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The Marl Slate: A Taphonomic and Petrographic Analysis.

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Abstract

The Marl Slate is the basal unit of the Upper Permian (Zechstein) in northeast England. A finely laminated, organic-rich, dolomitic siltstone, equivalent to the Kupferschiefer of the Southern North Sea Basin and northern Germany and Poland. Several lines of evidence indicate the Marl Slate/Kupferschiefer accumulated in the anoxic bottom waters of a shallow (<200m), stratified, epicontinental sea during the first Zechstein marine Transgression (Z1). The sea was formed virtually instantaneously when the Boreal Ocean broke into and flooded a chain of sub-sea-level inland drainage basins that were dominated by aeolian dune facies (Rotleigend) before flooding. Detailed investigation, undertaken as part of this study, of the sedimentology and petrography **(1)**, focussing on and around three sites in a transect through the edge of the Zechstein Z1 deposits across County Durham (Middridge Quarry, Crime Rigg Quarry and Claxheugh Rock) revealed that a cyclic pattern of freshwater influx and phytoplanktonic blooms initiated the formation of a stratified water column in the early stages of the Zechstein Sea. The induced anoxia in the bottom waters, alongside mass mortalities of the present fish fauna, resulted in the abundance of Marl Slate fossils **(2)**. SEM-EDS, X-CT and XRD were used on Permian fish specimens reposited in the Durham University collection to develop and further the understanding of the Permian fish taphonomy and overall preservation. A combination of apatite and pyrite mineralized and replaced the organic tissue, initiated by thin biofilms of sulphur reducing bacteria adhering the carcasses to the anoxic sea floor in low-energy conditions. Furthermore, micrometre thick, illite clay masks have been observed to have coated the fossil material. Biofilms of sulphur reducing bacteria, combined with clay nucleation on the outer surfaces of the films, had a central role in the decay and fossilization of the Marl Slate fishes. These results shed new light on how the sedimentology, petrography and palaeontology of the Marl Slate all factor into driving the taphonomy and the unique preservational pathway undergone by the fish fauna within the Marl Slate of northeast England. This research uses the Marl Slate to bridge the gap between taphonomy and the environment of preservation of early Permian fish fauna, it takes the first steps to generate visualized models representing the depositional and taphonomic environments of the Marl Slate involved in producing a high standard of fossilization.

Contents

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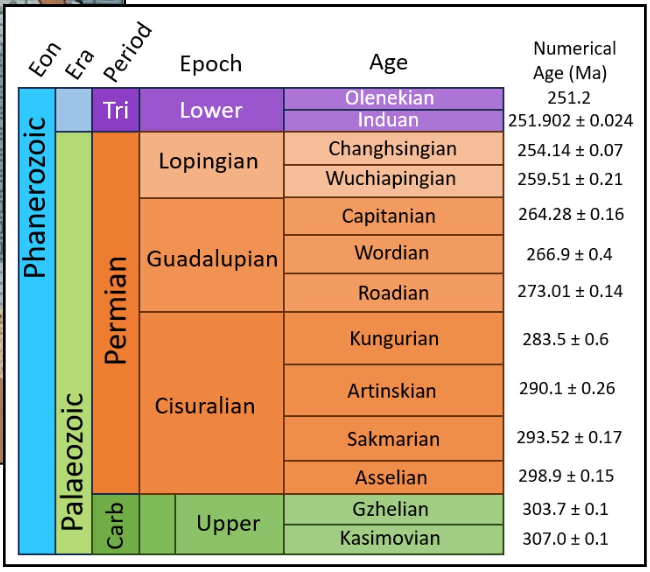
Introduction

The major continental collision that drove the Variscan Orogeny, during the late Carboniferous and early Permian, also created the Pangaean supercontinent (Stampfli et al, 2013). Within this landmass, Britain lay at a tropical latitude, approximately 30° north by the early Triassic. The depositional environments included widespread deserts, tropical and evaporitic seas, fluvial outwash plains, ephemeral lakes and mudflats (Ziegler, 1990). Erosion of the folded and uplifted Carboniferous strata had generated mature, gently rolling plains across which spread the early Permian desert (Sahney et al, 2010). By the late Permian, continental extension had opened seaways, flooding low ground across large inland drainage basins (Van Wees et al, 2000). On the western edge of northern England, the Bakevellia Sea developed, covering approximately the area of the present-day Irish Sea and its marginal areas (Pattison et al, 1973). To the east, the Zechstein Sea covered approximately the area

Figure 1.1: Map of northeast Europe displaying the extent of the Zechstein Sea. Particularly of note is where the sea reaches northeast England. Taken from the Geological Society Atlas of Palaeogeography and Lithofacies. Included is a Chronostratigraphy chart displaying the relevant ages within the Upper Carboniferous, Permian and Lower Triassic periods. Figure from the Atlas of Palaeogeography and Lithofacies, 1992. (3)



Eon	Era	Period	Epoch	Age	Numerical Age (Ma)
Phanerozoic		Tri	Lower	Olenekian	251.2
				Induan	251.902 ± 0.024
	Palaeozoic	Permian	Lopingian	Changhsingian	254.14 ± 0.07
				Wuchiapingian	259.51 ± 0.21
			Guadalupian	Capitanian	264.28 ± 0.16
				Wordian	266.9 ± 0.4
				Roadian	273.01 ± 0.14
			Cisuralian	Kungurian	283.5 ± 0.6
				Artinskian	290.1 ± 0.26
				Sakmarian	293.52 ± 0.17
				Asselian	298.9 ± 0.15
		Carb	Upper	Gzhelian	303.7 ± 0.1
				Kasimovian	307.0 ± 0.1

Figure 1.2: Geological time scale of the Permian. Clipped from Sedimentary Petrology from Tucker and Jones (2023) and therein Cohen et al, 2013, the ICS International Chronostratigraphic Chart.

of present-day North Sea and extended as far to the east as Lithuania and Poland. Today, Permian strata are preserved in northern England to the northwest of the Pennines, around Carlisle, in the Vale of Eden and West Cumbria as well as much of County Durham to the east of the Pennines. It is the Upper Permian sections across County Durham and the first transgression of the Zechstein Sea that forms the focus of this research.

County Durham of Northeast England is home to a variety of sedimentary facies; namely the Magnesian Limestone, deposited in the fully formed Zechstein Sea, and before that the Yellow Sands Formation deposited as aeolian dunes in the Early Permian desert. Yet it is what lies between those that is of interest in this study. The Marl Slate is the first sequence of the Zechstein Group (Z1 Cycle) in the Lopingian Epoch of the Late Permian. It began with an initial rapid transgression of the Zechstein Sea that flooded wide areas of the Early Permian desert (Figure 1.1). The Zechstein Transgression is studied in detail by Smith (1980). The Marl Sate represents one of the oldest marine Permian units preserved in northeast England and displays this initial transgression in the form of sapropelic, silty dolomitic mudstones. This formation is part of the Zechstein Group of rocks, and is equivalent to the Kupferschiefer of Germany and Northern Europe (Gibbons, 1987). It is overlain by the Magnesian Limestone and the contact often appears sharp; however, in many places a closer look reveals that it is in fact more transitional.

The Marl Slate varies in colour from beige-brown to greyish depending on the outcrop (Smith, 1980). Unweathered surfaces reveal thin (<mm thick) alternating bands of dark grey and near black sapropelic material as well as thicker, harder bands of more dolomitic material towards the upper sections of the Marl Slate (Hirst and Dunham, 1963). This matched descriptions of the Kupferschiefer (specifically the Fore-Sudetian monocline in Poland) by Haranczyk (1970). Interbedded throughout are thin (cm thick) bands of clay that are a brown colour akin to milk chocolate on unweathered surfaces. Detailed logging was undertaken at Claxheugh Rocks in northeast England in order to display these features graphically, as well as XRD analysis to figure out the composition of the clay.

Previous scanning electron microscopy (SEM) has revealed that three features are the most prominent components of the Marl Slate. i) The dolomite is very abundant, as is the illite clay filling pore space and coating a majority of grains (Turner and Magaritz, 1986). ii) Darker material, likely higher in organic carbon, is present in thin layers clearly visible in thin section (Turner et al, 1978). iii) While dolomite is the dominant carbonate, areas rich in primary calcite were also seen in a multitude of specimens, as well as clumps of spheroidal pyrite (framboids) that were scattered throughout (Sweeney et al, 1987). What was viewed here matches with the findings of Hirst and Dunham (1963). The final key component of the marl slate is the large abundance of fossil material, specifically the fish. EDX analysis of fragments of these fish is hypothesised to reveal that they are comprised primarily of apatite, the carcases likely providing their own source of phosphorus to initiate early apatite replacement of the organic material. **(4)**

The Marl Slate is a key point of interest, not only because of its well-preserved fossils but because it has the capacity to be of use in more applied fields. The first being the potentially large proportion of rare earth elements present within the lithology. The Kupferschiefer of Poland and Germany has been studied in detail regarding its enrichment in REEs and iron sulphides. Work by Love (1962) leaves no doubt as to the syngenetic/diagenetic origin of the bulk of the iron sulphide; but he also presents evidence that strongly confirms that sulphides, other than iron, crystallised later than pyrite. In addition, the Kupferschiefer is famous for being the host of one of the most important copper deposits in the world whilst also having an abundance of lead sulphide as well as iron sulphides. Regarding a more modern use, the Marl Slate may have the capacity to act as a regional seal for carbon capture and storage in the southern North Sea. If its capacity for this is proven to be viable, the Marl Slate and corresponding Kupferschiefer will be a key part of North Sea carbon storage in the future (see Monaghan et al, 2012 and Wilkinson et al, 2013). However, this study focusses on the Marl Slate from palaeontological and taphonomic perspectives, focussing on the abundance of well-preserved fish.

Fishes are primarily preserved as their hard parts via durpartic preservation, that is as skeletons or fragments of skeletons (Schopf, 1975). While the bones and shells of organisms do indeed provide useful information about how fossils are preserved, they lack the detail to explain the exceptional preservation the soft parts of some fossils undergo. Many vertebrate bones (including fish) are made up of apatite, $CaPO_4$, more specifically, $Ca_{10}(PO_4)_6(OH)_2$ (calcium hydroxyapatite) **(5)**. This apatite would be left behind, after decay of the soft-tissues and burial, and either mineralogically replaced or removed by environmental factors. Replacement of said hard parts can occur in multiple ways, mineralization (the replacement of organic matter with inorganic material) via microbial action is of note in this study (Briggs, 2003). There are multiple different factors that can influence the type and amount of mineral replacement an organism undergoes before complete fossilization. This study aims to discuss those factors and their end results, as well as the link between pre-burial processes (such as depositional environment and sedimentology) and post-burial processes like diagenesis, specifically the exact taphonomic pathway the organism followed, as well as any other exterior players that could alter the quality and the composition of the fossil.

The Taphonomy of the Marl Slate fishes is the unknown here. The sedimentology and palaeontology of the unit have been largely studied in the past, however research into the taphonomy of the fishes themselves has barely breached the surface **(6)**. Taphonomy itself is the combination of all of the processes occurring after an organism's death and before its final fossilization in rock (Behrensmeyer et al, 2000). It is very unlikely that an organism will ever end up as a fossil. For those that do however, there are three major processes commonly undergone by nearly all fossils before preservation: (1) decay of the soft tissues, (2) transport and breakage of hard tissues and (3) burial and modification of the hard tissues **(7)** (Benton and Harper, 2020). In some extremely rare cases, the soft-tissues of organisms may also be preserved. Examples of these exceptionally preserved fossils can be seen within Lagerstätten deposits such as the Burgess Shale of the Canadian Rockies or the Chengjiang deposit in southern China (Petrovich, 2001). However, more relevant examples can be found within the Marl Slate deposits of northeast England, correlating with the Kupferschiefer of eastern Germany. These soft-body tissues are the key to reconstructing the preservation pathways undergone by the organisms preserved in these rock bodies. Analysis of these tissues may provide the answers as to how and why some organisms are preserved so well. Soft-bodied organisms can make up 60% of organisms in some marine settings (Benton and Harper, 2020). Under normal conditions, the vast majority of those organisms would be lost to time.

Aims

Studying the Marl Slate offers a unique opportunity. The depositional setting and taphonomy are very niche, providing an excellent opportunity to delve into how well-preserved fossils form. The primary aim of this study is to explain how the fishes of the Marl Slate and corresponding Kupferschiefer became fossilised in such abundance and quality, while being roughly localized to the lower portion of the deposit. However, the environment where these fish live and die is niche meaning that the taphonomic pathways undertaken by these fish will be unique to the shallow Zechstein Sea and similar environments. In turn, in order to fulfil the primary aim, it needed to be split up into several key points of interest. These key points are set out below as three objectives. **(8)**

1. Petrography and Sedimentology. Understanding the petrography and sedimentology of the Marl Slate is essential to gaining an idea as to why such a large proportion of fish fossils are preserved within the Marl Slate, a relatively thin layer of the Zechstein Z1 cycle. An understanding of the rock itself will yield answers regarding what is so special about the Marl Slate.
2. The depositional setting and the biota. Understanding why the majority of fossils are found within the lower section of the Marl Slate requires, not only an idea of the unit's petrography and sedimentology, but a greater understanding of the depositional setting as well as its biota. While the palaeontology of the Marl Slate is largely understood, its exact depositional environment is unclear. If a new depositional model is put forward, it would lay the groundwork for fully understanding why the fishes were only preserved in abundance earlier in the Marl Slates deposition.
3. Taphonomy. Understanding the taphonomic pathway undergone by the fish carcasses is crucial to understanding how they were so well preserved in such abundance. Understanding the taphonomy of the fish fossils will answer the question as to why they are so well preserved, as well as uncover vital new data regarding the composition of the fossils themselves and likely hypotheses suggesting how they came to be preserved that way.

Chapter 1:

Marl Slate Stratigraphy and Fish Preservation

While the literature surrounding the Marl Slate is more sparse than other well preserved fossil beds, the absence presents a unique opportunity to shed some light on the understudied and underappreciated taphonomy of the unit. The lack of modern literature on the preservation or taphonomy of the vertebrate fossils of the Marl Slate is made up for by a larger number of older publications, discussing the taxonomy of the fossils, dating back to arguably the most comprehensive text by King (1850) whom does not delve into the newer fields of taphonomy or mode of preservation of the fish. This study aims to fill that gap in knowledge. The more modern literature revolves around the geochemistry of the Marl Slate itself; it has drifted from the fossils preserved which are potentially the key to discovering, or at least narrowing down, the environment of deposition as well as understanding the taphonomy. If the two were combined, it may lead to discoveries of how the fossils are so well preserved, as well as the environment they were preserved in. As the area of interest is largely understudied, this chapter aims to bring together relevant literature, regarding taphonomy and geochemistry, and link it back to the Marl Slate. It describes the general understanding of fossil preservation while highlighting how sparse the knowledge base is regarding Marl Slate taphonomy **(9)**. Understanding the taphonomy of the Marl Slate is critical when attempting to uncover how the fossil fish were preserved. Not only does this study aim to explain how the fish became preserved, but it will shed light on the understudied taphonomy of the Marl Slate. **(10)**

One excellent comparison to the Marl Slate would be the work done by Martill et al (1988), describing the Cretaceous Santana Formation of northeast Brazil. Early diagenesis of calcareous concretions allowed some fishes, killed in mass mortality events, to be preserved three dimensionally. It is thought that fluctuating salinities may have been responsible for the mass deaths of the dominantly marine fish fauna. It was early phosphatization, brought about by bacterial activity, that allowed a variety of soft tissues to be preserved within the cavity of a variety of fish taxa.

Pre-Burial Processes

Decay

Decay is often the first taphonomic process to affect a deceased organism. It begins almost immediately after the organism dies and continues until the organism is mineralized (Briggs and Kear, 1993). However, it is of note that mineralization of an organism does not necessarily prevent decay (Briggs, 1995). Although if mineralization begins early enough, both hard and soft-tissues have the potential to be preserved. If the onset of mineralization is late, decay processes will have removed many, if not all, of the soft tissues; and even have affected some of the hard tissues as well. The latter is most often the case.

Decay begins because deceased organisms are an enriched source of nutrients for other organisms to exploit (Lynch and Neufeld, 2015). Predation and scavenging are when larger organisms feed on smaller ones, alive or dead (Mellard et al, 2021). Decay, however, is the breakdown of organic matter by microbial organisms like bacteria, also known as putrefaction (Forbes, 2008). It is common for virtually all of an organism's flesh to be removed within days, simply due to decay (Glassic et al, 2023). The rate and amount of decay is generally controlled by three factors. The first is the oxygen supply. Bacterial decay is most productive in oxygen rich environments where they can break down the organic carbon, within the carcass, aerobically according to the following reaction (Dash and Das, 2020):

$CH_2O + O_2 \rightarrow CO_2 + H_2O$

The second factor influencing decay are environmental factors, the key controls being temperature and pH (Campobasso et al, 2001). Bacterial decay is promoted by higher temperatures and a neutral pH as these conditions favour microbial respiration. Bacterial action is slowed by cooler temperatures and conditions of unusual pH.

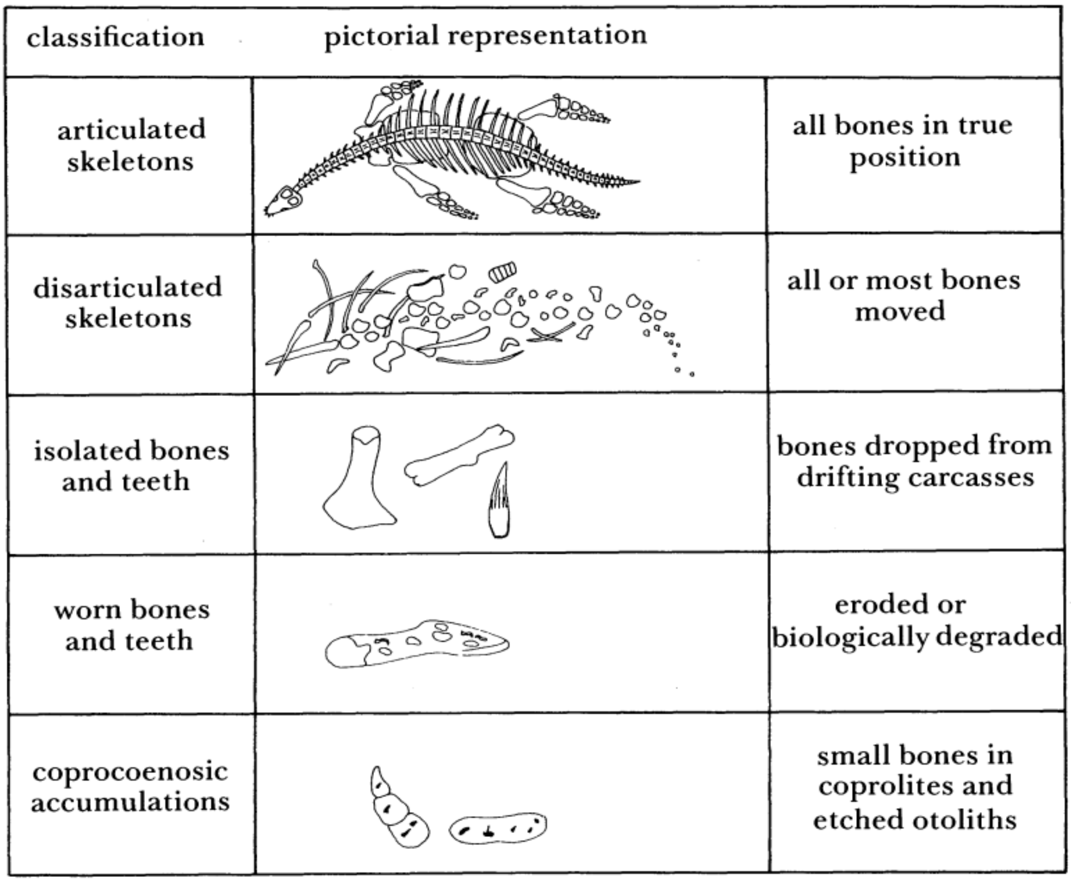
Thirdly, decay is dependent on the nature of the organic carbon the microbes are breaking down. Organic carbon can vary from highly labile (likely to decay early) to highly decay resistant (DeBruyn et al, 2025). Unfortunately, it is commonly the soft-tissues of organisms that are made up of more volatile organic carbon; this means that the usual end result of scavenging and the decay process is the organism's carcass being stripped of all of its soft tissue.

The breakdown of carcasses in aquatic settings depends on the availability of an energy source for the decay microbes. Anoxia is not a significant decay inhibitor, although it plays an important role in the promotion of the preservation of soft-bodied fossils by limiting scavenging and the turnover of sediment by bioturbators (Briggs, 2003). However, the exceptional preservation of soft tissues by this process requires elevated rather than restricted microbial activity (Sagemann et al, 1999).

Fragmentation and transport

The hard parts of an organism may simply be buried after they have decayed. However, more likely, they will be transported and broken up. Brenchley and Harper (1998) explain that the breakage of an organism's hard parts can be either; chemical (through processes like corrosion and dissolution) or physical (via disarticulation and fragmentation). This section will cover both.

Physical disarticulation is common in complicated skeletons made up of multiple parts. Disarticulation is more likely to occur after the decay or damaging of the connective tissues holding the bones together (Lyman, 1994). This can occur quickly by violent predation/scavenging of the



classification	pictorial representation	
articulated skeletons		all bones in true position
disarticulated skeletons		all or most bones moved
isolated bones and teeth		bones dropped from drifting carcasses
worn bones and teeth		eroded or biologically degraded
coprocoenosic accumulations		small bones in coprolites and etched otoliths

Figure 1.2: Table from Martill (1985) displaying the variations in preservation and amount of disarticulation in vertebrate remains. Shroat-Lewis et al (2012) provides an excellent grading scale for degree of disarticulation, ranking specimens from 0 to 6, least to most disarticulated.

organism, or if the organisms' connective tissues are already weak or prone to rapid decay. It could occur more slowly if the levels of scavenging are low and the organism's connective issues are resistant to aerobic decay. Anaerobic decay is commonly slower that aerobic decay (Tolunay et al, 2024).

Bones can fragment by breaking up along planes of weakness, usually caused by predation. Many predators break the bones of their prey when feeding and scavengers do the same to access more of the carcass's meat (Lyman, 1994). Fragmentation may also occur during transport of the bones/skeleton. Higher energy systems may cause bones to crash into rocks and break; continued wave action can cause thorough fragmentation over longer periods of time where bones and shells are ground down into a fine-grained sand (Benton and Harper, 2020).

Bioerosion is a common chemical process in carbonate environments where boring organisms bore into the calcite shells or skeletons of their hosts (El-Hedeny, 2007). They do this via dissolution of the calcareous material. Moreover, calcareous bones and shells are made up of carbonate; which is very liable to dissolution and corrosion in even the slightest acidic conditions (Guiney and Mucci, 2024). Bone materials more resistant to chemical disarticulation are those made from apatite (phosphate) or silicate, both of which are relatively unreactive.

Post-burial processes

Burial, modification and diagenesis

After an organism dies, it is prone to decay, scavenging and fragmentation/breakage. During and after burial, the carcass will be exposed to physical and chemical changes. As sediment is deposited on top of an organisms remains and it gets buried deeper and deeper, the first and most common physical change may occur. Flattening of fossil material, by the overlying sediment weight, often results in the specimen becoming compressed, to varying extents, in the plane of sedimentary bedding. Flattening can occur soon after burial, or long after depending on the sedimentation rate and type of sediment being deposited atop the specimen (Weigelt, 1989). The amount of flattening the remains undergo is largely dependent on the strength and composition of the specimen. For example, a thin skeleton with a cavity inside would be prone to collapse after burial. Whereas, larger forces would be required to collapse or fracture more rigid bones.

Diagenesis is the modification of sediments after burial. It can happen almost immediately after burial has occurred or thousands of years later due to chemically enriched solutions running through the rock or metamorphic processes directly altering the rock millions of years later. Early diagenesis however is a key factor amongst the complex processes leading to soft-part preservation (Allison, 1988). The most common diagenetic processes altering fossil material is the conversion of aragonite (in shells and skeletons of many shallow marine organisms) to calcite (Hashim and Kaczmarek, 2021). If an aragonite shell is all that remains of an organism, after it is buried, it may be surrounded by pore fluids poorly saturated in calcium carbonate. This would result in the aragonite shell dissolving completely leaving an open void in the sediment, a mould. Later on, pore fluids rich in calcium carbonate may flow through the void, allowing calcite to precipitate and fill the mould. This would, theoretically, produce an almost perfect replica of the original shell. It would create a cast.

In the upper to surface layers of finer muddy sediments, there is a zonation of chemical reactions promoted by bacterial activity (Figure 1.3). In the layer nearest the surface, the muddy sediment is oxygenated continuously through diffusion from the water above. The organic material is oxidised (it decays), mediated by bacteria. In the lower layers of sediment, microbes favour manganese oxides, nitrates, iron compounds and sulphates over oxygen for the reduction of organic matter (Brenchley and Harper, 1998). These suboxic zones are generally quite thin, and are important locations for the growth of phosphate and glauconite mineralization. It is the sulphate reduction zone in particular that plays an important role in the fossilization of organic matter through the growth of pyrite and chert. Within the sulphate reduction zone, soluble sulphide produces acidic, poorly saturated pore waters that favour the dissolution of shell material (Yin et al, 2021). When the sulphates are diminished (via reactions with iron) the resulting high alkalinity would then favour the precipitation of carbonate, forming a new cast of the shell. The availability of iron is a large factor in the preservation of shells. In sediments where iron content is low, acidity develops in the absence of iron reduction. Alkalinity and preservation of shells is favoured in sediments more enriched in iron.

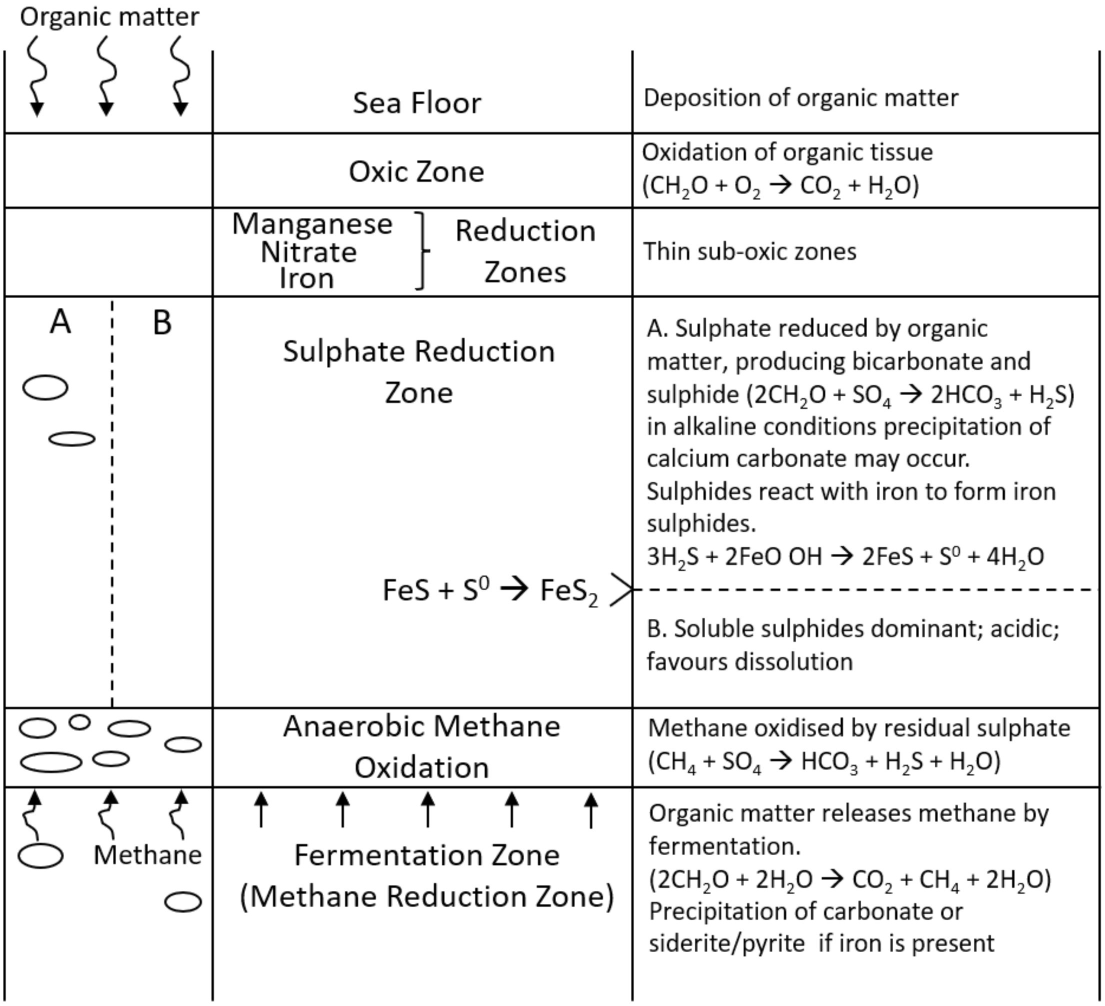


Figure 1.3: Table from Brenchley and Harper (1998), updated for enhanced visuals, displaying the diagenetic zones in near-surface layers or marine muds, highlighting the favoured locations for pyrite formation. Sulphate reduction is explained in chapter three of Sedimentary Petrology by Stuart Jones and Maurice Tucker.

Preservation in silica

Silica can replace dissolved calcite or aragonite, it can permineralise wood or pervasively fill burrows and trace fossils (Schubert et al, 1997). Permineralization is the process by which internal casts are formed within organisms by minerals carried by water (Mani, 1996). Internal shell structure would be destroyed during silicification, and some details of surface morphology can be distorted or lost. Silica deposition depends on a large enough silica supply and acidic conditions suitable for deposition within the diagenetic environment. Biogenic sources of silica are most common, this may explain why most silicification occurs during early burial. Precipitation of silica occurs in the sulphate reduction zone (Birnbaum et al, 1989). Environments that favour silicification are shallow-water marine basins and lacustrine settings, where evaporites may result in an increase in the pH, mobilizing the silica (Brenchley and Harper, 1998). It can also occur in highly acidic conditions like peat bogs.

Preservation in phosphate

Many cases of exceptional preservation display fossils preserved in phosphate. The replacement of the organic tissue may occur so early on that the original fine detail is preserved in the replacement. Phosphatization occurs through the replacement of organic matter by apatite. The phosphorous required for the process is found in two sources: (1) from the breakdown of organic matter during bacterial sulphate reduction and (2) from absorption sites on ferric oxyhydroxide, during iron reduction, where phosphate can be released (Strang et al., 2016). There may also be some detrital sources of phosphate. In the case of apatite, experiments on shrimps have shown that the decay of the organism itself may provide sufficient amounts of phosphorous to mineralize small areas of muscle (Briggs and Kear, 1993 and Hof and Briggs, 1997). However, a more substantial source of phosphorous would be needed to facilitate more extensive soft part preservation (Martill, 1988). In laboratory experiments, only crustaceans (and to a very limited extent squid) gave rise to phosphatized soft-tissue in the absence of an external source of phosphorous (Briggs and Kear, 1993 and Kear et al., 1995). However, in the Solnhofen Limestone, phosphatized soft-tissues were widely distributed; where they do occur in fish fossils (26% of 711 fish samples according to Wilby (1993)). Most of the soft-tissues in the Solnhofen Limestone retain subcellular details which may reflect a supersaturated source of phosphorous (Wilby, 1993). The phosphorous appears to have diffused from the sediment into the carcasses; as was evidenced by the depleted levels of sedimentary phosphate adjacent to some of the Solnhofen fossils compared to the background level (Briggs, 2003).

Preservation in pyrite

Most pyritized fossils are located within mudrocks due to their formation requiring organic carbon, iron and sulphate. These ingredients are commonly available in marine muds, however one or more is often deficient in other marine environments. For example, limestones often lack sedimentary pyrite as they are commonly depleted in iron. Pyritization occurs in sediments rich in sulphides mostly within the sulphate reduction zone. At that depth, H_2S (generated by bacterial sulphate reduction) combines with the reactive iron (Farrell, 2014). In well oxygenated muds, pyrite is sparse as the organic matter is often destroyed by oxidation (Brenchley and Harper, 1998). Pyrite more commonly forms in anaerobic bacterial environments within sediments or in sediments where the above water bodies are low in dissolved oxygen (anoxic or near-anoxic conditions) so sulphur reducing bacteria (SRB) can flourish. In addition to oxygen levels, sedimentation rate also has an impact on pyritization. If the sedimentation rate is low, organic matter is usually destroyed before it reaches the sulphate reduction zone (via scavenging or decay). If sedimentation rates are too high, organic matter may be buried too quickly so it is not in the sulphate reduction zone for long enough to generate any pyritization (Brenchley and Harper, 1998).

Early-formed-pyrite is often framboidal, as is the case within the Marl Slate (Hirst and Dunham, 1963). The pyrite in the Marl Slate is agreed to have formed very early diagenetically (Love, 1962), likely under the influence of SRB. It is also known that the Marl Slate was likely deposited under slow sedimentation rates (Hirst and Dunham, 1963), meaning the water conditions were relatively anoxic as the fish fossils show very little signs of thorough decay or scavenging.

Osés et al (2016) found that framboidal pyrite was the dominant microfabric making up fossil insects of the Cretaceous Crato Member in Brazil. They considered that biofilms of SRB had a central role in the decay and mineralization of the insect carcasses. Elemental analysis revealed that the iron was more concentrated in their fossils than in the rock matrix. Osés et al (2016) proposed that, during early diagenesis, SRB reduced sulphate (SO_4^{2-}) to hydrogen (H_2S) sulphide and ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}). This led to a reaction forming pyrite, which in turn mineralized the insect's exoskeletons. Moreover, the diffusion of pore water solutions into and through the insect carcasses may have also provided ions for SRB; which in turn infested the insects, mediating the precipitation of minerals (mainly framboidal pyrite), which covered the internal soft-tissues of the insects. This means that different soft-tissues have variable preservational potentials and that the fossilisation processes varied between carcasses.

Exceptional Preservation

Exceptional preservation is defined by the preservation of soft to lightly sclerotized organic tissues (Saleh et al, 2019) and requires a few key conditions; minimal/no pre-burial alteration of the specimen (whether that be decay, scavenging or fragmentation), as well as rapid burial to begin replacement of the soft-tissues early on (Varejão et al, 2025). The latter is required as the only process that can halt decay is mineralization. Early mineralization of soft tissues is most often achieved in carbonates, phosphates and pyrites (Figure 1.4). Each has more specific requirements in order to ensue. As mentioned previously, diagenesis is the overlying term for modifying processes that occur after burial. Early diagenetic pyritization is favoured by rapid burial, low organic content and the presence of sulphates in the deposited sediment (Benton and Harper, 2020). Whereas, early diagenetic phosphatization requires a lower rate of sedimentation (for slower burial) and higher organic content (Muscente et al, 2015). Carbonate preservation however, is more likely to occur when both the sedimentation rate and organic contents are high. Detailed preservation of soft-tissue

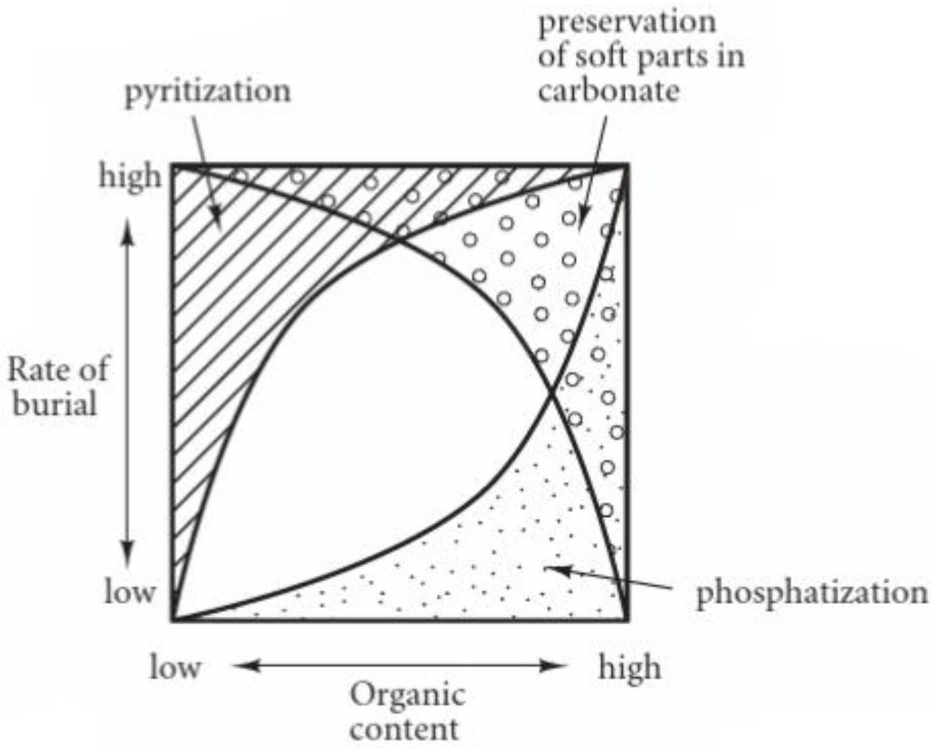


Figure 1.4: Chart from Benton and Harper (2020) displaying the conditions required for exceptional preservation of soft-tissue in pyrite, phosphate or carbonate.

in phosphate is rare; mineralization would have to occur extremely early, likely shortly after the organism's death. However, while still being a rare occurrence, the most common method of soft-tissue preservation occurs with the formation of mineral coats over the organic material, by either phosphate, pyrite or carbonate. These mineral coats are usually produced by bacterial action, perhaps as a biofilm covering the organic matter.

