe has the potential to be fractionated by many different processes, the lack of correlations suggests that later processes such as fractional crystallisation created $\delta^{56}\text{Fe}$ variations within the FAB and boninite suites, masking any potential geochemical indicators of partial melting and source depletion. By measuring Fe isotopes in a subduction system without an overlying plate,

we hoped to minimise geochemical complications and additional reservoirs to make it easier to deconvolve different Fe fractionation processes. The Bonin forearc lavas also allowed us to better isolate the processes and components that contribute to arc lava formation, by measuring rocks from different stages of subduction initiation which comprise distinct subduction components. However, even in this simplified scenario, it is still difficult to deconvolve Fe isotope fractionation processes through geochemical covariations alone. Using Fe isotopes to investigate subduction zone processes in isolation therefore appears problematic, and coupling Fe with additional isotope systems that have more selective fractionation mechanism may provide more robust constraints.

4.5. Conclusions

1. FAB and MORB $\delta^{56}\text{Fe}$ are not statistically distinct. This could be due to the similar petrogenetic origins of FABs and MORB.
2. Boninite $\delta^{56}\text{Fe}$ is statistically isotopically lighter than FAB $\delta^{56}\text{Fe}$, and statistically indistinguishable from global arc lava $\delta^{56}\text{Fe}$. The addition of slab melts, subducted sediments, and differing redox conditions are unconvincing mechanisms for creating isotopically light boninites.
3. Mantle melt modelling shows that source depletion and partial melting alone can reproduce the correct direction of fractionation and the observed FAB and boninite average Fe isotopic compositions with a FAB source slightly isotopically lighter than DMM ($\delta^{56}\text{Fe} = 0\text{‰}$). Therefore, increased source depletion may explain why arc lavas have lighter $\delta^{56}\text{Fe}$ than MORB.
4. Mantle partial melting and historic melt extraction are the most likely causes of the light $\delta^{56}\text{Fe}$ of arc lavas. However, the lack of geochemical correlations between $\delta^{56}\text{Fe}$ and major, trace and isotopic data makes using Fe isotopes to inform on igneous processes is difficult.
 - Pairing Fe isotope measurements with additional stable isotope data may aid interpretations in the future.

References

- Brounce, M., Reagan, M.K., Kelley, K.A., Cottrell, E., Shimizu, K. & Almeev, R. 2021. Co-variation of slab tracers, volatiles and oxidation during subduction initiation. *Geochemistry, Geophysics, Geosystems*, **22**, 1–30, <https://doi.org/10.1029/2021gc009823>.
- Brounce, M.N., Kelley, K.A. & Cottrell, E. 2014. Variations in $\text{Fe}^{3+}/\text{PFe}$ of Mariana Arc Basalts and Mantle Wedge fO₂. *Journal of Petrology*, **55**, 2514–2536, <https://doi.org/10.1093/petrology/egu065>.
- Chen, S., Niu, Y., Guo, P., Gong, H., Sun, P., Xue, Q., Duan, M. & Wang, X. 2019. Iron isotope fractionation during mid-ocean ridge basalt (MORB) evolution: Evidence from lavas on the East Pacific Rise at 10°30'N and its implications. *Geochimica et Cosmochimica Acta*, **267**, 227–

- 239, <https://doi.org/10.1016/j.gca.2019.09.031>.
- Coulthard, D.A., Reagan, M.K., Shimizu, K., Bindeman, I.N., Brounce, M., Almeev, R.R., Ryan, J., Chapman, T., Shervias, J. & Pearce, J.A. 2021. Magma Source Evolution Following Subduction Initiation: Evidence From the Element Concentrations, Stable Isotope Ratios, and Water Contents of Volcanic Glasses From the Bonin Forearc (IODP Expedition 352). *Geochemistry, Geophysics, Geosystems*, **22**, 1–30, <https://doi.org/10.1029/2020GC009054>.
- Craddock, P.R., Warren, J.M. & Dauphas, N. 2013. Abyssal peridotites reveal the near-chondritic Fe isotopic composition of the Earth. *Earth and Planetary Science Letters*, **365**, 63–76, <https://doi.org/10.1016/j.epsl.2013.01.011>.
- Dauphas, N., Craddock, P.R., Asimow, P.D., Bennett, V.C., Nutman, A.P. & Ohnenstetter, D. 2009. Iron isotopes may reveal the redox conditions of mantle melting from Archean to Present. *Earth and Planetary Science Letters*, **288**, 255–267, <https://doi.org/10.1016/j.epsl.2009.09.029>.
- Dauphas, N., Roskosz, M., Alp E., Neuville D., Hu M., Sio C., Tissot F., Zhao J., Tissandier L., Me'dard E. & Cordier C. 2014. Magma redox and structural controls on iron isotope variations in Earth's mantle and crust. *Earth and Planetary Science Letters*, **398**, 127–140, <https://doi.org/10.1016/j.epsl.2014.04.033>.
- Debret, B., Millet, M.A., Pons, M.L., Bouilhol, P., Inglis, E. & Williams, H. 2016. Isotopic evidence for iron mobility during subduction. *Geology*, **44**, 215–218, <https://doi.org/10.1130/G37565.1>.
- Debret, B., Bouilhol, P., Pons, M.L. & Williams, H. 2018. Carbonate transfer during the onset of slab devolatilization: New insights from Fe and Zn stable isotopes. *Journal of Petrology*, **59**, 1145–1166, <https://doi.org/10.1093/petrology/egy057>.
- Debret, B., Reekie, C.D.J., Mattielli, N., Beunon, H., Ménez, B., Savov, I. & Williams, H.M. 2020. Redox transfer at subduction zones: insights from Fe isotopes in the Mariana forearc. *Geochemical Perspectives Letters*, **12**, 46–51, <https://doi.org/10.7185/geochemlet.2003>.
- Debret, B., Garrido, C.J., Pons, M.L., Bouilhol, P., Inglis, E., López Sánchez-Vizcaíno, V. & Williams, H. 2021. Iron and zinc stable isotope evidence for open-system high-pressure dehydration of antigorite serpentinite in subduction zones. *Geochimica et Cosmochimica Acta*, **296**, 210–225, <https://doi.org/10.1016/j.gca.2020.12.001>.
- Deschamps, A. & Lallemand, S. 2002. The West Philippine Basin: An Eocene to early Oligocene back arc basin opened between two opposed subduction zones. *Journal of Geophysical Research*, **107**, <https://doi.org/10.1029/2001JB001706>.
- Dobson, P. F., Blank, J. G., Maruyama, S. & Liou, J. G. 2006. Petrology and Geochemistry of Boninite-Series Volcanic Rocks, Chichi-Jima, Bonin Islands, Japan. *International Geology Review*, **48**, 669–701, <https://doi.org/10.2747/0020-6814.48.8.669>.
- Evans, K.A. 2012. The redox budget of subduction zones. *Earth-Science Reviews*, **113**, 11–32, <https://doi.org/10.1016/j.earscirev.2012.03.003>.
- Evans, K.A. & Tomkins, A.G. 2011. The relationship between subduction zone redox budget and arc magma fertility. *Earth and Planetary Science Letters*, **308**, 401–409, <https://doi.org/10.1016/j.epsl.2011.06.009>.

- Foden, J., Sossi, P.A. & Wawryk, C.M. 2015. Fe isotopes and the contrasting petrogenesis of A-, I- and S-type granite. *Lithos*, **212**, 32–44, <https://doi.org/10.1016/j.lithos.2014.10.015>.
- Foden, J., Sossi, P.A. & Nebel, O. 2018. Controls on the iron isotopic composition of global arc magmas. *Earth and Planetary Science Letters*, **494**, 190–201, <https://doi.org/10.1016/j.epsl.2018.04.039>.
- Gleeson, M.L.M., Gibson, S.A. & Williams, H.M. 2020. Novel insights from Fe-isotopes into the lithological heterogeneity of Ocean Island Basalts and plume-influenced MORBs. *Earth and Planetary Science Letters*, **535**, 116–114, <https://doi.org/10.1016/j.epsl.2020.116114>.
- Hickey-vargas, R., Bizimis, M. & Deschamps, A. 2008. Onset of the Indian Ocean isotopic signature in the Philippine Sea Plate : Hf and Pb isotope evidence from Early Cretaceous terranes. *Earth and Planetary Science Letters*, **268**, 255–267, <https://doi.org/10.1016/j.epsl.2008.01.003>.
- Hickey-Vargas, R. 1998. Origin of the Indian Ocean-type isotopic signature in basalts from Philippine Sea plate spreading centers: An assessment of local versus large-scale processes. *Journal of Geophysical Research*, **103**, 20,963–20,979.
- Hickey-Vargas, R. 2005. Basalt and tonalite from the Amami Plateau , northern West Philippine Basin : New Early Cretaceous ages and geochemical results , and their petrologic and tectonic implications. *The Island Arc*, **14**, 653–665.
- Huang, F., Zhang, Z., Lundstrom, C.C. & Zhi, X. 2011. Iron and magnesium isotopic compositions of peridotite xenoliths from Eastern China. *Geochimica et Cosmochimica Acta*, **75**, 3318–3334, <https://doi.org/10.1016/j.gca.2011.03.036>.
- Huang, J., Guo, S., Jin, Q.Z. & Huang, F. 2020. Iron and magnesium isotopic compositions of subduction-zone fluids and implications for arc volcanism. *Geochimica et Cosmochimica Acta*, **278**, 376–391, <https://doi.org/10.1016/j.gca.2019.06.020>.
- Inglis, E., Debret, B., Burton, K.W., Millet, M.A., Pons, M-L., Dale, C.W., Bouilhol, P., Cooper, M., Nowell, G.M., McCoy-West, A.J. & Williams, H.M. 2017. The behavior of iron and zinc stable isotopes accompanying the subduction of mafic oceanic crust: A case study from Western Alpine ophiolites. *Geochemistry Geophysics Geosystems*, **18**, 2562–2579, <https://doi.org/10.1002/2016GC006735>.
- Ionov, D.A., Doucet, L.S. & Ashchepkov, I. V. 2010. Composition of the lithospheric mantle in the siberian craton: New constraints from fresh peridotites in the Udachnaya-East Kimberlite. *Journal of Petrology*, **51**, 2177–2210, <https://doi.org/10.1093/petrology/egq053>.
- Ishizuka, O., Taylor, R.N., Yuasa, M. & Ohara, Y. 2011a. Making and breaking an island arc: A new perspective from the Oligocene Kyushu-Palau arc, Philippine Sea. *Geochemistry, Geophysics, Geosystems*, **12**, 1–40, <https://doi.org/10.1029/2010GC003440>.
- Ishizuka, O., Tani, K., et al. 2011b. The timescales of subduction initiation and subsequent evolution of an oceanic island arc. *Earth and Planetary Science Letters*, **306**, 229–240, <https://doi.org/10.1016/j.epsl.2011.04.006>.
- Ishizuka, O., Taylor, R.N., Ohara, Y. & Yuasa, M. 2013. Upwelling , rifting , and age-progressive magmatism from the Oki-Daito mantle plume. *Geology*, **41**, 1011–1014, <https://doi.org/10.1130/G34525.1>.

- Ishizuka, O., Taylor, R.N., Umino, S. & Kanayama, K. 2020. Geochemical evolution of arc and slab following subduction initiation: A record from the Bonin islands, Japan. *Journal of Petrology*, **61**, 1–20, <https://doi.org/10.1093/petrology/egaa050>.
- Jenner, F.E. & O'Neill, H.S.C. 2012. Analysis of 60 elements in 616 ocean floor basaltic glasses. *Geochemistry, Geophysics, Geosystems*, **13**, 1–11, <https://doi.org/10.1029/2011GC004009>.
- Kelley, K.A. & Cottrell, E. 2009. Water and the oxidation state of subduction zone magmas. *Science*, **325**, 605–607, <https://doi.org/10.1126/science.1174156>.
- Kelley, K.A. & Cottrell, E. 2012. The influence of magmatic differentiation on the oxidation state of Fe in a basaltic arc magma. *Earth and Planetary Science Letters*, **329**, 109–121, <https://doi.org/10.1016/j.epsl.2012.02.010>.
- Konter, J.G., Pietruszka, A.J., Hanan, B.B., Finlayson, V.A., Craddock, P.R., Jackson, M.G. & Dauphas, N. 2016. Unusual $\delta^{56}\text{Fe}$ values in Samoan rejuvenated lavas generated in the mantle. *Earth and Planetary Science Letters*, **450**, 221–232, <https://doi.org/10.1016/j.epsl.2016.06.029>.
- Le Bas, M.J. 2000. IUGS reclassification of the high-Mg and picritic volcanic rocks. *Journal of Petrology*, **41**, 1467–1470, <https://doi.org/10.1093/petrology/41.10.1467>.
- Li, H.Y., Taylor, R.N., Prytulak, J., Kirchenbaur, M., Shervais, J.W., Ryan, J.G., Godard, M., Reagan, M.K. & Pearce, J.A. 2019. Radiogenic isotopes document the start of subduction in the Western Pacific. *Earth and Planetary Science Letters*, **518**, 197–210, <https://doi.org/10.1016/j.epsl.2019.04.041>.
- Li, Y.B., Kimura, J.I., Machida, S., Ishii, T., Ishiwatari, A., Maruyama, S., Qui, H.N., Ishikawa, T., Kato, Y., Haraguchi, S., Takahata, N., Hirahara, Y. & Miyazaki, T. 2013. High-Mg adakite and low-Ca boninite from a bonin fore-arc seamount: Implications for the reaction between slab melts and depleted mantle. *Journal of Petrology*, **54**, 1149–1175, <https://doi.org/10.1093/petrology/egt008>.
- Macris, C.A., Manning, C.E. & Young, E.D. 2015. Crystal chemical constraints on inter-mineral Fe isotope fractionation and implications for Fe isotope disequilibrium in San Carlos mantle xenoliths. *Geochimica et Cosmochimica Acta*, **154**, 168–185, <https://doi.org/10.1016/j.gca.2015.01.024>.
- Mallmann, G. & O'Neill, H.S.C. 2009. The crystal/melt partitioning of V during mantle melting as a function of oxygen fugacity compared with some other elements (Al, P, Ca, Sc, Ti, Cr, Fe, Ga, Y, Zr and Nb). *Journal of Petrology*, **50**, 1765–1794, <https://doi.org/10.1093/petrology/egp053>.
- Maunder, B., Prytulak, J., Goes, S. & Reagan, M. 2020. Rapid subduction initiation and magmatism in the Western Pacific driven by internal vertical forces. *Nature Communications*, **11**, 1–8, <https://doi.org/10.1038/s41467-020-15737-4>.
- Meijer, A., Anthony, E. & Reagan, M. 1982. Petrology of volcanic rocks from the fore-arc sites: Initial Reports of DSDP, **60**, 709–729.
- Nebel, O., Arculus, R.J., Sossi, P.A., Jenner, F.E. & Whan, T.H.E. 2013. Iron isotopic evidence for convective resurfacing of recycled arc-front mantle beneath back-arc basins. *Geophysical Research Letters*, **40**, 5849–5853, <https://doi.org/10.1002/2013GL057976>.

- Nebel, O., Sossi, P.A., Bénard, A., Wille, M., Vroon, P.Z. & Arculus, R.J. 2015. Redox-variability and controls in subduction zones from an iron-isotope perspective. *Earth and Planetary Science Letters*, **432**, 142–151, <https://doi.org/10.1016/j.epsl.2015.09.036>.
- Nebel, O., Sossi, P.A., Benard, A., Arculus, R.J., Yaxley, G.M., Woodhead, J.D., Rhodri, D.D. & Ruttor, S. 2019. Reconciling petrological and isotopic mixing mechanisms in the Pitcairn mantle plume using stable Fe isotopes. *Earth and Planetary Science Letters*, **521**, 60–67, <https://doi.org/10.1016/j.epsl.2019.05.037>.
- Parkinson, I.J. & Pearce, J.A. 1998. Peridotites from the Izu-Bonin-Mariana forearc (ODP Leg 125): evidence for mantle melting and melt-mantle interaction in a supra-subduction zone setting. *Journal of Petrology*, **39**, 1577–1618, <https://doi.org/10.1093/petroj/39.9.1577>.
- Parkinson, I.J., Hawkesworth, C.J. & Cohen, A.S. 1998. Ancient mantle in a modern arc: Osmium isotopes in Izu-Bonin-Mariana forearc peridotites. *Science*, **281**, 2011–2013, <https://doi.org/10.1126/science.281.5385.2011>.
- Pearce, J.A. 1992. Boninite and harzburgite from Leg 125 (Bonin-Mariana Forearc): a case study of magma genesis during the initial stages of subduction. *Proc., scientific results, ODP, Leg 125, Bonin/Mariana region*, **125**, 623–662, <https://doi.org/10.2973/odp.proc.sr.125.172.1992>.
- Pearce, J.A. & Reagan, M.K. 2019. Identification, classification, and interpretation of boninites from Anthropocene to Eoarchean using Si-Mg-Ti systematics. *Geosphere*, **15**, 1008–1037, <https://doi.org/10.1130/GES01661.1>.
- Peterson, J. 1891. Der Boninit von Peel Island, *Jahrb Hamburg Wiss Anst*, **8**, 341–349.
- Poitrasson, F., Delpech, G. & Grégoire, M. 2013. On the iron isotope heterogeneity of lithospheric mantle xenoliths: Implications for mantle metasomatism, the origin of basalts and the iron isotope composition of the Earth. *Contributions to Mineralogy and Petrology*, **165**, 1243–1258, <https://doi.org/10.1007/s00410-013-0856-7>.
- Polyakov, V.B. & Mineev, S.D. 2000. The use of Mossbauer spectroscopy in stable isotope geochemistry. *Geochimica et Cosmochimica Acta*, **64**, 849–865, [https://doi.org/10.1016/S0016-7037\(99\)00329-4](https://doi.org/10.1016/S0016-7037(99)00329-4).
- Reagan, M.K., Pearce, J.A., Petronotis, K., Almeev, R.R., Avery, A.J., Carvallo, C., Chapman, T., Christeson, G.L., Ferre, E.C., Godard, M., Heaton, D.E., Kirchenbaur, M., Kurz, W., Kutterolf, S., Li, H., Li, Y., Michibayashi, K., Morgan, S., Nelson, W.R., Prytulak, P., Python, M., Robertson, A.H.F., Ryan, J.G., Sager, W.W., Sakuyama, T., Shervais, J.W., Shimizu, K. & Whattam, S.A. 2015a. Expedition 352 core descriptions, Site U1439. *Proceedings of the International Ocean Discovery Program*, **352**, 1–290.
- Reagan, M.K., Pearce, J.A., Petronotis, K., Almeev, R.R., Avery, A.J., Carvallo, C., Chapman, T., Christeson, G.L., Ferre, E.C., Godard, M., Heaton, D.E., Kirchenbaur, M., Kurz, W., Kutterolf, S., Li, H., Li, Y., Michibayashi, K., Morgan, S., Nelson, W.R., Prytulak, P., Python, M., Robertson, A.H.F., Ryan, J.G., Sager, W.W., Sakuyama, T., Shervais, J.W., Shimizu, K. & Whattam, S.A. 2015b. Expedition 352 core descriptions, Site U1440. *Proceedings of the International Ocean Discovery Program*, **352**, 1–41.
- Reagan, M.K., Pearce, J.A., Petronotis, K., Almeev, R.R., Avery, A.J., Carvallo, C., Chapman, T., Christeson, G.L., Ferre, E.C., Godard, M., Heaton, D.E., Kirchenbaur, M., Kurz, W., Kutterolf, S., Li, H., Li, Y., Michibayashi, K., Morgan, S., Nelson, W.R., Prytulak, P., Python, M., Robertson,

- A.H.F., Ryan, J.G., Sager, W.W., Sakuyama, T., Shervais, J.W., Shimizu, K. & Whattam, S.A. 2015c. Expedition 352 core descriptions, Site U1441. *Proceedings of the International Ocean Discovery Program*, **352**, 1–162.
- Reagan, M.K., Pearce, J.A., Petronotis, K., Almeev, R.R., Avery, A.J., Carvallo, C., Chapman, T., Christeson, G.L., Ferre, E.C., Godard, M., Heaton, D.E., Kirchenbaur, M., Kurz, W., Kutterolf, S., Li, H., Li, Y., Michibayashi, K., Morgan, S., Nelson, W.R., Prytulak, P., Python, M., Robertson, A.H.F., Ryan, J.G., Sager, W.W., Sakuyama, T., Shervais, J.W., Shimizu, K. & Whattam, S.A. 2015d. Expedition 352 core descriptions, Site U1442. *Proceedings of the International Ocean Discovery Program*, **352**, 1–52.
- Reagan, M.K., Ishizuka, O., Stern, R.J., Kelley, K.A., Ohara, Y., Blichert-Toft, J., Bloomer, S.H., Cash, J., Fryer, P., Hanan, B.B., Hickey, Vargas, R., Ishii, T., Kimura, J.I., Peate, D.W., Rowe, M.C. & Woods, M. 2010. Fore-arc basalts and subduction initiation in the Izu-Bonin-Mariana system. *Geochemistry, Geophysics, Geosystems*, **11**, 1–17, <https://doi.org/10.1029/2009GC002871>.
- Reagan, M.K., McClelland, W.C., Girard, G., Goff, K.R., Peate, D.W., Ohara, Y. & Stern, R.J. 2013. The geology of the southern Mariana fore-arc crust: Implications for the scale of Eocene volcanism in the western Pacific. *Earth and Planetary Science Letters*, **380**, 41–51, <https://doi.org/10.1016/j.epsl.2013.08.013>.
- Reagan, M.K., Pearce, J.A., Petronotis, K., Almeev, R.R., Avery, A.J., Carvallo, C., Chapman, T., Christeson, G.L., Ferre, E.C., Godard, M., Heaton, D.E., Kirchenbaur, M., Kurz, W., Kutterolf, S., Li, H., Li, Y., Michibayashi, K., Morgan, S., Nelson, W.R., Prytulak, P., Python, M., Robertson, A.H.F., Ryan, J.G., Sager, W.W., Sakuyama, T., Shervais, J.W., Shimizu, K. & Whattam, S.A. 2015e. Expedition 352 summary. *Proceedings of the International Ocean Discovery Program*, **352**, <https://doi.org/10.14379/iodp.proc.352.101.2015>.
- Reagan, M.K., Pearce, J.A., Petronotis, K., Almeev, R.R., Avery, A.J., Carvallo, C., Chapman, T., Christeson, G.L., Ferre, E.C., Godard, M., Heaton, D.E., Kirchenbaur, M., Kurz, W., Kutterolf, S., Li, H., Li, Y., Michibayashi, K., Morgan, S., Nelson, W.R., Prytulak, P., Python, M., Robertson, A.H.F., Ryan, J.G., Sager, W.W., Sakuyama, T., Shervais, J.W., Shimizu, K. & Whattam, S.A. 2017. Subduction initiation and ophiolite crust: new insights from IODP drilling. *International Geology Review*, **59**, 1439–1450, <https://doi.org/10.1080/00206814.2016.1276482>.
- Reagan, M.K., Heaton, D.E., Schmitz, M.D., Pearce, J.A., Shervais, J.W. & Koppers, A.A.P. 2019. Forearc ages reveal extensive short-lived and rapid seafloor spreading following subduction initiation. *Earth and Planetary Science Letters*, **506**, 520–529, <https://doi.org/10.1016/j.epsl.2018.11.020>.
- Roskosz, M., Sio, C.K.I., Dauphas, N., Bi, W., Tissot, F.L.H., Hu, M.Y., Zhao, J. & Alp, E.E. 2015. Spinel-olivine-pyroxene equilibrium iron isotopic fractionation and applications to natural peridotites. *Geochimica et Cosmochimica Acta*, **169**, 184–199, <https://doi.org/10.1016/j.gca.2015.07.035>.
- Rouxel, O., Dobbek, N., Ludden, J. & Fouquet, Y. 2003. Iron isotope fractionation during oceanic crust alteration. *Chemical Geology*, **202**, 155–182, <https://doi.org/10.1016/j.chemgeo.2003.08.011>.

- Ryan, J.G., Shervais, J.W., et al. 2017. Application of a handheld X-ray fluorescence spectrometer for real-time, high-density quantitative analysis of drilled igneous rocks and sediments during IODP Expedition 352. *Chemical Geology*, **451**, 55–66, <https://doi.org/10.1016/j.chemgeo.2017.01.007>.
- Savov, I.P., Hickey-vargas, R., Antonio, M.D., Ryan, J.G. & Spadea, P. 2006. Petrology and Geochemistry of West Philippine Basin Basalts and Early Palau – Kyushu Arc Volcanic Clasts from ODP Leg 195 , Site 1201D : Implications for the Early History of the Izu – Bonin – Mariana Arc. *Journal of Petrology*, **47**, 277–299, <https://doi.org/10.1093/petrology/egi075>.
- Schauble, E.A. 2004. Applying Stable Isotope Fractionation Theory to New Systems. *Reviews in Mineralogy & Geochemistry*, **55**, 65–111.
- Schuessler, J.A., Schoenberg, R. & Sigmarsson, O. 2009. Iron and lithium isotope systematics of the Hekla volcano, Iceland - Evidence for Fe isotope fractionation during magma differentiation. *Chemical Geology*, **258**, 78–91, <https://doi.org/10.1016/j.chemgeo.2008.06.021>.
- Shahar, A., Young, E.D. & Manning, C.E. 2008. Equilibrium high-temperature Fe isotope fractionation between fayalite and magnetite: An experimental calibration. *Earth and Planetary Science Letters*, **268**, 330–338, <https://doi.org/10.1016/j.epsl.2008.01.026>.
- Shaw, D.M. 1970. Trace element fractionation during anatexis. *Geochimica et Cosmochimica Acta*, **34**, 237–243, [https://doi.org/10.1016/0016-7037\(70\)90009-8](https://doi.org/10.1016/0016-7037(70)90009-8).
- Shervais, J.W., Reagan, M., Haugen, E., Almeev, R.R., Pearce, J.A., Prytulak, J., Ryan, J.G., Whattam, S.A., Godard, M., Chapman, T., Li, H., Kurz, W., Nelson, W.R., Heaton, D., Kirchenbaur, M., Shimizu, K., Sakuyama, T., Li, Y. & Vetter, S.K. 2019. Magmatic Response to Subduction Initiation: Part 1. Fore-arc Basalts of the Izu-Bonin Arc From IODP Expedition 352. *Geochemistry, Geophysics, Geosystems*, **20**, 314–338, <https://doi.org/10.1029/2018GC007731>.
- Shervais, J.W., Reagan, M.K., Godard, M. & Prytulak, J. 2021. Magmatic Response to Subduction Initiation , Part II : Boninites and Related Rocks of the Izu-Bonin Arc From IODP Expedition 352 Geochemistry , Geophysics , Geosystems. *Geochemistry, Geophysics, Geosystems*, **22**, 1–34, <https://doi.org/10.1029/2020GC009093>.
- Shimizu, K., Ito, M., Chang, Q., Miyazaki, T., Ueki, K., Toyama, C., Senda, R., Vaglarov, B.S., Ishikawa, T. & Kimura, J.I. 2019. Identifying volatile mantle trend with the water–fluorine–cerium systematics of basaltic glass. *Chemical Geology*, **522**, 283–294, <https://doi.org/10.1016/j.chemgeo.2019.06.014>.
- Smyth, J.R. & Bish, D.L. 1988. Crystal Structures and Cation Sites of the Rock-Forming Minerals. *Boston, Allen and Unwin*, pp.332, <https://doi.org/10.5860/choice.26-0936>.
- Sobolev, A. V., Hofmann, A.W., Kuzmin, D.V., Yaxley, G.M., Arndt, N.T., Chung, S.L., Danyushevsky, L.V., Elliott, T., Frey, F.A., Garcia, M.O., Gurenko, A.A., Kamenetsky, V.S., Kerr, A.C., Krivolutsкая, N.A., Matvienkov, v.v., Nikogosian, I.K., Rocholl, A., Sigurdsson, I.A., Sushchevskaya, N.M. & Teklay, M. 2007. Supporting Online Material for The Amount of Recycled Crust in Sources of Mantle-Derived Melts. *Science*, **316**, 412–418.
- Soderman, C.R., Matthews, S., Shorttle, O., Jackson, M.G., Ruttor, S., Nebel, O., Turner, S., Beier, C., Millet, M.A., Widom, E., Humanyan, M. & Williams, H.M. 2021. Heavy $\delta^{57}\text{Fe}$ in ocean

- island basalts: A non-unique signature of processes and source lithologies in the mantle. *Geochimica et Cosmochimica Acta*, **292**, 309–332, <https://doi.org/10.1016/j.gca.2020.09.033>.
- Sossi, P.A. & O'Neill, H.S.C. 2017. The effect of bonding environment on iron isotope fractionation between minerals at high temperature. *Geochimica et Cosmochimica Acta*, **196**, 121–143, <https://doi.org/10.1016/j.gca.2016.09.017>.
- Sossi, P.A., Foden, J.D. & Halverson, G.P. 2012. Redox-controlled iron isotope fractionation during magmatic differentiation: An example from the Red Hill intrusion, S. Tasmania. *Contributions to Mineralogy and Petrology*, **164**, 757–772, <https://doi.org/10.1007/s00410-012-0769-x>.
- Sossi, P.A., Nebel, O. & Foden, J. 2016. Iron isotope systematics in planetary reservoirs. *Earth and Planetary Science Letters*, **452**, 295–308, <https://doi.org/10.1016/j.epsl.2016.07.032>.
- Stern, R.J., Fouch, M.J. & Klemperer, S.L. 2003. An overview of Izu Bonin Mariana subduction factory. *Geophysical Monograph-American Geophysical Union*, **138**, 175–222.
- Taylor, B. & Goodliffe, A.M. 2004. The West Philippine Basin and the initiation of subduction, revisited. *Geophysical Research Letters*, **31**, 2–5, <https://doi.org/10.1029/2004GL020136>.
- Teng, F., Dauphas, N. & Helz, R.T. 2008. Iron Isotope Fractionation During Magmatic Differentiation in Kilauea Iki Lava Lake. *Science*, **320**, 1620–1622, <https://doi.org/10.1126/science.1157166>.
- Teng, F.Z., Dauphas, N., Huang, S. & Marty, B. 2013. Iron isotopic systematics of oceanic basalts. *Geochimica et Cosmochimica Acta*, **107**, 12–26, <https://doi.org/10.1016/j.gca.2012.12.027>.
- Tollstrup, D., Gill, J., Kent, A., Prinkey, D., Williams, R., Tamura, Y. & Ishizuka, O. 2010. Across-arc geochemical trends in the Izu-Bonin arc: Contributions from the subducting slab, revisited. *Geochemistry, Geophysics, Geosystems*, **11**, 1–27, <https://doi.org/10.1029/2009GC002847>.
- Turner, S., Williams, H., Piazzolo, S., Blichert-Toft, J., Gerdes, M., Adam, J., Liu, X.M., Schaefer, B. & Maury, R. 2018. Sub-arc xenolith Fe-Li-Pb isotopes and textures tell tales of their journey through the mantle wedge and crust. *Geological Society of America*, **46**, 947–950, <https://doi.org/10.1130/G45359E.11034-1034>.
- Umino, S. 1986. Magma mixing in boninite sequence of Chichijima, Bonin Islands. *Journal of Volcanology and Geothermal Research*, **29**, 125–157.
- Urey, H.C. 1947. The Thermodynamic Properties of Isotopic Substances. *Journal of the Chemical Society*, 562–581.
- Walter, M.J. 1998. Melting of Garnet Peridotite and the Origin of Komatiite and Depleted Lithosphere. *Journal of Petrology*, **39**, 29–60, <https://doi.org/10.1093/petrology/39.1.29>.
- Wawryk, C.M. & Foden, J.D. 2017. Iron-isotope systematics from the Batu Hijau Cu-Au deposit, Sumbawa, Indonesia. *Chemical Geology*, **466**, 159–172, <https://doi.org/10.1016/j.chemgeo.2017.06.004>.
- Weyer, S. & Ionov, D.A. 2007. Partial melting and melt percolation in the mantle: The message from Fe isotopes. *Earth and Planetary Science Letters*, **259**, 119–133, <https://doi.org/10.1016/j.epsl.2007.04.033>.

- Weyer, S., Anbar, A.D., Brey, G.P., Münker, C., Mezger, K. & Woodland, A.B. 2005. Iron isotope fractionation during planetary differentiation. *Earth and Planetary Science Letters*, **240**, 251–264, <https://doi.org/10.1016/j.epsl.2005.09.023>.
- Whattam, S.A., Shervais, J.W., Reagan, M.K., Coulthard, D.A., Pearce, J.A., Jones, P., Seo, J., Putirka, K., Chapman, T., Heaton, D., Li, H., Nelson, W.R., Shimizu, K. & Stern, R.J. 2020. Mineral compositions and thermobarometry of basalts and boninites recovered during IODP Expedition 352 to the Bonin forearc. *American Mineralogist*, **105**, 1490–1507, <https://doi.org/10.2138/am-2020-6640>.
- Wilke, M. 2005. Fe in magma - An overview. *Annals of Geophysics*, **48**, 609–617.
- Williams, H.M. & Bizimis, M. 2014. Iron isotope tracing of mantle heterogeneity within the source regions of oceanic basalts. *Earth and Planetary Science Letters*, **404**, 396–407, <https://doi.org/10.1016/j.epsl.2014.07.033>.
- Williams, H.M., McCammon, C.A., Peslier, A.H., Halliday, A.N., Teutsch, N., Levasseur, S. & Burg, J.P. 2004. Iron isotope fractionation and the oxygen fugacity of the mantle. *Science*, **304**, 1656–1659, <https://doi.org/10.1126/science.1095679>.
- Williams, H.M., Peslier, A.H., McCammon, C., Halliday, A.N., Levasseur, S., Teutsch, N. & Burg, J.P. 2005. Systematic iron isotope variations in mantle rocks and minerals: The effects of partial melting and oxygen fugacity. *Earth and Planetary Science Letters*, **235**, 435–452, <https://doi.org/10.1016/j.epsl.2005.04.020>.
- Williams, H.M., Prytulak, J., Woodhead, J.D., Kelley, K.A., Brounce, M. & Plank, T. 2018. Interplay of crystal fractionation, sulfide saturation and oxygen fugacity on the iron isotope composition of arc lavas: An example from the Marianas. *Geochimica et Cosmochimica Acta*, **226**, 224–243, <https://doi.org/10.1016/j.gca.2018.02.008>.
- Wood, B.J. & Virgo, D. 1989. Upper mantle oxidation state: Ferric iron contents of Iherzolite spinels by ^{57}Fe Mössbauer spectroscopy and resultant oxygen fugacities. *Geochimica et Cosmochimica Acta*, **53**, 1277–1291, [https://doi.org/10.1016/0016-7037\(89\)90062-8](https://doi.org/10.1016/0016-7037(89)90062-8).
- Woodland, A.B. & Koch, M. 2003. Variation in oxygen fugacity with depth in the upper mantle beneath the Kaapvaal craton, Southern Africa. *Earth and Planetary Science Letters*, **214**, 295–310, [https://doi.org/10.1016/S0012-821X\(03\)00379-0](https://doi.org/10.1016/S0012-821X(03)00379-0).
- Workman, R.K. & Hart, S.R. 2005. Major and trace element composition of the depleted MORB mantle (DMM). *Earth and Planetary Science Letters*, **231**, 53–72, <https://doi.org/10.1016/j.epsl.2004.12.005>.
- Wu, J., Suppe, J., Lu, R. & Kanda, R. 2016. Philippine Sea and East Asian plate tectonics since 52Ma constrained by new subducted slab reconstruction methods. *Journal of Geophysical Research: Solid Earth*, **121**, 4670–4741, <https://doi.org/10.1002/2016JB012923>.
- Yaxley, G.M. & Green, D.H. 1998. Reactions between eclogite and peridotite: mantle refertilisation by subduction of oceanic crust. *Schweizerische Mineralogische und Petrographische Mitteilungen*, **78**, 243–255.
- Ye, H., Wu, C., Brzozowski, M.J., Yang, T., Zha, X., Zhao, S., Gao, B. & Li, W. 2020. Calibrating equilibrium Fe isotope fractionation factors between magnetite, garnet, amphibole, and

- biotite. *Geochimica et Cosmochimica Acta*, **271**, 78–95, <https://doi.org/10.1016/j.gca.2019.12.014>.
- Yogodzinski, G.M., Bizimis, M., Hickey-Vargas, R., McCarthy, A., Hocking, B.D., Savov, I.P., Ishizuka, O. & Arculus, R. 2018. Implications of Eocene-age Philippine Sea and forearc basalts for initiation and early history of the Izu-Bonin-Mariana arc. *Geochimica et Cosmochimica Acta*, **228**, 136–156, <https://doi.org/10.1016/j.gca.2018.02.047>.
- Young, E.D., Manning, C.E., Schauble, E.A., Shahar, A., Macris, C.A., Lazar, C. & Jordan, M. 2015. High-temperature equilibrium isotope fractionation of non-traditional stable isotopes: Experiments, theory, and applications. *Chemical Geology*, **395**, 176–195, <https://doi.org/10.1016/j.chemgeo.2014.12.013>.
- Zhao, X., Zhang, H., Zhu, X., Tang, S. & Tang, Y. 2010. Iron isotope variations in spinel peridotite xenoliths from North China Craton: Implications for mantle metasomatism. *Contributions to Mineralogy and Petrology*, **160**, 1–14, <https://doi.org/10.1007/s00410-009-0461-y>.
- Zhao, X., Zhang, H., Zhu, X., Tang, S. & Yan, B. 2012. Iron isotope evidence for multistage melt-peridotite interactions in the lithospheric mantle of eastern China. *Chemical Geology*, **292**, 127–139, <https://doi.org/10.1016/j.chemgeo.2011.11.016>.
- Zhao, X.M., Zhang, H.F., Zhu, X.K., Zhu, B. & Cao, H. hui. 2015. Effects of melt percolation on iron isotopic variation in peridotites from Yangyuan, North China Craton. *Chemical Geology*, **401**, 96–110, <https://doi.org/10.1016/j.chemgeo.2015.02.031>.

Chapter Five

The controls on zinc isotopic fractionation in IODP Expedition

352 subduction initiation lavas from the Bonin forearc

Abstract

Key components of subduction zone lavas are slab-derived melts and fluids. However, there are few robust approaches to tracing these inputs and there is no consensus on the scale of their contribution to arc lava geochemistry. Recently it has been suggested that Zn isotopes can be mobilised and fractionated by subduction-related fluids via complexation with sulphate, carbonate and/or halogen ions (e.g. Pons *et al.* 2016; Debret *et al.* 2018, 2021). Zinc isotopes may therefore trace subduction fluids through the mantle wedge. However, whether the Zn budget of subduction fluids is sufficient to influence the Zn budget of the mantle wedge and be recognised in arc lavas, is controversial.

This study measured Zn isotopic compositions of the IODP Expedition 352 fore-arc basalts (FABs) and boninites, with the aim of understanding if Zn isotopes are an effective tracer of arc lava source components. Boninites show clear geochemical evidence of subduction inputs, whereas FABs do not (Li *et al.* 2019; Shervais *et al.* 2019, 2021). This study finds no statistically significant $\delta^{66}\text{Zn}$ difference between FABs and boninites. There is therefore no evidence to suggest that subduction-derived fluids, melts and sediments have an observable influence over the $\delta^{66}\text{Zn}$ of boninites and arc lavas. This study also finds the largest partial melting attributed $\delta^{66}\text{Zn}$ range recorded so far in the literature. Expedition 352 FABs exhibit a 0.20 ‰ $\delta^{66}\text{Zn}$ range that correlates with $\text{CaO}/\text{Al}_2\text{O}_3$ and Zn concentrations, but cannot be fully accounted for by current mantle melting models. Mantle heterogeneity and melt mixing are currently the most likely causes of this large variance, and measuring the $\delta^{66}\text{Zn}$ of enriched FAB (E-FAB) samples in future work may shed more light on the large FAB $\delta^{66}\text{Zn}$ range. The clear message of this study is, however, that subduction-derived fluids, melts, and sediments do not have observable effects on the $\delta^{66}\text{Zn}$ of arc lavas.

CHAPTER FIVE TABLE OF CONTENTS

5.1. Introduction	195
5.1.1. Aims.....	198
5.2. IODP Expedition 352 Samples	198
5.3. Methods & Results.....	199
5.3.1. Fore-arc Basalt Zn Isotopic Compositions	202
5.3.2. Boninite Zn Isotopic Compositions	202
5.4. Discussion.....	204
5.4.1. Lack of Zn isotope difference between FABs and boninites	204
5.4.2. Boninite Zn Isotopic Compositions	205
5.4.2.1. Origin of the isotopically light boninites	205
5.4.2.2. Cause(s) of boninite $\delta^{66}\text{Zn}$ variations without anomalously light boninites?	210
5.4.3. Fore-arc Basalt Zn Isotopic Compositions	211
5.4.3.1. Could variable fluid addition or alteration account for the FAB $\delta^{66}\text{Zn}$ variation?	213
5.4.3.2. Magmatic differentiation and source depletion as $\delta^{66}\text{Zn}$ controls in FABs	215
5.4.3.3. Could melt mixing account for the FAB $\delta^{66}\text{Zn}$ variation?.....	221
5.4.3.4. Origin of the Depleted FAB Sample	224
5.4.4. Implications for isolating arc lava source components	225
5.5. Conclusions	226
References	226

5.1. Introduction

Arc lavas are geochemically distinct from mid-ocean ridge basalts (MORB). MORB forms by anhydrous decompression mantle melting due to seafloor spreading. Whereas, most arc lavas are hydrous, originating from melting of the mantle wedge via the injection of fluids, melts and sediments released from the subducting slab via dehydration and partial melting. Thus, arc lavas tend to be more enriched in LILEs, LREEs, and FMEs than MORB, but relatively depleted in HFSEs (e.g. Pearce & Peate 1995). The incorporation of subduction-derived sulphate and carbonate-bearing fluids and melts in subduction zones has been suggested to oxidise the mantle wedge (Parkinson & Arculus 1999; Evans 2012). However, there are few robust approaches to tracing sulphate transfer in subduction zones. There is therefore no consensus on the extent that sulphate and carbonate transfer from slab to mantle wedge occurs, and whether magmatic or subduction processes are the dominant controls on arc lava geochemistry.

Previous studies have attempted to use Fe stable isotopes to isolate different arc lava source components, and the influence of magmatic processes versus subduction inputs (e.g. Nebel *et al.* 2015; Foden *et al.* 2018; Williams *et al.* 2018). However, these studies and Fe isotope work from Chapter four have struggled to deconvolve Fe isotope fractionation mechanisms. Chapter four suggested that one of the obstacles to interpreting Fe isotope signatures in arc lavas is that Fe is a major element that is fluid mobile, compatible in most major mafic rock-forming minerals, and can therefore be fractionated by many different processes. It was therefore suggested that Fe should be coupled with additional isotope systems that have more selective fractionation mechanisms to provide more robust constraints that allow the different arc lava source components to be isolated and potentially traced.

Zinc isotopes have been increasingly applied to igneous geochemical applications as measurements have become more precise (**Fig. 5.1**; Chen *et al.* 2013; Doucet *et al.* 2016; Pons *et al.* 2016; Wang *et al.* 2017; Inglis *et al.* 2017; Debret *et al.* 2018, 2021; Huang *et al.* 2018a, b; Sossi *et al.* 2018; Beunon *et al.* 2020). Since Zn is less compatible than Fe in major mantle phases and only has one oxidation state, Zn isotope fractionation mechanisms likely differ from Fe mechanisms and therefore may be more selective. Zinc may therefore be able to aid deconvolving magmatic and subduction-related arc lava source components. Unfortunately, Zn isotope literature on terrestrial igneous systems is more limited than Fe isotope literature. Our understanding of Zn isotope fractionation, and the ultimate magnitudes of fractionation in response to different igneous processes is therefore limited. Non-metasomatic peridotites have been found to be fairly homogenous ($\delta^{66}\text{Zn} = 0.172 \pm 0.077 \text{ ‰}$, 2SD, (Wang *et al.* 2017; Huang *et al.* 2018a; Sossi *et al.* 2018b)) as have MORB ($\delta^{66}\text{Zn} = 0.270 \pm 0.056 \text{ ‰}$ 2SD (Wang *et al.* 2017; Huang *et al.* 2018b; Liao *et al.* 2020)). However, altered oceanic crust (AOC) ($\delta^{66}\text{Zn} = 0.18 - 0.55 \text{ ‰}$ (Huang *et al.* 2016)), sediments ($\delta^{66}\text{Zn} = 0.04 - 1.34 \text{ ‰}$; (Maréchal *et al.* 2000; Pichat *et al.* 2003; Bentahila *et al.* 2008; Pons *et al.* 2011)) and subducted serpentinites ($\delta^{66}\text{Zn} = -0.56 - 0.55 \text{ ‰}$ (Pons *et al.* 2016; Debret *et al.* 2018, 2021)) are significantly more variable and distinct from mantle and MORB compositions (**Fig. 5.1**). Thus, there is the potential for subduction inputs and fluids to influence arc lava $\delta^{66}\text{Zn}$ and be distinct enough for $\delta^{66}\text{Zn}$ to trace subduction inputs.

Recent $\delta^{66}\text{Zn}$ work on ultra-high pressure terrains and serpentinitised forearc mantle peridotites have suggested that Zn can be mobilised and fractionated by subduction-related fluids (e.g. Pons *et al.* 2016; Debret *et al.* 2018, 2021). Serpentine devolatilisation generated sulphate, carbonate and/or hypersaline fluids have been suggested to preferentially complex with isotopically heavy Zn (Zn-SO_4^{2-} , Zn-CO_3^{2-}) (Fujii *et al.* 2014; Ducher *et al.* 2016; Liu *et al.* 2016; Pons *et al.* 2016; Debret *et al.* 2018) which could influence $\delta^{66}\text{Zn}$ of the mantle wedge. Zinc isotopes may therefore be able to

trace carbonate and sulphate exchange between subducted slabs and the mantle wedge. The controversy lies in whether the Zn budget of subduction fluids is sufficient for them to have an observable effect on arc lava $\delta^{66}\text{Zn}$. A study of dehydrated slab residues from ophiolite complexes of the Western European Alps (Inglis *et al.* 2017) utilised Zn isotope measurements and modelling to suggest that even in the presence of aqueous sulphate and carbonate species, Zn solubility is not high enough to create an observable Zn isotope fractionation during slab devolatilisation. This is supported by Kamchatka and Aleutian arc lava $\delta^{66}\text{Zn}$ which do not correlate with geochemical indicators of subduction inputs such as Ba/Th and Ba/La (Huang *et al.* 2018b).

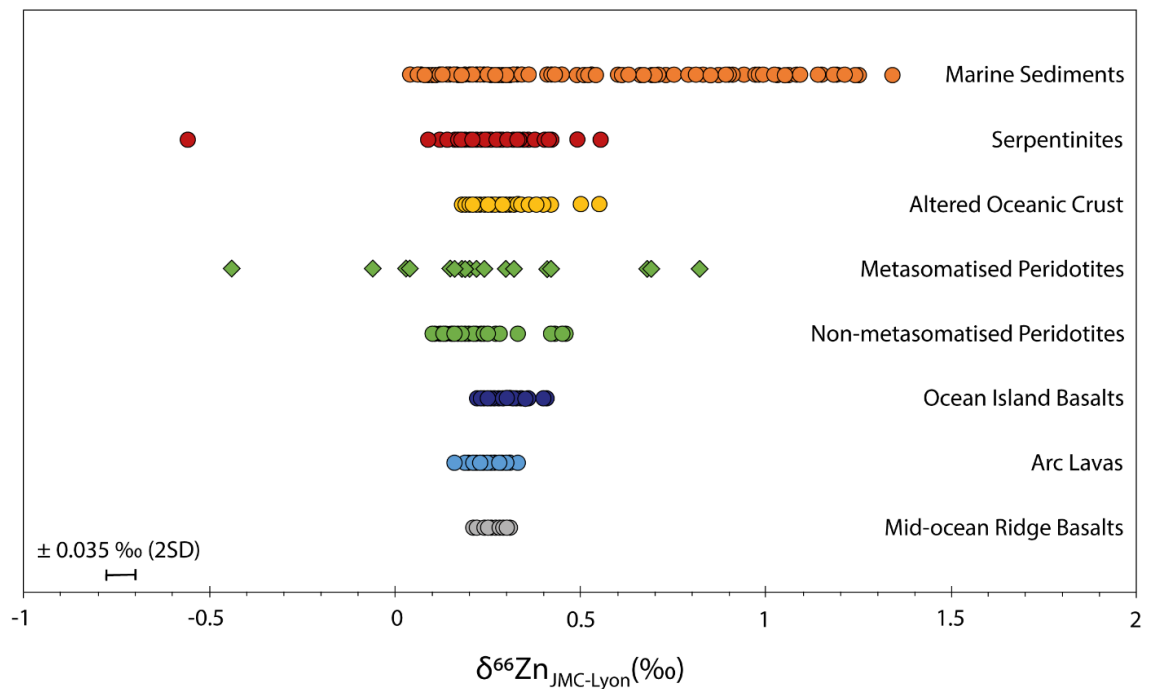


Figure 5.1: Summary comparison of $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$ literature data from studies relevant to this chapter. The data includes, MORB (Wang *et al.* 2017; Huang *et al.* 2018; Liao *et al.* 2020), arc lavas (Huang *et al.* 2018b), OIB (Herzog *et al.* 2009; Chen *et al.* 2013; Wang *et al.* 2017), peridotites (Doucet *et al.* 2016; Wang *et al.* 2017; Huang *et al.* 2018a; Sossi *et al.* 2018), AOC (Huang *et al.* 2016), serpentinites (Pons *et al.* 2016; Debret *et al.* 2018, 2021), and marine sediments (Maréchal *et al.* 2000; Pichat *et al.* 2003; Bentahila *et al.* 2008; Pons *et al.* 2011). The average error is ± 0.035 ‰ (2SD).

Mantle partial melting and fractional crystallisation of olivine and Fe-Ti oxides have both been suggested to fractionate Zn isotopes, creating heavy Zn enriched melts relative to their sources (e.g. Chen *et al.* 2013; Doucet *et al.* 2016; Wang *et al.* 2017; Sossi *et al.* 2018). However, the only major study of arc lava $\delta^{66}\text{Zn}$ (Huang *et al.* 2018b) attributes arc lava $\delta^{66}\text{Zn}$ to mantle partial melting. The study found that the Kamchatka and Aleutian arc lavas are isotopically similar to MORB, BABBs and OIBs, and there are no correlations between $\delta^{66}\text{Zn}$ and magmatic differentiation indicators. They therefore concluded that in subduction zones, fractional crystallisation has a minimal influence on arc lava $\delta^{66}\text{Zn}$. However, they attribute the isotopic offset between DMM estimates and the

Kamchatka and Aleutian arc lavas to partial melting-controlled $\delta^{66}\text{Zn}$ fractionation. One drawback of this study is that measuring arc lavas from established subduction zones to explore source and subduction-related processes can be complicated by the effects of magma transport and evolution through the crust.

The IODP Expedition 352 fore-arc basalts (FABs) and boninites measured for Fe isotopes in Chapter four negate the effects of magma transport and evolution through the crust. They also allow the comparison of $\delta^{66}\text{Zn}$ from two different lithologies, close in both space and time but with different inputs. FABs formed by anhydrous decompression melting in response to slab rollback and show no evidence of subduction inputs (Li *et al.* 2019; Shervais *et al.* 2019), whereas the boninites show clear evidence of subduction inputs (Li *et al.* 2019; Shervais *et al.* 2021). A direct comparison of FAB and boninite $\delta^{66}\text{Zn}$ should therefore address the debate surrounding whether subduction inputs are identifiable via arc lava $\delta^{66}\text{Zn}$. It should also allow the magmatic and subduction processes involved in arc lava formation to be better isolated, meaning we can better understand if Zn isotopes are an effective approach to tracing arc lava source components.

5.1.1. Aims

To address whether subduction-related or magmatic processes are the chief controls on the $\delta^{66}\text{Zn}$ of arc lavas, this chapter aims to answer the following questions:

4. Are IODP Expedition 352 fore-arc basalt and boninite $\delta^{66}\text{Zn}$ compositions isotopically distinct?
5. Does the addition of slab melts, fluids or sediments influence the Zn isotopic composition of boninites?
6. What process(es) are responsible for internal FAB and boninite $\delta^{66}\text{Zn}$ variation?

5.2. IODP Expedition 352 Samples

The Zn samples in this chapter include the same set of nine fore-arc basalts (FABs) and forty boninites from the Bonin forearc (**Fig. 5.2**), recovered by IODP Expedition 352 as used in Chapter four. The same six harzburgites and dunites from Chapter four are also included. The peridotites are interpreted as the closest available samples to the residues left after FAB and boninite extraction. For detailed descriptions of the peridotite samples, see Parkinson & Pearce (1998) and Parkinson *et al.* (1998). The Expedition 352 FAB and boninite samples are described in detail in Chapter four.

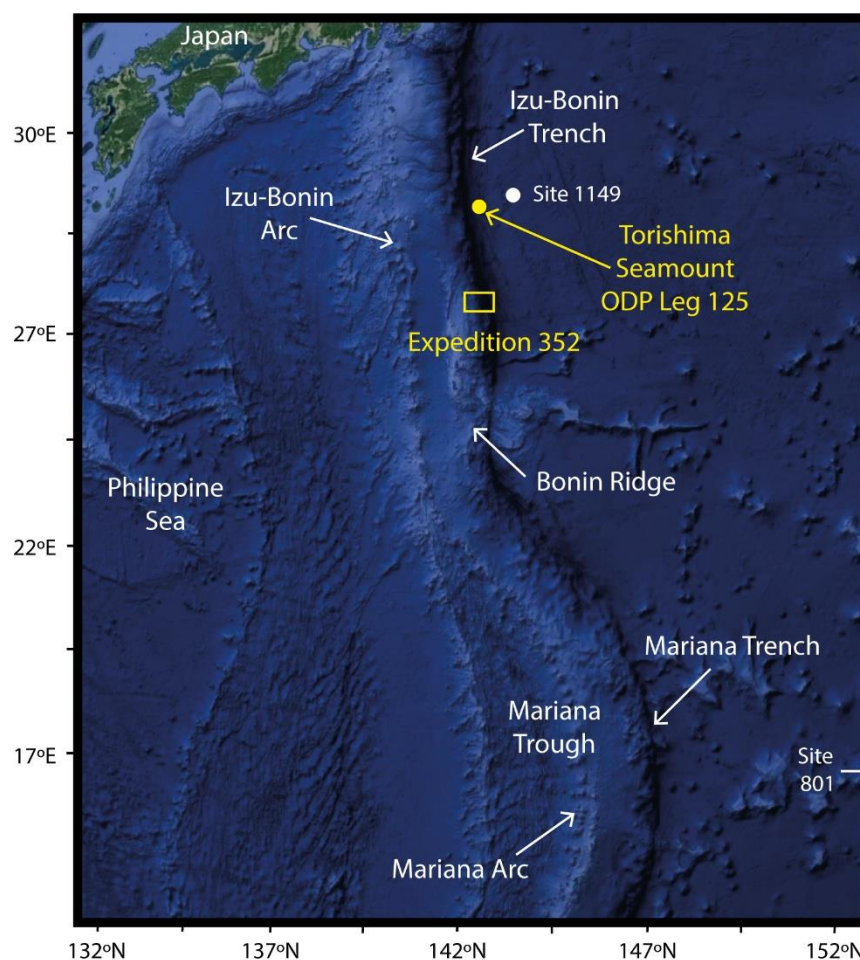


Figure 5.2: Location map of IODP Expedition 352 to the Bonin fore-arc from Chapter four. Topography map and coordinates taken from Google Earth, and annotations from Reagan et al. (2015b) and Parkinson & Pearce (1998).

5.3. Methods & Results

All samples are the IODP Expedition 352 POOL samples from Chapter four, acquired as pre-crushed whole-rock powders. All Zn isotope data was collected at Durham University. Full methods are outlined in Chapter two and all results are presented in **Table 4.2**. The Zn isotopic compositions of reference materials processed with the samples agree with accepted literature values, and are presented in Chapter 2. Total procedural blanks processed with every batch of 12 samples are detailed in Chapter 2 and were always $< 36 \text{ ng.g}^{-1} \text{ Zn}$ which is within the acceptable upper blank boundary for Zn relative to the total amount of Zn processed ($\sim 2\text{-}12 \text{ }\mu\text{g}$).

Table 5.1: Zinc isotope ratios measured in the IODP Expedition 352 FABs and boninites. Zinc isotopes as $\delta^{66}\text{Zn}$ (‰) relative to reference standard JMC-Lyon. Rock type abbreviations are as such: N-FAB (normal fore-arc basalt), P-FAB (primitive fore-arc basalt), D-FAB (depleted fore-arc basalt), LSB (low-silica boninite), HSB (high-silica boninite), BB (basaltic boninite), HMA (high-magnesian andesite). All isotope measurements were conducted on Neptune MC-ICP MS.

				Zinc Isotopes				
Sample	Series	Type	Depth (mbsl)	$\delta^{66}\text{Zn}_{\text{Lyon}}$ (‰)	error (2SD)	$\delta^{67}\text{Zn}_{\text{Lyon}}$ (‰)	error (2SD)	n
U1439C - Boninites								
U1439C 16R1-26/30	axial	LSB	299.76	0.225	0.023	-0.116	0.030	4
U1439C 22R1-89/95	axial	LSB	349.19	0.229	0.072	0.250	0.144	4
U1439C 41R1-99/106	axial	LSB	515.09	0.255	0.020	-0.064	0.074	4
U1439C-29R-4-W 78/82	axial	LSB	421.29	0.231	0.038	-0.123	0.085	8
U1439C-31R-5-W 12/17	axial	LSB	441.8	0.232	0.034	-0.140	0.040	4
U1439C 19R4 11/17	axial	LSB	333.16	0.289	0.034	-0.084	0.067	3
U1439C 40R1 33/38	axial	LSB	509.43	0.100	0.003	-0.312	0.075	3
U1439C 31R1 15/20	axial	LSB	436.25	0.220	0.014	-0.165	0.067	3
U1439C 26R1 132/137	axial	LSB	388.62	0.202	0.014	-0.186	0.084	3
U1439C 19R3 58/62	axial	LSB	332.22	-0.020	0.038	-0.591	0.098	6
U1439C 11R1 124/127	axial	LSB	266.64	0.262	0.033	-0.140	0.074	6
U1439C 33R2-W 23/30	axial	LSB	457.17	0.222	0.009	-0.085	0.115	3
U1439C 38R1 103/106	axial	LSB	495.63	0.261	0.025	-0.055	0.082	5
U1439C 27R3-W 80/87	axial	LSB	400.47	0.230	0.016	-0.076	0.078	4
U1439C 23R1-W 42/48	axial	LSB	358.52	0.248	0.025	-0.085	0.078	4
U1439C 28R2-W 66/71	axial	LSB	408.91	0.237	0.012	-0.128	0.037	4
U1439C-10R2-W 13/19	axial	BB	262.03	0.293	0.020	-0.023	0.021	4
U1439C-37R1-W 42/48	axial	HMA	485.22	0.324	0.027	0.044	0.092	7
U1439C 4R1-W 26/32	off-axis	HSB	201.86	0.257	0.016	-0.077	0.028	4
U1439C 6R1 25/30	off-axis	HSB	221.45	0.196	0.049	-0.274	0.093	6
U1439C 2R3-W 38/46	off-axis	HSB	185.13	0.216	0.016	-0.107	0.069	3
U1439A 23X1-W 0/3	off-axis	HSB	196.2	0.259	0.010	-0.070	0.023	4
U1439A 21X1-W 0/7	off-axis	HSB	182.5	0.230	0.014	-0.073	0.064	4
U1439C 5R1-W 92/96	off-axis	HSB	212.32	0.305	0.020	-0.005	0.072	4
U1442A - Boninites								
U1442A-35R-1-W 51/55	axial	LSB	306.01	-0.305	0.033	-0.790	0.059	4
U1442A 23R1 99/103	axial	LSB	189.69	0.347	0.036	0.013	0.115	3
U1442A 56R1 19/24	axial	LSB	510.49	0.262	0.035	-0.110	0.074	3

Table 5.1: continued

Sample	Series	Type	Depth (mbsl)	Zinc Isotopes				
				$\delta^{66}\text{Zn}_{\text{Lyon}}$ (‰)	error (2SD)	$\delta^{67}\text{Zn}_{\text{Lyon}}$ (‰)	error (2SD)	n
U1442A 49R2-W 60/65	axial	LSB	443.85	0.299	0.020	0.062	0.124	3
U1442A 36R2-W 17/22	axial	LSB	316.495	0.277	0.046	-0.044	0.093	7
U1442A 54R1-W 13/18	axial	LSB	490.93	0.266	0.042	-0.060	0.176	7
U1442A 57R2-W 116/121	axial	LSB	522.63	0.247	0.012	-0.070	0.109	3
U1442A 30R2-W 21/27	axial	BB	258.435	0.246	0.051	-0.118	0.169	6
U1442A 20R1-104/108	off-axis	HSB	160.64	0.280	0.046	-0.039	0.080	4
U1442A 22R1-122/125	off-axis	HSB	180.22	0.204	0.025	0.258	0.113	4
U1442A 47R1-W 50/55	off-axis	HSB	423.1	0.221	0.012	-0.146	0.091	3
U1442A 23R2-W 30/35	off-axis	HSB	190.46	0.254	0.037	-0.036	0.119	3
U1442A 28R1-W 10/14	off-axis	HSB	237.5	-0.012	0.008	-0.417	0.077	3
U1442A 48R1-W 87/92	off-axis	HSB	433.17	0.212	0.024	-0.100	0.051	3
U1442A 15R1-W 70/75	off-axis	HSB	119.4	0.223	0.013	-0.106	0.079	4
U1442A 13R1-W 4/10	off-axis	HSB	110.94	0.294	0.021	-0.017	0.043	4

U1440B - Fore-arc basalts								
U1440B 17R2-23/32	axial	N-FAB	213.8	0.375	0.013	0.086	0.052	4
U1440B 26R1-64/68	axial	N-FAB	271.14	0.176	0.044	0.242	0.020	4
U1440B 28R1-31/38	axial	N-FAB	290.31	0.211	0.027	0.086	0.138	4
U1440B-8R-1-W 20/23	off-axis	N-FAB	136.54	0.253	0.020	0.172	0.165	4
U1440B-12R-2-W 4/8	off-axis	P-FAB	165.14	0.230	0.063	0.160	0.122	4
U1440B-17R-1-W 11/13	axial	N-FAB	212.31	0.307	0.024	-0.040	0.027	4
U1440B-29R-1-W 5/8	axial	N-FAB	299.75	0.233	0.017	0.176	0.122	4

U1441A - Fore-arc basalts								
U1441A-21R-1-W 37/42	axial	N-FAB	190.27	0.237	0.024	0.135	0.057	4
U1441A-3-19R1-66/72	off-axis	D-FAB	171.16	-0.007	0.028	0.075	0.095	4

ODP Leg 125 - Torishima Peridotites								
783A-18R1-064/071	Torishima Forearc Seamount	Harz		0.254	0.038	-0.061	0.152	6
784A-38R2-072/077		Dunite		0.311	0.043	0.074	0.176	6
784A-40R2-070/075		Dunite		0.278	0.039	0.046	0.043	3
784A-45R2-33/38		Harz		0.274	0.011	0.049	0.100	3
784A-45R-CC-7/10		Harz		0.257	0.019	0.067	0.074	3
783A-18R1-119-124		Harz		0.289	0.034	0.103	0.126	3

5.3.1. Fore-arc Basalt Zn Isotopic Compositions

The Expedition 352 FABs have a $\delta^{66}\text{Zn}$ range of 0.382 ‰ and a mean of $0.224 \text{ ‰} \pm 0.208$ (2SD) (**Figure 5.3**). FAB $\delta^{66}\text{Zn}$ positively correlates with TiO_2 , Na_2O , Pb, U and Zn concentrations, plus Ce/Yb ratios, and negatively correlates with MgO concentrations and $\text{CaO}/\text{Al}_2\text{O}_3$ ratios. The D-FAB is significantly isotopically lighter than the other FABs and therefore skews the mean and enlarges the range. Since the D-FAB is also exceptionally chemically depleted in terms of trace element concentrations and radiogenic isotopes (Li *et al.* 2019; Shervais *et al.* 2019), it's inclusion in the FAB $\delta^{66}\text{Zn}$ population should be considered carefully (section 5.4.2). The FAB $\delta^{66}\text{Zn}$ mean is similar to that of MORB ($0.269 \text{ ‰} \pm 0.056$ (2SD) and $0.224 \text{ ‰} \pm 0.208$ (2SD) respectively). A student T-test shows comparing the FAB and MORB $\delta^{66}\text{Zn}$ means produced a P-value of 0.231, showing that at a 95% confidence interval there is not enough evidence for FAB and MORB $\delta^{66}\text{Zn}$ to be distinguished. However, the FAB $\delta^{66}\text{Zn}$ range is significantly larger than the MORB range, even if the D-FAB is excluded from the FAB population (0.199 ‰ vs 0.100 ‰).

5.3.2. Boninite Zn Isotopic Compositions

The Expedition 352 boninite $\delta^{66}\text{Zn}$ mean is $0.220 \text{ ‰} \pm 0.222$ (2SD), the HSB $\delta^{66}\text{Zn}$ mean is $0.224 \text{ ‰} \pm 0.152$ (2SD), and the LSB $\delta^{66}\text{Zn}$ mean is $0.209 \text{ ‰} \pm 0.265$ (2SD) (**Figure 5.3**). Student T-tests show that at 95% confidence intervals the boninite $\delta^{66}\text{Zn}$ compositions are statistically indistinguishably from literature arc lava $\delta^{66}\text{Zn}$ data (P-value = 0.275) and the HSB and LSB $\delta^{66}\text{Zn}$ compositions are also indistinguishable (P-value = 0.667). There are no correlations between boninite $\delta^{66}\text{Zn}$ and major or trace element concentrations or radiogenic isotope ratios. The boninite $\delta^{66}\text{Zn}$ range is 0.652 ‰ (**Figure 5.3**) which is larger than currently documented for FAB, MORB, and arc lavas (**Fig. 5.3**). The high variance is due to four isotopically light boninites, which include one extremely light sample ($\delta^{66}\text{Zn} = -0.305 \pm 0.033 \text{ ‰}$ 2SD, **Fig. 5.3**). It is therefore important to assess the cause(s) of these light signatures and whether the four light boninites should be considered independently from the main boninite population. However, the decision to include or exclude them from the boninite population does not affect T-test results (**Fig. 5.3**).

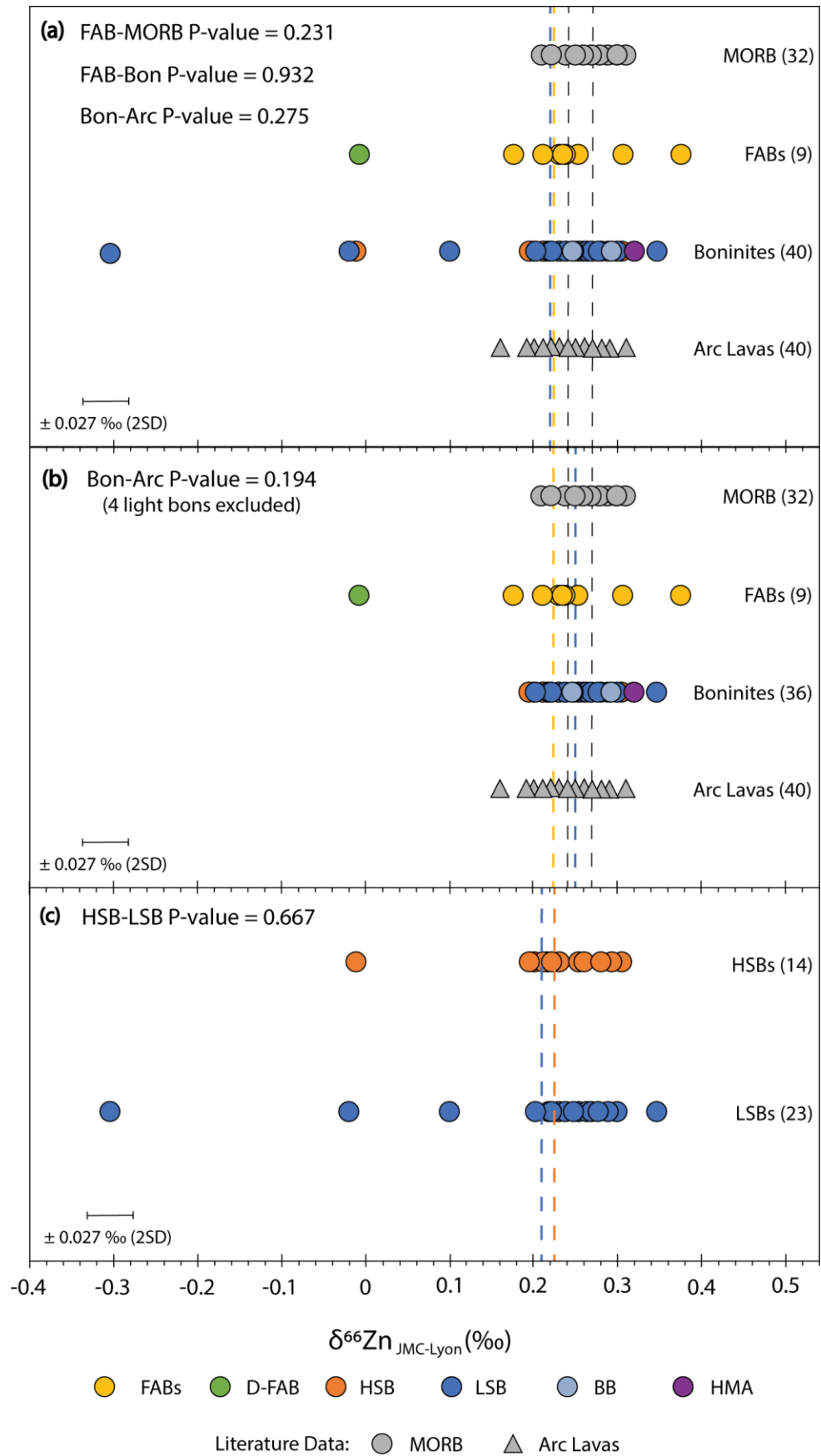


Figure 5.3: $\delta^{66}\text{Zn}$ comparison and student T-test results of (a) mid-ocean ridge basalt (MORB) fore-arc basalt (FAB), boninite, and arc lava $\delta^{66}\text{Zn}$ compositions; (b) mid-ocean ridge basalt (MORB) fore-arc basalt (FAB),

boninite, and arc lava $\delta^{66}\text{Zn}$ compositions, but excluding the four isotopically light boninite samples; **(c)** high-silica boninite (HSB) and low-silica boninite (LSB) $\delta^{66}\text{Zn}$ compositions. The FAB and boninite data is from this study, and the MORB data is from Wang *et al.* (2017), Huang *et al.* (2018b), Liao *et al.* (2020), and the arc lava data is from (Huang *et al.* 2018b). The vertical dashed lines represent the averages for each population that were compared in the student T-tests, and are colour coded to match the data point colours. The MORB $\delta^{66}\text{Zn}$ average = $0.269\text{‰} \pm 0.056$ (2SD), the FAB $\delta^{66}\text{Zn}$ average = $0.224\text{‰} \pm 0.208$ (2SD), the boninite $\delta^{66}\text{Zn}$ average = $0.220\text{‰} \pm 0.222$ (2SD), the HSB $\delta^{66}\text{Zn}$ average = $0.224\text{‰} \pm 0.152$ (2SD), and the LSB $\delta^{66}\text{Zn}$ average = $0.209\text{‰} \pm 0.265$ (2SD), and the arc lava $\delta^{66}\text{Zn}$ average = $0.241\text{‰} \pm 0.071$ (2SD). The average error on each data point is $\pm 0.027\text{‰}$ (2SD). The *p*-values represent the *p*-values from student T-tests. A *p*-value of less than 0.05 dictates that there is enough evidence for the population means to be distinguished at a 95% confidence interval.

5.4. Discussion

The aim of this chapter is broadly two-fold. First, comparing FABs and boninites directly addresses the debate surrounding whether subduction inputs are identifiable via arc lava $\delta^{66}\text{Zn}$. Therefore, statistical differences between the Zn isotopic composition of FABs and boninites are evaluated. Second, within each lithology (i.e FAB and boninite), co-variations of $\delta^{66}\text{Zn}$ and other geochemical parameters are examined, with evaluation of their potential cause(s). Finally, the implications of this work on deconvolving Zn isotope fractionation in arc lavas and subduction settings on a wider scale is discussed.

5.4.1. Lack of Zn isotope difference between FABs and boninites

One key difference between Expedition 352 FABs and boninites, is that unlike FABs, the boninites have distinctive trace element systematics, lower ϵHf_i and $^{208}\text{Pb}/^{204}\text{Pb}$ (**Fig. 5.4**) which are interpreted as evidence of distinct subducted slab components (Li *et al.* 2019). Previous work has suggested that Zn isotope fractionation can occur in response to devolatilisation of subducted slab material, by the preferential mobilisation of heavy Zn in slab-derived fluids via complexation with sulphate and/or carbonate ions (e.g. Pons *et al.* 2016; Debret *et al.* 2018, 2021). However, Expedition 352 FAB and boninite $\delta^{66}\text{Zn}$ is not statistically distinct; if anything, anomalous isotopic compositions tend towards light, not heavy isotopic values (**Fig. 5.3**). We therefore suggest that it is extremely unlikely that fluid or slab melt inputs had an observable impact on the Zn isotopic composition of the boninites. The lack of statistical difference between sediment-influenced HSB and sediment-poor LSB $\delta^{66}\text{Zn}$ also suggests that sediment addition from the slab does not have an observable impact on boninite $\delta^{66}\text{Zn}$. These findings are in broad agreement with Huang *et al.* (2018) whose study of the Kamchatka and Aleutian arcs found no systematic variations between $\delta^{66}\text{Zn}$ and indicators of subduction inputs. They also support mass balance calculations that suggest slab-derived fluids and melts have insufficient Zn to observably alter the mantle wedge Zn budget (Inglis *et al.* 2017). However, they disagree with Rosca *et al.* (2020) who suggest subduction-fluid

related $\delta^{66}\text{Zn}$ differences in Tonga arc lavas explain correlations with Ba/Th and Ce/Pb. We emphasize again that the FAB and boninite suites are closely related in space and time, and erupted in a seafloor spreading setting, thus removing the ambiguity of different mantle sources and/or crustal contamination. If a subduction-related Zn isotopic signature was to be distinguishable anywhere, it should be apparent in a comparison between FABs and boninites, and it is not.

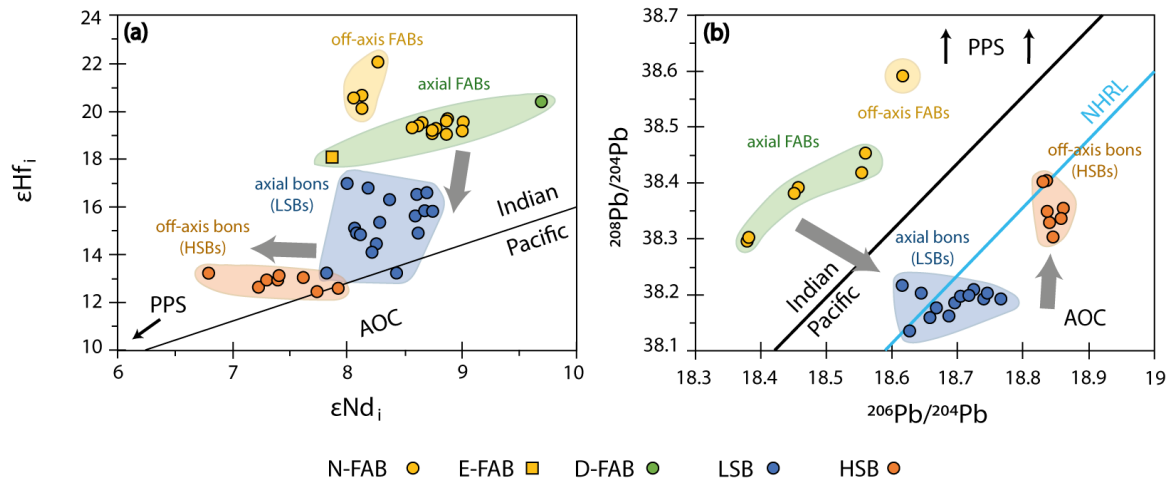


Figure 5.4: Nd, Hf, and Pb isotope measurements for IODP Expedition 352 fore-arc basalts (FABs) and boninites showing the evolution of magmatism throughout the early stages of subduction. Figure is adapted from Li *et al.* (2019).

5.4.2. Boninite Zn Isotopic Compositions

5.4.2.1. Origin of the isotopically light boninites

It is important to assess the cause(s) of the light $\delta^{66}\text{Zn}$ signatures of the four anomalously light boninites (**Fig. 5.3**) and whether they should be considered part of the main boninite population. Therefore, this section will discuss their origins, including discussions of magmatic differentiation, Zn-rich isotopically light phases, and alteration.

Zinc isotopes are thought to be sensitive to variable degrees of partial melting and magmatic differentiation (e.g. Chen *et al.* 2013; Doucet *et al.* 2016; Wang *et al.* 2017; Sossi *et al.* 2018b), with progressive magmatic differentiation creating isotopically heavy melts and light residues due to transitions between higher VI-fold Zn coordination in major mafic minerals such as olivine and pyroxenes, and lower IV-fold coordination in mafic melts. However, the four isotopically light boninites described in section 5.3.2 (**Fig. 5.3**) enlarge the boninite $\delta^{66}\text{Zn}$ range to 0.652 ‰, which is significantly larger than any previously reported melting or differentiation-induced Zn isotopic fractionation (~ 0.1 ‰ (Chen *et al.* 2013; Doucet *et al.* 2016; Wang *et al.* 2017)). There are also no correlations between boninite $\delta^{66}\text{Zn}$ and major element or trace elements (**Fig. 5.5**). It is therefore unlikely that the full boninite $\delta^{66}\text{Zn}$ range can be explained by variable degrees of magmatic

differentiation. Therefore, it is important to assess potential cause(s) for the anomalous isotopic compositions of the four light boninites, and whether they should be considered independent from the other boninites.