Exceptional preservation is usually resulted from conservation processes; where organisms are fossilised in ways that avoid decay, scavenging and diagenetic modification (Clements and Gabbott, 2022). For example, sedimentation could be so rapid that organisms are buried near-instantaneously. This could occur during a mudflow/landslip or on a delta front; anywhere where the deposition of fine enough sediment is particularly rapid. There are unusual conditions resulting in exceptional preservation as well. Entrapment in a particularly good preservative medium, like amber, are known to preserve a whole host of organisms; from frogs and lizards to insects and bacteria. However, there are very few geologic settings where the amber from resin-producing trees was recruited to the sedimentary record (Palmer, 2016). It is also agreed that certain clays enhance preservation of soft-tissues; Naimark et al (2018) proposes that kaolinite and chlorite enhance the preservation of Cambrian lagerstätten, with kaolinite being the more effective of the two.

Some sedimentary regimes may provide conditions resulting in a lack of predators, this would increase the chances of exceptional preservation as scavenging will be drastically reduced. These could be anoxic water columns in lakes or shallow seas, often called stagnation deposits. They often occur when bottom waters become stagnated and anoxic due to a lack of water circulation. Preservation in these environments depends on how much bacterial decay is actually inhibited. If favourable diagenetic conditions develop preservation will be aided, if the organisms are not disarticulated or modified drastically before burial by scavenging or decay. It is more common that pelagic organisms are preserved in these kinds of environments (Brenchley and Harper, 1998), however, it has been known that benthic fauna also get preserved in similar conditions where the bottom waters become are anoxic. It is likely that the Marl Slate represents one such deposit. The Solnhofen Limestone is another, and is famous for its preservation of *Archaeopteryx* as well as a majority of pelagic fauna and washed-in benthic animals. Under these conditions bioturbation would be rare, as the numbers of predators and scavengers would be reduced.

A good example of exceptional preservation would be the Chengjiang biota of Yunnan, China. The fossils are preserved in pyrite within a clay-rich host sediment containing pyrite of a framboidal habit, notably similar to the Marl Slate. Gabbott et al (2004) provides a detailed model explaining the two taphonomic pathways involved in the exceptional preservation as well as details of the decay process involving sulphur reducing bacteria. While framboidal pyrite is recognised in the Marl Slate, Hirst and Dunham (1963) state that the Marl Slate pyrite is closely and obviously associated with the bitumen also present within the Marl. Gabbott states that the clay-rich sediment of the Chengjiang deposit is depleted in organic carbon, a defining difference between the two. However, the defining difference is the oxygen content of the two deposits. The Chengjiang biota inhabited an oxygen-rich deltaic environment that was dominated by storm floods, unstable salinity and a high sedimentation rate. The Marl Slate was deposited in a lower energy, anoxic environment with seasonal, slower sedimentation resulting in varve-like bedding. This is a drastically different setting yet anoxia is often considered to be a factor in exceptional preservation, making the Marl Slate of suitable interest.

A large issue with exceptional preservation, however, is that it often requires specific and unique conditions that rarely occur. This can lead to modes of preservation that are "anactualistic", meaning they are restricted in time and can no longer occur exactly how they are shown in the fossil record (Gaines and Droser, 2025). Examples of biotas displaying an anactualistic mode of preservation are

Ediacara-type and Burgess Shale-type preservation, both no longer occurring in marine environments.

Anoxia

Anoxia is the term used to describe a severe lack of oxygen. Anoxia is commonly associated with marine environments either with poor circulation or deep basins where oxygen cannot reach the lower sections of the water column. Demaison and Moore (1980) proposed four states categorising modern aquatic anoxic settings. The first is large anoxic lakes where permanent stratification promotes development of anoxic bottom waters. This occurs more so in large, deep lakes that are not subject to seasonal overturn such as Lake Tanganyika in eastern Africa. The second setting is anoxic silled basins; landlocked silled basins with a positive water balance tend to become anoxic as water circulation is limited or cut off. Examples would be the Baltic and Black Seas. Setting three is anoxic layers, caused by upwelling, that develop only when the oxygen supply in deep water cannot match the demand by decaying organisms (for example, the Peru coastal upwelling). The final setting is anoxic layers in open oceans. They are found at intermediate depths due to distance from deep, oxygenated polar water sources like the northeastern Pacific and northern Indian Oceans.

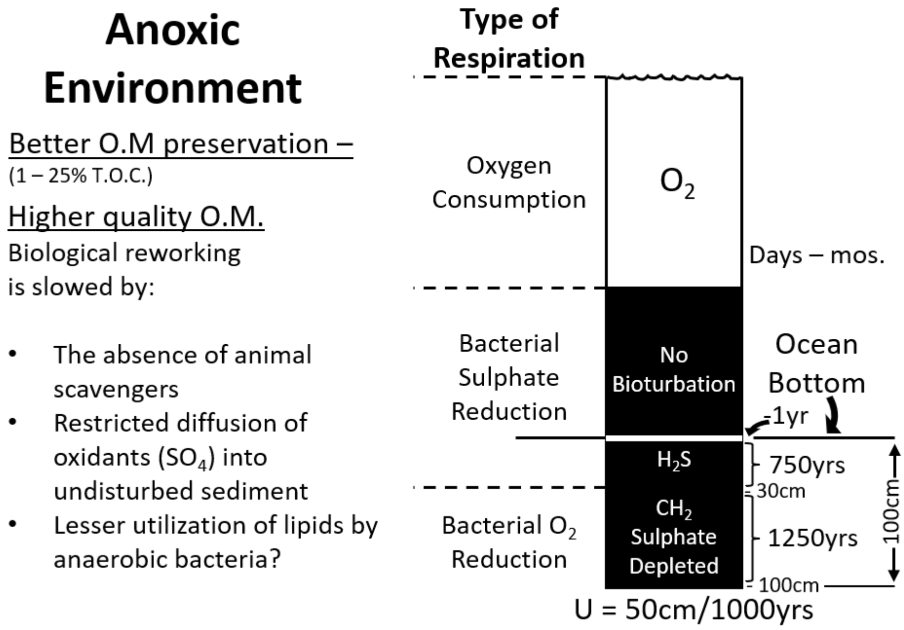


Figure 1.5: Diagram by Demaison and Moore (1980), updated for enhanced visuals, displaying a stratified water column with anoxic bottom waters with similarities to figure 1.3.

Anoxia is a key factor in exceptional preservation. If an environment has little or no oxygen, larger organisms will not survive; this will have a drastic reduction in predation and scavenging. Moreover, anoxia limits aerobic bacterial action, so the majority of aerobic bacterial decay of organic matter will cease, leaving only anaerobic bacteria (like SRB) to induce decay. However, the presence of anoxia does not significantly inhibit decay (Allison, 1988). There is a pronounced effect on benthic life at oxygen concentrations between 0.7 ml/L^{-1} and 0.3ml/L^{-1} (Demaison and Moore, 1980). Below those concentrations, deposit feeders become rare, less active and primarily soft-bodied. Eventually bioturbation will cease all together. Byers (1977) stated that oxygen concentrations of below 0.1 ml/L^{-1} kill almost all benthic organisms as well as suspension-feeders, and that anaerobic bacteria are the only organisms breaking down the organic matter. However, there is a Goldilocks zone between

0.4 ml/L^{-1} and 0.2 ml/L^{-1} where bioturbation is restricted, but the development of nektobenthic communities is not hindered. This is the probable depositional setting for the Sirius Passet Lagerstätte, where an anoxic water column developed over the depositional site, possibly in association with sea level change (Hammarlund et al., 2018). This Goldilocks zone may provide the perfect conditions for soft-tissue preservation. Oxygen levels would be low enough to decrease predation and scavenging, as well as decay by aerobic bacteria, providing the dead organisms time to be buried without pre-burial alteration/modification.

A note on Burgess Shale-type Preservation

BST preservation is the term commonly attributed to the fossilisation method of exceptionally preserved early animals. While a multitude of animals were preserved in the Burgess Shale, the most unique examples are soft-bodied organisms **(11)**. These animals lacked hard-tissue (skeletons or shells) and required exceptional conditions for preservation (Anderson et al, 2023). For example, the studies surrounding the Chengjiang deposit in China, by Gaines et al (2012), revealed that favourable sedimentary circumstances acted to restrict the flow of oxidants into the early burial environment, oxidant restriction was promoted by rapid entombment of soft-bodied organisms in the sediment, followed by early cementation at the sediment-water interface. The Burgess Shale has been intensively studied, resulting in the conclusion that five major factors contributed to its exceptional preservation:

1. A limited oxidant supply, both oxygen and sulphate.
2. Sediment that minimises porosity/permeability (e.g., clay) and provides an antibacterial burial environment.
3. Authigenic mineralisation that replaces the soft-tissues in geologically long-lived minerals, such as Al and Fe rich clays as well as pyrite and phosphate.
4. Polymerisation that enhances the decay resistance of organic remains.
5. Early cementation (e.g., from organic carbonate) that formed sedimentary seals stopping the diffusion of oxidants into the carcass (Gaines, 2014).

The clay minerals present, during BST preservation, are a key component of the sediment composition and authigenic mineralisation. They are key players in soft-tissue preservation on a wider scale (Anderson et al, 2011). Past experiments have proven that organisms undergo significantly less decay when clay minerals are present; specifically, the Al and Fe enriched clays kaolinite and berthierine, which have been previously shown to have antibacterial properties (McMahon et al, 2016). The probability of well-preserved fossils being present in mudstones is likely to increase when clays of any kind are present in the sediment. Clays may impact BST preservation either through being a part of the pervasive host sediment (Butterfield, 1990) or through direct chemical interactions between clay and organic material. When kaolinite and berthierine are present in the host sediment, they interfere with microbial decay, hence acting as decay inhibitors (Anderson et al, 2018). This is likely due to their constituent Al^{3+} and Fe^{2+}, although, the precise mechanisms by which they interfere with microbial activity remain to be determined (Anderson et al, 2023). Experiments by McMahon et al (2016) proved that both berthierine and kaolinite inhibit the growth of heterotrophic bacteria involved in decay of marine organisms in the modern-day (for example, *Pseodoalteromonas*). Limiting the growth of decay bacteria will, in turn, inhibit decay (Anderson et al, 2021). This provides a clear link between clay mineralogy and potential exceptional preservation of marine fossils. The role of clay in preservational potential, in relation to the Marl Slate, is explored further in this study. Petrovich (2001) concludes that illite coatings aided in the preservation of BST fossils. As illite is also present in the Marl Slate, it may have played a similar role.

Errors in the Fossil Record

The fossil record is largely incomplete, and there is significant taphonomic bias towards certain modes of preservation and depositional environments that preserve fossils better than others (Nanglu and Cullen, 2023). There is also a large biological bias towards organisms with harder, biomineralized body parts as softer tissue is much harder to preserve. There are numerous geological and biological explanations as to why there are large gaps within the fossil record. Raup (1972) explains the factors, that make the fossil record incomplete, in the form of filters:

1. *Anatomic Filters*: organisms are only likely to be preserved if they have hard parts. Skeletons of any sort are easier to preserve than entirely soft bodied organisms.
2. *Biological filters*: organism behaviour and population size are a dominating factor. The more of an organism there is, the higher the chance of preservation. Organisms with shorter life spans die more than longer living organisms, so are more likely to be preserved.
3. *Ecological factors*: the location of an organism's habitat may influence its preservation. Marine organisms or river dwelling creatures are more likely to be buried by sediment than birds or land mammals, so have a higher chance at being preserved in the fossil record.
4. *Sedimentary filters*: different depositional environments aid preservation. Lower energy environments where finer grained sediment is deposited (such as lagoons or lakes) have a much higher chance at preserving organisms living there than higher energy erosional environments (such as mountainsides or beaches).
5. *Preservation filters*: post-burial factors influence preservation. Chemical conditions must be precise, and the sediment must be relatively still. It cannot be constantly reworked as the carcass will break up.
6. *Diagenetic filters*: deposited rocks are influenced millions of years later by diagenetic processes. Mineralizing waters may percolate through, this could enhance fossil preservation by replacement, or could dissolve the fossil material.
7. *Metamorphic filters*: tectonic factors may influence the quality of a preserved fossil. Fossiliferous rock may be subject to contact or regional metamorphism which alters the very make-up of the rock. It is very rare that fossils survive this prominent alteration caused by metamorphism.
8. *Vertical movement filters*: the vast majority of fossils are located within sedimentary rocks that have been buried. By definition, burial requires the older rock to move to an increased depths to accommodate the younger rock above. Tectonic processes will subsequently have to bring the fossiliferous rock back up to the surface where it can be discovered. That is if the very same processed so not damage the fossils themselves.
9. *Human filters*: in order to be discovered and identified, the fossil must be seen and collected by a human being. Fossils may be washed away from view, eroded or simply discarded back into their environment. A found fossil must be registered in a museum before it becomes part of the collective paleontological record. Many fossils that are found are left in home displays.

Bias in the fossil record is amplified by the distribution of fossils, throughout the geological record, not being random. The distribution of fossils appears more random and less well preserved the older the rock is (Foote and Raup, 1996). This is due to it being subject to the above factors for longer periods of time. The fossil record will get filtered and filtered until the fossil remains discovered are negligible. Areas throughout geological time are not represented equally by the fossil record. Some intervals in time may be represented by thick successions of fossiliferous sedimentary rock, and so, are well documented (Nanglu and Cullen, 2023). This proves there is a strong link between the fossil record and the rock record.

The Marl Slate Specifically

The Marl Slate could be considered an example of exceptional preservation if lagerstätten bias is ignored (Flannery Sutherland et al, 2019); however, the exact mode of preservation is largely unknown. The rock itself is made up of laminated silty, dolomitic mudstones and sapropels that were most likely deposited in a low energy, anoxic marine environment (Hirst and Dunham, 1963). Deposition of the Marl Slate likely took place in a barren basin with stagnant waters, inducing the anoxic conditions that dominated the bottom waters. The organic rich, sapropelic layers are defined by their higher pyrite content and strongly negative $\delta^{18}O$ values in associated dolomites. There is no evidence that the $\delta^{18}O$ values were modified by later diagenesis (Turner and Magaritz, 1986). The association of sapropels and carbonates with low $\delta^{18}O$ values and fresh water influx is well known. The influx of fresh water induces the formation of a stratified water column, promoting more anoxic conditions in the bottom waters (Figure 1.5). Oszczepalski (1986) stated that the bottom anoxic conditions of the Zechstein Copper Shale, in Poland, had an oxygen concentration of below 0.1 ml L^{-1}. This could not be correlated with the Marl Slate as there is an abundance of nektobenthic fauna fossilised within the Marl Slate; predominantly bivalves, gastropods and fish. This implies that the oxygen concentrations of the Marl Slate were not completely anoxic; more sub-anoxic, likely ranging from 0.4 ml/L^{-1} and 0.2 ml/L^{-1} within that Goldilocks zone. This would explain the abundance of nektobenthic fauna present in the rock.

The depositional environment of the Marl Slate likely corresponds to the second anoxic setting proposed by Demaison and Moore (1980); landlocked anoxic silled basins. It is possible that the Marl Slate was deposited within a stagnating standing body of water, that was overwhelmed by the Zechstein transgression. If there was a significant amount of freshwater influx, then that stagnating water column would have become stratified, with the runoff bringing in huge amounts of nutrients. This would have generated the highly organic sapropelic layers seen within the Marl Slate. In the Holocene sediment record, several silled basins (namely the Baltic Sea and Black Sea) have deposited a layer enriched in organic carbon, often termed sapropel (Degens and Stoffers, 1980). This layer marks the change in depositional environment and biological production coincident with the post-glacial transgression (Emeis, 2009). The Marl Slate mode of deposition is analogous to conditions in the modern-day Black Sea; a stratified water column with relative anoxia causing the production of sapropel units rich in organic carbon (Arthur and Dean, 2010). Magaritz et al (1981) did record an increase in carbon content from the usual 0-2% to 3.5-4.5% at the base of the Zechstein which would explain the deposition of sapropelic layers enriched in carbon.

Key Points

Taphonomy is a complicated process with many factors influencing the overall preservation of an organism. Pre-burial processes break up, disarticulate and break down the organism’s soft tissues if they are not rapidly halted either by environmental factors or sudden burial (Lyman, 1994). Post-burial processes modify what remains of an organism; this may be flattening or modification of the organism’s mineralogy (Martill, 1985). After burial, preservation can occur in three materials: silica, replacing dissolved carbonates; phosphate, replacing softer tissues immediately after burial with apatite; or pyrite, preserving material in pyrite within sediments rich in iron and sulphates, usually at the sulphate reduction zone (Irwin et al, 1977). Several factors need to be present in order to achieve exceptional preservation. Rapid burial is essential as it prevents fragmentation and disarticulation of the carcass by scavenging and predation (Muscente et al, 2015). Anoxia drastically aids exceptional preservation as it limits bioturbation (Allison, 1988); reducing scavenging/predation as well as aerobic decay. However, if levels of anoxia become too high (oxygen concentrations of <0.1 ml L^{-1}) larger organisms will not be preserved as they likely will not inhabit that environment (Theede et al, 1969). There is a likely Goldilocks zone with oxygen concentrations of around 0.3 ml L^{-1} where bioturbation is limited, but benthic and some nektonic fauna still thrive, allowing for their preservation with limited decay or scavenging. Clays have also been shown to aid preservation (Naimark et al, 2018), kaolinite and berthierine specifically are antibacterial, likely due to their high iron content (Saleh et al (2019), limiting rates of decay within the host sediment. Despite this, there is still significant bias in the fossil record; mainly surrounding the type of environment an organism lives in.

This study puts forward that the Marl Slate itself represents an anoxic silled basin where the formation of a stratified water column, due to freshwater influx, increased levels of anoxia in the bottom waters. It is analogous to the modern-day Black Sea; both having generated prominent sapropelic layers (Degens and Stoffers (1980). The rock has a relatively high pyrite content (Turner and Magaritz, 1986) perhaps suggesting the fishes are preserved in pyrite, potentially induced by the action of anaerobic SRB within the sulphate reduction zone. On global scale, it can be agreed that the Marl Slate is Upper Capitanian (264Ma) in age (Swift, 1995), correlating to the initial assumption that the unit fell under the Guadalupian-Lopingian boundary in the Late Permian. What this study does not delve into however, is the wider use of the Marl Slate. As the western counterpart to the German Kupferschiefer, which is agreed to be younger than the Marl Slate (247±20Ma) according to Brauns et al (2003), it can be agreed that the Marl Slate is relatively enriched in REEs (Turner et al, 1978) that would be viable to mine if the unit was not so thin. SEM work as part of this study revealed that the Marl Slate is enriched in metal sulphides, particularly pyrite. However, the feature that puts the Marl Slate on the map is its abundance of well-preserved fossils. Fischer et al (2021) states that the equivalent Kupferschiefer acts as a stratigraphic marker horizon for the Upper Permian in Central and Northern Europe because of its outstanding fossils. It can be agreed that the Marl Slate is the continuation of this horizon in Western Europe.

Chapter 2:

Sedimentology and Stratigraphy of the Marl Slate, County Durham

Introduction to the Stratigraphy

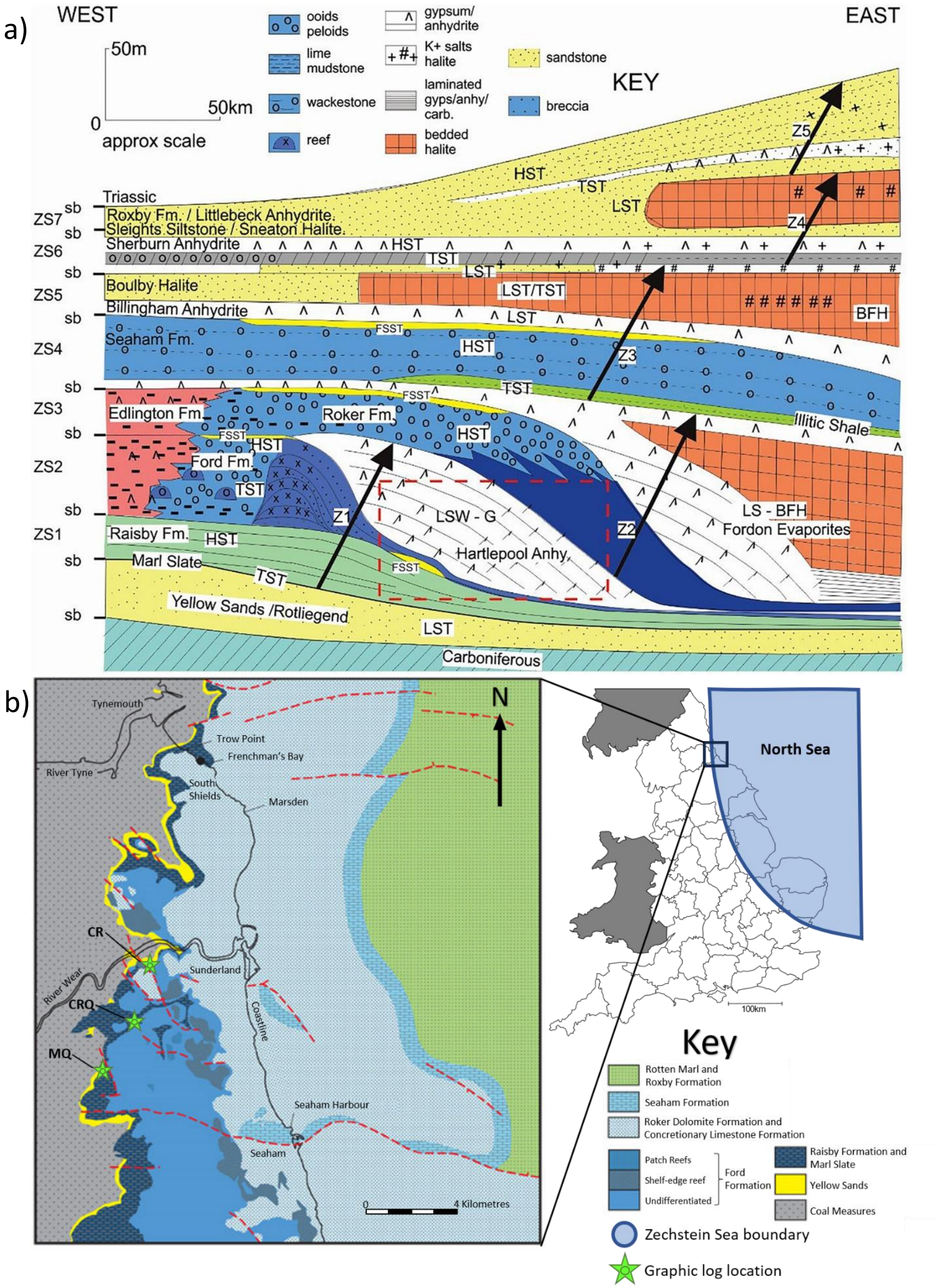


Figure 2.1: (a) Sequence stratigraphy diagram, from Daniels et al (2022), showcasing Zechstein cycles 1-7. It highlights the importance of the Marl Slate as one of the first depositions of the Z1 cycle. (b) Line map, adapted from Environment Agency: Durham Permian Sections, Figure 7 (Internal Report CR/07/115), showcasing where logs were recorded at Claxheugh Rocks (CR), Crime Rigg Quarry (CRQ) and Middridge Quarry (MQ). The logs were taken in such a way as to transect the edge of the Zechstein Basin through County Durham and Sunderland.

The exact age of the Marl Slate is up for debate. It was the first unit deposited as part of the Z1 cycle of the Zechstein transgression on the Guadalupian-Lopingian boundary within the Late Permian. Recent conodont biostratigraphy by Swift (1995) has suggested that the most appropriate age corresponding to the Marl Slate is Upper Capitanian (~264Ma), the last stage in the Guadalupian (C.M Henderson, pers comm).

While the age of the Marl Slate may be contested, its sedimentology is not. The overall section began as an aeolian environment represented by the Permian Yellow Sands. The Zechstein transgression induced shallow marine, almost lacustrine conditions incorporating the upstanding aeolian dunes (Mroczkowski and Mader, 1985). This is represented by the Marl Slate. After the complete development of the Zechstein Sea, the environment developed into a carbonate ramp represented by the Upper Magnesian Limestone divisions (Hardwood, 1986).

The Marl Slate itself is a laminated, silty dolomitic mudstone correlating to the German Kupferschiefer or "Copper Shale" (Vaughan et al, 1989). The unit shares a conformable lower boundary with the Permian Yellow Sands and, in some places, a non-conformable boundary with Carboniferous strata (usually Coal Measures) **(12)** and a more transitional upper boundary with the Raisby Formation, the lowest division of the Magnesian Limestone. The upper contact appears sharp from a distance. However, upon closer inspection, the contact is in fact transitional; the thin, extremely stratified layers of Marl Slate slowly fading into thicker blocks of Magnesian Limestone. The unit itself is thin, reaching no thicker than 2m with thin (cm thick) bands of clay running through it. The unit rarely appears at outcrop in the UK and is not present on many geological maps of northeast England due to its thinness (Figure 2.1). Where the Marl Slate does appear at outcrop, it has a tendency to taper off, disappearing between the Yellow Sands and Lower Magnesian Limestone. It is likely that the upstanding dunes of the Yellow Sands play a part in this odd depositional feature.

Field Sampling

(13) In order to glean a better understanding of the sedimentology of the Marl Slate three outcrops were visited in order to log and sample the Marl Slate as a transect through the edge of the Zechstein Basin (Figure 2.1): Middridge Quarry in Sedgefield (Figure 2.2a), Crime Rigg Quarry in Shadforth (Figure 2.2b) and Claxheugh Rocks in Sunderland (Figure 2.2c). Documentation of each individual lamination within the Marl Slate was not possible within the time frame. This was because the laminations are so thin and the surfaces of the Marl Slate at each locality were highly weathered (Figure 2.2). Middridge is a disused quarry so weathering of the quarry walls is extensive. The cliff face at Claxheugh was also significantly weathered, meaning Crime Rigg Quarry was the best chance at looking at fresh surfaces as it is an active quarry where fresh sections of Marl Slate are regularly exposed. Physical samples were taken from the upper, middle and lower sections of the Marl Slate. Due to Middridge having poorer exposure than Claxheugh and Crime Rigg, less samples were collected. Due to Crime Rigg being an active quarry, it was deemed more useful to spend longer at Claxheugh Rocks to perform detailed logging and sampling (Figure 2.4).

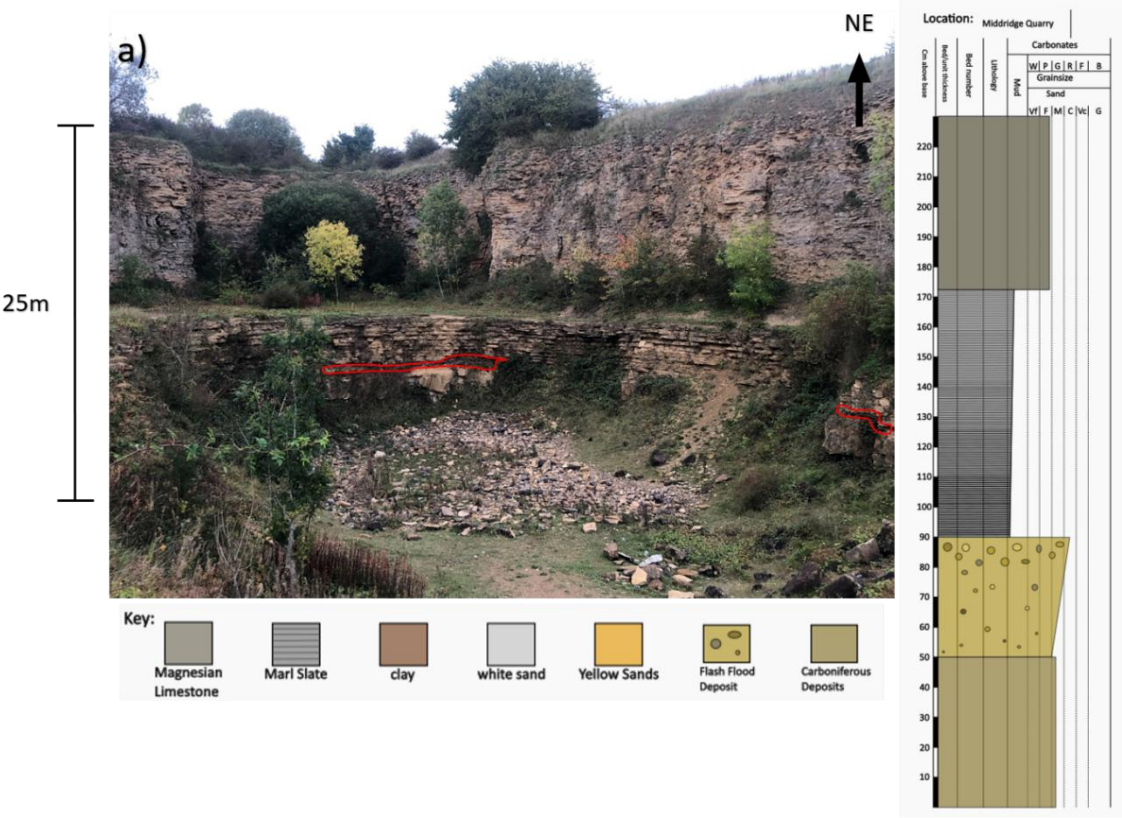
At each outcrop, the Marl Slate deposit was divided into three sections: upper Marl Slate (UMS), middle Marl Slate (MMS) and lower Marl Slate (LMS). These were then divided into compositional layers (DM1-3, indicating dolomite rich layers, and C1-6, indicating clay) **(14)**. Separate samples were taken from the dolomitic and clay bands of the log and sent off for X-ray diffraction analysis in order to gather precise measurements regarding the mineral wt% of each of these key layers (Figure 2.6). The XRD analysis was performed at X-ray Mineral Services UK using an XPert diffractometer. Preliminary data were provided using an older Philips instrument due to mechanical issues with the

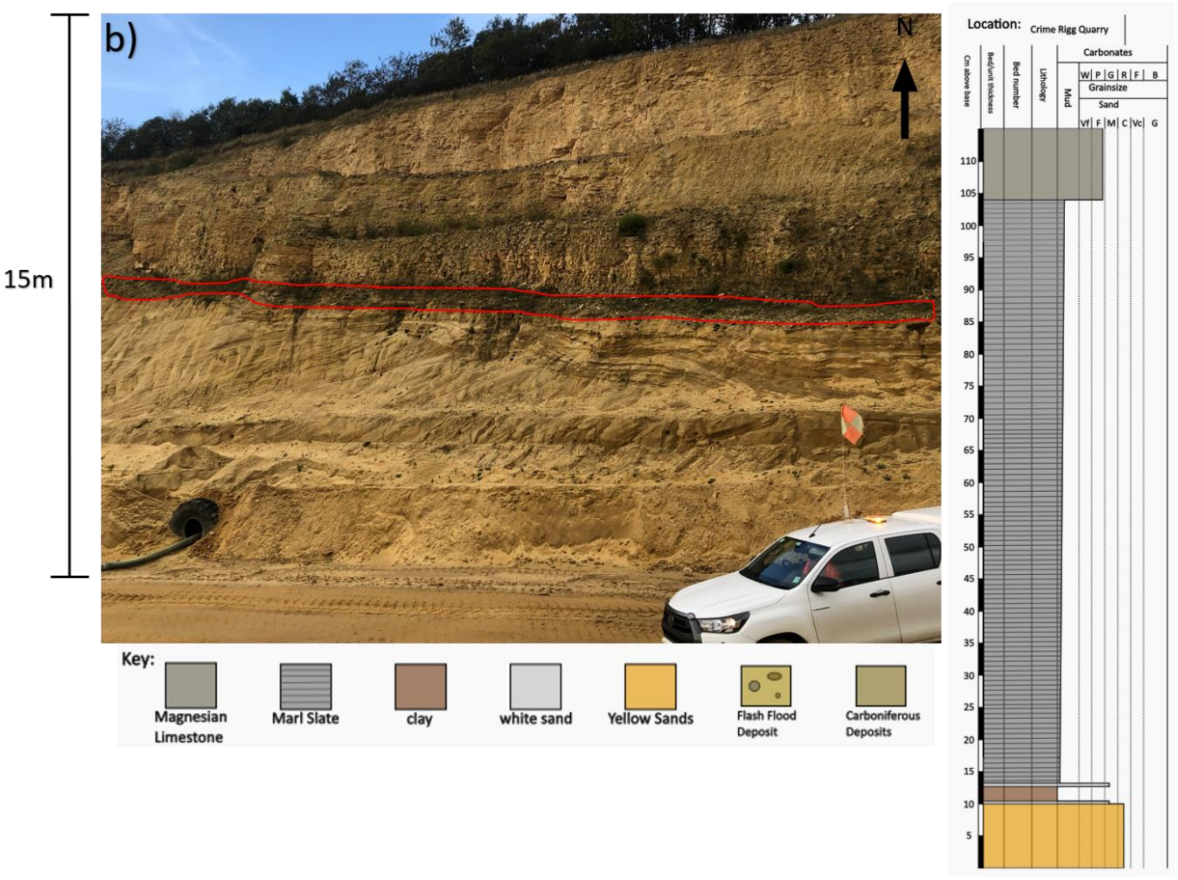
XPert diffractometer, however once it was up and running, the samples were re-run and more reliable results were provided.

Petrographic and Sedimentological Methods

(15) Analysis of rock chips and thin sections required the use of a Hitachi SU70 electron microscope; however, each required a different approach to its preparation and analysis. Sedimentary material, mounted as rock chips, was coated in 35nm of gold/palladium alloy using a Cressington Sputter Coater 108auto. This was to reduce thermal damage and improve the secondary electron signal required for topographic examination of the rock chip. Gold has a lower work function so is more efficient to coat with, it is also applied using a cooler sputter coater so there is hardly any heating of the sample surface compared to carbon coating. The thin sections were coated in carbon using a Cressington Carbon Coater, 108carbon/A. Each thin section was coated in 25nm of carbon.

For both thin sections and rock chips, the voltage was set to 15kv as standard. This is a high enough voltage for a sufficient interaction volume without degrading the spatial resolution of the image produced. The thin sections were viewed using BSEM (backscatter electron microscopy) as backscatter electrons are less influenced by charging (hence the carbon coating of thin sections rather than gold). However, they do give poorer spatial resolution than secondary electrons. Rock chips were imaged using secondary electron microscopy as secondary electrons scatter more broadly than backscatter electrons. Meaning they provide better resolution images more suited for topographic imaging of rock chips. These specific settings allowed for accurate EDS mapping and imaging of thin sections at no more than 5000x magnification, as well as detailed topographic imaging of rock chips up to 15000x magnification.