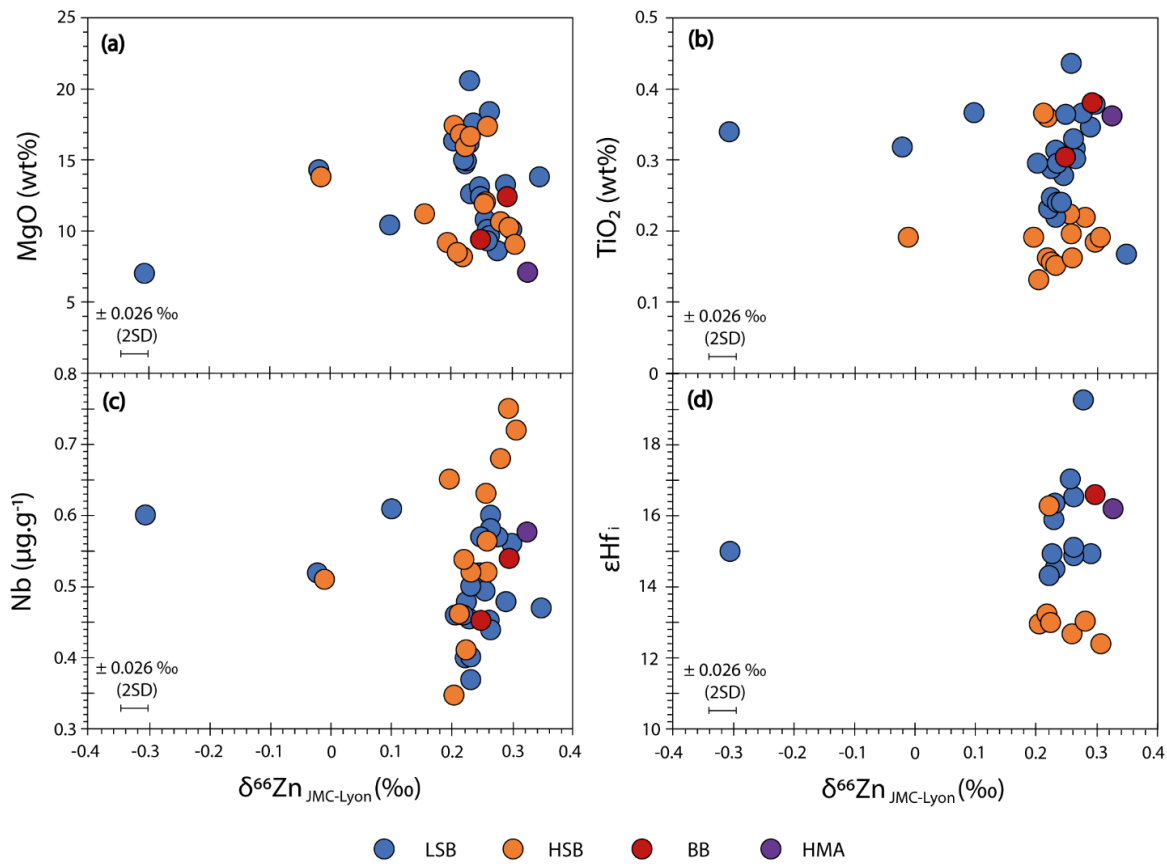


Figure 5.5: $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$ (‰) versus (a) MgO (wt%); (b) TiO_2 (wt%); (c) Nb ($\mu\text{g.g}^{-1}$); (d) ϵHf_i (initial) for IODP Expedition 352 boninites. The average error on each data point is ± 0.026 ‰ (2SD).

Can a minor Zn-rich isotopically light phase explain the anomalous boninites?

One way to explain an anomalously isotopically light whole-rock signature is the presence of a minor, Zn-rich, isotopically light phase. All four isotopically light boninites show petrographic evidence of minor oxides. Since oxides and in particular spinel have high Zn partition coefficients and concentrations ($K_{\text{Zn}}^{\text{sp}/\text{melt}} = 5.2$ (Davis *et al.* 2013) spinel [Zn] = $517 - 1567 \mu\text{g.g}^{-1}$ (Wang *et al.* 2017)), the presence of Zn-rich oxide phases may explain the anomalous $\delta^{66}\text{Zn}$ of the light boninites. However, spinel is isotopically heavier than the major boninite mineral phases, olivine, orthopyroxene, and clinopyroxene (Wang *et al.* 2017; **Fig. 5.6**). In addition, existing spinel $\delta^{66}\text{Zn}$ measurements are similar to the boninite $\delta^{66}\text{Zn}$ average (**Fig. 5.6**), not isotopically lighter. Therefore, the presence of spinel should not skew whole-rock boninite $\delta^{66}\text{Zn}$ towards lighter compositions, meaning that spinel cannot explain the $\delta^{66}\text{Zn}$ of the four isotopically light boninites. Similarly, despite olivine, clinopyroxene, and orthopyroxene being isotopically lighter than mafic

silicate melts (Sossi *et al.* 2015; Wang *et al.* 2017; Sossi *et al.* 2018b), they exhibit minimal $\delta^{66}\text{Zn}$ inter-mineral fractionation (Wang *et al.* 2017), and therefore a higher modal abundance of one should not alter the whole-rock $\delta^{66}\text{Zn}$ composition to the magnitude seen in the isotopically light samples. The four isotopically light boninites also do not have unusually high modal abundances of olivine, clinopyroxene or orthopyroxene compared to the other boninites from this study.

Some Expedition 352 thin sections contain minor sulphide minerals (Reagan *et al.* 2015a). The thin sections associated with the four isotopically anomalous boninites do not contain visible sulphides (Reagan *et al.* 2015a). However, this does not mean that sulphides were not present in the whole-rock that was crushed for chemical analyses. Common rock-forming sulphides include pyrite, pyrrhotite, galena, chalcopyrite, and sphalerite which are common products of hydrothermal alteration of oceanic crust. The chemical formula of sphalerite is ZnS , however, Zn can also substitute for metal ions in the other common sulphide minerals. Sphalerite's high Zn concentration means that sulphides could skew whole-rock $\delta^{66}\text{Zn}$ if they are isotopically distinct from the major boninite minerals, olivine, clinopyroxene, and orthopyroxene. Primary sphalerite $\delta^{66}\text{Zn}$ is between $\delta^{66}\text{Zn} = 1.33$ and -0.22 ‰, with an average of $\delta^{66}\text{Zn} = 0.184 \pm 0.421$ ‰ (2SD, $n = 101$, **Fig. 5.6**) (Wilkinson *et al.* 2005; Kelley *et al.* 2009; Gagnevin *et al.* 2012; Gao *et al.* 2018; Zhu *et al.* 2018). Isotopic compositions are thought to be highly variable due to Rayleigh fractionation as sulphides precipitate from hydrothermal fluids (Mason *et al.* 2005). But the enormous $\delta^{66}\text{Zn}$ range that reaches ratios lighter than all but one of the anomalous boninites suggests that minor sulphides have the potential to be responsible for the anomalously light boninite $\delta^{66}\text{Zn}$ compositions.

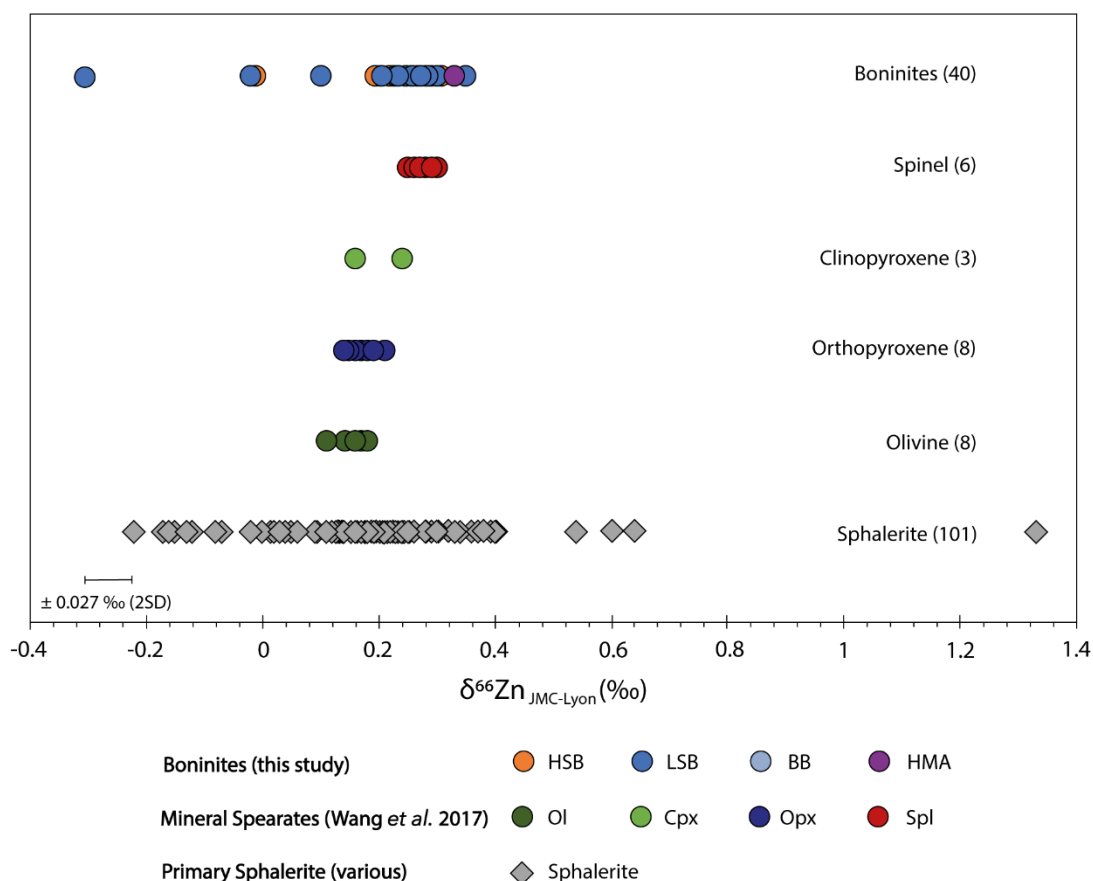
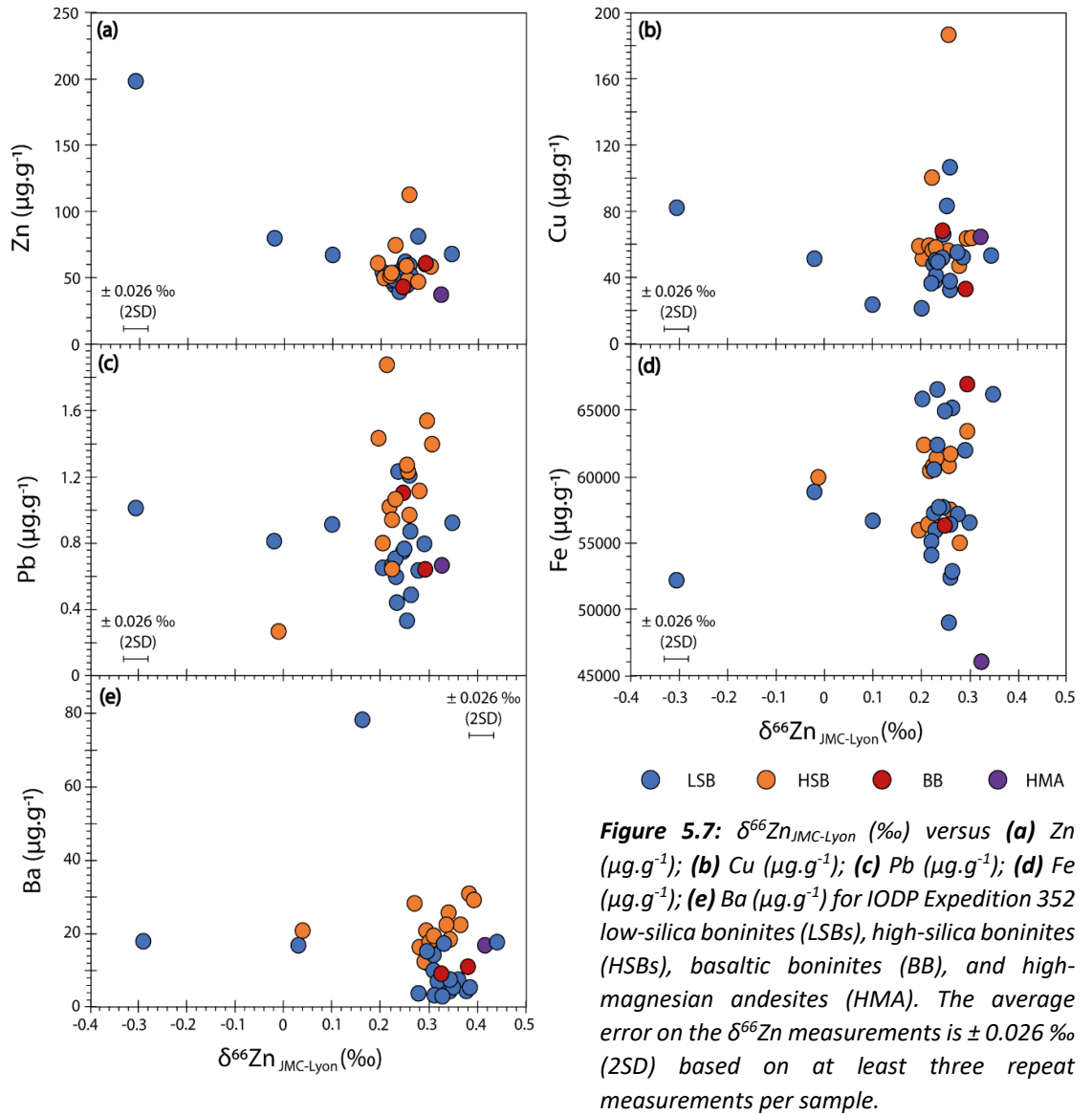


Figure 5.6: Comparison plot of $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$ (‰) measurements for IODP Expedition 352 boninites from this study, sphalerite $\delta^{66}\text{Zn}$ literature data measured against reference material JMC-Lyon (Wilkinson et al. 2005; Kelley et al. 2009; Gagnevin et al. 2012; Gao et al. 2018; Zhu et al. 2018), and olivine, clinopyroxene, orthopyroxene, and spinel mineral separate $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$ measurements from Wang et al. (2017).

Depending on the Zn budget of the other boninite phases, the presence of sulphide minerals may also create elevated abundances of common S-pairing elements such as Zn, Cu, Pb, Fe and Ba. The isotopically lightest LSB does indeed have an anomalously high Zn concentration ($[\text{Zn}] = 198 \mu\text{g.g}^{-1}$), and another light boninite has an anomalously high Ba concentration ($[\text{Ba}] = 78 \mu\text{g.g}^{-1}$) (Fig. 5.7). However, elevated chalcophile element concentrations are not consistent amongst the light boninites. For example, Zn concentrations are between 68.8 and 198 $\mu\text{g.g}^{-1}$ in the anomalous boninites, which at the lower end is similar to boninite average Zn concentration of 60.5 $\mu\text{g.g}^{-1}$.

Since sphalerite $\delta^{66}\text{Zn}$ can be very isotopically light (e.g. Wilkinson et al. 2005; Kelley et al. 2009; Gagnevin et al. 2012; Gao et al. 2018; Zhu et al. 2018), and there are high concentrations of common S-pairing elements such as Zn and Ba in some of the anomalous boninites, the presence of minor sulphides is a plausible explanation for the anomalously light $\delta^{66}\text{Zn}$ of four Expedition 352 boninites. Despite the lightest sphalerite $\delta^{66}\text{Zn}$ being heavier than the lightest boninite, the lightest boninite has an anomalously high Zn concentration. It may therefore be possible for sulphide

mineral $\delta^{66}\text{Zn}$ to reach such light isotopic compositions, but such a composition has not yet been observed.



Could secondary alteration explain the anomalous boninites?

A second option that may explain the light $\delta^{66}\text{Zn}$ of the anomalous boninites is secondary alteration. All Expedition 352 POOL samples were chosen to minimise alteration, however there is no way to guarantee that all the boninites in this study are alteration free. However, previous Zn isotope studies have suggested that secondary alteration creates heavy $\delta^{66}\text{Zn}$ in altered oceanic basalts (e.g. Huang *et al.* 2016). Therefore, secondary alteration is not considered to be a likely option for explaining the anomalous boninite $\delta^{66}\text{Zn}$ compositions.

The most probable cause of the light $\delta^{66}\text{Zn}$ of the four anomalously light boninites, and creating an artificially large range in boninite $\delta^{66}\text{Zn}$, is a Zn-rich isotopically light phase such as a sulphide mineral. However, the evidence is not conclusive. The anomalous boninites should be investigated further using S and O isotopes which should test the sulphide and alteration hypotheses. The four anomalously light boninites are very distinct from the $\delta^{66}\text{Zn}$ of the other 36 boninites in this study, and the very high Zn and Ba concentrations in two of them suggests that they are chemically different. Therefore, the four anomalous boninites will be excluded from the other boninites and treated as an independent population. This exclusion does not affect the FAB-boninite T-test result. The boninite $\delta^{66}\text{Zn}$ mean is still statistically indistinct from the FAB $\delta^{66}\text{Zn}$ mean, and HSBs and LSBs are also still statistically indistinguishable. The overall interpretations of this study will therefore also not change.

5.4.2.2. Cause(s) of boninite $\delta^{66}\text{Zn}$ variations without anomalously light boninites?

When the four anomalously isotopically light boninites are removed from the boninite population, there is a 0.151 ‰ $\delta^{66}\text{Zn}$ range, which is similar to the ~ 0.10 ‰ variations that have been attributed to partial melting and/or fractional crystallisation. There is no geochemical evidence that such a range is related to variable addition of subduction fluids or melts, since boninite $\delta^{66}\text{Zn}$ shows no covariation with subduction input indicators such as Ba/Th or Sm/Hf (**Fig. 5.8**). However, there are positive correlations between Nb and the lightest REE concentrations and the lightest REEs and $\delta^{66}\text{Zn}$, and a hint of a negative correlation with MgO in the LSBs (**Fig. 5.8**). Such correlations suggest that partial melting and fractional crystallisation may have influenced LSB $\delta^{66}\text{Zn}$ and may be responsible for the boninite $\delta^{66}\text{Zn}$ range. Since many of the boninites have high phenocryst abundances (up to 47 %) and are considered cumulative, fractional crystallisation may be responsible for some of the $\delta^{66}\text{Zn}$ scatter. This observation contrasts with Kamchatka and Aleutian arc $\delta^{66}\text{Zn}$ data from (Huang *et al.* 2018b) which found no evidence of a fractional crystallisation control on arc lava $\delta^{66}\text{Zn}$.

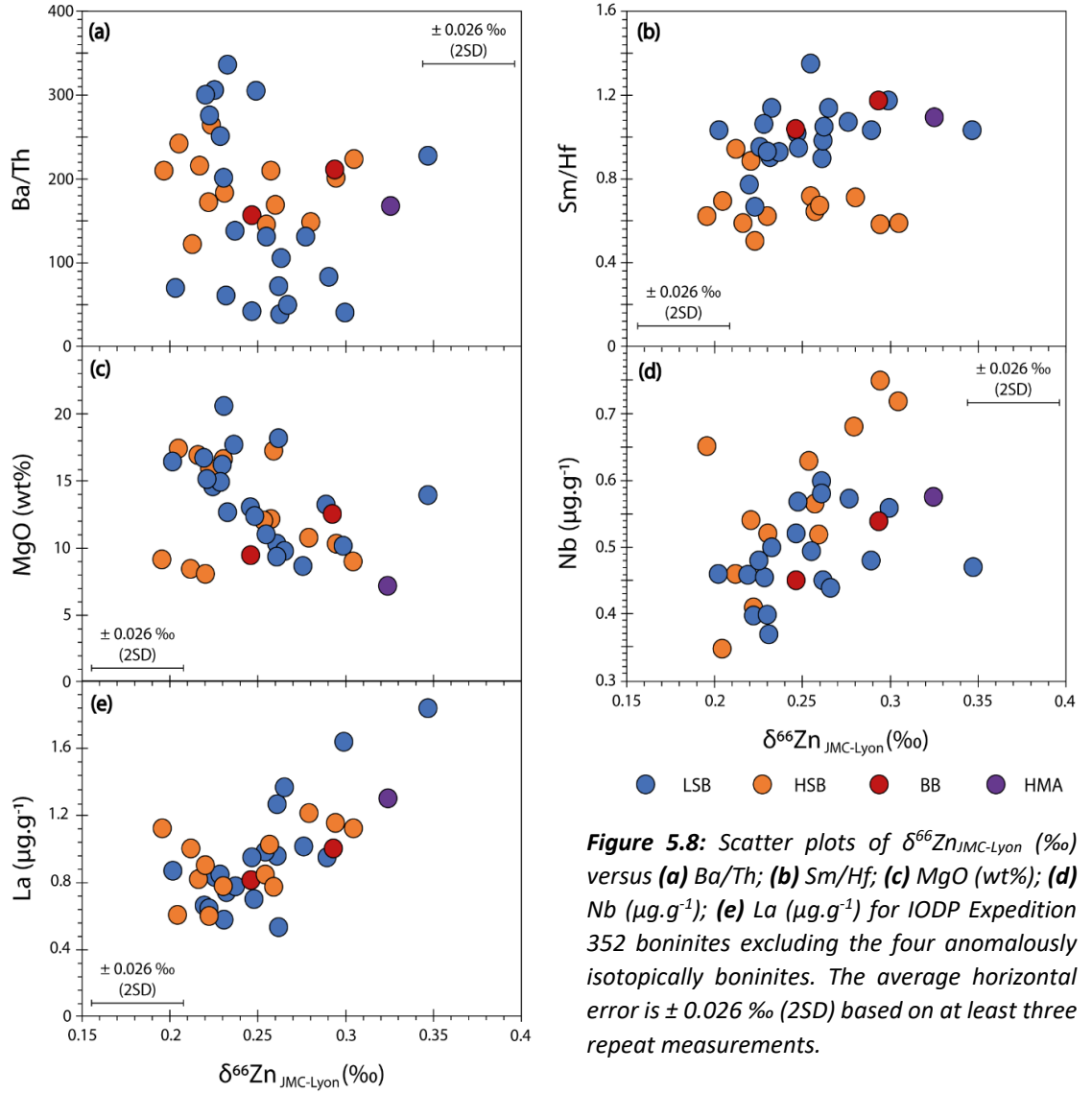


Figure 5.8: Scatter plots of $\delta^{66}\text{Zn}_{\text{JMC-Lyon}} (\text{‰})$ versus (a) Ba/Th; (b) Sm/Hf; (c) MgO (wt%); (d) Nb ($\mu\text{g.g}^{-1}$); (e) La ($\mu\text{g.g}^{-1}$) for IODP Expedition 352 boninites excluding the four anomalously isotopically boninites. The average horizontal error is $\pm 0.026 \text{ ‰}$ (2SD) based on at least three repeat measurements.

5.4.3. Fore-arc Basalt Zn Isotopic Compositions

The statistical similarity between FAB and MORB $\delta^{66}\text{Zn}$ (**Fig. 5.3**) is somewhat expected since FAB and MORB are not statistically different for Fe isotopes (Chapter four), and have similar petrogenic origins, having formed by anhydrous decompression melting due to seafloor spreading (Reagan *et al.* 2017). However, the large FAB $\delta^{66}\text{Zn}$ range (0.38 ‰), that is significantly larger than the MORB literature range of $\sim 0.10 \text{ ‰}$ (Wang *et al.* 2017; Huang *et al.* 2018b; Liao *et al.* 2020), is unexpected. Since there is no geochemical evidence of subduction inputs in FABs (Li *et al.* 2019; Shervais *et al.* 2019), possible explanatory Zn fractionation mechanisms are limited to magmatic processes such as source depletion, partial melting, and fractional crystallisation. There are correlations between FAB $\delta^{66}\text{Zn}$ and magmatic differentiation indicators (**Fig. 5.9**). However, the maximum reported differentiation-induced $\delta^{66}\text{Zn}$ fractionation is $\sim 0.1 \text{ ‰}$ (Chen *et al.* 2013; Doucet *et al.* 2016; Wang

et al. 2017), suggesting that ~ 0.38 ‰ is unlikely to be created by differentiation alone, particularly given the relatively restricted range of MgO that the FAB span (**Fig. 5.11**).

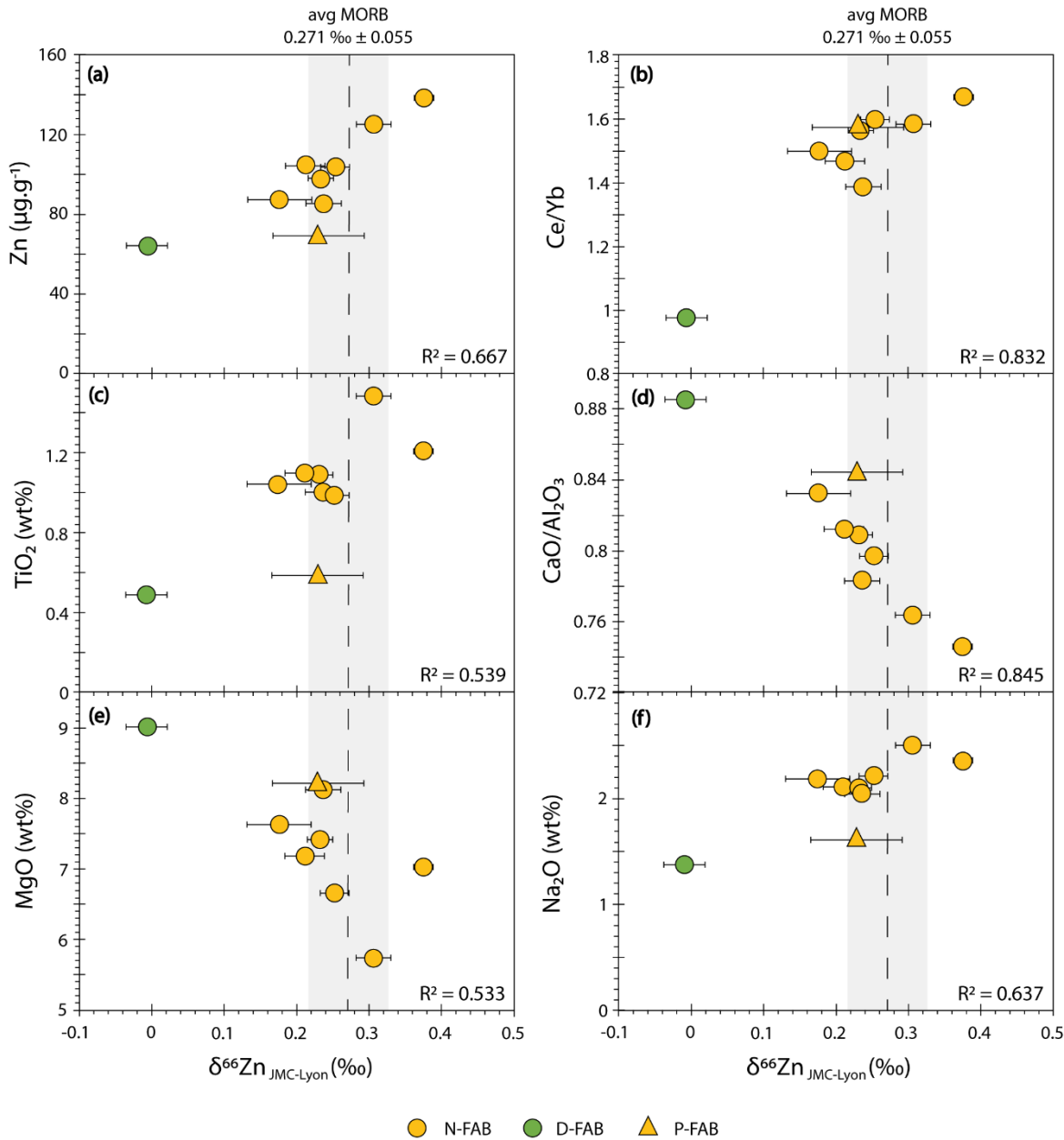
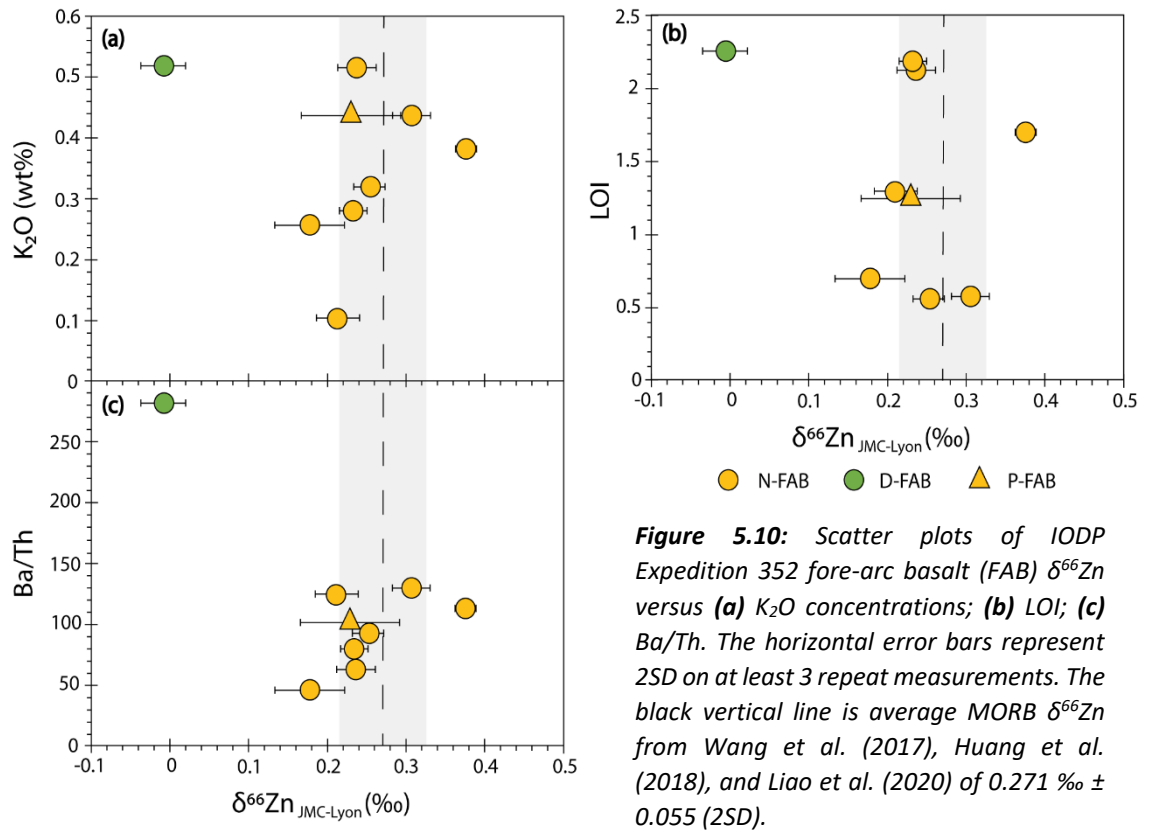


Figure 5.9: IODP Expedition 352 fore-arc basalt (FAB) $\delta^{66}\text{Zn}$ versus **(a)** Zn concentrations; **(b)** Ce/Yb; **(c)** TiO_2 concentrations; **(d)** $\text{CaO}/\text{Al}_2\text{O}_3$; **(e)** MgO concentrations; **(f)** Na_2O concentrations. The horizontal error bars represent 2SD on at least 3 repeat measurements. The black vertical line is the average MORB $\delta^{66}\text{Zn}$ from Wang *et al.* (2017), Huang *et al.* (2018b), Liao *et al.* (2020) of $0.271 \text{ ‰} \pm 0.055$ (2SD).

A key point to consider is whether D-FAB should be included in the FAB population throughout interpretation. D-FAB is isotopically distinct from the other FABs ($\delta^{66}\text{Zn} = -0.007 \pm 0.028$ ‰ 2SD), accounts for a substantial part of the FAB $\delta^{66}\text{Zn}$ range, and is exceptionally chemically depleted (Shervais *et al.* 2019). In addition, the D-FAB has the highest K_2O and LOI of the FABs, and very high Ba/Th (**Fig. 5.10**) which suggest it is more altered and/or experienced fluid interaction. In **Fig. 5.9**

D-FAB also appears to pin and exaggerate many of the correlations. We therefore suggest that D-FAB should be considered separate from the other FABs. Without D-FAB, the FAB range is halved to 0.20 ‰. Whilst 0.20 ‰ is still a large range for Zn isotopes, it may be easier to explain.



5.4.3.1. Could variable fluid addition or alteration account for the FAB $\delta^{66}\text{Zn}$ variation?

Whole-rock lavas originating from the seafloor will almost certainly have been affected by some form of secondary hydrothermal alteration and seafloor weathering. Despite IODP POOL sampling targeting the least altered core sections, there is no guarantee that the samples in this study are completely alteration free. A comparison of pristine Expedition 352 FAB glasses and whole-rock K_2O concentrations show that whole-rock samples have consistently higher K_2O concentrations than associated glasses (Coulthard et al. 2021), suggesting that whole-rock FABs are somewhat altered. Zinc isotope work on altered oceanic crust from the eastern equatorial Pacific suggests that high-T hydrothermal alteration ($> 350^\circ\text{C}$) can create large $\delta^{66}\text{Zn}$ ranges that exceed MORB (Fig. 5.1) and reach isotopically heavier compositions with increasing degrees of alteration (Huang et al. 2016). The 0.20 ‰ range in FAB $\delta^{66}\text{Zn}$ may therefore be explained by variable degrees of high-T hydrothermal alteration. However, there is no obvious correlation between FAB $\delta^{66}\text{Zn}$ and K_2O concentrations, or LOI (Fig. 5.10 & 5.11).

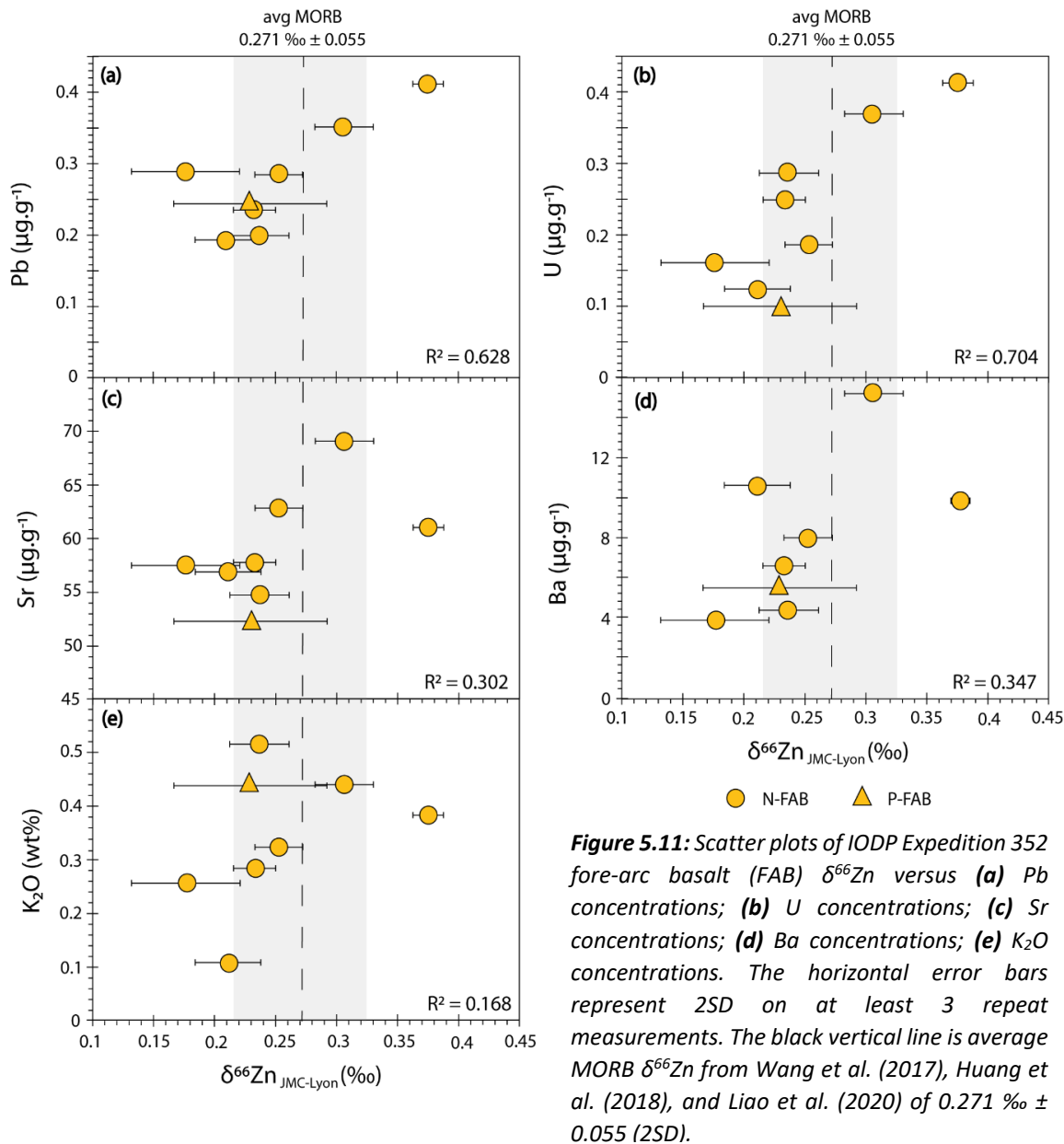


Figure 5.11: Scatter plots of IODP Expedition 352 fore-arc basalt (FAB) $\delta^{66}\text{Zn}$ versus (a) Pb concentrations; (b) U concentrations; (c) Sr concentrations; (d) Ba concentrations; (e) K_2O concentrations. The horizontal error bars represent 2SD on at least 3 repeat measurements. The black vertical line is average MORB $\delta^{66}\text{Zn}$ from Wang et al. (2017), Huang et al. (2018), and Liao et al. (2020) of $0.271 \text{ ‰} \pm 0.055$ (2SD).

Figure 5.11 shows that FAB $\delta^{66}\text{Zn}$ roughly positively correlates with FME concentrations Pb and U. A positive correlation suggests that greater FME concentrations, and therefore greater fluid interaction is associated with heavier $\delta^{66}\text{Zn}$. Previous slab dehydration Zn isotope work suggests that heavy Zn is preferentially complexed with chloride, sulphate, and/or carbonate ions in fluids (e.g. Pons et al. 2016; Debret et al. 2018, 2021), and therefore supports the idea of variable fluid-FAB interaction. However, an expected consequence of fluid input is an increase in H_2O and Cl concentrations, and FABs contain no absolute increase in H_2O or Cl compared to MORB (Fig. 5.12). There is also no correlation between FAB $\delta^{66}\text{Zn}$ and other FMEs Sr, Ba and K_2O (Fig 5.11d). It is therefore unlikely that the FAB genesis involved fluid interaction, and therefore a fluid interaction control on $\delta^{66}\text{Zn}$ fractionation in the Expedition 352 FABs is also unlikely.

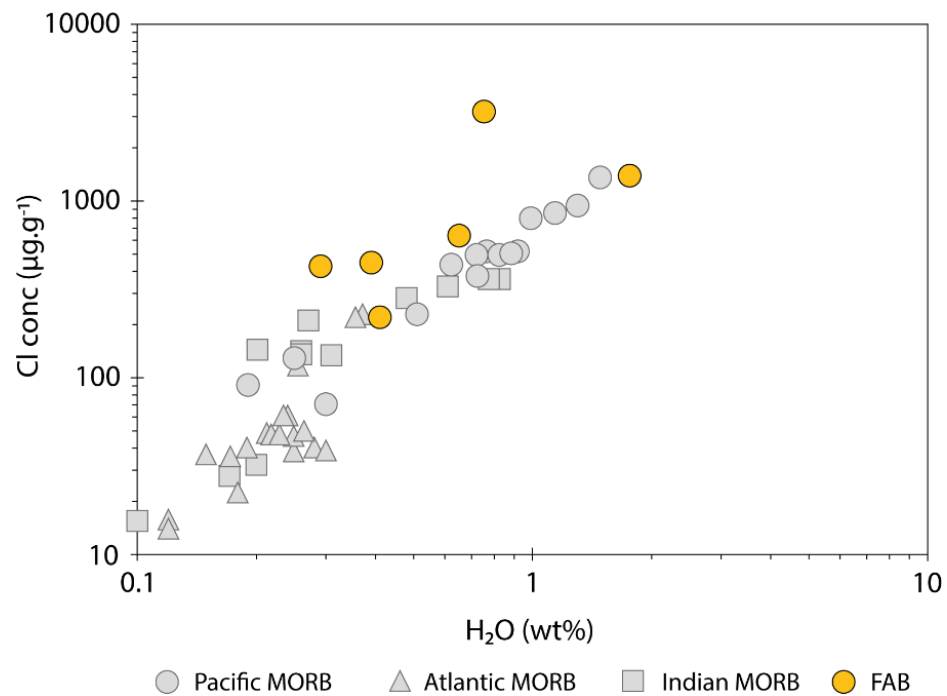


Figure 5.12: H_2O versus Cl concentration for IODP Expedition 352 fore-arc basalts (FABs) and Pacific, Atlantic, and Indian MORB. The FAB data is from Coulthard *et al.* (2021) and is on picked glass form near the POOL sample locations. Therefore, the glass data does not directly overlap with the samples from this study, and there is limited Cl and H_2O data available. The MORB data is from Kendrick *et al.* (2017).

5.4.3.2. Magmatic differentiation and source depletion as $\delta^{66}Zn$ controls in FABs

FABs tend to be more depleted in incompatible elements compared to MORB due to their greater source depletion, and often higher degrees of partial melting (Li *et al.* 2019; Shervais *et al.* 2019). When D-FAB is included in the FAB population, $\delta^{66}Zn$ correlates well with incompatible/more compatible element ratios such as Ce/Yb and indicators of differentiation such as MgO, Zn, TiO_2 , and Na_2O concentrations (**Fig. 5.9**), which could suggest a magmatic differentiation $\delta^{66}Zn$ control. However, when D-FAB is removed, many of those correlations are significantly weakened or disappear. **Figure 5.13** shows that without D-FAB, only CaO/Al_2O_3 and Zn concentrations convincingly correlate with $\delta^{66}Zn$. CaO/Al_2O_3 is commonly used as indicator of clinopyroxene-controlled partial melting, whereby the ratio increases with increasing degrees of partial melting as clinopyroxene is melted from the source. Such a correlation therefore suggests that increasing degrees of partial melting are associated with lighter melt $\delta^{66}Zn$ as it

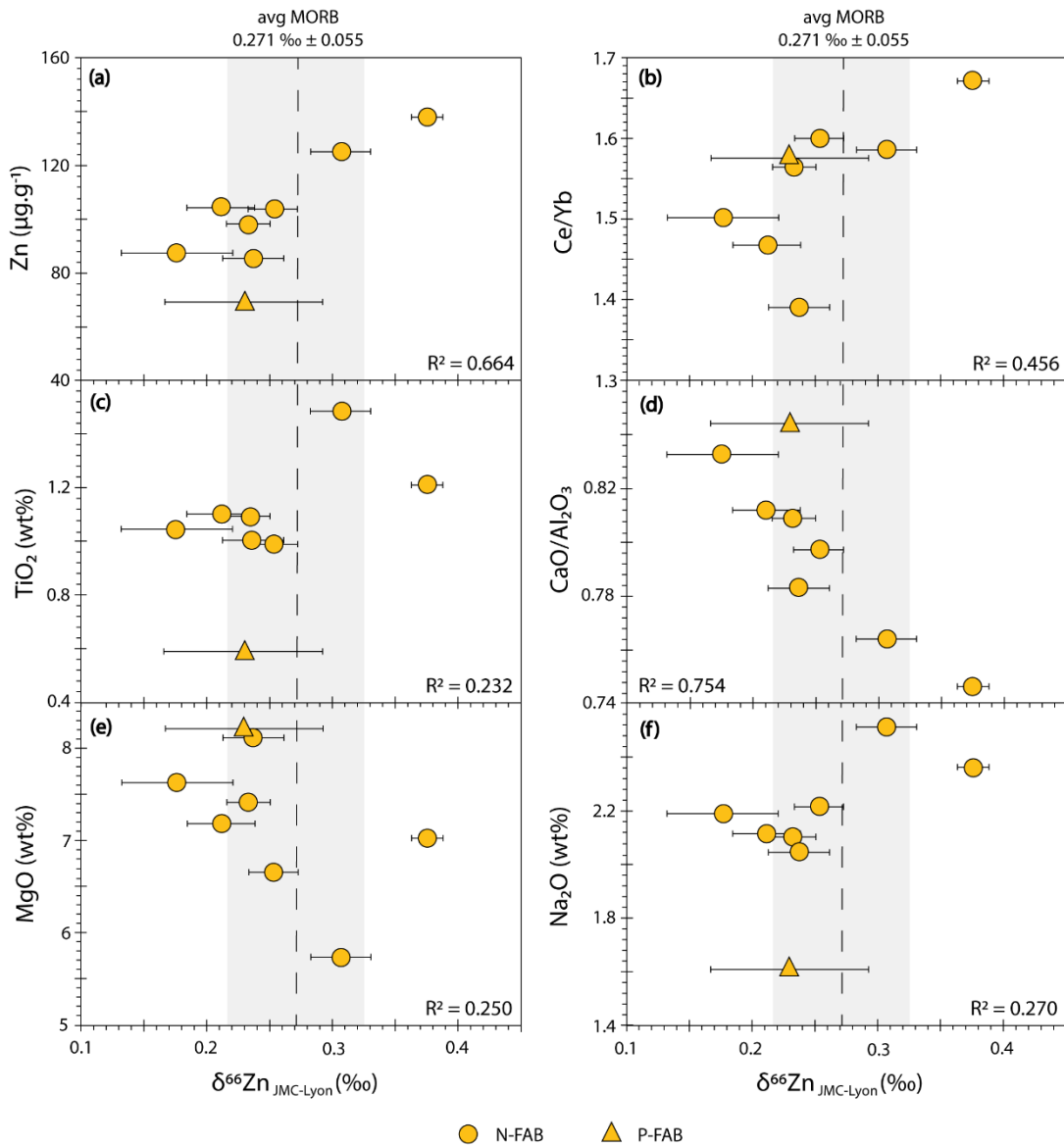


Figure 5.13: Scatter plots of IODP Expedition 352 FAB $\delta^{66}\text{Zn}$ versus (a) Zn concentrations; (b) Ce/Yb; (c) TiO_2 concentrations; (d) $\text{CaO}/\text{Al}_2\text{O}_3$; (e) MgO concentrations; (f) Na_2O concentrations. The D-FAB sample has been removed since it is chemically distinct. The horizontal error bars represent 2SD on at least 3 repeat measurements. The black vertical line is the average MORB $\delta^{66}\text{Zn}$ from Wang *et al.* (2017), Huang *et al.* (2018b), Liao *et al.* (2020) of $0.271 \text{ ‰} \pm 0.055$ (2SD).

approaches the source composition. This is consistent with previous Zn isotope work that found that Zn isotopes can be sensitive to mantle partial melting, creating initially isotopically heavy melts relative to the source that become progressively lighter with increasing degrees of melting (e.g. Doucet *et al.* 2016; Wang *et al.* 2017; Sossi *et al.* 2018; Beunon *et al.* 2020). The internal FAB $\delta^{66}\text{Zn}$ variation may therefore be related to mantle partial melting. However, this would be the largest partial melting induced $\delta^{66}\text{Zn}$ range reported in the literature to date, and at a more restricted range of evolution. Since previous Zn isotope studies have suggested that mantle partial melting can create a maximum $\sim 0.10 \text{ ‰}$ $\delta^{66}\text{Zn}$ fractionation, it may be that additional magmatic processes

exaggerated the FAB $\delta^{66}\text{Zn}$ range, but for some reason the geochemical indicators of such processes are masked. To determine if partial melting alone can create the observed FAB $\delta^{66}\text{Zn}$ range, further tests were conducted.

Testing a partial melting control on FAB $\delta^{66}\text{Zn}$

To test whether partial melting alone could account for the wide $\delta^{66}\text{Zn}$ FAB variation, $\delta^{66}\text{Zn}$ was modelled using Rayleigh fractionation equations as described in Beunon *et al.* (2020). Approximate melting degrees were taken from Shervais *et al.* (2019) who used trace element melt models to estimate that FABs experienced between 2 and 3 % garnet-field melting, followed by 7-25% spinel-field melting. The model assumed a garnet peridotite source ($\delta^{66}\text{Zn} = 0.16 \text{ ‰}$; Beunon *et al.* 2020) and subsequent spinel-field melting of the garnet melting residue. The concentration of Zn in the residue and melt were calculated using fractional modal melting equations from Shaw (1970), where the bulk Zn partition coefficient is the sum of the modal proportions and mineral-melt Zn partition coefficients of the major minerals in the source. All mineral modes, partition coefficients and $\delta^{66}\text{Zn}$ fractionation factors were taken from Beunon *et al.* (2020). Rayleigh distillation equations from Hoefs (2018) were then used to model the partial melting induced $\delta^{66}\text{Zn}$ fractionation in the residue and melt. To account for the variations in FAB melt degree, we performed a Monte Carlo simulation varying the garnet-field melting between 2 and 3%, and the spinel-field melting between 1 and 25%. **Figure 5.14** shows that partial melt modelling of a chemically homogenous, garnet peridotite source cannot reproduce the $\delta^{66}\text{Zn}$ variation observed in the Expedition 352 FABs. This could suggest that: (1) additional magmatic processes influenced FAB Zn isotopic compositions and their geochemical indicators were masked, or (2) current Zn isotopic melt modelling does not truly reflect what happens in nature. Additional magmatic processes could include fractional crystallisation, source depletion and melt mixing. Each of these is examined below.

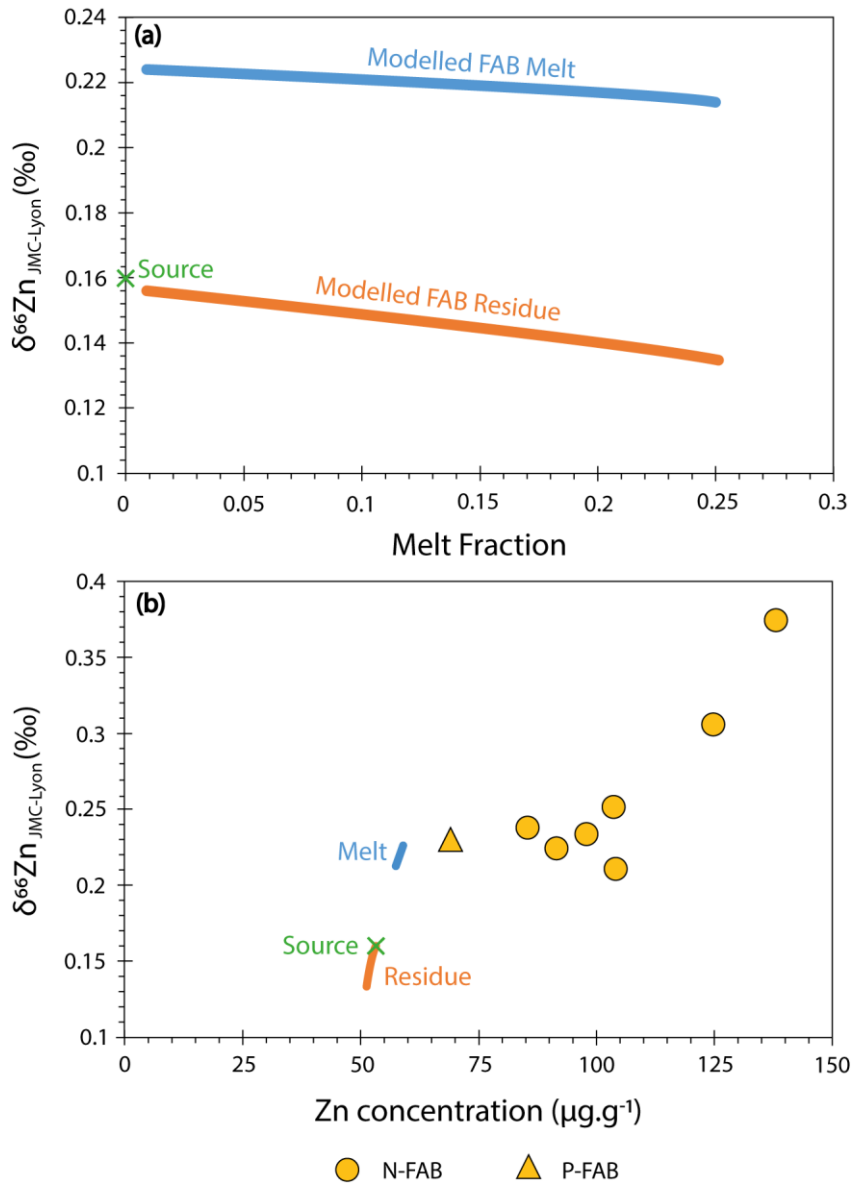


Figure 5.14: Zn isotopic melt modelling and Zn concentration versus $\delta^{66}\text{Zn}_{\text{Lyon}} (\text{‰})$ for IODP FABs. The blue crosses represent melt modelling from a garnet peridotite source ($\delta^{66}\text{Zn} = 0.16 \text{ ‰}$) with 2-3% melting and subsequent 1-25% melting of the residue in the spinel stability field.

Testing fractional crystallisation as a control on FAB $\delta^{66}\text{Zn}$ compositions

The most successful Shervais *et al.* (2019) fractional crystallisation models involved progressive crystallisation of olivine (1%); 30% olivine + 70% plagioclase (4-5%); and 7% olivine + 41% plagioclase + 52% augite (17-20%). There is no observable $\delta^{66}\text{Zn}$ fractionation between olivine and clinopyroxene (Wang *et al.* 2017), however both are typically isotopically lighter than basalts and mafic silicate melts (Sossi *et al.* 2015, 2018; Wang *et al.* 2017, **Table 5.2**). Whilst crystallisation of different ratios of olivine and clinopyroxene may not induce fractionation, variable total olv + cpx crystallisation may fractionate Zn isotopes, creating a progressively lighter solid and a heavier melt.

Fractional crystallisation of olivine has been invoked previously to explain $\delta^{66}\text{Zn}$ ranges of 0.11 ‰ (Chen *et al.* 2013).

It is harder to assess the role of plagioclase crystallisation, since no $\delta^{66}\text{Zn}$ measurements for plagioclase exist from mafic igneous systems. Zinc is very incompatible in plagioclase (**Table 5.2**), therefore, from a mass balance point of view, for plagioclase crystallisation to have an observable effect on $\delta^{66}\text{Zn}$, plagioclase would need to have an extreme $\delta^{66}\text{Zn}$. The general formula of plagioclase is MT_4O_8 . The M site contains large Ca^{2+} or Na^+ ions typically in VII to IX-fold coordination which cannot accommodate Zn^{2+} due to its small ionic radius. The T site is smaller, typically containing Al^{3+} or Si^{4+} in IV-fold coordination. The T site could accommodate Zn^{2+} , but due to Zn having a low K_D for plagioclase ($K_D \text{ Zn}^{\text{plag/melt}} = 0.11$ (Bougault & Hekinian 1974)), substitution is limited. Since Zn also adopts IV-fold coordination in spinel, plagioclase $\delta^{66}\text{Zn}$ may be similar to spinel, and heavier than olivine and pyroxenes where Zn is in VI-fold coordination. However, spinel and coexisting mafic silicate melts are thought to have the same $\delta^{66}\text{Zn}$ (Sossi *et al.* 2018, **Table 5.2**), therefore plagioclase fractional crystallisation should also have no effect on melt $\delta^{66}\text{Zn}$. If the $\delta^{66}\text{Zn}$ of plagioclase was sufficiently extreme for fractional crystallisation of minor plagioclase to have an observable effect on FAB $\delta^{66}\text{Zn}$, there should be a correlation between $\delta^{66}\text{Zn}$ and Eu/Eu^* , since Eu anomalies are ubiquitous indicators of plagioclase crystallisation (Drake and Weill, 1975). However, **Figure 5.15** shows no correlation is present. Therefore, the low D_{Zn} of plagioclase, and lack of correlation between $\delta^{66}\text{Zn}$ and Eu/Eu^* suggests that plagioclase crystallisation has negligible effects on $\delta^{66}\text{Zn}$ variation in the FAB population. Therefore, only the fractional crystallisation of isotopically light olivine and clinopyroxene have the potential create the observed FAB $\delta^{66}\text{Zn}$ variation. However, since there are no correlations between FAB $\delta^{66}\text{Zn}$ and magmatic differentiation indicators such as MgO or SiO_2 (**Fig. 5.13**), there is no compelling evidence that fractional crystallisation was a major contributor to FAB $\delta^{66}\text{Zn}$. This inference agrees with the work of Huang *et al.* (2018b) who suggest that a lack of correlations between $\delta^{66}\text{Zn}$, MgO and Zn/Fe_T , and the constant $\delta^{66}\text{Zn}$ of mafic and silicic Kamchatka arc lavas, means fractional crystallisation has an insignificant effect on Kamchatka and Aleutian arc lava $\delta^{66}\text{Zn}$.

Table 5.2: Zn partition coefficient and $\delta^{66}\text{Zn}$ fractionation factor between five major rock forming minerals and coexisting mafic silicate melts. The olivine, orthopyroxene, clinopyroxene and spinel data is from Sossi *et al.* (2018), and the plagioclase data is from Bougault & Hekinian (1974).

Phase	Partitioning	DZn	$\Delta^{66}\text{Zn}$ (‰)
Olivine	ol/melt	0.96	$-0.17 \times 10^6/T^2$
Orthopyroxene	opx/melt	0.65	$-0.17 \times 10^6/T^2$
Clinopyroxene	cpx/melt	0.40	$-0.17 \times 10^6/T^2$
Spinel	sp/melt	5.20	$0 \times 10^6/T^2$
Plagioclase	plag/melt	0.11	-

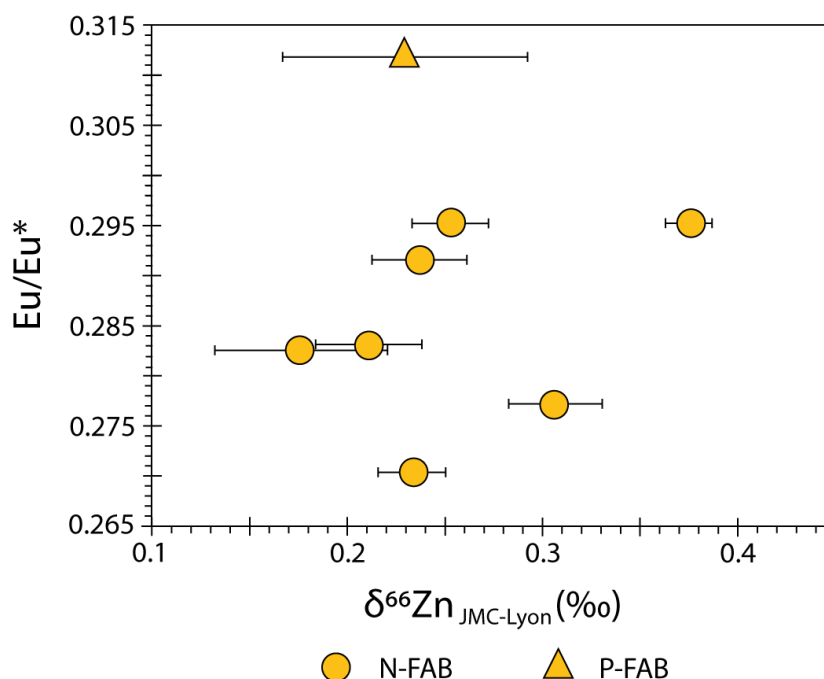


Figure 5.15: $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$ (‰) versus Eu anomaly ($\text{Eu}/\text{Eu}^* = \text{Eu}/(\text{Sm} \times \text{Gd})^{0.5}$) for IODP Expedition 352 fore-arc basalts (FABs). The horizontal error bars represent 2SD based on at least three repeat measurements.

Testing source depletion as a control on FAB $\delta^{66}\text{Zn}$

Depletion of the FAB source through multiple historic melt extraction events could potentially create $\delta^{66}\text{Zn}$ variation if the depletion created a heterogeneous source. However, if source depletion did contribute to the FAB $\delta^{66}\text{Zn}$ variation, a difference between FAB and MORB, and FAB and boninite $\delta^{66}\text{Zn}$ would be expected. FABs are more depleted than MORB, and the boninite source is thought to be the depleted FAB residue (Li *et al.* 2019; Shervais *et al.* 2021). However, there is no statistical difference between FAB and MORB or FAB and boninite $\delta^{66}\text{Zn}$ (Fig. 5.3). Therefore, it seems unlikely that the FAB $\delta^{66}\text{Zn}$ variation is related to source depletion. This is supported by the lack of a correlation between Cr# and $\delta^{66}\text{Zn}$ in the FABs when D-FAB is removed (Fig. 5.16).

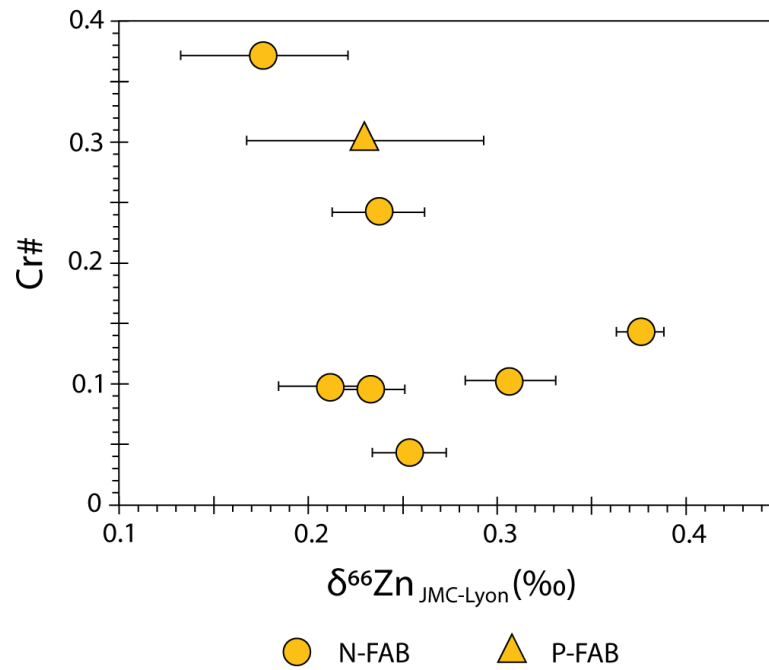


Figure 5.16: $\delta^{66}\text{Zn}_{\text{JMC-Lyon}} (\text{‰})$ versus whole-rock $\text{Cr\#} \left(\frac{\text{Cr} \times 100}{\text{Cr} + \text{Al}} \right)$ for IODP Expedition 352 fore-arc basalts (FABs). The horizontal error bars are 2SD on at least three repeat measurements.

5.4.3.3. Could melt mixing account for the FAB $\delta^{66}\text{Zn}$ variation?

Another option that could create a wider range of $\delta^{66}\text{Zn}$ and Zn concentrations is mixing the FAB melts with other reservoirs. The mantle is thought to be chemically heterogeneous. Zinc isotope measurements of mantle rocks have suggested that the Zn isotopic composition of the terrestrial mantle is also heterogeneous (e.g. Doucet *et al.* 2016). Therefore, mixing of melts from a heterogeneous mantle may be able to create observable Zn isotope variation. Melt mixing models derived from Beunon *et al.* (2020) were employed to assess the involvement of melt mixing in FAB formation. The melt mixing models employed accumulated fractional modal melting equations (Shaw 1970), Rayleigh distillation equations (Hoefs 2018), and mixing equations (DePaolo 1981) as described in Beunon *et al.* (2020) that mixed FAB melts with 40-60% Marianas sediments, C-bearing eclogite, low-garnet MORB-eclogite, and high-garnet MORB eclogite (**Fig. 5.19**). Previous Expedition 352 studies show no evidence of slab or sediment components in FABs (Li *et al.* 2019; Shervais *et al.* 2019), and **Figure 5.17** confirms that such mixing cannot reproduce the measured FAB compositional variation. Progressive mixing of FAB melts with C-bearing and MORB-eclogites create mixing lines towards higher Zn concentrations and heavier $\delta^{66}\text{Zn}$ which is in the same direction as the positive Zn/ $\delta^{66}\text{Zn}$ FAB correlation. However, the FAB melt is too isotopically heavy for the mixing lines to encompass the FAB data. For any of the eclogite mixing lines in **Figure 5.17** to pass through

the N-FAB and P-FAB data, the FAB source must have a $\delta^{66}\text{Zn}$ composition at least as light as 0.05 ‰. Of all existing peridotite $\delta^{66}\text{Zn}$ data, only three metasomatised peridotite samples have $\delta^{66}\text{Zn}$ around 0.05 ‰ (0.04 ‰, 0.03 ‰ and -0.06 ‰; Wang *et al.* 2017). These three samples are some of the lightest peridotites recorded (**Fig. 5.18**).

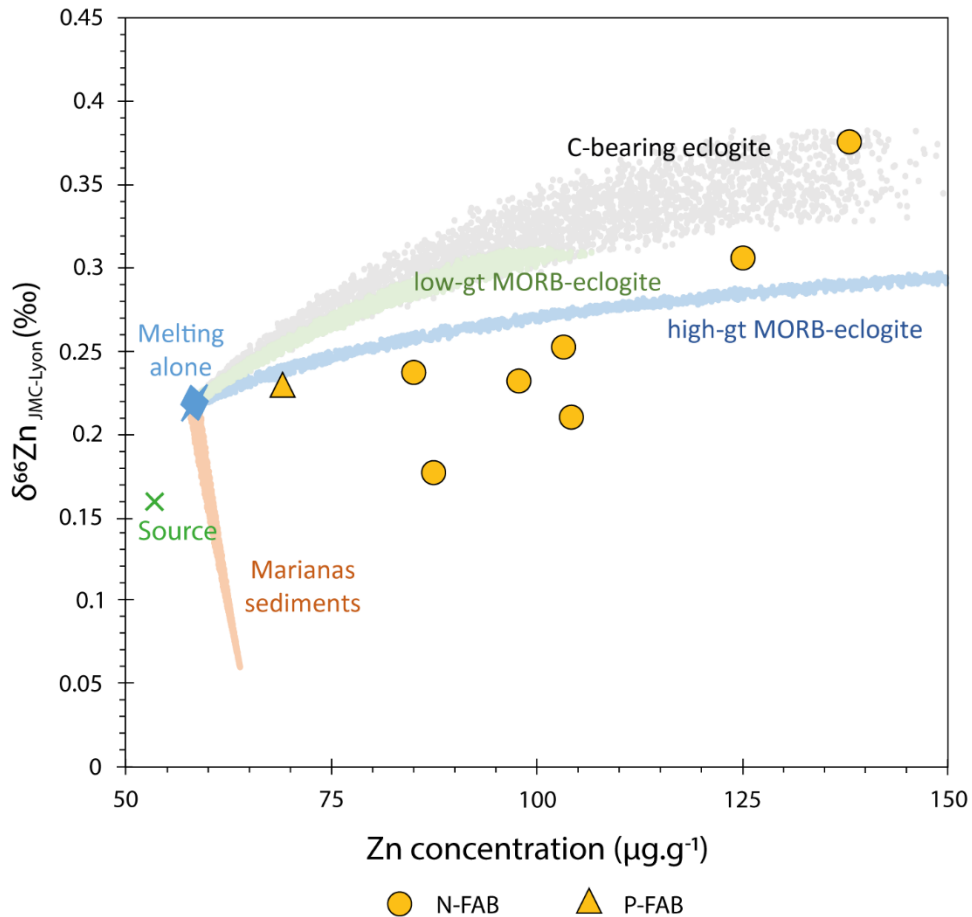


Figure 5.17: Zn concentration versus $\delta^{66}\text{Zn}_{\text{JMC-Lyon}}$ (‰) for IODP FABs. The blue crosses represent melt modelling from a garnet peridotite source ($\delta^{66}\text{Zn} = 0.16$ ‰) with 2-3% melting and subsequent 1-25% melting of the residue in the spinel stability field. The modelled FAB melt was mixed with various reservoirs according to Beunon *et al.* (2020).

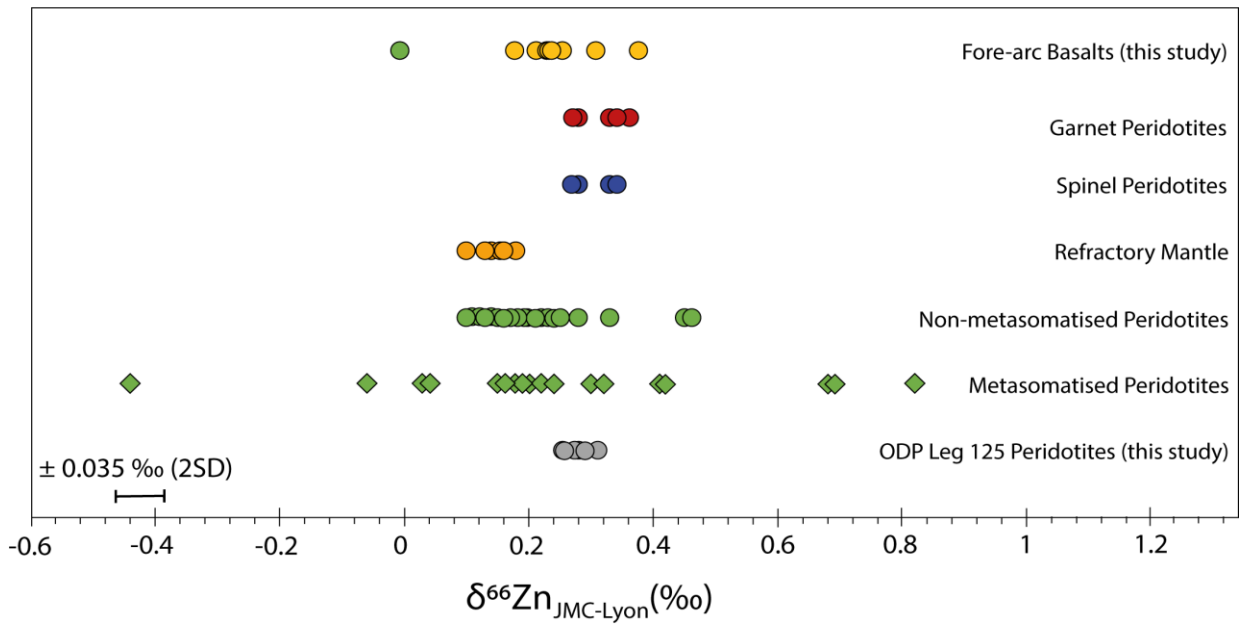


Figure 5.18: Available peridotite $\delta^{66}\text{Zn}$ data from literature (Doucet *et al.* 2016; Wang *et al.* 2017; Huang *et al.* 2018a; Sossi *et al.* 2018a) and the FAB and ODP Leg 125 peridotite $\delta^{66}\text{Zn}$ data from this study. D-FAB is the green FAB symbol.

Historic metasomatism of the FAB mantle source therefore has the potential to create a light enough source for mixing to reproduce the observed FAB $\delta^{66}\text{Zn}$ variance. Another potential way to create an extremely isotopically light FAB source is through multiple stages of large degree melt extraction, leaving behind a lighter $\delta^{66}\text{Zn}$, depleted residue, prior to the FAB melting event. Multiple events are required since a single melting event of a garnet peridotite source requires a melt degree of around 65% to go from 0.16 ‰ source to a 0.05 ‰ residue, which is very unlikely. A significant issue is that melting an increasingly depleted residue will become increasingly difficult, and therefore initiating FAB formation may also become extremely difficult. Also as mentioned above, since both FABs and MORB, and FABs and boninites differ in terms of source depletion but are not statistically distinct in $\delta^{66}\text{Zn}$, source depletion appears to have had minimal influence on $\delta^{66}\text{Zn}$ in this scenario. Potentially mixing the FAB source with sediments could create a lighter source as seen by the sediment mixing line in **Fig. 5.17**. But there is no geochemical evidence of a sediment component in FABs.

Melt mixing has the potential to create the range of FAB $\delta^{66}\text{Zn}$ observed in this study. Since partial melting and fractional crystallisation have only been reported to produce 0.10 ‰ variation in previous studies (e.g. Chen *et al.* 2013), melt mixing is a more likely candidate. However, the issues surrounding creating and then melting an isotopically light enough source are barriers to this idea. Previous suggestions of elevated mantle temperatures due to plume involvement however could maybe allow extremely depleted sources to melt (e.g. Shervais *et al.* 2019). The FABs are chemically

diverse due to variable degrees of trace element enrichment (Shervais *et al.* 2019) supporting a potentially chemically heterogeneous source and melt mixing. This study measured $\delta^{66}\text{Zn}$ in three of the four main FAB subgroups, and the most depleted FAB (D-FAB) is isotopically the lightest. Enriched FAB (E-FAB) is the least depleted of the FABs relative to MORB and thought to have formed by 2% garnet field melting, followed by 3-5% spinel field melting (Shervais *et al.* 2019). However, no E-FAB samples were available for this study. In the future, measuring E-FAB $\delta^{66}\text{Zn}$ may be a good test of whether enriched sources are isotopically heavy, in contrast with depleted sources, and therefore whether mantle heterogeneity could explain the large FAB $\delta^{66}\text{Zn}$ variance.

5.4.3.4. Origin of the Depleted FAB Sample

The D-FAB has the lightest $\delta^{66}\text{Zn}$ composition of the FAB population ($\delta^{66}\text{Zn} = -0.007 \pm 0.028$ ‰ 2SD), and is isotopically lighter than many boninite samples (**Fig. 5.3**). K_2O , LOI and Ba/Th ratios suggest that the D-FAB may be more altered than the other FABs or interacted with fluids (**Fig. 5.10**). However, since the boninite subduction fluid component did not create an observable $\delta^{66}\text{Zn}$ difference between FABs and boninites (**Fig. 5.3**), and previous studies suggest that fluids preferentially mobilise heavy Zn (Pons *et al.* 2016; Debret *et al.* 2018, 2021), fluid involvement is a dubious mechanism for creating the isotopically light D-FAB composition. With regards to alteration, since previous studies suggest that secondary alteration creates heavy $\delta^{66}\text{Zn}$ in altered oceanic basalts (e.g. Huang *et al.* 2016), alteration is also unlikely to create the light D-FAB $\delta^{66}\text{Zn}$. The D-FAB $\delta^{66}\text{Zn}$ cannot be accounted for by accumulation of mafic phases, since the D-FAB only has a 2% abundance of olivine, plagioclase and clinopyroxene phenocrysts combined (Shervais *et al.* 2019). To create the D-FAB composition from partial melting of a mantle source, a garnet peridotite source of $\delta^{66}\text{Zn} -0.07$ ‰ and a [Zn] of $58 \mu\text{g.g}^{-1}$ is required. There is one extreme metasomatised peridotite sample from Wang *et al.* (2017) that reaches and exceeds the $\delta^{66}\text{Zn}$ required to create the D-FAB ($\delta^{66}\text{Zn} = -0.44$ ‰; **Fig. 5.18**). It is therefore possible that a highly metasomatised peridotite could reach -0.07 ‰. However, such a source would need to exist as a small pod so as not to also be utilised by the other FABs. It seems strange that such extreme metasomatism would only affect one small, isolated part of the mantle. Another way to perhaps create a melt as isotopically light as the D-FAB is to have melted a small dunite pod in the upper mantle. As discussed above, olivine is isotopically lighter than mafic silicate melts, and fractional crystallisation of olivine should create an isotopically light solid. Subsequent melting of an uber depleted, olivine-rich pod should create a lighter melt, than a DMM melt. However, it is uncertain whether melting of a depleted olivine cumulate could reproduce the extreme D-FAB $\delta^{66}\text{Zn}$. It is also uncertain how such a depleted lithology would melt. The high D-FAB Ba/Th could suggest that the olivine cumulate interacted with a fluid that would lower the cumulate's solidus and allow melting

to occur. But then it is uncertain why such a fluid would not also interact with the FAB sources. Previous suggestions of plume involvement (Shervais *et al.* 2019) could raise mantle temperatures enough for a super depleted lithology to melt. An olivine cumulate D-FAB source could also be consistent with the D-FAB $\delta^{56}\text{Fe}$ value from Chapter four. The D-FAB does not have the lightest $\delta^{56}\text{Fe}$ of the FABs, but since $D(\text{Fe})^{\text{olv/melt}} \approx 1$, a high abundance of olivine may not have a significant effect on $\delta^{56}\text{Fe}$.

The D-FAB is an extremely unusual lithology and it is hard to explain its origin. Hopefully future Zn isotope studies that improve the breadth and diversity of Zn isotope measurements may be able to find an appropriately isotopically light source. However, at present, the two most likely contenders to explain the extremely light D-FAB $\delta^{66}\text{Zn}$ value are: (1) the melting of a highly metasomatised and isotopically light mantle source that was isolated from the primary FAB source; (2) the melting of a small olivine cumulate pod that's solidus was reduced by fluid fluxing.

5.4.4. Implications for isolating arc lava source components

This study provides strong evidence that subduction-derived fluids, melts, and sediments are unlikely to have an observable influence on the $\delta^{66}\text{Zn}$ of arc lavas. Zinc isotopes are therefore difficult to employ as a sulphate/carbonate/hypersaline fluid tracer through subduction zones.

Niobium, LREE, and MgO correlations with $\delta^{66}\text{Zn}$ suggest that mantle partial melting and magmatic differentiation may create $\delta^{66}\text{Zn}$ scatter in the Expedition 352 boninites, but these processes did not create a sizeable offset between FABs and boninites. However, since partial melting and magmatic differentiation have been invoked in previous Zn isotope studies to explain $\delta^{66}\text{Zn}$ differences between reservoirs such as mantle and MORB (e.g. Doucet *et al.* 2016; Wang *et al.* 2017; Sossi *et al.* 2018), this does not mean that such processes do not induce Zn isotope fractionation. Instead, it may be that the lack of a FAB-boninite $\delta^{66}\text{Zn}$ difference suggests the difference in degree of source depletion, partial melting, fractional crystallisation between FABs and boninites is not sizeable enough to create a $\delta^{66}\text{Zn}$ offset.

The Expedition 352 FABs record the largest partial melting attributed $\delta^{66}\text{Zn}$ range recorded so far in the literature. Correlations between, $\text{CaO}/\text{Al}_2\text{O}_3$, Zn concentrations, and FAB $\delta^{66}\text{Zn}$ and no other geochemical indicators suggest that partial melting is the dominant control on FAB $\delta^{66}\text{Zn}$. However, previous Zn isotope work has suggested that a $\delta^{66}\text{Zn}$ fractionation of only 0.10 ‰ is achievable. This could suggest that either current Zn melt models do not truly reflect nature, or there are additional processes influencing FAB $\delta^{66}\text{Zn}$ that for some reason are not visible geochemically. To test this, in the future enriched FAB (E-FAB) samples from Expedition 352 should be measured for $\delta^{66}\text{Zn}$. If E-

FAB $\delta^{66}\text{Zn}$ is the heaviest of the measured FAB data, it could suggest that the FAB $\delta^{66}\text{Zn}$ variation is controlled by mantle heterogeneity. The source of the potentially light E-FAB could be a mantle lithology poor in isotopically light olivine, complementing the potential light olivine-rich source of D-FAB. However, if E-FAB turns out to not be the isotopically heaviest FAB, it suggests that additional fractionation mechanisms are at play.

This work has highlighted some key questions about how Zn isotopes fractionate and what magnitude of fractionation is possible in different scenarios. However, one clear take home message is that the Zn budget of subduction-derived fluids, melts and sediments is insufficient to have an observable effect on the Zn budget of the mantle wedge and arc lavas.

5.5. Conclusions

1. FABs and boninites are statistically isotopically the same for Zn isotopes. Therefore, contrary to subducted serpentinite Zn isotope work (Pons *et al.* 2016; Debret *et al.* 2018, 2021) we suggest that slab-derived fluids and melts have insufficient Zn budgets to cause an observable $\delta^{66}\text{Zn}$ in arc lavas.
2. Covariations between boninite $\delta^{66}\text{Zn}$ and MgO and Nb concentrations suggest that boninite $\delta^{66}\text{Zn}$ variations are most likely caused by variable degrees of mantle partial melting and fractional crystallisation.
3. FAB $\delta^{66}\text{Zn}$ varies across 0.20 ‰.
 - There is no evidence that fluid interaction or secondary alteration contributed to this large range.
 - $\delta^{66}\text{Zn}$ covariations with $\text{CaO}/\text{Al}_2\text{O}_3$ suggest that FAB $\delta^{66}\text{Zn}$ was influenced by partial melting. However, current Zn melt models cannot reproduce the FAB $\delta^{66}\text{Zn}$ variation.
 - Therefore either, current Zn melt models do not truly reflect what happens in nature, or additional magmatic processes contributed to the FAB $\delta^{66}\text{Zn}$ range, but geochemical indicators were somehow masked.
 - Measuring $\delta^{66}\text{Zn}$ in enriched FABs (E-FAB) from Expedition 352 in the future may shed more light on this.

References

- Bentahila, Y., Othman, D. Ben & Luck, J. 2008. Strontium, lead and zinc isotopes in marine cores as tracers of sedimentary provenance: A case study around Taiwan orogen. *Chemical Geology*, **248**, 62–82, <https://doi.org/10.1016/j.chemgeo.2007.10.024>.

- Beunon, H., Mattielli, N., Doucet, L.S., Moine, B. & Debret, B. 2020. Mantle heterogeneity through Zn systematics in oceanic basalts: Evidence for a deep carbon cycling. *Earth-Science Reviews*, **205**, 103174, <https://doi.org/10.1016/j.earscirev.2020.103174>.
- Bougault, H. & Hekinian, R. 1974. Rift valley in the Atlantic Ocean near 36°50'N: Petrology and geochemistry of basaltic rocks. *Earth and Planetary Science Letters*, **24**, 249–261.
- Chen, H., Savage, P.S., Teng, F.Z., Helz, R.T. & Moynier, F. 2013. Zinc isotope fractionation during magmatic differentiation and the isotopic composition of the bulk Earth. *Earth and Planetary Science Letters*, **369**, 34–42, <https://doi.org/10.1016/j.epsl.2013.02.037>.
- Coulthard, D.A., Reagan, M.K., Shimizu, K., Bindeman, I.N., Brounce, M., Almeev, R.R., Ryan, J., Chapman, T., Shervias, J. & Pearce, J.A. 2021. Magma Source Evolution Following Subduction Initiation: Evidence From the Element Concentrations, Stable Isotope Ratios, and Water Contents of Volcanic Glasses From the Bonin Forearc (IODP Expedition 352). *Geochemistry, Geophysics, Geosystems*, **22**, 1–30, <https://doi.org/10.1029/2020GC009054>.
- Davis, F.A., Humayun, M., Hirschmann, M.M. & Cooper, R.S. 2013. Experimentally determined mineral/melt partitioning of first-row transition elements (FRTE) during partial melting of peridotite at 3GPa. *Geochimica et Cosmochimica Acta*, **104**, 232–260, <https://doi.org/10.1016/j.gca.2012.11.009>.
- Debret, B., Bouilhol, P., Pons, M.L. & Williams, H. 2018. Carbonate transfer during the onset of slab devolatilization: New insights from Fe and Zn stable isotopes. *Journal of Petrology*, **59**, 1145–1166, <https://doi.org/10.1093/petrology/egy057>.
- Debret, B., Garrido, C.J., Pons, M.L., Bouilhol, P., Inglis, E., López Sánchez-Vizcaíno, V. & Williams, H. 2021. Iron and zinc stable isotope evidence for open-system high-pressure dehydration of antigorite serpentinite in subduction zones. *Geochimica et Cosmochimica Acta*, **296**, 210–225, <https://doi.org/10.1016/j.gca.2020.12.001>.
- DePaolo, D.J. 1981. Trace element and isotopic effects of combined wallrock assimilation and fractional crystallization. *Earth and Planetary Science Letters*, **53**, 189–202. [https://doi.org/10.1016/0012-821X\(81\)90153-9](https://doi.org/10.1016/0012-821X(81)90153-9).
- Doucet, L.S., Mattielli, N., Ionov, D.A., Debouge, W. & Golovin, A. V. 2016. Zn isotopic heterogeneity in the mantle: A melting control? *Earth and Planetary Science Letters*, **451**, 232–240, <https://doi.org/10.1016/j.epsl.2016.06.040>.
- Drake, M.J. & Weill, D.F. 1975. Partition of Sr, Ba, Ca, Y, Eu²⁺, Eu³⁺, and other REE between plagioclase feldspar and magmatic liquid: an experimental study. *Geochimica et Cosmochimica Acta*, **39**, 689–712, [https://doi.org/10.1016/0016-7037\(75\)90011-3](https://doi.org/10.1016/0016-7037(75)90011-3).
- Ducher, M., Blanchard, M. & Balan, E. 2016. Equilibrium zinc isotope fractionation in Zn-bearing minerals from first-principles calculations. *Chemical Geology*, **443**, 87–96, <https://doi.org/10.1016/j.chemgeo.2016.09.016>.
- Evans, K.A. 2012. The redox budget of subduction zones. *Earth-Science Reviews*, **113**, 11–32, <https://doi.org/10.1016/j.earscirev.2012.03.003>.
- Foden, J., Sossi, P.A. & Nebel, O. 2018. Controls on the iron isotopic composition of global arc magmas. *Earth and Planetary Science Letters*, **494**, 190–201, <https://doi.org/10.1016/j.epsl.2018.04.039>.
- Fujii, T., Moynier, F., Blichert-Toft, J. & Albarède, F. 2014. Density functional theory estimation of isotope fractionation of Fe, Ni, Cu, and Zn among species relevant to geochemical and

- biological environments. *Geochimica et Cosmochimica Acta*, **140**, 553–576, <https://doi.org/10.1016/j.gca.2014.05.051>.
- Gagnevin, D., Boyce, A.J., Barrie, C.D., Menuge, J.F. & Blakeman, R.J. 2012. Zn, Fe and S isotope fractionation in a large hydrothermal system. *Geochimica et Cosmochimica Acta*, **88**, 183–198, <https://doi.org/10.1016/j.gca.2012.04.031>.
- Gao, Z., Zhu, X., Sun, J., Luo, Z., Bao, C., Tang, C. & Ma, J. 2018. Spatial evolution of Zn-Fe-Pb isotopes of sphalerite within a single ore body: A case study from the Dongshengmiao ore deposit, Inner Mongolia, China. *Mineralium Deposita*, **53**, 55–65, <https://doi.org/10.1007/s00126-017-0724-x>.
- Herzog, G.F., Moynier, F., Albarède, F. & Berezhnoy, A.A. 2009. Isotopic and elemental abundances of copper and zinc in lunar samples, Zagami, Pele's hairs, and a terrestrial basalt. *Geochimica et Cosmochimica Acta*, **73**, 5884–5904, <https://doi.org/10.1016/j.gca.2009.05.067>.
- Hoefs, J. 2018. Stable Isotope Geochemistry, *Springer Textbooks in Earth Sciences, Geography and Environment*, Springer International Publishing, <https://doi.org/10.1007/978-3-319-78527-1>.
- Huang, J., Liu, S.A., Gao, Y., Xiao, Y. & Chen, S. 2016. Copper and zinc isotope systematics of altered oceanic crust at IODP Site 1256 in the eastern equatorial Pacific. *Journal of Geophysical Research: Solid Earth*, **121**, 7086–7100, <https://doi.org/10.1002/2015JB012608>.
- Huang, J., Chen, S., Zhang, X.C. & Huang, F. 2018a. Effects of Melt Percolation on Zn Isotope Heterogeneity in the Mantle: Constraints From Peridotite Massifs in Ivrea-Verbano Zone, Italian Alps. *Journal of Geophysical Research: Solid Earth*, **123**, 2706–2722, <https://doi.org/10.1002/2017JB015287>.
- Huang, J., Zhang, X.C., Chen, S., Tang, L., Wörner, G., Yu, H. & Huang, F. 2018b. Zinc isotopic systematics of Kamchatka-Aleutian arc magmas controlled by mantle melting. *Geochimica et Cosmochimica Acta*, **238**, 85–101, <https://doi.org/10.1016/j.gca.2018.07.012>.
- Inglis, E., Debret, B., Burton, K.W., Millet, M.A., Pons, M-L., Dale, C.W., Bouilhol, P., Cooper, M., Nowell, G.M., McCoy-West, A.J. & Williams, H.M. 2017. The behavior of iron and zinc stable isotopes accompanying the subduction of mafic oceanic crust: A case study from Western Alpine ophiolites. *Geochemistry Geophysics Geosystems*, **18**, 2562–2579, <https://doi.org/10.1002/2016GC006735>.
- Kelley, K.D., Wilkinson, J.J., Chapman, J.B., Crowther, H.L. & Weiss, D.J. 2009. Zinc isotopes in sphalerite from base metal deposits in the Red Dog district, northern Alaska. *Economic Geology*, **104**, 767–773, <https://doi.org/10.2113/gsecongeo.104.6.767>.
- Kendrick, M.A., Hémond, C., Kamenetsky, V.S., Danyushevsky, L., Devey, C.W., Rodemanns, T., Jackson, M.G. & Perfit, M.R. 2017. Seawater cycled throughout Earth's mantle in partially serpentinized lithosphere. *Nature Geoscience*, **10**, 222–228, <https://doi.org/10.1038/ngeo2902>.
- Li, H.Y., Taylor, R.N., Prytulak, J., Kirchenbaur, M., Shervais, J.W., Ryan, J.G., Godard, M., Reagan, M.K. & Pearce, J.A. 2019. Radiogenic isotopes document the start of subduction in the Western Pacific. *Earth and Planetary Science Letters*, **518**, 197–210, <https://doi.org/10.1016/j.epsl.2019.04.041>.
- Liao, R., Zhu, H., Deng, J., Zhang, L., Li, H. & Li, C. 2020. Zinc isotopic systematics of the South China Sea basalts and implications for its behavior during plate subduction. **541**, <https://doi.org/10.1016/j.chemgeo.2020.119582>.

- Liu, S.A., Wang, Z.Z., Li, S.G., Huang, J. & Yang, W. 2016. Zinc isotope evidence for a large-scale carbonated mantle beneath eastern China. *Earth and Planetary Science Letters*, **444**, 169–178, <https://doi.org/10.1016/j.epsl.2016.03.051>.
- Maréchal, C.N., Nicolas, E., Douchet, C. & Albare, F. 2000. Abundance of zinc isotopes as a marine biogeochemical tracer. *Geochemistry, Geophysics, Geosystems*, **1**, 1–15, <https://doi.org/10.1029/1999GC000029>.
- Mason, T.F.D., Weiss, D.J., Chapman, J.B., Wilkinson, J.J., Tessalina, S.G., Spiro, B., Horstwood, W.S.A., Spratt, J. & Coles, B.J. 2005. Zn and Cu isotopic variability in the Alexandrinka volcanic-hosted massive sulphide (VHMS) ore deposit, Urals, Russia. *Chemical Geology*, **221**, 170–187, <https://doi.org/10.1016/j.chemgeo.2005.04.011>.
- Nebel, O., Sossi, P.A., Bénard, A., Wille, M., Vroon, P.Z. & Arculus, R.J. 2015. Redox-variability and controls in subduction zones from an iron-isotope perspective. *Earth and Planetary Science Letters*, **432**, 142–151, <https://doi.org/10.1016/j.epsl.2015.09.036>.
- Parkinson, I.J. & Arculus, R.J. 1999. The redox state of subduction zones: Insights from arc-peridotites. *Chemical Geology*, **160**, 409–423, [https://doi.org/10.1016/S0009-2541\(99\)00110-2](https://doi.org/10.1016/S0009-2541(99)00110-2).
- Parkinson, I.J. & Pearce, J.A. 1998. Peridotites from the Izu-Bonin-Mariana forearc (ODP Leg 125): evidence for mantle melting and melt-mantle interaction in a supra-subduction zone setting. *Journal of Petrology*, **39**, 1577–1618, <https://doi.org/10.1093/ptro/39.9.1577>.
- Parkinson, I.J., Hawkesworth, C.J. & Cohen, A.S. 1998. Ancient mantle in a modern arc: Osmium isotopes in Izu-Bonin-Mariana forearc peridotites. *Science*, **281**, 2011–2013, <https://doi.org/10.1126/science.281.5385.2011>.
- Pearce, J.A. & Peate, D.W. 1995. Tectonic Implications of the Composition of Volcanic Arc Magmas. *Annual Review of Earth and Planetary Sciences*, **23**, 251–285.
- Pichat, S., Douchet, C. & Albare, F. 2003. Zinc isotope variations in deep-sea carbonates from the eastern equatorial Pacific over the last 175 ka. *Earth and Planetary Science Letters*, **210**, 167–178, [https://doi.org/10.1016/S0012-821X\(03\)00106-7](https://doi.org/10.1016/S0012-821X(03)00106-7).
- Pons, M.-L., Debret, B., Bouilhol, P., Delacour, A. & Williams, H. 2016. Zinc isotope evidence for sulfate-rich fluid transfer across subduction zones. *Nature Communications*, **7**, 13794, <https://doi.org/10.1038/ncomms13794>.
- Pons, M., Quitté, G., Fujii, T., Rosing, M.T., Reynard, B. & Moynier, F. 2011. Early Archean serpentine mud volcanoes at Isua, Greenland, as a niche for early life. *PNAS*, **108**, 17639–17643, <https://doi.org/10.1073/pnas.1108061108>.
- Reagan, M.K., Pearce, J.A., Petronotis, K., Almeev, R.R., Avery, A.J., Carvallo, C., Chapman, T., Christeson, G.L., Ferre, E.C., Godard, M., Heaton, D.E., Kirchenbaur, M., Kurz, W., Kutterolf, S., Li, H., Li, Y., Michibayashi, K., Morgan, S., Nelson, W.R., Prytulak, P., Python, M., Robertson, A.H.F., Ryan, J.G., Sager, W.W., Sakuyama, T., Shervais, J.W., Shimizu, K. & Whattam, S.A. 2015a. Expedition 352 core descriptions, Site U1439. *Proceedings of the International Ocean Discovery Program*, **352**, 1–290.
- Reagan, M.K., Pearce, J.A., Petronotis, K., Almeev, R.R., Avery, A.J., Carvallo, C., Chapman, T., Christeson, G.L., Ferre, E.C., Godard, M., Heaton, D.E., Kirchenbaur, M., Kurz, W., Kutterolf, S., Li, H., Li, Y., Michibayashi, K., Morgan, S., Nelson, W.R., Prytulak, P., Python, M., Robertson, A.H.F., Ryan, J.G., Sager, W.W., Sakuyama, T., Shervais, J.W., Shimizu, K. & Whattam, S.A.

- 2015b. Expedition 352 summary. *Proceedings of the International Ocean Discovery Program*, **352**, <https://doi.org/10.14379/iodp.proc.352.101.2015>.
- Reagan, M.K., Pearce, J.A., Petronotis, K., Almeev, R.R., Avery, A.J., Carvallo, C., Chapman, T., Christeson, G.L., Ferre, E.C., Godard, M., Heaton, D.E., Kirchenbaur, M., Kurz, W., Kutterolf, S., Li, H., Li, Y., Michibayashi, K., Morgan, S., Nelson, W.R., Prytulak, P., Python, M., Robertson, A.H.F., Ryan, J.G., Sager, W.W., Sakuyama, T., Shervais, J.W., Shimizu, K. & Whattam, S.A. 2017. Subduction initiation and ophiolite crust: new insights from IODP drilling. *International Geology Review*, **59**, 1439–1450, <https://doi.org/10.1080/00206814.2016.1276482>.
- Rosca, C., König, S., Pons, M. & Schoenberg, R. 2020. Zinc isotope fractionation at destructive plate margins and potential implications for the global recycling signature. *EGU General Assembly 2020 Abstract*, Online.
- Shaw, D.M. 1970. Trace element fractionation during anatexis. *Geochimica et Cosmochimica Acta*, **34**, 237–243, [https://doi.org/10.1016/0016-7037\(70\)90009-8](https://doi.org/10.1016/0016-7037(70)90009-8).
- Shervais, J.W., Reagan, M., Haugen, E., Almeev, R.R., Pearce, J.A., Prytulak, J., Ryan, J.G., Whattam, S.A., Godard, M., Chapman, T., Li, H., Kurz, W., Nelson, W.R., Heaton, D., Kirchenbaur, M., Shimizu, K., Sakuyama, T., Li, Y. & Vetter, S.K. 2019. Magmatic Response to Subduction Initiation: Part 1. Fore-arc Basalts of the Izu-Bonin Arc From IODP Expedition 352. *Geochemistry, Geophysics, Geosystems*, **20**, 314–338, <https://doi.org/10.1029/2018 GC007731>.
- Shervais, J.W., Reagan, M.K., Godard, M. & Prytulak, J. 2021. Magmatic Response to Subduction Initiation , Part II : Boninites and Related Rocks of the Izu-Bonin Arc From IODP Expedition 352 Geochemistry , Geophysics , Geosystems. *Geochemistry, Geophysics, Geosystems*, **22**, 1–34, <https://doi.org/10.1029/2020GC009093>.
- Sossi, P.A., Halverson, G.P., Nebel, O. & Eggins, S.M. 2015. Combined separation of Cu, Fe and Zn from rock matrices and improved analytical protocols for stable isotope determination. *Geostandards and Geoanalytical Research*, **39**, 129–149, <https://doi.org/10.1111/j.1751-908X.2014.00298.x>.
- Sossi, P.A., Prytulak, J. & O'Neill, H.S.C. 2018a. Experimental calibration of vanadium partitioning and stable isotope fractionation between hydrous granitic melt and magnetite at 800 °C and 0.5 GPa. *Contributions to Mineralogy and Petrology*, **173**, 1451–1458, <https://doi.org/10.1007/s00410-018-1451-8>.
- Sossi, P.A., Nebel, O., St, H., Neill, C.O. & Moynier, F. 2018b. Zinc isotope composition of the Earth and its behaviour during planetary accretion. *Chemical Geology*, **477**, 73–84, <https://doi.org/10.1016/j.chemgeo.2017.12.006>.
- Wang, Z.Z., Liu, S.A., Liu, J., Huang, J., Xiao, Y., Chu, Z.Y., Zhao, X.M. & Tang, L. 2017. Zinc isotope fractionation during mantle melting and constraints on the Zn isotope composition of Earth's upper mantle. *Geochimica et Cosmochimica Acta*, **198**, 151–167, <https://doi.org/10.1016/j.gca.2016.11.014>.
- Wilkinson, J.J., Weiss, D.J., Mason, T.F.D. & Coles, B.J. 2005. Zinc isotope variation in hydrothermal systems: preliminary evidence from the Irish Midlands ore field. *Economic Geology*, **100**, 583–590.
- Williams, H.M., Prytulak, J., Woodhead, J.D., Kelley, K.A., Brounce, M. & Plank, T. 2018. Interplay of crystal fractionation, sulfide saturation and oxygen fugacity on the iron isotope composition

of arc lavas: An example from the Marianas. *Geochimica et Cosmochimica Acta*, **226**, 224–243, <https://doi.org/10.1016/j.gca.2018.02.008>.

Zhu, C., Liao, S., Wang, W., Zhang, Y., Yang, T., Fan, H. & Wen, H. 2018. Variations in Zn and S isotope chemistry of sedimentary sphalerite, Wusihe Zn-Pb deposit, Sichuan Province, China. *Ore Geology Reviews*, **95**, 639–648, <https://doi.org/10.1016/j.oregeorev.2018.03.018>.

CHAPTER SIX

The controls on vanadium and titanium isotopic fractionation in IODP Expedition 352 subduction initiation lavas from the Bonin forearc

Abstract

The $\text{Fe}^{3+}/\Sigma\text{Fe}$ of arc lavas is higher than MORB (e.g. Kelley & Cottrell 2009, 2012; Evans & Tomkins 2011; Evans 2012; Brounce *et al.* 2014). However, it is not certain whether elevated $\text{Fe}^{3+}/\Sigma\text{Fe}$ is related to higher $f\text{O}_2$ in arc sources (e.g. Wood *et al.* 1990; Parkinson & Arculus 1999), or magmatic processes *en route* to the surface such as fractional crystallisation, crustal assimilation, or degassing (e.g. Lee *et al.* 2005, 2010; Kelley & Cottrell 2009). Redox-sensitive stable isotopes such as V and Ti have the potential to trace arc lava $f\text{O}_2$. However, measurement protocols for V and Ti isotopes have only recently been developed to the precision needed for high-temperature applications. Therefore, arc lava $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ literature data is limited, and the controls on their fractionation are not well constrained.

This chapter compared the Ti and V isotopic compositions of IODP Expedition 352 fore-arc basalts (FABs) and boninites to determine if V and Ti isotopes reflect the evolving $f\text{O}_2$ of an arc setting from inception to the introduction of presumably oxidising slab inputs. Initial FABs formed by anhydrous decompression melting in a seafloor spreading setting akin to MORB. However, FABs and MORB are statistically distinct in both V and Ti isotopes. Surprisingly, the FAB-MORB offset is in opposing directions for Ti and V isotopes, with lighter FAB $\delta^{51}\text{V}$ and heavier FAB $\delta^{49}\text{Ti}$ compared to MORB. The $\delta^{51}\text{V}$ FAB-MORB offset is attributed to source depletion, and the $\delta^{49}\text{Ti}$ FAB-MORB offset to mantle heterogeneity. The boninites show clear evidence of subduction components and have higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Brounce *et al.* 2019; Li *et al.* 2019; Shervais *et al.* 2019, 2021). FAB have isotopically light $\delta^{49}\text{Ti}$ compared to boninites, whereas there is no statistically significant $\delta^{51}\text{V}$ FAB-boninite offset. The lack of $\delta^{51}\text{V}$ difference is explained by a two-step process, whereby a light isotopic composition in the mantle wedge from previous FAB extraction is counteracted by isotopically heavy oxidising slab fluids. Similarly, the $\delta^{49}\text{Ti}$ FAB-boninite offset is attributed to fluxing of the mantle wedge with halogen-rich slab-derived fluids. Strong correlations between fluid mobile elements and both $\delta^{49}\text{Ti}$ and $\delta^{51}\text{V}$ suggest that slab-derived halogen-rich fluids may mobilise V and Ti and induce isotopic fractionation.

CHAPTER SIX TABLE OF CONTENTS

6.1. Introduction	233
6.1.1. Aims.....	238
6.2. Methods	238
6.2.1. Vanadium Isotopes	238
6.2.2. Titanium Isotopes	238
6.2.3. Hafnium Isotopes	239
6.3. Results	243
6.3.1. FAB and MORB Ti and V isotopic compositions	243
6.3.2. FAB and boninite V and Ti Isotopic Compositions	244
6.4. Discussion.....	247
6.4.1. Effects of secondary Alteration.....	248
6.4.2. Cause(s) of FAB-MORB isotopic differences	249
6.4.2.1. Contribution of Slab-derived Fluids?	249
6.4.2.2. Contribution of Slab-derived Melts?.....	251
6.4.2.3. Different Redox Conditions?	252
6.4.2.4. Fractional Crystallisation	252
6.4.2.5. Mantle Partial Melting and Source Depletion	253
6.4.2.6. Titanium Isotopic Mantle Heterogeneity	255
6.4.2.7. Best Explanations for FAB-MORB $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ differences	256
6.4.3. Comparison of FAB-Boninite Ti- V isotopes	257
6.4.3.1. Source Depletion and Partial Melting.....	257
6.4.3.2. Fractional Crystallisation.....	257
6.4.3.3. Different Redox Conditions.....	259
6.4.3.4. Subduction-related Processes.....	260
6.4.4. Implications for using V and Ti isotopes in arcs	266
6.5. Conclusions	268
References	268

6.1. Introduction

The physical conditions in subduction zones such as pressure, temperature, and $f\text{O}_2$ are important to constrain because they control phase stability and element cycling. For example, the $f\text{O}_2$ of the

mantle wedge and of fluids from the subducting slab exert control on element speciation and mobility through subduction zones. Intuitively, arc lava sources, which are fluxed by fluids released from a subducting slab, should be more oxidised than MORB. Arc lavas contain components of hydrated and altered oceanic crust, sediments, and fluids from the subducting slab, whereas MORB form by anhydrous mantle decompression melting beneath a spreading centre. However, whether arc lavas are more oxidised than MORB, the specific agents of oxidation, and the magnitude of fO_2 differences between MORB and arc sources, are all active areas of debate. For example, arc lavas have higher measured $Fe^{3+}/\Sigma Fe$ than MORB (e.g. Kelley & Cottrell 2009, 2012; Evans & Tomkins 2011; Evans 2012; Brounce *et al.* 2014). However, it is uncertain whether the elevated $Fe^{3+}/\Sigma Fe$ of arc lavas is a primary signal related to higher fO_2 in their mantle sources (e.g. Wood *et al.* 1990; Parkinson & Arculus 1999), or created by magmatic processes *en route* to the surface such as fractional crystallisation, crustal assimilation, or degassing (e.g. Lee *et al.* 2005, 2010; Kelley & Cottrell 2009). Correlations between $Fe^{3+}/\Sigma Fe$ and H_2O in arc glasses suggest that elevated arc $Fe^{3+}/\Sigma Fe$ may be related to the addition of oxidised subduction zone fluids to mantle sources (Kelley & Cottrell 2009). Yet trace element ratio redox-proxies such as V/Sc and Zn/Fe surprisingly suggest there is little difference between arc and MORB mantle source fO_2 (Lee *et al.* 2005, 2010). Trace element redox proxies can, however, have large uncertainties because they are influenced by factors such as initial source concentration, mineralogy, pressure, and melt fraction. Redox-sensitive stable isotopes should be less affected by these factors. Iron isotopes were first used to investigate arc versus MORB fO_2 (e.g. Polyakov & Mineev 2000; Shahar *et al.* 2008; Young *et al.* 2015). Iron isotopes should theoretically reflect fO_2 due to multiple oxidation states, with more oxidised conditions favouring heavier $\delta^{56}Fe$ (Dauphas *et al.* 2009, 2014). However, $\delta^{56}Fe$ is lighter in arc lavas compared to MORB (e.g. Dauphas *et al.* 2009; Nebel *et al.* 2015; Foden *et al.* 2018; Williams *et al.* 2018). Chapter four interpreted the lighter $\delta^{56}Fe$ of arc lavas in terms of mantle source depletion, and highlighted that because Fe is a major element, there are a myriad of processes that can potentially fractionate Fe isotopes during melt generation and evolution, which complicates interpretations. Therefore, to further investigate subduction zone fO_2 , redox-sensitive stable isotope systems of minor elements should also be employed.

Titanium and vanadium are both refractory, multivalent, moderately incompatible elements, and both isotope systems have the capacity to be redox-sensitive (e.g. Canil 1997; Prytulak *et al.* 2013, 2017; Millet *et al.* 2016; Sossi *et al.* 2018; Hoare *et al.* 2020; Novella *et al.* 2020). Advances in MC-ICP-MS in the past decade (Nielsen *et al.* 2011; Prytulak *et al.* 2011; Zhang *et al.* 2011; Millet & Dauphas 2014) have allowed V and Ti isotopes to be measured to a great enough precision to be applied to high-temperature geologic systems. The investigation of V and Ti isotopes is in its infancy,

and the controls on $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ fractionation are not yet fully constrained. This chapter presents the first combined Ti-V isotopic investigation in any Earth materials.

Since Ti isotopes have only been recently applied to the study of magmatic processes (Millet *et al.* 2016; Greber *et al.* 2017; Deng *et al.* 2018, 2019; Johnson *et al.* 2019; Hoare *et al.* 2020; Zhao *et al.* 2020), there is limited published $\delta^{49}\text{Ti}$ data. Of particular relevance, Millet *et al.* (2016) found no $\delta^{49}\text{Ti}$ difference between peridotites and primitive basalts, and therefore suggested with support of MORB and komatiite $\delta^{49}\text{Ti}$ comparisons from Deng *et al.* (2018), that mantle partial melting does not fractionate Ti isotopes. However, a strong relationship between $\delta^{49}\text{Ti}$ and magmatic differentiation has been reported, with $\delta^{49}\text{Ti}$ increasing with the progressive fractional crystallisation and removal of Fe-Ti oxides (Millet *et al.* 2016; Deng *et al.* 2019; Johnson *et al.* 2019; Hoare *et al.* 2020; **Fig. 6.1**) which are the dominant hosts of Ti in igneous rocks. Whilst Ti is a multivalent element, under terrestrial conditions Ti only exists in Ti^{4+} speciation (Millet *et al.* 2016). Therefore, Ti is unlikely to respond directly to changes in redox. Instead, $\delta^{49}\text{Ti}$ may be able to trace melt $f\text{O}_2$ in oxide saturated rocks since the timing of oxide crystallisation is partially controlled by the interplay between $f\text{O}_2$ and H_2O content (Toplis & Carroll 1995, 1996). Hoare *et al.* (2020) showed that at a similar SiO_2 concentration, more oxidised calc-alkaline suites have higher $\delta^{49}\text{Ti}$ compared to more reduced tholeiitic magmas.

Only two previous Ti isotope studies have measured arc lavas (Millet *et al.* 2016; Hoare *et al.* 2020). Existing data shows a clear $\delta^{49}\text{Ti}$ difference between MORB and differentiated arc lavas that is attributed to the fractional crystallisation of oxides (**Figure 6.1**). However, the few primitive arc basalts that have not reached oxide crystallisation have $\delta^{49}\text{Ti}$ within error of MORB (**Figure 6.1**). This suggests that oxide crystallisation is the main mechanism of $\delta^{49}\text{Ti}$ fractionation in subduction zones, and that $f\text{O}_2$ differences between primitive rocks are difficult to trace with $\delta^{49}\text{Ti}$ alone. However, there is limited $\delta^{49}\text{Ti}$ data on primitive arc basalts at present, and more data is needed to confirm this.

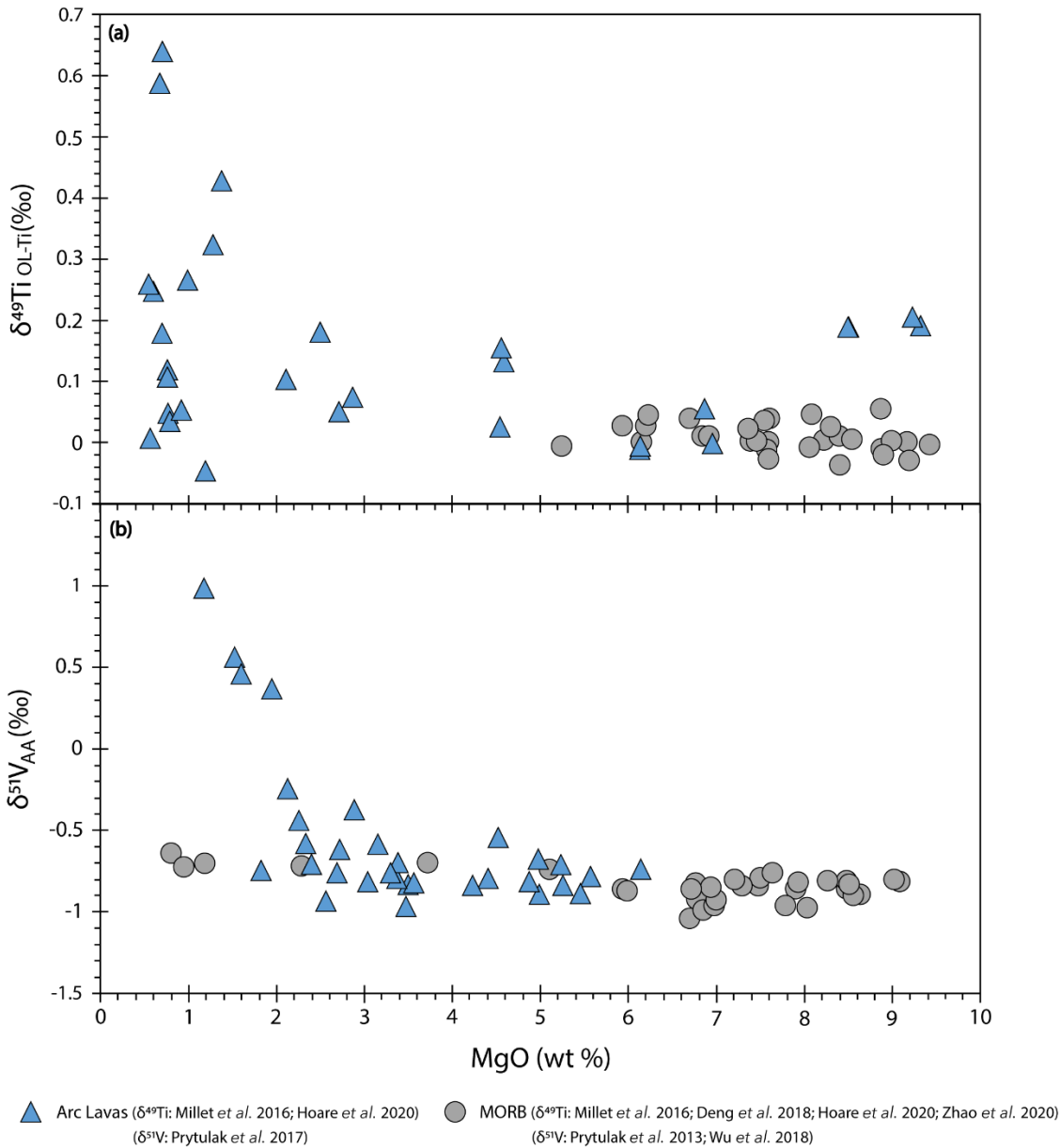


Figure 6.1: (a) $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ (‰) versus MgO (wt %) for literature MORB and arc lavas. MORB data is from Millet *et al.* (2016); Deng *et al.* (2018); Hoare *et al.* (2020); Zhao *et al.* (2020) and arc data is from Millet *et al.* (2016) and Hoare *et al.* (2020). The average y-axis error is ± 0.025 ‰ (95% c.i.) which is smaller than the data symbols. **(b)** $\delta^{51}\text{V}_{\text{AA}}$ (‰) versus MgO (wt %) for literature MORB and arc lavas. MORB data is from Prytulak *et al.* (2013) and Wu *et al.* (2018) and arc data is from Prytulak *et al.* (2017). The average y-axis error is ± 0.12 ‰ (2SD) which is the size of the data symbols.

Similar to Ti isotopes, the fractional crystallisation of isotopically light oxide phases is considered a key driver of $\delta^{51}\text{V}$ fractionation. Several studies have demonstrated that melts evolve to heavier $\delta^{51}\text{V}$ with differentiation, presumably due to Rayleigh removal of isotopically light oxides (Prytulak *et al.* 2017; Wu *et al.* 2018; Ding *et al.* 2020). However, unlike Ti isotopes, there is evidence to suggest V isotopes are fractionated during mantle partial melting. The few existing harzburgite measurements ($\delta^{51}\text{V} = -1.20 \pm 0.18$ ‰ 2SD, $n=4$ (Prytulak *et al.* 2013)) are significantly isotopically lighter than MORB ($\delta^{51}\text{V} = -0.84 \pm 0.18$ ‰ (Prytulak *et al.* 2013; Wu *et al.* 2018)). These observations

led Wu *et al.* (2018) to conclude that during the initial stages of mantle partial melting, melts are isotopically heavier than their source but become lighter with increasing melt fraction as they approach their source composition. Vanadium isotopes have been found to be insensitive to low temperature seafloor alteration (Prytulak *et al.* 2013; Wu *et al.* 2018), although Chapter two found that $\delta^{51}\text{V}$ can fractionate during higher temperature mantle metasomatism due to co-ordination differences. Likewise, Prytulak *et al.* (2017) and Novella *et al.* (2020) found that whilst $\delta^{51}\text{V}$ can respond indirectly to changes in $f\text{O}_2$, V coordination is likely a more significant control on $\delta^{51}\text{V}$.

Currently the only published $\delta^{51}\text{V}$ data for arc lavas is from Prytulak *et al.* (2017) who attempted to use $\delta^{51}\text{V}$ to determine whether arc lavas and MORB are isotopically distinct, and whether the elevated $\text{Fe}^{3+}/\Sigma\text{Fe}$ of arc lavas compared to MORB can be attributed to their sources. Similarly to Ti isotopic arc studies, Prytulak *et al.* (2017) found that prior to oxide crystallisation, there is no resolvable isotopic difference between arcs and MORB (**Figure 6.1**). If $\delta^{51}\text{V}$ is interpreted as a direct redox proxy, current arc and MORB $\delta^{51}\text{V}$ appear to agree with V/Sc inferences of a similar $f\text{O}_2$ in MORB and arc sources (Lee *et al.* 2005). However, $\delta^{51}\text{V}$ is typically lighter in more depleted peridotites (Prytulak *et al.* 2013). Therefore, if arc and MORB sources have the same $f\text{O}_2$, primitive arc lavas should be isotopically lighter than MORB. Prytulak *et al.* (2017) therefore suggested that the combined conditions of greater source depletion and higher $f\text{O}_2$ (so less compatible V) could result in similar arc and MORB V/Sc and, presumably, $\delta^{51}\text{V}$. However, it is still not certain whether the implied higher $f\text{O}_2$ of arc lavas is related to their source or processes *en route* to the surface.

The IODP Expedition 352 FABs and boninites from Chapters four and five represent two different lithologies, closely related in space and time from the Bonin forearc. The FABs formed by anhydrous decompression melting of a source more depleted than MORB, show no evidence of subducted slab components (Li *et al.* 2019; Shervais *et al.* 2019), and have similar $\text{Fe}^{3+}/\Sigma\text{Fe}$ to MORB (Cottrell & Kelley 2011; Zhang *et al.* 2018; Brounce *et al.* 2019). Whereas the boninites formed by flux melting of the mantle wedge induced by subducted slab-derived melts, fluids, and sediment inputs (Li *et al.* 2019; Shervais *et al.* 2021), and have higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ than MORB (Cottrell & Kelley 2011; Zhang *et al.* 2018; Brounce *et al.* 2019). A V and Ti isotopic comparison of the FABs and boninites may therefore allow the effects of $f\text{O}_2$ on $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ to be better constrained. The seafloor spreading setting of both FABs and boninites also negate the possible complicating effects of crustal assimilation and degassing during ascent through overlying crust. Both suites of examined samples also do not appear to have reached oxide saturation, thus removing a process that is known to cause isotopic fractionation in both Ti and V isotopes. A FAB-boninite comparison should therefore act as a test for whether elevated $f\text{O}_2$ in arc lavas is a primary signal related to higher $f\text{O}_2$ in their mantle sources, or if a higher $f\text{O}_2$ evolves during later magmatic differentiation.

6.1.1. Aims

To address whether V and Ti isotopes can be used to determine the origin of elevated fO_2 of arc lavas, this chapter aims to answer the following questions:

4. Are IODP Expedition 352 FAB and MORB $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ distinct?
5. Are IODP Expedition 352 FAB and boninite $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ distinct?
6. Can differences in source fO_2 between FAB and boninites influence V and Ti isotopic compositions?
7. Are magmatic processes or subduction inputs the most influential controls on the V and Ti isotopic compositions of the boninites?

6.2. Methods

The samples used in this Chapter are a subset set of IODP Expedition 352 fore-arc basalts (FABs) and boninites from Chapters four and five. Nine FABs and eleven boninites were measured since V ion chromatography takes significantly longer than Fe and Zn ion chromatography (Chapter 2). The samples chosen still encompass the full range of FAB and boninite subtypes displayed in Chapters four and five. In addition, the Ocean Drilling Program (ODP) Leg 125 six harzburgites and dunites from Chapters four and five were measured for V isotopes. The harzburgites and dunites were not measured for Ti isotopes due to low Ti concentrations (8 to 45 $\mu\text{g.g}^{-1}$ (Parkinson & Pearce 1998)) and insufficient sample material.

6.2.1. Vanadium Isotopes

All V isotope data was collected at Durham University in the Arthur Holmes isotope labs. Full methods are outlined in Chapter two and all results are presented in **Table 6.1**. The V isotopic composition of USGS reference materials processed with the samples as unknowns agree within error of accepted values from the literature and are displayed in Chapter two. The total procedural blanks processed with every batch of 12 samples and were always < 1.5 ng of V, which is negligible compared to the total V processed (~10-20 μg).

6.2.2. Titanium Isotopes

All Ti isotope data was collected at Cardiff University in the CELTIC labs under supervision of Dr Marc Alban-Millet. Full methods are described in Chapter two and all Ti isotope measurements are

in **Table 6.1**. The Ti isotopic composition of USGS reference materials processed with the samples as unknowns agree within error of accepted values from the literature and are in Chapter two.

6.2.3. Hafnium Isotopes

Hafnium isotopes were measured to fill in gaps in the literature data on the Expedition 352 FABs and boninites. Hafnium isotope measurements are reported for 10 of the FAB and boninite samples analysed in this chapter, plus 10 of the FABs and boninites used in Chapters four and five. Full methods are outlined in Chapter two and all results are in **Table 6.2**. The Hf isotopic composition of USGS reference materials processed with the samples as unknowns agree within error of accepted values from the literature and are in Chapter two.

Table 6.1: Titanium and vanadium isotope ratios measured in the IODP Expedition 352 FABs and boninites. Vanadium isotopes are reported as $\delta^{51}\text{V}$ (‰) relative to reference standard AA and titanium isotopes as $\delta^{49}\text{Ti}$ (‰) relative to reference standard OL-Ti. Rock type abbreviations are as such: N-FAB (normal fore-arc basalt), P-FAB (primitive fore-arc basalt), D-FAB (depleted fore-arc basalt), LSB (low-silica boninite), HSB (high-silica boninite), BB (basaltic boninite), HMA (high-magnesian andesite).

Sample	Series	Type	Depth (mbsl)	Vanadium Isotopes				Titanium Isotopes					
				$\delta^{51}\text{V}_{\text{AA}}$ (‰)	Digestions	error (2SD)	n	$\delta^{49}\text{Ti}_{\text{OL-Ti}}$ (‰)	Digestions	error (95% CI)	n		
U1439C - Boninites													
U1439C-4R-1-W 26/32	off-axis	HSB	201.86	-1.19	1	0.08	3	0.186	1	0.03	3		
U1439C 16R1-26/30	axial	LSB	299.76	-1.17	2	0.09	7	0.174	1	0.03	3		
U1439C 22R1-89/95	axial	LSB	349.19	-1.22	2	0.14	5	0.151	1	0.02	3		
U1439C 41R1-99/106	axial	LSB	515.09	-1.10	1	0.09	4	0.144	1	0.03	3		
U1439C-10R-2-W 13/19	axial	BB	262.03	-1.22	1	0.10	4						
U1439C-29R-4-W 78/82	axial	LSB	421.29	-1.12	1	0.07	4	0.133	1	0.03	3		
U1439C-31R-5-W 12/17	axial	LSB	441.80	-1.15	1	0.06	3						
U1439C-37R-1-W 42/48	axial	HMA	485.22	-0.91	1	0.06	4	0.159	1	0.02	3		
U1442A - Boninites													
U1442A 20R1-104/108	off-axis	HSB	160.64	-1.26	2	0.06	7	0.172	1	0.02	3		
U1442A 22R1-122/125	off-axis	HSB	180.22	-1.16	1	0.15	4	0.151	1	0.03	3		
U1442A-35R-1-W 51/55	axial	LSB	306.01	-1.21	1	0.05	3	0.152	1	0.02	3		
U1440B - Fore-arc basalts													
U1440B 17R2-23/32	axial	N-FAB	213.80	-0.97	1	0.02	3	0.082	1	0.02	3		
U1440B 26R1-64/68	axial	N-FAB	271.14	-1.04	1	0.05	3	0.128	1	0.03	3		
U1440B 28R1-31/38	axial	N-FAB	290.31	-1.00	1	0.12	4	0.104	1	0.02	3		
U1440B-8R-1-W 20/23	off-axis	N-FAB	136.54	-1.26	1	0.04	4						
U1440B-12R-2-W 4/8	off-axis	P-FAB	165.14	-1.22	1	0.06	3	0.097	1	0.03	3		
U1440B-17R-1-W 11/13	axial	N-FAB	212.31	-1.18	1	0.08	4	0.096	1	0.03	3		
U1440B-29R-1-W 5/8	axial	N-FAB	299.75	-0.98	1	0.09	5	0.076	1	0.02	3		

Table 6.1: continued

				Vanadium Isotopes				Titanium Isotopes			
Sample	Series	Type	Depth (mbsl)	$\delta^{51}\text{V}_{\text{AA}}$ (‰)	Digestions	error (2SD)	n	$\delta^{49}\text{Ti}_{\text{OL-Ti}}$ (‰)	Digestions	error (95% CI)	n
U1441A - Fore-arc basalts											
U1441A-21R-1-W 37/42	axial	N-FAB	190.27	-0.97	1	0.14	7	0.087	1	0.02	3
U1441-A3-19R1-66/72	off-axis	D-FAB	171.16	-1.26	2	0.13	6	0.118	1	0.02	3

Table 6.2: Hafnium isotope ratios measured in the IODP Expedition 352 FABs and boninites. Hafnium isotope ratios are reported as the measured ratio ($^{176}\text{Hf}/^{177}\text{Hf}_m$), the initial ratio age corrected to 50 Ma ($^{176}\text{Hf}/^{177}\text{Hf}_i$) and age corrected ϵHf . Rock type abbreviations are as such: N-FAB (normal fore-arc basalt), P-FAB (primitive fore-arc basalt), D-FAB (depleted fore-arc basalt), LSB (low-Si boninite), HSB (high-Si boninite), BB (basaltic boninite), HMA (high-magnesian andesite).

Sample	Series	Type	Depth (mbsl)	Hafnium Isotopes					
				$^{176}\text{Hf}/^{177}\text{Hf}_m$	$\pm 1s$	$^{176}\text{Hf}/^{177}\text{Hf}_i$	ϵHf_{50}	$\epsilon 2SE$	Reference
U1439C - Boninites									
U1439C-4R-1-W 26/32	off-axis	HSB	201.86	0.283128	± 4	0.283112	12.7	0.28	(Li <i>et al.</i> 2019)
U1439C 16R1-26/30	axial	LSB	299.76	0.283196	± 4	0.283176	14.9	0.28	(Li <i>et al.</i> 2019)
U1439C 22R1-89/95	axial	LSB	349.19	0.283223	± 4	0.283203	15.9	0.28	(Li <i>et al.</i> 2019)
U1439C 41R1-99/106	axial	LSB	515.09	0.283264	± 3	0.283235	17.0	0.21	(Li <i>et al.</i> 2019)
U1439C-10R-2-W 13/19	axial	BB	262.03	0.283243	± 2	0.283222	16.5	0.14	This study
U1439C-29R-4-W 78/82	axial	LSB	421.29	0.283183	± 2	0.283163	14.5	0.21	This study
U1439C-31R-5-W 12/17	axial	LSB	441.80	0.283241	± 2	0.283216	16.4	0.14	This study
U1439C-37R-1-W 42/48	axial	HMA	485.22	0.283231	± 3	0.283211	16.2	0.14	This study
U1442A - Boninites									
U1442A 20R1-104/108	off-axis	HSB	160.64	0.283137	± 4	0.283122	13.0	0.28	(Li <i>et al.</i> 2019)
U1442A 22R1-122/125	off-axis	HSB	180.22	0.283118	± 3	0.283095	12.1	0.21	This study
U1442A-35R-1-W 51/55	axial	LSB	306.01	0.283200	± 2	0.283181	15.1	0.14	This study

Table 6.2: continued

Sample	Series	Type	Depth (mbsl)	Hafnium Isotopes					
				$^{176}\text{Hf}/^{177}\text{Hf}_m$	$\pm 1s$	$^{176}\text{Hf}/^{177}\text{Hf}_i$	ϵHf_{50}	$\epsilon 2SE$	Reference
U1440B - Fore-arc basalts									
U1440B 17R2-23/32	axial	N-FAB (lower)	213.80	0.283339	± 1	0.283301	19.4	0.07	This study
U1440B 26R1-64/68	axial	N-FAB (lower)	271.14	0.283339	± 3	0.283299	19.3	0.21	(Li <i>et al.</i> 2019)
U1440B 28R1-31/38	axial	N-FAB (lower)	290.31	0.283118	± 3	0.283310	19.7	0.14	This study
U1440B-8R-1-W 20/23	off-axis	N-FAB (upper)	136.54	0.283386	± 3	0.283339	20.7	0.21	(Li <i>et al.</i> 2019)
U1440B-12R-2-W 4/8	off-axis	P-FAB (upper)	165.14	0.283406	± 2	0.283355	21.3	0.14	This study
U1440B-17R-1-W 11/13	axial	N-FAB (lower)	212.31	0.283345	± 3	0.283305	19.5	0.21	(Li <i>et al.</i> 2019)
U1440B-29R-1-W 5/8	axial	N-FAB (lower)	299.75	0.283342	± 5	0.283300	19.3	0.35	(Li <i>et al.</i> 2019)
U1441A - Fore-arc basalts									
U1441A-21R-1-W 37/42	axial	N-FAB	190.27	0.283352	± 2	0.283303	19.4	0.14	This study
U1441-A3-19R1-66/72	off-axis	D-FAB	171.16	0.283396	± 4	0.283335	20.6	0.28	(Li <i>et al.</i> 2019)

6.3. Results

6.3.1. FAB and MORB Ti and V isotopic compositions

The Expedition 352 FABs exhibit a smaller range in $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ than literature MORB data ($\delta^{51}\text{V}$ range = 0.29 ‰ and 0.40 ‰ respectively, and $\delta^{49}\text{Ti}$ range = 0.05 ‰ and 0.09 ‰ respectively) (**Figure 6.2**). Student T-tests comparing FAB and MORB mean isotopic compositions show that when variance is considered, the FAB and MORB means are statistically isotopically distinct in both $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ with P-values of 2.2×10^{-9} and 6.9×10^{-12} respectively at 95% confidence intervals (**Figure 6.2**). FABs have lighter $\delta^{51}\text{V}$ and heavier $\delta^{49}\text{Ti}$ than MORB (**Figure 6.2**). These differences contrast with the findings of Chapters four and five, where FAB and MORB were isotopically indistinguishable in terms of $\delta^{56}\text{Fe}$ and $\delta^{66}\text{Zn}$. As discussed, FAB and MORB have similar petrogenetic origins; both formed by anhydrous decompression melting during seafloor spreading, and thus might be expected to have similar stable isotopic compositions. One significant difference between these two lithologies is that FABs are considered to have a more depleted source than MORB (Li *et al.* 2019; Shervais *et al.* 2019). Therefore, differences in source depletion could in principle be responsible for the FAB-MORB Ti and V isotopic offsets. Since FAB and MORB are not isotopically distinct in $\delta^{56}\text{Fe}$ (Chapter four) or $\delta^{66}\text{Zn}$ (Chapter five), V and Ti isotopes are clearly either tracking a different process or are more sensitive to isotopic fractionation during FAB formation than Fe and Zn isotopes. Other potential causes of the Ti and V FAB-MORB differences are secondary alteration, the interaction of FABs with fluids or melts, differences in redox and/or the extent of magmatic differentiation.

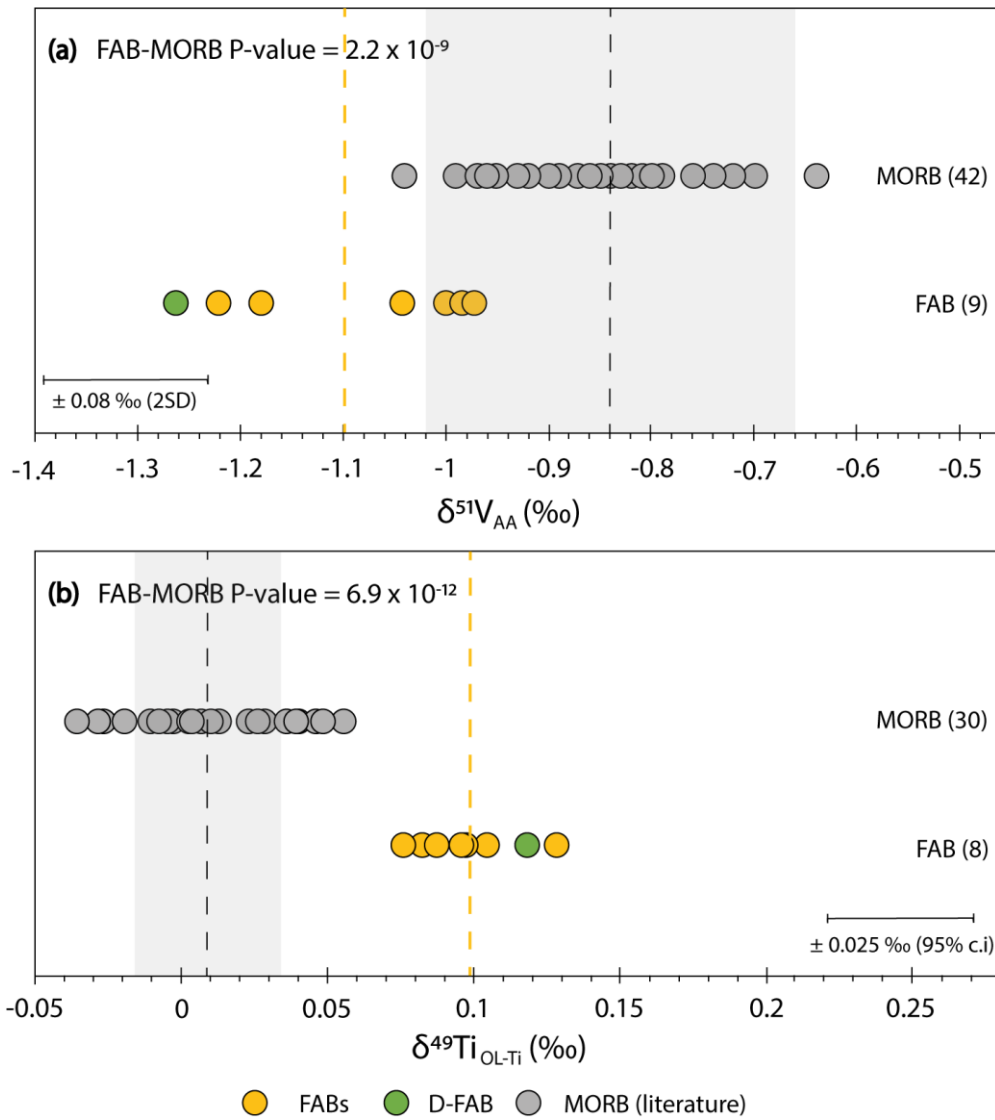


Figure 6.2: Comparison and student T-test results for $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$. **(a)** fore-arc basalts (FAB) and MORB $\delta^{51}\text{V}$ (Prytulak et al. 2013; Wu et al. 2018). **(b)** FAB and MORB $\delta^{49}\text{Ti}$ (Millet et al. 2016; Deng et al. 2018; Hoare et al. 2020; Zhao et al. 2020). The vertical dashed lines represent the average isotopic composition for the population of the corresponding colour. The grey shadow around the black dashed line represents the average error on the MORB average. The average error on the $\delta^{51}\text{V}$ measurements is ± 0.08 ‰ (2SD), and on the $\delta^{49}\text{Ti}$ measurements is ± 0.025 ‰ (95% c.i.). The p-values represent the p-values from student T-tests. A p-value of less than 0.05 dictates that there is enough evidence for the population means to be distinguished at a 95% confidence interval.

6.3.2. FAB and boninite V and Ti Isotopic Compositions

Student T-tests were also employed to assess the statistical similarity between FABs and boninites (**Figure 6.3**). **Figure 6.3a** shows that for V isotopes, there is not enough evidence to distinguish the FAB and boninite means (P-value = 0.122). There is an observable difference between the heavier, axial FABs and the boninites, but no difference between the lighter mostly off-axis FABs and the boninites.

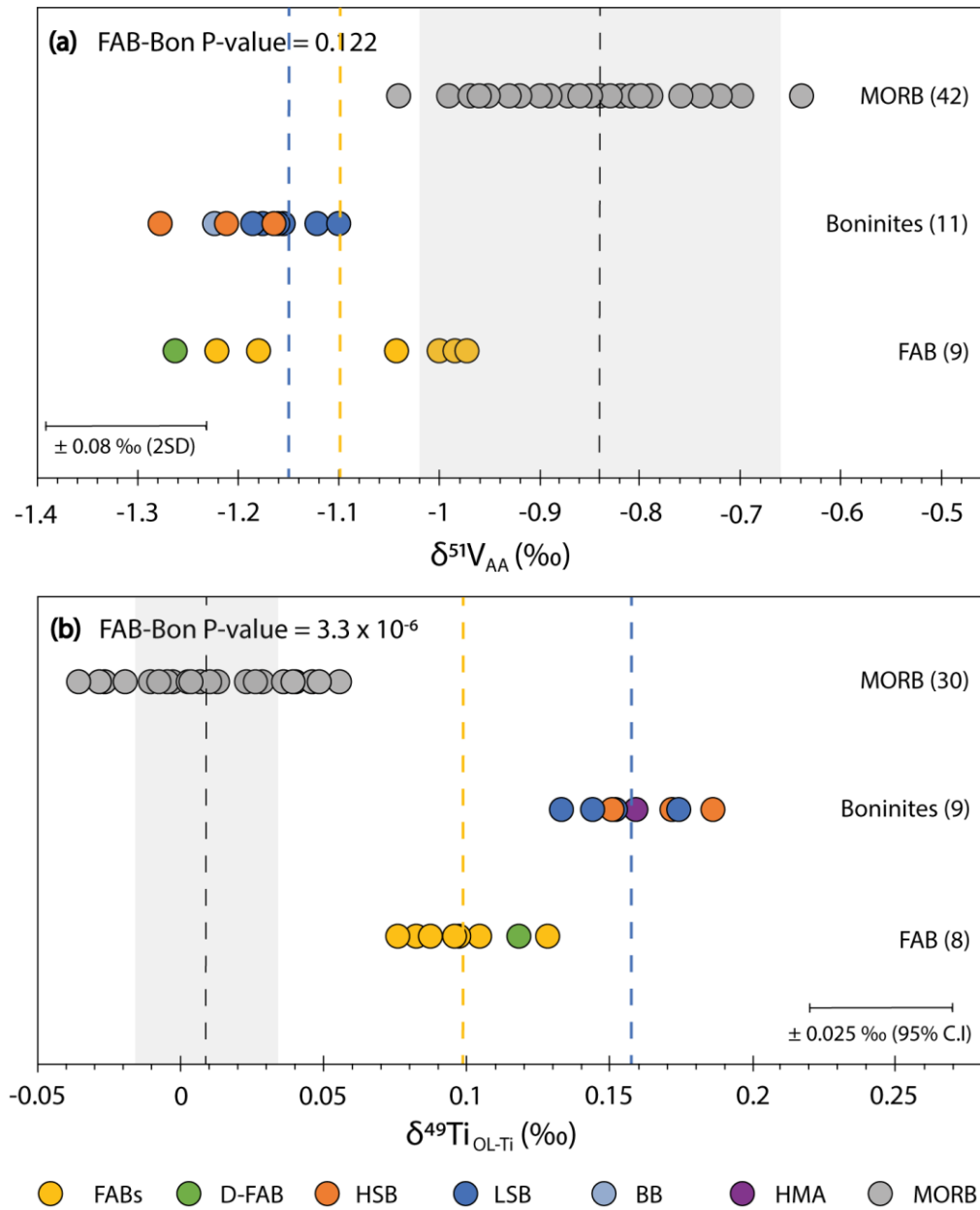


Figure 6.3: Comparison and student *T*-test results of **(a)** IODP Expedition 352 fore-arc basalt (FAB) and boninite $\delta^{51}\text{V}$; **(b)** fore-arc basalt (FAB) and boninite $\delta^{49}\text{Ti}$. All data is from this study. The vertical dashed lines represent the averages for each population that were compared in the student *T*-tests, and are colour coded to match the data point colours. The FAB $\delta^{49}\text{Ti}$ average = $0.099 \pm 0.035 \text{ ‰ (2SD)}$, the boninite $\delta^{49}\text{Ti}$ average = $0.158 \pm 0.033 \text{ ‰ (2SD)}$, the FAB $\delta^{51}\text{V}$ average = $-1.10 \pm 0.26 \text{ ‰ (2SD)}$, the boninite $\delta^{51}\text{V}$ average = $-1.15 \pm 0.19 \text{ ‰ (2SD)}$. The average error on each data point is $\pm 0.025 \text{ ‰ (95\% c.i.)}$ for the $\delta^{49}\text{Ti}$ data, and $\pm 0.09 \text{ ‰ (2SD)}$ for the $\delta^{51}\text{V}$ data. The *p*-values represent the *p*-values from student *T*-tests. A *p*-value of less than 0.05 dictates that there is enough evidence for the population means to be distinguished at a 95% confidence interval.

Contrary to V isotopes, **Figure 6.3b** shows that the FAB and boninite means are statistically distinct in Ti isotopes at a 95% confidence interval (*P*-value = 3.3×10^{-6}). The offset is in the same direction as the FAB-MORB $\delta^{49}\text{Ti}$ difference, but smaller in magnitude. There is a slight negative correlation between $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ in the boninites if the evolved high magnesium andesite HMA is ignored

(Figure 6.4). T-tests also show that the two main subgroups of boninites, LSBs and HSBs are not statistically distinct in either Ti or V isotopes (Figure 6.5).

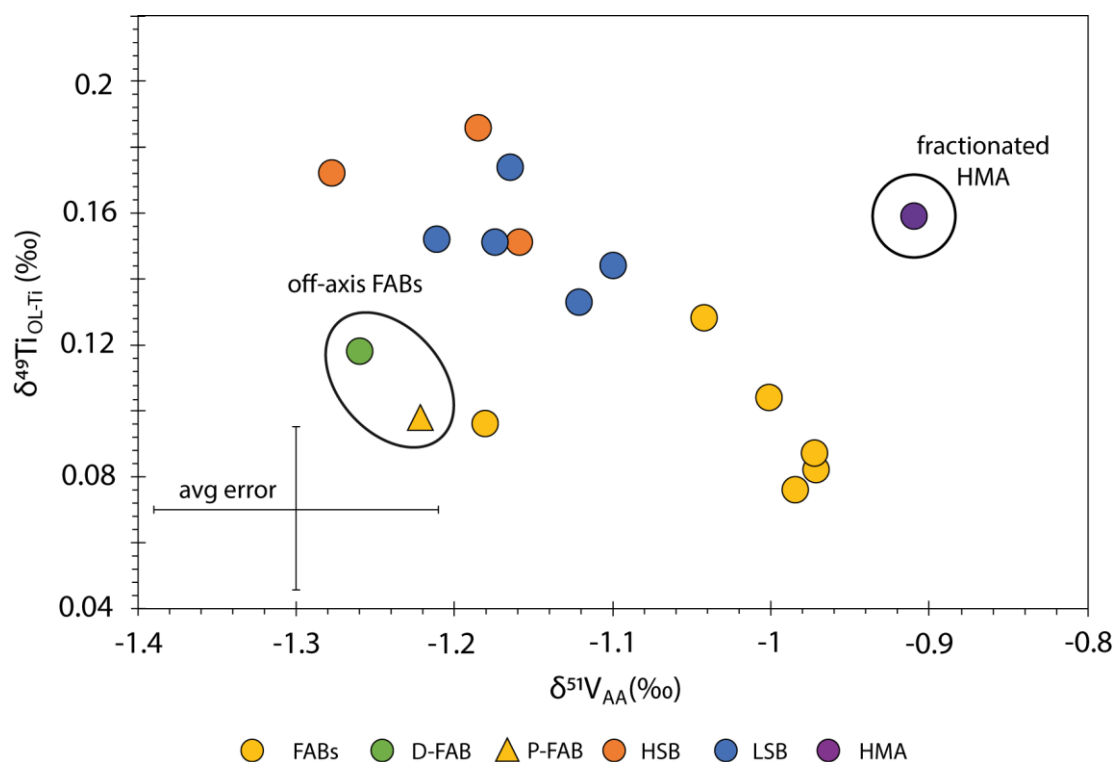


Figure 6.4: $\delta^{51}\text{V}_{\text{AA}}$ (‰) vs $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ (‰) for IODP FABs and boninites. The horizontal and vertical error bars are the average 2SD (± 0.09 ‰) and 95% c.i. (± 0.025 ‰) respectively for all samples.

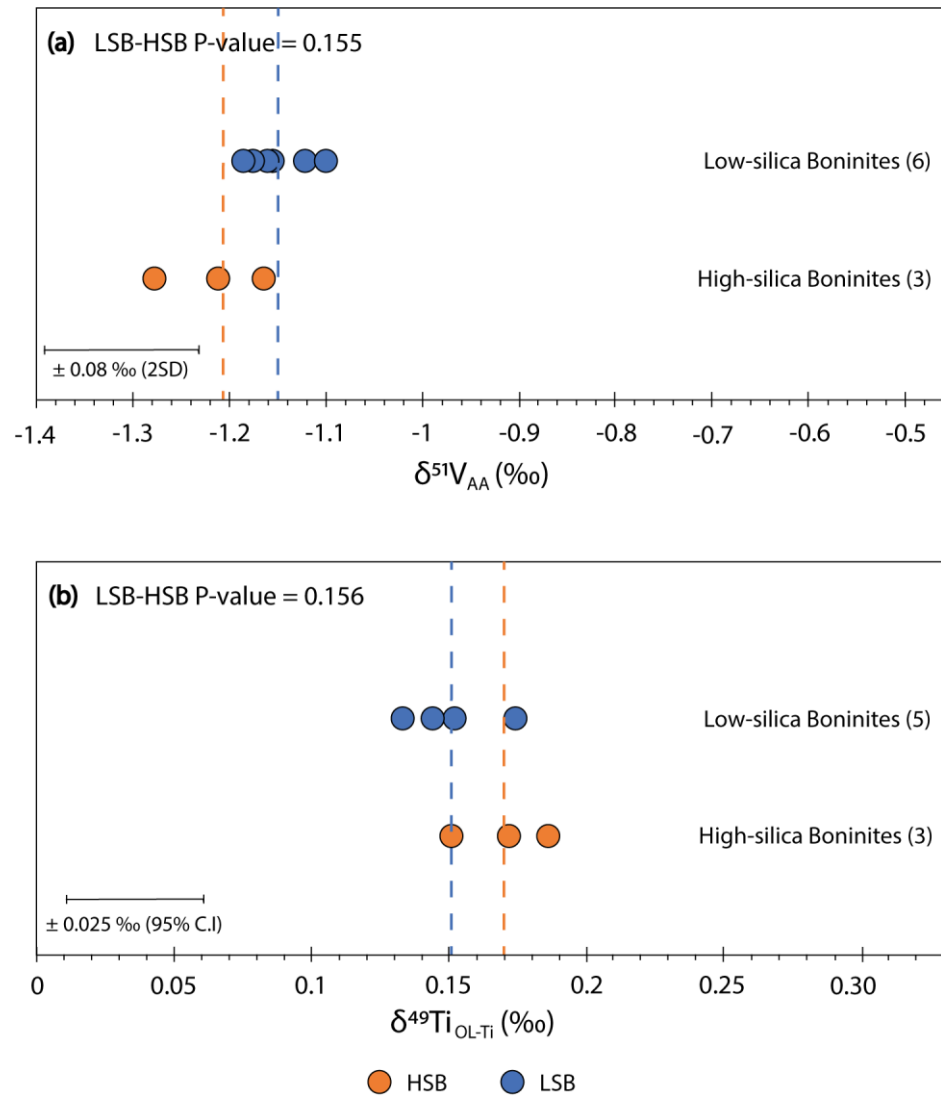


Figure 6.5: Comparison and student *T*-test results of **(a)** IODP Expedition 352 high-silica boninite (HSB) and low-silica boninite (LSB) $\delta^{49}\text{Ti}$; **(b)** high-silica boninite (HSB) and low-silica boninite (LSB) $\delta^{51}\text{V}$. All data is from this study. The vertical dashed lines represent the averages for each population that were compared in the student *T*-tests, and are colour coded to match the data point colours. The LSB $\delta^{49}\text{Ti}$ average = 0.151 ± 0.030 ‰ (2SD), the HSB $\delta^{49}\text{Ti}$ average = 0.170 ± 0.035 ‰ (2SD), the LSB $\delta^{51}\text{V}$ average = -1.15 ± 0.08 ‰ (2SD), the HSB $\delta^{51}\text{V}$ average = -1.21 ± 0.12 ‰ (2SD). The average error on each data point is ± 0.025 ‰ (95% c.i.) for the $\delta^{49}\text{Ti}$ data, and ± 0.09 ‰ (2SD) for the $\delta^{51}\text{V}$ data. The *p*-values represent the *p*-values from student *T*-tests. A *p*-value of less than 0.05 dictates that there is enough evidence for the population means to be distinguished at a 95% confidence interval.

6.4. Discussion

In contrast to Fe and Zn isotopes, FAB and MORB are statistically offset in terms of their Ti and V isotopic compositions. Furthermore, both Ti and V isotopes show greater variability in boninites that may reflect subduction zone inputs and/or changing intensive parameters. Below, the effects of secondary alteration, the causes of the observed FAB-MORB isotopic differences, the causes of

the FAB-boninite isotopic differences, and the implications of this work for using V and Ti isotopes in arc studies will be discussed.

6.4.1. Effects of secondary alteration

As discussed in previous chapters, the POOL sampling approach from Expedition 352 was designed to select the least altered samples for chemical characterisation. As discussed in Chapters four and five, there is no strong evidence that Fe or Zn isotopic compositions of FABs and boninites have been impacted by secondary alteration. However, it is worth re-visiting the argument, since, unlike Fe and Zn, there are clear differences between MORB and FAB Ti-V isotopic compositions. Whole-rock FABs have elevated and scattered K₂O concentrations compared to FAB glasses (Coulthard *et al.* 2021). Additionally, FMEs such as K, Rb, Ba, U, and Pb are found in higher concentrations in whole-rock analyses than predicted by Shervais *et al.* (2019) trace element models, and their concentrations vary between samples, and irregularly between elements. Thus whole-rock FABs are considered to have experienced some degree of secondary seafloor alteration.

Seafloor alteration has the potential to mobilise elements and fractionate isotopes. Leaching and fractionation of Fe isotopes from oceanic basalts in response to seafloor alteration is well documented (e.g. Sharma *et al.* 2001; Beard *et al.* 2003; Rouxel *et al.* 2003, 2008; Severmann *et al.* 2004; Bennett *et al.* 2009). However, Chapter four found no convincing evidence that Fe isotopes were affected by seafloor alteration in the FAB and boninite samples studied. In contrast to Fe, V and Ti are less prone to fluid mobilisation at low temperatures. Indeed, the effect of low-temperature (i.e. < 400 °C) seafloor alteration of mafic crust on the fractionation of V isotopes was specifically investigated via a suite of progressively altered oceanic crust. The isotopic composition of the variably altered MORB was identical to fresh MORB glass, presenting a strong argument against fractionation of V isotopes via seafloor and low temperature hydrothermal alteration (Prytulak *et al.* 2013; Wu *et al.* 2018). Unfortunately, a similar systematic study on the effects of seafloor and low temperature hydrothermal alteration has not yet been undertaken for Ti isotopes. However, since Ti has a very low solubility in low-temperature aqueous fluids, it is expected to be insusceptible to low-temperature seafloor alteration (Greber *et al.* 2017; Teng *et al.* 2017). Given the lack of evidence for secondary alteration affecting Fe and Zn isotopes, and previous work demonstrating that V is unlikely to be susceptible to secondary alteration, it is highly unlikely that Ti or V isotopes have been affected to a great enough degree to explain the FAB and MORB offset.

6.4.2. Cause(s) of FAB-MORB isotopic differences

The isotopic offsets between FAB and MORB in terms of Ti and V isotopes contrast with the lack of offsets between FAB and MORB in Fe and Zn isotopes. Therefore, because secondary alteration has been ruled out, Ti and V must be responding to a fundamentally different process or processes compared to Fe and Zn in this sample suite. Below the potential effects of the addition of slab-derived fluids and melts, differences in redox between FAB and MORB, fractional crystallisation, and source depletion are explored.

6.4.2.1. *Contribution of Slab-derived Fluids?*

The overwhelming consensus is that FABs are anhydrous (e.g. Reagan *et al.* 2017; Li *et al.* 2019; Shervais *et al.* 2019). However, the analysis of halogens, S, and, H and O isotopes in pristine FAB glasses has been used to suggest that FAB melting may have been accompanied by minor involvement of dilute slab-derived aqueous fluids (Coulthard *et al.* 2021). Previous work has shown that both Fe and Zn can be mobilised and isotopically fractionated by sulphate, carbonate, and halogen-rich slab-derived fluids (e.g. Debret *et al.* 2016, 2018, 2020, 2021; Pons *et al.* 2016; Debret & Sverjensky 2017; Turner *et al.* 2018). However, Chapters four and five found no evidence of slab-derived fluid fractionation of Fe and Zn isotopes in the FABs. Since V and Ti are less fluid mobile than Fe and Zn, minor subduction-derived aqueous fluids are unlikely to be responsible for the observed FAB-MORB $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ differences.

The dominant host of Ti in subducted slab material should be rutile, but the solubility of Ti in H_2O -rich fluids is very low, varying between 280 ppm at 0.5 GPa and 800 °C to 470 ppm at 0.5 GPa and 1000 °C (Rapp *et al.* 2010). However, halogen-rich fluids have been shown to mobilise Ti more readily. Titanium solubilities in Cl-rich brines at 0.5 GPa and 800-1000°C are between 631 ppm and 1753 ppm, 2 to 4 times greater than in H_2O -fluids, and up to 2965 ppm to 45,739 ppm, 10-100 times more in F-rich brines. The speciation of Ti in halogen brines is not certain, but Ti bonding should be different in halogen brines to rutile, thus causing isotopic fractionation (Millet *et al.* 2016). There is no previous work on the solubility, complexation, or fractionation of V in halogen-rich fluids. However, since V and Ti behave similarly in igneous processes, V may also be soluble in Cl-rich fluids. The involvement of aqueous fluids as suggested in Coulthard *et al.* (2021) is unlikely to explain the FAB-MORB $\delta^{49}\text{Ti}$ and $\delta^{51}\text{V}$ differences. However, if the fluids were halogen-rich and preferentially mobilised heavy Ti and light V, fluid involvement has the potential to create the observed $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ fractionation directions.

If FABs interacted with Cl-rich fluids that fractionated Ti and V isotopes, Cl and H₂O concentrations should be elevated in FABs relative to MORB, and FAB $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ may correlate with FAB Cl concentrations. **Figures 5.14 & 6.6** **Error! Reference source not found.** show that FABs are not enriched in Cl or H₂O relative to MORB. Unfortunately the only Cl and H₂O FAB data is from FAB glasses (Coulthard *et al.* 2021) and therefore there is no direct sample overlap with the FABs measured in this study. However, since neither Cl or H₂O are elevated in FABs relative to MORB, and there are no $\delta^{51}\text{V}$ or $\delta^{49}\text{Ti}$ correlations with fluid mobile elements in the FABs (**Figure 6.7**) we suggest that the interaction of FABs with subduction-derived halogen-rich fluids is an unlikely mechanism to explain the observed $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ FAB-MORB differences. In addition, Chapters four and five showed that even the complexation of more fluid mobile Fe and Zn with subduction-derived fluids is not sufficient to create observable isotopic differences between MORB, FABs, and boninites. It would therefore be unexpected for a similar mechanism to create very observable differences in fluid immobile isotope systems.