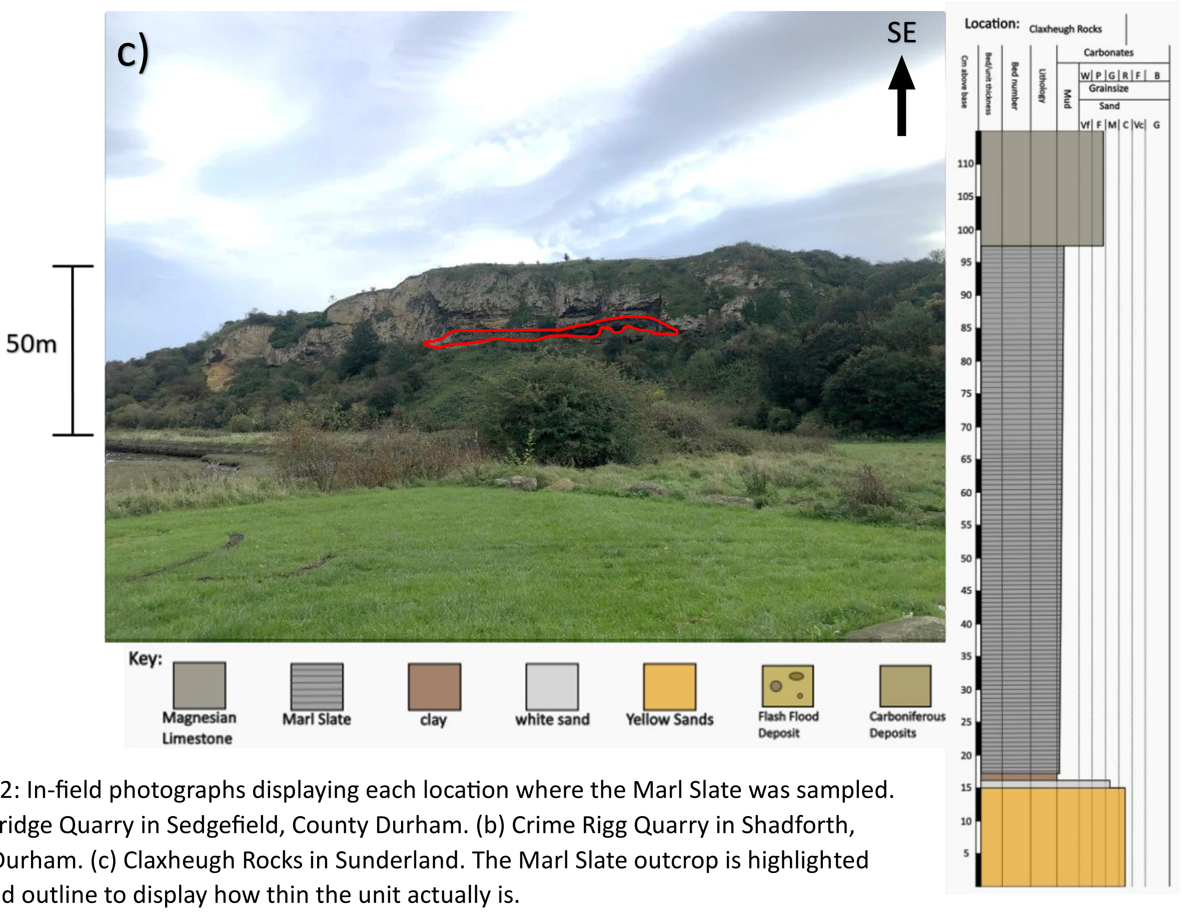


Figure 2.2: In-field photographs displaying each location where the Marl Slate was sampled. (a) Middridge Quarry in Sedgefield, County Durham. (b) Crime Rigg Quarry in Shadforth, County Durham. (c) Claxheugh Rocks in Sunderland. The Marl Slate outcrop is highlighted with a red outline to display how thin the unit actually is.

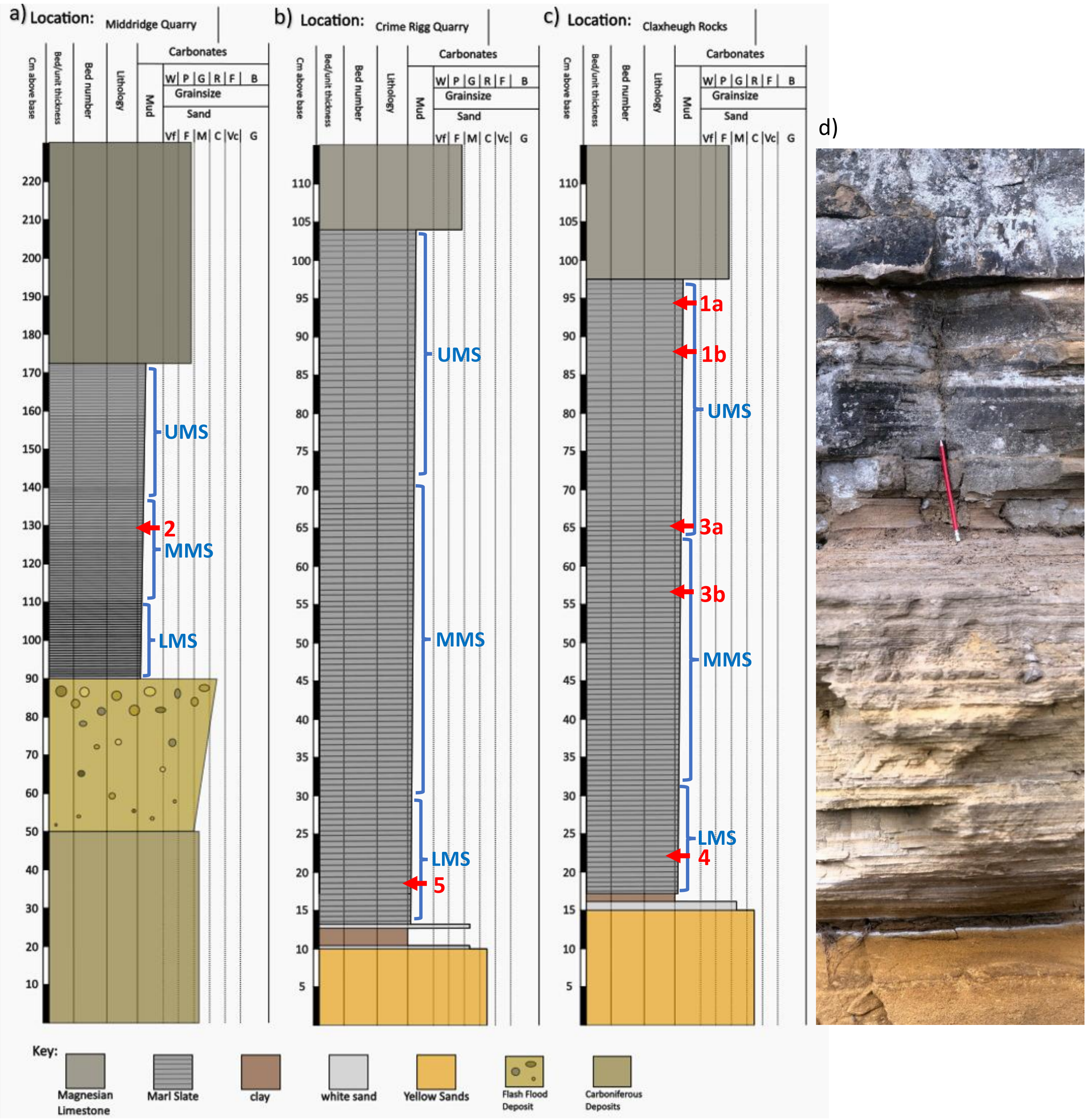


Figure 2.3: Each localities log, side-by-side, illustrating the stratigraphy and variation in Marl Slate thickness at three different localities across northeast England: (a) Middridge Quarry, Co. Durham. (b) Crime Rigg Quarry, Co. Durham. (c) Claxheugh Rocks, Sunderland. (d) In-field section at Claxheugh Rocks directly corresponding to the log taken. Red arrows display where each outcrop was sampled. Blue lines represent upper, middle and lower Marl Slate divisions.

Results

The Marl Slate was deposited as part of the initial rapid transgression of the Zechstein Sea that flooded wide areas of the Early Permian desert. One of these rapid flood deposits can be seen within the lower Marl Slate at Middridge Quarry in the form of a conglomerate (Figure 2.3a) (16). The Marl

Slate deposit varies in thickness from ~80cm at Claxheugh Rocks to 1m at Crime Rigg and Middridge. However, over much of northeast England the Marl Slate is less then 80cm thick (Smith, 1980). The Marl Slate itself can be split into three distinct subfacies first categorised by Turner and Magaritz (1986): (1) dark grey, organic rich, sapropelic siltstones that are much more abundant in the Lower Marl Slate. (2) organic-dolomite laminites more prominent in the Middle Marl Slate. (3) massive, finely crystalline dolostones that are more abundant in the Upper Marl Slate and represent the transition to the Magnesian Limestone.

(1) The Lower Marl Slate (LMS) often appears sandier, the sapropelic layers having a more yellow-beige colour likely due to reworking of the seafloor by benthic organisms like brachiopods. Demaison and Moore (1980) stated that there is little to no bioturbation in the Marl Slate; however, there was clear evidence of vertical burrows within the LMS at Claxheugh Rocks indicating that reworking of the Yellow Sands probably took place during early Marl Slate deposition. Its organic carbon content is generally between 8-10% and quartz 25-35% (Turner and Magaritz, 1986); the latter tends to occur within small lenses of silty, aluminium rich clay (Figure 2.4c). The key feature of the LMS is the high proportion of organics. The sediment here is more enriched in organic material which has led to a darker sediment colour as well as a higher abundance of fossil fish material due to the more oxygen depleted conditions required to deposit such material.

(2) The organic-dolomite laminites within the Middle Marl Slate (MMS) are grainier, still containing a large amount of siltier material as well as a higher proportion of dolomite compared to the LMS. The MMS is where the extreme lamination and stratification of the Marl Slate is much more obvious. Its organic carbon content drops to less than 6% which is paralleled by a decrease in quartz content to ~10% (Turner and Magaritz, 1986). The MMS is a lighter colour throughout than the LMS, corresponding with the lower organic carbon content, the MMS was likely deposited under less anoxic conditions than the LMS, yet still not entirely favourable for nektobenthic life.

(3) The Upper Marl Slate (UMS) does not present organic matter as discrete laminations. Instead, it is spread somewhat evenly throughout the lithotype. The crystalline dolostones are relatively homogenous and display negligible lamination while displaying a blockier appearance common among some limestones. The crystalline dolostone is also much harder, tending to release a dinging sound when struck by a hammer. While the UMS is made up of two thicker layers of crystalline dolostone separated by a band of predominantly Illite clay (Figure 2.4a), there is another apparent band of dolostone within the upper portion of the LMS showing the cyclicity of the Marl Slate on a larger scale than the laminations do.

The laminations are of key interest (Figure 2.3d). The laminae themselves are thin layers (appearing less than 0.25mm to the naked eye) of alternating dark organic, sapropelic material and lighter, less anoxic material. The Zechstein Sea must have been near stagnant to induce a slow enough sedimentation rate to preserve such fine layers. The depositional environment would have had to be extremely low energy as there are no ripples preserved either. The alternating laminations likely represent differences in oxygen levels either caused biologically or seasonally. The presence of dolomites, as well as preserved *Acentrophorus* fossils is evidence to suggest that each cycle of deposition was likely initiated by an influx of freshwater into the Zechstein basin, after the initial transgression. The influx of freshwater into a more saline basin would have promoted surface productivity of algal/phytoplanktonic blooms and induced water stratification (McNaughton et al, 2022) as well as regional anoxic conditions in the lower waters causing deposition of more sapropelic material and likely the deaths of larger organisms like fishes and brachiopods. The Key discovery is the change in organic content from the LMS through to the UMS. The abundance in the LMS and decrease towards the top of the unit implies a significant change in environmental conditions. The decrease in sedimentary organic content parallels an increase in oxygen content. As the environment becomes more oxygenated, preservation potential decreases. This is an important link between sedimentary deposition and fossil preservation and is evidenced by the decrease in fossil material from the LMS to the UMS.

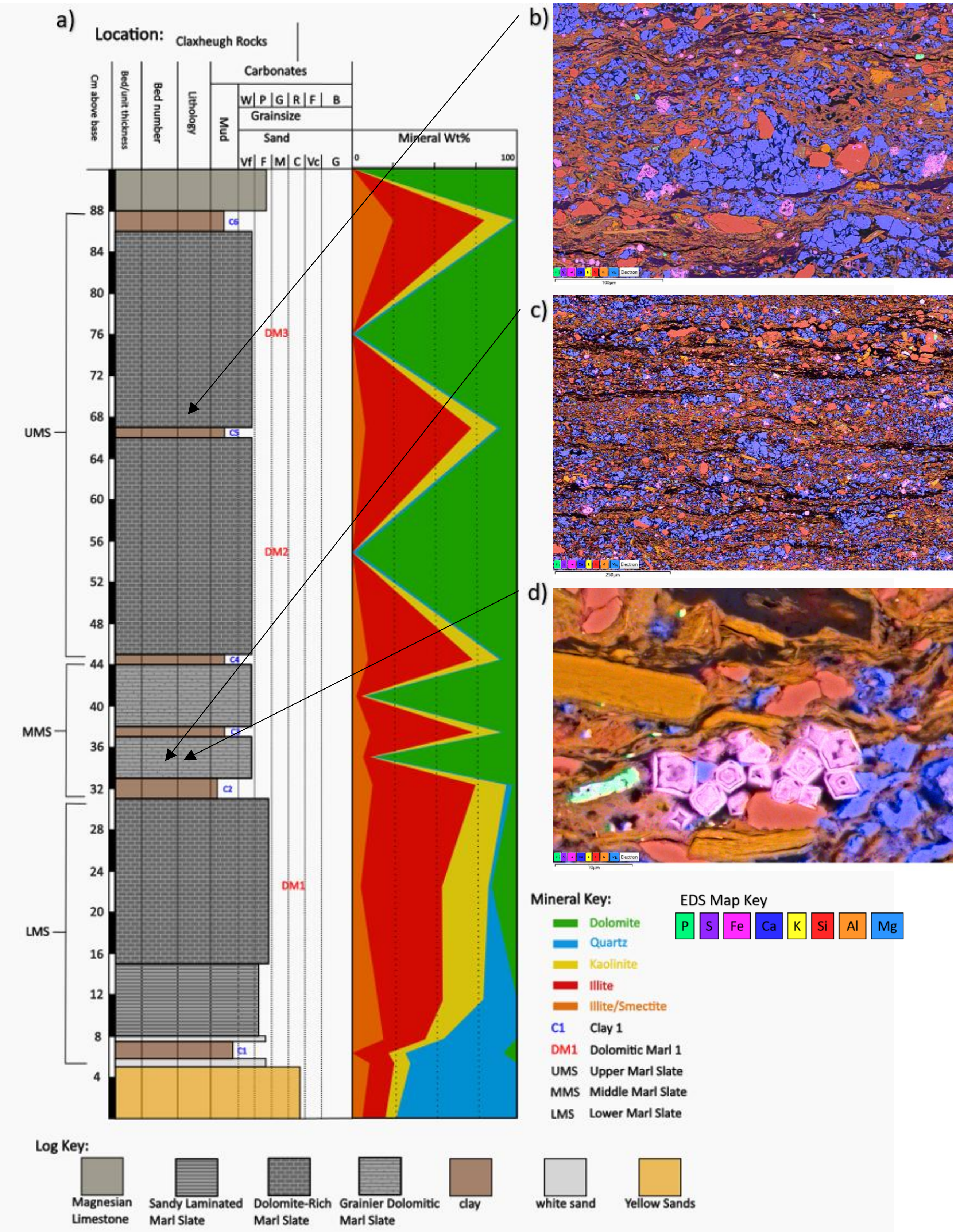


Figure 2.4: (a) A detailed graphic log through the Marl Slate at Claxheugh Rocks. Displaying the three most prominent subfacies within the Marl Slate as well as the mineral wt% throughout the section. Evidently, Illite is the most common clay, localised in and around six individual bands throughout the section labelled C1-6. The three bands of dolostone are highlighted as DM1-3. (b) Thin section EDS map showing the crystalline dolomite of the UMS. (c) Thin section EDS map displaying the organics and laminations within the MMS. (d) High magnification EDS map displaying the abundant framboidal pyrite clumps within the Marl Slate.

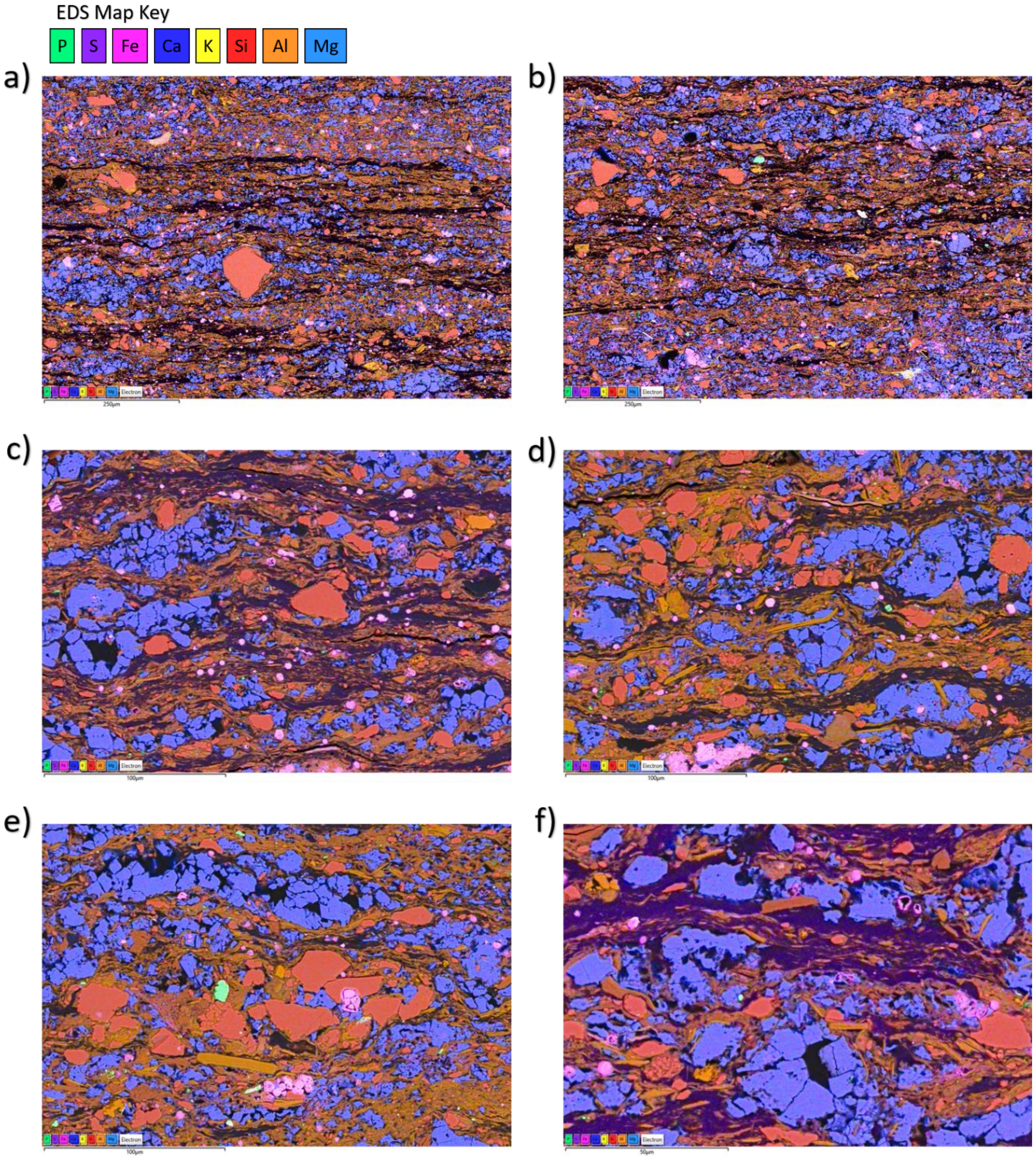
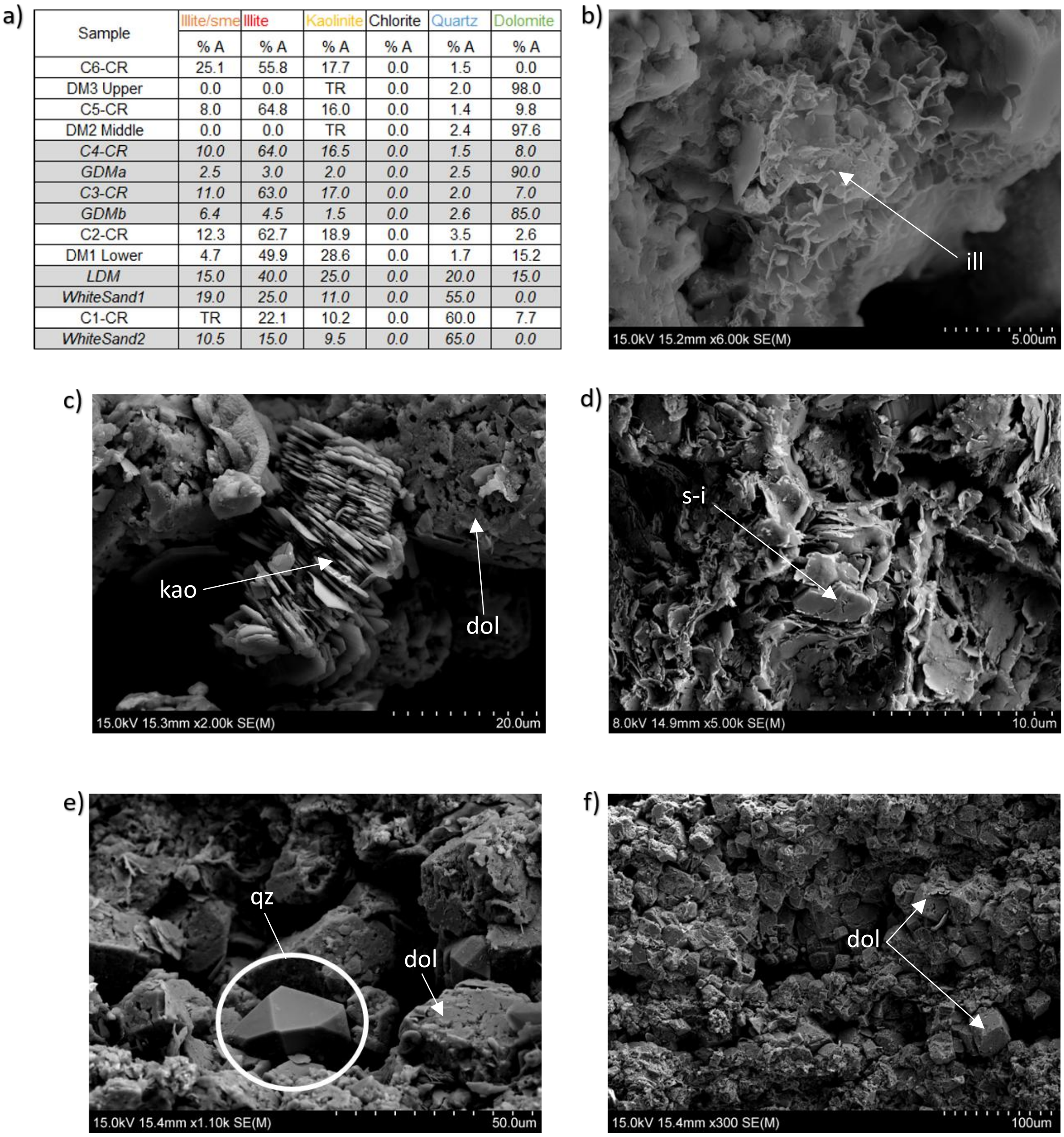


Figure 2.5: SEM micrographs from Claxheugh Rocks. (a) displays the prominent laminations within the DM1 subfaces, as well as the high organic content of the lower Marl Slate. (b) displays the lower organic content and higher abundance of dolomite within DM2. (c) a slightly higher magnification image of the laminations within DM1. (d) a higher magnification image from the top surface of DM1 displaying the increase in clay content near the interbedded clay bands. (d) a lower magnification image displaying the pyrite framboids (Figure 2.4d) next to quartz, dolomite and clay minerals. (f) a higher magnification image of the laminations compared to the dolomite crystals within DM1. All images use the same EDS map key as figure 2.4.

In thin section, the thinness of the Marl Slate laminations is clear (<60µm). They appear as alternating bands of dark organic material and lighter orange clays in conjunction with lilac dolomites as per the EDS colour selection. The laminations are prominent in the lower portions of the Marl Slate, as evidenced by their abundance in DM1 thin sections (Figure 2.5a). Further up the Marl Slate however, the laminations become fewer, transitioning into more blocky dolomite rich layers as the Marl Slate transitions into the Magnesian Limestone. This may occur because the environment changed from more anoxic conditions initially, resulting in darker, more organic rich sediment, to more oxygenated conditions later on with more freshwater influence, hence the increase in dolomite abundance.

XRD and SEM analysis



Sample	Illite/sme	Illite	Kaolinite	Chlorite	Quartz	Dolomite
	% A	% A	% A	% A	% A	% A
C6-CR	25.1	55.8	17.7	0.0	1.5	0.0
DM3 Upper	0.0	0.0	TR	0.0	2.0	98.0
C5-CR	8.0	64.8	16.0	0.0	1.4	9.8
DM2 Middle	0.0	0.0	TR	0.0	2.4	97.6
C4-CR	*10.0*	*64.0*	*16.5*	*0.0*	*1.5*	*8.0*
GDMa	*2.5*	*3.0*	*2.0*	*0.0*	*2.5*	*90.0*
C3-CR	*11.0*	*63.0*	*17.0*	*0.0*	*2.0*	*7.0*
GDMb	*6.4*	*4.5*	*1.5*	*0.0*	*2.6*	*85.0*
C2-CR	12.3	62.7	18.9	0.0	3.5	2.6
DM1 Lower	4.7	49.9	28.6	0.0	1.7	15.2
LDM	*15.0*	*40.0*	*25.0*	*0.0*	*20.0*	*15.0*
WhiteSand1	*19.0*	*25.0*	*11.0*	*0.0*	*55.0*	*0.0*
C1-CR	TR	22.1	10.2	0.0	60.0	7.7
WhiteSand2	*10.5*	*15.0*	*9.5*	*0.0*	*65.0*	*0.0*

Figure 2.6: (a) Table displaying the XRD results from hand samples taken from the Claxheugh Rocks outcrop of Marl Slate. Results are displayed as % Abundance of each mineral phase present within each hand sample. Minerals and sample names correspond to units on the Figure 2.4a graphic log. “CR” refers to the sampling location, Claxheugh Rocks. GDMa-b refer to the bands of grainy dolomitic marl (Figure 2.4a), LDM refers to the laminated marl layer beneath DM1 (Figure 2.4a) and WhiteSand1-2 refer to the bands of white sand (Figure 2.4a). Middridge and Crime Rigg Quarries. (b) Secondary electron image displaying fibrous illite (ill) from DM1. (c) SE image displaying a typical example of Kaolinite (kao) books from DM1. (d) SE image of smectite to fibrous illite (s-i). (e) SE image of a large quartz crystal (qz) surrounded by cubic dolomites. (f) Low magnification SE image of DM1 displaying the large cubic dolomite crystals (dol).

Conducting XRD analysis **(17)** on the Marl Slate was a detailed method used to understand the abundances of key minerals within the lithology. Claxheugh rocks was chosen because it displayed the full extent of the Marl Slate from top to bottom. As expected, the most abundant mineral in the crystalline dolostones is dolomite (up to 98%) with a negligible amount of anything else. The organic-dolomite layers are still a majority of dolomite but with minimal clay influence. The key minerals of interest, however, are the clays.

Clays are thought to aid in the preservation of fossils due to their extremely fine nature (Saleh et al, 2019). Their crystals are so small that they can preserve even the most minute details of fossils when deposited in low energy conditions. Some clays are considered to have antibacterial properties attributed to the toxicity of their metal content, berthierine in particular because of Al^{3+} and Fe^{2+} cations in its structure (Fu et al, 2015). XRD was used to gain an understanding, not only of which clays were present in the Marl Slate, but how much of each clay was present to understand whether they had an effect on the preservation of the Marl Slate Fish.

The XRD results revealed that the most abundant clay throughout the Marl Slate is illite. While low in the upper, more dolomitic regions of the UMS and MMS, illite is the primary mineral making up the clay bands C1-6, reaching as high as 64.8% in C5 (Figure 2.4a). The LMS is where the other clays phases become more abundant, kaolinite reaching up to 28.6% in DM1 (Figure 2.4a). Clays are common in marine shales, particularly illite, due to their low energy environments being sufficient enough for finer clays to precipitate out. However, the transition from illite to smectite can be attributed to post-burial diagenesis.

The abundance of illite is of note, not only because it matches the secondary electron SEM images of fibrous illite (Figure 2.4b), but because it is a known preservative clay and is often associated with exceptional preservation of marine fossils (Woltz et al, 2020). Illite is a common diagenetic mineral, and is likely present in the Marl Slate due to transformation of smectite to illite (Ferrell and Galán 2013). However, illite was also present in the Permian Yellow Sands (Pryor, 1971). Due to reworking and redeposition of the top layer of the Yellow Sands by the rapid flooding of the Zechstein Basin as well as benthic organisms inhabiting the Zechstein Sea, some of the already present illite would have been reworked into the lower Marl Slate deposits. Evidence of reworking can be seen in vertical burrows in the LMS as well as wet sediment deformation visible in the top layers of the Permian Yellow Sands.

Mineralogy and Anoxia

The mineralogy of the Marl Slate is one of the better understood aspects of its lithology. It is known that the trace metal content of the Marl Slate is greater than the average black shale (Wedenpohl, 1980). It is also understood that the metals were likely already present in the Zechstein seawater and were deposited within the Marl Slate as part of the biochemical cycle of the environment's phytoplankton (Brongersma-Sanders, 1965) **(18)**. However, the characteristic features of the Marl Slate mineralization were likely influenced by diagenetic factors. The increased content of elements like Cu, Mo, Ni, Pb, S and organic carbon is of particular interest because of how they relate to anoxia. Abundances of these particular elements indicate that the Marl Slate was deposited under anoxic conditions (Oszczepalski, 1986).

The distribution of base metals in the Marl Slate strongly suggests they were introduced by the same freshwater influx that initiated each depositional cycle. Cu and Zn contents are relatively low within the darker, more sapropelic laminae and become higher in the paler, more oxygenated laminae. This would mean that Cu and Zn sulphides were likely precipitated interstitially when more 'normal' marine conditions were re-established in the more oxygenated, later part of each depositional cycle. The earlier, sapropelic part of the cycle is characterised by high pyrite content (Figure 2.4c) and strongly negative $\delta^{18}O$ values in associated carbonate minerals, organic carbon is also much higher in these layers but diminished upwards in each depositional cycle (Turner and Magaritz, 1986). It is acknowledged that there is no evidence suggesting the $\delta^{18}O$ values had been modified by later diagenesis or recrystallisation, indicating that anoxia was the cause.

While the anoxia can be attributed to phytoplanktonic blooms initiated by freshwater influx the organic character and high abundance of sulphide minerals are more indicative of anoxic conditions as stated by Sweeny et al, 1987. It is likely that the sulphide minerals were produced by sulphate reducing bacteria (SRB) (Turner et al, 1978). The reduction of sulphates by anaerobic bacteria leads to the release of large quantities of H_2S into the bottom waters (Tissot and Welte, 1978); this results in the creation of metal-organic compounds which react with metal compounds, organic reductors and the now present H_2S to cause the precipitation of metal sulphides (Saxby, 1976) like pyrite and baryte, both of which occur in the Marl Slate (Figure 2.7).

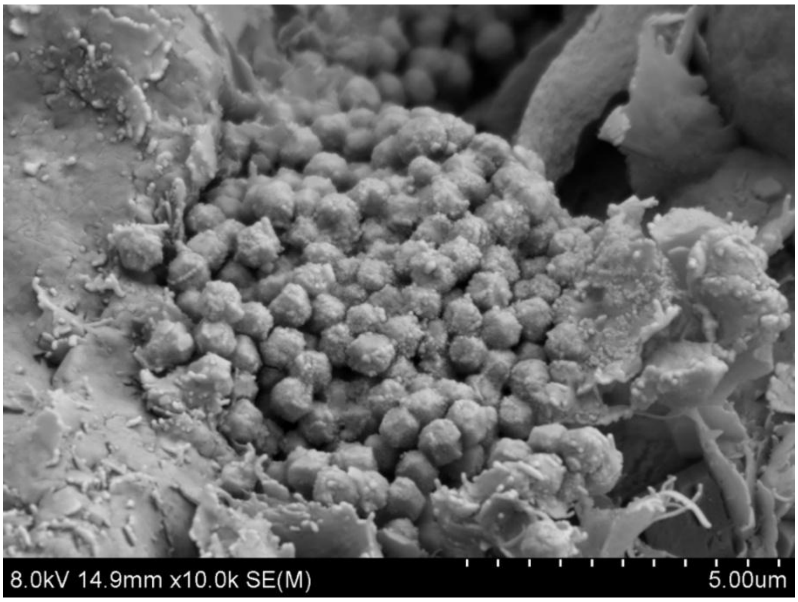


Figure 2.7: Secondary electron SEM image of a framboidal pyrite clump. The central lower section of the image displays early stage fibrous illite. The sample originates from the MMS at Middridge Quarry.

SEM data, as part of this study, further revealed that clumps of framboidal pyrite (Figures 17d and 19) are abundant throughout the Marl Slate (Figure 2.4c), but are more common within the laminations enriched in organic carbon. This can be attributed to their production by sulphate reducing bacteria. SRB are often correlated with anoxic waters (Theede et al, 1969). At oxygen concentrations between 0.7ml/L and 0.3ml/L benthic and nektonic life is supressed. Below 0.3ml/L deposit-feeders become rare, less active and soft bodied only. Eventually, bioturbation ceases altogether. Below 0.1ml/L suspension-feeders disappear as well, leaving anaerobic bacteria the only organisms effectively reworking of organic matter (Demaison and Moore, 1980). Oszczepalski (1986) stated that the bottom anoxic conditions of the Zechstein Copper Shale in Poland had an oxygen concentration of below 0.1ml/L. This means that the Marl Slate would have only had anaerobic SRB reworking the organic matter. As we know by the abundance of fossils present in the Marl Slate, it is clear that oxygen levels were not that low.

A complete lack of bioturbation and nektobenthic marine life would certainly slow bacterial sulphate reduction if not completely arrest it. It is more likely that the Marl Slate had a low oxygen concentration nearing 0.4-0.2ml/L which would have restricted bioturbation somewhat but not entirely. It would have allowed the development of nektobenthic communities resulting in the large proportion of fauna seen fossilised within the Marl Slate, while also allowing for anaerobic SRB to break down organic matter in the more stratified anoxic bottom waters (Figure 5) during freshwater induced phytoplanktonic blooms. As is evidenced by the exceptionally preserved fossil assemblages, decay of Marl Slate fauna was minimal so it is likely bacterial action was slowed by large scale 'suboxic' anoxia.

Depositional Environment

The Marl Slate was deposited early during the Zechstein transgression. Sea level rise, as part of the marine transgression, caused the upper waters to rise above the sand dunes, rapidly flooding the Zechstein Basin creating isolated almost stagnant marine environments between the large scale, upstanding dunes of the Permian desert. This is represented by the darker, more sapropelic, fine grained material (LMS). Seasonal freshwater influx from tributaries induced phytoplanktonic blooms that eventually stratified the water column, promoting suboxic conditions with anoxic bottom waters. This is represented by the increase in oxygen content and carbonate content in transition from the MMS to the UMS. There are four classifications of modern aquatic anoxic settings proposed by Demaison and Moore (1980):

(1) Large anoxic lakes form when permanent stratification promotes development of anoxic bottom water; particularly large, deep lakes not subject to seasonal overturn (e.g., Lake Tanganyika, Africa).
(2) Anoxic silled basins form when landlocked silled basins with positive water balance stratify and generate anoxic bottom waters (e.g., Baltic and Black seas).
(3) Anoxic layers caused by upwelling develop only when the oxygen supply in deep water cannot match the demand by decaying organisms (e.g., the Peru coastal upwelling).
(4) Open ocean anoxic layers are found at intermediate depths due to distance from deep, oxygenated polar water sources (e.g., the northeast Pacific and northern Indian oceans).

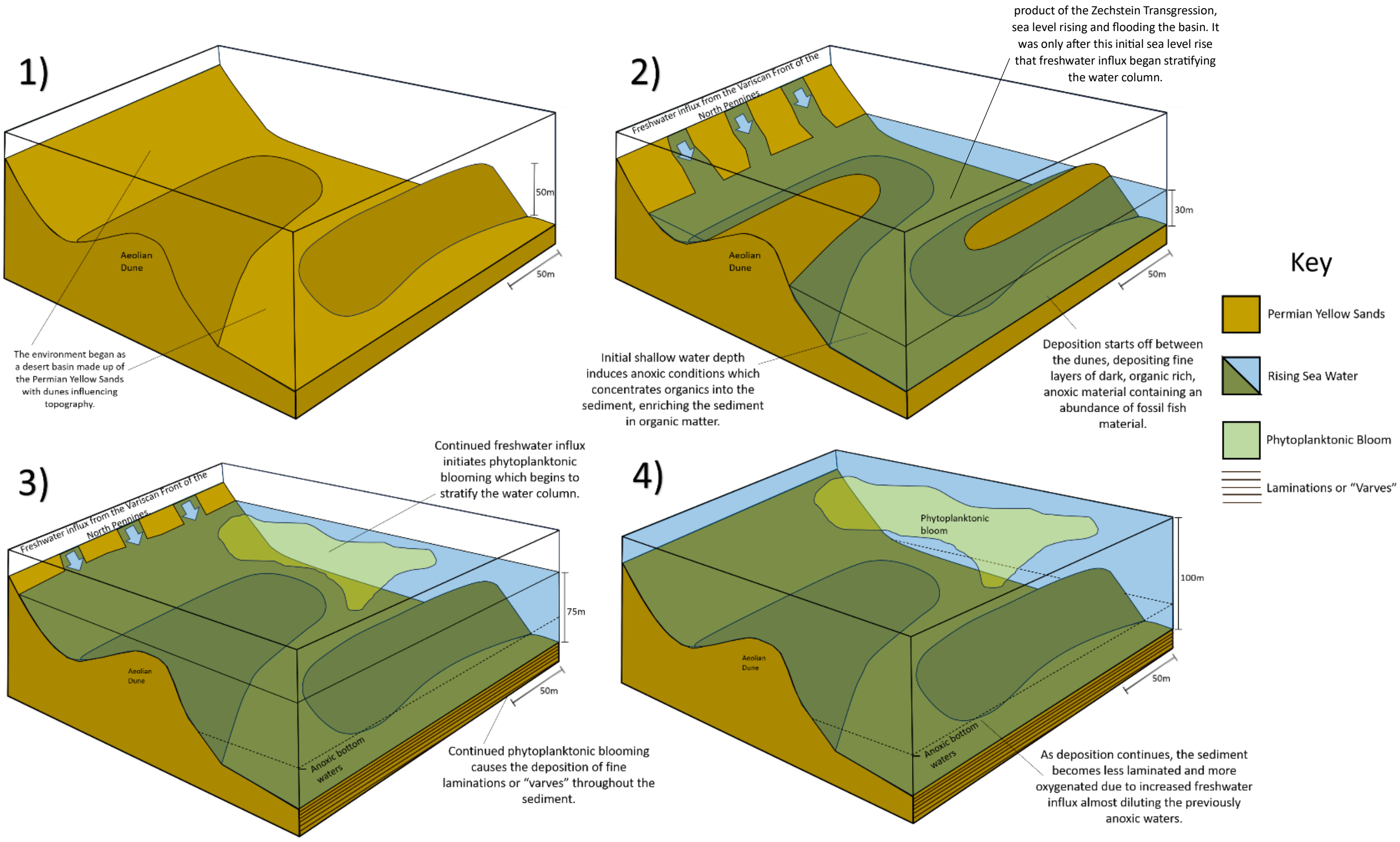
Deep-water facies have also been identified within the Kupferschiefer (Oszczepalski and Rydzewski, 1987) ranging between 20-60km thick and consisting of alternating organic rich shale with planar laminae of clay and planar-wavy laminated dolomitic calcareous clays. These deep-water facies formed either within the anaerobic zone or at the boundary with the dysaerobic zone. The shallow-water facies consist of varied thicknesses of mainly planar-wavy laminated dolomitic calcareous marl, deposited in dysaerobic (Poland) and aerobic (Germany) environments.

The Zechstein Sea was not an open ocean and was not affected by upwelling (Van Wees et al, 2000) and, on initial interpretation, could be considered a large anoxic lake. The anoxia seen in Marl Slate deposits was caused by an influx of freshwater (Turner and Magaritz, 1986) resulting in a stratified water column in what could be described as multiple smaller silled basins situated between large upstanding dunes all connected beneath the upper portion of the Zechstein water column. The Permian Zechstein Sea is often considered to be analogous to the modern Black Sea, both in depositional environment and common fauna. The only difference would be the upstanding dunes in the Zechstein Sea that created between them isolated anoxic environments that aided in prevention of water circulation. It is likely that these isolated basins were where the Marl Slate fish died and were preserved in times of increased anoxia caused by freshwater influx. This hypothesis is represented in Figure 2.8 and is evidence to suggest that the Zechstein Sea is more analogous to depositional environment (2), anoxic silled basins, hence the common comparison to the Black and Baltic seas.

Concluding Comments

Results from sedimentary and petrographic analysis reveal that the wider environment began with a transgression over the top of an aeolian environment, leading to shallow marine conditions and eventually a carbonate ramp. The Marl Slate itself is a finely laminated, illite rich dolomitic mud that displays sapropelic characteristics. The unit transitions from organic rich, more anoxic, fossiliferous layers into less anoxic, dolomite rich muds. The samples analysed evidence the variation in Marl Slate mineralogy as you move up the unit. They also allowed for detailed EDS and XRD analysis of the Marl Slate sedimentology to be conducted while recording images of what exactly was seen.

The sedimentology of the Marl Slate is complex, there are a multitude of factors influencing the seasonal deposition, as well as what is actually deposited. The initial shallow water environment would have been low energy and strongly anoxic (Figure 2.8, stage 2), around 0.3 ml/L^{-1}, where nektobenthic life is inhibited but not completely restricted. This resulted in the deposition of extremely laminated, "varved", sediments rich in organic matter and well-preserved fossils. Stage 2 of Figure 2.8 also explains why the Marl Slate is sporadic at outcrops; the initial layers of the Marl Slate were deposited between the large upstanding aeolian dunes of the Early Permian desert resulting in an incomplete picture of deposition. Hence why the Marl Slate is not seen or tapers off at certain outcrops between the Permian Yellow Sands and Magnesian Limestone. This means that the Permian Yellow Sands are a key pre-depositional factor in controlling the depositional environment of the Marl Slate.



The environment began as a desert basin made up of the Permian Yellow Sands with dunes influencing topography.

The environment was initially flooded as a product of the Zechstein Transgression, sea level rising and flooding the basin. It was only after this initial sea level rise that freshwater influx began stratifying the water column.

Initial shallow water depth induces anoxic conditions which concentrates organics into the sediment, enriching the sediment in organic matter.

Deposition starts off between the dunes, depositing fine layers of dark, organic rich, anoxic material containing an abundance of fossil fish material.

Continued freshwater influx initiates phytoplanktonic blooming which begins to stratify the water column.

Continued phytoplanktonic blooming causes the deposition of fine laminations or "varves" throughout the sediment.

As deposition continues, the sediment becomes less laminated and more oxygenated due to increased freshwater influx almost diluting the previously anoxic waters.

Figure 2.8: Block model portraying the depositional environment of the Marl Slate within the Zechstein Sea. (1) the environment began as a vast desert plain containing large scale aeolian dunes. (2) sea level rise as part of the Zechstein Transgression flooded the basin before seasonal freshwater influx from the Variscan Front induced relative anoxia to the shallow water environment between the upstanding dunes. (3) the freshwater initiated phytoplanktonic blooming in the surface waters, reducing the oxygen content of the bottom waters and stratifying the water column. The cyclic nature of the environment induced a repetitive depositional cycle not dissimilar to varving. (4) continued cyclicity of the environment slowly diluted the anoxia, depositing more oxygenated, lighter coloured sediment compared to the first deposited darker, more anoxic sediment. A key point to note is that the sediment input from the North Pennines was probably caused by small alluvial fans as per the stratigraphy at Middridge Quarry.

After the complete flooding of the Zechstein Basin (Figure 2.8, stage 4), the cyclicity of the Marl Slate depositional environment would have been in full swing. Alternating between more oxygen rich sediment pre-phytoplanktonic bloom and more anoxic, more organic rich sediment post-bloom. The majority of fish fossils are found preserved in the more anoxic sediment because the lack of oxygen in the bottom waters is a primary factor in aiding their preservation. However, the actual cause of the mass mortalities of the Marl Slate fishes is uncertain. The large majority of fish samples are located within the lowest anoxic bands of the Marl Slate. This means the initial mass dying event must have occurred in the earliest stages of Marl Slate deposition, either as a result of the induced anoxic conditions or in relation to the initial phytoplanktonic blooms. This study favours the idea that the increased anoxia was the primary facilitator of the dying event mainly due to the lack of fossils further up the Marl Slate deposit. If the fishes died as a result of seasonal blooming, there would be a higher abundance of fish fossils throughout the anoxic bands of the Marl Slate as the seasonal cyclicity of the deposit is a prominent feature of the whole unit yet the fossil fish are sparse everywhere except the lowest layers **(19)**. However, the mass mortalities could be a result of the initial blooming events drastically changing environmental conditions faster than the fishes could adapt, as suggested by Trewin (1986). The induced stratified water column would have resulted in bottom waters that were too anoxic to support the vast amount of life present elsewhere in the Zechstein Sea, creating an environment suitable for preservation. The key piece of information here is that there is a difference in oxygen content throughout Marl Slate deposition. The stronger anoxia at the beginning of deposition resulted in more organic rich sediment and a higher preservation potential for deceased fish. As water depth increased and the water column became stratified, preservation potential decreased as total oxygen content increased. More oxygenated water means more scavengers, more predators and overall lower preservation potential. In order to use this to understand taphonomy however, what the sediment has actually preserved needs to be understood first. Linking together the fossil material and the sediment it is preserved in is the next step to understanding the complex taphonomy of the Marl Slate.

Drawbacks

Regarding the Zechstein Sea as a whole, the insight from this study is restricted to the edge of the basin. Northeast England only reveals deposits from the edge of the Zechstein Basin, if the data gathered here is to be compared to the basin as a whole, samples would need to be analysed from different locations throughout the basin, preferably as a transect from the basins edge to its centre. To do this samples would have to be taken from Europe and potentially the North Sea. However, if a study like this was completed, it would reveal exceptional results. Not only would the variation in fossil preservation throughout the basin be uncovered, but it could lead to an understanding of how the whole environment changed. It could reveal how the Zechstein Transgression affected the whole basin. Is the Marl Slate uniform throughout the whole basin? Is the abundance of fossil fishes maintained throughout the basin? Is the mode of preservation the same throughout or does the taphonomy vary? The results of this study will trigger questions like that, a larger scale sedimentological and taphonomic study could potentially answer them.

The model suggested (Figure 2.8) is not an uncommon interpretation when considering anoxic environments in relation to phytoplanktonic blooms. Models of anoxia, as a result of algal blooms induced by run-off, are well known in a variety of settings, as summarized and categorized effectively by Demaison and Moore (1980). The difference this model proposes is the influence the upstanding dunes had on the wholesale anoxia of the Zechstein bottom waters. Rather than simply attributing the anoxia to freshwater influx and a stratified water column, the presence of upstanding dunes would have severely limited water circulation and, in turn, created isolated, stagnant pools in the early stages of the basins flooding. These pools would have been the precursor to the harshly anoxic bottom waters, and the likely factor influencing the higher abundance of fossilized fishes in the first anoxic layers of the Marl Slate deposit, described as the LMS. However, to test the hypothesis that the exact mechanism suggested in figure 2.8 is responsible for the petrography and sedimentology of the Marl Slate would require further study. **(20)**

Chapter 3:

The Marl Slate Biota and Preservation

Introduction to the biota

The palaeontology of the Marl Slate is a large field involving many diverse fossil groups. While it is an often-overlooked 2m thick unit, it offers a deep insight into the Z1 marine transgression of the Zechstein as well as excellent preservation of late Permian vertebrate palaeontology and associated palaeoecology. Not only does it contain fossils of some of the earliest jawed and ray-finned fish, it also contains an abundance of gastropods, bivalves, brachiopods, reptiles and a variety of flora, first compiled by King in 1850. All of the following fossils are Permian in age, originating from the Zechstein Marl Slate deposit of northeast England and the corresponding Kupferschiefer deposit of Germany. While the Marl Slate does contain a large variety of fossils, including fishes, sharks, brachiopods and plants, this study primarily focuses on the well-preserved fishes within the Durham University collection. The majority of these fishes were preserved in situ, not transported by currents. The fishes studied here are of extreme importance to the study. They are a fundamental factor in explaining the taphonomic pathway that led to the high standard of preservation seen within the Marl Slate biota. These fish are complicated organisms with a multitude of hard and soft tissues working in unison throughout the organism's life. In order to understand how the tissues came to be preserved, the diversity and anatomy of the Permian fish present within the Marl Slate must first be understood.

Permian fishes specifically have been described from several parts of the world and from both marine and non-marine deposits. The relatively well preserved and locally numerous examples from the Kupferschiefer of Germany and Marl Slate of County Durham attracted attention in the early 19th century, namely by King (1850). However, very little research has been undertaken recently and this project provides a timely reappraisal of the key Permian fish faunas from the Marl Slate of County Durham. Many museum specimens of fossil fish have been obtained in the past from many of the sites used in this study, specifically at Middridge and Crime Rigg Quarries, both from the Marl Slate formation (Figures 2.1 and 2.2).

Fish Genus	Average Organism Size	Preservation Standard	Fragmentation Level	% Abundance in Studied Samples	No. in Durham Collection
Palaeoniscum	20cm	Exceptional	Low	60.1%	21
Pygopterus	35cm	Exceptional	Medium	7.9%	1
Acrolepis	65cm	Exceptional	Medium	2.3%	1
Platysomus	18cm	Good	Medium	2.3%	3
Coelacanthus	70cm	Good	High	3.1%	2
Acentrophorus	10cm	Good	Medium	4.6%	0
Unknown	n/a	Poor	Very High	1.5%	2
Fish Teeth	<0.5mm	Exceptional	Low	16%	20
Reptiles	n/a	Exceptional	High	0%	n/a
Coprolites	<4cm	Good	Low	0.7%	1
Plants	n/a	Good	Medium	1.5%	2
Brachiopods	n/a	Exceptional	Medium	0%	n/a
Bivalves	n/a	Exceptional	Medium	0%	n/a

Figure 3.1: Table displaying the genera of the relevant organisms found within the Marl Slate. The organism size, average preservation standard, fragmentation level and abundance are displayed also. The number of samples within the Durham collection has also been noted.

The most abundant species of Permian fish, within the Durham University collection, is *Palaeoniscum freieslebeni* (Blainville, 1818). This aligns with the collection at the Natural History Museum as well as other reviews of the Marl Slate fauna, namely the work by Diedrich (2009). However, the overall abundance of *P. freieslebeni* is lower in the Durham Collection. *P. freieslebeni* is the most common taxon throughout the Marl Slate and Kupferschiefer, *Palaeoniscum* making up 80% of all fish fossils found within the deposit (Schaumberg, 1977). The differences in abundance between the two can be attributed to the much smaller size of the Durham collection. There were only thirty-four specimens available for analysis at Durham University compared to the hundreds that are part of the NHM collection. While it is the fishes that are of primary interest in this study, there is also an abundance of *Lingula* brachiopods (Bruguiere, 1797), bivalves and plants as stated by King (1850). However, it is only the fishes and fragments of fish that are of interest in this study, specifically the six genera mentioned in Figure 3.1.

The Marl Slate is also home to a number of reptiles, namely *Protorosaurus*, as there was only one recorded specimen of the lizard until 1993 when a second specimen was described from Quarrington Quarry, County Durham (Evans and King, 1988). The near-whole skeleton included skull fragments that were previously unknown to palaeontologists. The reason some reptilian fossils are often more fragmented is because terrestrial organisms are much more prone to decay and scavenging as they are often more subaerially exposed than marine fossils.

Palaeontological Methods

To understand the anatomy of these fish, it was deemed appropriate to send a single specimen of *P. freieslebeni*, specimen P.8114 (Figure 3.8), for two days of X-CT scanning at Southampton University (Figure 3.1). Two systems were used for the scan; a high-power Diondo d5 scanner was used with a flat-panel detector to obtain a full overview scan of the specimen and to measure the embedment depth of the fossil. The system was set up at medium-energy, high-power and relatively low spatial resolution (~0.4mm). A second scan was done on the region of the specimen that contained the fossil (a 'region of interest' scan) using a custom Nikon 450/225 kVp Hutch and curved linear array detector. This system was set up at high-energy, low-power and relatively high resolution (~0.13mm) for a specimen the size of P.8114.

X-CT Scan Results

The scan revealed that the specimen was embedded only millimetres into the Marl Slate country rock as well as which parts of the fish were best preserved. Figure 3.2 explains that the scales and skull bones are preserved well with nearly all of the fin material missing. This is a common occurrence within the large majority of fish specimens studied, likely due to the fineness and easily fragmentable nature of a fin. Scales and bones are harder, more solid structures with less moving parts so are much less likely to fragment. The scan conducted here also did not pick up any traces of soft tissues; this means that a longer, higher resolution scan would be necessary to uncover the presence, or lack, of any soft tissues. A smaller specimen would be required, perhaps the juvenile *P. freieslebeni* specimen, P.9299, from the Durham University collection or an external *Acentrophorus* (Traquair, 1877) specimen. Both being less than 6cm in length. However, the most fundamental factor in understanding the overall taphonomy of these fish is understanding the taxonomy of the fossils themselves.

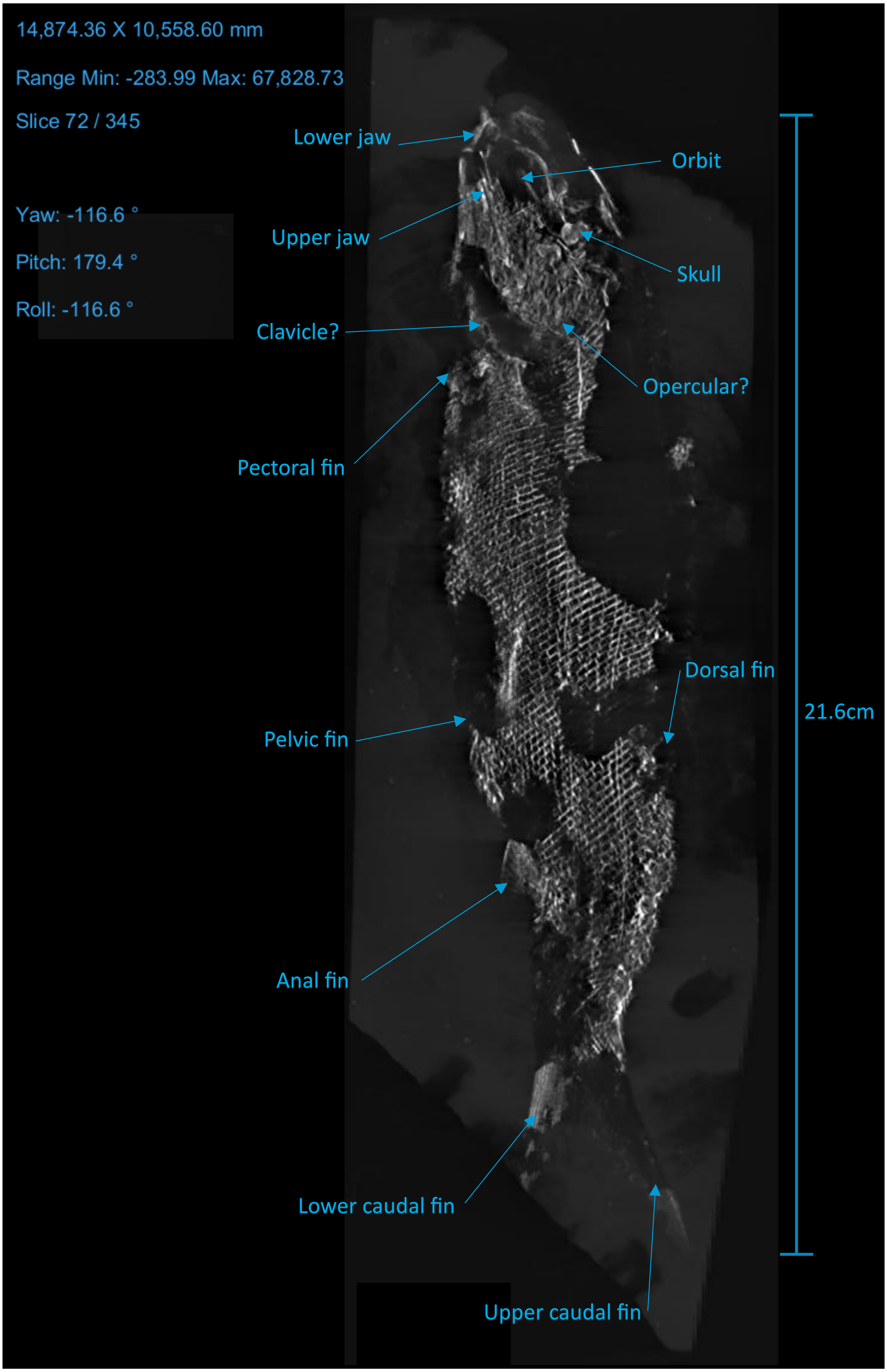


Figure 3.2: An X-CT scan of the top surface of *P. freieslebeni* specimen P.8114, highlighting the fossil material separated from the rock material. Fossil material is sharp white, rock material is greyed out.

Taxonomic Notes

Pygopterus

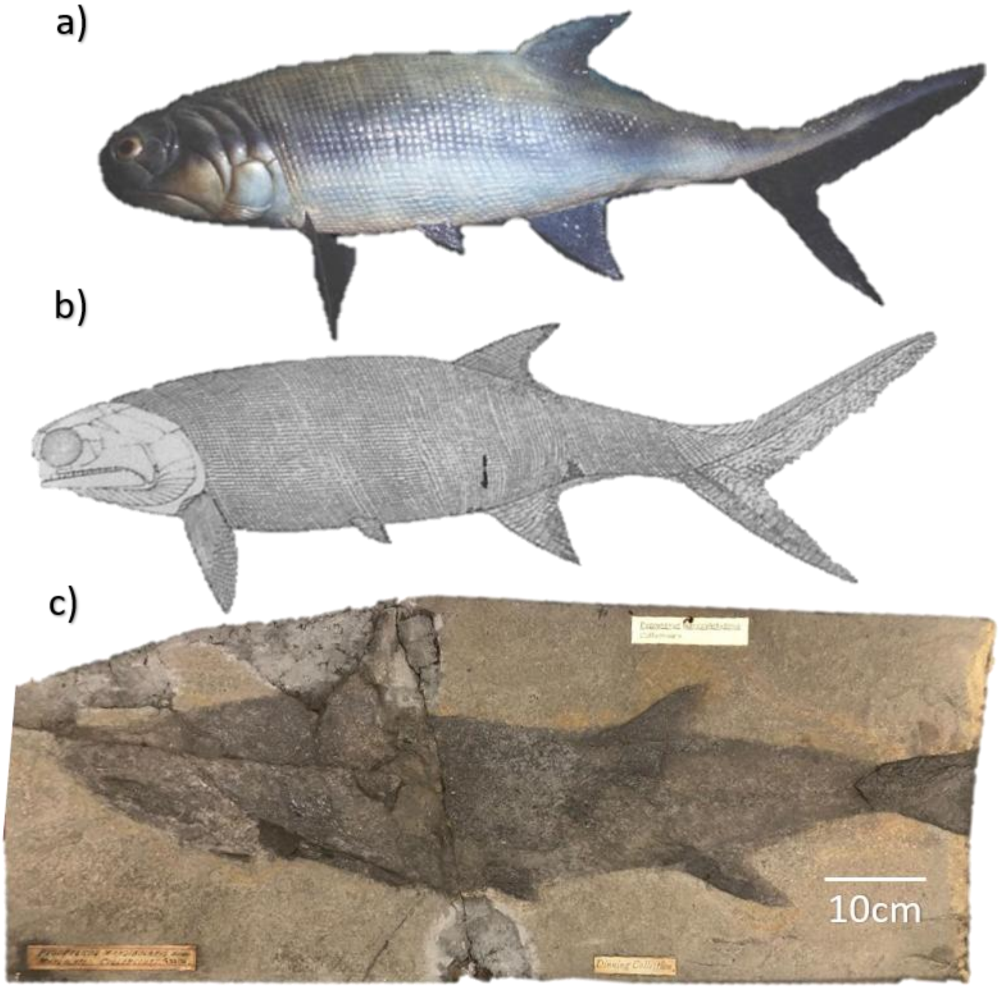


Figure 3.3: Comparison between three different representations of *Pygopterus*: (a) An artists 3D rendering of what a living *Pygopterus* would look like. (b) A restoration of *Pygopterus* from an exhibition held by Kipping Fossils, (c) An exceptionally preserved example of *Pygopterus* from the Hancock Museum, Newcastle.

Pygopterus (Blainville, 1818) was one of the physically larger genera of bony fishes living in the Permian. The type species, *Pygopterus humboldti*, appears larger than, yet visually similar to *Palaeoniscum* (Figure 3.8). Both have a torpedo shaped body with large eye sockets indicating both were predatory; however, the anal, pectoral and dorsal fins of Pygopterus are much larger (Figure 3.3b). Its upper caudal fin is also notably longer than the lower. The larger fins are likely an adaptation to aid in manoeuvrability. Pygopterus likely hunted much smaller, more agile prey and needed to be well equipped to catch them.

Platysomus

Platysomus (Agassiz, 1833) is one of the smaller fish in the Marl Slate. It was a ray-finned fish with a flattened body and elongated dorsal and anal fins (Figure 3.4b). Its pectoral fins were small and it lacked pelvic fins. The jaw of *Platysomus* had a large gape thought to have aided in feeding on plankton, indicating that it was not a primarily predatory fish, rather catching microscopic organisms in suspension. Compared to the rest of its body, the eyes of Platysomus are relatively small, indicating it relied more on mass consumption of food rather than targeted predation.

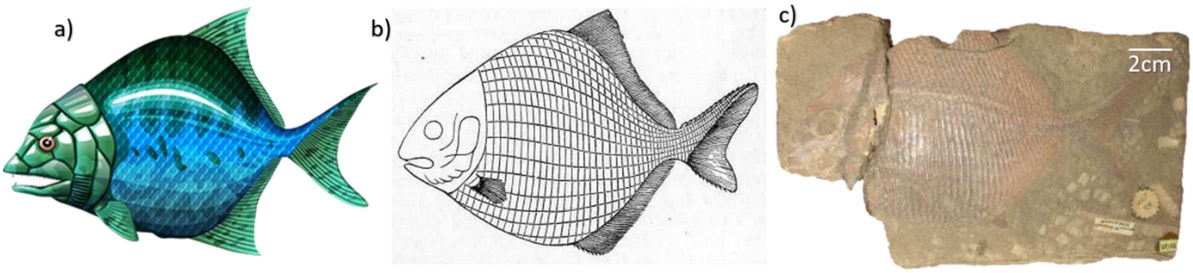


Figure 3.4: Comparison between three different representations of *Platysomus*: (a) An artist's recreation of what *Platysomus* would have looked like. (b) A reconstruction of *Platysomus* from the Ancient Life-History of Earth by Nicholson (2004), (c) An exceptionally preserved example of *Platysomus straitus* from the Hancock Museum, Newcastle.

Coelacanthus

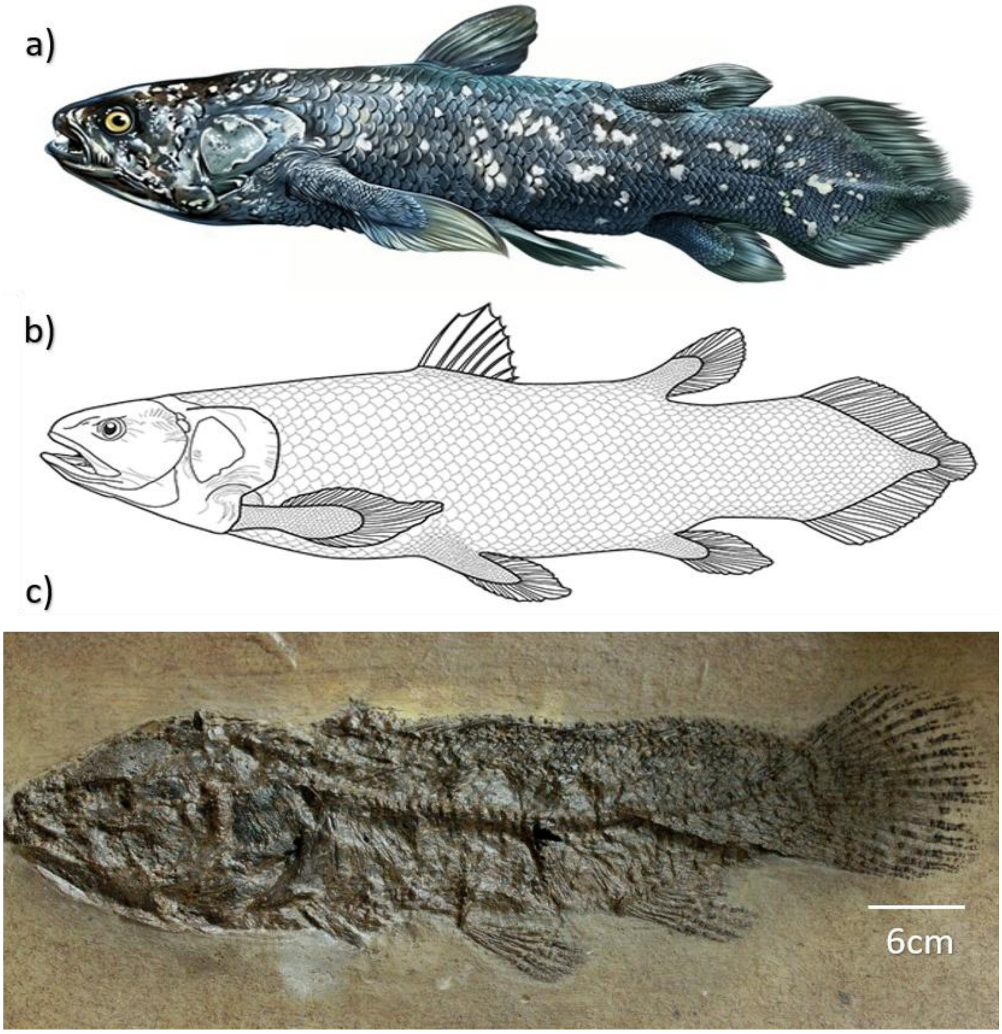


Figure 3.5: Comparison between three different representations of *Coelacanthus*: (a) An artist's recreation of what *Coelacanthus* would have looked like. (b) An illustrated reconstruction of *Coelacanthus*, (c) An exceptionally preserved example of *Coelacanthus granulatus* from the Natural History Museum, London.

Coelacanthus (Agassiz, 1839) was a Permian genus of coelacanth that bore a visual similarity to the modern, extant species coelacanth *Latimeria*. *Coelacanthus* had a more elongate head and was smaller with the larger specimens reaching upwards of 70cm in length. The type species, *Coelacanthus granulatus*, had small lobed fins as well as an additional anterior, sail-like dorsal fin (Figure 3.5). This alongside its bulbous, more elongate caudal fin suggest *Coelacanthus* were open-water predators. Many have also been found to only have teeth in the front of their mouths, indicating they tended to grasp live prey.

Acrolepis

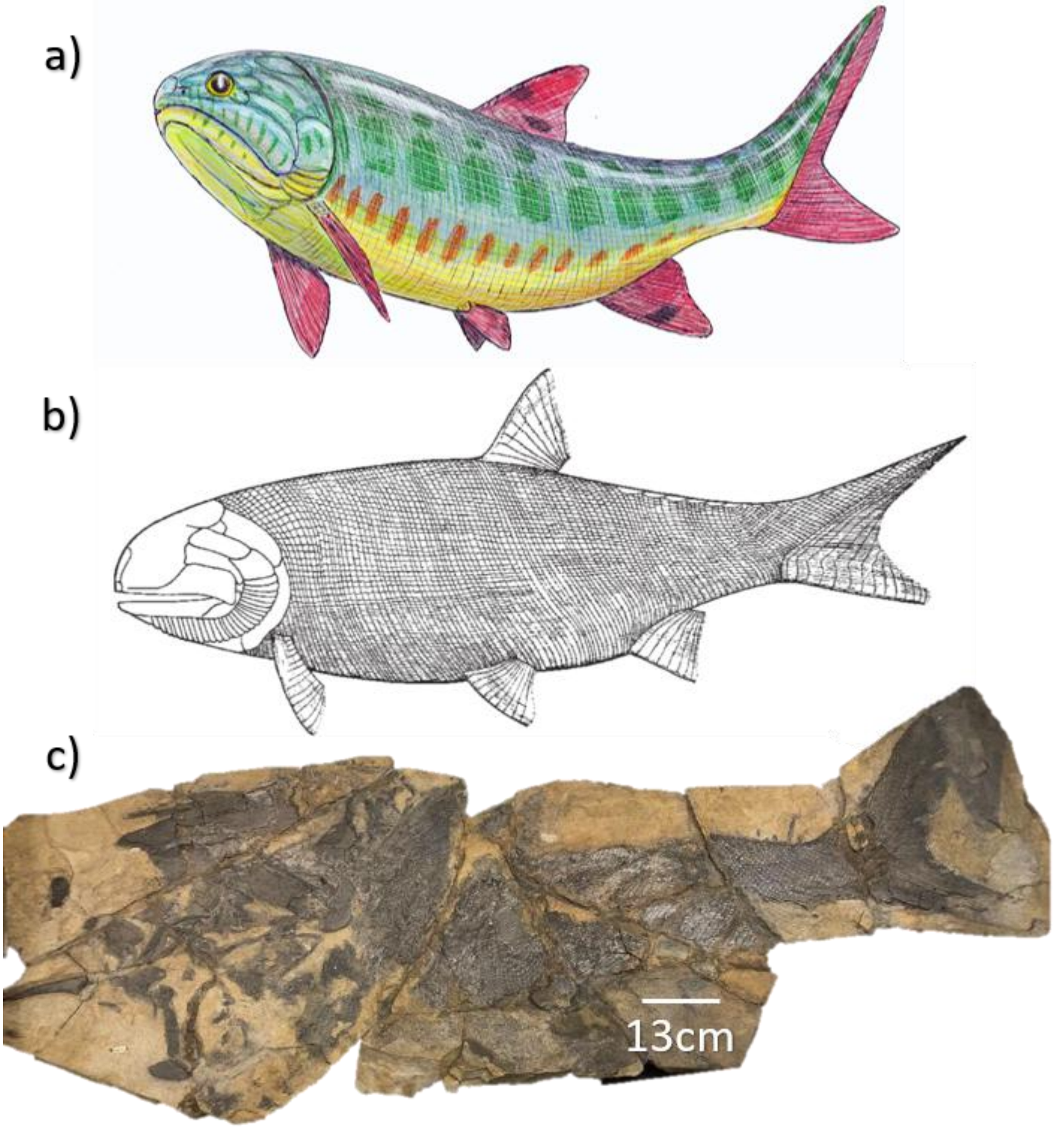


Figure 3.6: Comparison between three different representations of *Acrolepis*: (a) An artist's recreation of *Acrolepis*. (b) A reconstruction of *Acrolepis* by Stamberg (2006), (c) An exceptionally preserved example of *Acrolepis sedgewickii* from the Hancock Museum, Newcastle featuring an exploded head.

Acrolepis (Agassiz, 1933) was a genus of bony fish also living in the Permian. They were large piscivorous fish that were often the apex predator of their environment. The type species, *Acrolepis sedgewickii* averaged around 65cm in length; however, *Acrolepis gigas* often grew to lengths over 100cm. *Acrolepis* is morphologically similar to *Pygopterus*. Although it has a wider torpedo shaped body with less arched fins (Figure 3.6b). Its caudal fin is narrower and shorter also.

Acentrophorus

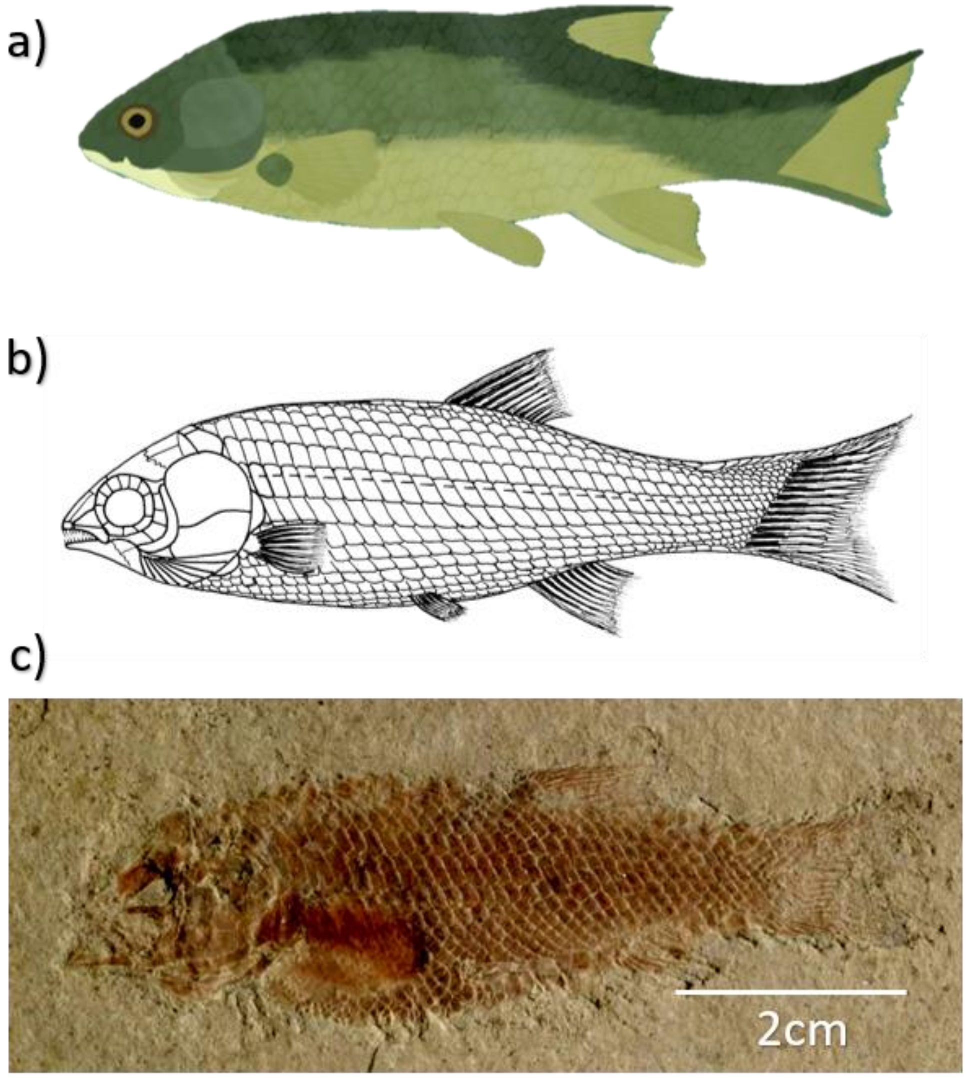


Figure 3.7: Comparison between three different representations of *Acentrophorus*: (a) An artist's recreation of a living *Acentrophorus*. (b) An artists drawn reconstruction of *Acentrophorus*, (c) An exceptionally preserved example of *Acentrophorus varians* from the Natural History Museum, London.