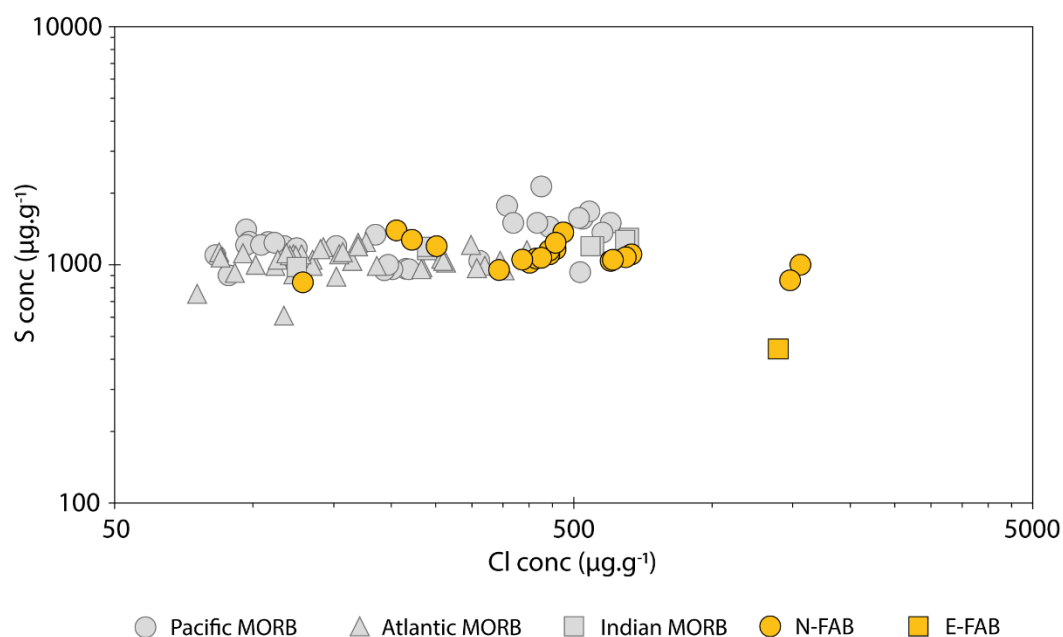


Figure 6.6: Chlorine versus sulphur concentrations in $\mu\text{g.g}^{-1}$ for IODP Expedition 352 FAB glasses (Coulthard *et al.* 2021) and an array of MORB glasses of Pacific, Atlantic and Indian provenance from Jenner & O'Neill (2012); Kendrick *et al.* (2017); Shimizu *et al.* (2019). Figure adapted from Coulthard *et al.* (2021).

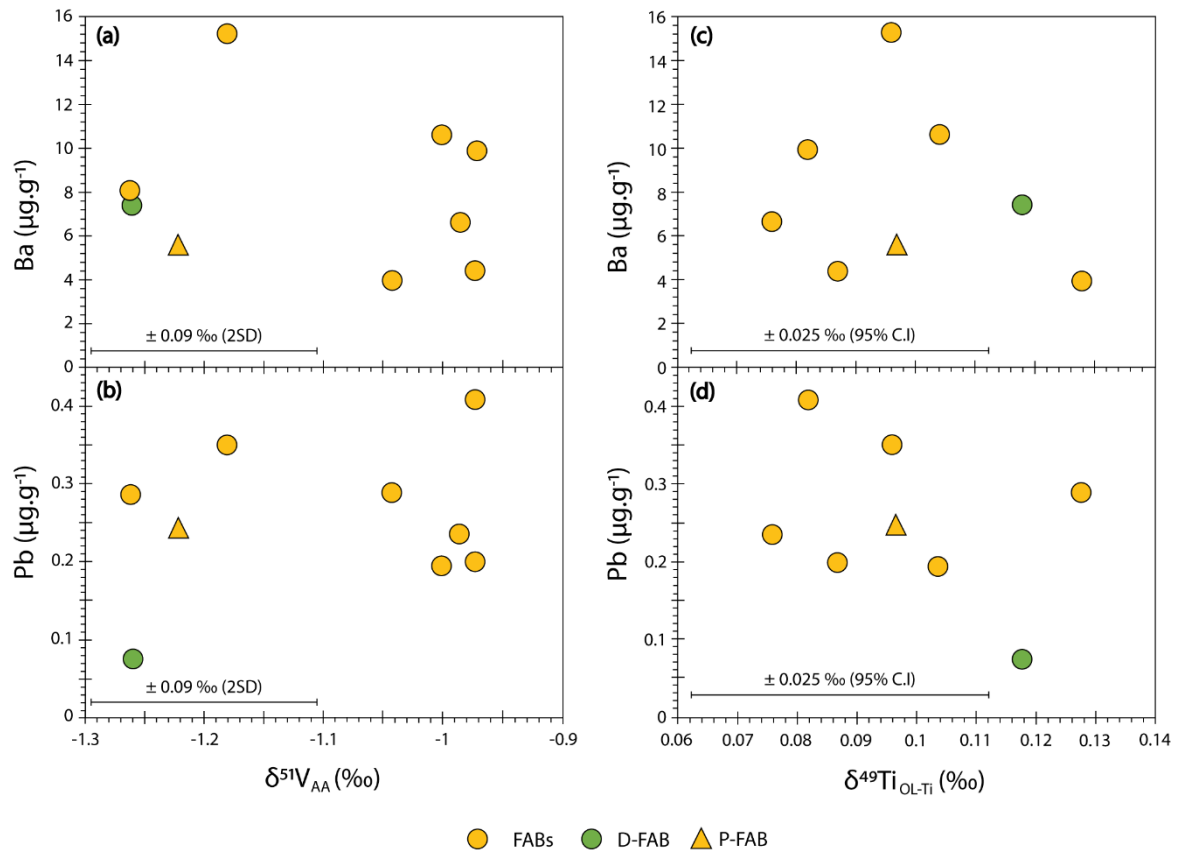


Figure 6.7: IODP Expedition 352 FAB $\delta^{51}\text{V}_{\text{AA}}$ and $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ versus FME concentrations. **(a)** $\delta^{51}\text{V}_{\text{AA}}$ (‰) versus Ba ($\mu\text{g.g}^{-1}$); **(b)** $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ (‰) versus Ba ($\mu\text{g.g}^{-1}$); **(c)** $\delta^{51}\text{V}_{\text{AA}}$ (‰) versus Pb ($\mu\text{g.g}^{-1}$); **(d)** $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ (‰) versus Pb ($\mu\text{g.g}^{-1}$). The average horizontal error in panels a and c is ± 0.09 ‰ (2SD), and in panels b and d ± 0.025 ‰ (95% c.i.).

6.4.2.2. Contribution of Slab-derived Melts?

Previous Expedition 352 work has found no geochemical evidence of the involvement of subducted slab melts in FAB formation (Li *et al.* 2019; Shervais *et al.* 2019). Since there are no covariations between FAB $\delta^{51}\text{V}$ or $\delta^{49}\text{Ti}$ and geochemical indicators of slab melts such as Sm/Hf (**Figure 6.8**) we suggest that slab melts are unlikely to explain the $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ differences between FABs and MORB.

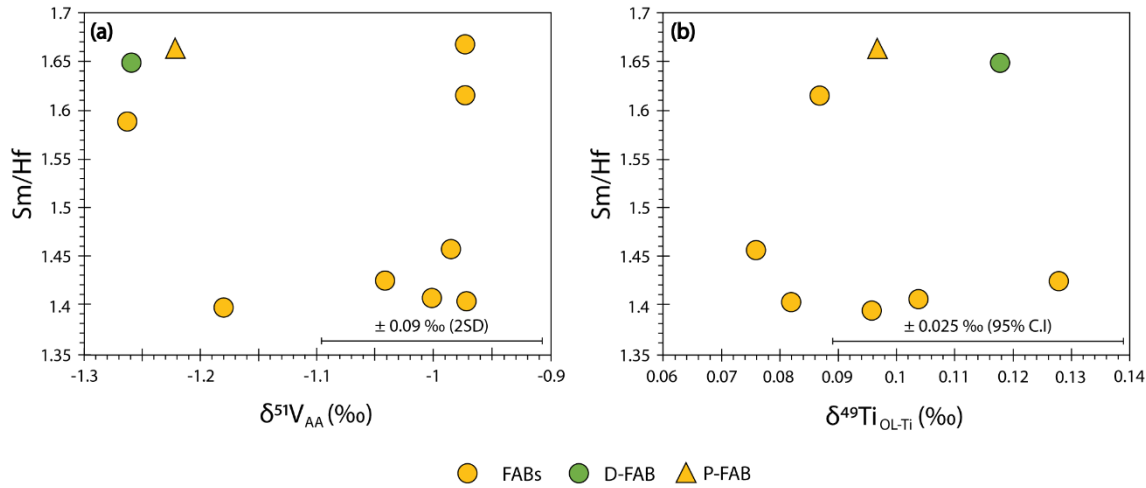


Figure 6.8: IODP Expedition 352 FAB $\delta^{51}\text{V}_{\text{AA}}$ and $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ versus Sm/Hf.

6.4.2.3. Different Redox Conditions?

Both V and Ti isotopes may respond to changes in redox conditions (e.g. Canil 1997; Prytulak *et al.* 2013, 2017; Millet *et al.* 2016; Sossi *et al.* 2018; Hoare *et al.* 2020; Novella *et al.* 2020). However, $\text{Fe}^{3+}/\Sigma\text{Fe}$ of FAB and MORB glasses by XANES show that FAB and MORB formed under similar redox conditions. MORB $\text{Fe}^{3+}/\Sigma\text{Fe}$ has been measured at between 0.143 and 0.160 ± 0.01 (1σ) on average (Cottrell & Kelley 2011; Zhang *et al.* 2018). IODP Expedition FAB glasses have $\text{Fe}^{3+}/\Sigma\text{Fe}$ between 0.136 and 0.177 (Brounce *et al.* 2019). Therefore, since FAB and MORB have similar $\text{Fe}^{3+}/\Sigma\text{Fe}$, it is unlikely that different redox conditions can account for the observed $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ FAB-MORB differences.

6.4.2.4. Fractional Crystallisation

Fractional crystallisation of oxide phases can cause significant Ti and V isotope fractionation. With progressive differentiation melts become isotopically heavier in both $\delta^{49}\text{Ti}$ (e.g. Millet *et al.* 2016; Deng *et al.* 2019; Aarons *et al.* 2020; Hoare *et al.* 2020) and $\delta^{51}\text{V}$ (e.g. Prytulak *et al.* 2017; Sossi *et al.* 2018; Wu *et al.* 2018; Ding *et al.* 2020). However, despite the FABs having experienced between 3 and 38 % fractional crystallisation, the most successful models do not involve the crystallisation of oxide phases (olivine (1%); 30% olivine + 70% plagioclase (4-5%); and 7% olivine + 41% plagioclase + 52% augite (17-20%) (Shervais *et al.* 2019)). Also, the $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ FAB-MORB offsets are in opposite directions, with FABs isotopically heavier in Ti and lighter in V. Therefore, fractional crystallisation would only be able to explain one of these isotope systems, depending on which lithology is more evolved. Since both isotope systems strongly respond to oxide crystallisation, it would be highly unlikely for only one system to respond. We therefore conclude that the fractional

crystallisation of oxide phases is unlikely to account for the observed $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ FAB-MORB differences.

6.4.2.5. Mantle Partial Melting and Source Depletion

Trace element and radiogenic isotope systematics suggest that FAB have more depleted sources than MORB (Li *et al.* 2019; Shervais *et al.* 2019). Previous V isotope work has suggested that since harzburgites are isotopically lighter than MORB (Prytulak *et al.* 2013; Wu *et al.* 2018), partial melting creates isotopically light residues and heavy melts (Wu *et al.* 2018). Therefore, previous melt extraction from the FAB source could explain a lighter FAB $\delta^{51}\text{V}$ compared to MORB.

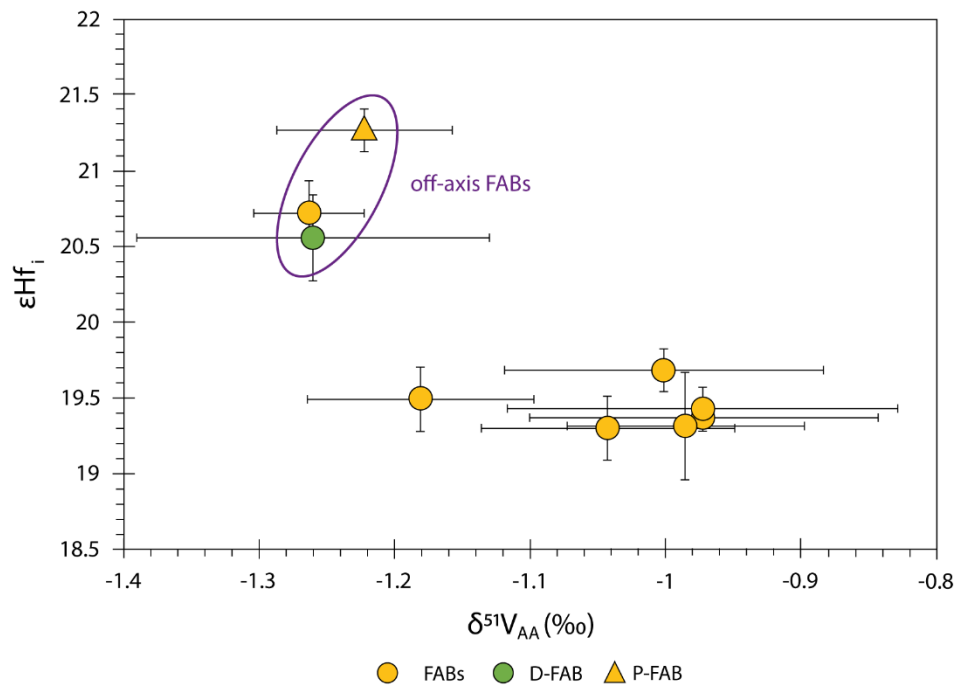


Figure 6.9: IODP Expedition 352 fore-arc basalt $\delta^{51}\text{V}_{\text{AA}}$ (‰) versus ϵHf_i . The x-axis error bars represent 2SD of at least three repeat $\delta^{51}\text{V}$ measurements for each sample. The y-axis error bars represent $\epsilon 2\text{SE}$.

One of the key observations of the FAB $\delta^{51}\text{V}$ dataset is that there appears to be two subgroups based on $\delta^{51}\text{V}$ differences (**Figure 6.2a**). Oxide phases such as magnetite are inferred to be isotopically light (e.g. Prytulak *et al.* 2017; Sossi *et al.* 2018; Ding *et al.* 2020) and have a high V partition coefficient, therefore a greater abundance of magnetite in the lightest FABs may explain the $\delta^{51}\text{V}$ groups. However, the isotopically lightest FABs do not have the highest oxide abundances (0 – 3 % oxides in the light FABs versus 0 – 5 % oxides in all FABs (Chapter four)), suggesting that a different process must be responsible for the $\delta^{51}\text{V}$ FAB groups. The isotopically lighter FAB group comprises three off-axis FABs and one axial FAB, whereas the heavier FABs are all axial FABs (**Figure 6.9**). Off-axis FAB have less radiogenic ϵHf_i . Thus the transition from axial to off-axis FAB is interpreted as a change to a more depleted FAB source (Li *et al.* 2019; Shervais *et al.* 2019). The

more depleted FABs in terms of radiogenic isotopes therefore have lighter $\delta^{51}\text{V}$, which reinforces the idea that source depletion fractionates V isotopes, and may be responsible for the $\delta^{51}\text{V}$ FAB-MORB offset. However, FAB $\delta^{51}\text{V}$ does not correlate with common source depletion indicators such as Cr# and $\text{Al}_2\text{O}_3/\text{SiO}_2$ (**Figure 6.10**). The lack of correlations could be due to additional processes masking such correlations, or the small population sizes. We therefore interpret the FAB-MORB $\delta^{51}\text{V}$ difference and the $\delta^{51}\text{V}$ separation between axial and off-axis FABs as being related to varying degrees of source depletion.

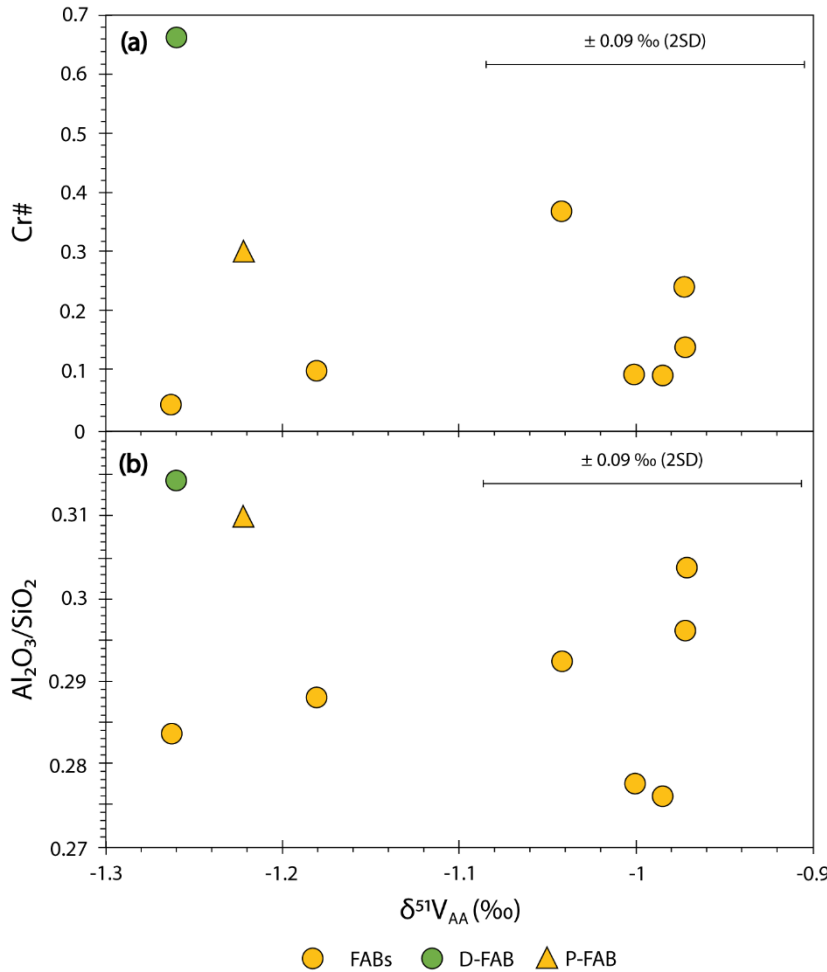


Figure 6.10: Expedition 352 FAB $\delta^{51}\text{V}_{\text{AA}}$ (‰) versus source depletion indicators **(a)** Cr# and **(b)** $\text{Al}_2\text{O}_3/\text{SiO}_2$. The average horizontal error is ± 0.09 ‰ (2SD) based on at least 3 repeat measurements of each sample.

In contrast to V isotopes, Ti isotopes show no significant fractionation between mantle peridotites and MORB (Millet *et al.* 2016; Deng *et al.* 2018), which suggests minimal $\delta^{49}\text{Ti}$ fractionation during mantle partial melting. This is consistent with mass balance considerations that suggest only melting under Ti-oxide saturation should cause melt-source $\delta^{49}\text{Ti}$ fractionation (Millet *et al.* 2016). FAB source depletion is thought to be a garnet facies melting event (Shervais *et al.* 2019), therefore it is unlikely that melting occurred under Ti-oxide saturation. Also, since V and Ti have similar

chemical properties and typically have similar coordination in mantle minerals, any partial melting induced Ti isotope fractionation would be expected to be in the same direction as V isotope fractionation. However, the FAB-MORB $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ differences are in opposite directions. Thus, source depletion is considered unlikely to account for the observed FAB-MORB $\delta^{49}\text{Ti}$ difference.

6.4.2.6. *Titanium Isotopic Mantle Heterogeneity*

After excluding other potential mechanisms for creating FABs that have isotopically heavier $\delta^{49}\text{Ti}$ than MORB, a remaining possibility is that the mantle $\delta^{49}\text{Ti}$ is heterogeneous. Expedition 352 FABs have Indian provenance (e.g. Dupre & Allegre 1983; Hart 1984). If Indian MORB is isotopically heavier than other types of MORB, it could support a source heterogeneity explanation. However, at present there are only four Indian N-MORB $\delta^{49}\text{Ti}$ measurements and one Indian E-MORB measurement in the published literature. The Indian N-MORB (average $\delta^{49}\text{Ti} = 0.004 \pm 0.020$ ‰, 2SD, $n = 4$ (Millet *et al.* 2016; Deng *et al.* 2018; Zhao *et al.* 2020)) is within error of the overall MORB average ($\delta^{49}\text{Ti} = 0.009 \pm 0.050$ ‰, 2SD, $n = 30$ (Millet *et al.* 2016; Deng *et al.* 2018; Hoare *et al.* 2020; Zhao *et al.* 2020)). However the E-MORB is isotopically heavier ($\delta^{49}\text{Ti} = 0.046 \pm 0.016$ ‰ 2SE (Deng *et al.* 2018)). Deng *et al.* (2018) attributed E-MORB's heavier $\delta^{49}\text{Ti}$ to a less depleted mantle source than N-MORB due to less crustal residue recycling. The limited Indian MORB data therefore hints at mantle heterogeneity, but more data is needed.

Another way to potentially test for source heterogeneity is to measure $\delta^{49}\text{Ti}$ in the ODP Leg 125 harzburgites and dunites. Parkinson *et al.* (1998) found that the ODP Leg 125 rocks have unusually unradiogenic Re/Os, and suggested the presence of delaminated subcontinental lithospheric mantle (SCLM) in the mantle wedge. However, the harzburgites and dunites were not measured since they are extremely depleted in Ti, and consequently exceptionally large sample masses are required to produce one Ti isotope measurement. Titanium isotope measurements of other subcontinental lithospheric rocks which are less depleted could be useful, but these would not represent a direct comparison with the Expedition 352 FABs and boninites.

Millet *et al.* (2016) suggested that the mantle is homogenous for $\delta^{49}\text{Ti}$ because MORB (0.001 ± 0.008 ‰, 95% c.i., $n = 7$), primitive arc lavas (0.007 ± 0.010 ‰, 95% c.i., $n = 8$), and primitive OIB (0.009 ± 0.019 ‰, 95% c.i., $n = 7$) are statistically indistinct. However, due to the infancy of Ti isotope analysis for high-temperature geologic systems means there is very limited Ti isotope data available. Therefore, Ti isotope mantle heterogeneity cannot be evaluated as well as mantle heterogeneity for more established isotope systems. Comparing $\delta^{49}\text{Ti}$ from different mantle settings such as abyssal peridotites that represent the depleted residues after MORB extraction, OIBs, and MORB can tell us about mantle heterogeneity. However, there is currently no abyssal peridotite $\delta^{49}\text{Ti}$ data

available, very limited primitive OIB data, and only 30 MORB samples from a limited range of spreading ridges. An unpublished PhD thesis (Kommischer 2020) contains $\delta^{49}\text{Ti}$ measurements that hint at a more complicated story than an isotopically homogenous mantle. They measured MORB-like basalts from the upper pillow lava sequence of the Troodos ophiolite on Cyprus. The Troodos ophiolite has been proposed to form above a subduction zone, and some have suggested that the upper pillow lavas maybe analogous to FAB. The Upper pillow lavas are isotopically heavier than MORB, and overlap more closely with the FAB data (**Figure 6.11**). These samples suggest that the mantle may have more variable $\delta^{49}\text{Ti}$ than previously thought.

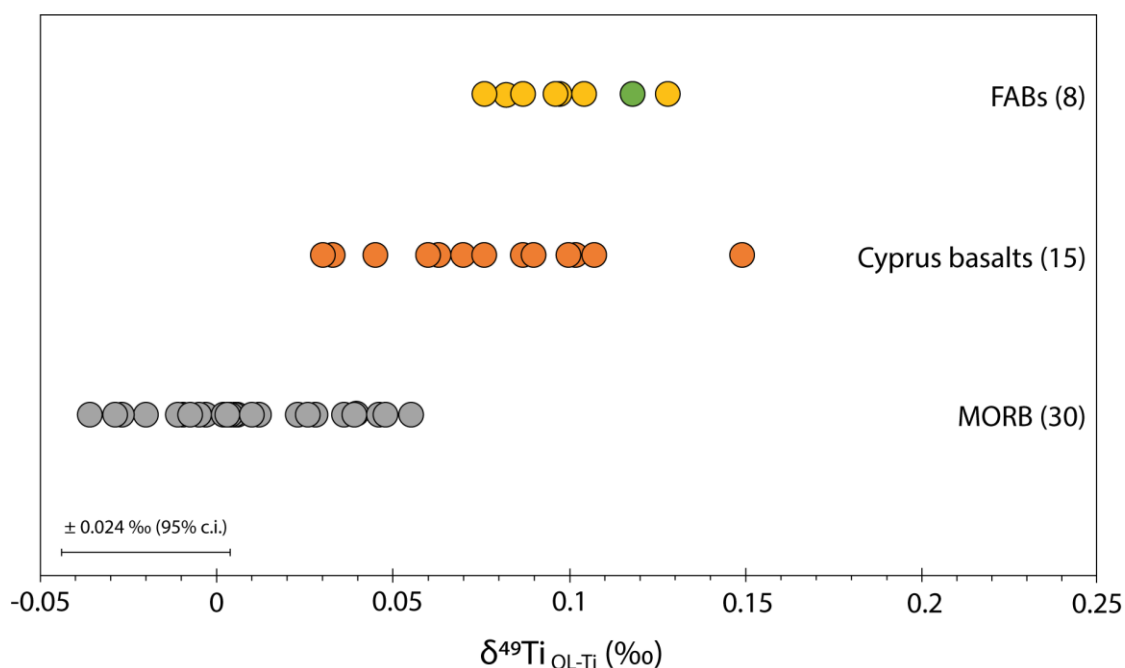


Figure 6.11: Comparison of MORB, FAB, and Cyprus basalt $\delta^{49}\text{Ti}$. MORB data is from Millet *et al.* (2016); Deng *et al.* (2018); Hoare *et al.* (2020); Zhao *et al.* (2020), the FAB data is from this study, and the MORB-like Cyprus basalt data is from Kommischer (2020). The average horizontal error is ± 0.024 ‰ (95% c.i.).

6.4.2.7. Current Explanations for FAB-MORB $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ differences

The above discussion highlights that none of the known mechanisms is likely to create V and Ti isotope fractionation in opposing directions as observed in the FAB-MORB isotopic offsets. There is the potential that complexation of Ti and V with Cl in fluids may fractionate V and Ti in opposite directions, but there is currently no supporting evidence, and there is very limited information on the coordination of V and Ti in Cl complexes. In addition, the lack of elevated Cl or H_2O concentrations in the FABs suggests that, despite the suggestion of Coulthard *et al.* (2021), FABs formed via anhydrous melting. Therefore, the processes that created the $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ FAB-MORB differences are likely different. This suggests that V and Ti isotopes are tracking different processes in the FAB dataset. The mechanism most likely to create the observed $\delta^{51}\text{V}$ FAB-MORB difference

is differing degrees of source depletion. Given the lack of evidence for any of the proposed $\delta^{49}\text{Ti}$ fractionation mechanisms, we suggest that the FAB-MORB $\delta^{49}\text{Ti}$ difference is related to $\delta^{49}\text{Ti}$ mantle heterogeneity, and that the FAB source was isotopically heavier than MORB sources.

6.4.3. Comparison of FAB-Boninite Ti- V isotopes

Figure 6.3 shows that FABs and boninites are isotopically distinct in $\delta^{49}\text{Ti}$ but not in $\delta^{51}\text{V}$. The V and Ti isotope data therefore suggest that the mechanism(s) responsible for the $\delta^{49}\text{Ti}$ difference are either: (1) decoupled from V isotope fractionation; or (2) the V and Ti isotope fractionation mechanisms are both of observable magnitudes in the same direction, but an additional $\delta^{51}\text{V}$ or $\delta^{49}\text{Ti}$ fractionation process occurred. The potential effects of source depletion, fractional crystallisation, and the addition of slab derived fluids, melts, and sediments on the V and Ti isotopic compositions of the boninites are discussed below.

6.4.3.1. *Source Depletion and Partial Melting*

The Expedition 352 boninites are suggested to have formed from the residue left behind after FAB extraction (Li *et al.* 2019; Shervais *et al.* 2021), therefore boninites should have a more depleted source than FABs. In Chapter four, source depletion was suggested to cause light $\delta^{56}\text{Fe}$ in arc lavas compared to MORB, and above, source depletion is suggested to create light $\delta^{51}\text{V}$ in FABs compared to MORB. Therefore, greater boninite source depletion should result in boninites having even lighter $\delta^{51}\text{V}$ than FAB. This is not observed (**Figure 6.3a**). Additionally, there is no previous Ti isotope work that has found convincing evidence for a significant Ti isotope fractionation in response to mantle partial melting (e.g. Millet *et al.* 2016; Deng *et al.* 2018). Therefore, the greater inferred source depletion of the boninites compared to the FABs is considered unlikely to explain the FAB-boninite $\delta^{49}\text{Ti}$ difference, and an additional $\delta^{51}\text{V}$ fractionation mechanism is needed to counteract $\delta^{51}\text{V}$ source depletion effects in the boninites.

6.4.3.2. *Fractional Crystallisation*

It is thought that Fe-Ti oxides are the major control on high-temperature igneous $\delta^{49}\text{Ti}$ fractionation. Positive correlations between $\delta^{49}\text{Ti}$ and SiO_2 and MgO (e.g. Millet *et al.* 2016; Deng *et al.* 2019; Aarons *et al.* 2020; Hoare *et al.* 2020) suggest that the crystallisation of light Fe-Ti oxides drives the remaining melt to increasingly heavier $\delta^{49}\text{Ti}$ during differentiation. This is because light Ti preferentially enters the VI-site in Fe-Ti oxides over the lower coordination sites of silicate melts (Millet *et al.* 2016). Such fractionation trends have been used to distinguish between tholeiitic and calc-alkaline suites because of their different oxide crystallisation timings (Hoare *et al.* 2020). The crystallisation of oxides is also suggested to fractionate V isotopes, likewise resulting in isotopically

heavier $\delta^{51}\text{V}$ in more differentiated magmas (e.g. Prytulak *et al.* 2017; Sossi *et al.* 2018; Wu *et al.* 2018; Ding *et al.* 2020). For example, high magnesium andesites are considered to be the fractionation products of LSBs, HSBs, and BBs (e.g. Shervais *et al.* 2021). The $\delta^{51}\text{V}$ of the HMA is distinctly heavier than all other boninite samples (**Figure 6.12**). It should be remembered that the FABs and boninites are not part of a cogenetic fractional crystallisation sequence, so it is not possible to interpret FAB-boninite isotopic differences as directly related to fractional crystallisation. Although, if the boninites experienced a different degree and/or timing of oxide crystallisation compared to FAB, with all else being equal, such a process could result in isotopically distinct FABs and boninites.

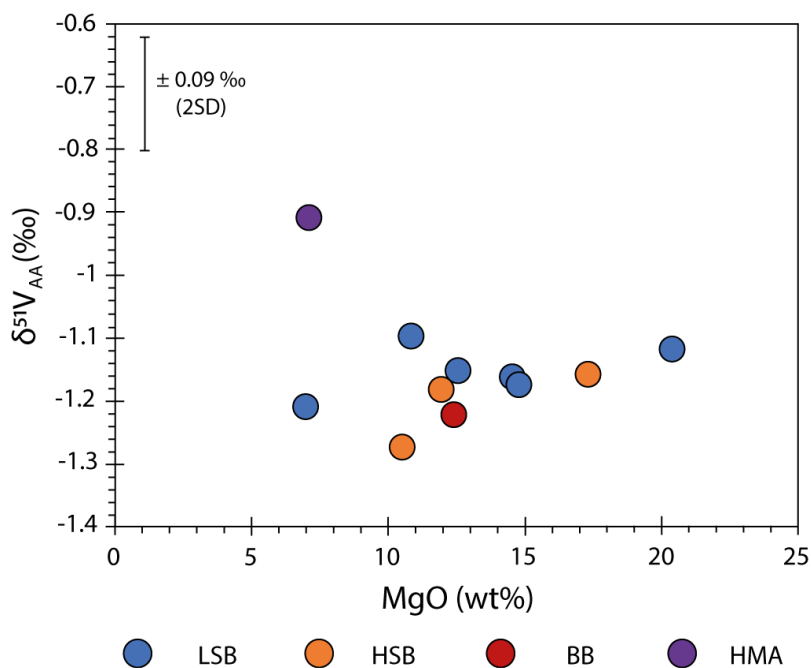


Figure 6.12: MgO (wt%) versus $\delta^{51}\text{V}_{\text{AA}}$ (‰) for IODP Expedition 352 boninites and high-magnesian andesite. The average vertical error is ± 0.09 ‰ based on the average 2SD of at least three repeat measurements for each sample.

The FABs are thought to have experienced between 3 % and 38 % fractional crystallisation (Shervais *et al.* 2019). In contrast, the boninites experienced minimal fractional crystallisation. Shervais *et al.* (2021) deemed that only boninites with less than 12 wt% MgO underwent net fractional crystallisation, and any with MgO greater than 12 wt% underwent net olivine accumulation. Only the high magnesium andesite and three of the ten boninites have MgO concentrations less than 12 wt%. Therefore, the extent of differentiation is distinct between FABs and boninites. However, since the boninites have heavier $\delta^{49}\text{Ti}$ than FABs, and differentiation creates progressively isotopically heavier melts (e.g. Millet *et al.* 2016; Deng *et al.* 2019; Aarons *et al.* 2020; Hoare *et al.* 2020), the FAB-boninite $\delta^{49}\text{Ti}$ difference is not in the direction expected for a fractional crystallisation process.

Furthermore, $\delta^{49}\text{Ti}$ fractionation is dependent on the crystallisation of oxide phases, and **Figure 6.13** highlights that Ti contents continue to increase with decreasing MgO, suggesting that the boninites studied did not reach oxide saturation.

The majority of the boninites experienced olivine accumulation. However, since Ti is incompatible in olivine and previous Ti isotope work has found minimal $\delta^{49}\text{Ti}$ fractionation during olivine fractionation (e.g. Deng *et al.* 2018), the effects of olivine accumulation are unlikely to be responsible for the FAB-boninite $\delta^{49}\text{Ti}$ offset. There are no olivine-melt $\delta^{51}\text{V}$ fractionation factors, although given the incompatibility of V in olivine, it is unlikely that olivine accumulation causes significant $\delta^{51}\text{V}$ fractionation. It is therefore unlikely that either differences in the degree of fractional crystallisation or olivine accumulation can explain the observed $\delta^{49}\text{Ti}$ FAB-boninite difference or be the process that counteracted source depletion $\delta^{51}\text{V}$ effects in the boninites.

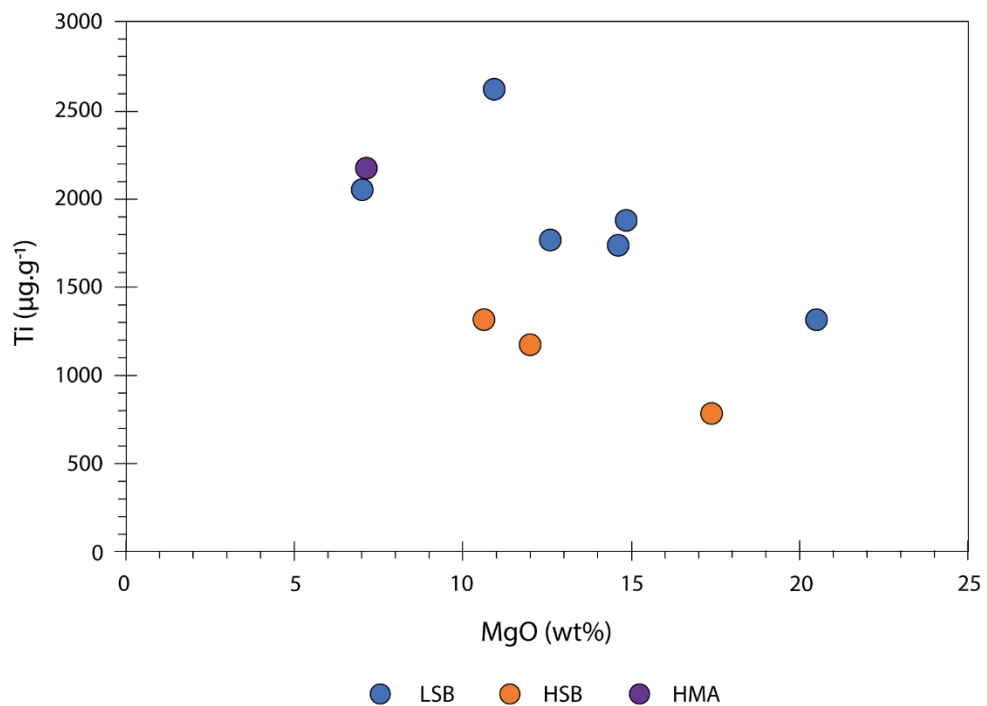


Figure 6.13: MgO (wt%) versus Ti concentration ($\mu\text{g.g}^{-1}$) for IODP Expedition 352 boninites. The data is from Goddard *et al.* (in prep).

6.4.3.3. Different Redox Conditions

Boninites are more oxidised than FABs ($\text{Fe}^{3+}/\Sigma\text{Fe} = 0.181 - 0.225$ and $0.136 - 0.177$ respectively (Brounce *et al.* 2021)). Vanadium and Ti isotopes both have the potential to fractionate in response to changes in redox conditions (Prytulak *et al.* 2013, 2017; Millet *et al.* 2016; Sossi *et al.* 2018; Hoare *et al.* 2020). Therefore, different redox conditions may be able to explain (1) the $\delta^{49}\text{Ti}$ FAB-boninite difference, (2) the covariation between boninite $\delta^{49}\text{Ti}$ and $\delta^{51}\text{V}$, and (3) partially or completely mask the effects of $\delta^{51}\text{V}$ fractionation during partial melting of an already depleted mantle source.

Previous V isotope studies (e.g. Prytulak *et al.* 2013, 2017; Sossi *et al.* 2018; Novella *et al.* 2020), Chapter three, and theoretical predictions suggest that greater fO_2 favours heavier $\delta^{51}V$. Whilst Ti does not have multiple terrestrial oxidation states, it has still been suggested to respond to changes in redox (e.g. Millet *et al.* 2016; Hoare *et al.* 2020). More oxidised calc-alkaline suites have higher $\delta^{49}Ti$ compared to more reduced tholeiitic lavas (Hoare *et al.* 2020), likely due to oxidised conditions favouring early saturation of titanomagnetite which preferentially incorporates light Ti isotopes compared to silicate melts due to its higher Ti coordination. Changes in redox therefore should cause V and Ti isotope fractionation in the same direction. The negative correlation between $\delta^{51}V$ and $\delta^{49}Ti$ (**Figure 6.4**) is therefore inconsistent with a straightforward relationship between FAB-boninite fO_2 differences and $\delta^{51}V$ and $\delta^{49}Ti$. Furthermore, the boninites experienced minimal fractional crystallisation and have not reached oxide saturation (**Figure 6.13**) suggesting that redox influenced oxide crystallisation can also not account for the observed $\delta^{49}Ti$ FAB-boninite differences. In contrast however, derivation of boninites from a more oxidised source may counteract $\delta^{51}V$ source depletion signatures. Unfortunately, there is no $Fe^{3+}/\Sigma Fe$ or fO_2 data for the exact samples measured in this study, so there is not yet a way to test the relationship between $\delta^{51}V$ and fO_2 .

6.4.3.4. Subduction-related Processes

Since there is little compelling evidence to suggest that the above processes can explain the $\delta^{49}Ti$ FAB-boninite offset, subduction-related processes such as the addition of slab-derived melts, fluids, and sediments must be explored. The isotopic similarity between low-silica boninites (LSBs) and high-silica boninites (HSBs) $\delta^{49}Ti$ (**Figure 6.5**) suggests an isotope fractionation mechanism common to both is responsible for the FAB-boninite $\delta^{49}Ti$ difference. There is geochemical evidence of both slab-derived melt and fluid components in LSBs and HSBs, however sediment inputs are restricted to HSBs (Li *et al.* 2019; Shervais *et al.* 2021). Therefore, since there is no difference between HSBs and LSBs, the addition of subducted sediments is not considered a candidate for creating the FAB-boninite $\delta^{49}Ti$ offset.

Chapters four and five found no evidence that slab-derived melts or fluids strongly influenced the $\delta^{56}Fe$ or $\delta^{66}Zn$ of the boninites. Since Ti is less fluid mobile than Fe and Zn, $\delta^{49}Ti$ is even less likely to be influenced by slab-derived fluids and/or melts. However, the boninite source is depleted in Ti compared to Fe and Zn, meaning, from a mass balance point of view, a smaller Ti flux is required to observably alter the Ti budget of the boninites. The average Ti concentration of the ODP Leg 125 harzburgites and dunites which are interpreted as the closest available samples to the residue after FAB and boninite extraction is $19.37 \mu g.g^{-1}$, compared to $62,293 \mu g.g^{-1}$ of Fe, and $37.30 \mu g.g^{-1}$ of Zn.

The addition of slab-derived melts and fluids therefore has the potential to explain the $\delta^{49}\text{Ti}$ difference between FABs and boninites, despite the low fluid mobility of Ti.

Titanium concentrations were modelled to determine the amount of Ti that can be contributed to the boninites by partial melting alone, and whether additional subduction-related sources are required. The model used batch melting equations from Shaw (1970), Ti partition coefficients from Kinzler (1997) and a DMM source from Workman & Hart (2005). **Figure 6.14** shows that a two-stage melt model that accounts for previous FAB melt extraction from a DMM source can account for the observed Ti budget of the Expedition 352 boninites. At FAB and boninite melt degrees (10 - 20 % FAB melt extraction and 10 - 15 % boninite melting (Shervais *et al.* 2019, 2021)), the modelled boninite melt Ti concentration is 1359 - 2269 $\mu\text{g.g}^{-1}$. This range encompasses the average boninite Ti concentration of 1687 $\mu\text{g.g}^{-1}$. However, since the FAB source is known to be more depleted than DMM (Li *et al.* 2019; Shervais *et al.* 2019), this range is likely an overestimate. Unfortunately, the Ti concentration of the FAB source or the degree of previous depletion is not known. A 10 % melt extraction from DMM creates a residue with a 43 % lower Ti concentration than DMM. If the FAB source was created by 10 % extraction from a DMM-like source, then the modelled boninite Ti concentrations no longer account for the full range of observed boninite Ti concentrations (**Figure 6.15**). The modelled boninite Ti concentrations range between 782 $\mu\text{g.g}^{-1}$ and 1657 $\mu\text{g.g}^{-1}$ (**Figure 6.15**). Only at lower melt degrees can the model reach the average boninite Ti concentration of 1687 $\mu\text{g.g}^{-1}$ (**Figure 6.15**). Assuming that the FAB source experienced at least 10 % melt extraction, it is possible that partial melting and source depletion alone may not fully account for the observed boninite Ti budgets. An additional Ti source such as subducted slab-derived fluids and/or melts may therefore be required.

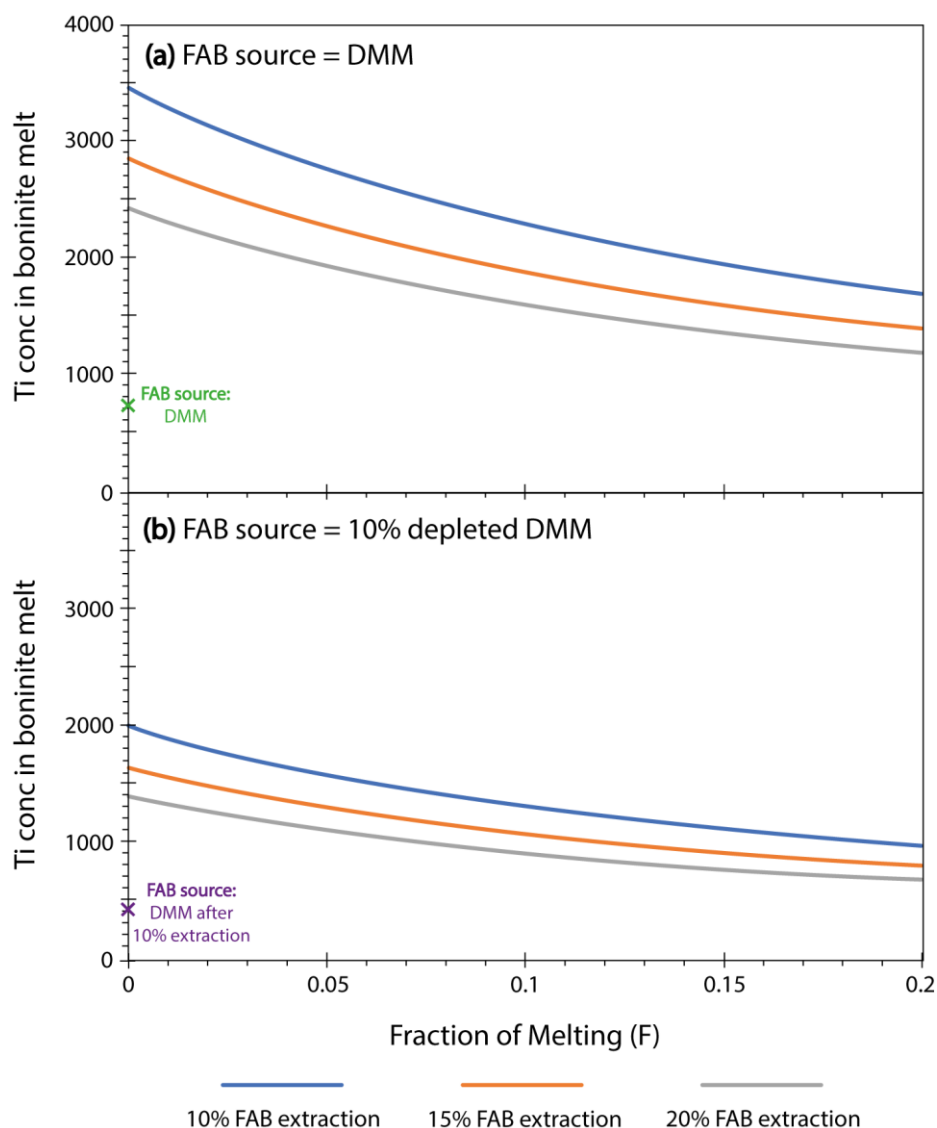


Figure 6.14: Titanium concentration melt modelling results. Models used batch melting equation from Shaw (1970), Ti partition coefficients from Kinzler (1997) and a DMM source from Workman & Hart (2005). Model (a) assumes a DMM source for FABs, 10-20% FAB melt extraction, and then 10-15% boninite melting. Model (b) assumes a more depleted FAB source. The source used had a Ti concentration equivalent to DMM after 10% melt extraction.

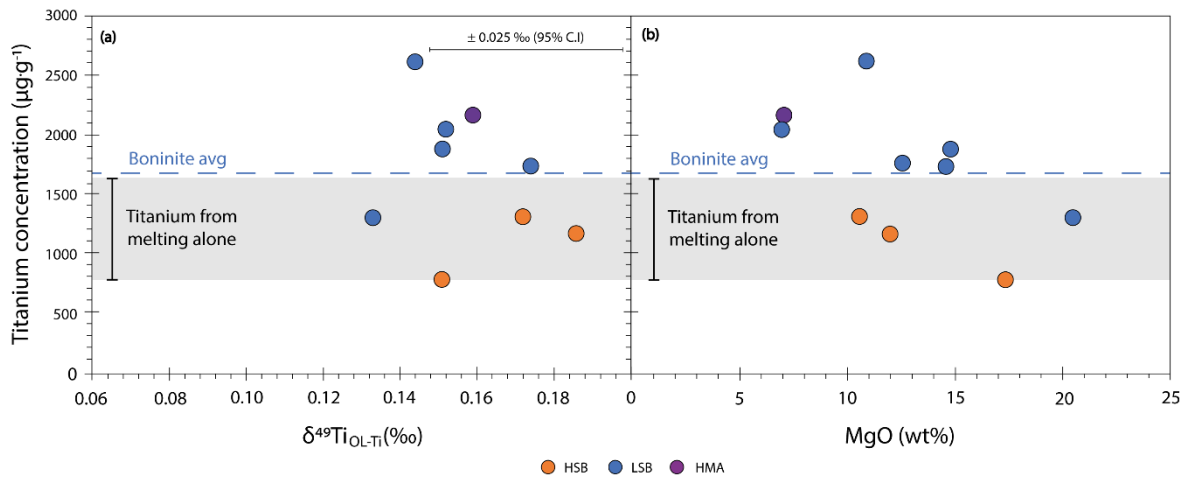


Figure 6.15: IODP Expedition 352 boninite Ti concentration ($\mu\text{g.g}^{-1}$) versus **(a)** $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ (‰) and **(b)** MgO (wt%). The grey horizontal bar represents the range in Ti concentration generated from Ti modelling in Fig. 6.15b assuming a DMM with a 10% historic source depletion event. The blue dashed horizontal line shows the average observed boninite Ti concentration.

Rutile (TiO_2) is a common slab accessory mineral that retains HFSEs during slab dehydration and melting (Ryerson & Watson 1987; Foley *et al.* 2000) and likely controls the Ti elemental budget of slab fluids and melts. Titanium is traditionally considered immobile, however, its mobility in subduction zones is debated. Experimental studies have shown that rutile has a low solubility in pure- H_2O fluids (Audetat & Keppler 2005; Rapp *et al.* 2010) and Ti, Nb and Ta have high rutile-aqueous fluid partition coefficients (Brenan *et al.* 1994). However, rutile has been found in subduction-fluid related veins (Gao *et al.* 2007), and rutile solubilities in Cl and F-rich fluids and albite-saturated fluids (Antignano & Manning 2008; Rapp *et al.* 2010) are several orders of magnitude higher than in aqueous fluids. Therefore, it appears that Ti can be mobilised from the subducting slab. Titanium occurs in VI-fold coordination in rutile. However, whilst the bonding environment of Ti in Cl and F-rich fluids is expected to be different from rutile, the exact speciation is not known, and therefore the direction and magnitude of $\delta^{49}\text{Ti}$ fractionation during rutile dissolution is unclear (Millet *et al.* 2016). Previous studies have found no isotopic difference between eclogites ($\delta^{49}\text{Ti} = -0.014 \pm 0.015$ ‰ 95% c.i. (Millet *et al.* 2016)), subduction-related serpentinites ($\delta^{49}\text{Ti} = +0.016 \pm 0.043$ ‰ 95% c.i. (Millet *et al.* 2016)), and MORB ($\delta^{49}\text{Ti} = +0.009 \pm 0.025$ ‰ 95% (Millet *et al.* 2016; Hoare *et al.* 2020; Zhao *et al.* 2020)) which implies any potential fluid-induced $\delta^{49}\text{Ti}$ fractionation is not sufficient to observably alter the Ti budget of the mantle wedge. However, FABs and boninites in this study display markedly different $\delta^{49}\text{Ti}$ (**Figure 6.3**) which magmatic processes such as partial melting, fractional crystallisation, and variable redox conditions struggle to explain.

Boninite $\delta^{49}\text{Ti}$ positively correlates with FME concentrations (**Figure 6.16**), suggesting that Ti complexation with slab derived fluids causes Ti isotope fractionation, with more fluid involvement

being associated with heavier $\delta^{49}\text{Ti}$. Slab-derived fluid induced $\delta^{49}\text{Ti}$ fractionation therefore may have contributed to the observed $\delta^{49}\text{Ti}$ FAB-boninite offset. Similar correlations are not seen with traditionally less mobile, incompatible elements (**Figure 6.17a-c**), enforcing the idea that the $\delta^{49}\text{Ti}$ correlations are related to fluid mobility and not incompatibility during partial melting. Boninite $\delta^{49}\text{Ti}$ also does not correlate with indicators of slab melt inputs such as Sm/Hf or Zr/Sm (**Figure 6.17d-f**). We suggest that the observed FAB-boninite $\delta^{49}\text{Ti}$ is related to the introduction of halogen-rich slab-derived fluids that partially dissolved rutile and transferred Ti to the mantle wedge. The depleted nature of the boninitic source meant that even limited Ti transfer can influence the Ti budget. Also, given the orders of magnitude greater solubility of Ti and rutile in halogen-rich fluids compared to aqueous fluids (Antignano & Manning 2008; Rapp *et al.* 2010), the fluids were likely Cl or F-rich. Boninite glasses do have slightly elevated Cl concentrations compared to FABs and MORB (**Fig. 4.18**) which supports the involvement of Cl-rich fluids.

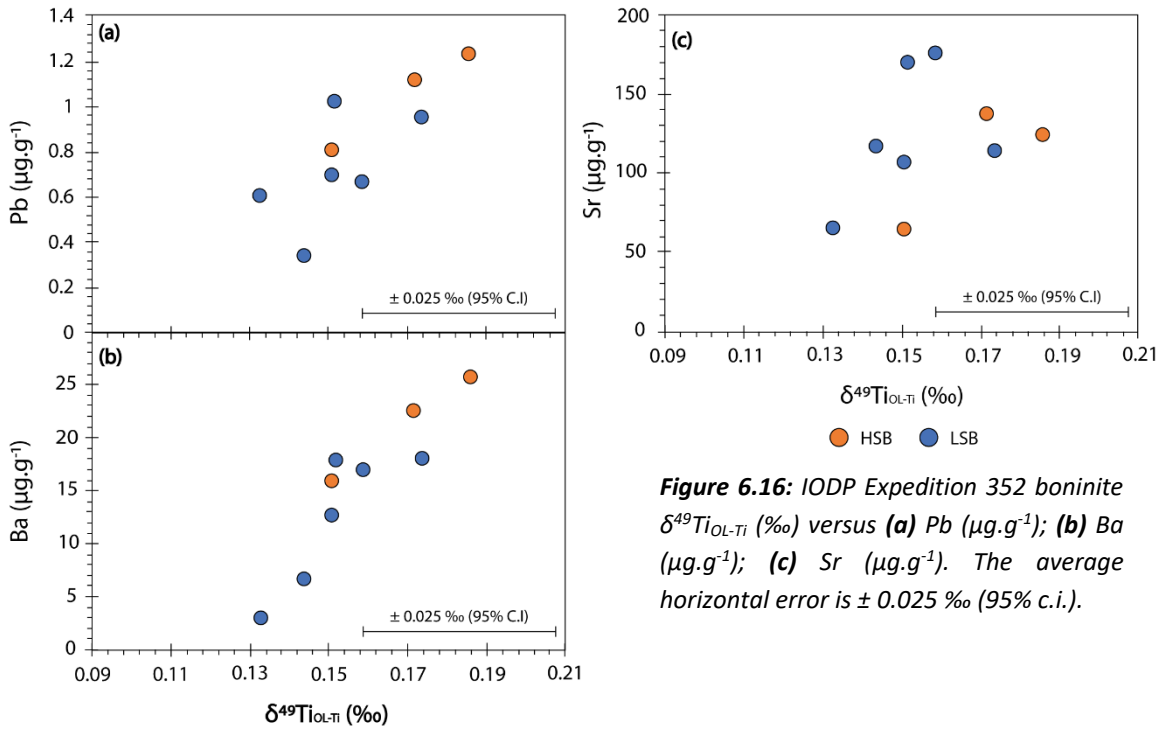


Figure 6.16: IODP Expedition 352 boninite $\delta^{49}\text{Ti}_{\text{OL-Ti}}$ (‰) versus (a) Pb ($\mu\text{g.g}^{-1}$); (b) Ba ($\mu\text{g.g}^{-1}$); (c) Sr ($\mu\text{g.g}^{-1}$). The average horizontal error is ± 0.025 ‰ (95% c.i.).

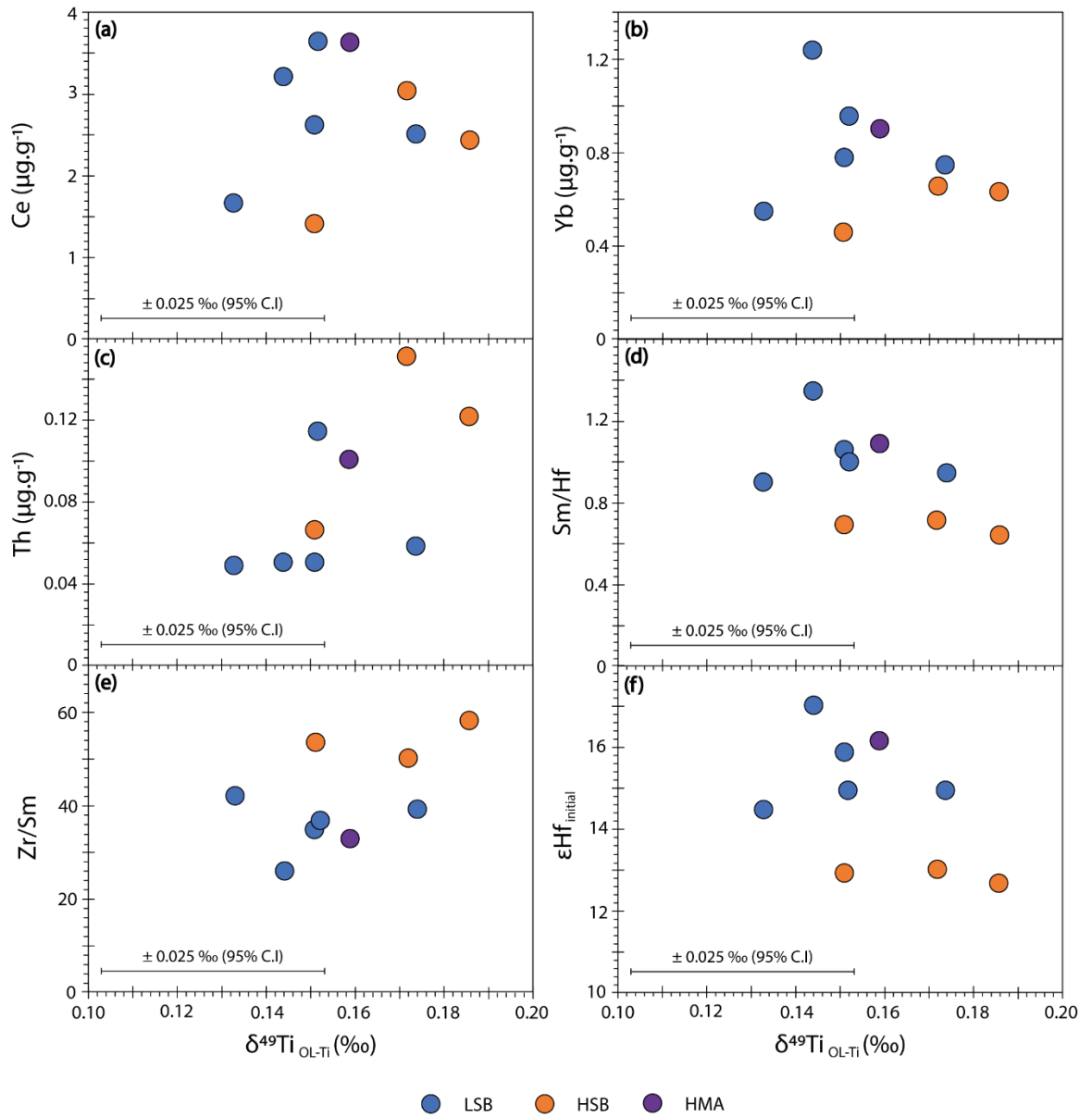


Figure 6.17: IODP Expedition 352 boninite $\delta^{49}\text{Ti}_{\text{OL-Ti}} (\text{‰})$ versus incompatible, immobile element concentrations (a-c) and slab melt indicators (d-f). (a) $\delta^{49}\text{Ti}_{\text{OL-Ti}} (\text{‰})$ versus Ce ($\mu\text{g.g}^{-1}$); (b) $\delta^{49}\text{Ti}_{\text{OL-Ti}} (\text{‰})$ versus Yb ($\mu\text{g.g}^{-1}$); (c) $\delta^{49}\text{Ti}_{\text{OL-Ti}} (\text{‰})$ versus Th ($\mu\text{g.g}^{-1}$); (d) $\delta^{49}\text{Ti}_{\text{OL-Ti}} (\text{‰})$ versus Sm/Hf; (e) $\delta^{49}\text{Ti}_{\text{OL-Ti}} (\text{‰})$ versus Zr/Sm; (f) $\delta^{49}\text{Ti}_{\text{OL-Ti}} (\text{‰})$ versus $\epsilon\text{Hf}_{\text{initial}}$. The average horizontal error is $\pm 0.025 \text{ ‰}$ (95% c.i.).

Vanadium's dominant valence state under typical terrestrial mantle $f\text{O}_2$ is V^{4+} (e.g. Sutton *et al.* 2005; Borisov 2012; Lanzirotti *et al.* 2018) which has a similar ionic charge and radius to Ti^{4+} in octahedral (VI) rutile coordination. Therefore, V is also compatible in rutile which can accommodate large V concentrations up to $2000 \mu\text{g.g}^{-1}$ (Barth *et al.* 2001; Hermann 2002; Zack *et al.* 2002; Liu *et al.* 2014; Guo *et al.* 2017). Whilst no $\delta^{51}\text{V}$ fractionation has been found in response to low-temperature seafloor alteration (e.g. Prytulak *et al.* 2013; Wu *et al.* 2019), Chapter three showed that higher temperature mantle metasomatism can induce $\delta^{51}\text{V}$ fractionation. Despite the temperatures and pressures of subduction fluids and melts being lower than those of the

metasomatic agents in Chapter three, the nature of subduction fluids is blurred between fluid and supercritical fluid (Ni *et al.* 2017). Thus, similarly to Ti isotopes, despite V's low fluid mobility, $\delta^{51}\text{V}$ may also fractionate in response to slab-derived fluid inputs. Indeed, boninite $\delta^{51}\text{V}$ also correlates with FME concentrations, albeit with large uncertainties (**Figure 6.18**). However, unlike $\delta^{49}\text{Ti}$, the $\delta^{51}\text{V}$ correlations are negative. The opposing fractionation directions of V and Ti isotopes suggests that slab-derived fluids could be responsible for the negative $\delta^{49}\text{Ti}$ - $\delta^{51}\text{V}$ correlation in **Figure 6.4**. The FME correlations suggest that subduction fluids preferentially mobilise isotopically light V. However, there are no existing rutile $\delta^{51}\text{V}$ fractionation factors or data on how V may complex with Cl or F-rich fluids, which is required to test such a mechanism.

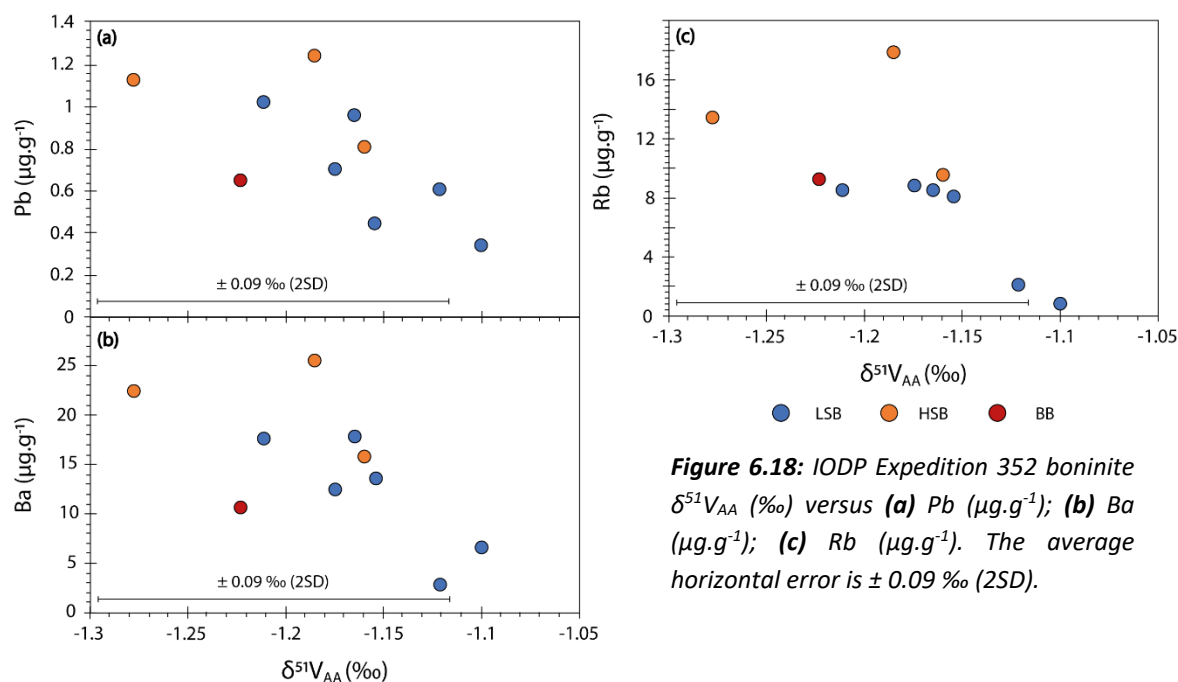


Figure 6.18: IODP Expedition 352 boninite $\delta^{51}\text{V}_{\text{AA}}$ (‰) versus **(a)** Pb ($\mu\text{g.g}^{-1}$); **(b)** Ba ($\mu\text{g.g}^{-1}$); **(c)** Rb ($\mu\text{g.g}^{-1}$). The average horizontal error is ± 0.09 ‰ (2SD).

6.4.4. Implications for using V and Ti isotopes in arcs

This chapter has shown that V and Ti isotopes have the potential to trace processes other than the fractional crystallisation of oxides. A statistically significant $\delta^{49}\text{Ti}$ difference is present between FAB and MORB. The lack of geochemical evidence for known $\delta^{49}\text{Ti}$ fractionation mechanisms leaves mantle heterogeneity as the most likely explanation for isotopically heavy FABs compared to MORB, despite their similar petrogenetic origins. Whilst this disagrees with Millet *et al.* (2016) who suggested the terrestrial mantle has homogenous $\delta^{49}\text{Ti}$, at present, a lack of diverse $\delta^{49}\text{Ti}$ data makes ruling out mantle heterogeneity difficult. Future studies that expand current MORB, OIB, arc, and peridotite $\delta^{49}\text{Ti}$ datasets will help constrain the extent of $\delta^{49}\text{Ti}$ mantle heterogeneity. Future studies could also measure $\delta^{49}\text{Ti}$ in the ODP Leg 125 harzburgites and dunites that sample the Bonin

forearc mantle, and subcontinental lithospheric mantle from other locations to test our source heterogeneity proposal.

In terms of $\delta^{51}\text{V}$, FAB are isotopically lighter than MORB. We attribute this offset to FAB derivation from a more depleted mantle source than MORB. This suggests that V isotopes could be an effective tracer of source depletion in igneous settings if samples without significant oxide crystallisation are examined. However, there are no correlations between FAB $\delta^{51}\text{V}$ and source depletion indicators, and it is not certain whether the FABs exist as two $\delta^{51}\text{V}$ distinct populations or one population with a spectrum of $\delta^{51}\text{V}$. To better test the effects of source depletion, more FAB samples should be measured in future studies, including E-FABs which represent the most enriched FABs. If source depletion does influence $\delta^{51}\text{V}$, E-FABs should be the isotopically heaviest. Since FAB and MORB are similar in Fe isotopes (Chapter four) despite FAB-boninite $\delta^{56}\text{Fe}$ differences being credited to source depletion and partial melting, the FAB-MORB $\delta^{51}\text{V}$ difference suggests that V isotopes could be a more effective source depletion tracer than $\delta^{56}\text{Fe}$.

Traditionally V and Ti are considered fluid immobile elements. However, this chapter has provided evidence that V and Ti isotopes may be mobilised and fractionated by subduction-derived fluids. Based on $\delta^{49}\text{Ti}$ correlations with FMEs, and that partial melting alone may not be able to fully account of the boninite Ti budget, we attribute the $\delta^{49}\text{Ti}$ FAB-boninite difference to the introduction of slab-derived fluids to the mantle wedge during boninite formation. In established subduction zones with more evolved lavas, the $\delta^{49}\text{Ti}$ effects of subduction-fluids are likely overshadowed by the effects of the fractional crystallisation of oxide phases. However, this is still an important finding that could change the way we think about Ti in subduction zones. We also found negative correlations between boninite $\delta^{51}\text{V}$ and FME concentrations that suggest that subduction fluids may fractionate V and Ti isotopes in different directions. Future investigations into the coordination of V and Ti in halogen-fluid complexes should improve our understanding of the mechanism behind these observations. Despite the $\delta^{51}\text{V}$ -FME correlations, the effects of subduction fluids on the overall boninite $\delta^{51}\text{V}$ are less pronounced than for Ti isotopes. Vanadium isotopes have been shown to observably fractionate via multiple mechanisms such as source depletion, and potentially variable redox conditions. The interaction of these different mechanisms with opposing directions of fractionation makes interpreting $\delta^{51}\text{V}$ signatures in arc lavas more challenging. Both the greater source depletion of the boninites and the involvement of subduction-fluids in boninite formation should mean that boninites are isotopically lighter than FABs. However, FABs and boninites are not statistically distinct. We suggest that the more oxidised nature of boninites could result in $\delta^{51}\text{V}$ fractionation towards heavier values that may counteract some of the source depletion and

subduction-fluid effects. However, to test this, $\text{Fe}^{3+}/\Sigma\text{Fe}$ and $f\text{O}_2$ data is needed on the samples from this study. Finally, measuring additional FAB and boninite $\delta^{51}\text{V}$ is needed to confirm whether the lack of $\delta^{51}\text{V}$ difference is statistically significant, or a function of small population sizes.

6.5. Conclusions

1. FABs are statistically isotopically lighter than MORB in $\delta^{51}\text{V}$, and heavier in $\delta^{49}\text{Ti}$.
 - The $\delta^{51}\text{V}$ difference is most likely caused by greater depletion of the FAB source compared to DMM. To test this, future studies should measure $\delta^{51}\text{V}$ in E-FAB samples.
 - The current best explanation for the $\delta^{49}\text{Ti}$ difference is that the FAB mantle is isotopically heavier than typical MORB due to $\delta^{49}\text{Ti}$ mantle heterogeneity.
2. Boninite and FAB $\delta^{51}\text{V}$ are similar despite boninites derivation from a more depleted source than FABs. An additional $\delta^{51}\text{V}$ fractionation mechanism may mask source depletion effects.
 - A viable mechanism to shift boninites to heavier $\delta^{51}\text{V}$ is the introduction of oxidising slab components. Future studies should measure $\text{Fe}^{3+}/\Sigma\text{Fe}$ and $f\text{O}_2$ in the samples from this study to test the $\delta^{51}\text{V}$ - $f\text{O}_2$ relationship.
3. $\delta^{49}\text{Ti}$ and $\delta^{51}\text{V}$ correlations with Ba, Pb, Sr, and Rb suggest that subduction-derived fluids may mobilise and fractionate V and Ti isotopes.
 - The input of subduction-derived fluids is the most likely mechanism to explain the boninites having heavier $\delta^{49}\text{Ti}$ than FABs.
 - Subduction-derived fluids may have also influenced the $\delta^{51}\text{V}$ of the boninites, creating lighter $\delta^{51}\text{V}$ with increasing fluid involvement. However, similar to source depletion, the introduction of oxidising slab components may have masked the effects of subduction fluids on $\delta^{51}\text{V}$.

References

- Aarons, S.M., Reimink, J.R., Greber, N.D., Heard, A.W., Zhang, Z. & Dauphas, N. 2020. Titanium isotopes constrain a magmatic transition at the Hadean-Archean boundary in the Acasta Gneiss Complex. *Science Advances*, **6**, 1–9, <https://doi.org/10.1126/sciadv.abc9959>.
- Antignano, A. & Manning, C.E. 2008. Rutile solubility in H_2O , H_2O - SiO_2 , and H_2O - $\text{NaAlSi}_3\text{O}_8$ fluids at 0.7–2.0 GPa and 700 – 1000°C: Implications for mobility of nominally insoluble elements. *Chemical Geology*, **255**, 283–293, <https://doi.org/10.1016/j.chemgeo.2008.07.001>.
- Audetat, A. & Keppler, H. 2005. Solubility of rutile in subduction zone fluids, as determined by experiments in the hydrothermal diamond anvil cell. *Earth and Planetary Science Letters*, **232**, 393–402, <https://doi.org/10.1016/j.epsl.2005.01.028>.

- Barth, M.G., Rudnick, R.L., Horn, I., McDonough, W.F., Spicuzza, M.J., Valley, J.W. & Haggerty, S.E. 2001. Geochemistry of xenolithic eclogites from West Africa, part I: A link between low MgO eclogites and Archean crust formation. *Geochimica et Cosmochimica Acta*, **65**, 1499–1527, [https://doi.org/10.1016/S0016-7037\(00\)00626-8](https://doi.org/10.1016/S0016-7037(00)00626-8).
- Beard, B.L., Johnson, C.M., Von Damm, K.L. & Poulson, R.L. 2003. Iron isotope constraints on Fe cycling and mass balance in oxygenated Earth oceans. *Geology*, **31**, 629–632, [https://doi.org/10.1130/0091-7613\(2003\)031<0629:ICOFC>2.0.CO;2](https://doi.org/10.1130/0091-7613(2003)031<0629:ICOFC>2.0.CO;2).
- Bennett, S.A., Rouxel, O., Schmidt, K., Garbe-Schönberg, D., Statham, P.J. & German, C.R. 2009. Iron isotope fractionation in a buoyant hydrothermal plume, 5°S Mid-Atlantic Ridge. *Geochimica et Cosmochimica Acta*, **73**, 5619–5634, <https://doi.org/10.1016/j.gca.2009.06.027>.
- Borisov, A.A. 2012. The Ti 4+/Ti 3+ ratio of magmatic melts: Application to the problem of the reduction of lunar basalts. *Petrology*, **20**, 391–398, <https://doi.org/10.1134/S0869591112040030>.
- Brenan, J., Shaw, H., Phinney, D. & Ryerson, F. 1994. Rutile-aqueous fluid partitioning of Nb, Ta, Hf, Zr, U and Th: implications for high field strength element depletions in island-arc basalts. *Earth and Planetary Science Letters*, **128**, 327–339, [https://doi.org/10.1016/0012-821X\(94\)90154-6](https://doi.org/10.1016/0012-821X(94)90154-6).
- Brounce, M., Cottrell, E. & Kelley, K.A. 2019. The redox budget of the Mariana subduction zone. *Earth and Planetary Science Letters*, **528**, 115859, <https://doi.org/10.1016/j.epsl.2019.115859>.
- Brounce, M., Reagan, M.K., Kelley, K.A., Cottrell, E., Shimizu, K. & Almeev, R. 2021. Co-variation of slab tracers, volatiles and oxidation during subduction initiation. *Geochemistry, Geophysics, Geosystems*, **22**, 1–30, <https://doi.org/10.1029/2021gc009823>.
- Brounce, M.N., Kelley, K.A. & Cottrell, E. 2014. Variations in Fe³⁺/PFe of Mariana Arc Basalts and Mantle Wedge fO₂. *Journal of Petrology*, **55**, 2514–2536, <https://doi.org/10.1093/petrology/egu065>.
- Canil, D. 1997. Vanadium partitioning and the oxidation state of Archean komatiite magmas. *Nature*, **389**, 842–845, <https://doi.org/10.1038/39860>.
- Cottrell, E. & Kelley, K.A. 2011. The oxidation state of Fe in MORB glasses and the oxygen fugacity of the upper mantle. *Earth and Planetary Science Letters*, **305**, 270–282, <https://doi.org/10.1016/j.epsl.2011.03.014>.
- Coulthard, D.A., Reagan, M.K., Shimizu, K., Bindeman, I.N., Brounce, M., Almeev, R.R., Ryan, J., Chapman, T., Shervias, J. & Pearce, J.A. 2021. Magma Source Evolution Following Subduction Initiation: Evidence From the Element Concentrations, Stable Isotope Ratios, and Water Contents of Volcanic Glasses From the Bonin Forearc (IODP Expedition 352). *Geochemistry, Geophysics, Geosystems*, **22**, 1–30, <https://doi.org/10.1029/2020GC009054>.
- Dauphas, N., Craddock, P.R., Asimow, P.D., Bennett, V.C., Nutman, A.P. & Ohnenstetter, D. 2009. Iron isotopes may reveal the redox conditions of mantle melting from Archean to Present. *Earth and Planetary Science Letters*, **288**, 255–267, <https://doi.org/10.1016/j.epsl.2009.09.029>.