Acentrophorus is an extinct genus of ray-finned fish that lived through the middle to late Permian. They occupied both freshwater and marine environments providing the first kernel of evidence suggesting the Zechstein Sea had prominent freshwater influxes (Romano et al, 2016). The type species, *Acentrophorus glaphyrus*, was first described as part of the *Palaeoniscum* by Agassiz. However, it was later assigned to a new genus, *Acentrophorus*, by Traquair.

Due to their size alone, it is likely that *Acentrophorus* was prey. *Acentrophorus* were very small fish, averaging around 6cm in length. While they have a similar torpedo shape to *Palaeoniscum*, their fins are noticeably different. The dorsal and anal fins of *Acentrophorus* are more square and less arched while still being relatively large compared to their body (Figure 3.7b). The pelvic fin is very small, and the pectoral fin is higher up and more symmetrical then *Palaeoniscum*. The caudal fin is of largest difference; it is more symmetrical and truncate compared to the uneven forking seen in *Palaeoniscum*.

Palaeoniscum

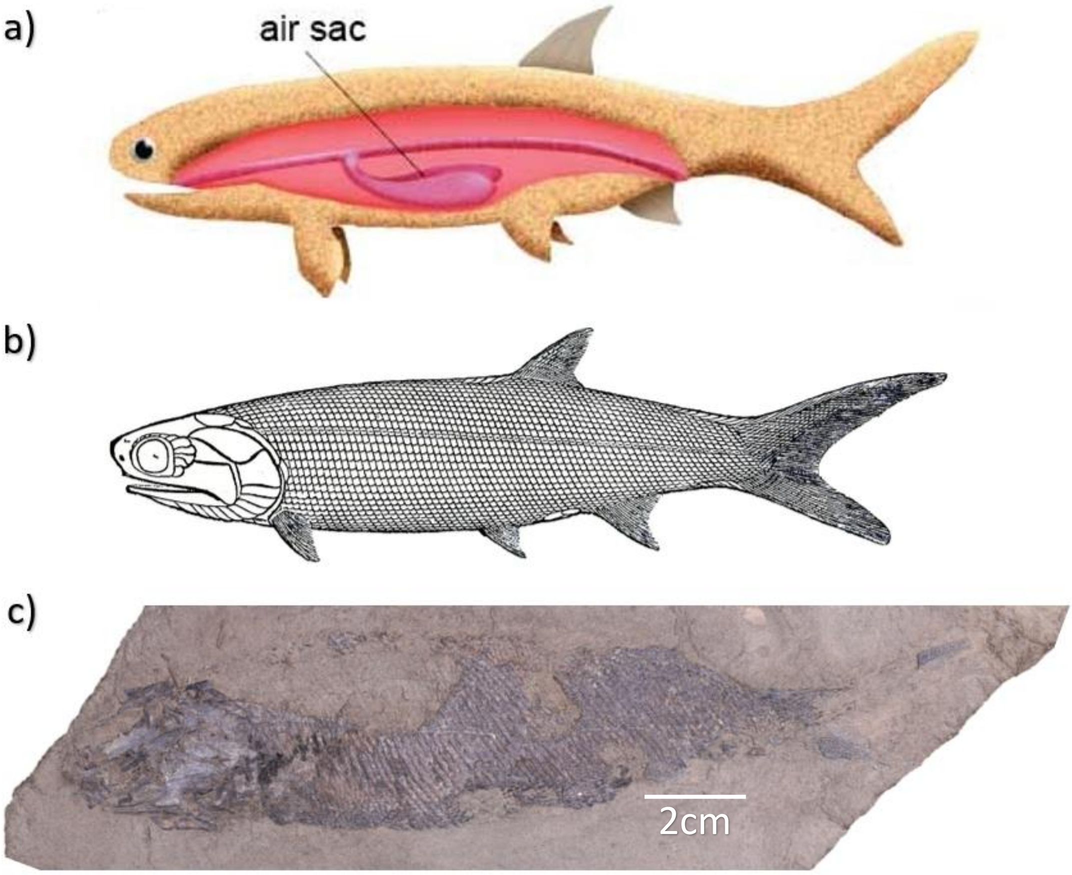


Figure 3.8: Comparison between three different representations of *Palaeoniscum*: (a) A recreation of *Palaeoniscum* by the BGS displaying how the air sacs are connected to the head. (b) A restoration of *Palaeoniscum* from the Guide to the Gallery of Fishes at the Natural History Museum in London by Traquair (1908), (c) The best-preserved example of *Palaeoniscum freieslebeni* from the Durham University collection (Sample P.8114).

P. freieslebeni is a Permian ray-finned fish and the type-species of the *genus Palaeoniscum*. It had a torpedo-shaped body varying in size between 20-30cm in adulthood. It had a deeply forked caudal fin with the upper fin often being longer than the lower. Alongside this, its relatively tall dorsal fin indicates that *P. freieslebeni* was a fast swimmer and likely an active predator. Palmer (1999) highlights that many species within the *Palaeoniscum* genus had easily replaceable teeth like that of modern sharks. They also had air sacks connected to the mouth that served as a primitive form of swim bladder.

What this array of fishes proves is that the ecology of the environment was already quite complex. It had already developed a complex food web consisting of a large number of different species (fishes, sharks, brachiopods and more) with each one varying in size and abundance. Each had their own niche adaptations to complement their place within the environment and food web, many being recorded in their preservation. However, the key is that all of the species must have thrived in the upper waters of the developing Zechstein Sea due to its higher oxygen content. The cyclical nature of the stratified water column would have provided seasonal nutrients for the fish populations, allowing for a more complex ecosystem to develop. What needs to be understood is how this complex array of fishes came to be preserved so well. Hence further examination of the fishes using scanning electron microscopy (SEM).

Teeth and Scales

P. freieslebeni was likely one of the key predators in Zechstein waters, having niche adaptations to aid in the capture of their prey (probably smaller fish). The large eye sockets are evidence for large eyes that were likely adapted for use in the shallow murky waters of the Zechstein Sea. SEM images of scales from sample P.8114 revealed small rounded bumps on the outer surface of the scales (Figure 3.9a). These were likely an adaptation to aid in generating or controlling turbulence in order to decrease drag when swimming through the water. Images of teeth taken by C.M. Henderson (Calgary) revealed asicobasal ridges which are a typical feature of aquatic reptiles and mammals (Figure 3.9b). The ridges are interpreted to aid in the predation of smaller fish, allowing the teeth within the animal's jaw to catch and hold onto slippery aquatic prey more effectively.

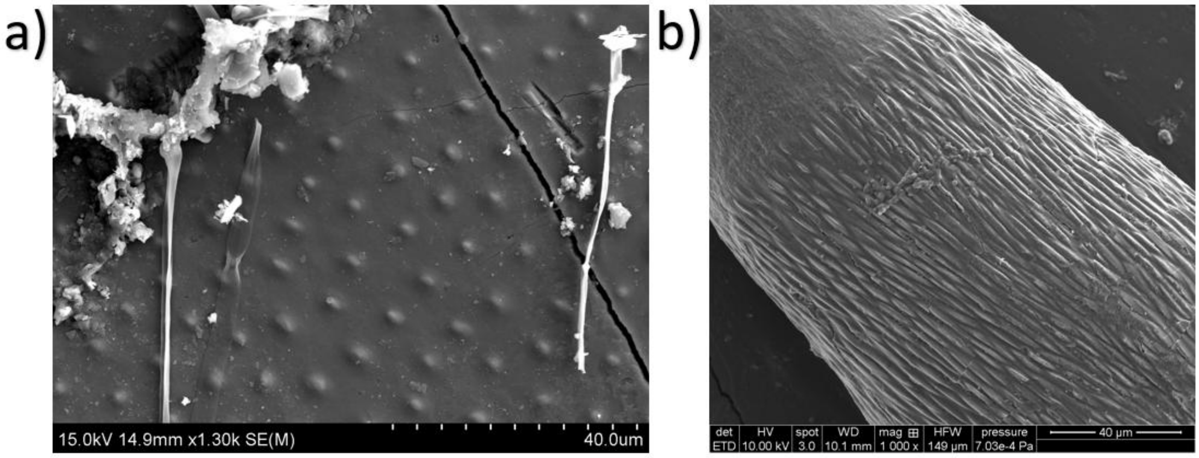


Figure 3.9: (a) Surface of a scale from sample P.478 (*P. freieslebeni*) from the Durham University collection. The small bumps are clearly visible protruding from the scales outer surface. (b) Surface of a Permian fish tooth of unknown species displaying the asicobasal ridges running parallel to the tooth. From C.M. Henderson (Calgary).

A multitude of scales were analysed from all six key species in this study, each one had a similar bumpy texture to the last. While scales were often cracked, the vast majority were whole and well preserved. The same can be said for the image of fish teeth sent for study by C.M. Henderson (Calgary). Very few of the teeth were fractured or broken, nearly every specimen was whole and well preserved.

Preservation Potential

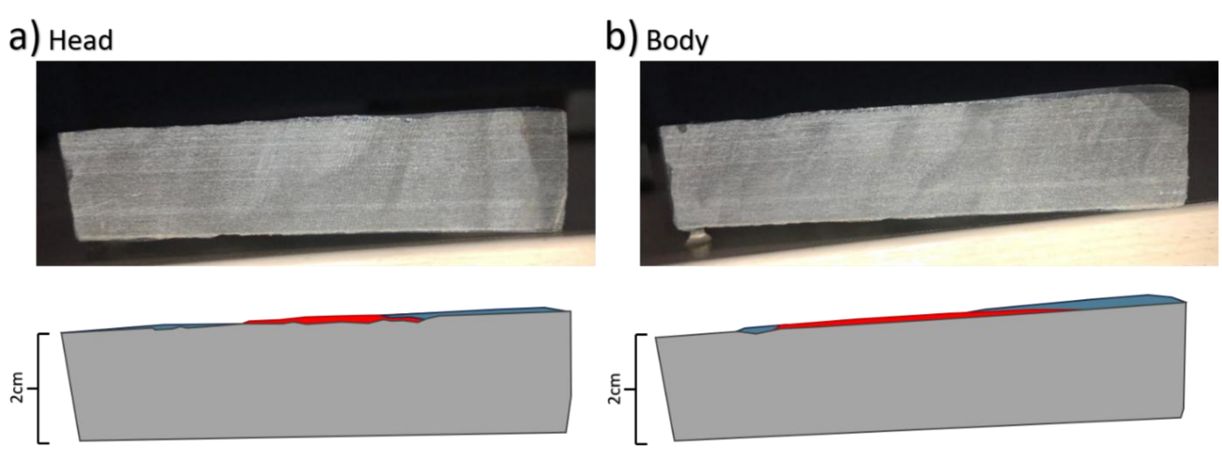


Figure 3.10: (a) a cross-sectional view through the head of *P. freieslebeni* specimen P.8114 alongside a sketch displaying the thinness of the fossil material, <1mm in places. (b) a cross-sectional view through the body of *P. freieslebeni* specimen P.8114 alongside a sketch displaying the thinness of the fossil material. The grey block represents the Marl Slate, red represents the fossil material and blue represents a resin used to keep the fossil material in place during cutting.

Regarding specimen P.8114 specifically (Figure 3.8c), the fossil was found to be exceptionally preserved in apatite with elements of pyrite incorporated into the uppermost surface of the fossil. The majority of the square scales are beautifully preserved alongside the caudal fin and pectoral fin that overlies the body scales. The anal, pelvic and dorsal fins are only preserved as impressions however. This is likely due to continuous movement of the specimen slowly chipping away at the fossil material. The specimen's skull is preserved in dorsal view towards the top left of the specimen with the left jaw and cheek bones visible in lateral view beneath that. A common feature of the smaller fish specimens is slight distortion of the bones in the head which is slightly visible in P.8114. The cause is most likely swelling of the head after death induced by movement of gasses from the primitive swim bladder (air sac) in the stomach to the organism's mouth and head. It is not uncommon for the heads of larger specimens to have exploded as a result of gas expulsion before preservation.

This level of preservation is the standard for Marl Slate fossils, with the thinness of the specimens (Figure 3.10) being the defining feature after the exceptional preservation. Specimen P.8114 is deemed the best only because it is a whole specimen large enough to see the finer details of its preservation better than most. The key trend in Marl Slate fishes is that the vast majority of them are preserved flat on their side. The actual fossil material of many of these fishes only extends a couple of millimetres deep into the rock they are preserved in (Figure 3.10). This could be a result of two things: compression of the carcass after burial or a release of gasses built up within the carcass after the organism's death resulting in flattening and depression of the carcass.

Unfortunately, a common attribute across these fossils is their destruction. Due to their extreme thinness, scales and finer fragments become dislodged from the rock matrix rather easily. This is not helped by the softness of the Marl Slate itself, often becoming quite crumbly and fissile when dry. While this did help with removal of scales for analysis; it meant that every specimen had to be handled with great care, especially when cutting them for thin section preparation.

What is Preserved?

The fish specimens from the Marl Slate, while well-preserved, are not often as complete as they seem. It is the harder, more resistant parts of the fish bodies that are more commonly preserved. These hard parts consist primarily of bones, scales and teeth and, as figure 3.9 displays, it is most often the scales and teeth that are preserved in the greatest detail, still maintaining their microscopic features. Bone structures are often larger and more brittle, often resulting in warping or fracture, whereas teeth and individual scales are small enough to be less affected by transport and breakage. While whole fish specimens do occur (see taxonomic notes for examples), they are often missing minor attributes.

The example of *P. freieslebeni* displayed in the taxonomic notes (Figure 3.8c) is missing the majority of its fin material. Only small sections of the upper and lower caudal fins remain, the dorsal, pectoral, pelvic and anal fins are only preserved as impressions within the Marl Slate material itself because the fossil material has been removed over time in storage. It is clear (Figure 3.6c) that the *Acrolepis* specimen has undergone significant damage to the head, the *Pygopterus* specimen (Figure 3.3c) is missing finer detail in the head and body. This differentiation only goes to show that each and every specimen that is a part of the Marl Slate biota is different from the next. While they have all undergone a similar taphonomic route, each fossil is unique.

An unexpected finding of the study however, was the complete absence of any conodonts in the Marl Slate samples. A total of 48.7kg of rock from the lower, middle and upper sections of the Marl

Slate at Middridge, Crime Rigg and Claxheugh Rocks was sent to C.M Henderson at the University of Calgary in Alberta, Canada for Conodont sampling. Having sampled the entirety of the 21 rock samples sent, not a single conodont was found. This was unexpected as Swift (1995) found a vast multitude of conodont species during his study of the Marl Slate. Swifts most productive region was the basal layer of Marl Slate just above the Permian Yellow Sands (C.M Henderson, pers comm) at Downhill Quarry in Sunderland, a mere 2.2km north of Claxheugh Rocks. The tremendous difference in abundance of conodonts is somewhat of a mystery, however it was suggested by C.M Henderson (pers comm) that the relative rarity of the conodonts here could be related to turbidity, but also could be a function of fluctuations between open marine and more restricted conditions. The anoxia near Zechstein Sea-floor would normally not be an issue since conodonts were nektic organisms, perhaps the seasonal overturn of the Zechstein Sea via phytoplanktonic blooming (Figure 2.8) had a large control over conodont populations in the more oxic upper waters? Moreover, the climate during the Middle and early Late Permian was likely relatively arid (Fluteau et al, 2001) in this part of northeast England, but with probable significant cyclic variation. It is suspected that the phytoplanktonic blooming was a result of estuarine circulation conditions and freshwater influx (Figure 2.8) that fluctuated with some cyclicity. This circulation and associated turbidity would have allowed some fish to migrate into the area (and a few conodonts as well) but seemed to preclude most benthic organisms, restricting those that could survive to select environments between or on the upstanding dunes. Simply, the environment may have been too harsh at times for conodonts to thrive which resulted in geographical gaps in their preservation; hence their abundance at Downhill Quarry and disappearance at Claxheugh Rocks.

The Marl Slate does contain benthic organisms within its biota, namely *Lingula* brachiopods, which are first noted by King (1850), so while benthic organisms were present in the lower waters of the Zechstein Sea they were most likely restricted to certain environments between upstanding dunes, perhaps similarly to conodonts, due to the circulation and turbidity of the early Zechstein Sea. The study and following report conducted by C.M Henderson is available in Appendix F.

A Note on Exploding Fish

It is not uncommon to see fish specimens from the Marl Slate with exploded heads (Figure 3.6c), most commonly the larger specimens. For Permian fish specifically, this occurrence can be attributed to their primitive swim bladder or air sac (Figure 3.8a), a structure acting like a small balloon aiding in buoyancy in the water. There is a small tube connecting the air sac to the gut and head. After the fish dies, the bacteria in its gut produce decay gasses that build up in the swim bladder. Due to the weak point leading to the head, the gasses rupture in that direction causing the head to explode. This is comparable to modern fish, like herring, where the swim bladder is connected to the brain and gut.

These “exploding heads” are a relatively common feature because the fragmented heads have been preserved in the fossil record. This is where this unique feature becomes more relevant to understanding Marl Slate taphonomy. As seen in modern fish, like goldfish, when the fish dies it tends to float near the surface of the tank a couple of days after death. This is due to the gas buildup in the gut and swim bladder. Fortunately for goldfish owners, their guts are too small to produce a sufficient amount of decay gasses for the stomach or head to explode. If the fish exploded while floating, the expulsion of gas would have scattered the skull fragments some distance away from the rest of the carcass. The Permian Marl Slate fish must have had something anchoring them on the seafloor when their heads exploded in order to preserve the remnants of the explosion. Moreover, if the fish floated after they died, their preservation potential would have been drastically lower due to a higher likelihood of scavenging. As is obvious in the quality of the Marl Slate fish fossils, there was minimal destruction of the fish after death and the exploded remains are close by the rest of the body as if the heads did indeed explode on the seafloor rather than in the water column.

For the Permian fish to have exploded on the seafloor, there must have been something preventing them from floating while still allowing decay gasses to build up in their guts and heads. This study will delve into the idea that the fish were adhered to the seafloor by the growth of bacteria covering the fish carcasses. These microbial mats can form and cover a dead fish within hours after the carcass has settled on the seafloor. Considering the high level of preservation in these fishes, it is not unlikely that microbial mats were involved. The potential creation of isolated environments for each fish to preserve could be a key factor in ensuring their preservation, especially when paired with the rapid burial necessary to produce fossils of this calibre.

Concluding Comments

The X-CT scan of specimen P.8114 (Figure 3.2) provided essential guidance on where to cut the specimen for thin sectioning in order to get an accurate representation of the whole fish. The best-preserved sections were the head, centre of the body and rear of the body, just before the tail. It is essential to analyse the upper most surface of the fossil that is in contact with the sediment to glean a better understanding of the contact on a microscopic scale. The specimen's part of the Durham University collection specifically, were observed to have a thin layer of dark material coating the fossil material. It is essential to analyse this feature microscopically to uncover the presence of biofilms or clay masks. Both of which play an important role in the preservation of marine organisms (O'Brien et al, 2008).

While the biota of the Marl Slate is large, the six species of fish prioritised in this study provide an excellent representation of how exceptional the preservation is. They are complex enough to display the intricacy of the preservation (incl. unique features like exploding heads) and are different enough to display the variation and diversity of the fish species present during the Marl Slates deposition. These six species are evidence that the preservation seen here is as close to exceptional as possible without the presence of preserved soft-tissue, the detail seen at macro and micro scales is sufficient to demonstrate this. However, the fishes studied do lack the exceptional soft-tissue preservation seen in Lagerstätten like the Burgess Shale, as well as the sheer volume of exceptionally preserved fossils seen in other Lagerstätten deposits. In conclusion; while the Marl Slate biota is diverse and well preserved, it lacks the exceptional preservation of soft-tissues and volume of exceptionally preserved fossils required to be considered a Lagerstätten. This conclusion does not negate the importance of these fossils however. The mineralogy and structure of the fossil specimens are important in understanding the unique taphonomic pathways undertaken by the fish; SEM and EDS analysis are the first steps taken to understanding the Marl Slates taphonomy as a whole. In order to link Marl Slate sedimentology and taxonomy with the complex systematics of fish preservation, a much more in depth understanding of the interaction between the fossil material and sediment is required. To effectively achieve this, a single specimen was analysed completely in microscopic detail, this provided the data required to begin understanding the essential link between the taxonomy and taphonomy of the Marl Slate fish.

Chapter 4:

Taphonomy

Introduction to Taphonomy

Gab et al (2020) explains that success or failure in the fossilisation of fish is decided soon after the fish dies. Taphonomy is the study of how organic remains transition from the biosphere into the lithosphere, specifically the processes affecting an organism between its time of death and discovery. In other words, it is a way of explaining an organism's pattern of death and dispersal of bones leading up to its preservation (Elder and Smith, 1988). Since the advent of experimental methods in palaeontological research, our understanding of taphonomic and fossilisation reactions has much improved. Today we realise how easily and rapidly organic tissue may be transformed into inorganic materials. Consensus is emerging that fossilisation reactions can take place within time frames accessible with laboratory experiments. A great comparison with this research would be experimental work done on the decay and mineralisation of shrimps by Briggs and Kear (1994) which resulted in extensive mineralisation associated with soft-tissues in a closed system. Compared to the open system, apatite crystal bundles were not as widespread, but localised to soft-tissues as poorly crystalline calcium phosphate where the primary source of phosphate was the carcass itself.

This study has uncovered that the taphonomy of the Marl Slate specifically is a rather complicated process, likely differing slightly between each individual organism. The standard taphonomic pathway undergone by the Marl Slate fish appears to be unique, involving a variety of different factors that influence the overall preservation. While the mineralisation of organisms is a common feature in exceptionally preserved fossils (Briggs, 2003), the steps taken before mineralization even begins within the Marl Slate are more niche. Rapid burial is a consistently recognised factor when discussing a high standard of preservation (Verajão et al, 2025), usually one of the more controlling factors as well. If an organism is not buried fast enough it will simply be destroyed by external factors like decay or scavenging. Pressure must also be high enough so that the carcass may sink to the bottom sediment, whether it stays there is another thing entirely. A low redox state may not delay soft-tissue decay, but anoxia may be essential in keeping scavengers at bay even if it is not a direct control on rate of decay (Allison, 1988). It is clear that rapid burial and anoxia, as well as high enough pressures, played a part in the high standard of preservation seen within the Marl Slate biota. But it cannot have been rapid burial alone that induced such a unique result, wider scale controls also need to be considered before narrowing in on the minute details.

The greater environment is an important factor when discussing taphonomy. It is the wider environment that influences the controls that affect taphonomy and overall preservation potential. Shortly after the transgression, it is believed that spatially heterogeneous reducing conditions presided in the Zechstein Basin (Pancost et al, 2002). The depositional environment put forward in this study suggests that permanent stagnant bottom-water conditions developed as a result of nutrient-rich water, leading to high organic productivity in the upper waters in combination with high evaporation rates. After the initial transgression, the water column in the Zechstein Sea may have been between 200-300m deep (Ziegler, 1990). Rates of deposition for the Marl Slate are estimated to be at 30-40cm in 17kyrs (Hirst and Dunham, 1963). The presence of green sulphur bacteria, which would have required both light and free hydrogen sulphide, indicates that photic zone euxinia, at a depth of 10-30m, occurred at least intermittently during the deposition of the Marl Slate and early history of the Zechstein Sea (Pancost et al, 2002 and Slowakiewicz et al, 2015). Primary production in the upper sections of the water column was dominated by photosynthetic cyanobacteria or green algae.

While sediment composition and the depositional environment both play a large role in the preservation of the Marl Slate fossils, it is likely there are more overlooked features that are the key to understanding the unique taphonomic pathway undertaken by these fish. The process of finding these key features begins with understanding in detail what the fossils are comprised of, requiring the destruction of one specimen for observational purposes. First of all, experimental work has indicated that the parameters most effective in early fossilisation are a high salinity and an alkaline pH (Briggs et al, 1993). When the salinity is less >10 wt.% of the NaCl equivalent or the pH in the alkaline region, bacterial attacks on soft-tissue are greatly reduced and a carcass can rest on the sediment-water interface for many weeks to months without decomposition until it is buried by sediment (Gab et al, 2020). These conditions, in combination with an adhering biofilm and protective clay mask, would ensure fish carcasses have the best chance to be preserved, even when gas expulsions threaten the integrity and completeness of the fossils.

Taphonomic Methods

Thin section and scale fragment analysis (in the form of rock chips) again required the use of a Hitachi SU70 electron microscope. Fish material, mounted as rock chips, was coated in 35nm of a gold/palladium alloy, using the Cressington Sputter Coater 108auto. Gold/palladium was used, not only to reduce charging, but also to prevent loss of detail during imaging. All new thin sections were coated in carbon using the Cressington Carbon Coater, 108carbon/A and were coated in 25nm of carbon.

The voltage was set to 15kv for thin sections and rock chips. The thin sections were again viewed using BSEM and rock chips were imaged using secondary electron microscopy. The specific settings were kept near identical to the sedimentological and petrographic analysis as to match the standard of EDS mapping and imaging. Thin sections were imaged at no more than 5000x magnification, and rock chips no more than 15000x magnification.

Thin Sectioning Specimen P.8114

Specimen P.8114 (Figure 3.8c) is a well-preserved example of *Palaeoniscum freieslebeni*, preserved almost completely with only small portions of the scales and fins missing (Figure 4.1). The X-CT scan of specimen P.8114 (Figure 3.2) revealed that it would be necessary to cut the specimen in three places in order to accurately represent the whole specimen in thin section while also viewing the fossil/Marl Slate boundary in microscopic detail. The scan proved that the most effective way to view the fossil in thin section was to cut sections through the head, body and rear of the body just before the tail. The aim to observe how the fossil material interacted with the rock material and how they differed in composition and structure by observing the upper and lower contacts between the outer fossil material and Marl Slate. The thin sections were also used to produce an array of line scans across the upper and lower surfaces of the fossil material (Figure 4.4). The goal, to gain an idea of whether the fossil was coated in any adhesive or protective material, such as a clay mask or microbial mat, and how that coating varied on each surface. **(21)**

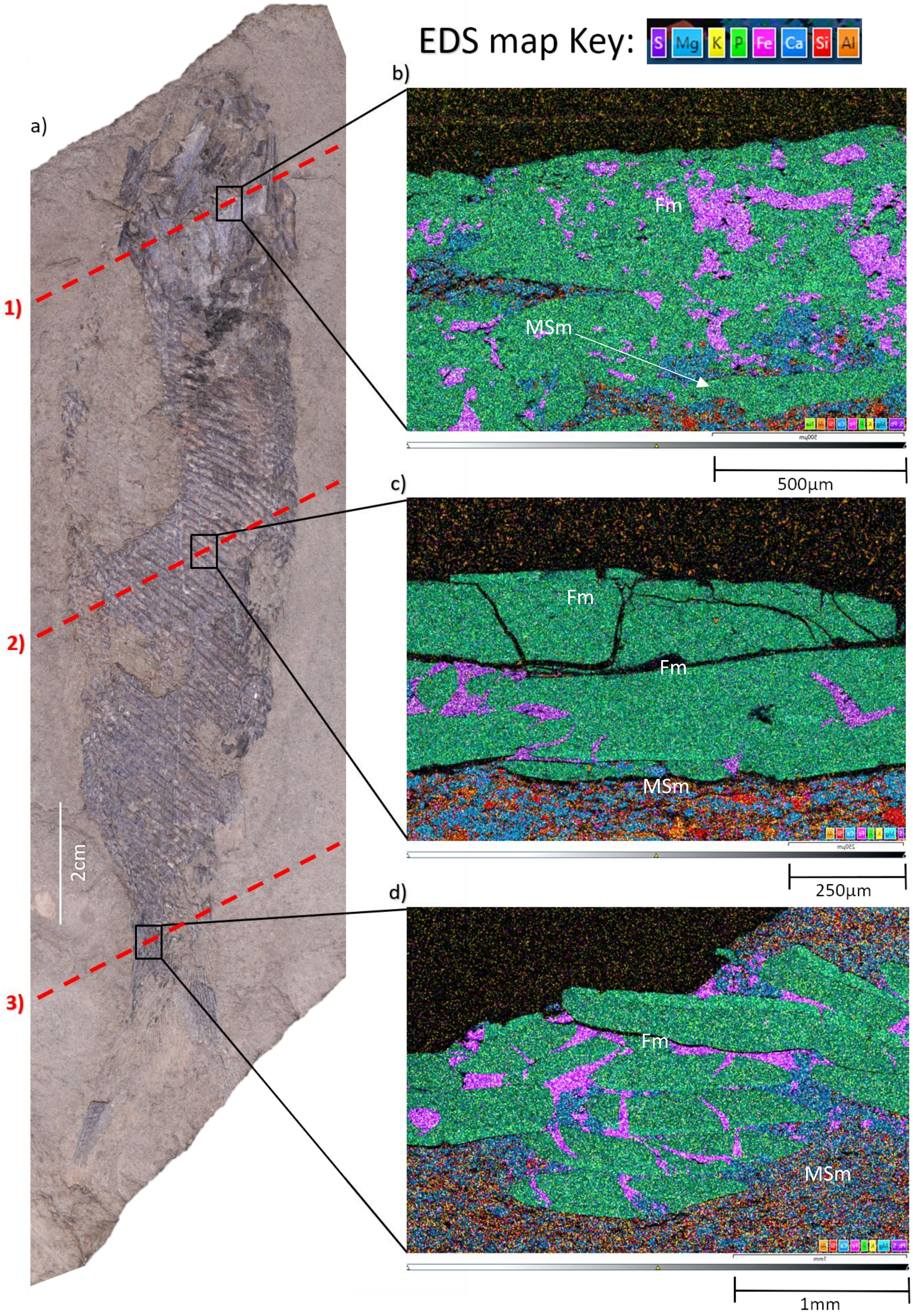


Figure 4.1: (a) a location map across *P. freieslebeni* specimen P.8114 (Figure 3.8c) displaying the lines at which serial sections were taken. (b) EDS map showcasing a cross section through the specimen's head. (c) EDS map of a cross section through the middle of the specimen's body. (d) EDS map through the base of the specimen's tail. Apatite = green, pyrite = pink. Fossil material (Fm), Marl Slate material (MSm).

The apatite/pyrite composition shown in figure 4.1 above is the standard for all studied specimens. Apatite is the primary component of the fossils, with areas of pyrite littered sporadically throughout the fossil material. The abundance of both pyrite and apatite within the fossil structure is evidence to suggest that mineralization of both occurred simultaneously during fossilisation, both minerals being the product of decay by SRB (Lepland et al, 2013 and Berg et al, 2020). The apatite is a result of the SRB using the fish material itself as a source of apatite, similar to the results found by Briggs and Kear (1994). The iron used to replace organic material with pyrite would have been sourced from iron sulphides already present in the sediment. The majority of pyrite within the Marl Slate is framboidal, indicating that it formed quite early diagenetically. As the Marl Slate is a thin unit, the diagenetic pyrite within must be recently formed and recycled by SRB during decay. Figure 4.1 makes clear that the composition of the fossils studied is continuous throughout the specimen. There is little change mineralogically throughout, the only variation is the size of the pyrite groups.

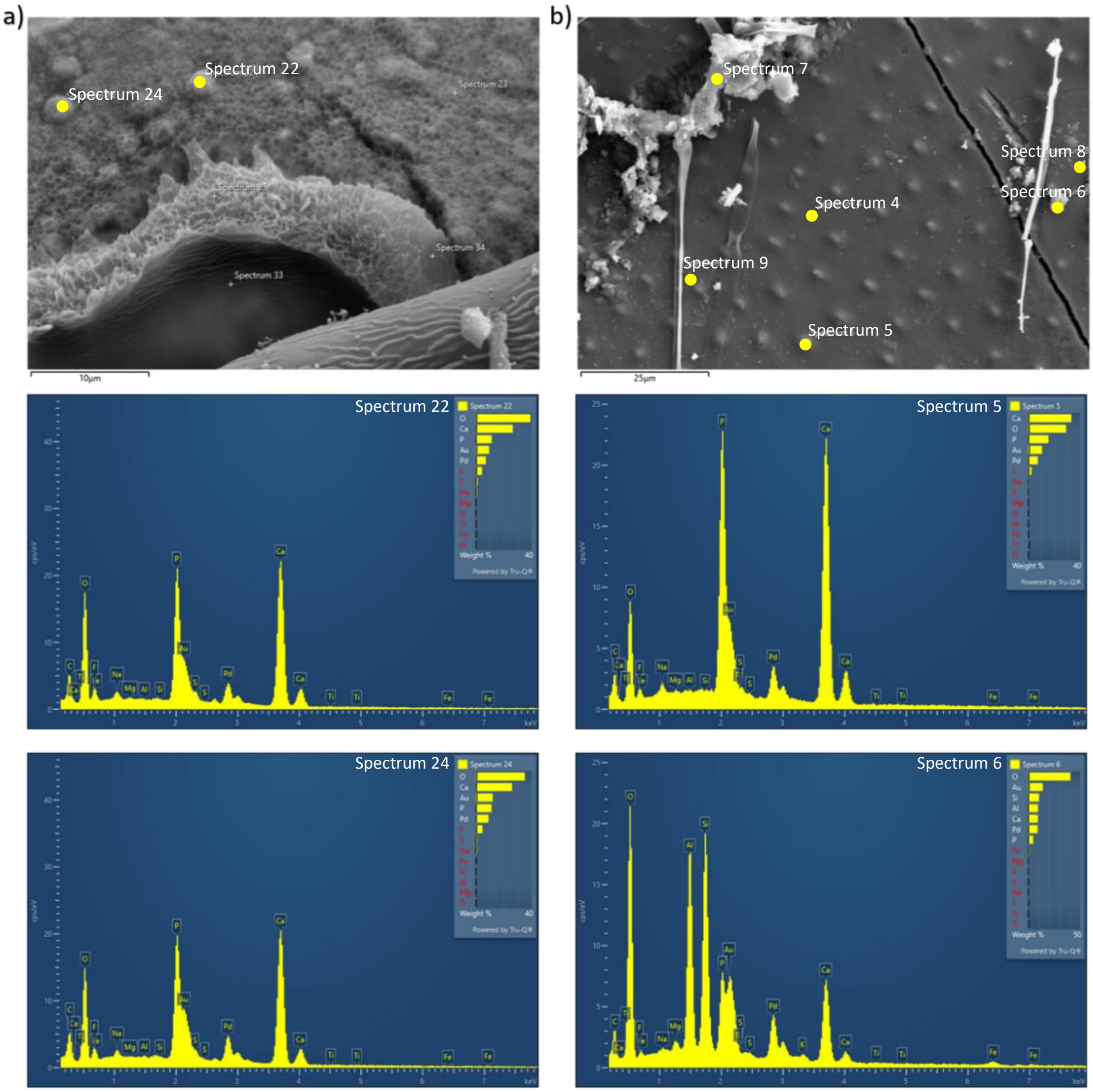


Figure 4.2: Point scan analysis of two fish scales from separate specimens. Each image displays a different texture of the scale surface. (a) specimen 39 displays a unique mesh-like texture, spectrums 22 and 24 showcasing the apatite structure (calcium phosphate) through identification of P and Ca elements. The carbon spike represents a carbon coating used on the samples during preparation. (b) specimen P.478 displays the more common “chicken skin” texture seen on the majority of fossil scale material studied here. Spectrum 5 showcases the apatite composition at the surface of the scale (results are the same for spectrums 4, 8 and 9). Spectrum 6 displays aluminium and silica peaks, likely representing clay (the same is true for spectrum 7).

The two specimens used in figure 4.2 provide the most distinct P and Ca peaks while also displaying the variation in scale textures, however results are coherent with all other specimens studied. Data found suggests that the pyrite within the fossil material is rarely at the surface of the fossil. Every point scan taken of fossil material, whether it is a scale, fin or bone, always displayed large phosphorus and calcium peaks, never iron or sulphur (Figure 4.2). The lack of pyrite in surface material may suggest that while replacement with apatite and pyrite did occur somewhat simultaneously, the initial surface replacement would have been purely recycled apatite. This is likely true as the first point of contact for SRB to begin decay and replacement would have been the hard parts of the outer part of the fish carcass, namely the skull bones and scales, both of which were comprised of apatite. This would have provided the initial source of P for apatite replacement before the need for iron sulphides in the sediment as primary apatite became sparser later on.

Presence of microbial mats

A microbial mat is a thin multi-layered sheet or biofilm of bacteria that grow at interfaces between different types of material, mostly on submerged surfaces like sea floors (Schieber et al, 2007). They have the capacity to adhere fossils to the sediment they lie on. They are often associated with decay and exceptional preservation of smaller marine fossils as they completely cover the carcass creating a microenvironment for the bacteria to feed on the organic matter within the carcass (O'Brien et al, 2008), eventually replacing it with whatever minerals are of sufficient amount to fuel the bacterial action. While this studies SEM analysis of the exposed surface of scales provided no direct evidence suggesting the presence of a biofilm over the top surface of the fossils, there is a significant piece of indirect evidence that can only be explained by the presence of an adhering material. Exploding fish (Figure 3.6c). The only way the fragmented skulls and stomachs of larger Marl Slate fish would have been preserved alongside the rest of the body is if the expulsion of gas occurred on the seafloor.

The only way a fish carcass full of gas would stay on the seafloor is if something was sticking it to the sediment, preventing floating. As seen in modern domestic fish, like goldfish, when they die their bodies sink to the bottom of the tank for a short period of time before the decaying stomach releases gasses into the head and stomach causing them to float upside down at the surface of the tank. In order to stay on the seafloor, a decaying fish carcass must be adhered to the sediment, the most likely way this occurred is via microbial mats (Figure 4.5, stage 2b). A biofilm would have covered the entirety of the fish carcass when it sank to the floor of the Zechstein Sea and adhered it to the sediment, cementing it down and preventing any floating. When the head or stomach exploded, the fragments would not travel far, keeping the carcass mostly whole and allowing the biofilm to extended over the fragments as well, preserving alongside the rest of the fossil.

The presence of microbial mats would help to explain the high standard of preservation seen in the Marl Slate fishes. When a carcass is completely covered by bacteria, all outlying decay factors are excluded. This allows the bacteria to replace the organic material in immense detail.

Presence of clay masks

Clays are often associated with exceptionally preserved fossils (Anderson et al, 2021). Similarly to microbial mats, clay masks completely cover the organism, limiting any outlying destructive factors (Gehling, 1999). Due to clay minerals being so fine, they preserve a mould of the outer surface of the organism in almost perfect detail (Locatelli et al, 2017). While evidence of a clay mask, in relation to the Marl Slate fish, could be considered minimal there is evidence within SEM work conducted during this study suggesting that a clay mask was indeed present (Figure 4.3). XRD data proves that clay is a vital component of Marl Slate sedimentology, specifically illite that likely formed via the transformation of smectite during early burial digenesis at low temperatures. The already present smectite merely needed a source of potassium to undergo the transformation, the majority of which likely arrived with the freshwater influx into the Zechstein Basin from the Variscan Front (Figure 2.8).

Kaolinite book structures are visible in the Marl Slate rock chips studied (Figure 2.6c), but are not as common as fibrous illite (Figure 2.6b) and smectite-illite structures (Figure 2.6d). The fact that illite is the dominant clay is important to note as green illite is known to display antibacterial properties because of its iron content (Hugget, 2005) and is often used in face masks for that very reason. While this is strong evidence suggesting that the sedimentology of the Marl Slate is the culprit for the high standard of preservation in these fossils, it also contradicts the presence of a biofilm. If illite is antibacterial then how was a strongly adhesive microbial mat able to form? The biota of the Marl Slate would not be as well preserved as it is with only the type of sediment influencing preservation. The answer to this question lies with the sulphur reducing bacteria and the original composition of the first clays deposited.

Confirmation of Biofilms and Clay Masks?

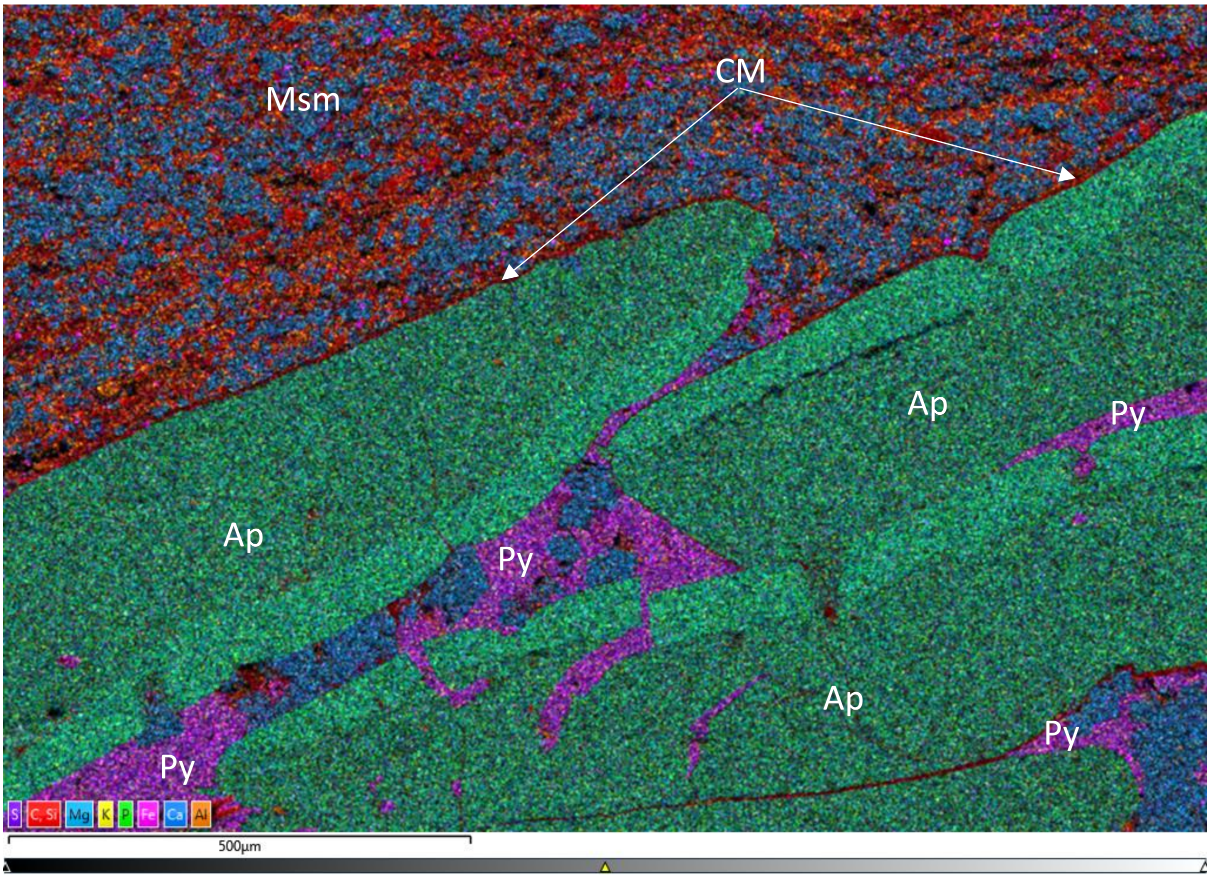


Figure 4.3: An EDS map covering an SEM image of a section of the tail from specimen P.8114. The image displays the standard apatite (Ap) and pyrite (Py) structure alongside the carbonate rich dolomitic muds of the Marl Slate (Msm). The feature of note is the thin red band covering the top surface of the green apatite material. The red band can be interpreted as silica rich clay or carbon rich matter, perhaps remnants of a biofilm and/or clay mask (CM).

SRB thrive in harsh anoxic conditions (Yuan et al, 2019), hence why they were the only organism able to initiate decay on the floor of the Zechstein Sea due to its stratified water column and more anoxic bottom waters. The anaerobic nature of the bacteria, as well as their natural resistance to the harshest of marine conditions, likely meant they already had some resistance to the antibacterial properties of some clays. Moreover, the originally precipitated clay was not illite at all, it was smectite pre-transformation. Meaning the clay in contact with the SRB would not have had the same antibacterial properties recognised in illite and would not have inhibited the growth of the bacteria. These factors in combination would have led to clay nucleation and mineral growth as a fine layer atop the SRB biofilm, adding another protective layer above the fish carcass and preventing any external decay factors from removing organic material. In other words, the biofilm would have

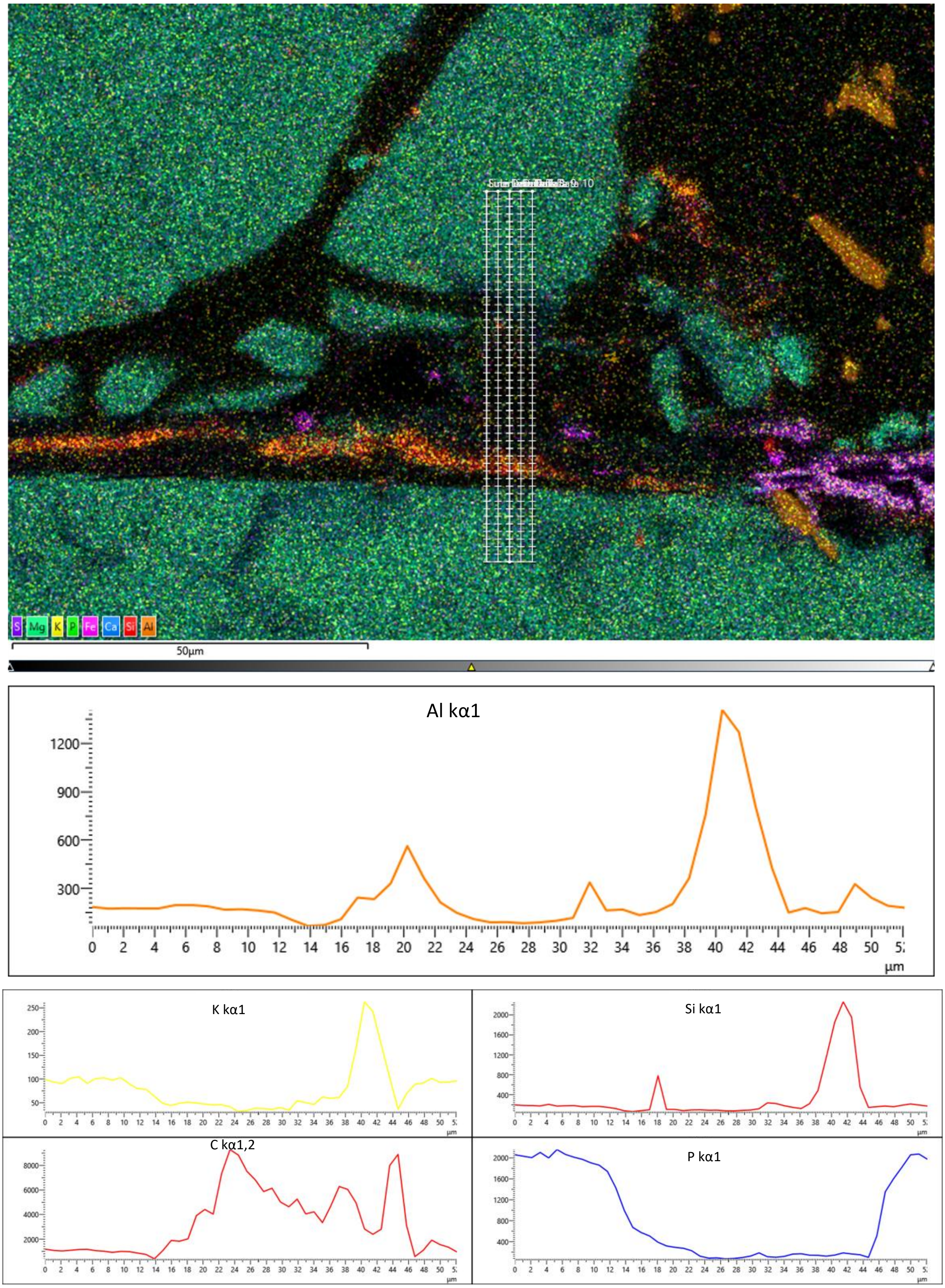


Figure 4.4: Microscopic line scans displaying the abundance of key elements through a section of the body thin section through specimen P.8114. The key proxy used for clay is Al (orange) alongside Si (Red) with K (yellow) confirming Illite. C (red) is the proxy for organic matter and P (blue) the proxy for apatite fossil material.

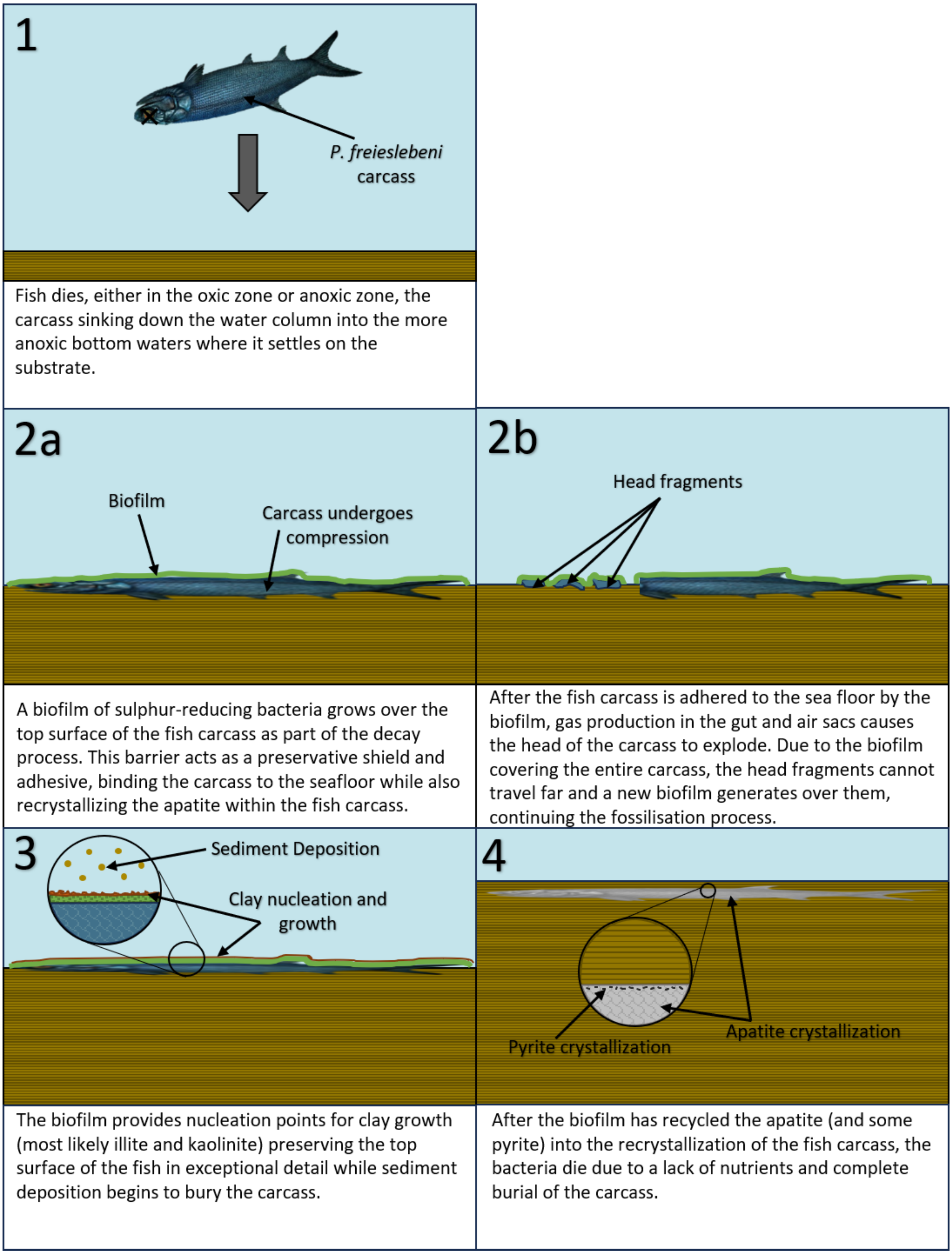
created nucleation points for clay mineral growth, further enhancing the preservation of the Marl Slate fish.

The direct evidence confirming the presence of a clay mask or microbial mat is small, however their presence cannot be denied. A thin layer of material is present in SEM results (Figure 4.3) and clearly displays a silica/carbon rich material covering the apatite fish material. In order to confirm the layer visible was indeed a clay mask or biofilm, higher magnification line scans were conducted to confirm the elemental composition of the layer (Figure 4.4). The data shown above is not unique, a multitude of scans were taken across all three slides through specimen P.8114, acquiring data from a vast number of locations across the fossil material. The scans were taken through the surface of the apatite material to ensure the targeted layer was scanned.

A microscopic line scan through the body of specimen P.8114 shows clear peaks displaying aluminium, silica and potassium on the outer surface of the apatite structures. These three elements indicate illite clay is present in the section, as can be seen in the SEM image also, even if it is faint. Also of interesting is the carbon peak. All thin sections were coated in carbon before use under SEM conditions which is why carbon will always be present in small amounts; yet the peak here is extremely high indicating that there is a strong source of carbon present. This is potentially organic carbon left behind as a trace of an organic biofilm that first coated the fish carcass. Biofilms would be extremely densely populated so such a high carbon signature wouldn’t be out of the ordinary. Notice also how the carbon peaks are in between the clay peaks and the apatite (indicated by phosphorus peaks). This may mean the biofilm atop the carcass provided a suitable surface for clay mineral growth to begin.

Taphonomic Pathway

This study defines a taphonomic pathway as the route of events undergone by an organism after its death that resulted in its preservation. The taphonomic pathway of the Marl Slate fish is unique in that the environment the fish lived and died in is largely different from any studied before.



Fish dies, either in the oxic zone or anoxic zone, the carcass sinking down the water column into the more anoxic bottom waters where it settles on the substrate.

A biofilm of sulphur-reducing bacteria grows over the top surface of the fish carcass as part of the decay process. This barrier acts as a preservative shield and adhesive, binding the carcass to the seafloor while also recrystallizing the apatite within the fish carcass.

After the fish carcass is adhered to the sea floor by the biofilm, gas production in the gut and air sacs causes the head of the carcass to explode. Due to the biofilm covering the entire carcass, the head fragments cannot travel far and a new biofilm generates over them, continuing the fossilisation process.

The biofilm provides nucleation points for clay growth (most likely illite and kaolinite) preserving the top surface of the fish in exceptional detail while sediment deposition begins to bury the carcass.

After the biofilm has recycled the apatite (and some pyrite) into the recrystallization of the fish carcass, the bacteria die due to a lack of nutrients and complete burial of the carcass.

Figure 4.5: Comic strip-style staged diagram displaying the taphonomic pathway of a *P. freieslebeni* carcass beginning with the organism's death and ending with its complete fossilization in apatite and pyrite within the Marl Slate.

To have the highest likelihood of preservation, a fish must die in the lower portions of the water column (Figure 4.5, stage 1). If death occurs in the upper waters the likelihood of predation and scavenging of the carcass increases dramatically due to the more oxygenated, less harsh waters containing a larger variation of marine life. If death occurs lower down in the water column, the carcass is more likely to sink to the sea floor, initiating the first steps of the taphonomic pathway (Figure 4.5). Once the carcass settles on the Zechstein Sea floor in the anoxic bottom waters, scavenging becomes negligible and decay rates slow down drastically due to a lack of aerobic bacteria. This allows for anaerobic, sulphur reducing bacteria to take over. With no significant competition, the bacteria spread over the organism, creating a film or microbial mat over the entire carcass (Figure 4.5, stage 2a). Not only does this initiate replacement of the organic material, it also creates a microenvironment where the carcass is subject to only bacterial action, all external forces acting on the carcass are minimized. This paired with the extreme low energy of the lower waters of the Zechstein Sea created the perfect environment for rapid decay and replacement of the fish carcasses.

The next major step is the onset of burial. With the microbial mat has formed fully, the outer surface provides nucleation points for clay growth (Figure 4.5, stage 3). Smectite, and potentially kaolinite, precipitate out of the water concealing the outer surface of the biofilm covered carcass in a thin layer of clay. This adds another protective layer between the carcass and the external environment, further enhancing preservation potential. During clay mineralisation, sediment deposition would have begun burying the carcass underneath dolomitic muds, likely darker in sediment colour due to the lower oxygen content. Burial finalises the beginning of the process, allowing early diagenesis to take over (Figure 4.5, stage 4). Bacterial action would continue for a short while in the sulphate reduction zone, continuing to replace organic material with hard apatite and initiating more concentrated pyrite replacement simultaneously as the local source of phosphorus lessens. Diagenesis would begin the transformation of smectite to illite and begin creating the picture seen today in the fossil record.

Concluding Comments

The taphonomic pathway undertaken by the Marl Slate fish is equally unique as it is complex. There are a multitude of factors influencing the preservation potential of the fishes yet there are three main factors controlling the high standard of preservation seen in the studied specimens. The first is the anoxic environment; the stratified water column of the shallow Zechstein Sea allowed for relatively undisturbed anaerobic bacterial action on the sea floor. The second is the high likelihood of a biofilm replacing the carcasses with apatite using the fish material itself as a local source of phosphorus while simultaneously inducing pyrite replacement due to being within the sulphate reduction zone. The third is burial, initiated by clay nucleation atop the biofilm. While the sedimentation rate of the Marl Slate was not particularly rapid geologically speaking, the complete concealment of these fish carcasses in a thin layer of clay would have been. Such an environment would have shielded the carcass from any external forces from the start; and combined with the low energy, hostile environment of the lower Zechstein Sea, it created a near perfect environment for the preservation of these fish.

Rapid burial is a key factor in the preservation of these fish, but would not be nearly as effective without the other two prerequisite factors. Rapid burial was not the driving factor in the preservation of these fish. It was the anoxic, low energy environment, combined with the presence of sulphur reducing bacteria and the likely formation of biofilms and clay masks, that created such a unique environment, somewhat individual to each fish that was preserved. With regards to biofilms and clay masks; due to the time frame and equipment available the evidence confirming the presence of both is not as concrete as it could be. However, there is enough evidence in the data gathered to suggest that they were an influential factor in the preservation of the fishes. There must have been something adhering the fish carcasses to the sea floor during the head explosions to keep the fragments so close to the rest of the organism. In such a harsh anoxic environment, microbial mats are the most likely suspect. Stage 2b of figure 4.5 explains their involvement in detail.

A drawback of the method used to study specimen P.8114 (Figure 3.8c) specifically was that partial destruction of the specimen was required in order to study it in the way that was required. In order to continue the study at a later date, more specimens may have to be cut into thin sections in order to gather a larger data pool. The results from multiple specimens would be extremely helpful in studying the internal pyrite and apatite structures as well as any differences within the external apatite. However, well preserved specimens would be required and there are not many collectors or museums that would allow the destruction of such a prized specimen. Even if higher magnification equipment could provide concrete confirmation of the presence of a biofilm and/or a clay mask.

Chapter 5:

Discussions and Conclusions

Summary and Key Findings

The problem with researching the Marl Slate, prior to this study, was that the large majority of literature surrounding the thin geological unit was answering questions about the palaeontology and taxonomy of the rock. The fossil biota had only been studied at face value, rather than being delved into on a microscopic level. Even less literature covered the sedimentology and geochemistry and there is next to nothing covering the taphonomy of the fossil fish, only comparative literature regarding lagerstätten like the Burgess Shale or Solnhofen Limestone, specifically work by Derek Briggs. This study has changed that by uncovering key information regarding the fossilisation of the Late Permian, Lopingian, Marl Slate fish. The information uncovered has been used to propose a model to explaining the taphonomic pathway the fishes followed in order to become preserved at a quality only a few steps below a lagerstätten like the Burgess Shale.

The key findings of this study included uncovering problems and missing stages in the taphonomic process that strongly suggested the involvement of biofilms and clay masks, not only to enhance the preservation potential of decaying fish, but to adhere them to the anoxic sea floor; keeping whole carcasses intact even when gas expulsions caused the heads and stomachs of decaying fish to explode. Not only do the results provide a detailed explanation of how the fish became preserved, but it has also gleaned more surface level answers like what the fishes are actually preserved in. SEM analysis revealed that 100% of the Marl Slate fish used as part of this study are preserved in a majority of apatite with sporadic bursts of pyrite throughout the apatite majority. Sulphur reducing bacteria require a source of phosphorus in order to replace organic matter with apatite, one of the most monumental findings during this study is that the SRB used the fish carcasses as a local source of phosphorus to replace the biological apatite within the fish bones and scales with harder, mineralised apatite, matching the findings of Briggs and Kear (1994). This may seem simple at base value; however, it was the key to confirming the involvement and role of sulphur reducing bacteria.

It is easy to invoke rapid burial as the sole mechanism explaining exceptional and near-exceptional preservation, however the study undertaken here proves the presence of several other complicating factors, arguably the most influential being the presence of sulphur reducing bacteria. However, in order for the SRB to be effective, the pressure must have been high enough so the fish carcasses could sink to the bottom sediment (Yuan et al, 2019) and the relative anoxia must have been high enough to significantly reduce scavenging. Only then would the SRB have condensed to form separate microbial mats over each decaying carcass. The relative anoxia of the Zechstein bottom waters would have induced pyritization within the sulphate reduction zone (Berg et al, 2020), which is recognised in SEM data. The nucleation and deposition of magnesium rich clays on top of these biofilms would have enhanced preservation potential even further by acting as antibacterial masks, illite specifically likely substituting aluminium with magnesium from the dolomite rich environment. The transformation of smectite into illite would likely have occurred after burial during diagenesis. While more effective antibacterial clays like berthierine and chlorite do exist, they are not present and were not recognised in any petrographic or taphonomic analysis during this study. Although, data from Bhattacharyya (1983) does suggest berthierine may form via progressive transformation from kaolinite with the addition of magnesium promoting the transformation. Perhaps, had the Marl Slate had a higher abundance of Mg rich kaolinite, berthierine may have formed.

Interpretations

The study was undertaken in a coherent way, beginning with the palaeontology of the fish fossils involved in the study. The analysis of the fishes resulted in the knowledge that they were preserved primarily as apatite, yet there was no evidence of an external source of apatite or phosphorus in the sedimentology or literature to explain how apatite had replaced the fish material. It was later uncovered that the fish carcasses had to have provided a sufficient enough local source of phosphorus for their own replacement. The calcium within apatite's structure was already spoken for within the dolomite rich sediment.

A combination of field and lab work allowed a conclusion to be made about the depositional environment of the early Zechstein Sea. As the basin filled with shallow, brackish waters the conditions were harsh and oxygen deprived, hence the dark, organic rich layers at the bottom of the Marl Slate unit. These conditions were harsh enough to play a role in the mass deaths of nektobenthic organisms, causing the increased abundance of fossil material in the lower portion of the Marl Slate. As freshwater influx stratified the water column and induced the more varved sediment pattern, more fish began to populate the upper, more oxygenated waters. Only when they died in the lower waters did they have a chance of being preserved. Understanding the depositional environment allowed for the final step to be made into figuring out the taphonomy of the Marl Slate.

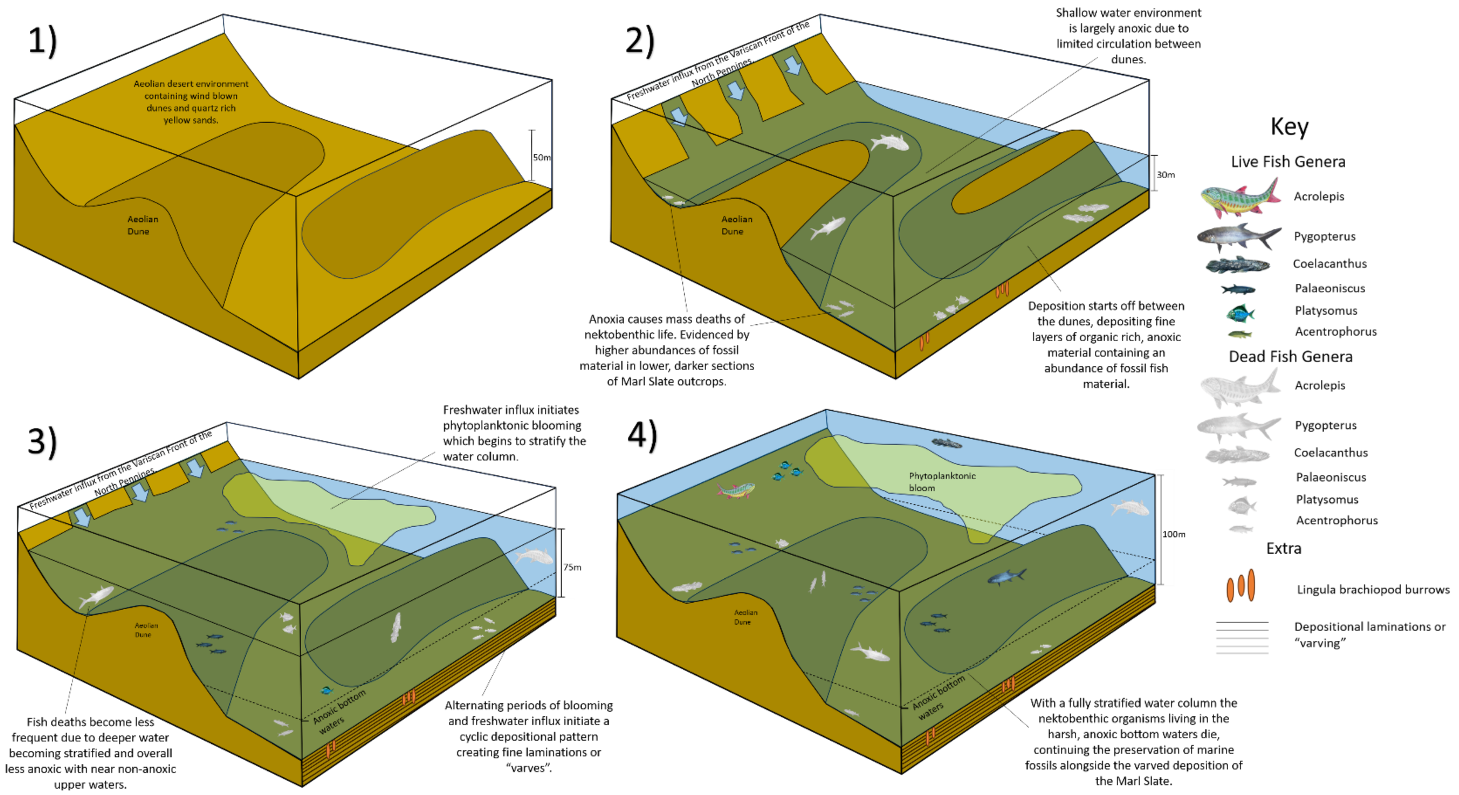


Figure 5.1: Block model portraying the depositional environment of the Marl Slate within the Zechstein Sea alongside the Marl Slate biota. (1) the environment began as a vast desert plain containing large scale aeolian dunes with the Permian Yellow Sands controlling the topography of the basin. (2) freshwater influx from the Variscan Front flooded the Early Permian desert and induced an anoxic, shallow water environment between the large dunes, initially culling the early nektobenthic life and depositing dark, organic rich sediment. (3) the freshwater initiated phytoplanktonic blooming in the surface waters, reducing the oxygen content of the bottom waters further and stratifying the water column. The cyclic nature of the environment induced a repetitive depositional cycle forming thin laminations or "varves". (4) the decrease in oxygen content increased the mortality rate of all benthic and nektonic life inhabiting the bottom waters between upstanding dunes inducing exceptional preservation in those areas, while increasing the oxygen content of the upper waters and completing the complex depositional environment.

The taphonomic pathway undergone by the Marl Slate fishes appears to be specific to the fish themselves. Mineralization appears to have occurred simultaneously with decay, specifically with pyrite and phosphate mineralization of internal and external structures respectively. The bacterial decay of the Marl Slate fish influenced local ion concentrations to favour the simultaneous pyrite and phosphate mineralization whilst also forming a biofilm over the top surface of the carcass allowing for the nucleation of clays as a protective mask preventing any external interference. A comparative example would be the Solnhofen Limestone of southern Germany. The unit is considered a lagerstätten due to its exceptionally preserved fossil assemblages, many of which contain phosphatized soft tissues; precisely 26% of 711 fish samples studied by Briggs and Kear (1993) and Kear et al (1995). While the phosphatised tissue is a similarity with the Marl Slate, it is interesting to note that the soft-tissues of the Solnhofen Limestone retain subcellular details which could reflect a supersaturated, external (likely sedimentary) source of phosphorus (Wilby, 1993). The interesting part is that the Solnhofen Limestone is thought to have been deposited within stagnant marine basins with high salt and low oxygen contents. This is remarkably similar to the depositional environment of the Marl Slate suggested in this study. But if the depositional environment was so similar, why is the Marl Slate biota preserved to a lesser degree, why is there an absence of soft-tissues preserved in the Marl Slate compared to the Solnhofen Limestone? To understand the similarities and differences, a closer comparison would have to be undertaken; looking microscopically at fossil material and sedimentary samples from each unit to determine the differences in the origin of the phosphorus and taphonomic pathways. This study is the first step towards attaining results like these, fossils need to be studied in such precise detail to uncover their history. Thin sections, as part of this study, accurately display the composition of the fossils compared to the sediment surrounding them. This study takes it one step further by using that data to forge models to explain the depositional environment of the Marl Slate and the taphonomic pathway undergone by its fish. If comparable data and models were available for other units, like the Solnhofen Limestone, it would be extremely beneficial to understanding the taphonomy of phosphatized tissues as well as better understanding exceptional preservation as a whole.

It would be wrong to say the results attained, regarding the fossilisation of the fish, were expected. While it was understood that the depositional environment of the Marl Slate would have to be shallow, near anoxic and of relatively low energy in order to preserve the complex anatomy of Permian fish, there was little to no literature mentioning how the fish actually got preserved. This meant that there were no expectations except that something must have caused such a good preservational standard throughout the Marl Slate unit. The early Zechstein Sea is often compared to the modern-day Black Sea. Demaison and Moore (1980) suggest that the Black Sea can be categorised as an anoxic silled basin, meaning the depositional environment of the Marl Slate cannot be that dissimilar. The results of this study confirm that the Marl Slate was deposited in an anoxic silled basin, the only differences are the presence of upstanding aeolian dunes (from the previous Early Permian desert) and a stratified water column induced by freshwater influx fuelling seasonal phytoplanktonic blooms.

While the majority of the study's findings fulfil the initial aims, there is one set of results that provide more questions than answers, specifically the lack of conodonts within the rock samples. The fact that no conodonts were found at all by C.M Henderson is an unexpected mystery, especially when Swift (1995) found them in high abundance at localities close by those samples here. It is thought that the conodonts present in the Marl Slate likely migrated into the Zechstein Basin alongside a large proportion of open water fishes after the water column became stratified (C.M Henderson, pers comm). The early Zechstein Sea would have been too harsh an environment to sustain large populations of nektobenthic conodonts. Shallow-water anoxia would have been localised between upstanding aeolian dunes; such an environment would inhibit any nektobenthic life. Conodonts may simply prefer more oxygenated, open water conditions. The outcrops sampled as part of this study were close to the basins edge and likely shallower environments. Perhaps more dense populations of conodonts could be found within Marl Slate deposits that are more centrally located within the Zechstein Basin. The water would have been deeper with a larger oxygenated zone in the upper part of the water column, a much more sustainable environment for nektobenthic organisms like conodonts.

Implications

It is correct to say that the results displayed here fill a void in the literature regarding Marl Slate taphonomy. Not only was the area previously understudied, but the results gleaned here not only fill that gap, but suggest a taphonomic pathway unique to the suggested environment of deposition. The research undertaken proposes a depositional model and environment for the Marl Slate, explaining how the environment developed from the Early Permian desert, as well as a taphonomic model of the fossilisation process the fishes went through in an area of study that is widely unknown and missing from the literature.