- Dauphas, N., Roskosz, M., Alp E., Neuville D., Hu M., Sio C., Tissot F., Zhao J., Tissandier L., Me´dard E. & Cordier C. 2014. Magma redox and structural controls on iron isotope variations in Earth’s mantle and crust. *Earth and Planetary Science Letters*, **398**, 127–140, <https://doi.org/10.1016/j.epsl.2014.04.033>.
- Debret, B. & Sverjensky, D.A. 2017. Highly oxidising fluids generated during serpentinite breakdown in subduction zones/704/2151/209/704/2151/431/119/118 article. *Scientific Reports*, **7**, 1–6, <https://doi.org/10.1038/s41598-017-09626-y>.
- Debret, B., Millet, M.A., Pons, M.L., Bouilhol, P., Inglis, E. & Williams, H. 2016. Isotopic evidence for iron mobility during subduction. *Geology*, **44**, 215–218, <https://doi.org/10.1130/G37565.1>.
- Debret, B., Bouilhol, P., Pons, M.L. & Williams, H. 2018. Carbonate transfer during the onset of slab devolatilization: New insights from Fe and Zn stable isotopes. *Journal of Petrology*, **59**, 1145–1166, <https://doi.org/10.1093/petrology/egy057>.
- Debret, B., Reekie, C.D.J., Mattielli, N., Beunon, H., Ménez, B., Savov, I. & Williams, H.M. 2020. Redox transfer at subduction zones: insights from Fe isotopes in the Mariana forearc. *Geochemical Perspectives Letters*, 46–51, <https://doi.org/10.7185/geochemlet.2003>.
- Debret, B., Garrido, C.J., Pons, M.L., Bouilhol, P., Inglis, E., López Sánchez-Vizcaíno, V. & Williams, H. 2021. Iron and zinc stable isotope evidence for open-system high-pressure dehydration of antigorite serpentinite in subduction zones. *Geochimica et Cosmochimica Acta*, **296**, 210–225, <https://doi.org/10.1016/j.gca.2020.12.001>.
- Deng, Z., Moynier, F., Sossi, P.A. & Chaussidon, M. 2018. Bridging the depleted morb mantle and the continental crust using titanium isotopes. *Geochemical Perspectives Letters*, **9**, 11–15, <https://doi.org/10.7185/geochemlet.1831>.
- Deng, Z., Chaussidon, M., Savage, P., Robert, F., Pik, R. & Moynier, F. 2019. Titanium isotopes as a tracer for the plume or island arc affinity of felsic rocks. *Proceedings of the National Academy of Sciences of the United States of America*, **116**, 1132–1135, <https://doi.org/10.1073/pnas.1809164116>.
- Ding, X., Helz, R.T., Qi, Y. & Huang, F. 2020. Vanadium isotope fractionation during differentiation of Kilauea Iki lava lake, Hawaii. *Geochimica et Cosmochimica Acta*, **289**, 114–129, <https://doi.org/10.1016/j.gca.2020.08.023>.
- Dupre, B. & Allegre, C.J. 1983. Pb-Sr isotope variation in Indian Ocean basalts and mixing phenomena. *Nature*, **303**, 142–146.
- Evans, K.A. 2012. The redox budget of subduction zones. *Earth-Science Reviews*, **113**, 11–32, <https://doi.org/10.1016/j.earscirev.2012.03.003>.
- Evans, K.A. & Tomkins, A.G. 2011. The relationship between subduction zone redox budget and arc magma fertility. *Earth and Planetary Science Letters*, **308**, 401–409, <https://doi.org/10.1016/j.epsl.2011.06.009>.
- Foden, J., Sossi, P.A. & Nebel, O. 2018. Controls on the iron isotopic composition of global arc magmas. *Earth and Planetary Science Letters*, **494**, 190–201, <https://doi.org/10.1016/j.epsl.2018.04.039>.
- Foley, S., Barth, M. & Jenner, G. 2000. Rutile/melt partition coefficients for trace elements and an assessment of the influence of rutile on the trace element characteristics of subduction zone

- magmas. *Geochimica et Cosmochimica Acta*, **64**, 933–938, [https://doi.org/10.1016/S0016-7037\(99\)00355-5](https://doi.org/10.1016/S0016-7037(99)00355-5).
- Gao, J., John, T., Klemm, R. & Xiong, X. 2007. Mobilization of Ti – Nb – Ta during subduction: Evidence from rutile-bearing dehydration segregations and veins hosted in eclogite, Tianshan, NW China. *Geochimica et Cosmochimica Acta*, **71**, 4974–4996, <https://doi.org/10.1016/j.gca.2007.07.027>.
- Greber, N.D., Dauphas, N., Puchtel, I.S., Hofmann, B.A. & Arndt, N.T. 2017. Titanium stable isotopic variations in chondrites, achondrites and lunar rocks. *Geochimica et Cosmochimica Acta*, **213**, 534–552, <https://doi.org/10.1016/j.gca.2017.06.033>.
- Guo, S., Tang, P., Su, B., Chen, Y., Ye, K., Zhang, L., Gao, Y., Liu, J. & Yang, Y. 2017. Unusual replacement of Fe - Ti oxides by rutile during retrogression in amphibolite - hosted veins (Dabie UHP terrane): A mineralogical record of fluid - induced oxidation processes in exhumed UHP slabs. *American Mineralogist*, **102**, 2268–2283.
- Hart, S.R. 1984. A large-scale isotopic anomaly in the southern hemisphere. *Nature*, **309**, 753–756.
- Hermann, J. 2002. Allanite: Thorium and light rare earth element carrier in subducted crust. *Chemical Geology*, **192**, 289–306, [https://doi.org/10.1016/S0009-2541\(02\)00222-X](https://doi.org/10.1016/S0009-2541(02)00222-X).
- Hoare, L., Klaver, M., Saji, N.S., Gillies, J., Parkinson, I.J., Lissenberg, C.J. & Millet, M.A. 2020. Melt chemistry and redox conditions control titanium isotope fractionation during magmatic differentiation. *Geochimica et Cosmochimica Acta*, **282**, 38–54, <https://doi.org/10.1016/j.gca.2020.05.015>.
- Jenner, F.E. & O'Neill, H.S.C. 2012. Analysis of 60 elements in 616 ocean floor basaltic glasses. *Geochemistry, Geophysics, Geosystems*, **13**, 1–11, <https://doi.org/10.1029/2011GC004009>.
- Johnson, A.C., Aarons, S.M., Dauphas, N., Nie, N.X., Zeng, H., Helz, R.T., Romaniello, S.J. & Anbar, A.D. 2019. Titanium isotopic fractionation in Kilauea Iki lava lake driven by oxide crystallization. *Geochimica et Cosmochimica Acta*, **264**, 180–190, <https://doi.org/10.1016/j.gca.2019.08.022>.
- Kelley, K.A. & Cottrell, E. 2009. Water and the oxidation state of subduction zone magmas. *Science*, **325**, 605–607, <https://doi.org/10.1126/science.1174156>.
- Kelley, K.A. & Cottrell, E. 2012. The influence of magmatic differentiation on the oxidation state of Fe in a basaltic arc magma. *Earth and Planetary Science Letters*, **329**, 109–121, <https://doi.org/10.1016/j.epsl.2012.02.010>.
- Kendrick, M.A., Hémond, C., Kamenetsky, V.S., Danyushevsky, L., Devey, C.W., Rodemanns, T., Jackson, M.G. & Perfit, M.R. 2017. Seawater cycled throughout Earth's mantle in partially serpentinized lithosphere. *Nature Geoscience*, **10**, 222–228, <https://doi.org/10.1038/ngeo2902>.
- Kinzler, R.J. 1997. Melting of mantle peridotite at pressures approaching the spinel to garnet transition: Application to mid-ocean ridge basalt petrogenesis. *Journal of Geophysical Research B: Solid Earth*, **102**, 853–874, <https://doi.org/10.1029/96jb00988>.
- Kommescher, S. 2020. Mass-dependent Titanium Isotope Variations in Terrestrial and Extra-Terrestrial Basalts: PhD Thesis, Universität zu Köln, p. 153.

- Lanzirotti, A., Darby Dyar, M., Sutton, S., Newville, M., Head, E., Carey, C., McCanta, M., Lee, L., King, P.L. & Jones, J. 2018. Accurate predictions of microscale oxygen barometry in basaltic glasses using v K-edge X-ray absorption spectroscopy: A multivariate approach. *American Mineralogist*, **103**, 1282–1297, <https://doi.org/10.2138/am-2018-6319>.
- Lee, C.T.A., Leeman, W.P., Canil, D. & Li, Z.X.A. 2005. Similar V/Sc systematics in MORB and arc basalts: Implications for the oxygen fugacities of their mantle source regions. *Journal of Petrology*, **46**, 2313–2336, <https://doi.org/10.1093/petrology/egi056>.
- Lee, C.T.A., Luffi, P., Le Roux, V., Dasgupta, R., Albarède, F. & Leeman, W.P. 2010. The redox state of arc mantle using Zn/Fe systematics. *Nature*, **468**, 681–685, <https://doi.org/10.1038/nature09617>.
- Li, H.Y., Taylor, R.N., Prytulak, J., Kirchenbaur, M., Shervais, J.W., Ryan, J.G., Godard, M., Reagan, M.K. & Pearce, J.A. 2019. Radiogenic isotopes document the start of subduction in the Western Pacific. *Earth and Planetary Science Letters*, **518**, 197–210, <https://doi.org/10.1016/j.epsl.2019.04.041>.
- Liu, L., Xiao, Y. & Aulbach, S. 2014. Vanadium and niobium behavior in rutile as a function of oxygen fugacity : evidence from natural samples. *Contributions to Mineralogy and Petrology*, **167**, <https://doi.org/10.1007/s00410-014-1026-2>.
- Millet, M.A. & Dauphas, N. 2014. Ultra-precise titanium stable isotope measurements by double-spike high resolution MC-ICP-MS. *Journal of Analytical Atomic Spectrometry*, **29**, 1444–1458, <https://doi.org/10.1039/c4ja00096j>.
- Millet, M.A., Dauphas, N., Greber, N.D., Burton, K.W., Dale, C.W., Debret, B., Macpherson, C.G., Nowell, G.M. & Williams, H.M. 2016. Titanium stable isotope investigation of magmatic processes on the Earth and Moon. *Earth and Planetary Science Letters*, **449**, 197–205, <https://doi.org/10.1016/j.epsl.2016.05.039>.
- Nebel, O., Sossi, P.A., Bénard, A., Wille, M., Vroon, P.Z. & Arculus, R.J. 2015. Redox-variability and controls in subduction zones from an iron-isotope perspective. *Earth and Planetary Science Letters*, **432**, 142–151, <https://doi.org/10.1016/j.epsl.2015.09.036>.
- Ni, H., Zhang, L., Xiong, X., Mao, Z. & Wang, J. 2017. Supercritical fluids at subduction zones: Evidence, formation condition, and physicochemical properties. *Earth-Science Reviews*, **167**, 62–71, <https://doi.org/10.1016/j.earscirev.2017.02.006>.
- Nielsen, S.G., Prytulak, J. & Halliday, A.N. 2011. Determination of Precise and Accurate 51V/50V Isotope Ratios by MC-ICP-MS, Part 1: Chemical Separation of Vanadium and Mass Spectrometric Protocols. *Geostandards and Geoanalytical Research*, **35**, 293–306, <https://doi.org/10.1111/j.1751-908X.2011.00106.x>.
- Novella, D., MacLennan, J., Shorttle, O., Prytulak, J. & Murton, B.J. 2020. A multi-proxy investigation of mantle oxygen fugacity along the Reykjanes Ridge. *Earth and Planetary Science Letters*, **531**, 115973, <https://doi.org/10.1016/j.epsl.2019.115973>.
- Parkinson, I.J. & Arculus, R.J. 1999. The redox state of subduction zones: Insights from arc-peridotites. *Chemical Geology*, **160**, 409–423, [https://doi.org/10.1016/S0009-2541\(99\)00110-2](https://doi.org/10.1016/S0009-2541(99)00110-2).

- Parkinson, I.J. & Pearce, J.A. 1998. Peridotites from the Izu-Bonin-Mariana forearc (ODP Leg 125): evidence for mantle melting and melt-mantle interaction in a supra-subduction zone setting. *Journal of Petrology*, **39**, 1577–1618, <https://doi.org/10.1093/петрол/39.9.1577>.
- Parkinson, I.J., Hawkesworth, C.J. & Cohen, A.S. 1998. Ancient mantle in a modern arc: Osmium isotopes in Izu-Bonin-Mariana forearc peridotites. *Science*, **281**, 2011–2013, <https://doi.org/10.1126/science.281.5385.2011>.
- Polyakov, V.B. & Mineev, S.D. 2000. The use of Mossbauer spectroscopy in stable isotope geochemistry. *Geochimica et Cosmochimica Acta*, **64**, 849–865, [https://doi.org/10.1016/S0016-7037\(99\)00329-4](https://doi.org/10.1016/S0016-7037(99)00329-4).
- Pons, M.-L., Debret, B., Bouilhol, P., Delacour, A. & Williams, H. 2016. Zinc isotope evidence for sulfate-rich fluid transfer across subduction zones. *Nature Communications*, **7**, <https://doi.org/10.1038/ncomms13794>.
- Prytulak, J., Nielsen, S.G. & Halliday, A.N. 2011. Determination of Precise and Accurate 51V/50V Isotope Ratios by Multi-Collector ICP-MS, Part 2: Isotopic Composition of Six Reference Materials plus the Allende Chondrite and Verification Tests. *Geostandards and Geoanalytical Research*, **35**, 307–318, <https://doi.org/10.1111/j.1751-908X.2011.00105.x>.
- Prytulak, J., Nielsen, S.G., Ionov, D.A., Halliday, A.N., Harvey, J., Kelley, K.A., Niu, Y.L., Peate, D.W., Shimizu, K. & Sims, K.W.W. 2013. The stable vanadium isotope composition of the mantle and mafic lavas. *Earth and Planetary Science Letters*, **365**, 177–189, <https://doi.org/10.1016/j.epsl.2013.01.010>.
- Prytulak, J., Sossi, P.A., Halliday, A.N., Plank, T., Savage, P.S. & Woodhead, J.D. 2017. Stable vanadium isotopes as a redox proxy in magmatic systems? *Geochemical Perspectives Letters*, **3**, 75–84, <https://doi.org/10.7185/geochemlet.1708>.
- Rapp, J.F., Klemme, S., Butler, I.B. & Harley, S.L. 2010. Extremely high solubility of rutile in chloride and fluoride-bearing metamorphic fluids: An experimental investigation. *Geology*, **38**, 323–326, <https://doi.org/10.1130/G30753.1>.
- Reagan, M.K., Pearce, J.A., Petronotis, K., Almeev, R.R., Avery, A.J., Carvallo, C., Chapman, T., Christeson, G.L., Ferre, E.C., Godard, M., Heaton, D.E., Kirchenbaur, M., Kurz, W., Kutterolf, S., Li, H., Li, Y., Michibayashi, K., Morgan, S., Nelson, W.R., Prytulak, P., Python, M., Robertson, A.H.F., Ryan, J.G., Sager, W.W., Sakuyama, T., Shervais, J.W., Shimizu, K. & Whattam, S.A. 2017. Subduction initiation and ophiolite crust: new insights from IODP drilling. *International Geology Review*, **59**, 1439–1450, <https://doi.org/10.1080/00206814.2016.1276482>.
- Rouxel, O., Dobbek, N., Ludden, J. & Fouquet, Y. 2003. Iron isotope fractionation during oceanic crust alteration. *Chemical Geology*, **202**, 155–182, <https://doi.org/10.1016/j.chemgeo.2003.08.011>.
- Rouxel, O., Sholkovitz, E., Charette, M. & Edwards, K.J. 2008. Iron isotope fractionation in subterranean estuaries. *Geochimica et Cosmochimica Acta*, **72**, 3413–3430, <https://doi.org/10.1016/j.gca.2008.05.001>.
- Ryerson, F. & Watson, E.B. 1987. Rutile saturation in magmas: implications for Ti-Nb-Ta depletion in island-arc basalts. *Earth and Planetary Science Letters*, **86**, 225–239.

- Severmann, S., Johnson, C.M., Beard, B.L., German, C.R., Edmonds, H.N., Chiba, H. & Green, D.R.H. 2004. The effect of plume processes on the Fe isotope composition of hydrothermally derived Fe in the deep ocean as inferred from the Rainbow vent site, Mid-Atlantic Ridge, 36°14'N. *Earth and Planetary Science Letters*, **225**, 63–76, <https://doi.org/10.1016/j.epsl.2004.06.001>.
- Shahar, A., Young, E.D. & Manning, C.E. 2008. Equilibrium high-temperature Fe isotope fractionation between fayalite and magnetite: An experimental calibration. *Earth and Planetary Science Letters*, **268**, 330–338, <https://doi.org/10.1016/j.epsl.2008.01.026>.
- Sharma, M., Polizzotto, M. & Anbar, A.D. 2001. Iron isotopes in hot springs along the Juan de Fuca Ridge. *Earth and Planetary Science Letters*, **194**, 39–51, [https://doi.org/10.1016/S0012-821X\(01\)00538-6](https://doi.org/10.1016/S0012-821X(01)00538-6).
- Shaw, D.M. 1970. Trace element fractionation during anatexis. *Geochimica et Cosmochimica Acta*, **34**, 237–243, [https://doi.org/10.1016/0016-7037\(70\)90009-8](https://doi.org/10.1016/0016-7037(70)90009-8).
- Shervais, J.W., Reagan, M., Haugen, E., Almeev, R.R., Pearce, J.A., Prytulak, J., Ryan, J.G., Whattam, S.A., Godard, M., Chapman, T., Li, H., Kurz, W., Nelson, W.R., Heaton, D., Kirchenbaur, M., Shimizu, K., Sakuyama, T., Li, Y. & Vetter, S.K. 2019. Magmatic Response to Subduction Initiation: Part 1. Fore-arc Basalts of the Izu-Bonin Arc From IODP Expedition 352. *Geochemistry, Geophysics, Geosystems*, **20**, 314–338, <https://doi.org/10.1029/2018 GC007731>.
- Shervais, J.W., Reagan, M.K., Godard, M. & Prytulak, J. 2021. Magmatic Response to Subduction Initiation , Part II : Boninites and Related Rocks of the Izu-Bonin Arc From IODP Expedition 352 Geochemistry , Geophysics , Geosystems. *Geochemistry, Geophysics, Geosystems*, **22**, 1–34, <https://doi.org/10.1029/2020GC009093>.
- Shimizu, K., Ito, M., Chang, Q., Miyazaki, T., Ueki, K., Toyama, C., Senda, R., Vaglarov, B.S., Ishikawa, T. & Kimura, J.I. 2019. Identifying volatile mantle trend with the water–fluorine–cerium systematics of basaltic glass. *Chemical Geology*, **522**, 283–294, <https://doi.org/10.1016/j.chemgeo.2019.06.014>.
- Sossi, P.A., Prytulak, J. & O'Neill, H.S.C. 2018. Experimental calibration of vanadium partitioning and stable isotope fractionation between hydrous granitic melt and magnetite at 800 °C and 0.5 GPa. *Contributions to Mineralogy and Petrology*, **173**, 1451–1458, <https://doi.org/10.1007/s00410-018-1451-8>.
- Sutton, S.R., Karner, J., Papike, J., Delaney, J.S., Shearer, C., Newville, M., Eng, P., Rivers, M. & Dyar, M.D. 2005. Vanadium K edge XANES of synthetic and natural basaltic glasses and application to microscale oxygen barometry. *Geochimica et Cosmochimica Acta*, **69**, 2333–2348, <https://doi.org/10.1016/j.gca.2004.10.013>.
- Teng, F.-Z., Dauphas, N. & Watkins, J.M. 2017. Non-Traditional Stable Isotopes: Retrospective and Prospective. *Reviews in Mineralogy & Geochemistry*, **82**, 1–26.
- Toplis, M.J. & Carroll, M.R. 1995. An experimental study of the influence of oxygen fugacity on Fe-ti oxide stability, phase relations, and mineral-melt equilibria in ferro-basaltic systems. *Journal of Petrology*, **36**, 1137–1170, <https://doi.org/10.1093/petrology/36.5.1137>.
- Toplis, M.J. & Carroll, M.R. 1996. Differentiation of ferro-basaltic magmas under conditions open and closed to oxygen: Implications for the skaergaard intrusion and other natural systems. *Journal of Petrology*, **37**, 837–858, <https://doi.org/10.1093/petrology/37.4.837>.

- Turner, S., Williams, H., Piazzolo, S., Blichert-Toft, J., Gerdes, M., Adam, J., Liu, X.M., Schaefer, B. & Maury, R. 2018. Sub-arc xenolith Fe-Li-Pb isotopes and textures tell tales of their journey through the mantle wedge and crust. *Geological Society of America*, **46**, 947-950, <https://doi.org/10.1130/G45359E.11034-1034>.
- Williams, H.M., Prytulak, J., Woodhead, J.D., Kelley, K.A., Brounce, M. & Plank, T. 2018. Interplay of crystal fractionation, sulfide saturation and oxygen fugacity on the iron isotope composition of arc lavas: An example from the Marianas. *Geochimica et Cosmochimica Acta*, **226**, 224–243, <https://doi.org/10.1016/j.gca.2018.02.008>.
- Wood, B.J., Bryndzia, L.T. & Johnson, K.E. 1990. Mantle oxidation state and its relationship to tectonic environment and fluid speciation. *Science*, **248**, 337–345, <https://doi.org/10.1126/science.248.4953.337>.
- Workman, R.K. & Hart, S.R. 2005. Major and trace element composition of the depleted MORB mantle (DMM). *Earth and Planetary Science Letters*, **231**, 53–72, <https://doi.org/10.1016/j.epsl.2004.12.005>.
- Wu, F., Qi, Y., Perfit, M.R., Gao, Y., Langmuir, C.H., Wanless, V.D., Yu, H. & Huang, F. 2018. Vanadium isotope compositions of mid-ocean ridge lavas and altered oceanic crust. *Earth and Planetary Science Letters*, **493**, 128–139, <https://doi.org/10.1016/j.epsl.2018.04.009>.
- Wu, F., Owens, J.D., Huang, T., Sarafian, A., Huang, K.F., Sen, I.S., Horner, T.J., Blusztajn, J., Morton, P. & Nielsen, S.G. 2019. Vanadium isotope composition of seawater. *Geochimica et Cosmochimica Acta*, **244**, 403–415, <https://doi.org/10.1016/j.gca.2018.10.010>.
- Young, E.D., Manning, C.E., Schauble, E.A., Shahar, A., Macris, C.A., Lazar, C. & Jordan, M. 2015. High-temperature equilibrium isotope fractionation of non-traditional stable isotopes: Experiments, theory, and applications. *Chemical Geology*, **395**, 176–195, <https://doi.org/10.1016/j.chemgeo.2014.12.013>.
- Zack, T., Kronz, A., Foley, S.F. & Rivers, T. 2002. Trace element abundances in rutiles from eclogites and associated garnet mica schists. **184**, 97–122, [https://doi.org/10.1016/S0009-2541\(01\)00357-6](https://doi.org/10.1016/S0009-2541(01)00357-6).
- Zhang, H.L., Cottrell, E., Solheid, P.A., Kelley, K.A. & Hirschmann, M.M. 2018. Determination of Fe³⁺/ΣFe of XANES basaltic glass standards by Mössbauer spectroscopy and its application to the oxidation state of iron in MORB. *Chemical Geology*, **479**, 166–175, <https://doi.org/10.1016/j.chemgeo.2018.01.006>.
- Zhang, J., Dauphas, N., Davis, A.M. & Pourmand, A. 2011. A new method for MC-ICPMS measurement of titanium isotopic composition: Identification of correlated isotope anomalies in meteorites. *Journal of Analytical Atomic Spectrometry*, **26**, 2197–2205, <https://doi.org/10.1039/c1ja10181a>.
- Zhao, X., Tang, S., Li, J., Wang, H., Helz, R., Marsh, B., Zhu, X. & Zhang, H. 2020. Titanium isotopic fractionation during magmatic differentiation. *Contributions to Mineralogy and Petrology*, **175**, 1–16, <https://doi.org/10.1007/s00410-020-01704-1>.

CHAPTER SEVEN

Conclusions & Future Work

Developments in MC-ICP MS have allowed transition metal stable isotope ratios to be applied to high-temperature igneous settings where they have the potential to fractionate in response to different magmatic processes. However, for some isotope systems literature data is still limited and there are gaps in our understanding of how and why they fractionate. This thesis studied V, Ti, Fe, and Zn isotope fractionation in high-temperature mantle and subduction zone settings with the initial aim of determining the effects of changing fO_2 and magmatic processes on isotopic fractionation. Whilst Covid-19 forced a slight shift in focus, the findings improve the collective understanding of high-temperature transition metal isotope behaviour. This final chapter summarises the main findings of the thesis, discusses limitations, and suggests avenues for future work.

7.1. Chapter Three

In Chapter Three garnet and clinopyroxene mineral separates from Slave craton mantle xenoliths were used to assess the effects of fO_2 , V bonding environment, and mantle metasomatism on V isotopic compositions in the mantle. Existing $Fe^{3+}/\Sigma Fe$ and fO_2 determinations, and mineral major and trace element data (Yaxley *et al.* 2017) were combined with new whole-rock and garnet and clinopyroxene mineral separate $\delta^{51}V$ and trace element data. Chapter Three is the first investigation into the effects of mantle metasomatism on $\delta^{51}V$. It also presents the first natural mineral separate $\delta^{51}V$ data and the first $\delta^{51}V$ measurements on oxide-free mantle rocks from > 3 GPa. The findings from this Chapter therefore make a significant contribution to the V isotope literature. The combined analysis of new and existing literature data on the same samples, coupled with mass balance reconstructions indicated that:

- i) fO_2 can influence mantle $\delta^{51}V$, evidenced by the positive trends between $\delta^{51}V$ and fO_2 in the metasomatic garnet and clinopyroxene phases.
- ii) Metasomatism can resolvably alter mantle $\delta^{51}V$, creating light signatures relative to BSE due to differences in V coordination between the metasomatic agent and the melt.

Whilst Chapter three improved our understanding of the controls on $\delta^{51}V$ fractionation in the mantle, there are some clear avenues for future work.

- Expand the Diavik $\delta^{51}V$ work to include a wider range of garnet types

The mantle xenoliths measured for $\delta^{51}\text{V}$ were limited in number and chemical variety due to sample availability. Previous studies found four types of Diavik xenoliths based on garnet REE patterns (e.g. Creighton *et al.* 2010; Yaxley *et al.* 2017), that are suggested to have experienced different degrees of metasomatism from the two metasomatic agents. Since Chapter Three showed that differences in V coordination between melt and metasomatic agent can cause significant $\delta^{51}\text{V}$ fractionation, the unrepresented sinusoidal and U-shaped garnet types may have different $\delta^{51}\text{V}$. Future studies should therefore measure $\delta^{51}\text{V}$ in sinusoidal and U-shaped garnet mineral separates to determine if different types and degrees of metasomatism cause $\delta^{51}\text{V}$ fractionation of different magnitudes and directions.

- *Measure $\delta^{51}\text{V}$ in olivine and orthopyroxene mineral separates from the Diavik xenoliths*

The observed $\delta^{51}\text{V}$ offset between garnet and clinopyroxene mineral separates and corresponding whole-rock powders was suggested to be caused by isotopic disequilibrium between metasomatic garnet and clinopyroxene and non-metasomatic olivine and orthopyroxene. However, this suggestion was based on modelling of olivine and orthopyroxene $\delta^{51}\text{V}$, and not measured $\delta^{51}\text{V}$ data. To determine for certain whether garnet and clinopyroxene are indeed in isotopic disequilibrium with olivine and orthopyroxene, $\delta^{51}\text{V}$ in olivine and orthopyroxene from the Chapter Three samples should be measured.

7.2. Chapters Four, Five, and Six

In Chapter Four the Fe isotopic compositions of 40 fore-arc basalts and boninites from IODP Expedition 352 to the Bonin forearc, and 6 ODP Leg 125 harzburgites and dunites were presented. Whilst there is existing arc lava $\delta^{56}\text{Fe}$ literature data (e.g. Dauphas *et al.* 2009; Nebel *et al.* 2015; Foden *et al.* 2018; Williams *et al.* 2018), previous studies have struggled to explain why arc lavas are isotopically lighter than MORB for $\delta^{56}\text{Fe}$. The new FAB and boninite $\delta^{56}\text{Fe}$ data were derived from samples free from the geochemical complications of an overlying plate and that allowed the effects of magmatic and subduction-related processes to be isolated. Chapter four therefore provided a new and unique insight into the origins of the light $\delta^{56}\text{Fe}$ of arc lavas. Iron isotopic compositions of the new FABs and boninites, and MORB samples from literature were compared, and correlations between $\delta^{56}\text{Fe}$ and major elements, trace elements, and radiogenic isotopes were examined. Iron isotopic fractionation during successive melt extraction events was modelled. The modelling found that source depletion and mantle partial melting can fully account for the $\delta^{56}\text{Fe}$ difference between FABs and boninites. The modelling results and the lack of correlations between boninite $\delta^{56}\text{Fe}$ and slab-derived fluid and melt indicators suggest that:

- i) Subduction inputs do not cause observable $\delta^{56}\text{Fe}$ fractionation in subduction zone lavas and can therefore not explain the light $\delta^{56}\text{Fe}$ of arc lavas.
- ii) The greater source depletion of arc lavas compared to MORB is the most likely candidate to explain the light $\delta^{56}\text{Fe}$ of arc lavas.

In Chapter five, new $\delta^{66}\text{Zn}$ data for the same 40 FABs and boninites and 6 peridotites was reported. These measurements represent a significant addition to the limited $\delta^{66}\text{Zn}$ arc lava literature (Huang *et al.* 2018) and allowed the effects of subduction-derived fluids, melts, and sediments on $\delta^{66}\text{Zn}$ fractionation to be determined. Comparisons of FAB, boninite and literature MORB $\delta^{66}\text{Zn}$, plus correlations with major and trace element concentrations found the following results:

- i) Despite suggestions from previous studies (e.g. Pons *et al.* 2016; Debret *et al.* 2018, 2021) Zn isotopes do not fractionate in response to the addition of subducted slab-derived fluids, melts, or sediments to a degree that these effects are recorded in erupted lavas.
- ii) Zinc isotopes cannot be used to trace sulphate and/or carbonate fluxes from the slab through subduction zones
- iii) Mantle heterogeneity and melt mixing may cause significant $\delta^{66}\text{Zn}$ fractionation.

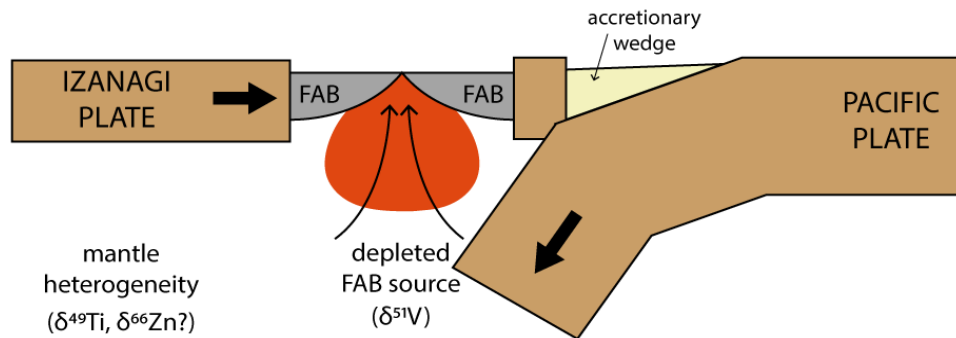
Chapter six presented new Ti and V isotopic measurements of 9 FABs and 11 of the boninites from Chapters four and five, and is the first combined V-Ti isotopic study of Earth materials. The precision of Ti and V isotope measurements has only recently been sufficient to apply to high-temperature geologic systems, therefore existing $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ arc lava data is limited (Millet *et al.* 2016; Prytulak *et al.* 2017; Hoare *et al.* 2020). The comparison of FAB and boninite $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ allowed the effects of source $f\text{O}_2$, magmatic processes, and the addition of slab-derived fluids, melts, and sediments to be determined. Comparisons of $\delta^{51}\text{V}$, $\delta^{49}\text{Ti}$, ϵHf , major and trace element data, and glass $\text{Fe}^{3+}/\Sigma\text{Fe}$, plus Ti concentration melt modelling led to the following results:

- i) Vanadium isotopes have the potential to trace source depletion in igneous rocks devoid of significant oxide crystallisation, and may be a more sensitive tracer than Fe isotopes.
- ii) Vanadium isotopes may also respond to changes in source $f\text{O}_2$ in subduction zones, causing $\delta^{51}\text{V}$ fractionation in the opposite direction to source depletion.
- iii) The mantle may be heterogenous in Ti isotopes.
- iv) Vanadium and Ti isotopes may be mobilised and fractionated by halogen-rich slab-derived fluids.

Chapters four, five, and six contributed significantly to our understanding of subduction zone geochemistry, and how V, Ti, Fe, and Zn isotopes fractionate in response to different magmatic and

subduction-related processes. **Figure 7.1** summarises the processes that this thesis suggests $\delta^{51}\text{V}$, $\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$, and $\delta^{49}\text{Ti}$ are sensitive to during subduction. Vanadium and Fe isotopes are both suggested to be sensitive to source depletion, however, **Figure 7.2** shows that $\delta^{51}\text{V}$ and $\delta^{56}\text{Fe}$ do not covary. The lack of covariation may be related to Fe being a major element in most rock-forming minerals, compatible, and fluid mobile, meaning there are a myriad of processes that may fractionate $\delta^{56}\text{Fe}$.

(a) Fore-arc basalt (FAB) formation:



(b) Boninite formation:

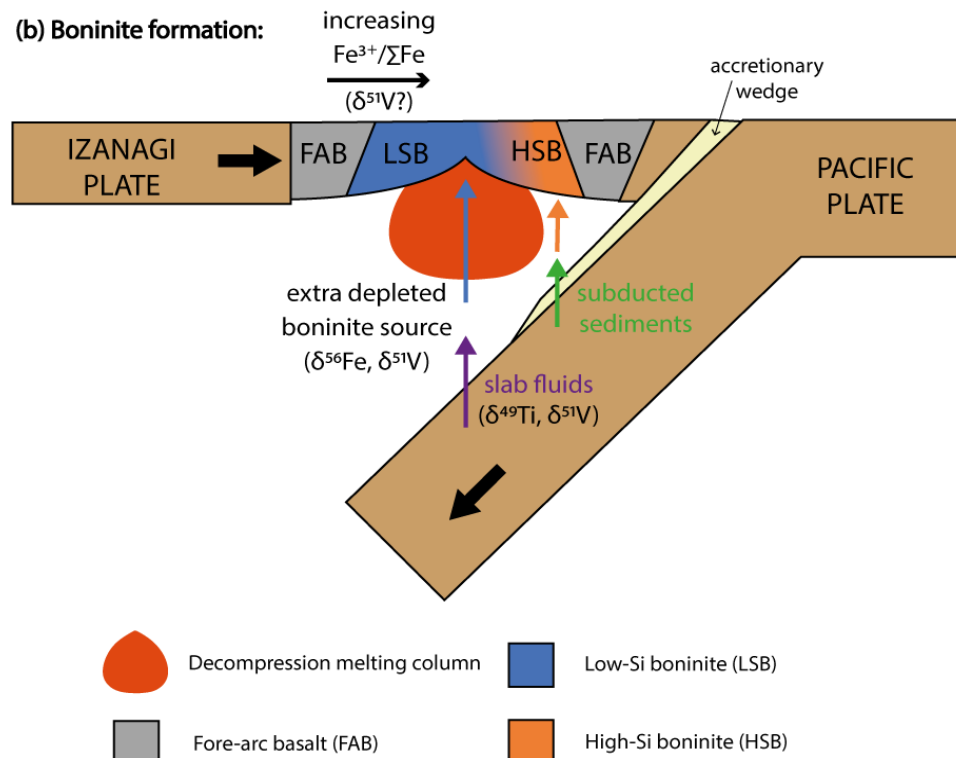


Figure 7.1: Schematic sketches of FAB and boninite formation outlining the magmatic processes that are suggested to fractionate V, Ti, Fe, and Zn isotopes in this study (see Chapters four, five, and six). The isotope systems in brackets beneath each magmatic or subduction-related process indicates the isotope system(s) that are suggested to be influenced by that process according to data from this study.

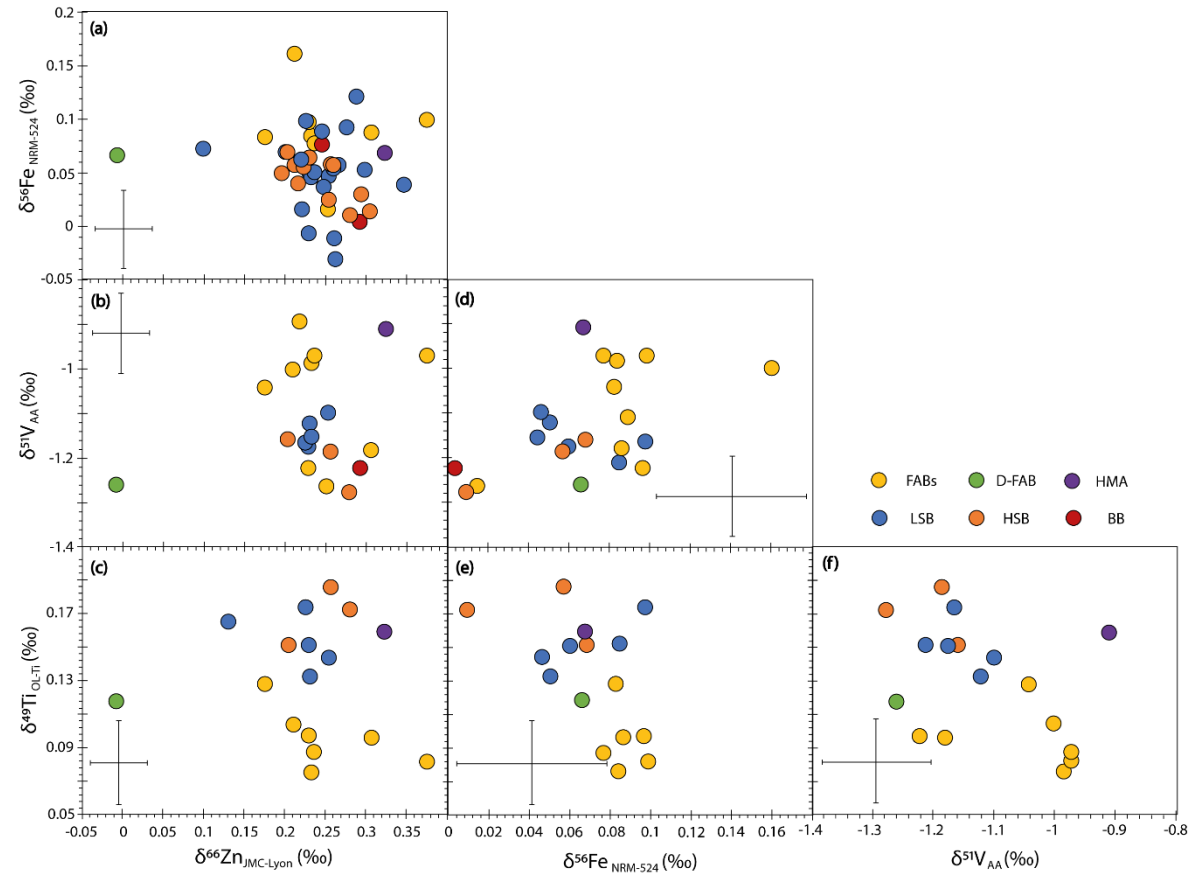


Figure 7.2: Compilation of $\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$, $\delta^{51}\text{V}$, and $\delta^{49}\text{Ti}$ versus each other for the IODP Expedition 352 FABs and boninites from Chapters four, five, and six. The average $\delta^{56}\text{Fe}$ error is $\pm 0.037 \text{ ‰}$ (2SD), the average $\delta^{66}\text{Zn}$ error is $\pm 0.027 \text{ ‰}$ (2SD), the average $\delta^{51}\text{V}$ error is $\pm 0.09 \text{ ‰}$ (2SD), and the average $\delta^{49}\text{Ti}$ error is $\pm 0.025 \text{ ‰}$ (95% c.i.).

There are several areas where future work could further improve our understanding of the controls on V, Ti, Fe, and Zn stable isotope fractionation.

- *Determine the $\delta^{51}\text{V}$, $\delta^{49}\text{Ti}$, $\delta^{56}\text{Fe}$, and $\delta^{66}\text{Zn}$ of E-FABs*

One of the limitations of Chapters four, five, and six is that the FAB sample size is limited and only the N-FAB, P-FAB, and D-FAB FAB sub-types were represented due to sample availability. The enriched FAB (E-FAB) sub-type is also of particular interest. Chapter five suggested that partial melting is likely responsible for the observed large FAB $\delta^{66}\text{Zn}$ range. However, Zn isotopic melt models cannot account for the observed FAB $\delta^{66}\text{Zn}$ range by partial melting alone. D-FAB is isotopically the lightest and suggested to reflect mantle heterogeneity, sampling an isotopically light, potentially olivine-rich source. Therefore, to further examine the cause of the large FAB $\delta^{66}\text{Zn}$ range, enriched FAB (E-FAB) samples from the Bonin forearc should be measured for Zn isotopes. If E-FAB $\delta^{66}\text{Zn}$ is the heaviest of the measured FAB data, it could suggest that the FAB $\delta^{66}\text{Zn}$ variation is controlled by mantle heterogeneity with the E-FAB sampling an isotopically lighter mantle lithology, complementary to the proposed isotopically light olivine-rich D-FAB source. In addition, $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ measurements of E-FAB may provide more evidence to support the respective source depletion and mantle heterogeneity explanations for $\delta^{51}\text{V}$ and $\delta^{49}\text{Ti}$ FAB-MORB differences.

- *Measure $\text{Fe}^{3+}/\Sigma\text{Fe}$ in FAB and boninite samples from this study*

Chapter six suggested that the $\delta^{51}\text{V}$ similarity between FABs and boninites, despite boninites having a more depleted source, may be related to the boninites being more oxidised. In Chapter three heavier $\delta^{51}\text{V}$ was suggested to be associated with higher $f\text{O}_2$, suggesting that more oxidised conditions could offset fractionation due to source depletion and slab-fluid $\delta^{51}\text{V}$ effects. However, there is no $\text{Fe}^{3+}/\Sigma\text{Fe}$ or $f\text{O}_2$ data on the samples used in Chapter six; the only $\text{Fe}^{3+}/\Sigma\text{Fe}$ data is on glass from different sections of the cores. To better determine if different $f\text{O}_2$ contributed to the lack of $\delta^{51}\text{V}$ difference between FABs and boninites, $\text{Fe}^{3+}/\Sigma\text{Fe}$ and $f\text{O}_2$ should be determined on the samples measured in Chapter six to allow a direct comparison of $\delta^{51}\text{V}$ and $f\text{O}_2$.

- *Measure $\delta^{49}\text{Ti}$ in samples from the subcontinental lithospheric mantle*

There are no clear geochemical correlations with FAB $\delta^{49}\text{Ti}$ in Chapter six, and the current best explanation for the statistically significant FAB-MORB $\delta^{49}\text{Ti}$ difference is mantle heterogeneity. However, previous Ti isotope studies have suggested that the mantle is homogeneous in $\delta^{49}\text{Ti}$ (Millet *et al.* 2016). These suggestions are however based on very limited $\delta^{49}\text{Ti}$ literature.

Therefore, to better assess mantle $\delta^{49}\text{Ti}$ heterogeneity and the cause of the heavy FAB $\delta^{49}\text{Ti}$, the $\delta^{49}\text{Ti}$ of subcontinental lithospheric mantle from various locations should be assessed.

References

- Creighton, S., Stachel, T., Eichenberg, D. & Luth, R.W. 2010. Oxidation state of the lithospheric mantle beneath Diavik diamond mine, central Slave craton, NWT, Canada. *Contributions to Mineralogy and Petrology*, **159**, 645–657, <https://doi.org/10.1007/s00410-009-0446-x>.
- Dauphas, N., Craddock, P.R., Asimow, P.D., Bennett, V.C., Nutman, A.P. & Ohnenstetter, D. 2009. Iron isotopes may reveal the redox conditions of mantle melting from Archean to Present. *Earth and Planetary Science Letters*, **288**, 255–267, <https://doi.org/10.1016/j.epsl.2009.09.029>.
- Debret, B., Bouilhol, P., Pons, M.L. & Williams, H. 2018. Carbonate transfer during the onset of slab devolatilization: New insights from Fe and Zn stable isotopes. *Journal of Petrology*, **59**, 1145–1166, <https://doi.org/10.1093/petrology/egy057>.
- Debret, B., Garrido, C.J., Pons, M.L., Bouilhol, P., Inglis, E., López Sánchez-Vizcaíno, V. & Williams, H. 2021. Iron and zinc stable isotope evidence for open-system high-pressure dehydration of antigorite serpentinite in subduction zones. *Geochimica et Cosmochimica Acta*, **296**, 210–225, <https://doi.org/10.1016/j.gca.2020.12.001>.
- Foden, J., Sossi, P.A. & Nebel, O. 2018. Controls on the iron isotopic composition of global arc magmas. *Earth and Planetary Science Letters*, **494**, 190–201, <https://doi.org/10.1016/j.epsl.2018.04.039>.
- Hoare, L., Klaver, M., Saji, N.S., Gillies, J., Parkinson, I.J., Lissenberg, C.J. & Millet, M.A. 2020. Melt chemistry and redox conditions control titanium isotope fractionation during magmatic differentiation. *Geochimica et Cosmochimica Acta*, **282**, 38–54, <https://doi.org/10.1016/j.gca.2020.05.015>.
- Huang, J., Zhang, X.C., Chen, S., Tang, L., Wörner, G., Yu, H. & Huang, F. 2018. Zinc isotopic systematics of Kamchatka-Aleutian arc magmas controlled by mantle melting. *Geochimica et Cosmochimica Acta*, **238**, 85–101, <https://doi.org/10.1016/j.gca.2018.07.012>.
- Millet, M.A., Dauphas, N., Greber, N.D., Burton, K.W., Dale, C.W., Debret, B., Macpherson, C.G., Nowell, G.M. & Williams, H.M. 2016. Titanium stable isotope investigation of magmatic processes on the Earth and Moon. *Earth and Planetary Science Letters*, **449**, 197–205, <https://doi.org/10.1016/j.epsl.2016.05.039>.
- Nebel, O., Sossi, P.A., Bénard, A., Wille, M., Vroon, P.Z. & Arculus, R.J. 2015. Redox-variability and controls in subduction zones from an iron-isotope perspective. *Earth and Planetary Science Letters*, **432**, 142–151, <https://doi.org/10.1016/j.epsl.2015.09.036>.
- Pons, M.-L., Debret, B., Bouilhol, P., Delacour, A. & Williams, H. 2016. Zinc isotope evidence for sulfate-rich fluid transfer across subduction zones. *Nature Communications*, **7**, <https://doi.org/10.1038/ncomms13794>.

- Prytulak, J., Sossi, P.A., Halliday, A.N., Plank, T., Savage, P.S. & Woodhead, J.D. 2017. Stable vanadium isotopes as a redox proxy in magmatic systems? *Geochemical Perspectives Letters*, **3**, 75–84, <https://doi.org/10.7185/geochemlet.1708>.
- Williams, H.M., Prytulak, J., Woodhead, J.D., Kelley, K.A., Brounce, M. & Plank, T. 2018. Interplay of crystal fractionation, sulfide saturation and oxygen fugacity on the iron isotope composition of arc lavas: An example from the Marianas. *Geochimica et Cosmochimica Acta*, **226**, 224–243, <https://doi.org/10.1016/j.gca.2018.02.008>.
- Yaxley, G.M., Berry, A.J., Rosenthal, A., Woodland, A.B. & Paterson, D. 2017. Redox preconditioning deep cratonic lithosphere for kimberlite genesis - Evidence from the central Slave Craton. *Scientific Reports*, **7**, 1–10, <https://doi.org/10.1038/s41598-017-00049-3>.

Appendix A - Major Element Oxide Concentration Data for Chapter Three Mineral Separates (Yaxley et al. 2017)

Diavik Garnet Lherzolite Mineral Separate Major Element Oxide Concentrations (wt%)													
Sample	Mineral	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃	FeO	MnO	NiO	MgO	CaO	Na ₂ O	Total
052	Gnt	41.76	0.56	16.97	7.79	0.80	6.62	0.36	0.01	20.26	6.25	0.06	101.44
	Cpx	55.38	0.15	1.24	1.30		2.84	0.11	0.06	18.14	19.66	1.25	100.12
	Opx	57.96	0.08	0.56	0.34		5.07	0.10	0.15	33.50	0.87	0.13	98.76
	Olv	42.22			0.05		8.23	0.11	0.40	50.49	0.04		101.53
108	Gnt	42.23	0.26	18.06	7.11	0.44	6.19	0.33	0.01	21.07	5.88	0.04	101.62
	Cpx	54.59	0.05	1.22	1.32		2.15	0.12	0.06	18.66	19.58	1.31	99.06
	Opx	57.75	0.03	0.53	0.30		4.31	0.13	0.12	35.58	0.71	0.12	99.57
	Olv	42.64			0.04		7.26	0.09	0.40	51.33	0.04		101.81
147	Gnt	42.10	0.30	17.57	7.70	0.47	5.95	0.33	0.01	20.91	6.08	0.04	101.44
	Cpx	54.76	0.05	1.07	1.19		2.08	0.09	0.06	18.34	20.23	0.94	98.82
	Opx	58.20	0.03	0.51	0.28		4.25	0.11	0.11	35.04	0.71	0.09	99.33
	Olv	40.64			0.04		7.11	0.08	0.36	50.03	0.04		98.30
422	Gnt	42.76	0.55	21.60	1.77	0.63	7.59	0.32	0.01	21.82	4.32	0.10	101.48
	Cpx	55.73	0.23	2.15	0.76		3.44	0.10	0.06	18.00	18.67	1.64	100.78
	Opx	58.59	0.12	0.72	0.14		5.82	0.11	0.12	34.26	0.86	0.20	100.95
	Olv	41.55			0.02		9.34	0.11	0.40	49.64	0.04		101.09
448	Gnt	41.97	0.03	20.04	5.25	0.19	7.78	0.45	0.00	19.95	5.79	0.03	101.48
	Cpx	57.09	0.00	1.98	2.00		1.42	0.06	0.04	15.81	22.73	1.97	103.09
	Opx	58.55	0.00	0.41	0.19		4.48	0.08	0.10	34.66	0.22	0.04	98.73
	Olv	42.57			0.01		7.02	0.08	0.39	51.56	0.01		101.63
450	Gnt	41.44	0.41	15.54	9.80	0.80	6.41	0.37	0.01	19.60	6.95	0.05	101.38
	Cpx	55.06	0.07	1.06	1.67		2.68	0.10	0.08	18.30	19.57	1.52	100.11
	Opx	58.04	0.05	0.55	0.40		5.08	0.11	0.14	34.83	0.79	0.16	100.14
	Olv	41.30			0.05		8.00	0.11	0.41	51.24	0.05		101.17
714	Gnt	41.95	0.74	18.13	5.95	0.92	7.08	0.34	0.01	20.72	5.67	0.08	101.61
	Cpx	55.85	0.20	1.54	1.25		3.37	0.11	0.06	18.82	17.70	1.43	100.33
	Opx	58.69	0.12	0.67	0.29		5.66	0.13	0.13	34.97	0.92	0.18	101.75
	Olv	41.62			0.04		9.59	0.08	0.40	48.52	0.07		100.32
1034	Gnt	42.62	0.27	19.45	5.29	0.60	6.57	0.33	0.01	21.51	5.24	0.05	101.93
	Cpx	55.15	0.05	1.38	1.19		2.68	0.09	0.06	18.41	19.74	1.45	100.21
	Opx	58.06	0.03	0.59	0.27		5.10	0.10	0.13	34.98	0.75	0.14	100.16
	Olv	41.25			0.04		7.97	0.10	0.39	51.28	0.04		101.08

Appendix B - Trace Element Concentration Data for Chapter Three Mineral Separates (Yaxley et al. 2017)

Diavik Garnet Lherzolite Mineral Separate Trace Element Concentrations ($\mu\text{g.g}^{-1}$)																
Sample	052		108		147		422		448		450		714		1034	
Mineral	Gnt	Cpx	Gnt	Cpx	Gnt	Cpx	Gnt	Cpx	Gnt	Cpx	Gnt	Cpx	Gnt	Cpx	Gnt	Cpx
P	92	12	116	10	211	25	298	137	74	33	162		182	31	107	17
Sc	147	16	123	10	124	10	84	16	116	16	171		108	15	107	11
Ti	2664	694	1364	214	1881	298	3686	1307	182	56	2523		4529	1083	1647	249
V	350	184	325	149	348	156	247	244	253	362	355		324	201	303	187
Co	46	27	44	21	37	22	55	28	40	15	43		47	29	46	26
Ni	86	474	74	385	67	402	95	457	16	275	83		103	484	81	450
Ga	7.59	3.06	5.66	1.74	6.39	2.10	16.14	8.42	3.57	4.24	8.64		12.3	5.44	11.1	3.31
Rb	0.27	0.08	0.04	0.06	0.02	0.60		2.33	0.07	0.28			0.37	0.28	0.01	0.03
Sr	0.65	141	0.47	131	1.40	279	0.34	141	0.12	167	1.35		0.73	119	0.37	127
Y	4.76	0.55	7.13	0.38	9.67	0.51	19.50	3.40	1.70	0.30	5.01		15.74	1.91	11.75	0.87
Zr	19.7	1.26	20.7	0.88	47.7	1.69	36.8	8.01	1.60	4.47	23.5		51.7	4.12	22.3	1.34
Nb	1.05	0.43	1.12	0.56	1.44	1.06	0.40	3.57	0.42	1.27	1.19		0.84	1.05	0.87	0.36
Cs		bdl		bdl		0.02		0.08		0.00				0.03		bdl
Ba	0.22	1.18	0.19	2.80	2.68	8.95		25.0	0.64	19.2	16.5		0.69	5.92	1.02	1.42
La	0.05	1.82	0.04	1.72	0.25	3.38	0.03	5.59	0.03	21.32	0.16		0.05	2.19	0.03	2.14
Ce		6.39	0.53	6.69	1.38	12.8	0.24	14.30	0.16	43.19	0.92		0.48	7.12	0.37	6.88
Pr	0.20	1.02	0.19	1.09	0.46	2.18	0.09	2.00	0.03	4.08	0.29		0.16	1.16	0.13	1.05
Nd	1.64	4.28	1.65	4.29	3.81	8.85	0.87	8.66	0.14	11.39	2.41		1.52	5.30	1.15	4.47
Sm	0.83	0.68	0.80	0.52	1.61	1.05	0.72	1.74	0.08	1.06	1.25		1.08	1.13	0.71	0.75
Eu	0.32	0.18	0.32	0.14	0.55	0.23	0.36	0.51	0.03	0.29	0.47		0.52	0.34	0.31	0.21
Gd	0.96	0.38	1.12	0.32	1.74	0.46	1.47	1.35	0.13	0.45	1.18		1.92	0.86	1.19	0.47
Tb	0.14	0.03	0.19	0.03	0.26	0.04	0.33	0.15	0.02	0.03	0.17		0.38	0.10	0.22	0.05
Dy	0.90	0.15	1.28	0.11	1.73	0.16	2.86	0.80	0.21	0.11	1.00		2.73	0.48	1.77	0.23
Ho	0.17	0.02	0.24	0.01	0.34	0.02	0.68	0.12	0.06	0.01	0.17		0.55	0.07	0.41	0.03
Er	0.46	0.05	0.67	0.03	0.99	0.04	2.15	0.28	0.23	0.02	0.51		1.57	0.16	1.35	0.07
Tm	0.07		0.09		0.14		0.33		0.05		0.07		0.23		0.21	
Yb	0.48	0.02	0.57	0.01	0.99	0.02	2.44	0.15	0.45	0.02	0.60		1.59	0.08	1.53	0.04
Lu	0.09	0.00	0.09	0.00	0.16	0.00	0.36	0.02	0.09	0.00	0.09		0.25	0.01	0.25	0.00
Hf	0.49	0.09	0.53	0.05	1.15	0.09	0.86	0.44	0.04	0.06	0.53		1.25	0.24	0.58	0.08
Ta	0.06	0.02	0.07	0.03	0.07	0.05	0.04	0.14	0.01	0.08	0.11		0.04	0.06	0.05	0.01
Pb	0.04	0.23	0.04	0.50	3.06	2.31	0.12	0.38	0.19	1.61	0.15		0.06	0.32	0.16	0.30
Th	0.01	0.11	0.02	0.04	0.05	0.09		0.19	0.01	0.97	0.05		0.01	0.08	0.01	0.02
U	0.03	0.01	0.03	0.01	0.06	0.02	0.03	0.07	0.01	0.15	0.05		0.02	0.02	0.02	0.01

Appendix C - Chapters Four, Five and Six Trace Element Data obtained from Open University and Labs A, C, D, E are from Godard et al. (in prep)

			Trace Element Concentrations (µg.g ⁻¹)																																				
Sample	Type	Source	Li	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Sn	Sb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Lu	Hf	Ta	Tl	Pb	Th	U
U1439 - Boninites																																							
U1439C 16R1-26/30	LSB	OU	8.81	26.98	136.8	343.91	978	43.47	312	48.38	43.75	8.51	113.59	7.14	29.46	0.48	0.14	0.09	0.12	17.85	0.83	2.51	0.39	2.20	0.75	0.27	0.95	0.17	1.13	0.26	0.74	0.74	0.11	0.79	0.06	0.11	0.95	0.06	0.04
U1439C 22R1-89/95	LSB	OU	11.71	28.88	135.6	535.97	988	48.42	368	52.72	45.58	8.78	105.70	7.55	29.22	0.45	0.23	0.07	0.13	12.52	0.84	2.62	0.42	2.40	0.83	0.30	1.07	0.19	1.21	0.27	0.78	0.77	0.12	0.78	0.04	0.12	0.69	0.05	0.04
U1439C 41R1-99/106	LSB	OU	10.36	39.04	186.3	554.66	973	39.30	164	83.29	45.12	0.87	116.25	12.50	31.31	0.49	0.32	0.02	0.02	6.59	0.98	3.21	0.55	3.29	1.19	0.45	1.61	0.29	1.94	0.44	1.25	1.23	0.19	0.88	0.07	0.01	0.33	0.05	0.02
U1439C-29R-4-W 78/82	LSB	OU	18.96	23.92	124.6	409.57	1617	63.07	618	38.03	47.78	2.10	64.70	5.05	21.93	0.37	0.14	0.05	0.06	2.90	0.57	1.65	0.27	1.51	0.52	0.19	0.66	0.12	0.80	0.19	0.54	0.55	0.09	0.57	0.03	0.01	0.60	0.05	0.05
U1439C-31R-5-W 12/17	LSB	OU	18.46	34.54	148.6	732.98	947	50.91	271	41.01	53.95	8.08	102.73	7.89	24.17	0.50	0.17	0.07	0.29	13.62	0.74	2.18	0.37	2.14	0.76	0.28	1.00	0.18	1.21	0.28	0.80	0.80	0.12	0.67	0.04	0.04	0.44	0.04	0.13
U1439C 19R4 11/17	LSB	OU	58.20	27.70	142.3	465.40	1013		361	51.90	59.30	4.21	123.10	8.17	29.55	0.48			0.09	4.32	0.95	2.62	0.44	2.40	0.82	0.31	1.03	0.19	1.21	0.28	0.80	0.92	0.13	0.80	0.03		0.80	0.05	0.07
U1439C 40R1 33/38	LSB	OU	25.10	33.30	164.4	191.50	1134	29.20	65	24.20	66.80	13.51	145.66	9.27	28.73	0.61			0.06	78.20	1.18	3.21	0.53	2.82	0.93	0.36	1.19	0.22	1.44	0.33	0.94	0.97	0.15	0.77	0.04		0.91	0.08	0.11
U1439C 31R1 15/20	LSB	OU	8.40	24.40	132.3	427.40		48.90	439	55.40	48.10	7.13	99.84	5.31	21.82	0.46			0.19	14.99	0.65	1.60	0.26	1.38	0.46	0.19	0.67	0.12	0.82	0.18	0.53	0.56	0.09	0.60	0.03		0.66	0.05	0.05
U1439C 26R1 132/137	LSB	OU	49.00	26.00	133.2	472.90	859	63.30	448	21.80	54.00	5.57	102.19	6.95	26.79	0.46			0.10	3.45	0.87	2.46	0.40	2.21	0.73	0.26	0.95	0.17	1.06	0.24	0.68	0.65	0.10	0.71	0.04		0.65	0.05	0.11
U1439C 19R3 58/62	LSB	OU	14.20	28.20	131.1	431.10	979	46.90	351	51.40	79.70	9.99	117.26	7.80	29.60	0.52			0.15	16.62	0.82	2.54	0.41	2.25	0.77	0.28	1.01	0.19	1.16	0.26	0.77	0.78	0.12	0.79	0.04		0.82	0.06	0.05
U1439C 11R1 124/127	LSB	OU	42.90	30.40	137.3	473.70	1688	57.80	504	38.00	58.80	6.12	64.01	6.87	24.07	0.45			0.08	4.26	0.53	1.90	0.32	1.89	0.70	0.26	0.94	0.17	1.08	0.25	0.69	0.65	0.10	0.68	0.05		0.48	0.04	0.06
U1439C 33R2-W 23/30	LSB	Lab A	39.20	23.20	128.7		906	48.50	464	36.60	46.20	2.07	101.82	5.27	23.84	0.40			0.07	11.62	0.64	1.75	0.30	1.56	0.51	0.21	0.74	0.13	0.87	0.19	0.53	0.55	0.08	0.76	0.04		0.66	0.04	0.04
U1439C 38R1 103/106	LSB	Lab E	18.50	29.40	176.5	194.80	945	33.30	82	106.90	51.40	1.78	161.97	8.71	35.55	0.58			0.02	7.37	0.95	2.92	0.46	2.47	0.85	0.32	1.10	0.20	1.29	0.30	0.86	0.87	0.14	0.95	0.04		1.21	0.10	0.08
U1439C 27R3-W 80/87	LSB	Lab A	17.30	24.50	125.5		915	50.30	432	50.80	48.10	5.00	108.75	5.20	20.49	0.40			0.10	9.50	0.78	1.95	0.32	1.69	0.53	0.20	0.71	0.12	0.82	0.19	0.54	0.58	0.09	0.58			0.71	0.05	0.04
U1439C 23R1-W 42/48	LSB	Lab A	18.80	32.00	162.3		1009	46.50	350	66.40	61.50	13.70	76.29	7.59	31.77	0.57			0.13	17.12	0.70	2.66	0.39	2.16	0.79	0.31	1.07	0.20	1.32	0.29	0.82	0.84	0.13	0.84	0.04		0.77	0.06	0.04
U1439C 28R2-W 66/71	LSB	Lab C	19.80	26.30	98.4	338.10		45.60	421	49.80	39.60	6.06	107.72	5.29	23.12				0.15	6.83	0.78	2.06	0.34	1.79	0.58	0.21	0.68	0.13	0.84	0.17	0.53	0.59	0.10	0.63			1.24	0.05	0.04
U1439C-10R2-W 13/19	BB	OU	16.08	35.07	179.6	479.49	965	50.49	226	33.65	60.31	9.25	100.09	9.44	29.82	0.54	0.26	0.29	0.14	10.69	0.99	2.94	0.48	2.83	0.97	0.35	1.30	0.23	1.49	0.34	0.95	0.87	0.13	0.83	0.04	0.07	0.64	0.05	0.12
U1439C-37R1-W 42/48	HMA	OU	6.87	30.03	185.3	67.50	476	26.74	33	64.55	36.52	2.50	174.61	9.15	33.57	0.58	0.19	0.03	0.02	16.78	1.30	3.63	0.56	3.07	1.01	0.37	1.26	0.22	1.45	0.33	0.94	0.90	0.14	0.93	0.04	0.01	0.66	0.10	0.09
U1439C 4R1-W 26/32	HSB	OU	9.38	29.68	145.5	560.78	1053	41.55	232	56.30	49.18	17.84	123.29	5.25	32.06	0.56	0.14	0.26	0.60	25.60	1.01	2.42	0.35	1.81	0.55	0.19	0.67	0.12	0.81	0.18	0.56	0.63	0.10	0.85	0.98	0.64	1.23	0.12	0.10
U1439C 6R1 25/30	HSB	OU	10.00	30.30	156.4	413.00	996	35.20	132	59.00	61.50	17.06	125.03	5.76	33.80	0.65			0.60	28.23	1.12	2.64	0.39	1.92	0.56	0.19	0.71	0.13	0.81	0.19	0.57	0.63	0.11	0.90	0.06		1.43	0.13	0.11
U1439C 2R3-W 38/46	HSB	Lab A	5.50	28.80	154.7		1034	49.70	342	59.50	54.40	11.79	77.15	4.15	21.30				0.47	20.54	0.82	1.79	0.27	1.32	0.41	0.16	0.54	0.09	0.64	0.14	0.43	0.51	0.08	0.69			1.02	0.10	0.09
U1439A 23X1-W 0/3	HSB	Lab A	9.60	29.40	154.8		1156	54.90	371	186.90	112.50	12.44	74.47	3.44	17.79	0.52			0.46	18.08	0.77	1.63	0.24	1.17	0.35	0.13	0.44	0.08	0.54	0.12	0.38	0.47	0.08	0.53	0.05		0.97	0.11	0.08
U1439A 21X1-W 0/7	HSB	Lab A	10.30	29.40	158.9		1118	57.90	346	58.30	75.20	13.24	78.48	3.64	19.04	0.52			0.50	19.02	0.78	1.68	0.25	1.21	0.35	0.13	0.46	0.08	0.57	0.13	0.41	0.48	0.08	0.57					

Appendix D - Vanadium Isotope Data

Sample Name	Type	Batch	Location	Date	Method	Sequence	RSE	RSD	$\delta^{51}\text{V}_{\text{AA}} (\text{‰})$	2SD	n
052 Gnt	garnet mineral separate	1	Imperial	07/12/2017	Nu II MC-ICP MS	10176	15	67	-1.21		
052 Gnt	garnet mineral separate	1	Durham	06/12/2018	Neptune MC-ICP MS	84		43	-1.21		
052 Gnt	garnet mineral separate	1	Durham	06/12/2018	Neptune MC-ICP MS	173		104	-1.27		
052 Gnt	garnet mineral separate	1	Durham	28/01/2019	Neptune MC-ICP MS	9		39	-1.26		
052 Gnt	garnet mineral separate	1	Durham	19/02/2019	Neptune MC-ICP MS	101		19	-1.28		
052 Gnt average									-1.25	0.07	5
108 Gnt	garnet mineral separate	1	Imperial	13/12/2017	Nu II MC-ICP MS	10625	16	41	-1.54		
108 Gnt	garnet mineral separate	1	Durham	06/12/2018	Neptune MC-ICP MS	90		61	-1.48		
108 Gnt	garnet mineral separate	1	Durham	06/12/2018	Neptune MC-ICP MS	179		173	-1.50		
108 Gnt	garnet mineral separate	1	Durham	28/01/2019	Neptune MC-ICP MS	15		48	-1.57		
108 Gnt	garnet mineral separate	1	Durham	19/02/2019	Neptune MC-ICP MS	131		32	-1.58		
108 Gnt - digestion 1 average									-1.53	0.09	5
108 Gnt	garnet mineral separate	2	Durham	26/11/2019	Neptune MC-ICP MS	6		87	-1.54		
108 Gnt	garnet mineral separate	2	Durham	26/11/2019	Neptune MC-ICP MS	21		69	-1.46		
108 Gnt	garnet mineral separate	2	Durham	26/11/2019	Neptune MC-ICP MS	48		46	-1.38		
108 Gnt	garnet mineral separate	2	Durham	27/11/2019	Neptune MC-ICP MS	104		67	-1.44		
108 Gnt - digestion 2 average									-1.46	0.14	4
108 Gnt average									-1.50	0.13	9
422 Gnt	garnet mineral separate	1	Imperial	09/12/2017	Nu II MC-ICP MS	10360	18	81	-1.52		
422 Gnt	garnet mineral separate	1	Imperial	13/12/2017	Nu II MC-ICP MS	10631	11	64	-1.65		
422 Gnt	garnet mineral separate	1	Durham	06/12/2018	Neptune MC-ICP MS	96		63	-1.43		
422 Gnt	garnet mineral separate	1	Durham	06/12/2018	Neptune MC-ICP MS	185		36	-1.60		
422 Gnt	garnet mineral separate	1	Durham	28/01/2019	Neptune MC-ICP MS	21		79	-1.50		
422 Gnt average									-1.54	0.17	5
714 Gnt	garnet mineral separate	1	Imperial	09/12/2017	Nu II MC-ICP MS	10368	16	70	-1.70		
714 Gnt	garnet mineral separate	1	Imperial	13/12/2017	Nu II MC-ICP MS	10637	15	55	-1.76		
714 Gnt	garnet mineral separate	1	Imperial	13/12/2017	Nu II MC-ICP MS	10699	10	80	-1.68		
714 Gnt	garnet mineral separate	1	Durham	06/12/2018	Neptune MC-ICP MS	191		69	-1.65		
714 Gnt	garnet mineral separate	1	Durham	28/01/2019	Neptune MC-ICP MS	27		55	-1.58		
714 Gnt	garnet mineral separate	1	Durham	19/02/2019	Neptune MC-ICP MS	125		35	-1.66		
714 Gnt average									-1.67	0.12	6
052 Cpx	clinopyroxene mineral separate	1	Durham	05/12/2018	Neptune MC-ICP MS	12		53	-1.30		
052 Cpx	clinopyroxene mineral separate	1	Durham	25/01/2019	Neptune MC-ICP MS	6		75	-1.36		
052 Cpx	clinopyroxene mineral separate	1	Durham	19/02/2019	Neptune MC-ICP MS	89		78	-1.35		
052 Cpx average									-1.34	0.07	3
108 Cpx	clinopyroxene mineral separate	2	Durham	27/11/2019	Neptune MC-ICP MS	9		22	-1.73		
108 Cpx average									-1.73		1
422 Cpx	clinopyroxene mineral separate	1	Durham	05/12/2018	Neptune MC-ICP MS	18		94	-1.46		
422 Cpx	clinopyroxene mineral separate	1	Durham	25/01/2019	Neptune MC-ICP MS	4		56	-1.43		
422 Cpx	clinopyroxene mineral separate	1	Durham	19/02/2019	Neptune MC-ICP MS	69		56	-1.56		
422 Cpx average									-1.48	0.14	3
714 Cpx	clinopyroxene mineral separate	1	Durham	05/12/2018	Neptune MC-ICP MS	24		57	-1.62		
714 Cpx	clinopyroxene mineral separate	1	Durham	06/12/2018	Neptune MC-ICP MS	113		42	-1.51		
714 Cpx	clinopyroxene mineral separate	1	Durham	06/12/2018	Neptune MC-ICP MS	211		48	-1.51		
714 Cpx	clinopyroxene mineral separate	1	Durham	25/01/2019	Neptune MC-ICP MS	10		77	-1.63		
714 Cpx	clinopyroxene mineral separate	1	Durham	19/02/2019	Neptune MC-ICP MS	75		32	-1.57		
714 Cpx average									-1.57	0.12	5
052	whole-rock lherzolite	1	Durham	18/02/2019	Neptune MC-ICP MS	15		32	-1.05		
052	whole-rock lherzolite	1	Durham	19/02/2019	Neptune MC-ICP MS	33		45	-1.12		
052 - digestion 1 average									-1.08	0.10	2

Appendix D - Vanadium Isotope Data

052	whole-rock lherzolite	2	Durham	08/09/2020	Neptune MC-ICP MS	69		77	-1.44			
052	whole-rock lherzolite	2	Durham	09/09/2020	Neptune MC-ICP MS	110		43	-1.49			
052	whole-rock lherzolite	2	Durham	09/09/2020	Neptune MC-ICP MS	146		44	-1.47			
052	whole-rock lherzolite	2	Durham	09/09/2020	Neptune MC-ICP MS	69		72	-1.44			
052	whole-rock lherzolite	2	Durham	10/09/2020	Neptune MC-ICP MS	110		58	-1.38			
052 - digestion 2 average									-1.44	0.08	5	
052	whole-rock lherzolite	3	Durham	08/09/2020	Neptune MC-ICP MS	81		54	-1.23			
052	whole-rock lherzolite	3	Durham	09/09/2020	Neptune MC-ICP MS	122		30	-1.36			
052	whole-rock lherzolite	3	Durham	09/09/2020	Neptune MC-ICP MS	158		20	-1.32			
052	whole-rock lherzolite	3	Durham	09/09/2020	Neptune MC-ICP MS	81		5	-1.30			
052	whole-rock lherzolite	3	Durham	10/09/2020	Neptune MC-ICP MS	122		40	-1.32			
052 - digestion 3 average									-1.30	0.09	5	
052 average									-1.33	0.27	12	

108	whole-rock lherzolite	1	Durham	05/12/2018	Neptune MC-ICP MS	30		39	-1.22			
108	whole-rock lherzolite	1	Durham	06/12/2018	Neptune MC-ICP MS	119		40	-1.20			
108	whole-rock lherzolite	1	Durham	06/12/2018	Neptune MC-ICP MS	217		30	-1.23			
108	whole-rock lherzolite	1	Durham	25/01/2019	Neptune MC-ICP MS	9		46	-1.23			
108 - digestion 1 average									-1.22	0.02	4	
108	whole-rock lherzolite	2	Durham	08/09/2020	Neptune MC-ICP MS	24		66	-1.38			
108	whole-rock lherzolite	2	Durham	08/09/2020	Neptune MC-ICP MS	36		32	-1.41			
108	whole-rock lherzolite	2	Durham	09/09/2020	Neptune MC-ICP MS	24		7	-1.29			
108	whole-rock lherzolite	2	Durham	09/09/2020	Neptune MC-ICP MS	36		16	-1.43			
108 - digestion 2 average									-1.38	0.13	4	
108	whole-rock lherzolite	3	Durham	08/09/2020	Neptune MC-ICP MS	30		42	-1.34			
108	whole-rock lherzolite	3	Durham	08/09/2020	Neptune MC-ICP MS	42		42	-1.25			
108	whole-rock lherzolite	3	Durham	09/09/2020	Neptune MC-ICP MS	30		52	-1.26			
108	whole-rock lherzolite	3	Durham	09/09/2020	Neptune MC-ICP MS	42		70	-1.31			
108 - digestion 3 average									-1.29	0.09	4	
108 average									-1.30	0.15	12	

147	whole-rock lherzolite	1	Durham	19/02/2019	Neptune MC-ICP MS	15		44	-1.18			
147 - digestion 1 average									-1.18		1	
147	whole-rock lherzolite	2	Durham	18/02/2019	Neptune MC-ICP MS	57		32	-0.78			
147	whole-rock lherzolite	2	Durham	20/02/2019	Neptune MC-ICP MS	60		60	-0.92			
147 - digestion 2 average									-0.85	0.20	2	
147 average									-0.96	0.40	3	

422	whole-rock lherzolite	2	Durham	05/12/2018	Neptune MC-ICP MS	72		37	-1.20			
422	whole-rock lherzolite	2	Durham	06/12/2018	Neptune MC-ICP MS	161		84	-1.02			
422	whole-rock lherzolite	2	Durham	07/12/2018	Neptune MC-ICP MS	259		47	-0.98			
422	whole-rock lherzolite	2	Durham	18/02/2019	Neptune MC-ICP MS	33		36	-1.08			
422	whole-rock lherzolite	2	Durham	20/02/2019	Neptune MC-ICP MS	84		31	-1.11			
422 - digestion 2 average									-1.08	0.16	5	
422	whole-rock lherzolite	3	Durham	27/11/2019	Neptune MC-ICP MS	15		42	-1.57			
422 - digestion 3 average									-1.57		1	
422 average									-1.16	0.43	6	

448	whole-rock lherzolite	1	Durham	19/02/2019	Neptune MC-ICP MS	15		40	-1.47			
448	whole-rock lherzolite	2	Durham	06/12/2018	Neptune MC-ICP MS	78		98	-1.25			
448	whole-rock lherzolite	2	Durham	07/12/2018	Neptune MC-ICP MS	265		71	-1.37			
448 - digestion 2 average									-1.31	0.17	2	
448	whole-rock lherzolite	3	Durham	08/09/2020	Neptune MC-ICP MS	87		12	-1.61			
448	whole-rock lherzolite	3	Durham	09/09/2020	Neptune MC-ICP MS	128		47	-1.56			
448	whole-rock lherzolite	3	Durham	09/09/2020	Neptune MC-ICP MS	164		16	-1.59			
448	whole-rock lherzolite	3	Durham	09/09/2020	Neptune MC-ICP MS	87		37	-1.60			
448	whole-rock lherzolite	3	Durham	10/09/2020	Neptune MC-ICP MS	128		20	-1.60			
448 - digestion 3 average									-1.59	0.04	5	
448 average									-1.51	0.27	8	

Appendix D - Vanadium Isotope Data

450	whole-rock lherzolite	1	Durham	19/02/2019	Neptune MC-ICP MS	21		53	-1.21		
450 - digestion 1 average									-1.21		1
450	whole-rock lherzolite	2	Durham	20/02/2019	Neptune MC-ICP MS	72		36	-1.15		
450 - digestion 2 average									-1.15		2
450 average									-1.18	0.09	2

714	whole-rock lherzolite	1	Durham	19/02/2019	Neptune MC-ICP MS	9		52	-1.19		
714 - digestion 1 average									-1.19		1
714	whole-rock lherzolite	2	Durham	18/02/2019	Neptune MC-ICP MS	27		52	-0.86		
714 - digestion 2 average									-0.86		2
714	whole-rock lherzolite	3	Durham	27/11/2019	Neptune MC-ICP MS	3		53	-0.95		
714 - digestion 3 average									-0.95		1
714 average									-1.00	0.34	3

1034	whole-rock lherzolite	1	Durham	19/02/201	Neptune MC-ICP MS	33		25	-1.01		
1034 average									-1.01		1

031 kimberlite	whole-rock lherzolite	1	Durham	08/09/2020	Neptune MC-ICP MS	128		77	-1.27		
031 kimberlite	whole-rock lherzolite	1	Durham	09/09/2020	Neptune MC-ICP MS	134		29	-1.27		
031 kimberlite	whole-rock lherzolite	1	Durham	09/09/2020	Neptune MC-ICP MS	93		68	-1.31		
031 kimberlite - digestion 1 average									-1.29	0.04	3
031 kimberlite	whole-rock lherzolite	2	Durham	08/09/2020	Neptune MC-ICP MS	54		69	-1.25		
031 kimberlite	whole-rock lherzolite	2	Durham	09/09/2020	Neptune MC-ICP MS	48		52	-1.21		
031 kimberlite	whole-rock lherzolite	2	Durham	09/09/2020	Neptune MC-ICP MS	54		75	-1.27		
031 kimberlite - digestion 2 average									-1.24	0.06	3
031 kimberlite average									-1.26	0.07	6

Sample Name	Type	Batch	Location	Date	Method	Sequence	RSE	RSD	$\delta^{51}\text{V}_{\text{AA}} (\text{‰})$	2SD	n
U1440B-8R-1-W 20/23	whole-rock N-FAB	1	Durham	15/10/2020	Neptune MC-ICP MS	24	23	48	-1.27		
U1440B-8R-1-W 20/23	whole-rock N-FAB	1	Durham	16/10/2020	Neptune MC-ICP MS	90	18	29	-1.25		
U1440B-8R-1-W 20/23	whole-rock N-FAB	1	Durham	16/10/2020	Neptune MC-ICP MS	33	21	85	-1.29		
U1440B-8R-1-W 20/23	whole-rock N-FAB	1	Durham	16/10/2020	Neptune MC-ICP MS	27	24	71	-1.24		
U1440B-8R-1-W 20/23 average									-1.26	0.04	4

U1440B-29R-1-W 5/8	whole-rock N-FAB	1	Durham	14/10/2020	Neptune MC-ICP MS	30	17	17	-0.93		
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	Durham	15/10/2020	Neptune MC-ICP MS	30	22	51	-0.97		
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	Durham	16/10/2020	Neptune MC-ICP MS	96	18	55	-1.05		
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	Durham	16/10/2020	Neptune MC-ICP MS	36	19	81	-0.99		
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	Durham	16/10/2020	Neptune MC-ICP MS	30	17	96	-0.98		
U1440B-29R-1-W 5/8 average									-0.98	0.09	5

U1440B 26R-1-64/68	whole-rock N-FAB	1	Durham	24/01/2019	Neptune MC-ICP MS	39		36	-1.02		
U1440B 26R-1-64/68	whole-rock N-FAB	1	Durham	25/01/2019	Neptune MC-ICP MS	115		30	-1.04		
U1440B 26R-1-64/68	whole-rock N-FAB	1	Durham	29/01/2019	Neptune MC-ICP MS	125		21	-1.07		
U1440B 26R-1-64/68 average									-1.04	0.05	3