The results improve the overall understanding of taphonomy in anoxic environments while providing insight to palaeontology as a whole. The research not only uncovers key information about the Marl Slate and the taphonomy of its biota, but it sheds light on the rock unit as a whole. The Marl Slate displays many of the properties important in cap rocks, and with the Permian Yellow Sands beneath, could be an area of study regarding carbon capture and storage or potentially other approaches to green energy. The Marl Slate does contain chlorite, which is considered a key mineral for preserving reservoir quality by Charlaftis et al (2021). While the Marl Slate is unlikely to contain a viable source of fossil fuels, the unit may provide useful if studied with regards to carbon capture and storage (CCS). In relation to the Permian Yellow Sands below the Marl Slate, Charlaftis et al (2022) discuss the quality of sandstone reservoirs which may be useful in the assessment for CCS if paired with a study assessing the Marl Slates viability as a suitable cap rock. Additionally, the Marl Slate is the western equivalent of the German Kupferschiefer deposit or “Copper Shale” (Vaughan and Turner, 1980). That unit in particular is home to an abundance of rare earth elements and has been mined for copper for centuries. While the Marl Slate is too thin to be viable for REE mining it could provide insight on the type lithologies where REEs are most common as well as the environments required for the formation/deposition of REEs.

Limitations

With a field of research so widely understudied, the limitations were unknown to begin with. Other than the lack of literature on the topic of Marl Slate taphonomy, there was nothing preventing the go forward the research had initially. However, it was quickly realised that the Durham University collection of Marl Slate fish was not that large. With 34 total specimens, it was decided to look elsewhere for other examples to help provide a more accurate representation of the Marl Slate biota. The Durham University collection largely consisted of many specimens of the same species (*P. Freieslebeni*), all of which were small and broken up with age. The Natural History Museum in London was consulted as well as the Hancock Museum in Newcastle; both had a much larger collection of fossils on display and in storage, many of which were of higher quality **(22)**. The visits provided insight to the large variety of species present within the early Zechstein Sea. However, a major step in this study was gleaning an idea of what the fish fossils looked like in cross section and as expected, neither museum would allow the destruction of one of their specimens. As a result, the best example of *P. freieslebeni* (specimen P.8114) from the Durham collection was used and it provided informative, high-resolution results of the specimen in cross section at a microscopic scale and revealed that the fossils were not only comprised of apatite but pyrite as well, a key revelation during the study.

Two more minor limitations include the training requirement for use of Durham Universities TEM. If the TEM was used, it would accurately confirm or deny the presence of a biofilm or clay mask within the thin sections through specimen P.8114, both of which are essential parts of the taphonomic model this study puts forward. There is also the lack of comparable data. The Early Zechstein Sea is analogous to the modern-day Black Sea according to classifications by Demaison and Moore (1980); and the final product of Black Sea deposition will not be visible for millions of years.

Recommendations

The study could be advanced through the use of a TEM. Such equipment would allow for atomic level analysis of the Marl Slate, sedimentologically and paleontologically. The results gained from such a study would be essential to backing up the results found in this one, as well as solidifying the relevance and accuracy of the models proposed. If the study were to be conducted on a wider scale, it would be beneficial to create thin sections through more than one specimen in order to cement the results found from the single sample studied here. It would be beneficial to conduct XRD analysis on multiple fossil specimens to gain a higher resolution dataset explaining the exact composition of the fossil material, similar to work conducted by Bartsiokas and Middleton (1992), perhaps suggesting a precise apatite/pyrite ratio. It would be essential to confirm or deny the presence of biofilms and clay masks beyond any doubt, as they are an important part of the taphonomic model. It would also be essential to delve deeper into how diagenesis affected the fossils from their immediate burial at such a shallow depth and afterward as they were buried further. In short, while the study provides the answers it is supposed to, there is still more to be done to finalise and cement those answers in place.

Conclusion

The aims of the study were to understand how the Marl Slate fishes became preserved in such a thin layer of the Zechstein Z1 cycle, to understand why the fishes are so well preserved and to gain an idea of the depositional environment of the Marl Slate and why it is so special in relation to the preservation of these fishes. The key question being how exactly the Marl Slate fishes became preserved. It can be confidently stated that the results of the study do indeed fulfil the aims. The Marl Slate unit was deposited during a short period of geological time during the Capitanian stage of the Upper Guadalupian Epoch (approximately 264Ma). Many fishes would have migrated into the Zechstein Basin with the first transgression; however, the depositional environment was initially too harsh for nektobenthic organisms, anoxia causing the deaths of the fishes, initiating their preservation early on during Marl Slate deposition. Both of these factors explain the fish's preservation within such a thin unit. As to why the fishes are so well preserved, there are a multitude of factors aiding in their preservation. The fish were adhered to an anoxic sea floor via microbial mats and replaced with hard apatite as well as pyrite before being buried by a mixture of antibacterial clays and dolomite. The anoxic environment would have prevented any scavenging and would have been low enough in energy to mitigate any fragmentation. The microbial mat and resulting clay mask would have further prevented any external destructive factors leading to near-exceptional preservation of fish scales and bones. With relation to the depositional environment, the taphonomic pathway would have begun in the anoxic bottom waters of a stratified water column. The environment in question was localised between upstanding aeolian dunes remnant from the early Permian desert. The dunes would have limited any water circulation even with freshwater influx and seasonal overturn via phytoplanktonic blooms, eventually leading to the near-exceptional preservation of the Marl Slate fish. Figure 5.1 combines all of this information in a compacted 3D storyboard of block diagrams.

The results found here have significant sedimentological, palaeontological and taphonomic importance because not only is the unique preservation of the Marl Slate fishes explained, but the depositional environment is uncovered as well. Past literature regarding the Marl Slate is limited to the taxonomy of the biota; this study deepens the knowledge of the environment where the fishes lived while also providing an explanation of how they became so well preserved. The taphonomic pathway suggested is unique to the depositional environment, only comparable to the modern-day Black Sea where the end product is millions of years from completion. Higher magnification could narrow the results of the study, confirming the presence of microbial mats and clay masks while using multiple fish specimens for thin sectioning. It is appreciated that the destruction of such prized specimens is preferably avoidable, however when tasked with the uncovering of such a unique environment and taphonomic pathway, all options should be considered. These fossils required detailed analysis of their external surface, the main limitations of the study were the lack of excellent specimens available for thin sectioning and the time required to study them.

The Marl Slate is a small unit within the Upper Permian; however, it is unique both taphonomically and sedimentologically and should not be brushed over. This study provides essential insight into the inner workings of the depositional environment and taphonomy of the Marl Slate, proposing the first models for the taphonomic pathway undertaken by the Marl Slate fish, as well as the formation and development of its depositional environment. The quality of the fossils is not that of a Lagerstätten, however the process of how they preserved may provide insight into the formation of similar, exceptionally preserved fossil deposits elsewhere. This research recognises the Marl Slate as a unique opportunity to fully appreciate the harsh, anoxic environment of the first Zechstein transgression as well as the significant impact the understanding of its taphonomy has on palaeoecology and fossil preservation as a whole.

Future Work

- It would be beneficial to understanding how the Zechstein Sea changed from the basins edge to its centre. To study fish fossils found along that transect would be an opportunity to understand how the environment changed, and how the taphonomic pathway of the fishes varied across the whole environment.
- The study of a larger pool of thin sectioned specimens would be necessary in order to find a trend regarding the occurrence of biofilms and clay masks, as well as study of their composition.
- It would be extremely useful to delve into which species of bacteria would form the most adhesive biofilm or whether decay rates are influenced by the type of bacteria involved.
- It would be essential to discover which types of clay would provide the best preservational potential, whether the transformation of smectite to illite truly would have enhanced preservation of the fish.
- More general study could include the viability of the Marl Slate for REEs or the potential for the Marl Slate to be used as a cap rock when injecting carbon into the Yellow Sands formation below. The latter being of large relevance and importance currently.
- More extensive and more detailed X-CT and chemical 3D mapping of multiple samples would be beneficial to understanding the relationship between fossil material and sediment.

- Conducting experimental work on the decay and mineralisation of small sections of modern fish, similar to *P. freieslebeni*, would provide an exceptional understanding of how fish scales and marine soft tissues react to certain decay and mineralisation conditions.
- It would be useful to sample more sites throughout County Durham, perhaps from the Kupferschiefer also, for sedimentary as well as fossil samples to gain a greater understanding of the Marl Slate Zh1 transgression across NW Europe.

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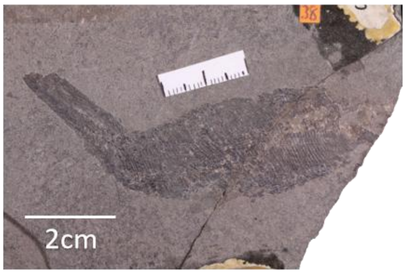
Appendix A: Durham Marl Slate Fossil Collection

a) Palaeoniscum freieslebeni (P.8114) – Durham University

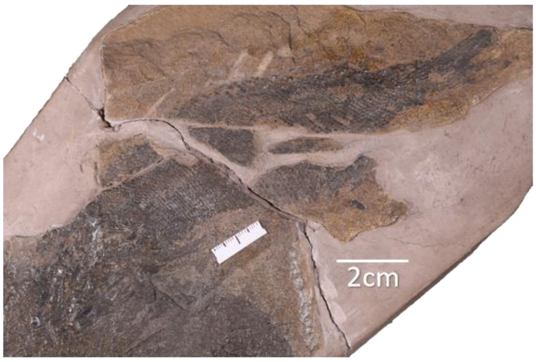
b) Palaeoniscum freieslebeni (P.471) – Durham University



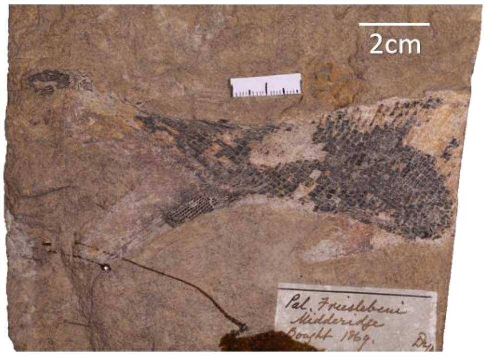
c) Palaeoniscum freieslebeni (P.473) – Durham University

d) Palaeoniscum freieslebeni (P.476) – Durham University

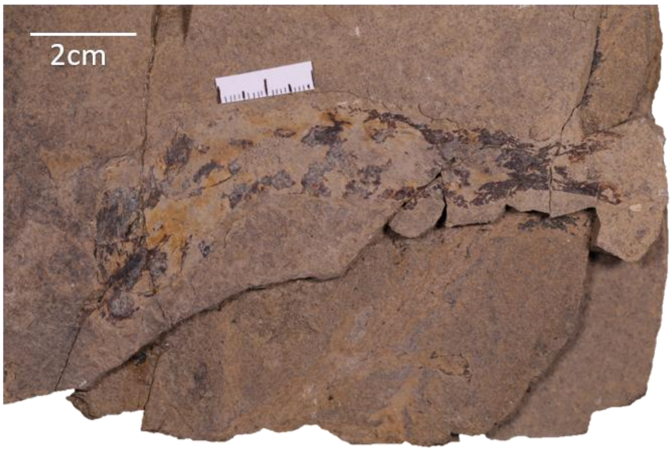
e) Palaeoniscum freieslebeni (P.477) – Durham University



g) Palaeoniscum freieslebeni (P.479) – Durham University



f) Palaeoniscum freieslebeni (P.478) – Durham University

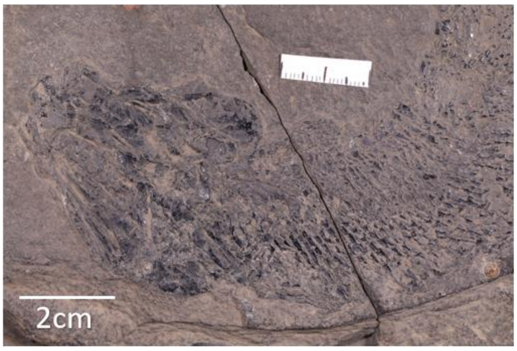


a) *Palaeoniscum freieslebeni* (P.8118) – Durham University

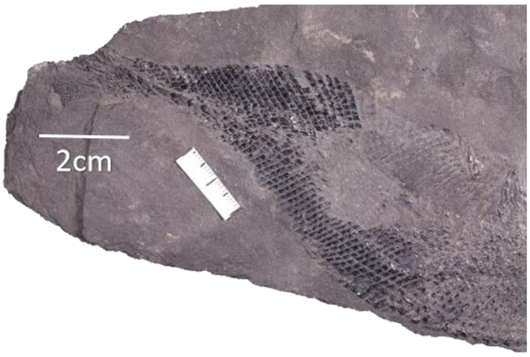
b) *Palaeoniscum freieslebeni* (P.8119) – Durham University

c) *Palaeoniscum freieslebeni* (P.9254) – Durham University

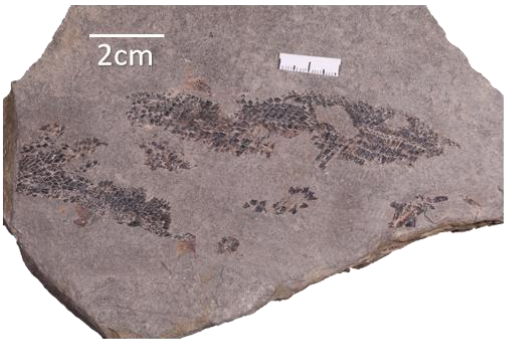
d) Juvenile *Palaeoniscum freieslebeni* (P.9299) – Durham University



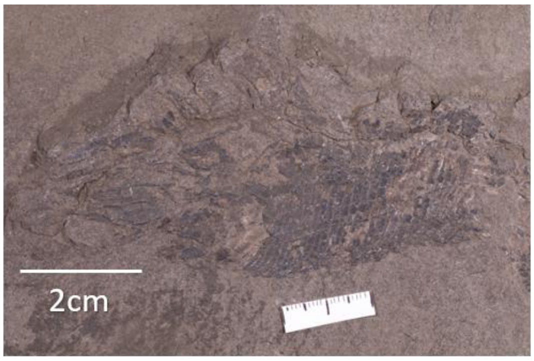
a) *Palaeoniscum freieslebeni* (P.1478) – Durham University



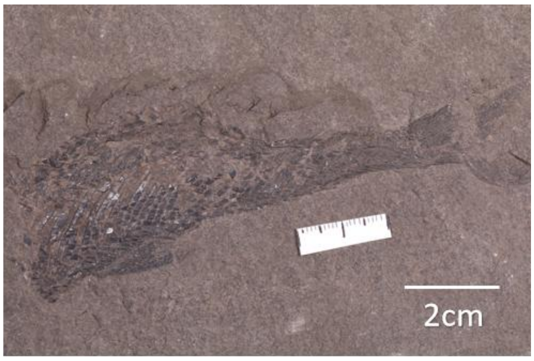
e) *Palaeoniscum freieslebeni* (P.469) – Durham University



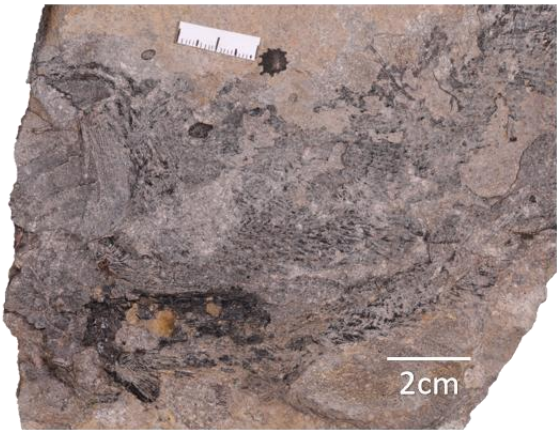
e) *Palaeoniscum freieslebeni* (P.8795) – Durham University



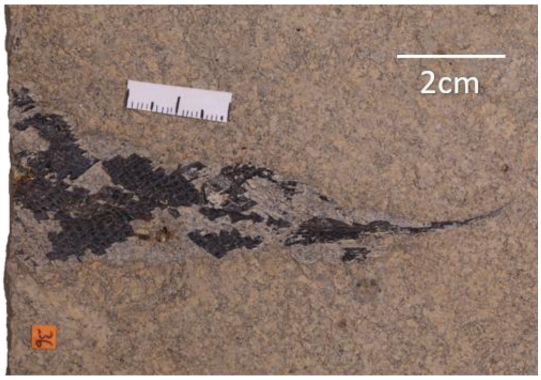
a) *Palaeoniscum freieslebeni* (32)
– Durham University



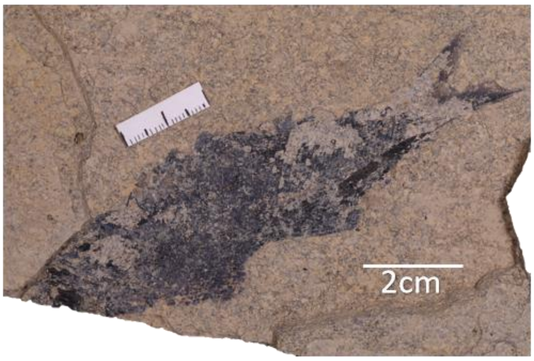
b) *Palaeoniscum freieslebeni* (33)
– Durham University



c) *Palaeoniscum freieslebeni* (34)
– Durham University



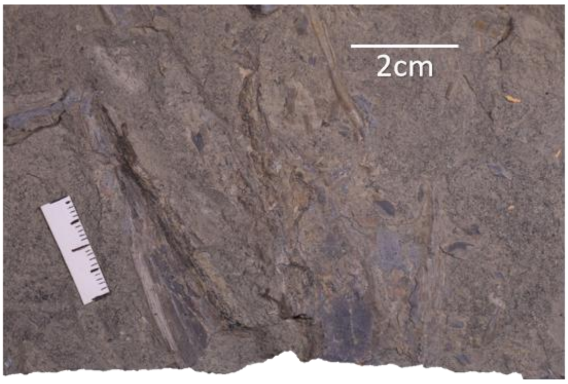
d) *Palaeoniscum freieslebeni* (36a)
– Durham University



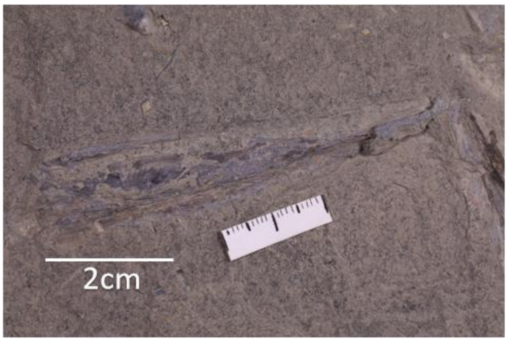
e) *Palaeoniscum freieslebeni* (36b)
– Durham University

f) *Palaeoniscum freieslebeni* (37)
– Durham University

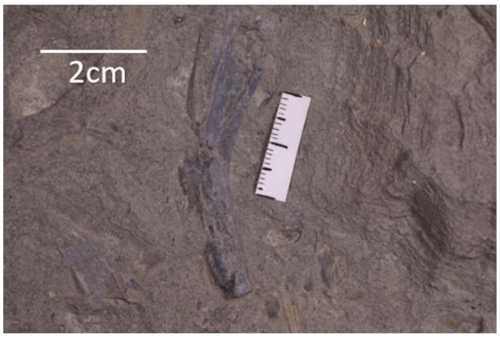
g) *Palaeoniscum freieslebeni* (39)
– Durham University



a) *Palaeoniscum comtus* Fragments (V.44a) – Durham University



b) *Palaeoniscum comtus* Fragments (V.44b) – Durham University

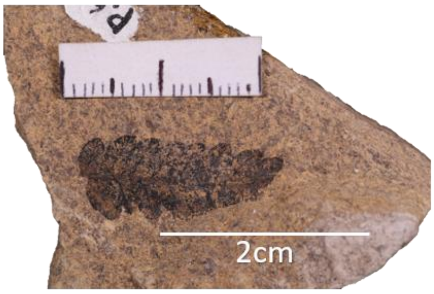


c) *Palaeoniscum comtus* Fragments (V.44c) – Durham University

d) Cranidial Bone, unknown species (P.8043) – Durham University

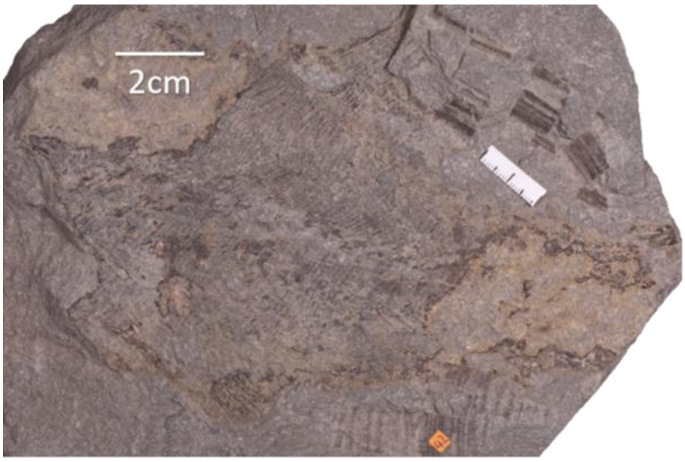
e) Coprolite, unknown species (P.8354) – Durham University

f) *Acrolepis sedgewickii* Scale (P.6614) – Durham University

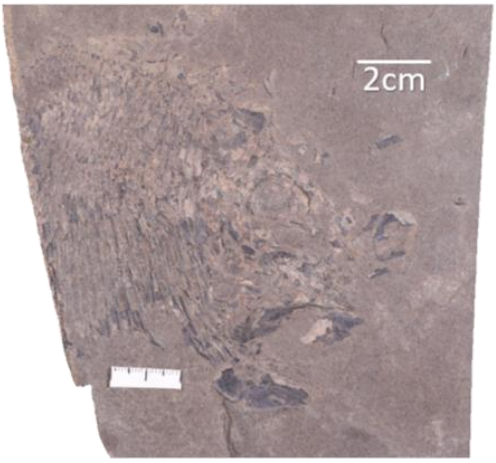


h) *Neuropteris* (P.6613) – Durham University

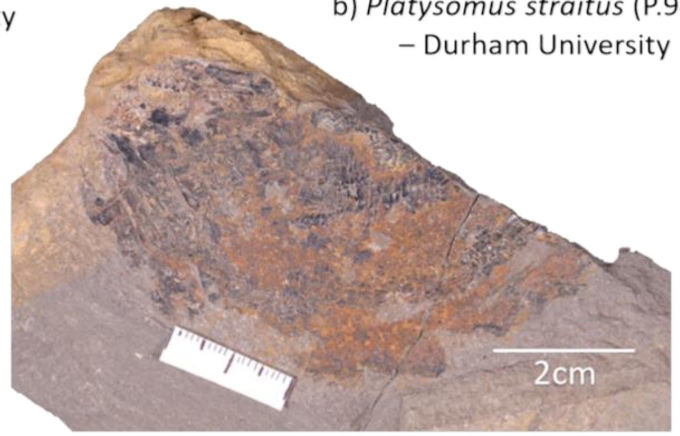
g) *Neuropteris* (P.1844) – Durham University



a) *Platysomus straitus* (P.8120)
– Durham University



b) *Platysomus straitus* (P.9413)
– Durham University

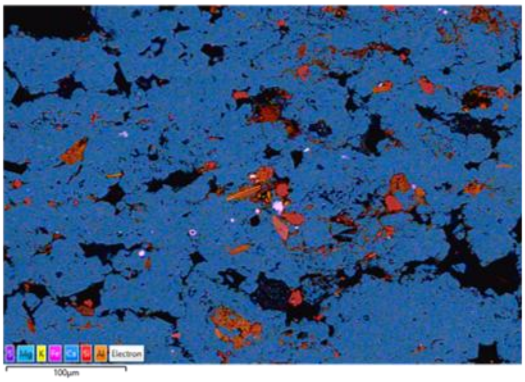


c) *Platysomus straitus* (P.8117)
– Durham University

Appendix B: Sedimentary SEM data

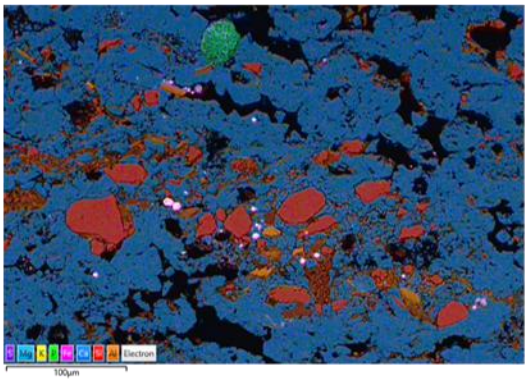
Sample 1a_Claxheugh Rocks

Location 1



HM_x300_15kv

Location 2



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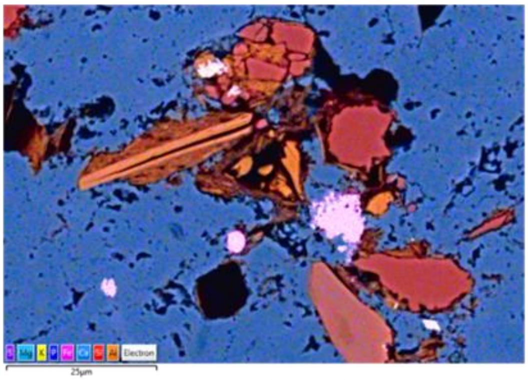
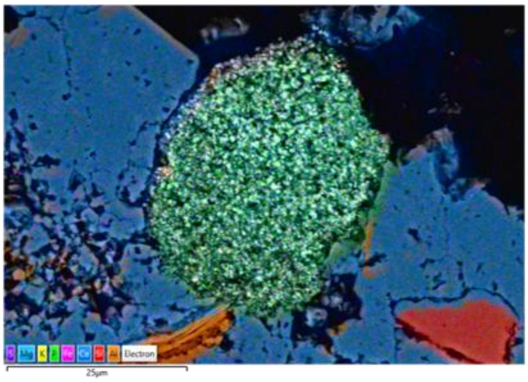


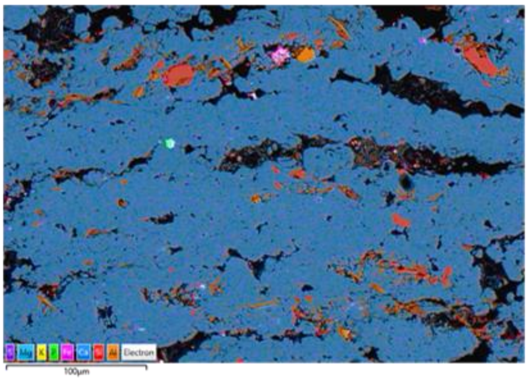
HM_x1.5k_15kv



HM_x1.8k_15kv
(Fish Fragment)

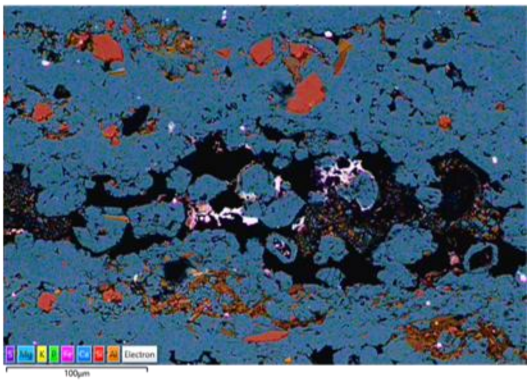
Sample 1b_Claxheugh Rocks

Location 1



HM_x300_15kv

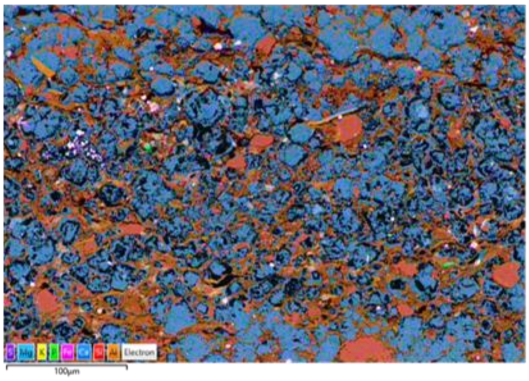
Location 2



HM_x300_15kv

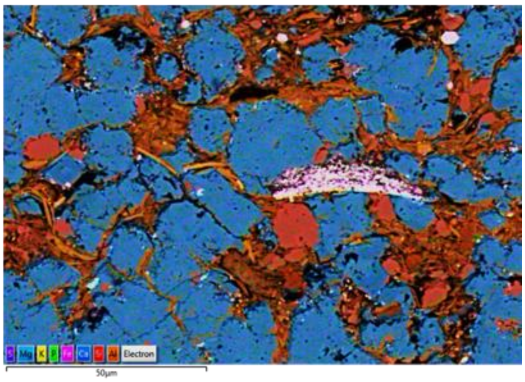
Sample 2_Middridge Quarry

Location 1



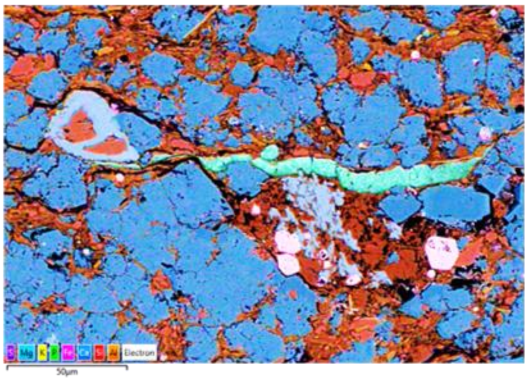
HM_x200_15kv

Location 2

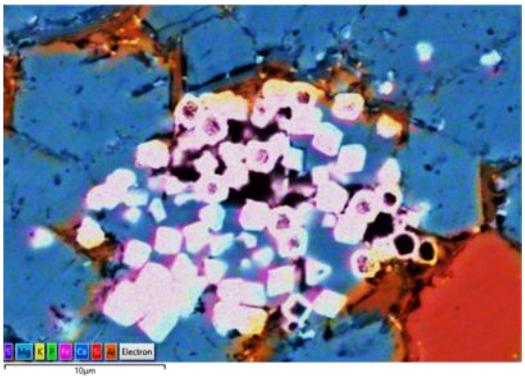


HM_x600_15kv

Location 3



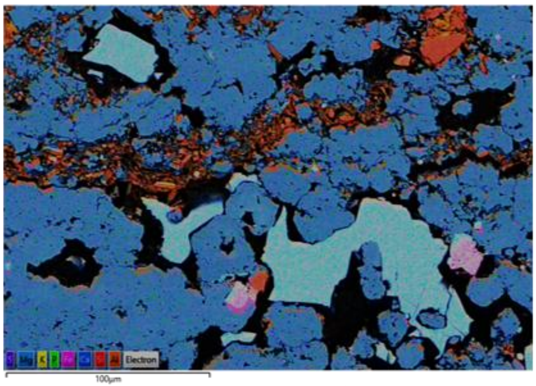
HM_x500_15kv
(Fish Material)



HM_x2.1k_15kv
(Pyrite Framboids)

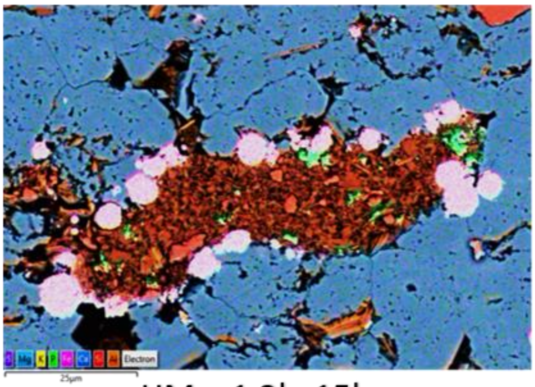
Sample 3a_Claxheugh Rocks

Location 1

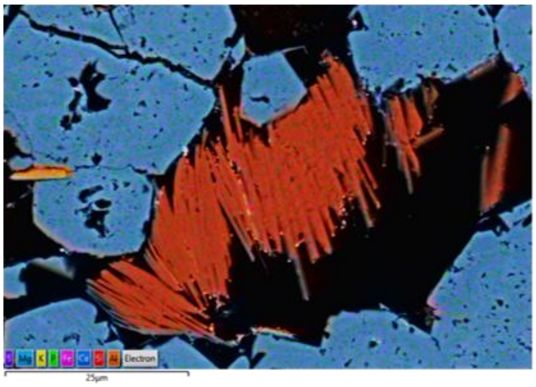


HM_x500_15kv

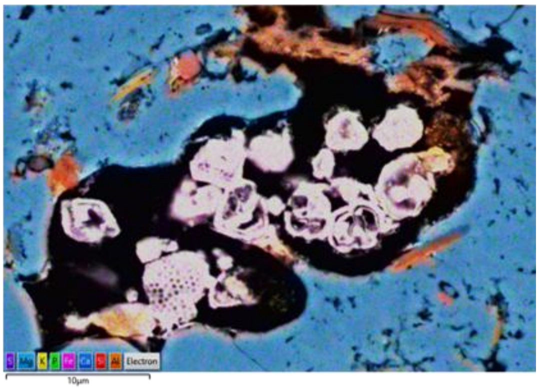
Location 2



HM_x1.3k_15kv



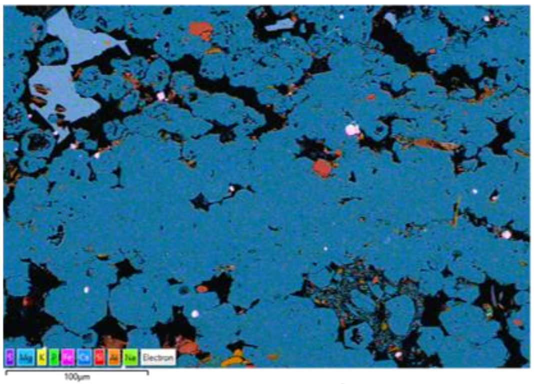
HM_x1.8k_15kv
(Kaolinite Books)



HM_x1.9k_15kv
(Pyrite Framboids)