U1440B-17R-1-W 11/13	whole-rock N-FAB	1	Durham	13/03/2020	Neptune MC-ICP MS	15	19	41	-1.18		
U1440B-17R-1-W 11/13	whole-rock N-FAB	1	Durham	13/03/2020	Neptune MC-ICP MS	75	18	51	-1.23		
U1440B-17R-1-W 11/13	whole-rock N-FAB	1	Durham	14/03/2020	Neptune MC-ICP MS	140	18	97	-1.18		
U1440B-17R-1-W 11/13	whole-rock N-FAB	1	Durham	16/03/2020	Neptune MC-ICP MS	134	20	56	-1.13		
U1440B-17R-1-W 11/13 average									-1.18	0.08	4

U1440B 17R-2-23/32	whole-rock N-FAB	1	Durham	24/01/2019	Neptune MC-ICP MS	45		36	-0.96		
U1440B 17R-2-23/32	whole-rock N-FAB	1	Durham	25/01/2019	Neptune MC-ICP MS	121		55	-0.97		
U1440B 17R-2-23/32	whole-rock N-FAB	1	Durham	29/01/2019	Neptune MC-ICP MS	131		33	-0.98		
U1440B 17R-2-23/32 average									-0.97	0.02	3

U1440B-12R-2-W 4/8	whole-rock P-FAB	1	Durham	14/10/2020	Neptune MC-ICP MS	42	20	56	-1.19		

Appendix D - Vanadium Isotope Data

U1440B-12R-2-W 4/8	whole-rock P-FAB	1	Durham	15/10/2020	Neptune MC-ICP MS	42	26	62	-1.25			
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	Durham	16/10/2020	Neptune MC-ICP MS	119	21	75	-1.23			
U1440B-12R-2-W 4/8 average									-1.22	0.06	3	
U1440B 28R-1-31/38	whole-rock N-FAB	1	Durham	15/10/2020	Neptune MC-ICP MS	48	20	36	-0.95			
U1440B 28R-1-31/38	whole-rock N-FAB	1	Durham	16/10/2020	Neptune MC-ICP MS	122	19	69	-1.01			
U1440B 28R-1-31/38	whole-rock N-FAB	1	Durham	16/10/2020	Neptune MC-ICP MS	39	21	43	-0.97			
U1440B 28R-1-31/38	whole-rock N-FAB	1	Durham	16/10/2020	Neptune MC-ICP MS	36	22	52	-1.08			
U1440B 28R-1-31/38 average									-1.00	0.12	4	
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	Durham	15/10/2020	Neptune MC-ICP MS	54	23	75	-0.87			
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	Durham	16/10/2020	Neptune MC-ICP MS	125	21	66	-1.07			
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	Durham	16/10/2020	Neptune MC-ICP MS	18	19	41	-0.90			
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	Durham	16/10/2020	Neptune MC-ICP MS	24	17	94	-0.99			
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	Durham	16/10/2020	Neptune MC-ICP MS	27	19	75	-0.95			
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	Durham	16/10/2020	Neptune MC-ICP MS	18	27	74	-1.05			
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	Durham	16/10/2020	Neptune MC-ICP MS	21	23	67	-0.98			
U1441A-21R-1-W 37/42 average									-0.97	0.14	7	
U1441 A3 19R-1-66/72	whole-rock D-FAB	1	Durham	24/01/2019	Neptune MC-ICP MS	33		67	-1.22			
U1441 A3 19R-1-66/72	whole-rock D-FAB	1	Durham	25/01/2019	Neptune MC-ICP MS	109		21	-1.34			
U1441 A3 19R-1-66/72	whole-rock D-FAB	1	Durham	29/01/2019	Neptune MC-ICP MS	119		38	-1.34			
U1441 A3 19R-1-66/72 - digestion 1 average									-1.30	0.14	3	
U1441 A3 19R-1-66/72	whole-rock D-FAB	2	Durham	15/10/2020	Neptune MC-ICP MS	60	19	79	-1.19			
U1441 A3 19R-1-66/72	whole-rock D-FAB	2	Durham	16/10/2020	Neptune MC-ICP MS	131	24	31	-1.25			
U1441 A3 19R-1-66/72	whole-rock D-FAB	2	Durham	16/10/2020	Neptune MC-ICP MS	39	26	30	-1.23			
U1441 A3 19R-1-66/72 - digestion 2 average									-1.22	0.06	3	
U1441A-21R-1-W 37/42 average									-1.26	0.13	6	
U1439C 22R-1-89/95	whole-rock LSB	1	Durham	24/01/2019	Neptune MC-ICP MS	21		37	-1.31			
U1439C 22R-1-89/95	whole-rock LSB	1	Durham	25/01/2019	Neptune MC-ICP MS	92		15	-1.28			
U1439C 22R-1-89/95	whole-rock LSB	1	Durham	29/01/2019	Neptune MC-ICP MS	107		22	-1.36			
U1439C 22R-1-89/95 - digestion 1 average									-1.32	0.08	3	
U1439C 22R-1-89/95	whole-rock LSB	2	Durham	15/10/2020	Neptune MC-ICP MS	78	17	62	-1.17			
U1439C 22R-1-89/95	whole-rock LSB	2	Durham	16/10/2020	Neptune MC-ICP MS	78	25	53	-1.14			
U1439C 22R-1-89/95	whole-rock LSB	2	Durham	16/10/2020	Neptune MC-ICP MS	143	24	77	-1.21			
U1439C 22R-1-89/95 - digestion 2 average									-1.17	0.07	3	
U1439C 22R-1-89/95 average									-1.24	0.17	6	
U1442A 20R-1-104/108	whole-rock HSB	1	Durham	24/01/2019	Neptune MC-ICP MS	9		67	-1.23			
U1442A 20R-1-104/108	whole-rock HSB	1	Durham	25/01/2019	Neptune MC-ICP MS	80		45	-1.21			
U1442A 20R-1-104/108	whole-rock HSB	1	Durham	29/01/2019	Neptune MC-ICP MS	95		22	-1.23			
U1442A 20R-1-104/108 - digestion 1 average									-1.22	0.03	3	
U1442A 20R-1-104/108	whole-rock HSB	2	Durham	13/03/2020	Neptune MC-ICP MS	27	21	41	-1.30			
U1442A 20R-1-104/108	whole-rock HSB	2	Durham	13/03/2020	Neptune MC-ICP MS	87	17	14	-1.27			
U1442A 20R-1-104/108	whole-rock HSB	2	Durham	14/03/2020	Neptune MC-ICP MS	152	19	24	-1.26			
U1442A 20R-1-104/108	whole-rock HSB	2	Durham	16/03/2020	Neptune MC-ICP MS	140	21	60	-1.29			
U1442A 20R-1-104/108 - digestion 2 average									-1.28	0.04	4	
U1442A 20R-1-104/108 average									-1.26	0.06	7	
U1442A-35R-1 W 51/55	whole-rock LSB	1	Durham	15/10/2020	Neptune MC-ICP MS	66	18	95	-1.22			
U1442A-35R-1 W 51/55	whole-rock LSB	1	Durham	15/10/2020	Neptune MC-ICP MS	66	24	102	-1.18			
U1442A-35R-1 W 51/55	whole-rock LSB	1	Durham	16/10/2020	Neptune MC-ICP MS	134	17	57	-1.23			
U1442A-35R-1 W 51/55 average									-1.21	0.05	3	
U1442A 22R-1-122/125	whole-rock HSB	1	Durham	15/10/2020	Neptune MC-ICP MS	72	19	9	-1.11			
U1442A 22R-1-122/125	whole-rock HSB	1	Durham	16/10/2020	Neptune MC-ICP MS	72	21	98	-1.27			
U1442A 22R-1-122/125	whole-rock HSB	1	Durham	16/10/2020	Neptune MC-ICP MS	137	20	40	-1.17			
U1442A 22R-1-122/125	whole-rock HSB	1	Durham	16/10/2020	Neptune MC-ICP MS	45	22	48	-1.17			

Appendix D - Vanadium Isotope Data

U1442A 22R-1-122/125	whole-rock HSB	1	Durham	16/10/2020	Neptune MC-ICP MS	42	22	23	-1.07		
U1442A 22R-1-122/125 average									-1.16	0.15	5
U1439C-31R-5-W 12/17	whole-rock LSB	1	Durham	13/03/2020	Neptune MC-ICP MS	93	18	8	-1.13		
U1439C-31R-5-W 12/17	whole-rock LSB	1	Durham	14/03/2020	Neptune MC-ICP MS	158	22	61	-1.15		
U1439C-31R-5-W 12/17	whole-rock LSB	1	Durham	15/03/2020	Neptune MC-ICP MS	27	18	23	-1.18		
U1439C-31R-5-W 12/17 average									-1.15	0.06	3
U1439C-10R-2-W 13/19	whole-rock BB	1	Durham	13/03/2020	Neptune MC-ICP MS	39	19	81	-1.17		
U1439C-10R-2-W 13/19	whole-rock BB	1	Durham	13/03/2020	Neptune MC-ICP MS	99	22	25	-1.21		
U1439C-10R-2-W 13/19	whole-rock BB	1	Durham	14/03/2020	Neptune MC-ICP MS	164	21	22	-1.29		
U1439C-10R-2-W 13/19	whole-rock BB	1	Durham	15/03/2020	Neptune MC-ICP MS	69	22	51	-1.22		
U1439C-10R-2-W 13/19 average									-1.22	0.10	4
U1439C-37R-1-W 42/48	whole-rock HMA	1	Durham	13/03/2020	Neptune MC-ICP MS	45	17	44	-0.91		
U1439C-37R-1-W 42/48	whole-rock HMA	1	Durham	14/03/2020	Neptune MC-ICP MS	110	20	76	-0.95		
U1439C-37R-1-W 42/48	whole-rock HMA	1	Durham	14/03/2020	Neptune MC-ICP MS	170	19	36	-0.88		
U1439C-37R-1-W 42/48	whole-rock HMA	1	Durham	15/03/2020	Neptune MC-ICP MS	63	16	19	-0.90		
U1439C-37R-1-W 42/48 average									-0.91	0.06	4
U1439C-4R-1-W 26/32	whole-rock HSB	1	Durham	14/03/2020	Neptune MC-ICP MS	116	24	58	-1.18		
U1439C-4R-1-W 26/32	whole-rock HSB	1	Durham	14/03/2020	Neptune MC-ICP MS	176	20	23	-1.22		
U1439C-4R-1-W 26/32	whole-rock HSB	1	Durham	15/03/2020	Neptune MC-ICP MS	57	17	46	-1.15		
U1439C-4R-1-W 26/32 average									-1.19	0.08	3
U1439C 41R-1-99/106	whole-rock LSB	1	Durham	13/03/2020	Neptune MC-ICP MS	57	14	29	-1.07		
U1439C 41R-1-99/106	whole-rock LSB	1	Durham	14/03/2020	Neptune MC-ICP MS	122	21	79	-1.05		
U1439C 41R-1-99/106	whole-rock LSB	1	Durham	15/03/2020	Neptune MC-ICP MS	51	23	21	-1.14		
U1439C 41R-1-99/106	whole-rock LSB	1	Durham	16/03/2020	Neptune MC-ICP MS	99	13	48	-1.14		
U1439C 41R-1-99/106 average									-1.10	0.09	4
U1439C-29R-4-W 78/82	whole-rock LSB - cumulative	1	Durham	13/03/2020	Neptune MC-ICP MS	63	19	28	-1.08		
U1439C-29R-4-W 78/82	whole-rock LSB - cumulative	1	Durham	14/03/2020	Neptune MC-ICP MS	128	19	30	-1.13		
U1439C-29R-4-W 78/82	whole-rock LSB - cumulative	1	Durham	15/03/2020	Neptune MC-ICP MS	45	16	75	-1.11		
U1439C-29R-4-W 78/82	whole-rock LSB - cumulative	1	Durham	16/03/2020	Neptune MC-ICP MS	93	17	58	-1.17		
U1439C-29R-4-W 78/82 average									-1.12	0.07	4
U1439C 16R-1-26/30	whole-rock LSB	1	Durham	24/01/2019	Neptune MC-ICP MS	27		30	-1.16		
U1439C 16R-1-26/30	whole-rock LSB	1	Durham	25/01/2019	Neptune MC-ICP MS	98		59	-1.16		
U1439C 16R-1-26/30	whole-rock LSB	1	Durham	29/01/2019	Neptune MC-ICP MS	113		63	-1.18		
U1439C 16R-1-26/30 - digestion 1 average									-1.17	0.02	3
U1439C 16R-1-26/30	whole-rock LSB	2	Durham	13/03/2020	Neptune MC-ICP MS	69	16	17	-1.09		
U1439C 16R-1-26/30	whole-rock LSB	2	Durham	14/03/2020	Neptune MC-ICP MS	134	19	44	-1.15		
U1439C 16R-1-26/30	whole-rock LSB	2	Durham	15/03/2020	Neptune MC-ICP MS	39	19	21	-1.23		
U1439C 16R-1-26/30	whole-rock LSB	2	Durham	16/03/2020	Neptune MC-ICP MS	87	17	97	-1.19		
U1439C 16R-1-26/30 - digestion 2 average									-1.17	0.12	4
U1439C 16R-1-26/30 average									-1.17	0.09	7
783A-18R1-064/071	Torishima Forearc Seamount, harzburgite	1	Durham	11/03/2021	Neptune MC-ICP MS	6	23	25	-0.78		
783A-18R1-064/071 average									-0.78	-	1
784A-38R2-072/077	Torishima Forearc Seamount, dunite	1	Durham	11/03/2021	Neptune MC-ICP MS	12	20	17	-1.11		
784A-38R2-072/077 average									-1.11	-	1
784A-40R2-070/075	Torishima Forearc Seamount, dunite	1	Durham	11/03/2021	Neptune MC-ICP MS	18	19	25	-0.82		
784A-40R2-070/075 average									-0.82	-	1
784A-45R2-33/38	Torishima Forearc Seamount, harzburgite	1	Durham	11/03/2021	Neptune MC-ICP MS	24	18	36	-0.98		
784A-45R2-33/38 average									-0.98	-	1

Appendix D - Vanadium Isotope Data

784A-45R-CC-7/10	Torishima Forearc Seamount, harzburgite	1	Durham	11/03/2021	Neptune MC-ICP MS	21	25	67	-1.20			
784A-45R-CC-7/10	Torishima Forearc Seamount, harzburgite	1	Durham	11/03/2021	Neptune MC-ICP MS	51	19	61	-1.16			
784A-45R-CC-7/10	Torishima Forearc Seamount, harzburgite	1	Durham	11/03/2021	Neptune MC-ICP MS	63	22	28	-1.26			
784A-45R-CC-7/10 average									-1.21	0.10	3	

783A-18R1-119-124	Torishima Forearc Seamount, harzburgite	1	Durham	11/03/2021	Neptune MC-ICP MS	15	19	33	-1.03			
783A-18R1-119-124	Torishima Forearc Seamount, harzburgite	1	Durham	11/03/2021	Neptune MC-ICP MS	45	16	16	-1.11			
783A-18R1-119-124	Torishima Forearc Seamount, harzburgite	1	Durham	11/03/2021	Neptune MC-ICP MS	57	21	26	-1.02			
783A-18R1-119-124 average									-1.05	0.10	3	

												Literature		
Sample Name	Type	Batch	Location	Date	Method	Sequence	RSE	RSD	$\delta^{51}\text{V}_{\text{AA}}$ (‰)	2SD	n	$\delta^{51}\text{V}_{\text{AA}}$ (‰)	2SD	Reference
BCR-2	USGS reference material	1	Imperial	10/12/2017	Nu II MC-ICP MS		13	82	-1.05					
BCR-2	USGS reference material	1	Imperial	13/12/2017	Nu II MC-ICP MS		16	84	-1.01					
BCR-2	USGS reference material	1	Imperial	17/01/2018	Nu II MC-ICP MS		8	45	-0.95					
BCR-2 - digestion 1 average									-1.00	0.10	3			
BCR-2	USGS reference material	1	Durham	28/01/2019	Neptune MC-ICP MS			50	-0.66					
BCR-2	USGS reference material	1	Durham	29/01/2019	Neptune MC-ICP MS			49	-0.74					
BCR-2	USGS reference material	1	Durham	30/01/2019	Neptune MC-ICP MS			93	-0.69					
BCR-2	USGS reference material	1	Durham	18/02/2019	Neptune MC-ICP MS			53	-0.84					
BCR-2	USGS reference material	1	Durham	19/02/2019	Neptune MC-ICP MS			50	-0.76					
BCR-2 - digestion 1 average									-0.74	0.14	5			
BCR-2	USGS reference material	2	Durham	28/01/2019	Neptune MC-ICP MS			11	-0.82					
BCR-2	USGS reference material	2	Durham	29/01/2019	Neptune MC-ICP MS			29	-0.84					
BCR-2	USGS reference material	2	Durham	30/01/2019	Neptune MC-ICP MS			76	-0.81					
BCR-2	USGS reference material	2	Durham	20/02/2019	Neptune MC-ICP MS			21	-0.77					
BCR-2 - digestion 2 average									-0.81	0.06	4			
BCR-2	USGS reference material	3	Durham	28/01/2019	Neptune MC-ICP MS			32	-0.70					
BCR-2	USGS reference material	3	Durham	29/01/2019	Neptune MC-ICP MS			67	-0.66					
BCR-2	USGS reference material	3	Durham	30/01/2019	Neptune MC-ICP MS			71	-0.65					
BCR-2	USGS reference material	3	Durham	18/02/2019	Neptune MC-ICP MS			53	-0.72					
BCR-2	USGS reference material	3	Durham	20/02/2019	Neptune MC-ICP MS			42	-0.68					
BCR-2 - digestion 3 average									-0.68	0.06	5			
BCR-2	USGS reference material	4	Durham	21/05/2019	Neptune MC-ICP MS		32	21	-0.94					
BCR-2	USGS reference material	4	Durham	22/05/2019	Neptune MC-ICP MS		34	42	-0.93					
BCR-2 - digestion 4 average									-0.94	0.01	2			
BCR-2	USGS reference material	5	Durham	22/05/2019	Neptune MC-ICP MS		34	52	-0.96					
BCR-2	USGS reference material	5	Durham	22/05/2019	Neptune MC-ICP MS		33	18	-1.00					
BCR-2 - digestion 5 average									-0.98	0.05	2			
BCR-2	USGS reference material	6	Durham	22/05/2019	Neptune MC-ICP MS		29	53	-0.77					
BCR-2	USGS reference material	6	Durham	22/05/2019	Neptune MC-ICP MS		25	46	-0.73					
BCR-2 - digestion 6 average									-0.75	0.06	2			
BCR-2 average									-0.81	0.25	23	-0.78	0.08	Wu <i>et al.</i> (2016)

BIR-1a	USGS reference material	1	Imperial	07/12/2017	Nu II MC-ICP MS		13	92	-1.07		
BIR-1a	USGS reference material	1	Imperial	07/12/2017	Nu II MC-ICP MS		12	53	-1.16		
BIR-1a	USGS reference material	1	Imperial	09/12/2017	Nu II MC-ICP MS		17	93	-1.29		
BIR-1a	USGS reference material	1	Imperial	11/12/2017	Nu II MC-ICP MS		15	36	-1.30		
BIR-1a - digestion 1 average									-1.20	0.22	4
BIR-1a	USGS reference material	2	Durham	28/01/2019	Neptune MC-ICP MS			52	-0.93		
BIR-1a	USGS reference material	2	Durham	29/01/2019	Neptune MC-ICP MS			37	-0.90		
BIR-1a	USGS reference material	2	Durham	30/01/2019	Neptune MC-ICP MS			33	-0.84		
BIR-1a	USGS reference material	2	Durham	18/02/2019	Neptune MC-ICP MS			57	-0.90		
BIR-1a - digestion 2 average									-0.89	0.08	4
BIR-1a	USGS reference material	3	Durham	29/01/2019	Neptune MC-ICP MS			22	-0.75		
BIR-1a	USGS reference material	3	Durham	29/01/2019	Neptune MC-ICP MS			49	-0.91		
BIR-1a	USGS reference material	3	Durham	30/01/2019	Neptune MC-ICP MS			20	-0.94		

Appendix D - Vanadium Isotope Data

BIR-1a - digestion 3 average									-0.86	0.20	3			
BIR-1a	USGS reference material	4	Durham	29/01/2019	Neptune MC-ICP MS			34	-0.84					
BIR-1a	USGS reference material	4	Durham	30/01/2019	Neptune MC-ICP MS			39	-0.85					
BIR-1a - digestion 4 average									-0.85	0.00	2			
BIR-1a	USGS reference material	5	Durham	21/05/2019	Neptune MC-ICP MS			28	55	-0.95				
BIR-1a	USGS reference material	5	Durham	22/05/2019	Neptune MC-ICP MS			26	48	-0.96				
BIR-1a - digestion 5 average									-0.95	0.00	2			
BIR-1a	USGS reference material	6	Durham	21/05/2019	Neptune MC-ICP MS			33	32	-1.05				
BIR-1a	USGS reference material	6	Durham	22/05/2019	Neptune MC-ICP MS			34	36	-0.96				
BIR-1a - digestion 6 average									-1.01	0.12	2			
BIR-1a	USGS reference material	7	Durham	07/09/2020	Neptune MC-ICP MS				32	-1.00				
BIR-1a	USGS reference material	7	Durham	07/09/2020	Neptune MC-ICP MS				62	-1.05				
BIR-1a	USGS reference material	7	Durham	07/09/2020	Neptune MC-ICP MS				47	-1.01				
BIR-1a	USGS reference material	7	Durham	08/09/2020	Neptune MC-ICP MS				91	-1.02				
BIR-1a	USGS reference material	7	Durham	08/09/2020	Neptune MC-ICP MS				63	-0.95				
BIR-1a	USGS reference material	7	Durham	08/09/2020	Neptune MC-ICP MS				56	-1.07				
BIR-1a	USGS reference material	7	Durham	09/09/2020	Neptune MC-ICP MS				30	-1.01				
BIR-1a	USGS reference material	7	Durham	16/10/2020	Neptune MC-ICP MS				54	-1.04				
BIR-1a	USGS reference material	7	Durham	16/10/2020	Neptune MC-ICP MS				91	-0.96				
BIR-1a	USGS reference material	7	Durham	16/10/2020	Neptune MC-ICP MS				87	-0.96				
BIR-1a - digestion 7 average									-1.01	0.08	10			
BIR-1a average									-0.99	0.25	27			
										-0.92	0.09	Wu <i>et al.</i> (2016)		

BHVO-2	USGS reference material	1	Durham	29/01/2019	Neptune MC-ICP MS			50	-0.90						
BHVO-2	USGS reference material	1	Durham	29/01/2019	Neptune MC-ICP MS			43	-0.83						
BHVO-2	USGS reference material	1	Durham	30/01/2019	Neptune MC-ICP MS			45	-0.88						
BHVO-2 - digestion 1 average									-0.87		0.07	3			
BHVO-2	USGS reference material	2	Durham	29/01/2019	Neptune MC-ICP MS			40	-0.88						
BHVO-2	USGS reference material	2	Durham	29/01/2019	Neptune MC-ICP MS			31	-0.90						
BHVO-2	USGS reference material	2	Durham	19/02/2019	Neptune MC-ICP MS			47	-0.90						
BHVO-2	USGS reference material	2	Durham	20/02/2019	Neptune MC-ICP MS			24	-0.91						
BHVO-2 - digestion 2 average									-0.90		0.03	4			
BHVO-2	USGS reference material	3	Durham	29/01/2019	Neptune MC-ICP MS			52	-0.97						
BHVO-2	USGS reference material	3	Durham	29/01/2019	Neptune MC-ICP MS			32	-0.94						
BHVO-2	USGS reference material	3	Durham	19/02/2019	Neptune MC-ICP MS			19	-0.99						
BHVO-2 - digestion 3 average									-0.97		0.06	3			
BHVO-2	USGS reference material	4	Durham	21/05/2019	Neptune MC-ICP MS		26	15	-0.95						
BHVO-2	USGS reference material	4	Durham	22/05/2019	Neptune MC-ICP MS		31	57	-0.93						
BHVO-2 - digestion 4 average									-0.94	0.03	2				
BHVO-2	USGS reference material	5	Durham	21/05/2019	Neptune MC-ICP MS		28	28	-0.71						
BHVO-2	USGS reference material	5	Durham	22/05/2019	Neptune MC-ICP MS		35	32	-0.81						
BHVO-2 - digestion 5 average									-0.76		0.14	2			
BHVO-2	USGS reference material	6	Durham	21/05/2019	Neptune MC-ICP MS		30	59	-0.90						
BHVO-2	USGS reference material	6	Durham	22/05/2019	Neptune MC-ICP MS		29	69	-1.01						
BHVO-2 - digestion 6 average									-0.96	0.15	2				
BHVO-2	USGS reference material	7	Durham	08/09/2020	Neptune MC-ICP MS			19	-0.86						
BHVO-2	USGS reference material	7	Durham	08/09/2020	Neptune MC-ICP MS			56	-0.92						
BHVO-2	USGS reference material	7	Durham	08/09/2020	Neptune MC-ICP MS			63	-0.86						
BHVO-2	USGS reference material	7	Durham	09/09/2020	Neptune MC-ICP MS			29	-0.81						
BHVO-2 - digestion 7 average									-0.86		0.09	4			
BHVO-2	USGS reference material	8	Durham	14/10/2020	Neptune MC-ICP MS			31	-0.86						
BHVO-2	USGS reference material	8	Durham	15/10/2020	Neptune MC-ICP MS			47	-0.97						
BHVO-2 - digestion 8 average									-0.91		0.15	2			
BHVO-2 average									-0.90		0.14	22	-0.83	0.09	Wu <i>et al.</i> (2016)

GSP-2	USGS reference material	1	Durham	21/05/2019	Neptune MC-ICP MS			33	37	-0.71				
GSP-2	USGS reference material	1	Durham	22/05/2019	Neptune MC-ICP MS			35	66	-0.82				

Appendix D - Vanadium Isotope Data

GSP-2 - digestion 1 average									-0.77	0.15	2				
GSP-2	USGS reference material	2	Durham	21/05/2019	Neptune MC-ICP MS		28	49	-0.71						
GSP-2 - digestion 2 average									-0.71		1				
GSP-2 average									-0.75	0.13	3				-0.62
PCC-1	USGS reference material	1	Durham	08/09/2020	Neptune MC-ICP MS			37	-1.72						
PCC-1	USGS reference material	1	Durham	09/09/2020	Neptune MC-ICP MS			43	-1.71						
PCC-1	USGS reference material	1	Durham	09/09/2020	Neptune MC-ICP MS			23	-1.76						
PCC-1	USGS reference material	1	Durham	09/09/2020	Neptune MC-ICP MS			30	-1.68						
PCC-1	USGS reference material	1	Durham	10/09/2020	Neptune MC-ICP MS			47	-1.66						
PCC-1 - digestion 1 average									-1.71	0.08	5	-1.02	0.08	Sossi <i>et al.</i> (2018)	

Appendix E - Titanium Isotope Data

Sample	Type	Batch	Location	Date	Method	$\delta^{49}\text{Ti}_{\text{OL-Ti}}$ (‰)	95% c.i	n
U1439C-4R-1-W 26/32	whole-rock HSB	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.186	0.03	3
U1439C 16R-1-26/30	whole-rock LSB	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.174	0.03	3
U1439C 22R-1-89/95	whole-rock LSB	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.151	0.02	3
U1439C 41R-1-99/106	whole-rock LSB	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.144	0.03	3
U1439C-29R-4-W 78/82	whole-rock LSB -cumulative	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.133	0.03	3
U1439C-37R-1-W 42/48	whole-rock HMA	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.159	0.02	3
U1442A 20R-1-104/108	whole-rock HSB	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.172	0.02	3
U1442A 22R-1-122/125	whole-rock HSB	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.151	0.03	3
U1442A-35R-1-W 51/55	whole-rock LSB	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.152	0.02	3
U1440B 17R-2-23/32	whole-rock N-FAB	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.082	0.02	3
U1440B 26R-1-64/68	whole-rock N-FAB	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.128	0.03	3
U1440B 28R-1-31/38	whole-rock N-FAB	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.104	0.02	3
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.097	0.03	3
U1440B-17R-1-W 11/13	whole-rock N-FAB	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.096	0.03	3
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.076	0.02	3
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.087	0.02	3
U1441-A3-19R-1-66/72	whole-rock D-FAB	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.118	0.02	3
BHVO-2	USGS Reference Material	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.010	0.03	2
BCR-2	USGS Reference Material	1	Cardiff	12/12/2018	Nu II MC-ICP MS	0.011	0.03	2
OL-Ti DS	Titanium Solution Standard	1	Cardiff	12/12/2018	Nu II MC-ICP MS	-0.001	0.02	11

Appendix F - Iron Isotope Data

Sample Name	Type	Digestion	Batch no.	Location	Date	Method	RSE	RSD	$\delta^{56}\text{Fe}_{\text{NRM524}} (\text{‰})$	2SD	$\delta^{57}\text{Fe}_{\text{NRM524}} (\text{‰})$	2SD	n
U1440B-17R-1-W 11/13	whole-rock N-FAB	1	449-03	Durham	08/02/2020	SSB Neptune MC-ICP MS	7	3	0.158		0.235		
U1440B-17R-1-W 11/13	whole-rock N-FAB	1	449-03	Durham	08/02/2020	SSB Neptune MC-ICP MS	7	18	0.149		0.220		
U1440B-17R-1-W 11/13	whole-rock N-FAB	1	449-03	Durham	08/02/2020	SSB Neptune MC-ICP MS	7	13	0.123		0.196		
U1440B-17R-1-W 11/13 SSB average									0.143	0.037	0.217	0.039	3
U1440B-17R-1-W 11/13	whole-rock N-FAB	1	449-03	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	13	97	0.034		0.054		
U1440B-17R-1-W 11/13	whole-rock N-FAB	1	449-03	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	11	176	0.099		0.156		
U1440B-17R-1-W 11/13	whole-rock N-FAB	1	449-03	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	10	72	0.068		0.111		
U1440B-17R-1-W 11/13	whole-rock N-FAB	1	449-03	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	20	159	0.095		0.139		
U1440B-17R-1-W 11/13	whole-rock N-FAB	1	449-03	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	17	220	0.094		0.123		
U1440B-17R-1-W 11/13	whole-rock N-FAB	1	449-03	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	19	70	0.096		0.134		
U1440B-17R-1-W 11/13	whole-rock N-FAB	1	449-03	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	20	42	0.115		0.166		
U1440B-17R-1-W 11/13	whole-rock N-FAB	1	449-03	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	17	41	0.091		0.150		
U1440B-17R-1-W 11/13 Ni doped average									0.086	0.050	0.129	0.070	8
U1440B 17R-2-23/33	whole-rock N-FAB	1	449-04	Durham	08/02/2020	SSB Neptune MC-ICP MS	9	13	0.156		0.219		
U1440B 17R-2-23/33	whole-rock N-FAB	1	449-04	Durham	08/02/2020	SSB Neptune MC-ICP MS	7	14	0.161		0.196		
U1440B 17R-2-23/34	whole-rock N-FAB	1	449-04	Durham	08/02/2020	SSB Neptune MC-ICP MS	5	7	0.151		0.232		
U1440B 17R-2-23/32 SSB average									0.156	0.010	0.216	0.036	3
U1440B 17R-2-23/33	whole-rock N-FAB	1	449-04	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	9	193	0.097		0.159		
U1440B 17R-2-23/33	whole-rock N-FAB	1	449-04	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	8	147	0.121		0.164		
U1440B 17R-2-23/33	whole-rock N-FAB	1	449-04	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	12	104	0.079		0.110		
U1440B 17R-2-23/32 Ni doped average									0.099	0.042	0.144	0.059	3
U1440B-8R-1-W 20/23	whole-rock N-FAB	1	2-1	Durham	11/09/2019	SSB Neptune MC-ICP MS	8	42	0.039		0.062		
U1440B-8R-1-W 20/23	whole-rock N-FAB	1	2-1	Durham	09/03/2020	SSB Neptune MC-ICP MS	8	27	0.080		0.104		
U1440B-8R-1-W 20/23	whole-rock N-FAB	1	2-1	Durham	09/03/2020	SSB Neptune MC-ICP MS	7	4	0.097		0.123		
U1440B-8R-1-W 20/23 SSB average									0.072	0.059	0.096	0.063	3
U1440B-8R-1-W 20/23	whole-rock N-FAB	1	2-1	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	14	25	0.021		0.003		
U1440B-8R-1-W 20/23	whole-rock N-FAB	1	2-1	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	10	17	0.001		-0.004		
U1440B-8R-1-W 20/23	whole-rock N-FAB	1	2-1	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	7	44	0.024		0.033		
U1440B-8R-1-W 20/23 Ni doped average									0.015	0.025	0.011	0.039	3
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	2-2	Durham	11/09/2019	SSB Neptune MC-ICP MS	11	11	0.074		0.118		
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	2-2	Durham	12/09/2019	SSB Neptune MC-ICP MS	12	18	0.089		0.147		
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	2-2	Durham	12/09/2019	SSB Neptune MC-ICP MS	12	12	0.085		0.129		
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	2-2	Durham	09/03/2020	SSB Neptune MC-ICP MS	8	14	0.105		0.168		
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	2-2	Durham	09/03/2020	SSB Neptune MC-ICP MS	9	17	0.111		0.163		
U1440B-29R-1-W 5/8 SSB average									0.093	0.030	0.145	0.043	5
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	2-2	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	8	195	0.107		0.164		
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	2-2	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	6	232	0.061		0.067		
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	2-2	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	5	272	0.083		0.135		
U1440B-29R-1-W 5/8 Ni doped average									0.084	0.046	0.122	0.099	3
U1440B 26R-1-64/68	whole-rock N-FAB	1	2-3	Durham	11/09/2019	SSB Neptune MC-ICP MS	12	13	0.118		0.163		
U1440B 26R-1-64/68	whole-rock N-FAB	1	2-3	Durham	11/09/2019	SSB Neptune MC-ICP MS	12	12	0.133		0.174		
U1440B 26R-1-64/68	whole-rock N-FAB	1	2-3	Durham	12/09/2019	SSB Neptune MC-ICP MS	10	8	0.127		0.194		
U1440B 26R-1-64/68	whole-rock N-FAB	1	2-3	Durham	12/09/2019	SSB Neptune MC-ICP MS	12	7	0.115		0.186		
U1440B 26R-1-64/68 SSB average									0.123	0.017	0.179	0.027	4
U1440B 26R-1-64/68	whole-rock N-FAB	1	2-3	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	10	73	0.071		0.089		
U1440B 26R-1-64/68	whole-rock N-FAB	1	2-3	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	6	65	0.105		0.163		
U1440B 26R-1-64/68	whole-rock N-FAB	1	2-3	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	6	47	0.072		0.104		
U1440B 26R-1-64/68 Ni doped average									0.083	0.038	0.119	0.078	3
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	2-4	Durham	11/09/2019	SSB Neptune MC-ICP MS	10	6	0.053		0.080		
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	2-4	Durham	11/09/2019	SSB Neptune MC-ICP MS	11	2	0.072		0.097		
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	2-4	Durham	12/09/2019	SSB Neptune MC-ICP MS	11	5	0.057		0.102		

Appendix F - Iron Isotope Data

U1440B-12R-2-W 4/8	whole-rock P-FAB	1	2-4	Durham	09/03/2020	SSB Neptune MC-ICP MS	8	21	0.086		0.147		
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	2-4	Durham	09/03/2020	SSB Neptune MC-ICP MS	7	17	0.083		0.154		
U1440B-12R-2-W 4/8 SSB average									0.070	0.030	0.116	0.065	5
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	2-4	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	6	13	0.078		0.110		
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	2-4	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	4	25	0.066		0.126		
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	2-4	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	7	18	0.115		0.188		
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	2-4	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	13	424	0.086		0.105		
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	2-4	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	12	428	0.113		0.130		
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	2-4	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	12	444	0.123		0.165		
U1440B-12R-2-W 4/8 Ni doped average									0.097	0.046	0.137	0.065	6
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	11/09/2019	SSB Neptune MC-ICP MS	9	0	0.125		0.211		
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	11/09/2019	SSB Neptune MC-ICP MS	8	17	0.168		0.244		
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	12/09/2019	SSB Neptune MC-ICP MS	11	15	0.151		0.238		
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	12/09/2019	SSB Neptune MC-ICP MS	9	7	0.170		0.266		
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	09/03/2020	SSB Neptune MC-ICP MS	9	14	0.184		0.267		
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	09/03/2020	SSB Neptune MC-ICP MS	7	23	0.161		0.287		
U1440B 28R-1-31/38 SSB average									0.160	0.040	0.252	0.054	6
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	7	21	0.146		0.216		
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	9	33	0.118		0.171		
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	8	4	0.172		0.263		
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	11	37	0.171		0.276		
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	10	43	0.162		0.249		
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	10	16	0.195		0.302		
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	17	8	0.156		0.213		
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	19	6	0.149		0.215		
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	18	25	0.174		0.251		
U1440B 28R-1-31/38 Ni doped average									0.160	0.043	0.239	0.079	9
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	2-8	Durham	11/09/2019	SSB Neptune MC-ICP MS	10	8	0.105		0.143		
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	2-8	Durham	11/09/2019	SSB Neptune MC-ICP MS	10	8	0.123		0.154		
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	2-8	Durham	12/09/2019	SSB Neptune MC-ICP MS	9	37	0.117		0.160		
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	2-8	Durham	12/09/2019	SSB Neptune MC-ICP MS	10	6	0.117		0.200		
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	2-8	Durham	09/03/2020	SSB Neptune MC-ICP MS	10	2	0.167		0.262		
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	2-8	Durham	09/03/2020	SSB Neptune MC-ICP MS	7	11	0.155		0.228		
U1441A-21R-1-W 37/42 SSB average									0.131	0.049	0.191	0.095	6
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	2-8	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	8	10	0.084		0.129		
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	2-8	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	7	9	0.076		0.119		
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	2-8	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	7	48	0.072		0.116		
U1441A-21R-1-W 37/42 Ni doped average									0.077	0.012	0.121	0.014	3
U1441-A3-19R-1-66/72	whole-rock D-FAB	1	2-9	Durham	11/09/2019	SSB Neptune MC-ICP MS	11	3	0.060		0.087		
U1441-A3-19R-1-66/72	whole-rock D-FAB	1	2-9	Durham	11/09/2019	SSB Neptune MC-ICP MS	10	9	0.053		0.088		
U1441-A3-19R-1-66/72	whole-rock D-FAB	1	2-9	Durham	12/09/2019	SSB Neptune MC-ICP MS	11	32	0.082		0.129		
U1441-A3-19R-1-66/72	whole-rock D-FAB	1	2-9	Durham	12/09/2019	SSB Neptune MC-ICP MS	12	50	0.061		0.091		
U1441-A3-19R-1-66/72 SSB average									0.064	0.025	0.099	0.041	4
U1441-A3-19R-1-66/72	whole-rock D-FAB	1	2-9	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	6	26	0.071		0.103		
U1441-A3-19R-1-66/72	whole-rock D-FAB	1	2-9	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	13	63	0.084		0.124		
U1441-A3-19R-1-66/72	whole-rock D-FAB	1	2-9	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	14	52	0.018		0.028		
U1441-A3-19R-1-66/72	whole-rock D-FAB	1	2-9	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	14	47	0.074		0.102		
U1441-A3-19R-1-66/72	whole-rock N-FAB	1	2-9	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	23	27	0.053		0.069		
U1441-A3-19R-1-66/72	whole-rock N-FAB	1	2-9	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	22	3	0.070		0.114		
U1441-A3-19R-1-66/72	whole-rock N-FAB	1	2-9	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	17	17	0.093		0.135		
U1441-A3-19R-1-66/72 Ni doped average									0.066	0.049	0.096	0.073	7
U1442A-35R-1-W 51/55	whole-rock LSB	1	2-10	Durham	11/09/2019	SSB Neptune MC-ICP MS	11	3	0.049		0.072		
U1442A-35R-1-W 51/55	whole-rock LSB	1	2-10	Durham	11/09/2019	SSB Neptune MC-ICP MS	11	12	0.096		0.145		
U1442A-35R-1-W 51/55	whole-rock LSB	1	2-10	Durham	12/09/2019	SSB Neptune MC-ICP MS	12	1	0.062		0.101		
U1442A-35R-1-W 51/55	whole-rock LSB	1	2-10	Durham	12/09/2019	SSB Neptune MC-ICP MS	12	6	0.104		0.149		

Appendix F - Iron Isotope Data

U1442A-35R-1-W 51/55	whole-rock LSB	1	2-10	Durham	09/03/2020	SSB Neptune MC-ICP MS	7	5	0.109		0.166		
U1442A-35R-1-W 51/55	whole-rock LSB	1	2-10	Durham	09/03/2020	SSB Neptune MC-ICP MS	8	2	0.106		0.158		
U1442A-35R-1-W 51/55 SSB average									0.088	0.051	0.132	0.074	6
U1442A-35R-1-W 51/55	whole-rock LSB	1	2-10	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	13	221	0.077		0.129		
U1442A-35R-1-W 51/55	whole-rock LSB	1	2-10	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	11	150	0.070		0.094		
U1442A-35R-1-W 51/55	whole-rock LSB	1	2-10	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	11	125	0.108		0.153		
U1442A-35R-1-W 51/55 Ni doped average									0.085	0.041	0.125	0.059	3
U1442A 22R-1-122/125	whole-rock HSB	1	2-12	Durham	12/09/2019	SSB Neptune MC-ICP MS	13	11	0.059		0.107		
U1442A 22R-1-122/125	whole-rock HSB	1	2-12	Durham	09/03/2020	SSB Neptune MC-ICP MS	10	6	0.081		0.139		
U1442A 22R-1-122/125	whole-rock HSB	1	2-12	Durham	09/03/2020	SSB Neptune MC-ICP MS	6	19	0.082		0.153		
U1442A 22R-1-122/125 SSB average									0.074	0.026	0.133	0.047	3
U1442A 22R-1-122/125	whole-rock HSB	1	2-12	Durham	09/03/2020	Ni doped Neptune MC-ICP MS	5	56	0.078		0.110		
U1442A 22R-1-122/125	whole-rock HSB	1	2-12	Durham	09/03/2020	Ni doped Neptune MC-ICP MS	10	34	0.075		0.103		
U1442A 22R-1-122/125	whole-rock HSB	1	2-12	Durham	09/03/2020	Ni doped Neptune MC-ICP MS	14	10	0.100		0.135		
U1442A 22R-1-122/125	whole-rock HSB	1	2-12	Durham	09/03/2020	Ni doped Neptune MC-ICP MS	10	43	0.046		0.073		
U1442A 22R-1-122/125	whole-rock HSB	1	2-12	Durham	09/03/2020	Ni doped Neptune MC-ICP MS	10	48	0.043		0.052		
U1442A 22R-1-122/125 Ni doped average									0.069	0.047	0.095	0.064	5
U1439C 22R-1-89/95	whole-rock LSB	1	2-18	Durham	12/09/2019	SSB Neptune MC-ICP MS	12	32	0.056		0.095		
U1439C 22R-1-89/95	whole-rock LSB	1	2-18	Durham	12/09/2019	SSB Neptune MC-ICP MS	9	11	0.083		0.108		
U1439C 22R-1-89/95 SSB average									0.069	0.038	0.101	0.018	2
U1439C 22R-1-89/95	whole-rock LSB	1	2-18	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	12	97	0.063		0.098		
U1439C 22R-1-89/95	whole-rock LSB	1	2-18	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	10	15	0.046		0.064		
U1439C 22R-1-89/95	whole-rock LSB	1	2-18	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	10	124	0.071		0.098		
U1439C 22R-1-89/95 Ni doped average									0.060	0.026	0.086	0.039	3
U1442A 20R-1-104/108	whole-rock HSB	1	449-05	Durham	02/03/2020	SSB Neptune MC-ICP MS	8	34	0.088		0.110		
U1442A 20R-1-104/108	whole-rock HSB	1	449-05	Durham	02/03/2020	SSB Neptune MC-ICP MS	8	35	0.119		0.193		
U1442A 20R-1-104/108 SSB average									0.104	0.044	0.152	0.117	2
U1442A 20R-1-104/108	whole-rock HSB	1	449-05	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	14	19	0.009		0.041		
U1442A 20R-1-104/108	whole-rock HSB	1	449-05	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	8	73	0.028		0.044		
U1442A 20R-1-104/108	whole-rock HSB	1	449-05	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	5	11	-0.009		-0.008		
U1442A 20R-1-104/108 Ni doped average									0.009	0.037	0.026	0.058	3
U1439C-31R-5-W 12/17	whole-rock LSB	1	449-06	Durham	02/03/2020	SSB Neptune MC-ICP MS	7	18	0.106		0.152		
U1439C-31R-5-W 12/17	whole-rock LSB	1	449-06	Durham	02/03/2020	SSB Neptune MC-ICP MS	7	28	0.080		0.104		
U1439C-31R-5-W 12/17	whole-rock LSB	1	449-06	Durham	02/03/2020	SSB Neptune MC-ICP MS	10	33	0.116		0.170		
U1439C-31R-5-W 12/17 SSB average									0.101	0.037	0.142	0.067	3
U1439C-31R-5-W 12/17	whole-rock LSB	1	449-06	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	6	153	0.016		0.023		
U1439C-31R-5-W 12/17	whole-rock LSB	1	449-06	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	7	161	0.059		0.073		
U1439C-31R-5-W 12/17	whole-rock LSB	1	449-06	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	7	64	0.012		0.026		
U1439C-31R-5-W 12/17	whole-rock LSB	1	449-06	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	12	162	0.058		0.083		
U1439C-31R-5-W 12/17	whole-rock LSB	1	449-06	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	7	153	0.068		0.123		
U1439C-31R-5-W 12/17	whole-rock LSB	1	449-06	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	7	154	0.019		0.024		
U1439C-31R-5-W 12/17	whole-rock LSB	1	449-06	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	15	75	0.047		0.065		
U1439C-31R-5-W 12/17	whole-rock LSB	1	449-06	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	19	48	0.077		0.101		
U1439C-31R-5-W 12/17 Ni doped average									0.045	0.051	0.065	0.075	8
U1439C-10R-2-W 13/19	whole-rock BB	1	449-07	Durham	02/03/2020	SSB Neptune MC-ICP MS	10	11	-0.031		-0.025		
U1439C-10R-2-W 13/19	whole-rock BB	1	449-07	Durham	02/03/2020	SSB Neptune MC-ICP MS	10	1	0.009		-0.006		
U1439C-10R-2-W 13/19	whole-rock BB	1	449-07	Durham	02/03/2020	SSB Neptune MC-ICP MS	11	2	-0.005		0.026		
U1439C-10R-2-W 13/19 SSB average									-0.009	0.041	-0.002	0.052	3
U1439C-10R-2-W 13/19	whole-rock BB	1	449-07	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	6	80	0.001		-0.003		
U1439C-10R-2-W 13/19	whole-rock BB	1	449-07	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	5	27	0.012		0.024		
U1439C-10R-2-W 13/19	whole-rock BB	1	449-07	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	9	117	-0.010		-0.010		
U1439C-10R-2-W 13/19	whole-rock BB	1	449-07	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	7	102	0.005		-0.001		
U1439C-10R-2-W 13/19	whole-rock BB	1	449-07	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	8	99	0.010		0.015		
U1439C-10R-2-W 13/19 Ni doped average									0.004	0.018	0.005	0.028	5

Appendix F - Iron Isotope Data

U1439C-37R-1-W 42/48	whole-rock HMA	1	449-08	Durham	02/03/2020	SSB Neptune MC-ICP MS	8	75	0.141		0.228		
U1439C-37R-1-W 42/48	whole-rock HMA	1	449-08	Durham	02/03/2020	SSB Neptune MC-ICP MS	8	41	0.157		0.219		
U1439C-37R-1-W 42/48	whole-rock HMA	1	449-08	Durham	02/03/2020	SSB Neptune MC-ICP MS	8	1	0.100		0.181		
U1439C-37R-1-W 42/48 average									0.133	0.059	0.209	0.050	3
U1439C-37R-1-W 42/48	whole-rock HMA	1	449-08	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	13	130	0.070		0.121		
U1439C-37R-1-W 42/48	whole-rock HMA	1	449-08	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	8	100	0.084		0.140		
U1439C-37R-1-W 42/48	whole-rock HMA	1	449-08	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	7	67	0.085		0.074		
U1439C-37R-1-W 42/48	whole-rock HMA	1	449-08	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	11	28	0.039		0.082		
U1439C-37R-1-W 42/48	whole-rock HMA	1	449-08	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	11	50	0.061		0.116		
U1439C-37R-1-W 42/48 Ni doped average									0.068	0.038	0.107	0.056	5

U1439C-4R-1-W 26/32	whole-rock HSB	1	449-09	Durham	08/02/2020	SSB Neptune MC-ICP MS	9	50	0.104		0.142		
U1439C-4R-1-W 26/32	whole-rock HSB	1	449-09	Durham	08/02/2020	SSB Neptune MC-ICP MS	6	44	0.093		0.164		
U1439C-4R-1-W 26/32	whole-rock HSB	1	449-09	Durham	08/02/2020	SSB Neptune MC-ICP MS	6	30	0.129		0.177		
U1439C-4R-1-W 26/32	whole-rock HSB	1	449-09	Durham	02/03/2020	SSB Neptune MC-ICP MS	7	36	0.091		0.170		
U1439C-4R-1-W 26/32	whole-rock HSB	1	449-09	Durham	02/03/2020	SSB Neptune MC-ICP MS	9	28	0.137		0.223		
U1439C-4R-1-W 26/32	whole-rock HSB	1	449-09	Durham	02/03/2020	SSB Neptune MC-ICP MS	10	13	0.158		0.273		
U1439C-4R-1-W 26/32 SSB average									0.119	0.054	0.191	0.096	6
U1439C-4R-1-W 26/32	whole-rock HSB	1	449-09	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	5	78	0.062		0.109		
U1439C-4R-1-W 26/32	whole-rock HSB	1	449-09	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	8	73	0.054		0.087		
U1439C-4R-1-W 26/32	whole-rock HSB	1	449-09	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	7	71	0.056		0.077		
U1439C-4R-1-W 26/32 Ni doped average									0.057	0.008	0.091	0.033	3

U1439C 41R-1-99/106	whole-rock LSB	1	449-11	Durham	08/02/2020	SSB Neptune MC-ICP MS	9	14	0.033		0.057		
U1439C 41R-1-99/106	whole-rock LSB	1	449-11	Durham	08/02/2020	SSB Neptune MC-ICP MS	7	31	0.066		0.118		
U1439C 41R-1-99/106	whole-rock LSB	1	449-11	Durham	02/03/2020	SSB Neptune MC-ICP MS	8	14	0.059		0.102		
U1439C 41R-1-99/106	whole-rock LSB	1	449-11	Durham	02/03/2020	SSB Neptune MC-ICP MS	9	5	0.101		0.144		
U1439C 41R-1-99/106	whole-rock LSB	1	449-11	Durham	02/03/2020	SSB Neptune MC-ICP MS	10	36	0.108		0.149		
U1439C 41R-1-99/106 SSB average									0.073	0.062	0.114	0.074	5
U1439C 41R-1-99/106	whole-rock LSB	1	449-11	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	10	13	0.040		0.076		
U1439C 41R-1-99/106	whole-rock LSB	1	449-11	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	6	59	0.047		0.057		
U1439C 41R-1-99/106	whole-rock LSB	1	449-11	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	6	47	0.069		0.108		
U1439C 41R-1-99/106	whole-rock LSB	1	449-11	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	10	15	0.025		0.044		
U1439C 41R-1-99/106	whole-rock LSB	1	449-11	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	8	21	0.084		0.108		
U1439C 41R-1-99/106	whole-rock LSB	1	449-11	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	8	19	0.027		0.025		
U1439C 41R-1-99/106	whole-rock LSB	1	449-11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	11	18	0.031		0.059		
U1439C 41R-1-99/106 Ni doped average									0.046	0.045	0.068	0.063	7

U1439C-29R-4-W 78/82	whole-rock LSB	1	468-02	Durham	02/03/2020	SSB Neptune MC-ICP MS	9	34	0.110		0.154		
U1439C-29R-4-W 78/82 SSB average									0.110		0.154		1
U1439C-29R-4-W 78/82	whole-rock LSB	1	468-02	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	8	83	0.061		0.083		
U1439C-29R-4-W 78/82	whole-rock LSB	1	468-02	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	9	34	0.061		0.092		
U1439C-29R-4-W 78/82	whole-rock LSB	1	468-02	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	11	14	0.039		0.060		
U1439C-29R-4-W 78/82	whole-rock LSB	1	468-02	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	11	68	0.070		0.086		
U1439C-29R-4-W 78/82	whole-rock LSB	1	468-02	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	11	136	0.027		0.052		
U1439C-29R-4-W 78/82	whole-rock LSB	1	468-02	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	14	61	0.047		0.069		
U1439C-29R-4-W 78/82 Ni doped average									0.051	0.032	0.074	0.031	6

U1439C 16R-1-26/30	whole-rock LSB	1	468-03	Durham	02/03/2020	SSB Neptune MC-ICP MS	8	38	0.096		0.142		
U1439C 16R-1-26/30	whole-rock LSB	1	468-03	Durham	02/03/2020	SSB Neptune MC-ICP MS	10	6	0.090		0.151		
U1439C 16R-1-26/30	whole-rock LSB	1	468-03	Durham	02/03/2020	SSB Neptune MC-ICP MS	11	24	0.124		0.184		
U1439C 16R-1-26/30 SSB average									0.104	0.037	0.159	0.044	3
U1439C 16R-1-26/30	whole-rock LSB	1	468-03	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	23	47	0.099		0.178		
U1439C 16R-1-26/30	whole-rock LSB	1	468-03	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	38	37	0.109		0.188		
U1439C 16R-1-26/30	whole-rock LSB	1	468-03	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	18	105	0.091		0.166		
U1439C 16R-1-26/30	whole-rock LSB	1	468-03	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	21	109	0.054		0.093		
U1439C 16R-1-26/30	whole-rock LSB	1	468-03	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	19	16	0.095		0.153		
U1439C 16R-1-26/30 Ni doped average									0.090	0.042	0.156	0.074	5

Appendix F - Iron Isotope Data

U1439C 19R4 11/17	whole-rock LSB	1	512-03	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	13	5	0.128		0.177		
U1439C 19R4 11/17	whole-rock LSB	1	512-03	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	17	44	0.112		0.177		
U1439C 19R4 11/17	whole-rock LSB	1	512-03	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	23	18	0.135		0.195		
U1439C 19R4 11/17	whole-rock LSB	1	512-03	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	19	30	0.107		0.164		
U1439C 19R4 11/17 average									0.120	0.026	0.178	0.026	4
U1442A 47R1-W 50/55	whole-rock HSB	1	512-04	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	12	16	0.076		0.137		
U1442A 47R1-W 50/55	whole-rock HSB	1	512-04	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	7	53	0.029		0.070		
U1442A 47R1-W 50/55	whole-rock HSB	1	512-04	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	9	38	0.066		0.125		
U1442A 47R1-W 50/55 average									0.057	0.050	0.111	0.071	3
U1442A 23R1 99/103	whole-rock LSB	1	512-05	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	12	45	0.036		0.038		
U1442A 23R1 99/103	whole-rock LSB	1	512-05	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	9	48	0.025		0.082		
U1442A 23R1 99/103	whole-rock LSB	1	512-05	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	11	10	0.051		0.091		
U1442A 23R1 99/103 average									0.037	0.026	0.070	0.056	3
U1442A 56R1 19/24	whole-rock LSB	1	512-06	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	8	6	0.041		0.072		
U1442A 56R1 19/24	whole-rock LSB	1	512-06	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	9	85	0.064		0.118		
U1442A 56R1 19/24	whole-rock LSB	1	512-06	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	12	35	0.056		0.067		
U1442A 56R1 19/24	whole-rock LSB	1	512-06	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	14	9	0.057		0.095		
U1442A 56R1 19/24 average									0.054	0.019	0.088	0.046	4
U1439C 40R1 33/38	whole-rock LSB	1	512-07	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	10	64	0.079		0.117		
U1439C 40R1 33/38	whole-rock LSB	1	512-07	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	8	62	0.063		0.119		
U1439C 40R1 33/38	whole-rock LSB	1	512-07	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	13	96	0.058		0.112		
U1439C 40R1 33/38	whole-rock LSB	1	512-07	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	15	187	0.093		0.146		
U1439C 40R1 33/38	whole-rock LSB	1	512-07	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	11	0	0.067		0.096		
U1439C 40R1 33/38 average									0.072	0.028	0.118	0.037	5
U1439C 31R1 15/20	whole-rock LSB	1	512-08	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	12	109	0.080		0.075		
U1439C 31R1 15/20	whole-rock LSB	1	512-08	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	7	53	0.061		0.110		
U1439C 31R1 15/20	whole-rock LSB	1	512-08	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	8	9	0.043		0.073		
U1439C 31R1 15/20	whole-rock LSB	1	512-08	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	14	32	0.038		0.092		
U1439C 31R1 15/20 average									0.056	0.038	0.087	0.034	4
U1439C 26R1 132/137	whole-rock LSB	1	512-09	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	11	76	0.057		0.094		
U1439C 26R1 132/137	whole-rock LSB	1	512-09	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	10	85	0.069		0.096		
U1439C 26R1 132/137	whole-rock LSB	1	512-09	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	12	142	0.052		0.065		
U1439C 26R1 132/137	whole-rock LSB	1	512-09	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	7	109	0.096		0.148		
U1439C 26R1 132/137 average									0.068	0.039	0.101	0.069	4
U1439C 19R3 58/62	whole-rock LSB	1	512-10	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	11	76	0.045		0.075		
U1439C 19R3 58/62	whole-rock LSB	1	512-10	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	14	39	0.083		0.131		
U1439C 19R3 58/62	whole-rock LSB	1	512-10	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	18	68	0.049		0.057		
U1439C 19R3 58/62	whole-rock LSB	1	512-10	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	17	24	0.048		0.076		
U1439C 19R3 58/62 average									0.056	0.036	0.085	0.065	4
U1439C 6R1 25/30	whole-rock HSB	1	512-11	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	11	62	0.036		0.052		
U1439C 6R1 25/30	whole-rock HSB	1	512-11	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	10	16	0.061		0.099		
U1439C 6R1 25/30	whole-rock HSB	1	512-11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	12	24	0.029		0.080		
U1439C 6R1 25/30 average									0.042	0.034	0.077	0.047	3
U1439C 11R1 134/127	whole-rock LSB	1	512-12	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	16	49	-0.046		-0.076		
U1439C 11R1 134/127	whole-rock LSB	1	512-12	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	14	75	-0.033		-0.064		
U1439C 11R1 134/127	whole-rock LSB	1	512-12	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	13	97	-0.028		-0.035		
U1439C 11R1 134/127	whole-rock LSB	1	512-12	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	20	4	-0.021		-0.040		
U1439C 11R1 134/127 average									-0.032	0.021	-0.054	0.038	4

Appendix F - Iron Isotope Data

U1442A 49R2W 60/65	whole-rock LSB	1	515-03	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	11	177	0.042		0.049			
U1442A 49R2W 60/65	whole-rock LSB	1	515-03	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	12	129	0.070		0.062			
U1442A 49R2W 60/65	whole-rock LSB	1	515-03	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	13	6	0.092		0.116			
U1442A 49R2W 60/65	whole-rock LSB	1	515-03	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	14	5	0.097		0.149			
U1442A 49R2W 60/65	whole-rock LSB	1	515-03	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	12	37	0.076		0.120			
U1442A 49R2W 60/65 average									0.075	0.043	0.099	0.084	5	
U1442A 30R2W 21/27	whole-rock BB	1	515-04	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	11	177	0.042		0.049			
U1442A 30R2W 21/27	whole-rock BB	1	515-04	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	12	129	0.070		0.062			
U1442A 30R2W 21/27	whole-rock BB	1	515-04	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	13	6	0.092		0.116			
U1442A 30R2W 21/27	whole-rock BB	1	515-04	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	14	5	0.097		0.149			
U1442A 30R2W 21/27	whole-rock BB	1	515-04	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	12	37	0.076		0.120			
U1442A 30R2W 21/27 average									0.075	0.043	0.099	0.084	5	
U1442A 36R2W 17/22	whole-rock LSB	1	515-05	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	21	24	0.116		0.148			
U1442A 36R2W 17/22	whole-rock LSB	1	515-05	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	15	100	0.075		0.123			
U1442A 36R2W 17/22	whole-rock LSB	1	515-05	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	14	30	0.052		0.091			
U1442A 36R2W 17/22	whole-rock LSB	1	515-05	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	20	21	0.092		0.144			
U1442A 36R2W 17/22	whole-rock LSB	1	515-05	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	20	21	0.095		0.132			
U1442A 36R2W 17/22	whole-rock LSB	1	515-05	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	20	9	0.110		0.175			
U1442A 36R2W 17/22	whole-rock LSB	1	515-05	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	18	20	0.121		0.165			
U1442A 36R2W 17/22	whole-rock LSB	1	515-05	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	16	48	0.074		0.127			
U1442A 36R2W 17/22 average									0.092	0.048	0.138	0.053	8	
U1439C 2R3W 38/46	whole-rock HSB	1	515-06	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	17	21	0.054		0.081			
U1439C 2R3W 38/46	whole-rock HSB	1	515-06	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	10	26	0.057		0.066			
U1439C 2R3W 38/46	whole-rock HSB	1	515-06	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	15	35	0.017		0.042			
U1439C 2R3W 38/46	whole-rock HSB	1	515-06	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	16	85	0.050		0.084			
U1439C 2R3W 38/46	whole-rock HSB	1	515-06	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	16	20	0.061		0.083			
U1439C 2R3W 38/46	whole-rock HSB	1	515-06	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	17	21	0.002		0.013			
U1439C 2R3W 38/46 average									0.040	0.049	0.062	0.057	6	
U1442A 54R-1W 13/18	whole-rock LSB	1	515-07	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	14	9	0.050		0.063			
U1442A 54R-1W 13/18	whole-rock LSB	1	515-07	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	10	69	0.093		0.149			
U1442A 54R-1W 13/18	whole-rock LSB	1	515-07	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	11	66	0.033		0.042			
U1442A 54R-1W 13/18	whole-rock LSB	1	515-07	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	7	0	0.071		0.088			
U1442A 54R-1W 13/18	whole-rock LSB	1	515-07	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	21	18	0.041		0.067			
U1442A 54R-1W 13/18	whole-rock LSB	1	515-07	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	19	15	0.039		0.074			
U1442A 54R-1W 13/18	whole-rock LSB	1	515-07	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	20	14	0.069		0.136			
U1442A 54R-1W 13/18 average									0.056	0.044	0.089	0.079	7	
U1442A 23R-2W 30/35	whole-rock HSB	1	515-08	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	7	79	0.000		-0.006			
U1442A 23R-2W 30/35	whole-rock HSB	1	515-08	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	7	225	0.016		0.003			
U1442A 23R-2W 30/35	whole-rock HSB	1	515-08	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	13	67	0.045		0.077			
U1442A 23R-2W 30/35	whole-rock HSB	1	515-08	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	9	24	0.032		0.027			
U1442A 23R-2W 30/35 average									0.023	0.039	0.025	0.075	4	
U1442A 28R-1W 10/14	whole-rock HSB	1	515-09	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	15	32	0.062		0.075			
U1442A 28R-1W 10/14	whole-rock HSB	1	515-09	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	22	108	0.063		0.083			
U1442A 28R-1W 10/14	whole-rock HSB	1	515-09	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	12	1	0.112		0.146			
U1442A 28R-1W 10/14	whole-rock HSB	1	515-09	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	18	22	0.092		0.128			
U1442A 28R-1W 10/14 average									0.082	0.048	0.108	0.069	4	
U1439C 33R-2W 23/30-ICP	whole-rock LSB	1	515-10	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	12	60	-0.017		-0.022			
U1439C 33R-2W 23/30-ICP	whole-rock LSB	1	515-10	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	11	60	0.029		0.039			
U1439C 33R-2W 23/30-ICP	whole-rock LSB	1	515-10	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	13	37	0.036		0.031			
U1439C 33R-2W 23/30-ICP	whole-rock LSB	1	515-10	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	13	56	0.017		0.008			
U1439C 33R-2W 23/30-ICP average									0.016	0.047	0.014	0.054	4	

Appendix F - Iron Isotope Data

U1442A 57R-2W 116/121	whole-rock LSB	1	515-11	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	9	93	0.105		0.150		
U1442A 57R-2W 116/121	whole-rock LSB	1	515-11	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	13	37	0.088		0.117		
U1442A 57R-2W 116/121	whole-rock LSB	1	515-11	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	13	154	0.091		0.145		
U1442A 57R-2W 116/121	whole-rock LSB	1	515-11	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	10	20	0.067		0.107		
U1442A 57R-2W 116/121 average									0.088	0.032	0.130	0.043	4
U1442A 48R-1W 87/92	whole-rock HSB	1	515-12	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	18	77	0.066		0.091		
U1442A 48R-1W 87/92	whole-rock HSB	1	515-12	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	19	50	0.038		0.016		
U1442A 48R-1W 87/92	whole-rock HSB	1	515-12	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	13	86	0.062		0.087		
U1442A 48R-1W 87/92	whole-rock HSB	1	515-12	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	20	102	0.070		0.099		
U1442A 48R-1W 87/92	whole-rock HSB	1	515-12	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	13	132	0.043		0.078		
U1442A 48R-1W 87/92 average									0.056	0.029	0.074	0.067	5
U1439C 38R1 103/106	whole-rock LSB	1	517-03	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	19	11	-0.016		-0.019		
U1439C 38R1 103/106	whole-rock LSB	1	517-03	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	18	32	0.004		-0.011		
U1439C 38R1 103/106	whole-rock LSB	1	517-03	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	20	2	-0.025		-0.054		
U1439C 38R1 103/106 average									-0.012	0.030	-0.028	0.046	3
U1439A 23X-1-W 0/3	whole-rock HSB	1	517-04	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	20	24	0.058		0.091		
U1439A 23X-1-W 0/3	whole-rock HSB	1	517-04	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	18	7	0.063		0.087		
U1439A 23X-1-W 0/3	whole-rock HSB	1	517-04	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	17	21	0.046		0.071		
U1439A 23X-1-W 0/3 average									0.056	0.018	0.083	0.021	3
U1442A 15R-1-W 70/75	whole-rock HSB	1	517-05	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	22	24	0.044		0.066		
U1442A 15R-1-W 70/75	whole-rock HSB	1	517-05	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	15	7	0.079		0.093		
U1442A 15R-1-W 70/75	whole-rock HSB	1	517-05	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	21	77	0.041		0.039		
U1442A 15R-1-W 70/75 average									0.055	0.043	0.066	0.055	3
U1439A 21X-1-W 0/7-ICP	whole-rock HSB	1	517-06	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	17	36	0.081		0.115		
U1439A 21X-1-W 0/7-ICP	whole-rock HSB	1	517-06	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	17	17	0.041		0.060		
U1439A 21X-1-W 0/7-ICP	whole-rock HSB	1	517-06	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	21	14	0.069		0.106		
U1439A 21X-1-W 0/7-ICP average									0.064	0.042	0.094	0.059	3
U1439C 27R-3-W 80/87	whole-rock LSB	1	517-07	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	17	6	0.031		0.055		
U1439C 27R-3-W 80/87	whole-rock LSB	1	517-07	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	20	4	-0.046		-0.065		
U1439C 27R-3-W 80/87	whole-rock LSB	1	517-07	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	22	20	0.007		0.012		
U1439C 27R-3-W 80/87	whole-rock LSB	1	517-07	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	21	24	-0.046		-0.067		
U1439C 27R-3-W 80/87	whole-rock LSB	1	517-07	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	19	50	0.000		0.022		
U1439C 27R-3-W 80/87	whole-rock LSB	1	517-07	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	23	9	-0.031		-0.042		
U1439C 27R-3-W 80/87	whole-rock LSB	1	517-07	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	21	13	-0.012		-0.002		
U1439C 27R-3-W 80/87	whole-rock LSB	1	517-07	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	21	49	-0.007		-0.061		
U1439C 27R-3-W 80/87	whole-rock LSB	1	517-07	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	16	61	0.013		-0.002		
U1439C 27R-3-W 80/87	whole-rock LSB	1	517-07	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	19	1	0.013		0.020		
U1439C 27R-3-W 80/87 average									-0.008	0.052	-0.021	0.076	9
U1439C 23R-1-W 42/48	whole-rock LSB	1	517-08	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	18	34	0.017		0.029		
U1439C 23R-1-W 42/48	whole-rock LSB	1	517-08	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	19	20	0.059		0.085		
U1439C 23R-1-W 42/48	whole-rock LSB	1	517-08	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	17	77	0.043		0.075		
U1439C 23R-1-W 42/48	whole-rock LSB	1	517-08	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	17	33	0.025		0.062		
U1439C 23R-1-W 42/48 average									0.036	0.037	0.063	0.048	4
U1439C 28R-2-W 66/71	whole-rock LSB	1	517-09	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	21	16	0.035		0.065		
U1439C 28R-2-W 66/71	whole-rock LSB	1	517-09	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	19	41	0.040		0.072		
U1439C 28R-2-W 66/71	whole-rock LSB	1	517-09	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	19	47	0.073		0.101		
U1439C 28R-2-W 66/71 average									0.049	0.041	0.079	0.038	3
U1442A 13R-1-W 4/10	whole-rock HSB	1	517-10	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	19	29	0.021		0.069		
U1442A 13R-1-W 4/10	whole-rock HSB	1	517-10	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	19	12	0.038		0.067		
U1442A 13R-1-W 4/10	whole-rock HSB	1	517-10	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	19	7	0.057		0.093		

Appendix F - Iron Isotope Data

U1442A 13R-1-W 4/10	whole-rock HSB	1	517-10	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	16	3	0.027		0.071			
U1442A 13R-1-W 4/10	whole-rock HSB	1	517-10	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	22	12	0.002		0.019			
U1442A 13R-1-W 4/10 average									0.029	0.041	0.064	0.055	5	
U1439C 5R-1-W 92/96	whole-rock HSB	1	517-11	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	15	28	0.017		0.041			
U1439C 5R-1-W 92/96	whole-rock HSB	1	517-11	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	17	7	0.012		0.042			
U1439C 5R-1-W 92/96	whole-rock HSB	1	517-11	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	21	2	-0.003		0.022			
U1439C 5R-1-W 92/96	whole-rock HSB	1	517-11	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	16	12	0.035		0.031			
U1439C 5R-1-W 92/96	whole-rock HSB	1	517-11	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	19	48	0.026		0.022			
U1439C 5R-1-W 92/96	whole-rock HSB	1	517-11	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	21	17	-0.012		-0.010			
U1439C 5R-1-W 92/96 average									0.013	0.035	0.025	0.038	6	
783A-18R1-064/071	whole-rock harzburgite	1	509-01	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	17	7	0.012		0.021			
783A-18R1-064/071	whole-rock harzburgite	1	509-01	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	20	16	0.001		0.004			
783A-18R1-064/071	whole-rock harzburgite	1	509-01	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	17	5	-0.029		-0.036			
783A-18R1-064/071 average									-0.005	0.043	-0.004	0.059	3	
784A-38R2-072/077	whole-rock dunite	1	509-03	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	18	16	0.099		0.135			
784A-38R2-072/077	whole-rock dunite	1	509-03	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	19	12	0.078		0.110			
784A-38R2-072/077	whole-rock dunite	1	509-03	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	21	22	0.129		0.211			
784A-38R2-072/077	whole-rock dunite	1	509-03	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	15	20	0.094		0.171			
784A-38R2-072/077 average									0.100	0.042	0.157	0.089	4	
784A-40R2-070/075	whole-rock dunite	1	509-05	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	15	42	-0.017		-0.023			
784A-40R2-070/075	whole-rock dunite	1	509-05	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	18	1	0.004		-0.029			
784A-40R2-070/075	whole-rock dunite	1	509-05	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	15	27	-0.045		-0.063			
784A-40R2-070/075 average									-0.020	0.049	-0.038	0.043	3	
784A-45R2-33/38	whole-rock harzburgite	1	509-09	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	23	58	0.000		0.006			
784A-45R2-33/38	whole-rock harzburgite	1	509-09	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	17	0	-0.069		-0.095			
784A-45R2-33/38	whole-rock harzburgite	1	509-09	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	18	3	-0.045		-0.059			
784A-45R2-33/38	whole-rock harzburgite	1	509-09	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	20	45	-0.044		-0.068			
784A-45R2-33/38	whole-rock harzburgite	1	509-09	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	16	7	-0.005		0.016			
784A-45R2-33/38	whole-rock harzburgite	1	509-09	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	20	18	-0.022		-0.021			
784A-45R2-33/38	whole-rock harzburgite	1	509-09	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	19	71	-0.056		-0.084			
784A-45R2-33/38	whole-rock harzburgite	1	509-09	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	23	31	-0.061		-0.104			
784A-45R2-33/38	whole-rock harzburgite	1	509-09	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	21	0	-0.031		-0.049			
784A-45R2-33/38 average									-0.037	0.048	-0.051	0.086	9	
784A-45R-CC-7/10	whole-rock harzburgite	1	509-11	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	23	15	0.018		0.028			
784A-45R-CC-7/10	whole-rock harzburgite	1	509-11	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	21	3	-0.004		0.015			
784A-45R-CC-7/10	whole-rock harzburgite	1	509-11	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	17	46	0.055		0.072			
784A-45R-CC-7/10	whole-rock harzburgite	1	509-11	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	15	89	0.031		0.060			
784A-45R-CC-7/10	whole-rock harzburgite	1	509-11	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	19	4	0.050		0.071			
784A-45R-CC-7/10	whole-rock harzburgite	1	509-11	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	22	51	0.018		-0.002			
784A-45R-CC-7/10	whole-rock harzburgite	1	509-11	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	22	18	0.040		0.049			
784A-45R-CC-7/10	whole-rock harzburgite	1	509-11	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	19	12	0.001		0.032			
784A-45R-CC-7/10 average									0.026	0.043	0.041	0.054	8	
783A-18R1-119-124	whole-rock harzburgite	1	509-13	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	19	18	0.082		0.132			
783A-18R1-119-124	whole-rock harzburgite	1	509-13	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	20	8	0.074		0.103			
783A-18R1-119-124	whole-rock harzburgite	1	509-13	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	17	13	0.054		0.070			
783A-18R1-119-124 average									0.070	0.029	0.102	0.062	3	
Sample Name	Type	Digestion	Batch no.	Location	Date	Method	RSE	RSD	$\delta^{56}\text{Fe}_{\text{IRMM-014}} (\text{‰})$	2SD	$\delta^{57}\text{Fe}_{\text{IRMM-014}} (\text{‰})$	2SD	n	
F05JM10 Gnt	garnet mineral separate	1	446-11	Durham	08/02/2020	SSB Neptune MC-ICP MS	7	41	0.071		0.123			
F05JM10 Gnt	garnet mineral separate	1	446-11	Durham	08/02/2020	SSB Neptune MC-ICP MS	6	52	0.088		0.146			
F05JM10 Gnt average									0.079	0.024	0.135	0.033	2	

Appendix F - Iron Isotope Data

BD3692 Gnt	garnet mineral separate	1	446-12	Durham	08/02/2020	SSB Neptune MC-ICP MS	9	15	0.022		0.024		
BD3692 Gnt	garnet mineral separate	1	446-12	Durham	08/02/2020	SSB Neptune MC-ICP MS	7	17	0.015		0.023		
BD3692 Gnt	garnet mineral separate	1	446-12	Durham	08/02/2020	SSB Neptune MC-ICP MS	7	24	-0.002		-0.001		
BD3692 Gnt average									0.012	0.024	0.015	0.028	3

														Literature		
Sample Name	Type	Digestion	Batch no.	Location	Date	Method	RSE	RSD	$\delta^{56}\text{Fe}_{\text{IRMM-014}}$ (‰)	2SD	$\delta^{57}\text{Fe}_{\text{NRM524}}$ (‰)	2SD	n	$\delta^{56}\text{Fe}_{\text{IRMM-014}}$ (‰)	2SD	Reference
BCR-2	USGS reference material	1		Durham	11/09/2019	SSB Neptune MC-ICP MS	9	28	0.097		0.142					
BCR-2	USGS reference material	1		Durham	11/09/2019	SSB Neptune MC-ICP MS	10	16	0.090		0.141					
BCR-2	USGS reference material	1		Durham	11/09/2019	SSB Neptune MC-ICP MS	7	36	0.094		0.127					
BCR-2	USGS reference material	1		Durham	11/09/2019	SSB Neptune MC-ICP MS	12	4	0.098		0.147					
BCR-2	USGS reference material	1		Durham	12/09/2019	SSB Neptune MC-ICP MS	9	5	0.091		0.134					
BCR-2	USGS reference material	1		Durham	12/09/2019	SSB Neptune MC-ICP MS	9	24	0.107		0.161					
BCR-2	USGS reference material	1		Durham	12/09/2019	SSB Neptune MC-ICP MS	10	16	0.089		0.126					
BCR-2 Digestion 1 average									0.095	0.013	0.140	0.024	7			
BCR-2	USGS reference material	2		Durham	21/04/2021	Ni doped Neptune MC-ICP MS	8	101	0.052		0.078					
BCR-2	USGS reference material	2		Durham	21/04/2021	Ni doped Neptune MC-ICP MS	10	6	0.078		0.145					
BCR-2	USGS reference material	2		Durham	22/04/2021	Ni doped Neptune MC-ICP MS	12	125	0.111		0.183					
BCR-2	USGS reference material	2		Durham	22/04/2021	Ni doped Neptune MC-ICP MS	10	65	0.073		0.093					
BCR-2	USGS reference material	2		Durham	23/04/2021	Ni doped Neptune MC-ICP MS	18	215	0.133		0.208					
BCR-2	USGS reference material	2		Durham	23/04/2021	Ni doped Neptune MC-ICP MS	17	335	0.080		0.159					
BCR-2	USGS reference material	2		Durham	26/04/2021	Ni doped Neptune MC-ICP MS	7	99	0.107		0.143					
BCR-2 Digestion 2 average									0.090	0.055	0.144	0.092	7			
BCR-2 average									0.093	0.039	0.142	0.065	14	0.08	0.04	Gong <i>et al.</i> (2020)

GSP-2	USGS reference material	1		Durham	11/09/2019	SSB Neptune MC-ICP MS	9	1	0.153		0.235					
GSP-2	USGS reference material	1		Durham	11/09/2019	SSB Neptune MC-ICP MS	9	11	0.159		0.235					
GSP-2	USGS reference material	1		Durham	11/09/2019	SSB Neptune MC-ICP MS	10	40	0.153		0.210					
GSP-2	USGS reference material	1		Durham	11/09/2019	SSB Neptune MC-ICP MS	11	49	0.155		0.204					
GSP-2	USGS reference material	1		Durham	12/09/2019	SSB Neptune MC-ICP MS	10	23	0.169		0.230					
GSP-2	USGS reference material	1		Durham	12/09/2019	SSB Neptune MC-ICP MS	9	23	0.159		0.234					
GSP-2	USGS reference material	1		Durham	12/09/2019	SSB Neptune MC-ICP MS	11	18	0.167		0.238					
GSP-2	USGS reference material	1		Durham	03/07/2019	SSB Neptune MC-ICP MS	15	1	0.187		0.273					
GSP-2	USGS reference material	1		Durham	03/07/2019	SSB Neptune MC-ICP MS	17	44	0.168		0.222					
GSP-2	USGS reference material	1		Durham	04/07/2019	SSB Neptune MC-ICP MS	16	35	0.134		0.204					
GSP-2	USGS reference material	1		Durham	04/07/2019	SSB Neptune MC-ICP MS	22	2	0.160		0.229					
GSP-2 average									0.160	0.026	0.229	0.039	11	0.15	0.04	Gong <i>et al.</i> (2020)

BIR-1a	USGS reference material	1		Durham	16/04/2021	Ni doped Neptune MC-ICP MS	24	204	0.102		0.146					
BIR-1a	USGS reference material	1		Durham	16/04/2021	Ni doped Neptune MC-ICP MS	17	168	0.060		0.100					
BIR-1a	USGS reference material	1		Durham	16/04/2021	Ni doped Neptune MC-ICP MS	11	123	0.082		0.137					
BIR-1a	USGS reference material	1		Durham	19/04/2021	Ni doped Neptune MC-ICP MS	5	46	0.092		0.125					
BIR-1a	USGS reference material	1		Durham	20/04/2021	Ni doped Neptune MC-ICP MS	10	13	0.030		0.038					
BIR-1a	USGS reference material	1		Durham	21/04/2021	Ni doped Neptune MC-ICP MS	8	154	0.080		0.087					
BIR-1a	USGS reference material	1		Durham	21/04/2021	Ni doped Neptune MC-ICP MS	11	31	0.092		0.159					
BIR-1a	USGS reference material	1		Durham	21/04/2021	Ni doped Neptune MC-ICP MS	17	218	0.088		0.119					
BIR-1a	USGS reference material	1		Durham	22/04/2021	Ni doped Neptune MC-ICP MS	20	231	0.090		0.131					
BIR-1a	USGS reference material	1		Durham	22/04/2021	Ni doped Neptune MC-ICP MS	19	258	0.086		0.132					
BIR-1a Digestion 1 average									0.080	0.041	0.117	0.070	10			
BIR-1a	USGS reference material	2		Durham	16/04/2021	Ni doped Neptune MC-ICP MS	20	144	0.097		0.131					
BIR-1a	USGS reference material	2		Durham	16/04/2021	Ni doped Neptune MC-ICP MS	15	121	0.070		0.109					
BIR-1a	USGS reference material	2		Durham	16/04/2021	Ni doped Neptune MC-ICP MS	10	60	0.052		0.079					
BIR-1a	USGS reference material	2		Durham	19/04/2021	Ni doped Neptune MC-ICP MS	6	20	0.014		0.015					
BIR-1a	USGS reference material	2		Durham	20/04/2021	Ni doped Neptune MC-ICP MS	9	80	0.048		0.089					
BIR-1a	USGS reference material	2		Durham	21/04/2021	Ni doped Neptune MC-ICP MS	9	153	0.051		0.123					
BIR-1a	USGS reference material	2		Durham	21/04/2021	Ni doped Neptune MC-ICP MS	11	124	0.028		0.052					
BIR-1a	USGS reference material	2		Durham	22/04/2021	Ni doped Neptune MC-ICP MS	13	73	0.048		0.086					
BIR-1a	USGS reference material	2		Durham	22/04/2021	Ni doped Neptune MC-ICP MS	13	20	0.084		0.137					

Appendix F - Iron Isotope Data

BIR-1a	USGS reference material	2		Durham	23/04/2021	Ni doped Neptune MC-ICP MS	15	63	0.087		0.133							
BIR-1a	USGS reference material	2		Durham	26/04/2021	Ni doped Neptune MC-ICP MS	17	50	0.053		0.095							
BIR-1a	USGS reference material	2		Durham	27/04/2021	Ni doped Neptune MC-ICP MS	19	138	0.085		0.107							
BIR-1a	USGS reference material	2		Durham	17/05/2021	Ni doped Neptune MC-ICP MS	15	14	0.095		0.161							
BIR-1a	USGS reference material	2		Durham	17/05/2021	Ni doped Neptune MC-ICP MS	13	5	0.082		0.119							
BIR-1a Digestion 2 average									0.064	0.051	0.103	0.075	14					
BIR-1a	USGS reference material	3		Durham	18/05/2021	Ni doped Neptune MC-ICP MS	22	28	0.024		0.054							
BIR-1a	USGS reference material	3		Durham	18/05/2021	Ni doped Neptune MC-ICP MS	17	17	0.076		0.124							
BIR-1a	USGS reference material	3		Durham	18/05/2021	Ni doped Neptune MC-ICP MS	17	22	0.058		0.076							
BIR-1a	USGS reference material	3		Durham	19/05/2021	Ni doped Neptune MC-ICP MS	17	67	0.066		0.117							
BIR-1a	USGS reference material	3		Durham	19/05/2021	Ni doped Neptune MC-ICP MS	22	65	0.029		0.058							
BIR-1a	USGS reference material	3		Durham	19/05/2021	Ni doped Neptune MC-ICP MS	14	23	0.074		0.097							
BIR-1a	USGS reference material	3		Durham	20/05/2021	Ni doped Neptune MC-ICP MS	20	73	0.080		0.137							
BIR-1a	USGS reference material	3		Durham	20/05/2021	Ni doped Neptune MC-ICP MS	18	26	0.052		0.060							
BIR-1a	USGS reference material	3		Durham	20/05/2021	Ni doped Neptune MC-ICP MS	19	58	0.067		0.096							
BIR-1a	USGS reference material	3		Durham	20/05/2021	Ni doped Neptune MC-ICP MS	22	40	0.086		0.122							
BIR-1a	USGS reference material	3		Durham	20/05/2021	Ni doped Neptune MC-ICP MS	21	14	0.074		0.093							
BIR-1a	USGS reference material	3		Durham	20/05/2021	Ni doped Neptune MC-ICP MS	23	3	0.053		0.087							
BIR-1a Digestion 3 average									0.062	0.039	0.093	0.056	12					
BIR-1a average									0.068	0.046	0.068	0.046	36	0.06	0.01	Sossi <i>et al.</i> (2015)		
BHVO-2	USGS reference material	1		Durham	28/04/2021	Ni doped Neptune MC-ICP MS	7	9	0.140		0.199							
BHVO-2	USGS reference material	1		Durham	28/04/2021	Ni doped Neptune MC-ICP MS	5	6	0.107		0.163							
BHVO-2	USGS reference material	1		Durham	29/04/2021	Ni doped Neptune MC-ICP MS	10	26	0.129		0.218							
BHVO-2	USGS reference material	1		Durham	29/04/2021	Ni doped Neptune MC-ICP MS	11	74	0.144		0.220							
BHVO-2	USGS reference material	1		Durham	29/04/2021	Ni doped Neptune MC-ICP MS	11	11	0.098		0.165							
BHVO-2 Digestion 1 average									0.124	0.040	0.193	0.055	5	0.11	0.04	Gong <i>et al.</i> (2020)		

Appendix G - Zinc Isotope Data

Sample Name	Type	Digestion	Batch no.	Location	Date	Method	RSE	RSD	$\delta^{66}\text{Zn}_{\text{ETH}} (\text{‰})$	$\delta^{66}\text{Zn}_{\text{LYON}} (\text{‰})$	2SD	$\delta^{67}\text{Zn}_{\text{ETH}} (\text{‰})$	2SD	$\delta^{68}\text{Zn}_{\text{ETH}} (\text{‰})$	2SD	n
U1440B-8R-1-W 20/23	whole-rock N-FAB	1	2-1	Durham	06/06/2019	Neptune MC-ICP MS	13	52	-0.029	0.251		0.277		-0.122		
U1440B-8R-1-W 20/23	whole-rock N-FAB	1	2-1	Durham	06/06/2019	Neptune MC-ICP MS	13	29	-0.015	0.265		0.129		-0.078		
U1440B-8R-1-W 20/23	whole-rock N-FAB	1	2-1	Durham	06/06/2019	Neptune MC-ICP MS	13	16	-0.026	0.254		0.195		-0.102		
U1440B-8R-1-W 20/23	whole-rock N-FAB	1	2-1	Durham	06/06/2019	Neptune MC-ICP MS	12	11	-0.038	0.242		0.088		-0.132		
U1440B-8R-1-W 20/23 average									-0.027	0.253	0.020	0.172	0.165	-0.108	0.048	4
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	2-2	Durham	06/06/2019	Neptune MC-ICP MS	13	5	-0.053	0.227		0.236		-0.149		
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	2-2	Durham	06/06/2019	Neptune MC-ICP MS	15	16	-0.041	0.239		0.185		-0.107		
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	2-2	Durham	06/06/2019	Neptune MC-ICP MS	14	32	-0.038	0.242		0.091		-0.133		
U1440B-29R-1-W 5/8	whole-rock N-FAB	1	2-2	Durham	06/06/2019	Neptune MC-ICP MS	13	18	-0.055	0.225		0.192		-0.092		
U1440B-29R-1-W 5/8 average									-0.047	0.233	0.017	0.176	0.122	-0.120	0.051	4
U1440B 26R-1-64/68	whole-rock N-FAB	1	2-3	Durham	06/06/2019	Neptune MC-ICP MS	15	7	-0.121	0.159		0.240		-0.161		
U1440B 26R-1-64/68	whole-rock N-FAB	1	2-3	Durham	06/06/2019	Neptune MC-ICP MS	10	23	-0.071	0.209		0.251		-0.132		
U1440B 26R-1-64/68	whole-rock N-FAB	1	2-3	Durham	06/06/2019	Neptune MC-ICP MS	13	25	-0.112	0.168		0.229		-0.124		
U1440B 26R-1-64/68	whole-rock N-FAB	1	2-3	Durham	06/06/2019	Neptune MC-ICP MS	13	25	-0.110	0.170		0.247		-0.162		
U1440B 26R-1-64/68 average									-0.104	0.176	0.044	0.242	0.020	-0.144	0.039	4
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	2-4	Durham	06/06/2019	Neptune MC-ICP MS	13	14	-0.006	0.274		0.196		-0.074		
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	2-4	Durham	06/06/2019	Neptune MC-ICP MS	17	12	-0.061	0.219		0.219		-0.132		
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	2-4	Durham	06/06/2019	Neptune MC-ICP MS	13	3	-0.054	0.226		0.140		-0.123		
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	2-4	Durham	06/06/2019	Neptune MC-ICP MS	13	17	-0.080	0.200		0.083		-0.153		
U1440B-12R-2-W 4/8 average									-0.050	0.230	0.063	0.160	0.122	-0.120	0.067	3
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	06/06/2019	Neptune MC-ICP MS	8	15	-0.067	0.213		0.183		-0.103		
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	06/06/2019	Neptune MC-ICP MS	13	30	-0.069	0.211		0.087		-0.156		
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	06/06/2019	Neptune MC-ICP MS	12	27	-0.086	0.194		0.028		-0.197		
U1440B 28R-1-31/38	whole-rock N-FAB	1	2-7	Durham	06/06/2019	Neptune MC-ICP MS	15	11	-0.053	0.227		0.047		-0.150		
U1440B 28R-1-31/38 average									-0.069	0.211	0.027	0.086	0.138	-0.152	0.077	4
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	2-8	Durham	06/06/2019	Neptune MC-ICP MS	13	7	-0.061	0.219		0.170		-0.091		
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	2-8	Durham	06/06/2019	Neptune MC-ICP MS	15	1	-0.035	0.245		0.147		-0.047		
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	2-8	Durham	06/06/2019	Neptune MC-ICP MS	14	44	-0.039	0.241		0.111		-0.113		
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	2-8	Durham	06/06/2019	Neptune MC-ICP MS	11	15	-0.037	0.243		0.113		-0.166		
U1441A-21R-1-W 37/42 average									-0.043	0.237	0.024	0.135	0.057	-0.104	0.099	4
U1441-A3-19R-1-66/72	whole-rock D-FAB	1	2-9	Durham	06/06/2019	Neptune MC-ICP MS	12	7	-0.294	-0.014		0.144		-0.466		
U1441-A3-19R-1-66/72	whole-rock D-FAB	1	2-9	Durham	06/06/2019	Neptune MC-ICP MS	9	8	-0.290	-0.010		0.037		-0.406		
U1441-A3-19R-1-66/72	whole-rock D-FAB	1	2-9	Durham	06/06/2019	Neptune MC-ICP MS	12	42	-0.266	0.014		0.055		-0.373		
U1441-A3-19R-1-66/72	whole-rock D-FAB	1	2-9	Durham	06/06/2019	Neptune MC-ICP MS	13	7	-0.298	-0.018		0.064		-0.466		
U1441-A3-19R-1-66/72 average									-0.287	-0.007	0.028	0.075	0.095	-0.428	0.093	4
U1440B 17R-1-W 11/13	whole-rock N-FAB	1	487-03	Durham	11/05/2021	Neptune MC-ICP MS	9	8	0.015	0.295		-0.029		0.031		
U1440B 17R-1-W 11/13	whole-rock N-FAB	1	487-03	Durham	11/05/2021	Neptune MC-ICP MS	11	13	0.029	0.309		-0.032		0.052		
U1440B 17R-1-W 11/13	whole-rock N-FAB	1	487-03	Durham	11/05/2021	Neptune MC-ICP MS	9	1	0.037	0.317		-0.039		0.056		
U1440B 17R-1-W 11/13	whole-rock N-FAB	1	487-03	Durham	11/05/2021	Neptune MC-ICP MS	8	1	0.013	0.293		-0.060		0.059		
U1440B 17R-1-W 11/13 average									0.027	0.307	0.024	-0.040	0.027	0.049	0.026	3

Appendix G - Zinc Isotope Data

U1440B 17R-2 23/32	whole-rock N-FAB	1	487-04	Durham	11/05/2021	Neptune MC-ICP MS	8	2	0.094	0.374		0.100		0.147			
U1440B 17R-2 23/32	whole-rock N-FAB	1	487-04	Durham	11/05/2021	Neptune MC-ICP MS	9	4	0.103	0.383		0.114		0.214			
U1440B 17R-2 23/32	whole-rock N-FAB	1	487-04	Durham	11/05/2021	Neptune MC-ICP MS	7	15	0.092	0.372		0.074		0.189			
U1440B 17R-2 23/32	whole-rock N-FAB	1	487-04	Durham	11/05/2021	Neptune MC-ICP MS	7	11	0.092	0.372		0.056		0.184			
U1440B 17R2 23/32 average									0.095	0.375	0.013	0.086	0.052	0.183	0.056	3	

U1442A-35R-1-W 51/55	whole-rock LSB	1	2-10	Durham	06/06/2019	Neptune MC-ICP MS	12	44	-0.603	-0.323		-0.811		-1.201			
U1442A-35R-1-W 51/55	whole-rock LSB	1	2-10	Durham	06/06/2019	Neptune MC-ICP MS	14	11	-0.590	-0.310		-0.764		-1.206			
U1442A-35R-1-W 51/55	whole-rock LSB	1	2-10	Durham	06/06/2019	Neptune MC-ICP MS	11	31	-0.583	-0.303		-0.767		-1.121			
U1442A-35R-1-W 51/55	whole-rock LSB	1	2-10	Durham	06/06/2019	Neptune MC-ICP MS	14	4	-0.563	-0.283		-0.820		-1.155			
U1442A-35R-1-W 51/55 average									-0.585	-0.305	0.033	-0.790	0.059	-1.171	0.080	4	

U1442A 22R-1-122/125	whole-rock HSB	1	2-12	Durham	06/06/2019	Neptune MC-ICP MS	12	25	-0.074	0.206		0.298		-0.113			
U1442A 22R-1-122/125	whole-rock HSB	1	2-12	Durham	06/06/2019	Neptune MC-ICP MS	13	1	-0.061	0.219		0.314		-0.078			
U1442A 22R-1-122/125	whole-rock HSB	1	2-12	Durham	06/06/2019	Neptune MC-ICP MS	14	26	-0.091	0.189		0.199		-0.143			
U1442A 22R-1-122/125	whole-rock HSB	1	2-12	Durham	06/06/2019	Neptune MC-ICP MS	14	11	-0.076	0.204		0.221		-0.173			
U1442A 22R-1-122/125 average									-0.076	0.204	0.025	0.258	0.113	-0.127	0.082	4	

U1439C 22R-1-89/95	whole-rock LSB	1	2-18	Durham	06/06/2019	Neptune MC-ICP MS	15	39	-0.006	0.274		0.320		-0.020			
U1439C 22R-1-89/95	whole-rock LSB	1	2-18	Durham	06/06/2019	Neptune MC-ICP MS	13	23	-0.047	0.233		0.180		-0.068			
U1439C 22R-1-89/95	whole-rock LSB	1	2-18	Durham	06/06/2019	Neptune MC-ICP MS	12	16	-0.059	0.221		0.197		-0.116			
U1439C 22R-1-89/95	whole-rock LSB	1	2-18	Durham	06/06/2019	Neptune MC-ICP MS	16	4	-0.093	0.187		0.304		-0.116			
U1439C 22R-1-89/95 average									-0.051	0.229	0.072	0.250	0.144	-0.080	0.092	4	

U1439C-37R-1-W 42/48	whole-rock HMA	1	511-05	Durham	24/03/2021	Neptune MC-ICP MS	10	31	0.040	0.320		0.126		0.068			
U1439C-37R-1-W 42/48	whole-rock HMA	1	511-05	Durham	24/03/2021	Neptune MC-ICP MS	8	18	0.066	0.346		0.029		0.109			
U1439C-37R-1-W 42/48	whole-rock HMA	1	511-05	Durham	24/03/2021	Neptune MC-ICP MS	8	7	0.038	0.318		0.034		0.087			
U1439C-37R-1-W 42/48 digestion 1 average									0.048	0.328	0.032	0.063	0.110	0.088	0.041	3	
U1439C-37R-1-W 42/48	whole-rock HMA	2	487-08	Durham	11/05/2021	Neptune MC-ICP MS	8	29	0.047	0.327		0.080		0.080			
U1439C-37R-1-W 42/48	whole-rock HMA	2	487-08	Durham	11/05/2021	Neptune MC-ICP MS	11	11	0.057	0.337		0.007		0.110			
U1439C-37R-1-W 42/48	whole-rock HMA	2	487-08	Durham	11/05/2021	Neptune MC-ICP MS	9	17	0.028	0.308		0.044		0.061			
U1439C-37R-1-W 42/48	whole-rock HMA	2	487-08	Durham	11/05/2021	Neptune MC-ICP MS	9	8	0.035	0.315		-0.010		0.098			
U1439C-37R-1-W 42/48 digestion 2 average									0.042	0.322	0.026	0.030	0.081	0.088	0.043	3	
U1439C-37R-1-W 42/48 average									0.044	0.324	0.027	0.044	0.092	0.088	0.039	7	

U1439C 19R4 11/17	whole-rock LSB	1	512-03	Durham	23/03/2021	Neptune MC-ICP MS	10	36	-0.010	0.270		-0.071		-0.024			
U1439C 19R4 11/17	whole-rock LSB	1	512-03	Durham	23/03/2021	Neptune MC-ICP MS	11	13	0.023	0.303		-0.122		-0.045			
U1439C 19R4 11/17	whole-rock LSB	1	512-03	Durham	23/03/2021	Neptune MC-ICP MS	7	14	0.015	0.295		-0.059		0.036			
U1439C 19R4 11/17 average									0.009	0.289	0.034	-0.084	0.067	-0.011	0.085	3	

U1442A 47R1-W 50/55	whole-rock HSB	1	512-04	Durham	23/03/2021	Neptune MC-ICP MS	10	16	-0.052	0.228		-0.094		-0.103			
U1442A 47R1-W 50/55	whole-rock HSB	1	512-04	Durham	23/03/2021	Neptune MC-ICP MS	8	1	-0.064	0.216		-0.178		-0.141			
U1442A 47R1-W 50/55	whole-rock HSB	1	512-04	Durham	23/03/2021	Neptune MC-ICP MS	9	24	-0.062	0.218		-0.165		-0.119			
U1442A 47R1-W 50/55 average									-0.059	0.221	0.012	-0.146	0.091	-0.121	0.038	3	

U1442A 23R1 99/103	whole-rock LSB	1	512-05	Durham	23/03/2021	Neptune MC-ICP MS	8	7	0.084	0.364		0.074		0.117			
U1442A 23R1 99/103	whole-rock LSB	1	512-05	Durham	23/03/2021	Neptune MC-ICP MS	9	8	0.069	0.349		0.006		0.109			
U1442A 23R1 99/103	whole-rock LSB	1	512-05	Durham	23/03/2021	Neptune MC-ICP MS	7	7	0.048	0.328		-0.040		0.087			
U1442A 23R1 99/103 average									0.067	0.347	0.036	0.013	0.115	0.105	0.031	3	

Appendix G - Zinc Isotope Data

U1442A 56R1 19/24	whole-rock LSB	1	512-06	Durham	23/03/2021	Neptune MC-ICP MS	7	14	0.001	0.281		-0.072		-0.001		
U1442A 56R1 19/24	whole-rock LSB	1	512-06	Durham	23/03/2021	Neptune MC-ICP MS	8	18	-0.022	0.258		-0.146		-0.057		
U1442A 56R1 19/24	whole-rock LSB	1	512-06	Durham	23/03/2021	Neptune MC-ICP MS	8	9	-0.034	0.246		-0.113		-0.055		
U1442A 56R1 19/24 average									-0.018	0.262	0.035	-0.110	0.074	-0.038	0.064	3
U1439C 40R1 33/38	whole-rock LSB	1	512-07	Durham	23/03/2021	Neptune MC-ICP MS	9	11	-0.180	0.100		-0.273		-0.315		
U1439C 40R1 33/38	whole-rock LSB	1	512-07	Durham	23/03/2021	Neptune MC-ICP MS	11	7	-0.182	0.098		-0.348		-0.362		
U1439C 40R1 33/38	whole-rock LSB	1	512-07	Durham	23/03/2021	Neptune MC-ICP MS	10	10	-0.178	0.102		-0.316		-0.346		
U1439C 40R1 33/38 average									-0.180	0.100	0.003	-0.312	0.075	-0.341	0.048	3
U1439C 31R1 15/20	whole-rock LSB	1	512-08	Durham	23/03/2021	Neptune MC-ICP MS	9	14	-0.054	0.226		-0.128		-0.108		
U1439C 31R1 15/20	whole-rock LSB	1	512-08	Durham	23/03/2021	Neptune MC-ICP MS	8	28	-0.067	0.213		-0.172		-0.130		
U1439C 31R1 15/20	whole-rock LSB	1	512-08	Durham	23/03/2021	Neptune MC-ICP MS	11	25	-0.060	0.220		-0.193		-0.120		
U1439C 31R1 15/20 average									-0.060	0.220	0.014	-0.165	0.067	-0.119	0.021	3
U1439C 26R1 132/137	whole-rock LSB	1	512-09	Durham	23/03/2021	Neptune MC-ICP MS	9	12	-0.074	0.206		-0.158		-0.165		
U1439C 26R1 132/137	whole-rock LSB	1	512-09	Durham	23/03/2021	Neptune MC-ICP MS	10	4	-0.074	0.206		-0.234		-0.201		
U1439C 26R1 132/137	whole-rock LSB	1	512-09	Durham	23/03/2021	Neptune MC-ICP MS	8	13	-0.086	0.194		-0.165		-0.186		
U1439C 26R1 132/137 average									-0.078	0.202	0.014	-0.186	0.084	-0.184	0.037	3
U1439C 19R3 58/62	whole-rock LSB	1	512-10	Durham	23/03/2021	Neptune MC-ICP MS	7	9	-0.309	-0.029		-0.498		-0.592		
U1439C 19R3 58/62	whole-rock LSB	1	512-10	Durham	23/03/2021	Neptune MC-ICP MS	9	3	-0.276	0.004		-0.583		-0.622		
U1439C 19R3 58/62	whole-rock LSB	1	512-10	Durham	23/03/2021	Neptune MC-ICP MS	7	16	-0.320	-0.040		-0.596		-0.620		
U1439C 19R3 58/62	whole-rock LSB	1	512-10	Durham	23/03/2021	Neptune MC-ICP MS	9	8	-0.303	-0.023		-0.625		-0.596		
U1439C 19R3 58/62	whole-rock LSB	1	512-10	Durham	23/03/2021	Neptune MC-ICP MS	9	14	-0.312	-0.032		-0.611		-0.577		
U1439C 19R3 58/62	whole-rock LSB	1	512-10	Durham	23/03/2021	Neptune MC-ICP MS	7	5	-0.277	0.003		-0.633		-0.536		
U1439C 19R3 58/62 average									-0.300	-0.020	0.038	-0.591	0.098	-0.590	0.063	6
U1439C 6R1 25/30	whole-rock HSB	1	512-11	Durham	23/03/2021	Neptune MC-ICP MS	10	5	-0.055	0.225		-0.188		-0.136		
U1439C 6R1 25/30	whole-rock HSB	1	512-11	Durham	23/03/2021	Neptune MC-ICP MS	10	14	-0.079	0.201		-0.255		-0.183		
U1439C 6R1 25/30	whole-rock HSB	1	512-11	Durham	23/03/2021	Neptune MC-ICP MS	9	29	-0.115	0.165		-0.292		-0.196		
U1439C 6R1 25/30	whole-rock HSB	1	512-11	Durham	23/03/2021	Neptune MC-ICP MS	8	23	-0.093	0.187		-0.314		-0.171		
U1439C 6R1 25/30	whole-rock HSB	1	512-11	Durham	23/03/2021	Neptune MC-ICP MS	10	1	-0.106	0.174		-0.303		-0.180		
U1439C 6R1 25/30	whole-rock HSB	1	512-11	Durham	23/03/2021	Neptune MC-ICP MS	8	0	-0.060	0.220		-0.293		-0.112		
U1439C 6R1 25/30 average									-0.084	0.196	0.049	-0.274	0.093	-0.163	0.064	6
U1439C 11R1 124/127	whole-rock LSB	1	512-12	Durham	23/03/2021	Neptune MC-ICP MS	10	15	0.002	0.282		-0.066		0.003		
U1439C 11R1 124/127	whole-rock LSB	1	512-12	Durham	23/03/2021	Neptune MC-ICP MS	8	5	-0.048	0.232		-0.149		-0.098		
U1439C 11R1 124/127	whole-rock LSB	1	512-12	Durham	23/03/2021	Neptune MC-ICP MS	11	15	-0.013	0.267		-0.156		-0.040		
U1439C 11R1 124/127	whole-rock LSB	1	512-12	Durham	23/03/2021	Neptune MC-ICP MS	7	12	-0.018	0.262		-0.147		-0.046		
U1439C 11R1 124/127	whole-rock LSB	1	512-12	Durham	23/03/2021	Neptune MC-ICP MS	9	8	-0.021	0.259		-0.146		0.009		
U1439C 11R1 124/127	whole-rock LSB	1	512-12	Durham	23/03/2021	Neptune MC-ICP MS	11	4	-0.009	0.271		-0.172		-0.014		
U1439C 11R1 124/127 average									-0.018	0.262	0.033	-0.140	0.074	-0.031	0.079	6
U1442A 49R2-W 60/65	whole-rock LSB	1	515-03	Durham	24/03/2021	Neptune MC-ICP MS	7	10	0.014	0.294		0.133		0.050		
U1442A 49R2-W 60/65	whole-rock LSB	1	515-03	Durham	24/03/2021	Neptune MC-ICP MS	8	2	0.031	0.311		0.023		0.072		
U1442A 49R2-W 60/65	whole-rock LSB	1	515-03	Durham	24/03/2021	Neptune MC-ICP MS	10	7	0.012	0.292		0.029		0.087		
U1442A 49R2-W 60/65 average									0.019	0.299	0.020	0.062	0.124	0.070	0.037	3
U1442A 30R2-W 21/27	whole-rock BB	1	515-04	Durham	24/03/2021	Neptune MC-ICP MS	11	57	0.010	0.290		0.017		0.007		

Appendix G - Zinc Isotope Data

U1442A 30R2-W 21/27	whole-rock BB	1	515-04	Durham	24/03/2021	Neptune MC-ICP MS	10	5	-0.015	0.265		-0.041		-0.040			
U1442A 30R2-W 21/27	whole-rock BB	1	515-04	Durham	25/03/2021	Neptune MC-ICP MS	7	6	-0.043	0.237		-0.162		-0.107			
U1442A 30R2-W 21/27	whole-rock BB	1	515-04	Durham	25/03/2021	Neptune MC-ICP MS	10	15	-0.055	0.225		-0.180		-0.124			
U1442A 30R2-W 21/27	whole-rock BB	1	515-04	Durham	25/03/2021	Neptune MC-ICP MS	9	16	-0.050	0.230		-0.170		-0.104			
U1442A 30R2-W 21/27	whole-rock BB	1	515-04	Durham	25/03/2021	Neptune MC-ICP MS	9	16	-0.050	0.230		-0.170		-0.104			
U1442A 30R2-W 21/27 average									-0.034		0.246	0.051	-0.118	0.169	-0.079	0.102	6

U1442A 36R2-W 17/22	whole-rock LSB	1	515-05	Durham	24/03/2021	Neptune MC-ICP MS	11	23	-0.024	0.256		0.016		-0.042			
U1442A 36R2-W 17/22	whole-rock LSB	1	515-05	Durham	24/03/2021	Neptune MC-ICP MS	10	0	0.019	0.299		0.024	0.000				
U1442A 36R2-W 17/22	whole-rock LSB	1	515-05	Durham	24/03/2021	Neptune MC-ICP MS	8	3	0.012	0.292		-0.046	0.012				
U1442A 36R2-W 17/22	whole-rock LSB	1	515-05	Durham	25/03/2021	Neptune MC-ICP MS	7	11	0.000	0.280		-0.090	-0.045				
U1442A 36R2-W 17/22	whole-rock LSB	1	515-05	Durham	25/03/2021	Neptune MC-ICP MS	12	3	-0.046	0.234		-0.060	-0.038				
U1442A 36R2-W 17/22	whole-rock LSB	1	515-05	Durham	25/03/2021	Neptune MC-ICP MS	9	10	0.007	0.287		-0.067	-0.027				
U1442A 36R2-W 17/22	whole-rock LSB	1	515-05	Durham	25/03/2021	Neptune MC-ICP MS	10	22	0.007	0.287		-0.087	0.001				
U1442A 36R2-W 17/22 average									-0.003		0.277	0.046	-0.044	0.093	-0.020	0.047	7

U1439C 2R3-W 38/46	whole-rock HSB	1	515-06	Durham	24/03/2021	Neptune MC-ICP MS	7	13	-0.073	0.207		-0.104		-0.183		
U1439C 2R3-W 38/46	whole-rock HSB	1	515-06	Durham	24/03/2021	Neptune MC-ICP MS	9	6	-0.058	0.222		-0.075		-0.152		
U1439C 2R3-W 38/46	whole-rock HSB	1	515-06	Durham	24/03/2021	Neptune MC-ICP MS	8	10	-0.061	0.219		-0.143		-0.133		
U1439C 2R3-W 38/46 average									-0.064	0.216	0.016	-0.107	0.069	-0.156	0.051	3

U1442A 54R1-W 13/18	whole-rock LSB	1	515-07	Durham	23/03/2021	Neptune MC-ICP MS	9	10	0.024	0.304	0.042	0.056	0.176	0.066	0.108	7
U1442A 54R1-W 13/18	whole-rock LSB	1	515-07	Durham	23/03/2021	Neptune MC-ICP MS	10	9	0.005	0.285		0.052		-0.011		
U1442A 54R1-W 13/18	whole-rock LSB	1	515-07	Durham	23/03/2021	Neptune MC-ICP MS	11	1	-0.022	0.258		-0.052		-0.059		
U1442A 54R1-W 13/18	whole-rock LSB	1	515-07	Durham	23/03/2021	Neptune MC-ICP MS	11	17	-0.019	0.261		-0.145		-0.049		
U1442A 54R1-W 13/18	whole-rock LSB	1	515-07	Durham	23/03/2021	Neptune MC-ICP MS	9	33	-0.038	0.242		-0.167		-0.085		
U1442A 54R1-W 13/18	whole-rock LSB	1	515-07	Durham	23/03/2021	Neptune MC-ICP MS	8	3	-0.027	0.253		-0.098		-0.092		
U1442A 54R1-W 13/18	whole-rock LSB	1	515-07	Durham	23/03/2021	Neptune MC-ICP MS	11	18	-0.024	0.256		-0.066		-0.026		
U1442A 54R1-W 13/18 average									-0.014	0.266		-0.060		-0.037		

U1442A 23R2-W 30/35	whole-rock HSB	1	515-08	Durham	24/03/2021	Neptune MC-ICP MS	10	19	-0.043	0.237		0.031		-0.085		
U1442A 23R2-W 30/35	whole-rock HSB	1	515-08	Durham	24/03/2021	Neptune MC-ICP MS	11	19	-0.006	0.274		-0.056		-0.042		
U1442A 23R2-W 30/35	whole-rock HSB	1	515-08	Durham	24/03/2021	Neptune MC-ICP MS	9	18	-0.027	0.253		-0.082		-0.040		
U1442A 23R2-W 30/35 average									-0.026	0.254	0.037	-0.036	0.119	-0.056	0.051	3

U1442A 28R1-W 10/14	whole-rock HSB	1	515-09	Durham	24/03/2021	Neptune MC-ICP MS	9	6	-0.292	-0.012		-0.392		-0.574		
U1442A 28R1-W 10/14	whole-rock HSB	1	515-09	Durham	24/03/2021	Neptune MC-ICP MS	8	18	-0.295	-0.015		-0.398		-0.576		
U1442A 28R1-W 10/14	whole-rock HSB	1	515-09	Durham	24/03/2021	Neptune MC-ICP MS	9	20	-0.288	-0.008		-0.462		-0.598		
U1442A 28R1-W 10/14 average									-0.292	-0.012	0.008	-0.417	0.077	-0.582	0.027	3

U1439C 33R2-W 23/30	whole-rock LSB	1	515-10	Durham	24/03/2021	Neptune MC-ICP MS	8	7	-0.063	0.217		-0.019		-0.096		
U1439C 33R2-W 23/30	whole-rock LSB	1	515-10	Durham	24/03/2021	Neptune MC-ICP MS	7	6	-0.055	0.225		-0.110		-0.115		
U1439C 33R2-W 23/30	whole-rock LSB	1	515-10	Durham	24/03/2021	Neptune MC-ICP MS	10	13	-0.056	0.224		-0.126		-0.130		
U1439C 33R2-W 23/30 average									-0.058	0.222	0.009	-0.085	0.115	-0.114	0.034	3

U1442A 57R2-W 116/121	whole-rock LSB	1	515-11	Durham	24/03/2021	Neptune MC-ICP MS	11	6	-0.037	0.243		-0.035		-0.053		
U1442A 57R2-W 116/121	whole-rock LSB	1	515-11	Durham	24/03/2021	Neptune MC-ICP MS	9	9	-0.026	0.254		-0.043		-0.062		
U1442A 57R2-W 116/121	whole-rock LSB	1	515-11	Durham	24/03/2021	Neptune MC-ICP MS	9	4	-0.037	0.243		-0.133		-0.082		
U1442A 57R2-W 116/121 average									-0.033	0.247	0.012	-0.070	0.109	-0.066	0.029	3

Appendix G - Zinc Isotope Data

U1442A 48R1-W 87/92	whole-rock HSB	1	515-12	Durham	24/03/2021	Neptune MC-ICP MS	10	0	-0.081	0.199		-0.112		-0.113			
U1442A 48R1-W 87/92	whole-rock HSB	1	515-12	Durham	24/03/2021	Neptune MC-ICP MS	11	13	-0.058	0.222		-0.071		-0.147			
U1442A 48R1-W 87/92	whole-rock HSB	1	515-12	Durham	24/03/2021	Neptune MC-ICP MS	8	12	-0.065	0.215		-0.117		-0.133			
U1442A 48R1-W 87/92 average									-0.068	0.212	0.024	-0.100	0.051	-0.131	0.034	3	
U1439C 38R1 103/106	whole-rock LSB	1	517-03	Durham	10/05/2021	Neptune MC-ICP MS	10	6	-0.032	0.248		-0.055		-0.068			
U1439C 38R1 103/106	whole-rock LSB	1	517-03	Durham	10/05/2021	Neptune MC-ICP MS	8	10	-0.004	0.276		0.013		0.027			
U1439C 38R1 103/106	whole-rock LSB	1	517-03	Durham	10/05/2021	Neptune MC-ICP MS	8	8	-0.024	0.256		-0.064		-0.013			
U1439C 38R1 103/106	whole-rock LSB	1	517-03	Durham	10/05/2021	Neptune MC-ICP MS	9	1	-0.006	0.274		-0.073		-0.021			
U1439C 38R1 103/106	whole-rock LSB	1	517-03	Durham	10/05/2021	Neptune MC-ICP MS	10	3	-0.027	0.253		-0.096		-0.023			
U1439C 38R1 103/106 average									-0.019	0.261	0.025	-0.055	0.082	-0.019	0.068	5	
U1439A 23X-1-W 0/3	whole-rock HSB	1	517-04	Durham	10/05/2021	Neptune MC-ICP MS	8	15	-0.027	0.253		-0.085		-0.042			
U1439A 23X-1-W 0/3	whole-rock HSB	1	517-04	Durham	10/05/2021	Neptune MC-ICP MS	8	2	-0.022	0.258		-0.061		-0.050			
U1439A 23X-1-W 0/3	whole-rock HSB	1	517-04	Durham	10/05/2021	Neptune MC-ICP MS	9	5	-0.014	0.266		-0.073		0.000			
U1439A 23X-1-W 0/3	whole-rock HSB	1	517-04	Durham	10/05/2021	Neptune MC-ICP MS	6	1	-0.021	0.259		-0.061		-0.049			
U1439A 23X-1-W 0/3 average									-0.021	0.259	0.010	-0.070	0.023	-0.035	0.047	4	
U1442A 15R-1-W 70/75	whole-rock HSB	1	517-05	Durham	10/05/2021	Neptune MC-ICP MS	9	7	-0.059	0.221		-0.126		-0.089			
U1442A 15R-1-W 70/75	whole-rock HSB	1	517-05	Durham	10/05/2021	Neptune MC-ICP MS	8	10	-0.051	0.229		-0.050		-0.075			
U1442A 15R-1-W 70/75	whole-rock HSB	1	517-05	Durham	10/05/2021	Neptune MC-ICP MS	6	13	-0.066	0.214		-0.140		-0.142			
U1442A 15R-1-W 70/75	whole-rock HSB	1	517-05	Durham	10/05/2021	Neptune MC-ICP MS	7	0	-0.053	0.227		-0.108		-0.108			
U1442A 15R-1-W 70/75 average									-0.057	0.223	0.013	-0.106	0.079	-0.104	0.057	4	
U1439A 21X-1-W 0/7-ICP	whole-rock HSB	1	517-06	Durham	10/05/2021	Neptune MC-ICP MS	8	6	-0.051	0.229		-0.029		-0.103			
U1439A 21X-1-W 0/7-ICP	whole-rock HSB	1	517-06	Durham	10/05/2021	Neptune MC-ICP MS	9	5	-0.059	0.221		-0.095		-0.074			
U1439A 21X-1-W 0/7-ICP	whole-rock HSB	1	517-06	Durham	10/05/2021	Neptune MC-ICP MS	8	1	-0.044	0.236		-0.069		-0.089			
U1439A 21X-1-W 0/7-ICP	whole-rock HSB	1	517-06	Durham	10/05/2021	Neptune MC-ICP MS	10	7	-0.044	0.236		-0.099		-0.073			
U1439A 21X-1-W 0/7-ICP average									-0.050	0.230	0.014	-0.073	0.064	-0.085	0.029	4	
U1439C 27R-3-W 80/87	whole-rock LSB	1	517-07	Durham	10/05/2021	Neptune MC-ICP MS	9	17	-0.038	0.242		-0.034		-0.087			
U1439C 27R-3-W 80/87	whole-rock LSB	1	517-07	Durham	10/05/2021	Neptune MC-ICP MS	8	10	-0.055	0.225		-0.061		-0.109			
U1439C 27R-3-W 80/87	whole-rock LSB	1	517-07	Durham	10/05/2021	Neptune MC-ICP MS	10	4	-0.051	0.229		-0.083		-0.095			
U1439C 27R-3-W 80/87	whole-rock LSB	1	517-07	Durham	10/05/2021	Neptune MC-ICP MS	7	1	-0.056	0.224		-0.126		-0.119			
U1439C 27R-3-W 80/87 average									-0.050	0.230	0.016	-0.076	0.078	-0.103	0.029	4	
U1439C 23R-1-W 42/48	whole-rock LSB	1	517-08	Durham	10/05/2021	Neptune MC-ICP MS	8	7	-0.024	0.256		-0.071		-0.025			
U1439C 23R-1-W 42/48	whole-rock LSB	1	517-08	Durham	10/05/2021	Neptune MC-ICP MS	6	16	-0.021	0.259		-0.036		-0.072			
U1439C 23R-1-W 42/48	whole-rock LSB	1	517-08	Durham	10/05/2021	Neptune MC-ICP MS	9	5	-0.035	0.245		-0.113		-0.057			
U1439C 23R-1-W 42/48	whole-rock LSB	1	517-08	Durham	10/05/2021	Neptune MC-ICP MS	9	1	-0.048	0.232		-0.120		-0.067			
U1439C 23R-1-W 42/48 average									-0.032	0.248	0.025	-0.085	0.078	-0.055	0.042	4	
U1439C 28R-2-W 66/71	whole-rock LSB	1	517-09	Durham	10/05/2021	Neptune MC-ICP MS	9	13	-0.046	0.234		-0.103		-0.083			
U1439C 28R-2-W 66/71	whole-rock LSB	1	517-09	Durham	10/05/2021	Neptune MC-ICP MS	8	6	-0.051	0.229		-0.126		-0.074			
U1439C 28R-2-W 66/71	whole-rock LSB	1	517-09	Durham	10/05/2021	Neptune MC-ICP MS	7	14	-0.038	0.242		-0.142		-0.072			
U1439C 28R-2-W 66/71	whole-rock LSB	1	517-09	Durham	10/05/2021	Neptune MC-ICP MS	6	2	-0.038	0.242		-0.142		-0.050			
U1439C 28R-2-W 66/71 average									-0.043	0.237	0.012	-0.128	0.037	-0.070	0.028	4	
U1442A 13R-1-W 4/10	whole-rock HSB	1	517-10	Durham	10/05/2021	Neptune MC-ICP MS	9	13	0.006	0.286		-0.008		0.032			
U1442A 13R-1-W 4/10	whole-rock HSB	1	517-10	Durham	10/05/2021	Neptune MC-ICP MS	8	3	0.012	0.292		0.010		0.055			

Appendix G - Zinc Isotope Data

U1442A 13R-1-W 4/10	whole-rock HSB	1	517-10	Durham	10/05/2021	Neptune MC-ICP MS	10	4	0.030	0.310		-0.034		0.075		
U1442A 13R-1-W 4/10	whole-rock HSB	1	517-10	Durham	10/05/2021	Neptune MC-ICP MS	8	7	0.009	0.289		-0.035		-0.007		
U1442A 13R-1-W 4/10 average									0.014	0.294	0.021	-0.017	0.043	0.039	0.070	4
U1439C 5R-1-W 92/96	whole-rock HSB	1	517-11	Durham	10/05/2021	Neptune MC-ICP MS	8	8	0.022	0.302		0.039		0.038		
U1439C 5R-1-W 92/96	whole-rock HSB	1	517-11	Durham	10/05/2021	Neptune MC-ICP MS	8	3	0.022	0.302		-0.025		0.070		
U1439C 5R-1-W 92/96	whole-rock HSB	1	517-11	Durham	10/05/2021	Neptune MC-ICP MS	9	12	0.039	0.319		-0.042		0.059		
U1439C 5R-1-W 92/96	whole-rock HSB	1	517-11	Durham	10/05/2021	Neptune MC-ICP MS	10	9	0.016	0.296		0.009		0.027		
U1439C 5R-1-W 92/96 average									0.025	0.305	0.020	-0.005	0.072	0.048	0.039	4
U1439C 31R-5-W 12/17	whole-rock LSB	1	487-06	Durham	11/05/2021	Neptune MC-ICP MS	6	11	-0.071	0.209		-0.164		-0.094		
U1439C 31R-5-W 12/17	whole-rock LSB	1	487-06	Durham	11/05/2021	Neptune MC-ICP MS	8	9	-0.049	0.231		-0.119		-0.077		
U1439C 31R-5-W 12/17	whole-rock LSB	1	487-06	Durham	11/05/2021	Neptune MC-ICP MS	6	5	-0.036	0.244		-0.130		-0.063		
U1439C 31R-5-W 12/17	whole-rock LSB	1	487-06	Durham	11/05/2021	Neptune MC-ICP MS	7	2	-0.034	0.246		-0.148		-0.073		
U1439C 31R-5-W 12/17 average									-0.048	0.232	0.034	-0.140	0.040	-0.077	0.026	4
U1439C 10R-2-W 13/19	whole-rock BB	1	487-07	Durham	11/05/2021	Neptune MC-ICP MS	7	12	0.015	0.295		-0.020		0.033		
U1439C 10R-2-W 13/19	whole-rock BB	1	487-07	Durham	11/05/2021	Neptune MC-ICP MS	10	23	0.004	0.284		-0.036		0.017		
U1439C 10R-2-W 13/19	whole-rock BB	1	487-07	Durham	11/05/2021	Neptune MC-ICP MS	8	14	0.008	0.288		-0.024		0.034		
U1439C 10R-2-W 13/19	whole-rock BB	1	487-07	Durham	11/05/2021	Neptune MC-ICP MS	9	2	0.026	0.306		-0.011		0.045		
U1439C 10R-2-W 13/19 average									0.013	0.293	0.020	-0.023	0.021	0.032	0.023	4
U1439C 4R-1-W 26/32	whole-rock HSB	1	487-09	Durham	11/05/2021	Neptune MC-ICP MS	9	18	-0.017	0.263		-0.066		-0.019		
U1439C 4R-1-W 26/32	whole-rock HSB	1	487-09	Durham	11/05/2021	Neptune MC-ICP MS	8	3	-0.015	0.265		-0.065		-0.029		
U1439C 4R-1-W 26/32	whole-rock HSB	1	487-09	Durham	11/05/2021	Neptune MC-ICP MS	9	1	-0.028	0.252		-0.093		-0.028		
U1439C 4R-1-W 26/32	whole-rock HSB	1	487-09	Durham	11/05/2021	Neptune MC-ICP MS	9	9	-0.031	0.249		-0.086		-0.016		
U1439C 4R-1-W 26/32 average									-0.023	0.257	0.016	-0.077	0.028	-0.023	0.013	4
U1439C 16R-1 26/30	whole-rock LSB	1	487-10	Durham	11/05/2021	Neptune MC-ICP MS	8	13	-0.060	0.220		-0.099		-0.090		
U1439C 16R-1 26/30	whole-rock LSB	1	487-10	Durham	11/05/2021	Neptune MC-ICP MS	9	7	-0.055	0.225		-0.108		-0.089		
U1439C 16R-1 26/30	whole-rock LSB	1	487-10	Durham	11/05/2021	Neptune MC-ICP MS	9	9	-0.039	0.241		-0.131		-0.053		
U1439C 16R-1 26/30	whole-rock LSB	1	487-10	Durham	11/05/2021	Neptune MC-ICP MS	8	2	-0.065	0.215		-0.125		-0.121		
U1439C 16R-1 26/30 average									-0.055	0.225	0.023	-0.116	0.030	-0.088	0.056	4
U1439C 41R-1 99/106	whole-rock LSB	1	487-11	Durham	11/05/2021	Neptune MC-ICP MS	10	11	-0.036	0.244		-0.091		-0.048		
U1439C 41R-1 99/106	whole-rock LSB	1	487-11	Durham	11/05/2021	Neptune MC-ICP MS	7	15	-0.013	0.267		-0.016		-0.033		
U1439C 41R-1 99/106	whole-rock LSB	1	487-11	Durham	11/05/2021	Neptune MC-ICP MS	7	21	-0.030	0.250		-0.053		-0.035		
U1439C 41R-1 99/106	whole-rock LSB	1	487-11	Durham	11/05/2021	Neptune MC-ICP MS	8	2	-0.022	0.258		-0.095		-0.045		
U1439C 41R-1 99/106 average									-0.025	0.255	0.020	-0.064	0.074	-0.040	0.014	4
U1439C 29R-4-W 74/82	whole-rock LSB	1	487-12	Durham	11/05/2021	Neptune MC-ICP MS	9	7	-0.036	0.244		-0.150		-0.101		
U1439C 29R-4-W 74/82	whole-rock LSB	1	487-12	Durham	11/05/2021	Neptune MC-ICP MS	10	18	-0.052	0.228		-0.156		-0.096		
U1439C 29R-4-W 74/82	whole-rock LSB	1	487-12	Durham	11/05/2021	Neptune MC-ICP MS	8	4	-0.074	0.206		-0.136		-0.118		
U1439C 29R-4-W 74/82	whole-rock LSB	1	487-12	Durham	11/05/2021	Neptune MC-ICP MS	9	6	-0.069	0.211		-0.181		-0.136		
U1439C 29R-4-W 74/82 digestion 1 average									-0.058	0.222	0.034	-0.156	0.037	-0.113	0.037	4
U1439C 29R-4-W 74/82		2	468-02	Durham	10/05/2021	Neptune MC-ICP MS	9	26	-0.063	0.217		-0.127		-0.085		
U1439C 29R-4-W 74/82	whole-rock LSB	2	468-02	Durham	10/05/2021	Neptune MC-ICP MS	9	7	-0.042	0.238		-0.063		-0.058		
U1439C 29R-4-W 74/82	whole-rock LSB	2	468-02	Durham	10/05/2021	Neptune MC-ICP MS	7	5	-0.034	0.246		-0.066		-0.041		
U1439C 29R-4-W 74/82	whole-rock LSB	2	468-02	Durham	10/05/2021	Neptune MC-ICP MS	8	3	-0.019	0.261		-0.103		-0.030		
U1439C 29R-4-W 74/82 digestion 2 average									-0.040	0.240	0.037	-0.090	0.062	-0.054	0.048	4

Appendix G - Zinc Isotope Data

U1439C 29R-4-W 74/82 average										-0.049	0.231	0.038	-0.123	0.085	-0.083	0.075	8
U1442A 20R-1 104/108	whole-rock HSB	1	487-05	Durham	11/05/2021	Neptune MC-ICP MS	8	10	0.007	0.287		-0.008		0.028			
U1442A 20R-1 104/108	whole-rock HSB	1	487-05	Durham	11/05/2021	Neptune MC-ICP MS	8	2	-0.025	0.255		-0.027		-0.037			
U1442A 20R-1 104/108	whole-rock HSB	1	487-05	Durham	11/05/2021	Neptune MC-ICP MS	9	15	-0.011	0.269		-0.098		0.002			
U1442A 20R-1 104/108	whole-rock HSB	1	487-05	Durham	11/05/2021	Neptune MC-ICP MS	6	2	0.028	0.308		-0.023		0.049			
U1442A 20R-1 104/108 average										0.000	0.280	0.046	-0.039	0.080	0.010	0.074	4
783A-18R1-064/071	Torishima Forearc Seamount Harzburgite	1	509-01	Durham	23/03/2021	Neptune MC-ICP MS	12	5	0.007	0.287		0.027		0.035			
783A-18R1-064/071	Torishima Forearc Seamount Harzburgite	1	509-01	Durham	23/03/2021	Neptune MC-ICP MS	10	13	-0.036	0.244		-0.017		-0.006			
783A-18R1-064/071	Torishima Forearc Seamount Harzburgite	1	509-01	Durham	23/03/2021	Neptune MC-ICP MS	9	16	-0.034	0.246		-0.037		-0.040			
783A-18R1-064/071	Torishima Forearc Seamount Harzburgite	1	509-01	Durham	24/03/2021	Neptune MC-ICP MS	9	8	-0.014	0.266		-0.076		0.036			
783A-18R1-064/071	Torishima Forearc Seamount Harzburgite	1	509-01	Durham	24/03/2021	Neptune MC-ICP MS	9	0	-0.031	0.249		-0.069		0.030			
783A-18R1-064/071	Torishima Forearc Seamount Harzburgite	1	509-01	Durham	24/03/2021	Neptune MC-ICP MS	7	17	-0.044	0.236		-0.196		0.007			
783A-18R1-064/071 average										-0.026	0.254	0.038	-0.061	0.152	0.010	0.060	6
784A-38R2-072/077	Torishima Forearc Seamount Dunite	1	509-03	Durham	23/03/2021	Neptune MC-ICP MS	10	62	0.055	0.335		0.179		0.152			
784A-38R2-072/077	Torishima Forearc Seamount Dunite	1	509-03	Durham	23/03/2021	Neptune MC-ICP MS	11	13	0.005	0.285		0.110		0.085			
784A-38R2-072/077	Torishima Forearc Seamount Dunite	1	509-03	Durham	23/03/2021	Neptune MC-ICP MS	10	5	0.057	0.337		0.112		0.131			
784A-38R2-072/077	Torishima Forearc Seamount Dunite	1	509-03	Durham	24/03/2021	Neptune MC-ICP MS	8	16	0.022	0.302		0.105		0.109			
784A-38R2-072/077	Torishima Forearc Seamount Dunite	1	509-03	Durham	24/03/2021	Neptune MC-ICP MS	8	5	0.033	0.313		0.002		0.111			
784A-38R2-072/077	Torishima Forearc Seamount Dunite	1	509-03	Durham	24/03/2021	Neptune MC-ICP MS	10	21	0.014	0.294		-0.063		0.102			
784A-38R2-072/077 average										0.031	0.311	0.043	0.074	0.176	0.115	0.047	6
784A-40R2-070/075	Torishima Forearc Seamount Dunite	1	509-05	Durham	23/03/2021	Neptune MC-ICP MS	12	17	-0.008	0.272		0.059		0.050			
784A-40R2-070/075	Torishima Forearc Seamount Dunite	1	509-05	Durham	23/03/2021	Neptune MC-ICP MS	8	32	-0.018	0.262		0.058		-0.010			
784A-40R2-070/075	Torishima Forearc Seamount Dunite	1	509-05	Durham	23/03/2021	Neptune MC-ICP MS	10	0	0.020	0.300		0.021		0.019			
784A-40R2-070/075 average										-0.002	0.278	0.039	0.046	0.043	0.020	0.060	3
784A-45R2-33/38	Torishima Forearc Seamount Harzburgite	1	509-09	Durham	23/03/2021	Neptune MC-ICP MS	11	10	0.000	0.280		0.008		0.049			
784A-45R2-33/38	Torishima Forearc Seamount Harzburgite	1	509-09	Durham	23/03/2021	Neptune MC-ICP MS	9	3	-0.010	0.270		0.105		0.010			
784A-45R2-33/38	Torishima Forearc Seamount Harzburgite	1	509-09	Durham	23/03/2021	Neptune MC-ICP MS	12	6	-0.008	0.272		0.033		0.029			
784A-45R2-33/38 average										-0.006	0.274	0.011	0.049	0.100	0.029	0.039	3
784A-45R-CC-7/10	Torishima Forearc Seamount Harzburgite	1	509-11	Durham	23/03/2021	Neptune MC-ICP MS	12	28	-0.033	0.247		0.033		-0.045			
784A-45R-CC-7/10	Torishima Forearc Seamount Harzburgite	1	509-11	Durham	23/03/2021	Neptune MC-ICP MS	8	26	-0.015	0.265		0.106		-0.029			
784A-45R-CC-7/10	Torishima Forearc Seamount Harzburgite	1	509-11	Durham	23/03/2021	Neptune MC-ICP MS	9	16	-0.020	0.260		0.061		-0.025			
784A-45R-CC-7/10 average										-0.023	0.257	0.019	0.067	0.074	-0.033	0.021	3
783A-18R1-119-124	Torishima Forearc Seamount Harzburgite	1	509-13	Durham	23/03/2021	Neptune MC-ICP MS	10	36	-0.010	0.270		0.071		0.022			
783A-18R1-119-124	Torishima Forearc Seamount Harzburgite	1	509-13	Durham	23/03/2021	Neptune MC-ICP MS	11	13	0.023	0.303		0.175		0.096			
783A-18R1-119-124	Torishima Forearc Seamount Harzburgite	1	509-13	Durham	23/03/2021	Neptune MC-ICP MS	7	14	0.015	0.295		0.062		0.048			
783A-18R1-119-124 average										0.009	0.289	0.034	0.103	0.126	0.055	0.075	3

Sample Name	Type	Digestion	Batch no.	Location	Date	Method	RSE	RSD	$\delta^{66}\text{Zn}_{\text{ETH}}$ (‰)	$\delta^{66}\text{Zn}_{\text{LYON}}$ (‰)	2SD					n
F05JM10 Gnt	garnet mineral separate (Finsch)	1	446-11	Durham	21/10/2019	Neptune MC-ICP MS	13	39	0.000	0.280						
F05JM10 Gnt	garnet mineral separate (Finsch)	1	446-11	Durham	21/10/2019	Neptune MC-ICP MS	12	0	-0.073	0.207						
F05JM10 Gnt	garnet mineral separate (Finsch)	1	446-11	Durham	21/10/2019	Neptune MC-ICP MS	14	18	-0.033	0.247						
F05JM10 Gnt	garnet mineral separate (Finsch)	1	446-11	Durham	22/10/2019	Neptune MC-ICP MS	12	4	-0.036	0.244						
F05JM10 Gnt	garnet mineral separate (Finsch)	1	446-11	Durham	22/10/2019	Neptune MC-ICP MS	12	7	-0.061	0.219						

Appendix G - Zinc Isotope Data

F05JM10 Gnt average								-0.041	0.239	0.057					5

BD3692 Gnt	garnet mineral separate (Finsch)	1	446-12	Durham	21/10/2019	Neptune MC-ICP MS	15	16	-0.058	0.222					
BD3692 Gnt	garnet mineral separate (Finsch)	1	446-12	Durham	21/10/2019	Neptune MC-ICP MS	12	8	-0.060	0.220					
BD3692 Gnt	garnet mineral separate (Finsch)	1	446-12	Durham	22/10/2019	Neptune MC-ICP MS	10	13	-0.025	0.255					
BD3692 Gnt	garnet mineral separate (Finsch)	1	446-12	Durham	22/10/2019	Neptune MC-ICP MS	12	3	-0.057	0.223					
BD3692 Gnt average								-0.050	0.230	0.034					4

Sample Name	Type	Digestion	Batch no.	Location	Date	Method	RSE	RSD	$\delta^{66}\text{Zn}_{\text{ETH}} (\text{‰})$	$\delta^{66}\text{Zn}_{\text{LYON}} (\text{‰})$	2SD				n
052	whole-rock lherzolite (Diavik)	1	446-03	Durham	21/10/2019	Neptune MC-ICP MS	9	13	-0.058	0.222					
052	whole-rock lherzolite (Diavik)	1	446-03	Durham	21/10/2019	Neptune MC-ICP MS	13	2	-0.080	0.200					
052	whole-rock lherzolite (Diavik)	1	446-03	Durham	21/10/2019	Neptune MC-ICP MS	10	7	-0.084	0.196					
052	whole-rock lherzolite (Diavik)	1	446-03	Durham	21/10/2019	Neptune MC-ICP MS	9	27	-0.083	0.197					
052	whole-rock lherzolite (Diavik)	1	446-03	Durham	21/10/2019	Neptune MC-ICP MS	11	1	-0.087	0.193					
052	whole-rock lherzolite (Diavik)	1	446-03	Durham	22/10/2019	Neptune MC-ICP MS	15	15	-0.047	0.233					
052	whole-rock lherzolite (Diavik)	1	446-03	Durham	22/10/2019	Neptune MC-ICP MS	11	1	-0.070	0.210					
052	whole-rock lherzolite (Diavik)	1	446-03	Durham	22/10/2019	Neptune MC-ICP MS	11	7	-0.054	0.226					
052 average									-0.070	0.210	0.031				8

108	whole-rock lherzolite (Diavik)	1	446-04	Durham	21/10/2019	Neptune MC-ICP MS	14	11	-0.060	0.220					
108	whole-rock lherzolite (Diavik)	1	446-04	Durham	21/10/2019	Neptune MC-ICP MS	14	7	-0.047	0.233					
108	whole-rock lherzolite (Diavik)	1	446-04	Durham	21/10/2019	Neptune MC-ICP MS	14	16	-0.059	0.221					
108	whole-rock lherzolite (Diavik)	1	446-04	Durham	21/10/2019	Neptune MC-ICP MS	12	1	-0.059	0.221					
108	whole-rock lherzolite (Diavik)	1	446-04	Durham	21/10/2019	Neptune MC-ICP MS	13	9	-0.086	0.194					
108	whole-rock lherzolite (Diavik)	1	446-04	Durham	22/10/2019	Neptune MC-ICP MS	9	18	-0.056	0.224					
108	whole-rock lherzolite (Diavik)	1	446-04	Durham	22/10/2019	Neptune MC-ICP MS	11	5	-0.055	0.225					
108	whole-rock lherzolite (Diavik)	1	446-04	Durham	22/10/2019	Neptune MC-ICP MS	9	10	-0.077	0.203					
052 average									-0.063	0.217	0.026				8

422	whole-rock lherzolite (Diavik)	1	446-05	Durham	21/10/2019	Neptune MC-ICP MS	10	13	-0.089	0.191					
422	whole-rock lherzolite (Diavik)	1	446-05	Durham	21/10/2019	Neptune MC-ICP MS	17	6	-0.106	0.174					
422	whole-rock lherzolite (Diavik)	1	446-05	Durham	21/10/2019	Neptune MC-ICP MS	13	5	-0.046	0.234					
422	whole-rock lherzolite (Diavik)	1	446-05	Durham	21/10/2019	Neptune MC-ICP MS	12	0	-0.066	0.214					
422	whole-rock lherzolite (Diavik)	1	446-05	Durham	21/10/2019	Neptune MC-ICP MS	10	22	-0.081	0.199					
422	whole-rock lherzolite (Diavik)	1	446-05	Durham	22/10/2019	Neptune MC-ICP MS	12	7	-0.052	0.228					
422	whole-rock lherzolite (Diavik)	1	446-05	Durham	22/10/2019	Neptune MC-ICP MS	12	11	-0.063	0.217					
422	whole-rock lherzolite (Diavik)	1	446-05	Durham	22/10/2019	Neptune MC-ICP MS	10	13	-0.061	0.219					
422 average									-0.071	0.209	0.040				8

448	whole-rock lherzolite (Diavik)	1	446-06	Durham	21/10/2019	Neptune MC-ICP MS	13	2	-0.145	0.135					
448	whole-rock lherzolite (Diavik)	1	446-06	Durham	21/10/2019	Neptune MC-ICP MS	16	5	-0.117	0.163					
448	whole-rock lherzolite (Diavik)	1	446-06	Durham	21/10/2019	Neptune MC-ICP MS	11	25	-0.124	0.156					
448	whole-rock lherzolite (Diavik)	1	446-06	Durham	21/10/2019	Neptune MC-ICP MS	15	4	-0.126	0.154					
448	whole-rock lherzolite (Diavik)	1	446-06	Durham	21/10/2019	Neptune MC-ICP MS	10	4	-0.096	0.184					
448	whole-rock lherzolite (Diavik)	1	446-06	Durham	22/10/2019	Neptune MC-ICP MS	11	10	-0.084	0.196					
422 average									-0.115	0.165	0.044				6

450	whole-rock lherzolite (Diavik)	1	446-07	Durham	21/10/2019	Neptune MC-ICP MS	15	30	-0.166	0.114					
450	whole-rock lherzolite (Diavik)	1	446-07	Durham	21/10/2019	Neptune MC-ICP MS	12	11	-0.175	0.105					
450	whole-rock lherzolite (Diavik)	1	446-07	Durham	21/10/2019	Neptune MC-ICP MS	10	28	-0.134	0.146					

Appendix G - Zinc Isotope Data

450	whole-rock lherzolite (Diavik)	1	446-07	Durham	21/10/2019	Neptune MC-ICP MS	13	20	-0.150	0.130						
450	whole-rock lherzolite (Diavik)	1	446-07	Durham	21/10/2019	Neptune MC-ICP MS	14	5	-0.152	0.128						
450	whole-rock lherzolite (Diavik)	1	446-07	Durham	22/10/2019	Neptune MC-ICP MS	9	33	-0.157	0.123						
450	whole-rock lherzolite (Diavik)	1	446-07	Durham	22/10/2019	Neptune MC-ICP MS	10	2	-0.180	0.100						
450	whole-rock lherzolite (Diavik)	1	446-07	Durham	22/10/2019	Neptune MC-ICP MS	10	15	-0.161	0.119						
450 average									-0.159	0.121	0.029					8
714	whole-rock lherzolite (Diavik)	1	446-08	Durham	21/10/2019	Neptune MC-ICP MS	9	5	-0.092	0.188						
714	whole-rock lherzolite (Diavik)	1	446-08	Durham	21/10/2019	Neptune MC-ICP MS	12	4	-0.093	0.187						
714	whole-rock lherzolite (Diavik)	1	446-08	Durham	21/10/2019	Neptune MC-ICP MS	12	39	-0.099	0.181						
714	whole-rock lherzolite (Diavik)	1	446-08	Durham	21/10/2019	Neptune MC-ICP MS	13	22	-0.040	0.240						
714	whole-rock lherzolite (Diavik)	1	446-08	Durham	21/10/2019	Neptune MC-ICP MS	12	0	-0.084	0.196						
714	whole-rock lherzolite (Diavik)	1	446-08	Durham	22/10/2019	Neptune MC-ICP MS	11	25	-0.071	0.209						
714	whole-rock lherzolite (Diavik)	1	446-08	Durham	22/10/2019	Neptune MC-ICP MS	10	17	-0.113	0.167						
714	whole-rock lherzolite (Diavik)	1	446-08	Durham	22/10/2019	Neptune MC-ICP MS	11	19	-0.078	0.202						
714 average									-0.084	0.196	0.044					8
108 Gnt	whole-rock lherzolite (Diavik)	1	446-09	Durham	21/10/2019	Neptune MC-ICP MS	14	23	-0.075	0.205						
108 Gnt	whole-rock lherzolite (Diavik)	1	446-09	Durham	21/10/2019	Neptune MC-ICP MS	12	35	-0.125	0.155						
108 Gnt	whole-rock lherzolite (Diavik)	1	446-09	Durham	21/10/2019	Neptune MC-ICP MS	13	20	-0.138	0.142						
108 Gnt	whole-rock lherzolite (Diavik)	1	446-09	Durham	22/10/2019	Neptune MC-ICP MS	12	13	-0.106	0.174						
108 Gnt	whole-rock lherzolite (Diavik)	1	446-09	Durham	22/10/2019	Neptune MC-ICP MS	10	4	-0.118	0.162						
108 Gnt average									-0.112	0.168	0.048					5
Sample Name	Type	Digestion	Batch no.	Location	Date	Method	RSE	RSD	$\delta^{66}\text{Zn}_{\text{ETH}} (\text{‰})$	$\delta^{66}\text{Zn}_{\text{LYON}} (\text{‰})$	2SD	$\delta^{67}\text{Zn}_{\text{ETH}} (\text{‰})$	2SD	$\delta^{68}\text{Zn}_{\text{ETH}} (\text{‰})$	2SD	n
BIR-1a	USGS reference material	1		Durham	27/06/2019	Neptune MC-ICP MS			-0.091	0.189						
BIR-1a	USGS reference material	1		Durham	27/06/2019	Neptune MC-ICP MS			-0.051	0.229						
BIR-1a	USGS reference material	1		Durham	27/06/2019	Neptune MC-ICP MS			-0.094	0.186						
BIR-1a digestion 1 average									-0.079	0.201	0.048					3
BIR-1a	USGS reference material	2		Durham	23/03/2021	Neptune MC-ICP MS	10	48	-0.031	0.249						
BIR-1a	USGS reference material	2		Durham	23/03/2021	Neptune MC-ICP MS	10	6	-0.045	0.235						
BIR-1a	USGS reference material	2		Durham	23/03/2021	Neptune MC-ICP MS	9	14	-0.032	0.248						
BIR-1a	USGS reference material	2		Durham	24/03/2021	Neptune MC-ICP MS	7	17	-0.019	0.261						
BIR-1a	USGS reference material	2		Durham	24/03/2021	Neptune MC-ICP MS	9	9	-0.022	0.258						
BIR-1a	USGS reference material	2		Durham	24/03/2021	Neptune MC-ICP MS	6	5	-0.010	0.270						
BIR-1a	USGS reference material	2		Durham	25/03/2021	Neptune MC-ICP MS	9	23	-0.031	0.249						
BIR-1a digestion 2 average									-0.027	0.253	0.023					7
BIR-1a	USGS reference material	3		Durham	23/03/2021	Neptune MC-ICP MS	12	15	-0.031	0.249						
BIR-1a	USGS reference material	3		Durham	23/03/2021	Neptune MC-ICP MS	11	12	-0.037	0.243						
BIR-1a	USGS reference material	3		Durham	23/03/2021	Neptune MC-ICP MS	7	12	-0.033	0.247						
BIR-1a	USGS reference material	3		Durham	24/03/2021	Neptune MC-ICP MS	8	5	-0.041	0.239						
BIR-1a	USGS reference material	3		Durham	24/03/2021	Neptune MC-ICP MS	9	4	-0.043	0.237						
BIR-1a	USGS reference material	3		Durham	24/03/2021	Neptune MC-ICP MS	9	11	-0.064	0.216						
BIR-1a digestion 3 average									-0.042	0.238	0.024					6
BIR-1a average									-0.042	0.238	0.047					16
BHVO-2	USGS reference material	1		Durham	27/06/2019	Neptune MC-ICP MS			0.001	0.281						
BHVO-2	USGS reference material	1		Durham	27/06/2019	Neptune MC-ICP MS			0.049	0.329						
BHVO-2	USGS reference material	1		Durham	27/06/2019	Neptune MC-ICP MS			0.057	0.337						

Appendix G - Zinc Isotope Data

BHVO-2 average									0.036	0.316	0.061					3
GSP-2	USGS reference material	1		Durham	27/06/2019	Neptune MC-ICP MS			0.773	1.053						
GSP-2	USGS reference material	1		Durham	27/06/2019	Neptune MC-ICP MS			0.758	1.038						
GSP-2	USGS reference material	1		Durham	27/06/2019	Neptune MC-ICP MS			0.774	1.054						
GSP-2 average									0.768	1.048	0.019					3
BCR-2	USGS reference material	1		Durham	27/06/2019	Neptune MC-ICP MS			-0.015	0.265						
BCR-2	USGS reference material	1		Durham	27/06/2019	Neptune MC-ICP MS			-0.007	0.273						
BCR-2	USGS reference material	1		Durham	27/06/2019	Neptune MC-ICP MS			-0.026	0.254						
BCR-2 digestion 1 average									-0.016	0.264	0.020					3
BCR-2	USGS reference material	2		Durham	23/03/2021	Neptune MC-ICP MS	11	2	-0.029	0.251						
BCR-2	USGS reference material	2		Durham	23/03/2021	Neptune MC-ICP MS	8	9	-0.038	0.242						
BCR-2	USGS reference material	2		Durham	23/03/2021	Neptune MC-ICP MS	8	2	-0.041	0.239						
BCR-2	USGS reference material	2		Durham	24/03/2021	Neptune MC-ICP MS	7	23	-0.027	0.253						
BCR-2	USGS reference material	2		Durham	24/03/2021	Neptune MC-ICP MS	8	15	-0.050	0.230						
BCR-2	USGS reference material	2		Durham	24/03/2021	Neptune MC-ICP MS	9	9	-0.035	0.245						
BCR-2 digestion 2 average									-0.036	0.244	0.017					6
BCR-2	USGS reference material	3		Durham	10/05/2021	Neptune MC-ICP MS	8	14	-0.037	0.243		-0.079		-0.050		
BCR-2	USGS reference material	3		Durham	10/05/2021	Neptune MC-ICP MS	8	6	0.002	0.282		-0.025		-0.002		
BCR-2	USGS reference material	3		Durham	10/05/2021	Neptune MC-ICP MS	9	0	-0.018	0.262		-0.037		-0.028		
BCR-2	USGS reference material	3		Durham	10/05/2021	Neptune MC-ICP MS	7	8	-0.011	0.269		-0.041		-0.051		
BCR-2	USGS reference material	3		Durham	10/05/2021	Neptune MC-ICP MS	9	8	-0.031	0.249		-0.102		-0.052		
BCR-2 digestion 3 average									-0.019	0.261	0.032	-0.057	0.065	-0.036	0.044	5
BCR-2	USGS reference material	4		Durham	11/05/2021	Neptune MC-ICP MS	10	0	-0.010	0.270		-0.078		-0.020		
BCR-2	USGS reference material	4		Durham	11/05/2021	Neptune MC-ICP MS	10	24	-0.015	0.265		-0.062		-0.003		
BCR-2	USGS reference material	4		Durham	11/05/2021	Neptune MC-ICP MS	6	15	0.000	0.280		-0.068		-0.007		
BCR-2	USGS reference material	4		Durham	11/05/2021	Neptune MC-ICP MS	11	5	-0.008	0.272		-0.054		-0.013		
BCR-2 digestion 4 average									-0.008	0.272	0.013	-0.066	0.020	-0.011	0.015	4
BCR-2 average									-0.022	0.258	0.030	-0.061	0.048	-0.025	0.042	18

Appendix H - Hafnium Isotope Data

Sample Name	Type	Batch	Location	Date	Method	¹⁷⁶ Hf/ ¹⁷⁷ Hf _m	±1s	¹⁷⁶ Hf/ ¹⁷⁷ Hf _i	εHfi	ε2SE
U1439C-10R-2-W 13/19	whole-rock BB	1	Durham	27/11/2020	Neptune MC-ICP MS	0.283243	±2	0.283222	16.5	0.14
U1439C-29R-4-W 78/82	whole-rock LSB	1	Durham	27/11/2020	Neptune MC-ICP MS	0.283183	±2	0.283163	14.5	0.21
U1439C-31R-5-W 12/17	whole-rock LSB	1	Durham	27/11/2020	Neptune MC-ICP MS	0.283241	±2	0.283216	16.4	0.14
U1439C-37R-1-W 42/48	whole-rock HMA	1	Durham	27/11/2020	Neptune MC-ICP MS	0.283231	±3	0.283211	16.2	0.14
U1442A-35R-1-W 51/55	whole-rock LSB	1	Durham	27/11/2020	Neptune MC-ICP MS	0.283200	±2	0.283181	15.1	0.14
U1442A 22R1-122/125	whole-rock HSB	1	Durham	27/11/2020	Neptune MC-ICP MS	0.283118	±3	0.283095	12.1	0.21
U1440B 17R2-23/32	whole-rock N-FAB	1	Durham	27/11/2020	Neptune MC-ICP MS	0.283339	±1	0.283301	19.4	0.07
U1440B 28R1-31/38	whole-rock N-FAB	1	Durham	27/11/2020	Neptune MC-ICP MS	0.283118	±3	0.283310	19.7	0.14
U1440B-12R-2-W 4/8	whole-rock P-FAB	1	Durham	27/11/2020	Neptune MC-ICP MS	0.283406	±2	0.283355	21.3	0.14
U1441A-21R-1-W 37/42	whole-rock N-FAB	1	Durham	27/11/2020	Neptune MC-ICP MS	0.283352	±2	0.283303	19.4	0.14

								Literature	
Sample Name	Type	Batch	Location	Date	Method	¹⁷⁶ Hf/ ¹⁷⁷ Hf _m	±2se	¹⁷⁶ Hf/ ¹⁷⁷ Hf _m	Reference
AGV-1	USGS reference material	1	Durham	25/11/2020	Neptune MC-ICP MS	0.282981	0.000003		
AGV-1	USGS reference material	1	Durham	25/11/2020	Neptune MC-ICP MS	0.282982	0.000005		
AGV-1	USGS reference material	1	Durham	25/11/2020	Neptune MC-ICP MS	0.282979	0.000003		
AGV-1 average						0.282980	0.000003	0.282979	Weis <i>et al.</i> (2007)

BCR-2	USGS reference material	1	Durham	25/11/2020	Neptune MC-ICP MS	0.282867	0.000003		
BCR-2	USGS reference material	1	Durham	25/11/2020	Neptune MC-ICP MS	0.282867	0.000003		
BCR-2	USGS reference material	1	Durham	25/11/2020	Neptune MC-ICP MS	0.282860	0.000003		
BCR-2	USGS reference material	1	Durham	25/11/2020	Neptune MC-ICP MS	0.282868	0.000003		
BCR-2	USGS reference material	1	Durham	27/11/2020	Neptune MC-ICP MS	0.282861	0.000002		
BCR-2 average						0.282863	0.000009	0.282870	Weis <i>et al.</i> (2007)

BIR-1a	USGS reference material	1	Durham	25/11/2020	Neptune MC-ICP MS	0.283253	0.000007		
BIR-1a	USGS reference material	1	Durham	25/11/2020	Neptune MC-ICP MS	0.283261	0.000009		
BIR-1a	USGS reference material	1	Durham	25/11/2020	Neptune MC-ICP MS	0.283254	0.000005		
BIR-1a	USGS reference material	1	Durham	25/11/2020	Neptune MC-ICP MS	0.283248	0.000006		
BIR-1a average						0.283254	0.000013	0.283243	Weis <i>et al.</i> (2007)

BHVO-2	USGS reference material	1	Durham	25/11/2020	Neptune MC-ICP MS	0.283099	0.000003		
BHVO-2	USGS reference material	1	Durham	25/11/2020	Neptune MC-ICP MS	0.283094	0.000003		
BHVO-2	USGS reference material	1	Durham	25/11/2020	Neptune MC-ICP MS	0.283100	0.000003		
BHVO-2	USGS reference material	1	Durham	25/11/2020	Neptune MC-ICP MS	0.283099	0.000003		
BHVO-2	USGS reference material	1	Durham	27/11/2020	Neptune MC-ICP MS	0.283094	0.000002		
BHVO-2 average						0.283097	0.000006	0.283105	Weis <i>et al.</i> (2007)

Appendix I - Trace Element Data

					Trace Element Concentrations (µg.g ⁻¹)																	
Sample Name	Type	Location	Method	Date	Sc	Ti	V	Cr	Mn	Co	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Cs	Ba	La	
052	whole-rock lherzolite	O.U	ICP-QQQ-MS	02/04/2019	5.89	497.61	25.01	2211.72	1713.05	113.44	2301.61	13.35	41.28	5.053	74.768	0.885	4.169	13.730	0.088	157.884	9.929	
052	whole-rock lherzolite	O.U	ICP-QQQ-MS	30/09/2020	6.62	554.22	25.84	2217.58	1698.84	110.91	2459.51	14.17	43.38	5.085	74.962	0.883	3.874	14.092	0.087	154.340	10.468	
052 average					6.62	554.22	25.84	2217.58	1698.84	110.91	2459.51	14.17	43.38	5.085	74.962	0.883	3.874	14.092	0.087	154.340	10.468	
108	whole-rock lherzolite	O.U	ICP-QQQ-MS	30/09/2020	1.92	168.57	16.18	1066.19	779.95	104.80	2280.92	4.77	36.30	1.038	41.883	0.157	0.795	3.115	0.020	21.082	2.806	
147	whole-rock lherzolite	O.U	ICP-QQQ-MS	30/09/2020	4.68	307.51	22.94	2273.13	1059.39	113.74	2321.69	9.47	39.61	3.985	54.334	1.141	3.623	7.181	0.040	48.082	26.619	
422	whole-rock lherzolite	O.U	ICP-QQQ-MS	02/04/2019	15.02	1038.90	60.99	2893.30	1032.53	116.00	2021.58	14.91	49.80	11.151	30.423	3.591	8.343	11.297	0.115	68.220	7.540	
422	whole-rock lherzolite	O.U	ICP-QQQ-MS	30/09/2020	15.83	1122.49	62.78	2869.65	1003.99	114.66	2171.91	16.51	51.86	10.592	30.136	3.522	8.337	11.291	0.119	60.753	7.870	
422 average					15.83	1122.49	62.78	2869.65	1003.99	114.66	2171.91	16.51	51.86	10.592	30.136	3.522	8.337	11.291	0.119	60.753	7.870	
448	whole-rock lherzolite	O.U	ICP-QQQ-MS	02/04/2019	6.37	721.70	32.20	2966.33	1684.65	102.81	1870.42	14.59	38.27	21.984	142.893	0.909	7.057	28.238	0.190	186.221	21.036	
448	whole-rock lherzolite	O.U	ICP-QQQ-MS	30/09/2020	6.71	755.56	31.61	2759.76	1537.27	98.02	1932.31	15.12	37.75	21.155	133.200	0.825	6.573	29.222	0.187	170.408	21.260	
448 average					6.71	755.56	31.61	2759.76	1537.27	98.02	1932.31	15.12	37.75	21.155	133.200	0.825	6.573	29.222	0.187	170.408	21.260	
450	whole-rock lherzolite	O.U	ICP-QQQ-MS	02/04/2019	7.28	357.61	27.83	3232.30	772.45	148.43	2953.86	19.82	55.50	4.001	59.172	0.505	4.134	9.927	0.154	100.321	6.688	
450	whole-rock lherzolite	O.U	ICP-QQQ-MS	30/09/2020	8.53	409.19	29.04	3409.69	761.11	151.68	3232.85	21.81	57.82	3.966	58.558	0.502	4.237	10.464	0.161	96.910	7.249	
450 average					8.53	409.19	29.04	3409.69	761.11	151.68	3232.85	21.81	57.82	3.966	58.558	0.502	4.237	10.464	0.161	96.910	7.249	
714	whole-rock lherzolite	O.U	ICP-QQQ-MS	02/04/2019	4.55	527.45	26.61	1545.36	1807.26	123.53	2332.41	10.82	52.46	3.651	93.004	0.821	4.364	12.103	0.063	148.339	8.794	
714	whole-rock lherzolite	O.U	ICP-QQQ-MS	30/09/2020	5.22	597.52	27.57	1588.39	1738.39	123.58	2520.76	10.52	56.93	3.506	90.248	0.807	4.150	12.237	0.065	140.009	8.978	
714 average					5.22	597.52	27.57	1588.39	1738.39	123.58	2520.76	10.52	56.93	3.506	90.248	0.807	4.150	12.237	0.065	140.009	8.978	
kimberlite (031)	whole-rock	O.U	ICP-QQQ-MS	30/09/2020	4.87	2538.73	43.76	1651.33	667.77	98.15	1748.31	42.76	42.82	16.423	395.846	2.182	22.600	63.124	0.422	804.581	52.794	
kimberlite (031)	whole-rock	O.U	ICP-QQQ-MS	30/09/2020	11.29	2566.27	43.92	1917.25	845.16	112.57	1820.29	37.72	51.72	17.372	475.088	3.237	40.869	86.768	0.441	1331.153	65.273	
kimberlite (031) average					8.08	2552.50	43.84	1784.29	756.47	105.36	1784.30	40.24	47.27	16.897	435.467	2.709	31.734	74.946	0.432	1067.867	59.034	
108 Gnt	garnet mineral separate	O.U	ICP-QQQ-MS	07/10/2020	127.70	1457.84	328.58	48198.88	2271.25	39.78	75.83	26.26	31.04	0.579	1.557	7.661	20.636	0.999	0.006	31.652	0.148	
108 Cpx	clinopyroxene mineral separate	O.U	ICP-QQQ-MS	07/10/2020	10.08	342.93	138.67	8108.65	640.81	21.68	404.59	9.80	39.71	0.710	130.630	0.773	2.092	1.276	0.010	8.030	2.563	
PCC-1	USGS Reference Material	O.U	ICP-QQQ-MS	02/04/2019	7.19	23.91	26.78	3007.27	816.71	107.49	2128.25	5.92	38.64	0.064	0.356	0.077	0.171	0.015	0.004	0.923	0.025	
PCC-1	USGS Reference Material	O.U	ICP-QQQ-MS	02/04/2019	7.27	23.80	26.33	2936.46	809.49	106.29	2082.26	5.79	38.29	0.063	0.351	0.076	0.165	0.018	0.004	0.910	0.027	
PCC-1	USGS Reference Material	O.U	ICP-QQQ-MS	02/04/2019	7.32	23.74	26.67	2943.54	811.56	105.50	2059.17	5.72	38.02	0.059	0.358	0.079	0.173	0.024	0.004	0.943	0.027	
PCC-1 average					7.26	23.82	26.59	2962.42	812.59	106.42	2089.89	5.81	38.32	0.062	0.355	0.077	0.170	0.019	0.004	0.925	0.026	
DTS-2	USGS Reference Material	O.U	ICP-QQQ-MS	02/04/2019	3.30	21.08	9.47	4598.43	933.60	142.71	2309.81	5.74	45.70	0.096	0.309	0.037	0.172	0.018	0.005	0.320	0.023	
DTS-2	USGS Reference Material	O.U	ICP-QQQ-MS	02/04/2019	3.28	21.06	9.37	4475.87	922.95	139.97	2264.01	5.57	44.88	0.088	0.322	0.036	0.165	0.019	0.005	0.321	0.022	
DTS-2	USGS Reference Material	O.U	ICP-QQQ-MS	02/04/2019	3.32	21.18	9.34	4437.70	927.09	137.45	2226.19	5.55	44.85	0.083	0.304	0.036	0.174	0.021	0.005	0.335	0.023	
DTS-2 average					3.30	21.11	9.39	4504.00	927.88	140.04	2266.67	5.62	45.14	0.089	0.311	0.036	0.170	0.019	0.005	0.326	0.023	
BIR-1a	USGS Reference Material	O.U	ICP-QQQ-MS	30/09/2020	26.34	6436.61	332.24	438.02	1274.54	56.58	191.26	127.41	66.30	0.112	91.119	14.653	16.444	0.584	0.003	6.592	0.599	
BIR-1a	USGS Reference Material	O.U	ICP-QQQ-MS	30/09/2020	25.36	6319.78	333.25	443.85	1237.52	56.01	192.03	127.44	65.97	0.109	90.071	14.519	16.000	0.596	0.003	6.511	0.597	
BIR-1a	USGS Reference Material	O.U	ICP-QQQ-MS	07/10/2020	25.96	6544.57	355.58	460.45	1365.17	58.84	195.06	131.27	71.51	0.127	94.830	14.376	15.522	0.622	0.003	7.079	0.671	
BIR-1a	USGS Reference Material	O.U	ICP-QQQ-MS	07/10/2020	25.77	6561.42	348.50	449.23	1339.16	57.08	192.71	128.33	69.47	0.119	94.906	14.259	15.382	0.621	0.004	7.250	0.662	
BIR-1a average					25.86	6465.60	342.39	447.89	1304.10	57.12	192.76	128.61	68.31	0.117	92.732	14.452	15.837	0.606	0.003	6.858	0.632	
BHVO-2	USGS Reference Material	O.U	ICP-QQQ-MS	30/09/2020	33.06	17439.36	315.18	323.60	1297.39	46.54	126.74	129.28	106.68	9.125	387.687	28.138	180.516	11.417	0.102	135.006	15.015	
BHVO-2	USGS Reference Material	O.U	ICP-QQQ-MS	30/09/2020	32.42	17145.66	312.08	326.15	1254.30	46.62	129.06	130.73	107.00	8.931	385.760	27.690	178.341	10.061	0.098	135.653	14.717	
BHVO-2	USGS Reference Material	O.U	ICP-QQQ-MS	07/10/2020	34.30	17614.47	322.46	328.62	1347.82	47.44	126.83	129.34	104.67	9.851	406.862	28.688	185.915	10.504	0.104	137.355	16.714	
BHVO-2	USGS Reference Material	O.U	ICP-QQQ-MS	07/10/2020	33.71	17719.52	321.75	329.23	1343.97	47.67	124.83	129.83	104.50	9.592	403.014	28.806	185.760	10.005	0.103	137.116	16.214	
BHVO-2 average					33.37	17479.75	317.87	326.90	1310.87	47.06	126.86	129.80	105.71	9.375	395.831	28.331	182.633	10.497	0.102	136.282	15.665	

Appendix I - Trace Element Data

Trace Element Concentrations (µg.g ⁻¹)																	
Ce	Pr	Nd	Sm	Eu	Gd	Tb	Hf	Dy	Ho	Er	Yb	Lu	Ta	Tl	Pb	Th	U
18.324	1.886	5.970	0.634	0.193	0.367	0.038	0.198	0.183	0.032	0.072	0.050	0.008	0.648	0.073	0.681	1.186	0.274
17.806	1.796	5.750	0.654	0.193	0.379	0.042	0.202	0.190	0.034	0.080	0.056	0.009	0.555	0.073	0.599	1.280	0.304
17.806	1.796	5.750	0.654	0.193	0.379	0.042	0.202	0.190	0.034	0.080	0.056	0.009	0.555	0.073	0.599	1.280	0.304
4.519	0.442	1.328	0.142	0.037	0.082	0.009	0.026	0.035	0.006	0.013	0.013	0.002	0.237	0.006	0.264	0.364	0.056
33.204	2.952	8.999	0.714	0.229	0.436	0.040	0.149	0.172	0.033	0.072	0.050	0.008	0.489	0.017	0.719	0.748	0.164
12.989	1.338	4.560	0.632	0.195	0.542	0.090	0.228	0.560	0.133	0.383	0.392	0.060	0.440	0.031	3.377	0.665	0.235
12.329	1.264	4.241	0.618	0.202	0.566	0.093	0.241	0.592	0.133	0.398	0.403	0.058	0.443	0.028	3.163	0.677	0.251
12.329	1.264	4.241	0.618	0.202	0.566	0.093	0.241	0.592	0.133	0.398	0.403	0.058	0.443	0.028	3.163	0.677	0.251
36.986	3.582	10.826	1.045	0.275	0.533	0.052	0.704	0.204	0.032	0.070	0.053	0.008	1.276	0.025	1.297	2.945	0.375
34.240	3.209	9.679	0.969	0.264	0.525	0.051	0.677	0.207	0.033	0.069	0.059	0.008	0.875	0.026	1.302	2.909	0.388
34.240	3.209	9.679	0.969	0.264	0.525	0.051	0.677	0.207	0.033	0.069	0.059	0.008	0.875	0.026	1.302	2.909	0.388
12.035	1.193	3.713	0.401	0.122	0.226	0.026	0.255	0.103	0.019	0.043	0.034	0.007	0.497	0.063	1.003	0.774	0.285
11.975	1.172	3.609	0.429	0.120	0.249	0.026	0.293	0.117	0.020	0.048	0.046	0.006	0.489	0.063	0.680	0.869	0.320
11.975	1.172	3.609	0.429	0.120	0.249	0.026	0.293	0.117	0.020	0.048	0.046	0.006	0.489	0.063	0.680	0.869	0.320
14.938	1.437	4.435	0.463	0.141	0.282	0.035	0.123	0.166	0.031	0.078	0.057	0.010	0.618	0.023	0.537	1.022	0.212
13.640	1.324	3.996	0.440	0.137	0.285	0.036	0.122	0.168	0.032	0.078	0.060	0.009	0.520	0.025	0.546	1.076	0.234
13.640	1.324	3.996	0.440	0.137	0.285	0.036	0.122	0.168	0.032	0.078	0.060	0.009	0.520	0.025	0.546	1.076	0.234
89.956	8.693	26.827	2.785	0.699	1.491	0.141	0.499	0.583	0.094	0.212	0.163	0.022	3.709	0.088	3.727	5.408	1.266
107.448	10.602	32.445	3.343	0.874	1.769	0.177	0.889	0.717	0.116	0.260	0.207	0.029	4.124	0.087	3.983	16.677	1.350
98.702	9.648	29.636	3.064	0.787	1.630	0.159	0.694	0.650	0.105	0.236	0.185	0.026	3.917	0.088	3.855	11.043	1.308
0.728	0.219	1.802	0.838	0.331	1.208	0.219	0.588	1.347	0.284	0.728	0.659	0.093	0.081	-0.002	1.522	0.034	0.045
8.151	1.214	4.941	0.666	0.156	0.366	0.042	0.098	0.191	0.031	0.073	0.051	0.008	0.075	-0.001	1.008	0.123	0.026
0.056	0.007	0.029	0.005	0.001	0.006	0.001	0.004	0.007	0.003	0.010	0.026	0.004	0.003	0.001	7.555	0.009	0.003
0.054	0.008	0.028	0.005	0.001	0.006	0.001	0.005	0.009	0.003	0.011	0.025	0.004	0.003	0.001	7.495	0.010	0.004
0.055	0.008	0.031	0.005	0.001	0.005	0.001	0.005	0.008	0.003	0.011	0.023	0.004	0.004	0.000	7.636	0.010	0.003
0.055	0.007	0.029	0.005	0.001	0.006	0.001	0.005	0.008	0.003	0.010	0.025	0.004	0.003	0.001	7.562	0.010	0.003
0.052	0.007	0.026	0.004	0.001	0.003	0.001	0.006	0.004	0.001	0.005	0.008	0.002	0.001	<0.000	7.594	0.009	0.003
0.051	0.007	0.023	0.005	0.001	0.004	0.001	0.004	0.004	0.001	0.004	0.012	0.002	0.001	0.000	7.583	0.008	0.004
0.052	0.007	0.026	0.004	0.001	0.003	0.001	0.005	0.004	0.001	0.005	0.005	0.002	0.002	<0.000	7.698	0.009	0.003
0.052	0.007	0.025	0.004	0.001	0.003	0.001	0.005	0.004	0.001	0.005	0.009	0.002	0.002	0.000	7.625	0.009	0.003
1.917	0.385	2.449	1.142	0.539	1.904	0.379	0.611	2.601	0.594	1.749	1.651	0.239	0.051	0.000	2.997	0.028	0.010
1.913	0.384	2.438	1.139	0.557	1.917	0.379	0.615	2.598	0.602	1.760	1.697	0.237	0.046	0.000	2.972	0.027	0.011
2.151	0.394	2.690	1.247	0.544	2.084	0.415	0.610	2.736	0.631	1.825	1.894	0.252	0.043	-0.003	3.153	0.026	0.015
2.083	0.393	2.620	1.198	0.575	2.013	0.404	0.620	2.720	0.625	1.785	1.789	0.252	0.051	-0.003	3.100	0.030	0.013
2.016	0.389	2.549	1.182	0.554	1.979	0.394	0.614	2.664	0.613	1.780	1.758	0.245	0.048	-0.001	3.056	0.028	0.012
37.991	5.436	25.062	6.220	2.163	6.324	0.975	4.409	5.428	1.019	2.613	2.175	0.281	0.386	0.023	2.457	1.319	0.428
38.062	5.336	24.392	6.173	2.144	6.235	0.963	4.387	5.338	1.016	2.604	2.115	0.272	0.267	0.021	2.392	1.291	0.427
41.235	5.478	26.851	6.701	2.102	6.821	1.051	4.541	5.609	1.089	2.746	2.234	0.295	0.330	0.016	2.553	1.367	0.455
39.890	5.437	25.943	6.556	2.165	6.545	1.009	4.456	5.521	1.048	2.691	2.240	0.287	0.241	0.017	2.538	1.332	0.429
39.294	5.422	25.562	6.412	2.143	6.481	1.000	4.448	5.474	1.043	2.664	2.191	0.284	0.306	0.019	2.485	1.327	0.435

Appendix J - Vanadium BDH Standard Solution Data

Sample Name	Type	Batch	Location	Date	Method	RSE	RSD	$\delta^{51}\text{V}_{\text{AA}} (\text{‰})$	2SD	n
BDH	V standard solution	1	Imperial	07/12/2017	Nu II MC-ICP MS	12	50	-1.25		
BDH	V standard solution	1	Imperial	07/12/2017	Nu II MC-ICP MS	14	59	-1.29		
BDH	V standard solution	1	Imperial	07/12/2017	Nu II MC-ICP MS	10	46	-1.21		
BDH	V standard solution	1	Imperial	07/12/2017	Nu II MC-ICP MS	16	12	-1.16		
BDH	V standard solution	1	Imperial	07/12/2017	Nu II MC-ICP MS	13	73	-0.94		
BDH	V standard solution	1	Imperial	07/12/2017	Nu II MC-ICP MS	14	103	-1.11		
Session 1 BDH average								-1.16	0.25	6
BDH	V standard solution	2	Imperial	09/12/2017	Nu II MC-ICP MS	10	52	-1.22		
BDH	V standard solution	2	Imperial	09/12/2017	Nu II MC-ICP MS	12	121	-1.28		
BDH	V standard solution	2	Imperial	09/12/2017	Nu II MC-ICP MS	13	30	-1.02		
BDH	V standard solution	2	Imperial	09/12/2017	Nu II MC-ICP MS	14	74	-1.43		
BDH	V standard solution	2	Imperial	09/12/2017	Nu II MC-ICP MS	14	73	-1.15		
BDH	V standard solution	2	Imperial	09/12/2017	Nu II MC-ICP MS	13	56	-1.26		
BDH	V standard solution	2	Imperial	09/12/2017	Nu II MC-ICP MS	15	67	-1.27		
BDH	V standard solution	2	Imperial	09/12/2017	Nu II MC-ICP MS	12	45	-1.22		
BDH	V standard solution	2	Imperial	09/12/2017	Nu II MC-ICP MS	10	65	-1.28		
BDH	V standard solution	2	Imperial	09/12/2017	Nu II MC-ICP MS	11	43	-1.26		
BDH	V standard solution	2	Imperial	09/12/2017	Nu II MC-ICP MS	11	16	-1.19		
BDH	V standard solution	2	Imperial	09/12/2017	Nu II MC-ICP MS	11	98	-1.05		
Session 2 BDH average								-1.22	0.22	12
BDH	V standard solution	3	Imperial	13/12/2017	Nu II MC-ICP MS	13	124	-1.13		
BDH	V standard solution	3	Imperial	13/12/2017	Nu II MC-ICP MS	12	70	-1.17		
BDH	V standard solution	3	Imperial	13/12/2017	Nu II MC-ICP MS	12	80	-1.26		
BDH	V standard solution	3	Imperial	13/12/2017	Nu II MC-ICP MS	15	110	-1.08		
BDH	V standard solution	3	Imperial	13/12/2017	Nu II MC-ICP MS	16	93	-1.22		
BDH	V standard solution	3	Imperial	13/12/2017	Nu II MC-ICP MS	13	88	-1.12		
BDH	V standard solution	3	Imperial	13/12/2017	Nu II MC-ICP MS	17	57	-0.94		
BDH	V standard solution	3	Imperial	13/12/2017	Nu II MC-ICP MS	10	69	-1.04		
BDH	V standard solution	3	Imperial	13/12/2017	Nu II MC-ICP MS	15	41	-1.34		
BDH	V standard solution	3	Imperial	13/12/2017	Nu II MC-ICP MS	15	61	-1.23		
BDH	V standard solution	3	Imperial	13/12/2017	Nu II MC-ICP MS	13	76	-1.16		
Session 3 BDH average								-1.15	0.22	11
BDH	V standard solution	4	Durham	05/12/2018	Neptune MC-ICP MS		83	-1.24		
BDH	V standard solution	4	Durham	05/12/2018	Neptune MC-ICP MS		114	-1.23		
BDH	V standard solution	4	Durham	05/12/2018	Neptune MC-ICP MS		33	-1.15		
BDH	V standard solution	4	Durham	05/12/2018	Neptune MC-ICP MS		67	-1.24		
BDH	V standard solution	4	Durham	05/12/2018	Neptune MC-ICP MS		32	-1.36		
BDH	V standard solution	4	Durham	05/12/2018	Neptune MC-ICP MS		84	-1.26		
BDH	V standard solution	4	Durham	05/12/2018	Neptune MC-ICP MS		69	-1.20		
BDH	V standard solution	4	Durham	05/12/2018	Neptune MC-ICP MS		102	-1.35		
BDH	V standard solution	4	Durham	05/12/2018	Neptune MC-ICP MS		101	-1.01		
BDH	V standard solution	4	Durham	05/12/2018	Neptune MC-ICP MS		84	-1.23		
BDH	V standard solution	4	Durham	05/12/2018	Neptune MC-ICP MS		115	-1.13		
BDH	V standard solution	4	Durham	05/12/2018	Neptune MC-ICP MS		56	-1.12		
BDH	V standard solution	4	Durham	05/12/2018	Neptune MC-ICP MS		101	-1.05		
BDH	V standard solution	4	Durham	05/12/2018	Neptune MC-ICP MS		70	-1.36		
BDH	V standard solution	4	Durham	05/12/2018	Neptune MC-ICP MS		43	-1.27		
BDH	V standard solution	4	Durham	05/12/2018	Neptune MC-ICP MS		74	-1.20		
Session 4 BDH average								-1.21	0.20	16
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		87	-1.12		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		34	-1.18		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		61	-1.21		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		37	-1.31		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		53	-1.19		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		74	-1.20		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		79	-1.30		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		81	-1.05		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		89	-1.34		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		68	-1.11		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		72	-1.06		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		57	-1.09		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		59	-1.13		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		82	-1.27		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		55	-1.17		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		107	-1.23		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		91	-1.28		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		68	-1.28		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		46	-1.08		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		107	-1.19		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		84	-1.10		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		35	-1.19		
BDH	V standard solution	5	Durham	06/12/2018	Neptune MC-ICP MS		19	-1.19		
Session 5 BDH average								-1.19	0.17	23
BDH	V standard solution	6	Durham	23/01/2019	Neptune MC-ICP MS		24	-1.21		
BDH	V standard solution	6	Durham	23/01/2019	Neptune MC-ICP MS		22	-1.23		
BDH	V standard solution	6	Durham	23/01/2019	Neptune MC-ICP MS		42	-1.18		
BDH	V standard solution	6	Durham	23/01/2019	Neptune MC-ICP MS		50	-1.17		
BDH	V standard solution	6	Durham	23/01/2019	Neptune MC-ICP MS		31	-1.23		
BDH	V standard solution	6	Durham	23/01/2019	Neptune MC-ICP MS		38	-1.21		
BDH	V standard solution	6	Durham	23/01/2019	Neptune MC-ICP MS		30	-1.15		
BDH	V standard solution	6	Durham	23/01/2019	Neptune MC-ICP MS		49	-1.23		
BDH	V standard solution	6	Durham	23/01/2019	Neptune MC-ICP MS		19	-1.21		

Appendix J - Vanadium BDH Standard Solution Data

BDH	V standard solution	24	Durham	10/09/2020	Neptune MC-ICP MS		27	-1.30
BDH	V standard solution	24	Durham	10/09/2020	Neptune MC-ICP MS		35	-1.30
BDH	V standard solution	24	Durham	10/09/2020	Neptune MC-ICP MS		59	-1.23
BDH	V standard solution	24	Durham	10/09/2020	Neptune MC-ICP MS		29	-1.34
BDH	V standard solution	24	Durham	10/09/2020	Neptune MC-ICP MS		70	-1.27
BDH	V standard solution	24	Durham	10/09/2020	Neptune MC-ICP MS		49	-1.31
BDH	V standard solution	24	Durham	10/09/2020	Neptune MC-ICP MS		43	-1.25
BDH	V standard solution	24	Durham	10/09/2020	Neptune MC-ICP MS		67	-1.24
Session 24 BDH average							-1.28	0.07 27

BDH	V standard solution	25	Durham	14/10/2020	Neptune MC-ICP MS	21	81	-1.15
BDH	V standard solution	25	Durham	14/10/2020	Neptune MC-ICP MS	19	28	-1.10
BDH	V standard solution	25	Durham	14/10/2020	Neptune MC-ICP MS	18	20	-1.20
BDH	V standard solution	25	Durham	14/10/2020	Neptune MC-ICP MS	20	46	-1.14
BDH	V standard solution	25	Durham	14/10/2020	Neptune MC-ICP MS	18	48	-1.19
BDH	V standard solution	25	Durham	14/10/2020	Neptune MC-ICP MS	17	47	-1.27
BDH	V standard solution	25	Durham	14/10/2020	Neptune MC-ICP MS	19	29	-1.20
BDH	V standard solution	25	Durham	14/10/2020	Neptune MC-ICP MS	16	80	-1.15
BDH	V standard solution	25	Durham	14/10/2020	Neptune MC-ICP MS	19	48	-1.08
BDH	V standard solution	25	Durham	14/10/2020	Neptune MC-ICP MS	17	34	-1.14
BDH	V standard solution	25	Durham	14/10/2020	Neptune MC-ICP MS	19	15	-1.15
BDH	V standard solution	25	Durham	14/10/2020	Neptune MC-ICP MS	22	38	-1.14
BDH	V standard solution	25	Durham	14/10/2020	Neptune MC-ICP MS	18	92	-1.17
BDH	V standard solution	25	Durham	15/10/2020	Neptune MC-ICP MS	17	54	-1.17
BDH	V standard solution	25	Durham	15/10/2020	Neptune MC-ICP MS	17	63	-1.08
BDH	V standard solution	25	Durham	15/10/2020	Neptune MC-ICP MS	18	54	-1.08
Session 25 BDH average							-1.15	0.10 16

BDH	V standard solution	26	Durham	15/10/2020	Neptune MC-ICP MS	31	78	-1.25
BDH	V standard solution	26	Durham	15/10/2020	Neptune MC-ICP MS	19	31	-1.22
BDH	V standard solution	26	Durham	15/10/2020	Neptune MC-ICP MS	23	78	-1.29
BDH	V standard solution	26	Durham	15/10/2020	Neptune MC-ICP MS	22	42	-1.19
BDH	V standard solution	26	Durham	15/10/2020	Neptune MC-ICP MS	27	53	-1.15
BDH	V standard solution	26	Durham	15/10/2020	Neptune MC-ICP MS	22	48	-1.21
BDH	V standard solution	26	Durham	15/10/2020	Neptune MC-ICP MS	17	63	-1.25
BDH	V standard solution	26	Durham	15/10/2020	Neptune MC-ICP MS	26	68	-1.15
BDH	V standard solution	26	Durham	15/10/2020	Neptune MC-ICP MS	22	99	-1.03
BDH	V standard solution	26	Durham	15/10/2020	Neptune MC-ICP MS	18	57	-1.08
BDH	V standard solution	26	Durham	15/10/2020	Neptune MC-ICP MS	23	62	-1.06
BDH	V standard solution	26	Durham	15/10/2020	Neptune MC-ICP MS	23	72	-1.08
BDH	V standard solution	26	Durham	15/10/2020	Neptune MC-ICP MS	15	27	-1.10
BDH	V standard solution	26	Durham	15/10/2020	Neptune MC-ICP MS	20	52	-1.19
BDH	V standard solution	26	Durham	16/10/2020	Neptune MC-ICP MS	21	33	-1.09
BDH	V standard solution	26	Durham	16/10/2020	Neptune MC-ICP MS	22	40	-1.16
BDH	V standard solution	26	Durham	16/10/2020	Neptune MC-ICP MS	19	67	-1.18
BDH	V standard solution	26	Durham	16/10/2020	Neptune MC-ICP MS	24	87	-1.16
BDH	V standard solution	26	Durham	16/10/2020	Neptune MC-ICP MS	18	58	-1.21
BDH	V standard solution	26	Durham	16/10/2020	Neptune MC-ICP MS	24	70	-1.19
BDH	V standard solution	26	Durham	16/10/2020	Neptune MC-ICP MS	26	69	-1.14
BDH	V standard solution	26	Durham	16/10/2020	Neptune MC-ICP MS	18	33	-1.17
BDH	V standard solution	26	Durham	16/10/2020	Neptune MC-ICP MS	18	81	-1.25
Session 26 BDH average							-1.16	0.13 23

BDH	V standard solution	27	Durham	16/10/2020	Neptune MC-ICP MS	22	47	-1.32
BDH	V standard solution	27	Durham	16/10/2020	Neptune MC-ICP MS	15	56	-1.12
BDH	V standard solution	27	Durham	16/10/2020	Neptune MC-ICP MS	23	92	-1.09
BDH	V standard solution	27	Durham	16/10/2020	Neptune MC-ICP MS	20	22	-1.20
BDH	V standard solution	27	Durham	16/10/2020	Neptune MC-ICP MS	20	103	-1.29
BDH	V standard solution	27	Durham	16/10/2020	Neptune MC-ICP MS	20	98	-1.23
BDH	V standard solution	27	Durham	16/10/2020	Neptune MC-ICP MS	21	90	-1.21
BDH	V standard solution	27	Durham	16/10/2020	Neptune MC-ICP MS	20	78	-1.10
BDH	V standard solution	27	Durham	16/10/2020	Neptune MC-ICP MS	19	67	-1.21
BDH	V standard solution	27	Durham	17/10/2020	Neptune MC-ICP MS	25	73	-1.11
Session 27 BDH average							-1.19	0.16 10

BDH	V standard solution	28	Durham	09/03/2021	Neptune MC-ICP MS	21	30	-1.22
BDH	V standard solution	28	Durham	09/03/2021	Neptune MC-ICP MS	19	7	-1.17
BDH	V standard solution	28	Durham	09/03/2021	Neptune MC-ICP MS	23	43	-1.21
BDH	V standard solution	28	Durham	09/03/2021	Neptune MC-ICP MS	21	20	-1.24
BDH	V standard solution	28	Durham	09/03/2021	Neptune MC-ICP MS	22	41	-1.27
BDH	V standard solution	28	Durham	09/03/2021	Neptune MC-ICP MS	25	16	-1.19
BDH	V standard solution	28	Durham	09/03/2021	Neptune MC-ICP MS	21	26	-1.24
BDH	V standard solution	28	Durham	09/03/2021	Neptune MC-ICP MS	23	32	-1.24
BDH	V standard solution	28	Durham	09/03/2021	Neptune MC-ICP MS	25	20	-1.22
Session 28 BDH average							-1.22	0.06 9

BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		19	-1.16
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		17	-1.27
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		34	-1.21
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		31	-1.21
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		37	-1.21
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		15	-1.16
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		82	-1.23
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		60	-1.11
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		29	-1.15
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		29	-1.19
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		18	-1.20
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		34	-1.19

Appendix J - Vanadium BDH Standard Solution Data

BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		30	-1.15		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		52	-1.21		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		29	-1.15		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		32	-1.16		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		57	-1.15		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		54	-1.18		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		39	-1.26		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		45	-1.22		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		35	-1.20		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		39	-1.16		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		58	-1.13		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		57	-1.22		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		47	-1.26		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		49	-1.25		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		70	-1.21		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		34	-1.25		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		35	-1.19		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		79	-1.16		
BDH	V standard solution	29	Durham	10/03/2021	Neptune MC-ICP MS		46	-1.21		
Session 29 BDH average								-1.19	0.08	31

BDH	V standard solution	30	Durham	11/03/2021	Neptune MC-ICP MS	22	27	-1.27		
BDH	V standard solution	30	Durham	11/03/2021	Neptune MC-ICP MS	24	38	-1.21		
BDH	V standard solution	30	Durham	11/03/2021	Neptune MC-ICP MS	22	18	-1.12		
BDH	V standard solution	30	Durham	11/03/2021	Neptune MC-ICP MS	27	34	-1.21		
BDH	V standard solution	30	Durham	11/03/2021	Neptune MC-ICP MS	23	58	-1.13		
BDH	V standard solution	30	Durham	11/03/2021	Neptune MC-ICP MS	28	14	-1.22		
BDH	V standard solution	30	Durham	11/03/2021	Neptune MC-ICP MS	23	48	-1.20		
BDH	V standard solution	30	Durham	11/03/2021	Neptune MC-ICP MS	23	27	-1.19		
BDH	V standard solution	30	Durham	11/03/2021	Neptune MC-ICP MS	27	22	-1.14		
BDH	V standard solution	30	Durham	11/03/2021	Neptune MC-ICP MS	20	35	-1.18		
BDH	V standard solution	30	Durham	11/03/2021	Neptune MC-ICP MS	20	40	-1.20		
BDH	V standard solution	30	Durham	11/03/2021	Neptune MC-ICP MS	25	19	-1.14		
BDH	V standard solution	30	Durham	11/03/2021	Neptune MC-ICP MS	17	44	-1.23		
BDH	V standard solution	30	Durham	11/03/2021	Neptune MC-ICP MS	23	52	-1.19		
BDH	V standard solution	30	Durham	11/03/2021	Neptune MC-ICP MS	20	32	-1.30		
BDH	V standard solution	30	Durham	11/03/2021	Neptune MC-ICP MS	23	40	-1.24		
Session 30 BDH average								-1.20	0.10	16

Appendix K - Iron Standard Solution Data

Sample Name	Type	Session	Location	Date	Method	RSE	RSD	$\delta^{56}\text{Fe}_{\text{NRM-524}} (\text{‰})$	2SD	$\delta^{57}\text{Fe}_{\text{NRM524}} (\text{‰})$	2SD	n
Romil Fe	Fe standard solution	1	Durham	11/09/2019	SSB Neptune MC-ICP MS	8	6	0.144		0.203		
Romil Fe	Fe standard solution	1	Durham	11/09/2019	SSB Neptune MC-ICP MS	9	15	0.154		0.225		
Romil Fe	Fe standard solution	1	Durham	11/09/2019	SSB Neptune MC-ICP MS	10	31	0.151		0.224		
Romil Fe	Fe standard solution	1	Durham	11/09/2019	SSB Neptune MC-ICP MS	10	21	0.172		0.247		
Session 1 Romil Fe average								0.156	0.024	0.225	0.036	4

Romil Fe	Fe standard solution	2	Durham	12/09/2019	SSB Neptune MC-ICP MS	10	31	0.179		0.235		
Romil Fe	Fe standard solution	2	Durham	12/09/2019	SSB Neptune MC-ICP MS	10	1	0.145		0.207		
Romil Fe	Fe standard solution	2	Durham	12/09/2019	SSB Neptune MC-ICP MS	11	49	0.158		0.218		
Romil Fe	Fe standard solution	2	Durham	12/09/2019	SSB Neptune MC-ICP MS	10	48	0.182		0.285		
Session 2 Romil Fe average								0.166	0.035	0.236	0.069	4

Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	7	46	0.151		0.241		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	6	29	0.129		0.229		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	7	18	0.135		0.182		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	8	53	0.149		0.196		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	8	62	0.145		0.223		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	7	189	0.152		0.207		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	6	106	0.145		0.216		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	6	98	0.164		0.231		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	6	59	0.160		0.215		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	18	14	0.132		0.183		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	8	114	0.151		0.201		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	6	74	0.136		0.177		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	7	79	0.161		0.243		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	6	42	0.163		0.244		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	6	35	0.146		0.161		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	7	85	0.144		0.234		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	5	65	0.160		0.227		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	6	78	0.157		0.235		
Romil Fe	Fe standard solution	3	Durham	08/02/2020	SSB Neptune MC-ICP MS	6	53	0.127		0.188		
Session 3 Romil Fe average								0.148	0.023	0.212	0.050	19

Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	8	20	0.139		0.223		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	7	6	0.161		0.255		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	9	26	0.159		0.241		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	8	1	0.177		0.254		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	7	32	0.171		0.257		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	6	47	0.173		0.269		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	8	29	0.192		0.275		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	9	20	0.158		0.275		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	7	61	0.190		0.268		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	7	127	0.190		0.273		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	9	66	0.181		0.292		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	9	25	0.159		0.274		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	8	18	0.188		0.280		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	6	49	0.177		0.275		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	8	4	0.172		0.260		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	7	19	0.170		0.256		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	6	13	0.200		0.302		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	7	83	0.162		0.262		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	7	51	0.193		0.281		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	8	40	0.176		0.273		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	7	44	0.163		0.263		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	10	0	0.181		0.270		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	7	31	0.175		0.260		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	7	90	0.179		0.343		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	10	108	0.167		0.268		
Romil Fe	Fe standard solution	4	Durham	09/03/2020	SSB Neptune MC-ICP MS	10	32	0.168		0.312		
Session 4 Romil Fe average								0.174	0.027	0.272	0.046	26

Romil Fe	Fe standard solution	5	Durham	12/04/2021	SSB Neptune MC-ICP MS	4	35	0.128		0.185		
Romil Fe	Fe standard solution	5	Durham	12/04/2021	SSB Neptune MC-ICP MS	4	55	0.126		0.180		
Romil Fe	Fe standard solution	5	Durham	12/04/2021	SSB Neptune MC-ICP MS	4	25	0.141		0.211		
Romil Fe	Fe standard solution	5	Durham	12/04/2021	SSB Neptune MC-ICP MS	4	32	0.154		0.212		
Romil Fe	Fe standard solution	5	Durham	12/04/2021	SSB Neptune MC-ICP MS	5	17	0.139		0.205		
Romil Fe	Fe standard solution	5	Durham	12/04/2021	SSB Neptune MC-ICP MS	4	17	0.128		0.193		
Romil Fe	Fe standard solution	5	Durham	12/04/2021	SSB Neptune MC-ICP MS	5	66	0.111		0.178		
Romil Fe	Fe standard solution	5	Durham	12/04/2021	SSB Neptune MC-ICP MS	5	22	0.138		0.213		
Romil Fe	Fe standard solution	5	Durham	12/04/2021	SSB Neptune MC-ICP MS	4	31	0.106		0.161		
Romil Fe	Fe standard solution	5	Durham	12/04/2021	SSB Neptune MC-ICP MS	5	2	0.142		0.212		
Session 5 Romil Fe average								0.131	0.029	0.195	0.036	10

Appendix K - Iron Standard Solution Data

Romil Fe	Fe standard solution	6	Durham	13/04/2021	SSB Neptune MC-ICP MS	4	3	0.161		0.243	
Romil Fe	Fe standard solution	6	Durham	13/04/2021	SSB Neptune MC-ICP MS	4	13	0.199		0.296	
Romil Fe	Fe standard solution	6	Durham	13/04/2021	SSB Neptune MC-ICP MS	3	12	0.188		0.272	
Romil Fe	Fe standard solution	6	Durham	13/04/2021	SSB Neptune MC-ICP MS	4	32	0.234		0.355	
Romil Fe	Fe standard solution	6	Durham	13/04/2021	SSB Neptune MC-ICP MS	4	6	0.177		0.258	
Romil Fe	Fe standard solution	6	Durham	13/04/2021	SSB Neptune MC-ICP MS	4	24	0.208		0.313	
Romil Fe	Fe standard solution	6	Durham	13/04/2021	SSB Neptune MC-ICP MS	4	23	0.186		0.268	
Romil Fe	Fe standard solution	6	Durham	13/04/2021	SSB Neptune MC-ICP MS	4	37	0.212		0.305	
Romil Fe	Fe standard solution	6	Durham	13/04/2021	SSB Neptune MC-ICP MS	3	42	0.194		0.283	
Romil Fe	Fe standard solution	6	Durham	13/04/2021	SSB Neptune MC-ICP MS	4	16	0.173		0.257	
Session 6 Romil Fe average								0.193	0.043	0.285	0.066 10

Romil Fe	Fe standard solution	7	Durham	14/04/2021	SSB Neptune MC-ICP MS	5	30	0.210		0.302	
Romil Fe	Fe standard solution	7	Durham	14/04/2021	SSB Neptune MC-ICP MS	4	8	0.207		0.295	
Romil Fe	Fe standard solution	7	Durham	14/04/2021	SSB Neptune MC-ICP MS	4	46	0.183		0.279	
Romil Fe	Fe standard solution	7	Durham	14/04/2021	SSB Neptune MC-ICP MS	4	13	0.152		0.223	
Romil Fe	Fe standard solution	7	Durham	14/04/2021	SSB Neptune MC-ICP MS	4	18	0.231		0.347	
Romil Fe	Fe standard solution	7	Durham	14/04/2021	SSB Neptune MC-ICP MS	5	11	0.257		0.399	
Romil Fe	Fe standard solution	7	Durham	14/04/2021	SSB Neptune MC-ICP MS	4	45	0.207		0.320	
Romil Fe	Fe standard solution	7	Durham	14/04/2021	SSB Neptune MC-ICP MS	5	63	0.203		0.300	
Romil Fe	Fe standard solution	7	Durham	14/04/2021	SSB Neptune MC-ICP MS	4	40	0.207		0.308	
Romil Fe	Fe standard solution	7	Durham	14/04/2021	SSB Neptune MC-ICP MS	5	6	0.195		0.282	
Romil Fe	Fe standard solution	7	Durham	14/04/2021	SSB Neptune MC-ICP MS	3	35	0.196		0.294	
Romil Fe	Fe standard solution	7	Durham	14/04/2021	SSB Neptune MC-ICP MS	4	9	0.234		0.339	
Romil Fe	Fe standard solution	7	Durham	14/04/2021	SSB Neptune MC-ICP MS	3	24	0.175		0.272	
Session 7 Romil Fe average								0.204	0.053	0.305	0.084 13

Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	20	559	0.115		0.171	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	17	328	0.119		0.189	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	15	99	0.103		0.182	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	17	80	0.203		0.316	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	14	137	0.130		0.218	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	13	0	0.160		0.251	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	13	154	0.163		0.226	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	12	122	0.177		0.268	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	12	57	0.177		0.261	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	13	18	0.187		0.287	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	9	70	0.149		0.223	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	11	61	0.143		0.228	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	10	40	0.194		0.298	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	7	18	0.143		0.211	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	9	16	0.128		0.201	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	7	52	0.126		0.204	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	7	99	0.092		0.163	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	8	33	0.163		0.253	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	6	142	0.141		0.229	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	6	17	0.139		0.220	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	7	36	0.152		0.227	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	5	76	0.147		0.225	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	4	39	0.144		0.253	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	5	19	0.112		0.188	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	4	92	0.151		0.258	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	4	32	0.134		0.207	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	4	86	0.165		0.247	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	4	98	0.144		0.214	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	5	36	0.133		0.195	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	3	58	0.150		0.224	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	4	87	0.134		0.229	
Romil Fe	Fe standard solution	8	Durham	16/04/2021	Ni doped Neptune MC-ICP MS	6	37	0.136		0.214	
Session 8 Romil Fe average								0.145	0.050	0.228	0.070 32

Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	9	136	0.176		0.242	
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	9	65	0.161		0.234	
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	16	55	0.189		0.268	
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	9	67	0.154		0.231	
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	9	12	0.187		0.231	
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	8	51	0.202		0.269	
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	10	28	0.168		0.229	
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	9	23	0.197		0.241	
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	9	109	0.168		0.250	
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	11	300	0.165		0.250	
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	9	58	0.155		0.234	
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	6	40	0.198		0.294	

Appendix K - Iron Standard Solution Data

Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	9	35	0.206		0.314		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	8	55	0.194		0.299		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	7	99	0.231		0.353		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	9	81	0.224		0.310		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	9	115	0.178		0.269		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	8	79	0.160		0.266		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	10	33	0.222		0.331		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	13	41	0.201		0.290		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	7	116	0.209		0.315		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	8	34	0.166		0.248		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	6	36	0.162		0.246		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	8	15	0.207		0.298		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	7	17	0.226		0.315		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	9	10	0.201		0.267		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	13	28	0.226		0.282		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	8	25	0.230		0.336		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	7	156	0.180		0.321		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	10	96	0.210		0.328		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	7	24	0.223		0.341		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	10	48	0.197		0.252		
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	13	80	0.212	0.316			
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	10	30	0.203	0.277			
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	8	3	0.196	0.313			
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	10	38	0.202	0.271			
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	15	80	0.184	0.281			
Romil Fe	Fe standard solution	9	Durham	20/04/2021	Ni doped Neptune MC-ICP MS	8	1	0.235	0.319			
Session 9 Romil Fe average								0.195	0.047	0.282	0.072	38

Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	9	263	0.184		0.294		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	5	23	0.166		0.268		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	7	7	0.204		0.319		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	8	11	0.216		0.326		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	8	118	0.247		0.343		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	11	220	0.182		0.250		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	8	18	0.130		0.214		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	9	201	0.162		0.248		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	9	198	0.126		0.192		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	13	20	0.196		0.297		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	9	40	0.143		0.247		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	7	12	0.172		0.275		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	11	13	0.187		0.282		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	7	164	0.157		0.248		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	9	12	0.139		0.204		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	8	2	0.141		0.212		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	7	60	0.212		0.302		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	9	47	0.112		0.164		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	9	97	0.166		0.258		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	10	40	0.185		0.284		
Romil Fe	Fe standard solution	10	Durham	21/04/2021	Ni doped Neptune MC-ICP MS	8	2	0.220	0.304			
Session 10 Romil Fe average								0.174	0.070	0.263	0.094	21

Romil Fe	Fe standard solution	11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	15	147	0.144		0.245		
Romil Fe	Fe standard solution	11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	13	116	0.142		0.233		
Romil Fe	Fe standard solution	11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	11	59	0.132		0.230		
Romil Fe	Fe standard solution	11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	10	13	0.168		0.249		
Romil Fe	Fe standard solution	11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	11	12	0.148		0.237		
Romil Fe	Fe standard solution	11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	8	150	0.195		0.304		
Romil Fe	Fe standard solution	11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	9	138	0.170		0.285		
Romil Fe	Fe standard solution	11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	8	93	0.217		0.322		
Romil Fe	Fe standard solution	11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	7	25	0.193		0.313		
Romil Fe	Fe standard solution	11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	11	97	0.170		0.274		
Romil Fe	Fe standard solution	11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	8	16	0.161		0.262		
Romil Fe	Fe standard solution	11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	10	108	0.123		0.197		
Romil Fe	Fe standard solution	11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	9	184	0.188		0.274		
Romil Fe	Fe standard solution	11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	7	225	0.208		0.309		
Romil Fe	Fe standard solution	11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	7	112	0.154		0.251		
Romil Fe	Fe standard solution	11	Durham	22/04/2021	Ni doped Neptune MC-ICP MS	8	29	0.244		0.339		
Session 11 Romil Fe average								0.172	0.066	0.270	0.079	16

Romil Fe	Fe standard solution	12	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	9	352	0.177		0.281
Romil Fe	Fe standard solution	12	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	12	242	0.158		0.258
Romil Fe	Fe standard solution	12	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	11	154	0.189		0.269
Romil Fe	Fe standard solution	12	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	12	345	0.201		0.298
Romil Fe	Fe standard solution	12	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	13	66	0.196		0.298

Appendix K - Iron Standard Solution Data

Romil Fe	Fe standard solution	12	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	14	8	0.167		0.258	
Romil Fe	Fe standard solution	12	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	10	137	0.170		0.245	
Romil Fe	Fe standard solution	12	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	10	133	0.176		0.244	
Romil Fe	Fe standard solution	12	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	13	175	0.211		0.318	
Romil Fe	Fe standard solution	12	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	20	125	0.170		0.241	
Romil Fe	Fe standard solution	12	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	12	179	0.183		0.280	
Romil Fe	Fe standard solution	12	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	16	109	0.117		0.180	
Romil Fe	Fe standard solution	12	Durham	23/04/2021	Ni doped Neptune MC-ICP MS	18	208	0.198		0.283	
Session 12 Romil Fe average								0.178	0.048	0.266	0.070 13

Romil Fe	Fe standard solution	13	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	17	64	0.176		0.281	
Romil Fe	Fe standard solution	13	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	7	23	0.173		0.264	
Romil Fe	Fe standard solution	13	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	19	7	0.166		0.240	
Romil Fe	Fe standard solution	13	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	17	9	0.195		0.286	
Romil Fe	Fe standard solution	13	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	12	61	0.188		0.307	
Romil Fe	Fe standard solution	13	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	10	8	0.188		0.300	
Romil Fe	Fe standard solution	13	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	12	77	0.175		0.268	
Romil Fe	Fe standard solution	13	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	13	21	0.153		0.243	
Romil Fe	Fe standard solution	13	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	15	36	0.234		0.336	
Romil Fe	Fe standard solution	13	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	8	73	0.142		0.202	
Romil Fe	Fe standard solution	13	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	9	51	0.236		0.351	
Romil Fe	Fe standard solution	13	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	17	50	0.158		0.249	
Romil Fe	Fe standard solution	13	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	16	145	0.174		0.266	
Romil Fe	Fe standard solution	13	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	18	28	0.175		0.281	
Romil Fe	Fe standard solution	13	Durham	27/04/2021	Ni doped Neptune MC-ICP MS	10	27	0.210		0.326	
Session 13 Romil Fe average								0.183	0.054	0.280	0.080 15

Romil Fe	Fe standard solution	14	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	7	108	0.183		0.268	
Romil Fe	Fe standard solution	14	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	8	11	0.202		0.300	
Romil Fe	Fe standard solution	14	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	9	24	0.162		0.234	
Romil Fe	Fe standard solution	14	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	11	73	0.173		0.261	
Romil Fe	Fe standard solution	14	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	7	39	0.207		0.309	
Romil Fe	Fe standard solution	14	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	5	106	0.190		0.290	
Romil Fe	Fe standard solution	14	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	6	158	0.147		0.245	
Romil Fe	Fe standard solution	14	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	7	45	0.219		0.332	
Romil Fe	Fe standard solution	14	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	5	132	0.198		0.287	
Romil Fe	Fe standard solution	14	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	6	58	0.163		0.266	
Romil Fe	Fe standard solution	14	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	5	175	0.195		0.300	
Romil Fe	Fe standard solution	14	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	7	108	0.162		0.253	
Romil Fe	Fe standard solution	14	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	7	28	0.187		0.277	
Romil Fe	Fe standard solution	14	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	9	132	0.171		0.271	
Romil Fe	Fe standard solution	14	Durham	28/04/2021	Ni doped Neptune MC-ICP MS	6	37	0.203		0.305	
Session 14 Romil Fe average								0.184	0.041	0.280	0.053 15

Romil Fe	Fe standard solution	15	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	9	74	0.150		0.230	
Romil Fe	Fe standard solution	15	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	9	21	0.141		0.221	
Romil Fe	Fe standard solution	15	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	14	125	0.162		0.240	
Romil Fe	Fe standard solution	15	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	11	12	0.177		0.281	
Romil Fe	Fe standard solution	15	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	8	21	0.191		0.309	
Romil Fe	Fe standard solution	15	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	10	173	0.164		0.257	
Romil Fe	Fe standard solution	15	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	7	181	0.175		0.259	
Romil Fe	Fe standard solution	15	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	12	4	0.217		0.307	
Romil Fe	Fe standard solution	15	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	4	201	0.143		0.221	
Romil Fe	Fe standard solution	15	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	6	129	0.163		0.243	
Romil Fe	Fe standard solution	15	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	7	41	0.154		0.257	
Romil Fe	Fe standard solution	15	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	10	122	0.170		0.295	
Romil Fe	Fe standard solution	15	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	11	137	0.193		0.264	
Romil Fe	Fe standard solution	15	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	7	57	0.174		0.260	
Romil Fe	Fe standard solution	15	Durham	29/04/2021	Ni doped Neptune MC-ICP MS	10	12	0.213		0.322	
Session 15 Romil Fe average								0.172	0.046	0.264	0.064 15

Romil Fe	Fe standard solution	16	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	18	39	0.167		0.248	
Romil Fe	Fe standard solution	16	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	17	11	0.170		0.240	
Romil Fe	Fe standard solution	16	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	19	18	0.204		0.323	
Romil Fe	Fe standard solution	16	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	20	59	0.178		0.256	
Romil Fe	Fe standard solution	16	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	24	1	0.106		0.179	
Romil Fe	Fe standard solution	16	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	18	27	0.178		0.279	
Romil Fe	Fe standard solution	16	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	23	20	0.181		0.297	
Romil Fe	Fe standard solution	16	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	16	5	0.190		0.304	
Romil Fe	Fe standard solution	16	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	20	10	0.215		0.357	
Romil Fe	Fe standard solution	16	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	20	32	0.201		0.312	
Romil Fe	Fe standard solution	16	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	18	48	0.206		0.313	
Romil Fe	Fe standard solution	16	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	19	21	0.193		0.287	
Romil Fe	Fe standard solution	16	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	17	80	0.130		0.176	

Appendix K - Iron Standard Solution Data

Romil Fe	Fe standard solution	16	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	18	56	0.234		0.368		
Romil Fe	Fe standard solution	16	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	17	17	0.189		0.287		
Romil Fe	Fe standard solution	16	Durham	17/05/2021	Ni doped Neptune MC-ICP MS	14	67	0.211		0.310		
Session 16 Romil Fe average								0.185	0.064	0.284	0.108	16
Romil Fe	Fe standard solution	17	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	17	17	0.192		0.288		
Romil Fe	Fe standard solution	17	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	19	20	0.185		0.276		
Romil Fe	Fe standard solution	17	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	19	12	0.179		0.257		
Romil Fe	Fe standard solution	17	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	19	15	0.176		0.268		
Romil Fe	Fe standard solution	17	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	20	4	0.194		0.285		
Romil Fe	Fe standard solution	17	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	19	5	0.229		0.336		
Romil Fe	Fe standard solution	17	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	17	23	0.170		0.264		
Romil Fe	Fe standard solution	17	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	15	7	0.216		0.293		
Romil Fe	Fe standard solution	17	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	16	19	0.215		0.324		
Romil Fe	Fe standard solution	17	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	19	63	0.177		0.265		
Romil Fe	Fe standard solution	17	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	15	45	0.139		0.195		
Romil Fe	Fe standard solution	17	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	17	9	0.191		0.291		
Romil Fe	Fe standard solution	17	Durham	18/05/2021	Ni doped Neptune MC-ICP MS	15	7	0.193		0.271		
Session 17 Romil Fe average								0.189	0.046	0.278	0.068	13
Romil Fe	Fe standard solution	18	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	17	86	0.140		0.221		
Romil Fe	Fe standard solution	18	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	18	98	0.206		0.315		
Romil Fe	Fe standard solution	18	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	21	4	0.201		0.290		
Romil Fe	Fe standard solution	18	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	19	58	0.213		0.324		
Romil Fe	Fe standard solution	18	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	18	45	0.179		0.285		
Romil Fe	Fe standard solution	18	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	18	90	0.141		0.231		
Romil Fe	Fe standard solution	18	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	19	3	0.133		0.211		
Romil Fe	Fe standard solution	18	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	23	14	0.149		0.235		
Romil Fe	Fe standard solution	18	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	20	80	0.172		0.260		
Romil Fe	Fe standard solution	18	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	21	40	0.172		0.249		
Romil Fe	Fe standard solution	18	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	19	43	0.215		0.324		
Romil Fe	Fe standard solution	18	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	20	47	0.208		0.318		
Romil Fe	Fe standard solution	18	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	19	63	0.168		0.259		
Romil Fe	Fe standard solution	18	Durham	19/05/2021	Ni doped Neptune MC-ICP MS	18	42	0.161		0.235		
Session 18 Romil Fe average								0.176	0.058	0.268	0.081	14
Romil Fe	Fe standard solution	19	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	18	27	0.220		0.327		
Romil Fe	Fe standard solution	19	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	22	66	0.150		0.228		
Romil Fe	Fe standard solution	19	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	18	22	0.170		0.255		
Romil Fe	Fe standard solution	19	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	19	34	0.191		0.269		
Romil Fe	Fe standard solution	19	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	17	63	0.232		0.319		
Romil Fe	Fe standard solution	19	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	22	0	0.178		0.238		
Romil Fe	Fe standard solution	19	Durham	20/05/2021	Ni doped Neptune MC-ICP MS	19	2	0.195		0.274		
Session 19 Romil Fe average								0.191	0.056	0.273	0.076	7

Appendix L - Zinc Solution Standard Data

Sample Name	Type	Session	Location	Date	Method	RSE	RSD	$\delta^{66}\text{Zn}_{\text{ETH}} (\text{‰})$	2SD	$\delta^{67}\text{Zn}_{\text{ETH}} (\text{‰})$	$\delta^{68}\text{Zn}_{\text{ETH}} (\text{‰})$	n
Romil Zn	Zn standard solution	3	Durham	05/06/2019	Neptune MC-ICP MS	10	38	-2.970	0.070	-4.471	-5.913	12
Romil Zn	Zn standard solution	3	Durham	05/06/2019	Neptune MC-ICP MS	14	32	-2.988		-4.407	-5.923	
Romil Zn	Zn standard solution	3	Durham	05/06/2019	Neptune MC-ICP MS	15	36	-3.031		-4.489	-5.954	
Romil Zn	Zn standard solution	3	Durham	05/06/2019	Neptune MC-ICP MS	12	1	-2.954		-4.354	-5.834	
Romil Zn	Zn standard solution	3	Durham	05/06/2019	Neptune MC-ICP MS	12	58	-2.913		-4.377	-5.802	
Romil Zn	Zn standard solution	3	Durham	05/06/2019	Neptune MC-ICP MS	13	46	-2.944		-4.332	-5.821	
Romil Zn	Zn standard solution	3	Durham	05/06/2019	Neptune MC-ICP MS	15	15	-2.996		-4.458	-5.863	
Romil Zn	Zn standard solution	3	Durham	05/06/2019	Neptune MC-ICP MS	12	16	-3.020		-4.499	-5.866	
Romil Zn	Zn standard solution	3	Durham	05/06/2019	Neptune MC-ICP MS	12	22	-3.013		-4.574	-5.927	
Romil Zn	Zn standard solution	3	Durham	05/06/2019	Neptune MC-ICP MS	12	1	-2.967		-4.415	-5.877	
Romil Zn	Zn standard solution	3	Durham	05/06/2019	Neptune MC-ICP MS	13	16	-2.973		-4.435	-5.843	
Romil Zn	Zn standard solution	3	Durham	05/06/2019	Neptune MC-ICP MS	12	16	-2.942		-4.411	-5.835	
Session 1 Romil Zn average								-2.976	0.070	-4.435	-5.871	12

Romil Zn	Zn standard solution	1	Durham	21/10/2019	Neptune MC-ICP MS	11	8	-2.988	0.051	-4.339	-5.846	15
Romil Zn	Zn standard solution	1	Durham	21/10/2019	Neptune MC-ICP MS	25	3	-2.957		-4.225	-5.811	
Romil Zn	Zn standard solution	1	Durham	21/10/2019	Neptune MC-ICP MS	22	17	-2.913		-4.183	-5.708	
Romil Zn	Zn standard solution	1	Durham	21/10/2019	Neptune MC-ICP MS	17	17	-2.973		-4.232	-5.843	
Romil Zn	Zn standard solution	1	Durham	21/10/2019	Neptune MC-ICP MS	27	45	-2.956		-4.245	-5.823	
Romil Zn	Zn standard solution	1	Durham	21/10/2019	Neptune MC-ICP MS	13	18	-2.931		-4.273	-5.771	
Romil Zn	Zn standard solution	1	Durham	21/10/2019	Neptune MC-ICP MS	14	19	-2.972		-4.255	-5.773	
Romil Zn	Zn standard solution	1	Durham	21/10/2019	Neptune MC-ICP MS	15	9	-2.956		-4.256	-5.796	
Romil Zn	Zn standard solution	1	Durham	21/10/2019	Neptune MC-ICP MS	11	3	-2.969		-4.325	-5.739	
Romil Zn	Zn standard solution	1	Durham	21/10/2019	Neptune MC-ICP MS	15	27	-2.972		-4.415	-5.837	
Romil Zn	Zn standard solution	1	Durham	21/10/2019	Neptune MC-ICP MS	14	10	-3.000		-4.278	-5.793	
Romil Zn	Zn standard solution	1	Durham	21/10/2019	Neptune MC-ICP MS	12	6	-2.969		-4.322	-5.807	
Romil Zn	Zn standard solution	1	Durham	21/10/2019	Neptune MC-ICP MS	17	0	-2.906		-4.263	-5.696	
Romil Zn	Zn standard solution	1	Durham	21/10/2019	Neptune MC-ICP MS	12	6	-2.958		-4.250	-5.832	
Romil Zn	Zn standard solution	1	Durham	21/10/2019	Neptune MC-ICP MS	9	10	-2.967		-4.338	-5.823	
Session 2 Romil Zn average								-2.959	0.051	-4.280	-5.793	15

Romil Zn	Zn standard solution	2	Durham	22/10/2019	Neptune MC-ICP MS	13	17	-2.921	0.048	-4.302	-5.777	5
Romil Zn	Zn standard solution	2	Durham	22/10/2019	Neptune MC-ICP MS	11	4	-2.929		-4.297	-5.772	
Romil Zn	Zn standard solution	2	Durham	22/10/2019	Neptune MC-ICP MS	9	9	-2.938		-4.194	-5.770	
Romil Zn	Zn standard solution	2	Durham	22/10/2019	Neptune MC-ICP MS	14	24	-2.983		-4.297	-5.842	
Romil Zn	Zn standard solution	2	Durham	22/10/2019	Neptune MC-ICP MS	12	26	-2.943		-4.233	-5.842	
Session 3 Romil Zn average								-2.943	0.048	-4.265	-5.801	5

Romil Zn	Zn standard solution	4	Durham	22/03/2021	Neptune MC-ICP MS	13	3	-2.946	0.038	-4.491	-5.891	4
Romil Zn	Zn standard solution	4	Durham	22/03/2021	Neptune MC-ICP MS	13	2	-2.924		-4.476	-5.873	
Romil Zn	Zn standard solution	4	Durham	22/03/2021	Neptune MC-ICP MS	16	5	-2.969		-4.469	-5.850	
Romil Zn	Zn standard solution	4	Durham	22/03/2021	Neptune MC-ICP MS	13	27	-2.935		-4.408	-5.861	
Session 4 Romil Zn average								-2.943	0.038	-4.461	-5.869	4

Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	12	39	-2.903	0.040	-4.159	-5.674	22
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	10	12	-2.909		-4.146	-5.660	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	12	10	-2.943		-4.524	-5.819	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	10	21	-2.935		-4.493	-5.824	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	9	24	-2.944		-4.485	-5.808	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	9	19	-2.947		-4.484	-5.824	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	10	2	-2.960		-4.474	-5.829	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	7	20	-2.955		-4.422	-5.802	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	10	27	-2.933		-4.388	-5.769	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	9	11	-2.953		-4.506	-5.847	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	12	23	-2.934		-4.426	-5.814	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	9	7	-2.935		-4.406	-5.824	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	9	23	-2.973		-4.460	-5.805	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	9	2	-2.983		-4.504	-5.841	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	10	5	-2.960		-4.401	-5.835	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	10	2	-2.944		-4.385	-5.817	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	12	2	-2.966		-4.454	-5.827	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	9	4	-2.941		-4.407	-5.799	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	10	4	-2.962		-4.445	-5.810	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	10	11	-2.970		-4.445	-5.811	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	8	18	-2.954		-4.479	-5.824	
Romil Zn	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	12	7	-2.974		-4.436	-5.866	
Session 5 Romil Zn average								-2.949	0.040	-4.424	-5.806	22

Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	10	46	-2.934		-4.398	-5.738	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	9	25	-2.942		-4.424	-5.805	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	12	23	-2.943		-4.403	-5.750	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	9	12	-2.950		-4.347	-5.787	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	8	2	-2.924		-4.370	-5.789	

Appendix L - Zinc Solution Standard Data

Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	10	28	-2.943		-4.417	-5.790	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	7	11	-2.935		-4.338	-5.728	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	9	14	-2.937		-4.344	-5.785	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	6	1	-2.939		-4.408	-5.780	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	10	4	-2.929		-4.383	-5.788	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	8	1	-2.967		-4.339	-5.812	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	10	1	-2.944		-4.321	-5.766	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	7	12	-2.933		-4.388	-5.797	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	10	6	-2.931		-4.346	-5.752	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	9	2	-2.939		-4.325	-5.786	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	8	13	-2.961		-4.383	-5.801	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	7	18	-2.929		-4.372	-5.737	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	8	5	-2.942		-4.397	-5.762	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	9	13	-2.912		-4.365	-5.791	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	8	8	-2.934		-4.354	-5.760	
Romil Zn	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	10	17	-2.947		-4.348	-5.782	
Session 6 Romil Zn average								-2.939	0.024	-4.370	-5.776	21

Romil Zn	Zn standard solution	7	Durham	25/03/2021	Neptune MC-ICP MS	11	8	-2.941		-4.429	-5.770	
Romil Zn	Zn standard solution	7	Durham	25/03/2021	Neptune MC-ICP MS	13	13	-2.907		-4.332	-5.700	
Romil Zn	Zn standard solution	7	Durham	25/03/2021	Neptune MC-ICP MS	10	11	-2.945		-4.394	-5.773	
Session 7 Romil Zn average								-2.931	0.041	-4.385	-5.748	3

Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	9	3	-2.967		-4.385	-5.861	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	6	23	-2.959		-4.377	-5.857	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	8	8	-2.963		-4.433	-5.841	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	7	14	-2.961		-4.386	-5.859	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	7	28	-2.953		-4.351	-5.822	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	8	13	-2.966		-4.361	-5.840	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	9	19	-2.946		-4.396	-5.850	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	8	17	-2.954		-4.339	-5.831	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	8	16	-2.958		-4.398	-5.855	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	10	84	-2.918		-4.384	-5.778	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	7	8	-2.951		-4.393	-5.860	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	13	0	-2.916		-4.349	-5.775	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	10	7	-2.956		-4.330	-5.833	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	11	31	-2.927		-4.370	-5.825	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	6	5	-2.958		-4.393	-5.860	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	9	9	-2.983		-4.408	-5.885	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	11	4	-2.963		-4.396	-5.894	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	8	9	-2.931		-4.379	-5.821	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	8	0	-2.942		-4.361	-5.848	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	9	5	-2.941		-4.380	-5.837	
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	10	3	-2.969	-4.337	-5.869		
Romil Zn	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	7	7	-2.958	-4.350	-5.854		
Session 8 Romil Zn average								-2.952	0.034	-4.375	-5.843	22

Romil Zn	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	9	1	-2.953		-4.394	-5.846	
Romil Zn	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	9	19	-2.973		-4.384	-5.892	
Romil Zn	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	9	6	-2.947		-4.363	-5.841	
Romil Zn	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	8	21	-2.976		-4.395	-5.882	
Romil Zn	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	9	7	-2.934		-4.402	-5.838	
Romil Zn	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	9	34	-2.964		-4.433	-5.865	
Romil Zn	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	7	22	-2.948		-4.384	-5.828	
Romil Zn	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	9	3	-2.957		-4.402	-5.857	
Romil Zn	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	10	8	-2.938		-4.429	-5.854	
Romil Zn	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	7	10	-2.951		-4.377	-5.872	
Romil Zn	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	9	14	-2.959		-4.412	-5.877	
Romil Zn	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	10	16	-2.962		-4.401	-5.866	
Romil Zn	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	10	11	-2.916		-4.410	-5.805	
Romil Zn	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	8	6	-2.951		-4.420	-5.861	
Session 9 Romil Zn average								-2.952		0.031	-4.400	-5.856

IRMM3702	Zn standard solution	1	Durham	05/06/2019	Neptune MC-ICP MS	14	22	0.013		0.050	0.049	
IRMM3702	Zn standard solution	1	Durham	05/06/2019	Neptune MC-ICP MS	18	29	-0.015		0.027	0.011	
IRMM3702	Zn standard solution	1	Durham	05/06/2019	Neptune MC-ICP MS	11	0	-0.005		0.053	0.031	
IRMM3702	Zn standard solution	1	Durham	05/06/2019	Neptune MC-ICP MS	12	29	0.028		0.068	0.101	
IRMM3702	Zn standard solution	1	Durham	05/06/2019	Neptune MC-ICP MS	12	48	0.034		0.047	-0.009	
IRMM3702	Zn standard solution	1	Durham	05/06/2019	Neptune MC-ICP MS	14	1	0.032		0.054	0.078	
IRMM3702	Zn standard solution	1	Durham	05/06/2019	Neptune MC-ICP MS	14	40	0.012		0.000	0.024	
IRMM3702	Zn standard solution	1	Durham	05/06/2019	Neptune MC-ICP MS	14	16	-0.023		-0.121	-0.051	
IRMM3702	Zn standard solution	1	Durham	05/06/2019	Neptune MC-ICP MS	12	69	-0.004		-0.118	-0.055	
IRMM3702	Zn standard solution	1	Durham	05/06/2019	Neptune MC-ICP MS	15	15	0.005		-0.057	-0.007	
Session 1 IRMM3702 average								0.008	0.040	0.000	0.017	10

Appendix L - Zinc Solution Standard Data

IRMM3702	Zn standard solution	2	Durham	21/10/2019	Neptune MC-ICP MS	26	4	0.009		0.034	0.001	
IRMM3702	Zn standard solution	2	Durham	21/10/2019	Neptune MC-ICP MS	20	28	-0.019		0.114	-0.051	
IRMM3702	Zn standard solution	2	Durham	21/10/2019	Neptune MC-ICP MS	15	36	0.021		0.125	-0.009	
IRMM3702	Zn standard solution	2	Durham	21/10/2019	Neptune MC-ICP MS	13	29	0.001		0.126	-0.029	
IRMM3702	Zn standard solution	2	Durham	21/10/2019	Neptune MC-ICP MS	26	9	0.006		0.190	0.011	
IRMM3702	Zn standard solution	2	Durham	21/10/2019	Neptune MC-ICP MS	19	15	-0.004		0.135	-0.021	
IRMM3702	Zn standard solution	2	Durham	21/10/2019	Neptune MC-ICP MS	9	15	0.008		0.053	-0.015	
IRMM3702	Zn standard solution	2	Durham	21/10/2019	Neptune MC-ICP MS	12	26	0.006		0.058	-0.032	
IRMM3702	Zn standard solution	2	Durham	21/10/2019	Neptune MC-ICP MS	15	16	0.001		0.118	-0.004	
IRMM3702	Zn standard solution	2	Durham	21/10/2019	Neptune MC-ICP MS	12	5	-0.002		0.101	0.042	
IRMM3702	Zn standard solution	2	Durham	21/10/2019	Neptune MC-ICP MS	13	5	-0.003		0.140	-0.014	
IRMM3702	Zn standard solution	2	Durham	21/10/2019	Neptune MC-ICP MS	14	7	-0.011		0.082	-0.007	
IRMM3702	Zn standard solution	2	Durham	21/10/2019	Neptune MC-ICP MS	11	7	-0.029		0.030	-0.053	
IRMM3702	Zn standard solution	2	Durham	21/10/2019	Neptune MC-ICP MS	12	7	-0.007		0.057	-0.028	
IRMM3702	Zn standard solution	2	Durham	21/10/2019	Neptune MC-ICP MS	13	14	-0.029		0.054	-0.050	
IRMM3702	Zn standard solution	2	Durham	21/10/2019	Neptune MC-ICP MS	14	29	-0.032		-0.014	-0.048	
Session 2 IRMM3702 average								-0.005	0.031	0.088	-0.019	16

IRMM3702	Zn standard solution	3	Durham	22/10/2019	Neptune MC-ICP MS	11	14	-0.026		0.036	-0.021	
IRMM3702	Zn standard solution	3	Durham	22/10/2019	Neptune MC-ICP MS	15	10	0.012		0.062	0.004	
IRMM3702	Zn standard solution	3	Durham	22/10/2019	Neptune MC-ICP MS	10	9	-0.016		0.096	-0.009	
IRMM3702	Zn standard solution	3	Durham	22/10/2019	Neptune MC-ICP MS	16	4	0.017		0.004	-0.018	
IRMM3702	Zn standard solution	3	Durham	22/10/2019	Neptune MC-ICP MS	11	1	0.007		0.039	-0.023	
IRMM3702	Zn standard solution	3	Durham	22/10/2019	Neptune MC-ICP MS	14	15	-0.005		0.065	-0.027	
Session 3 IRMM3702 average								-0.002	0.034	0.050	-0.015	6

IRMM3702	Zn standard solution	4	Durham	22/03/2021	Neptune MC-ICP MS	15	15	-0.038		-0.123	-0.117	
IRMM3702	Zn standard solution	4	Durham	22/03/2021	Neptune MC-ICP MS	11	12	-0.004		-0.121	-0.089	
IRMM3702	Zn standard solution	4	Durham	22/03/2021	Neptune MC-ICP MS	11	41	0.000		-0.067	-0.041	
Session 4 IRMM3702 average								-0.014	0.042	-0.104	-0.082	3

IRMM3702	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	12	3	0.052		0.267	0.193	
IRMM3702	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	9	10	0.045		0.293	0.175	
IRMM3702	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	9	8	-0.013		-0.041	0.021	
IRMM3702	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	12	18	-0.007		-0.007	0.017	
IRMM3702	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	13	10	-0.027		-0.065	0.026	
IRMM3702	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	8	13	-0.015		0.015	0.073	
IRMM3702	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	10	7	-0.002		-0.015	0.057	
IRMM3702	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	8	2	-0.019		0.031	0.057	
IRMM3702	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	8	6	-0.025		-0.065	0.029	
IRMM3702	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	10	3	-0.012		0.003	0.065	
IRMM3702	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	10	3	-0.004		0.064	0.077	
IRMM3702	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	9	5	-0.017		0.043	0.037	
IRMM3702	Zn standard solution	5	Durham	23/03/2021	Neptune MC-ICP MS	10	16	-0.021		0.055	0.023	
Session 5 IRMM3702 average								-0.005	0.050	0.044	0.065	13

IRMM3702	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	8	17	0.013		0.060	0.075	
IRMM3702	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	9	13	0.014		0.070	0.085	
IRMM3702	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	11	14	0.008		0.117	0.078	
IRMM3702	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	11	23	0.012		0.102	0.073	
IRMM3702	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	9	10	0.022		0.105	0.090	
IRMM3702	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	9	12	-0.010		0.077	0.057	
IRMM3702	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	11	0	0.021		0.090	0.086	
IRMM3702	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	8	12	-0.014		0.054	0.062	
IRMM3702	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	7	0	0.003		-0.009	0.047	
IRMM3702	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	11	24	0.005		0.112	0.052	
IRMM3702	Zn standard solution	6	Durham	24/03/2021	Neptune MC-ICP MS	7	13	-0.017		0.042	0.071	
Session 6 IRMM3702 average								0.005	0.027	0.075	0.071	11

IRMM3702	Zn standard solution	7	Durham	25/03/2021	Neptune MC-ICP MS	10	5	0.005		0.026	0.073	
IRMM3702	Zn standard solution	7	Durham	25/03/2021	Neptune MC-ICP MS	10	6	0.005		0.071	0.049	
IRMM3702	Zn standard solution	7	Durham	25/03/2021	Neptune MC-ICP MS	9	12	0.011		0.046	0.091	
Session 7 IRMM3702 average								0.007	0.008	0.048	0.071	3

IRMM3702	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	11	16	0.035		0.116	0.144
IRMM3702	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	8	6	0.068		0.153	0.199
IRMM3702	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	9	18	0.035		0.096	0.126
IRMM3702	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	9	12	0.029		0.077	0.139
IRMM3702	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	9	17	0.028		0.112	0.136
IRMM3702	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	9	4	0.014		0.068	0.108
IRMM3702	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	8	12	0.025		0.108	0.100
IRMM3702	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	7	12	0.022		0.096	0.127
IRMM3702	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	7	12	0.044		0.075	0.109

Appendix L - Zinc Solution Standard Data

IRMM3702	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	8	2	0.027		0.100	0.129	
IRMM3702	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	7	1	0.006		0.073	0.082	
IRMM3702	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	8	20	0.013		0.089	0.104	
IRMM3702	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	9	10	0.014		0.086	0.087	
IRMM3702	Zn standard solution	8	Durham	10/05/2021	Neptune MC-ICP MS	9	3	-0.008		0.029	0.089	
Session 8 IRMM3702 average								0.025	0.036	0.091	0.120	14
IRMM3702	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	11	18	0.044		0.059	0.148	
IRMM3702	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	9	9	0.041		0.013	0.157	
IRMM3702	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	6	7	0.044		0.091	0.139	
IRMM3702	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	8	32	0.016		0.003	0.091	
IRMM3702	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	8	32	0.024		0.071	0.147	
IRMM3702	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	8	7	0.053		0.044	0.161	
IRMM3702	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	9	0	0.025		0.086	0.123	
IRMM3702	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	9	8	0.039		0.085	0.142	
IRMM3702	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	7	11	0.017		0.055	0.137	
IRMM3702	Zn standard solution	9	Durham	11/05/2021	Neptune MC-ICP MS	9	16	0.036		0.061	0.161	
Session 9 IRMM3702 average								0.033	0.025	0.057	0.140	10