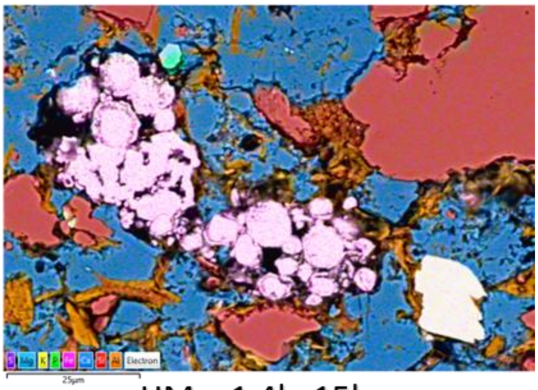
Sample 3b_Claxheugh Rocks

Location 1



HM_x300_15kv

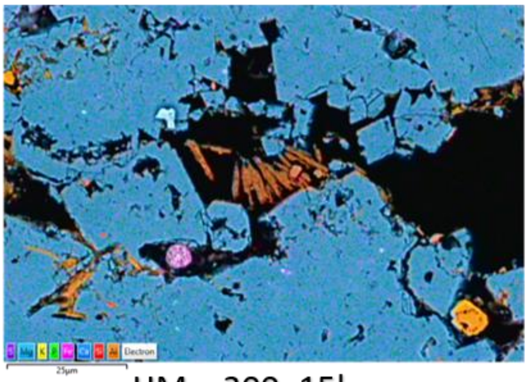
Location 2



HM_x1.4k_15kv

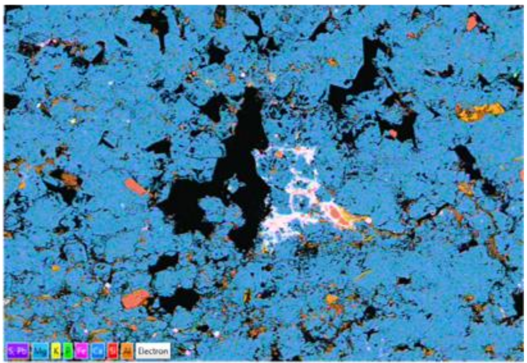
Sample 4_Claxheugh Rocks

Location 1



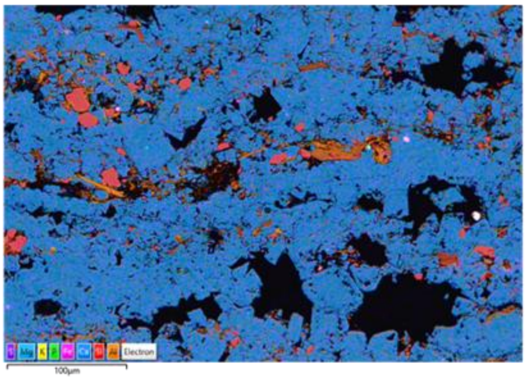
HM_x300_15kv

Location 2



HM_x200_15kv

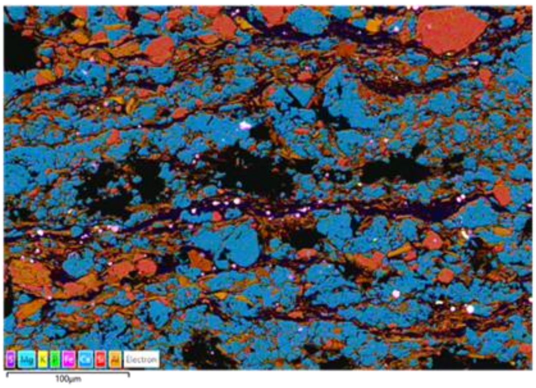
Location 3



HM_x300_15kv

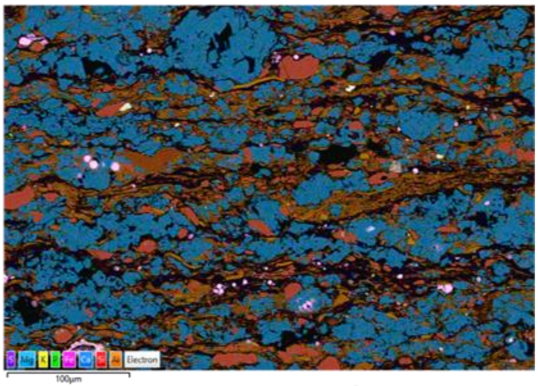
Sample 5_Crime Rigg Quarry

Location 1



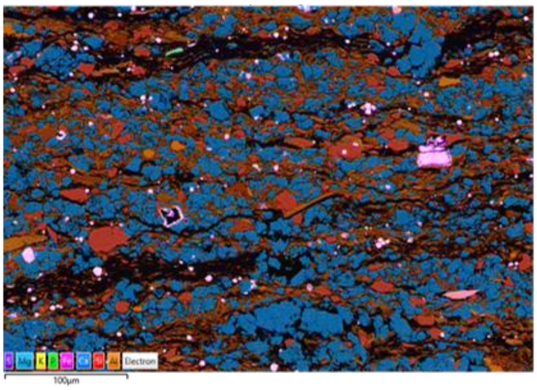
HM_x300_15kv

Location 2



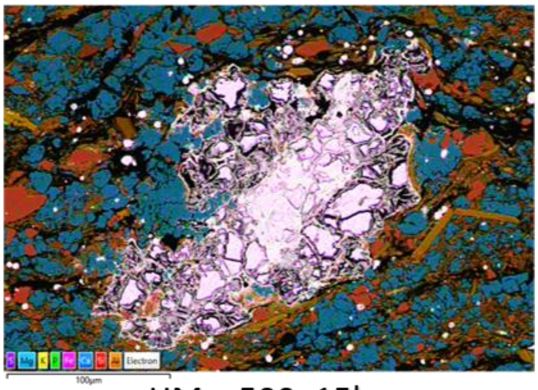
HM_x300_15kv

Location 2



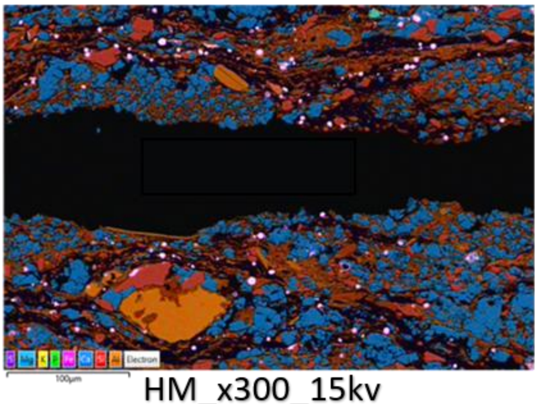
HM_x300_15kv

Location 4



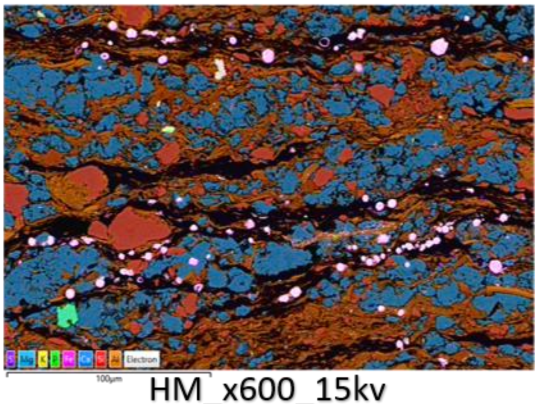
HM_x500_15kv

Location 5



HM_x300_15kv

Location 6

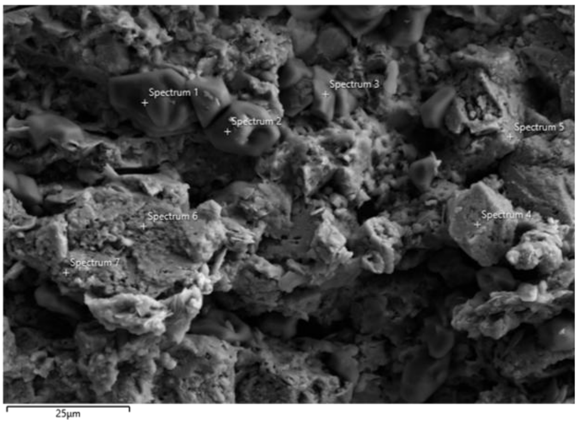


HM_x600_15kv

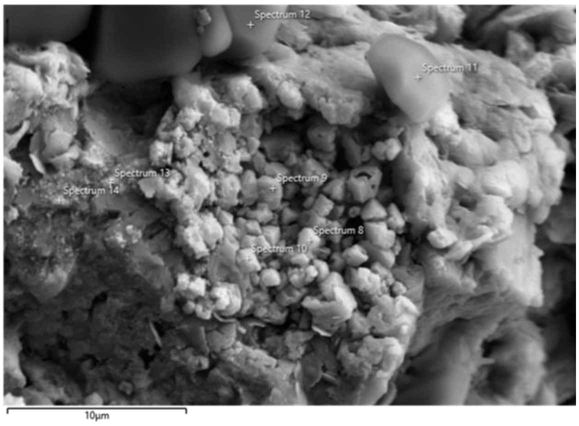
Appendix C: Sedimentary Rock Chips

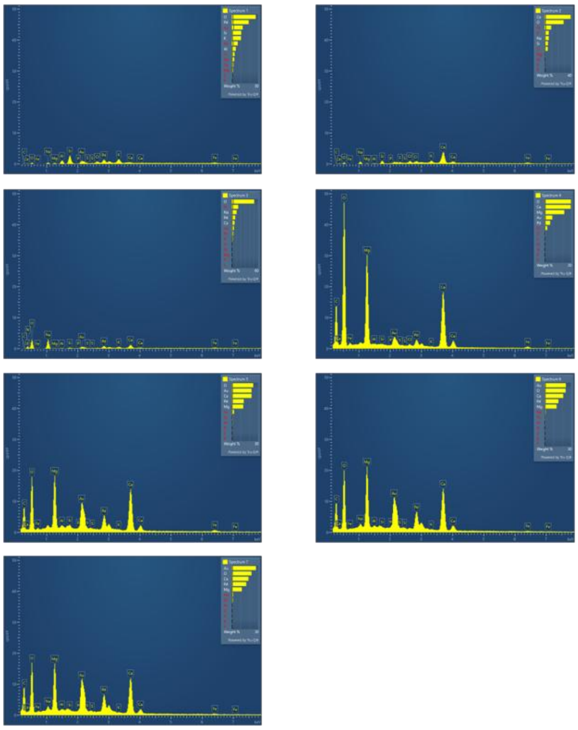
C1 LMS_Claxheugh Rocks

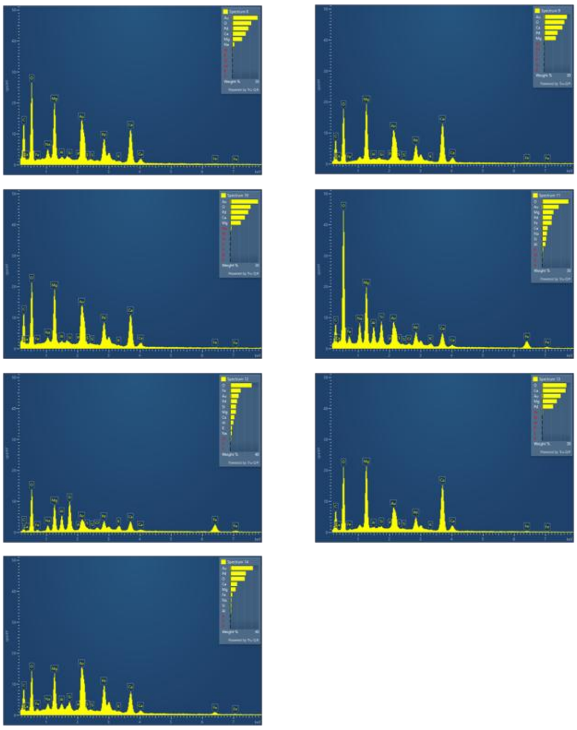
Site 1



Site 2

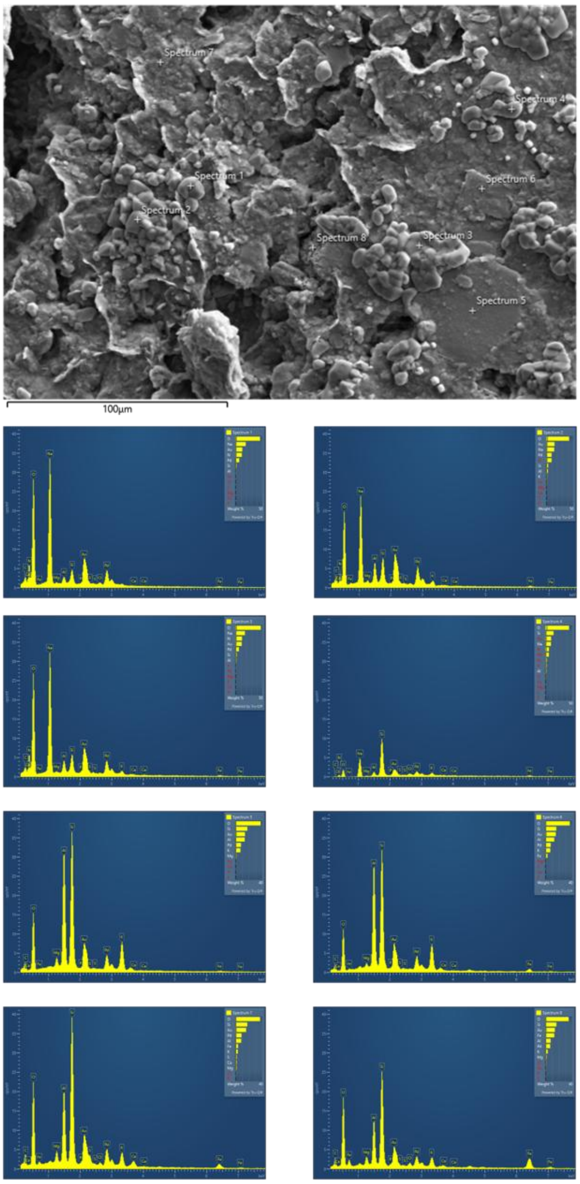




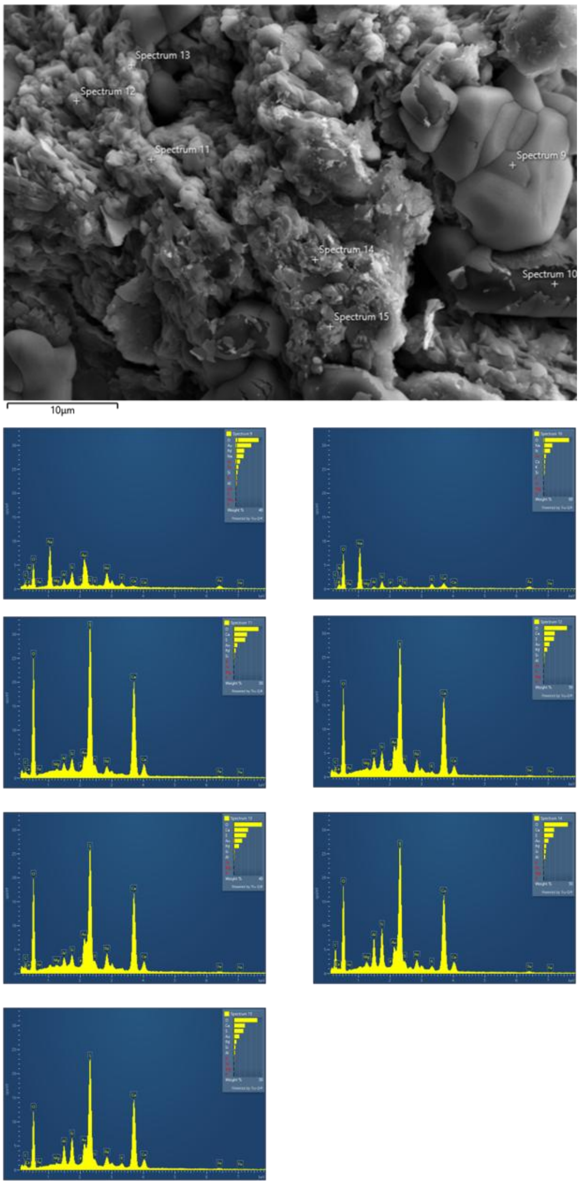


Between C2 and C3_Claxheugh Rocks

Site 1

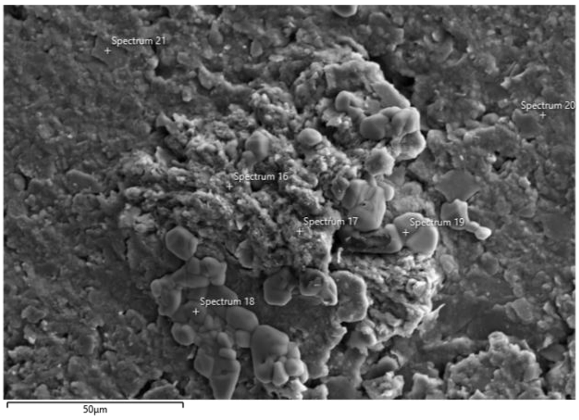


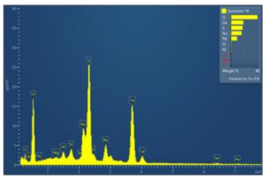
Site 2

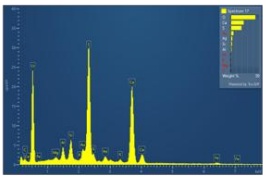


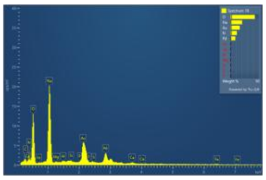
Between C2 and C3_Claxheugh Rocks

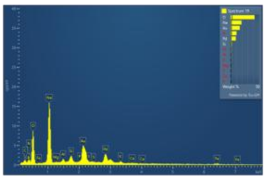
Site 3

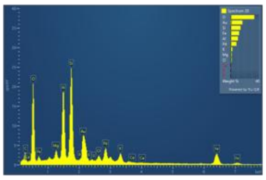


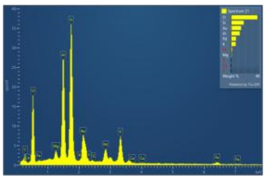




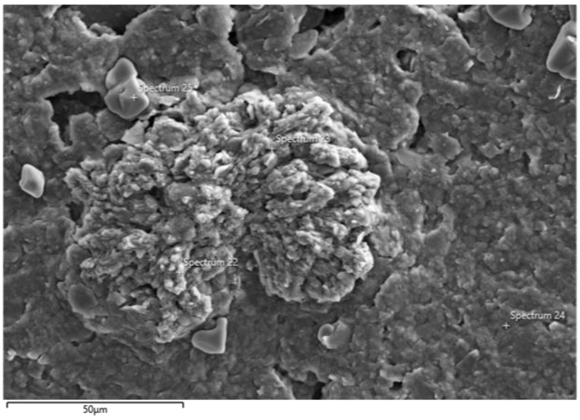


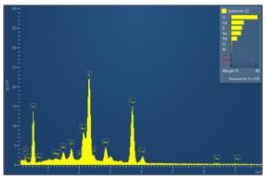


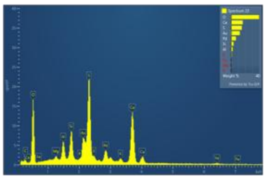


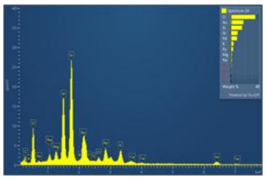


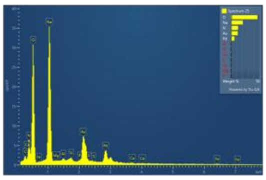
Site 4





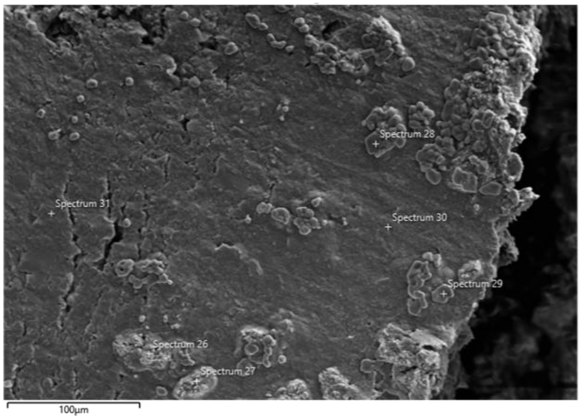


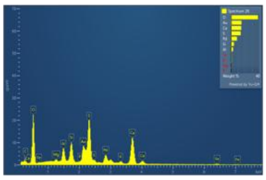


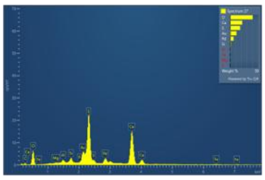


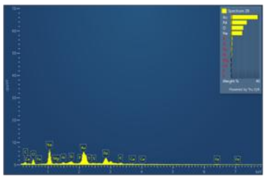
Between C2 and C3_Claxheugh Rocks

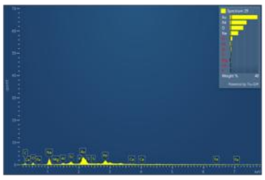
Site 5

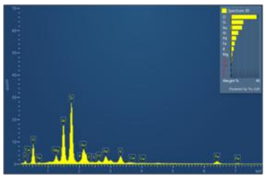


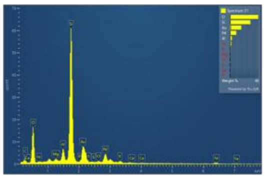






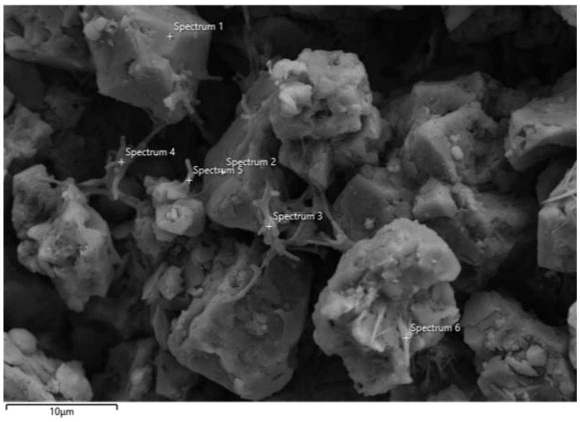




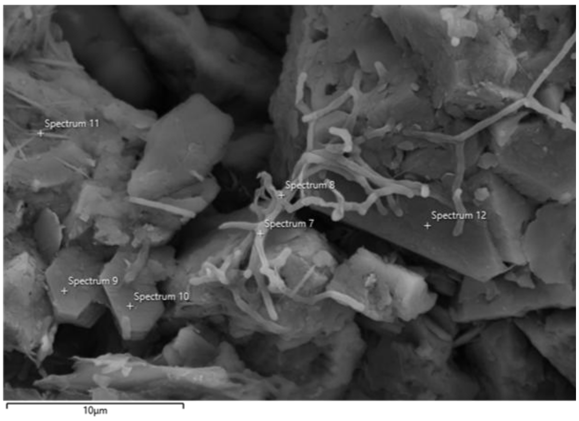


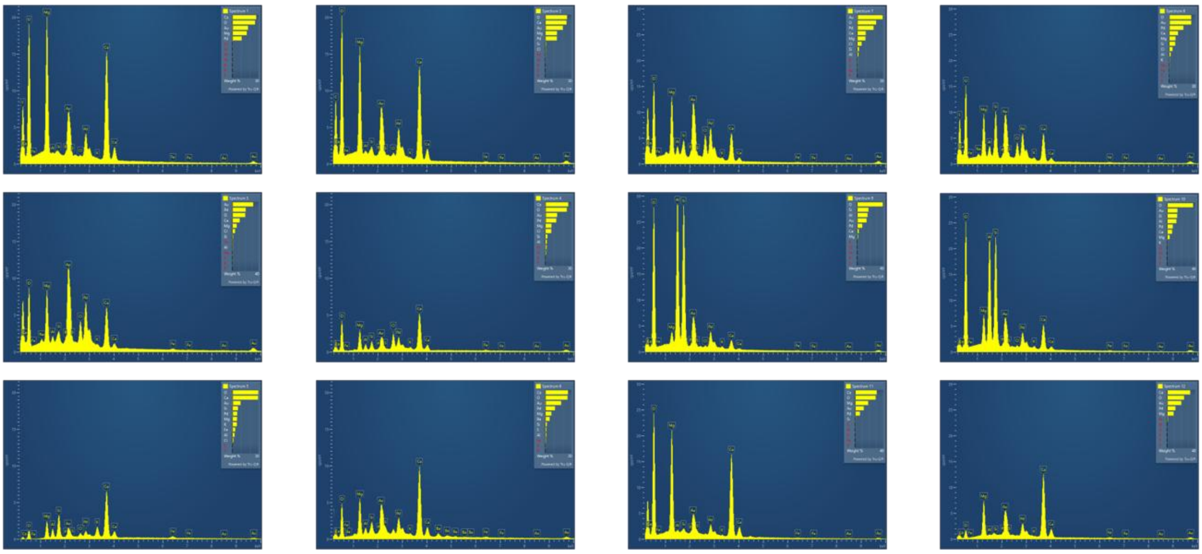
DM1_Claxheugh Rocks

Site 1



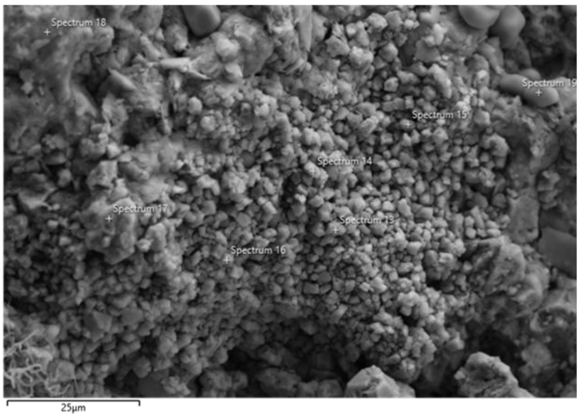
Site 2



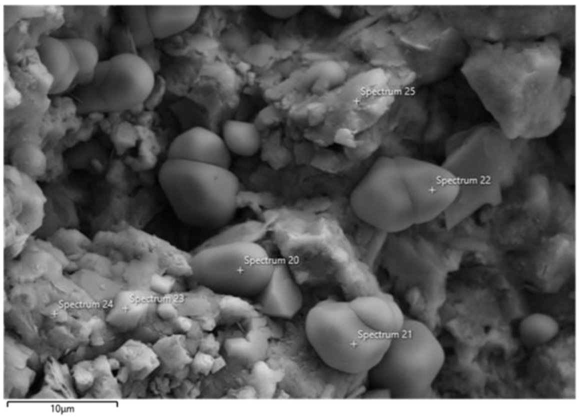


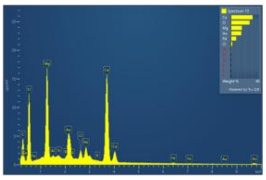
DM1_Claxheugh Rocks

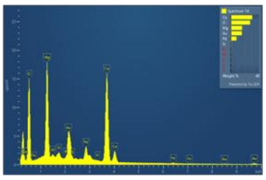
Site 3

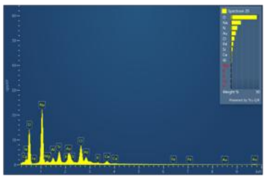


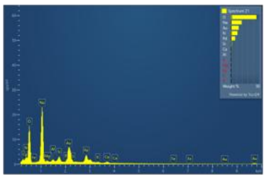
Site 4

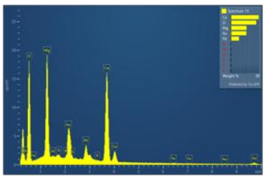


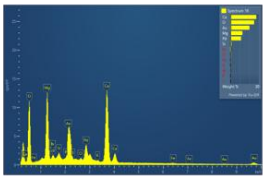


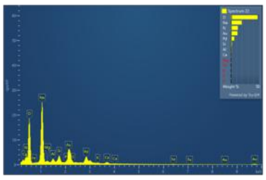


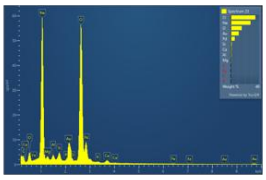


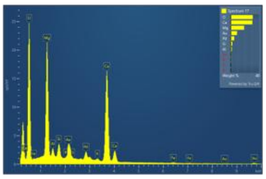


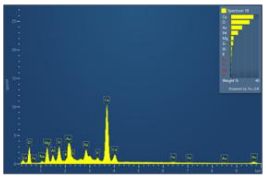


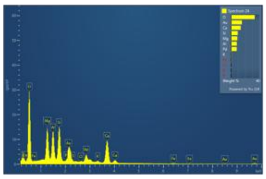


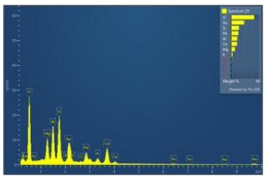


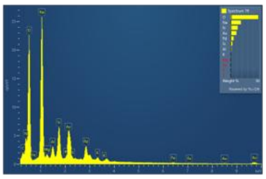






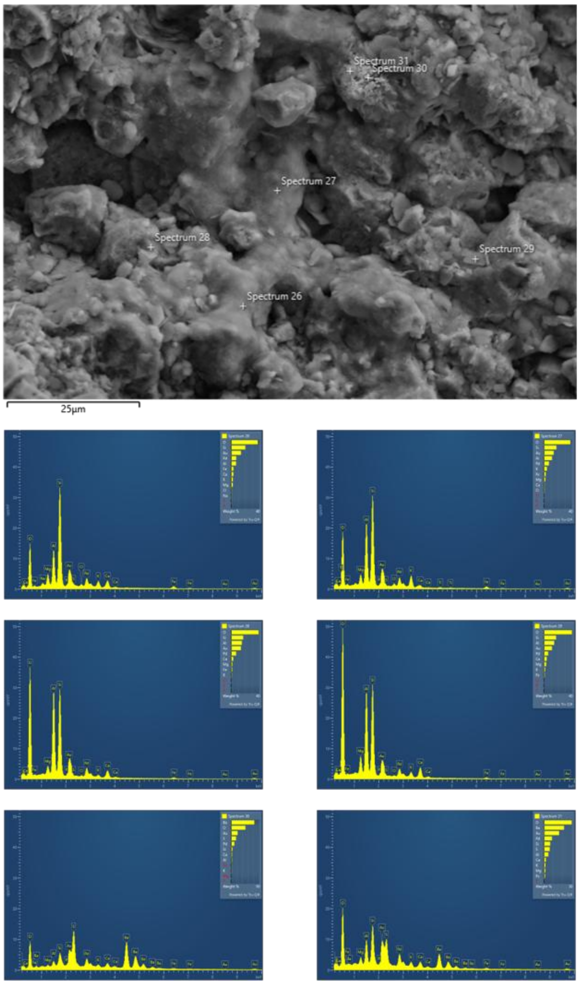




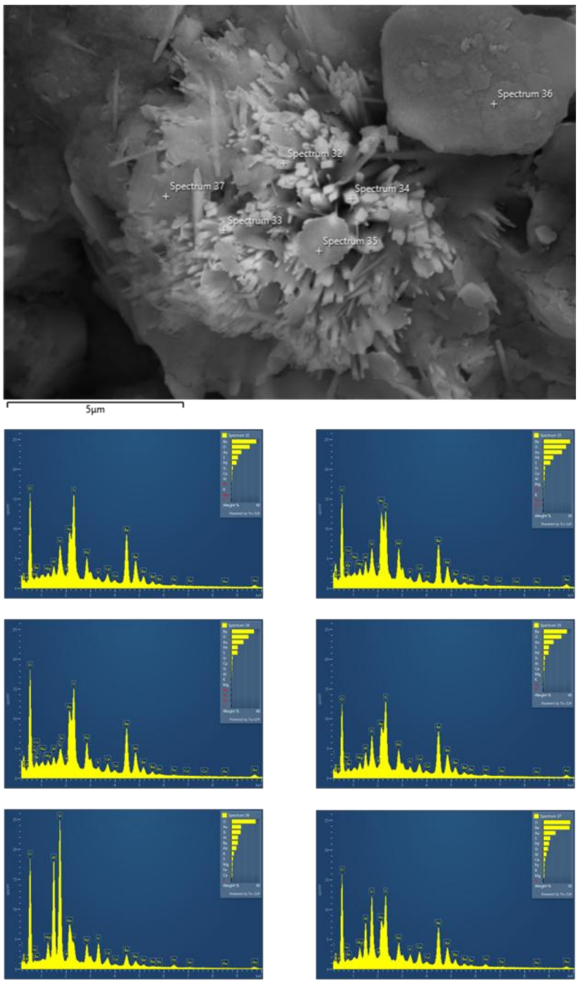


DM1_Claxheugh Rocks

Site 5

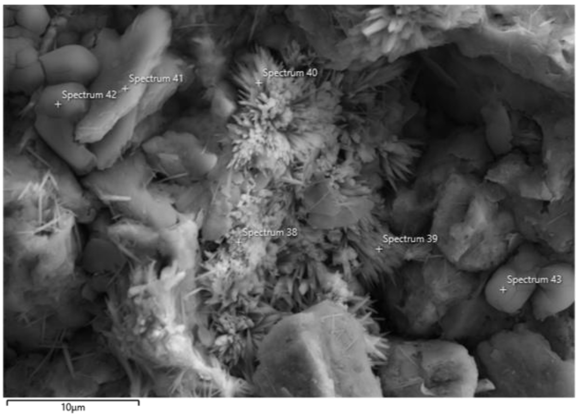


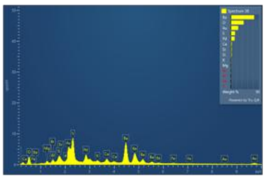
Site 6

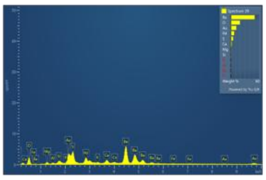


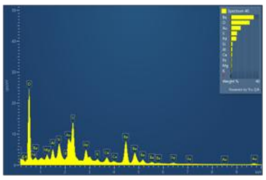
DM1_Claxheugh Rocks

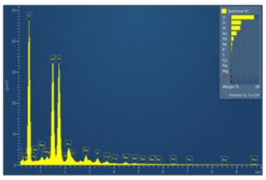
Site 7

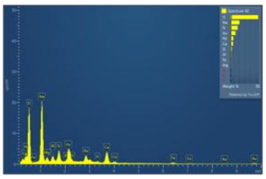


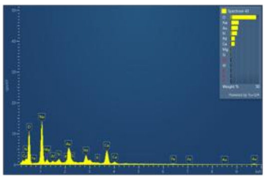






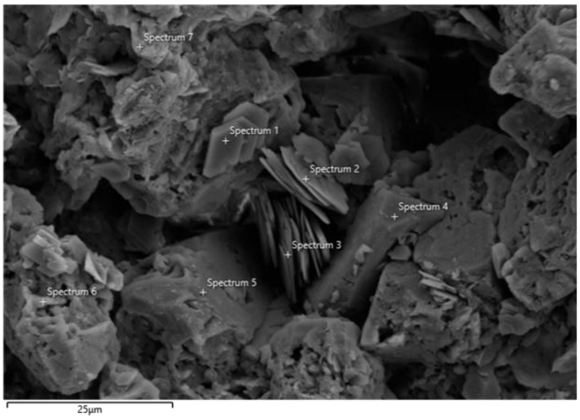


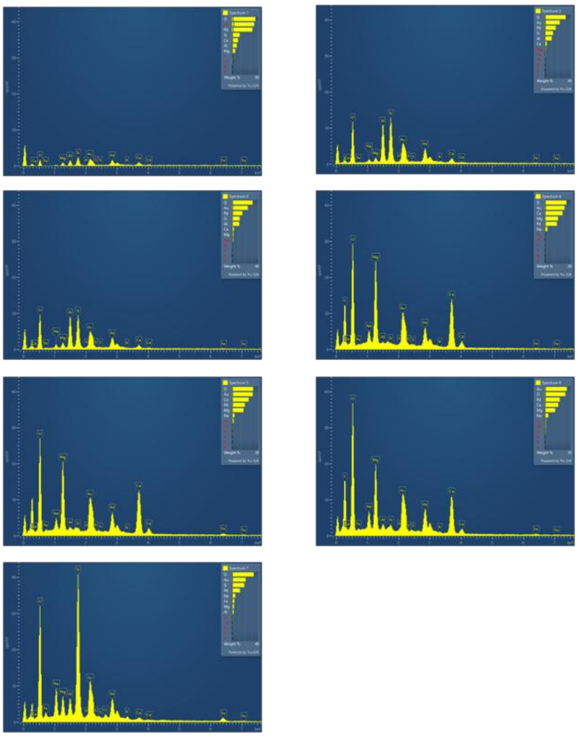




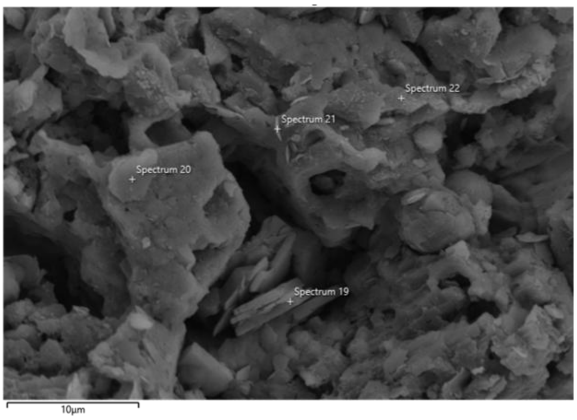
DM2_Claxheugh Rocks

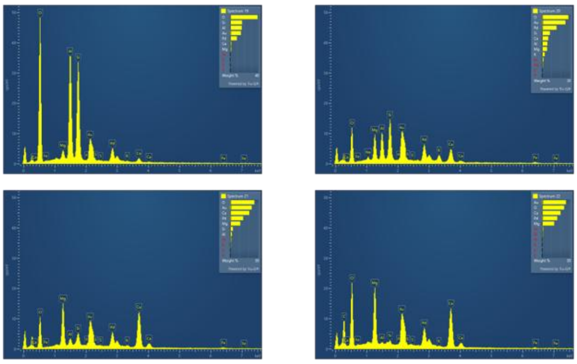
Site 1





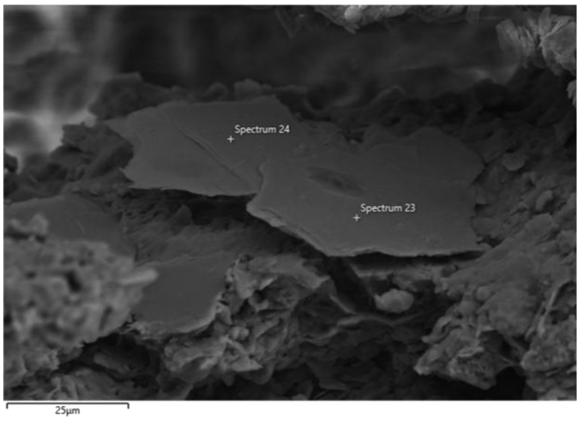
Site 2

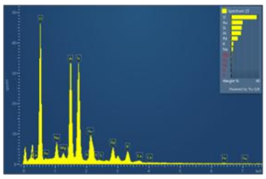


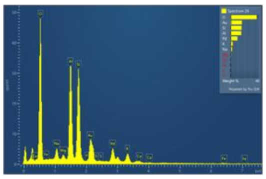


DM2_Claxheugh Rocks

Site 3

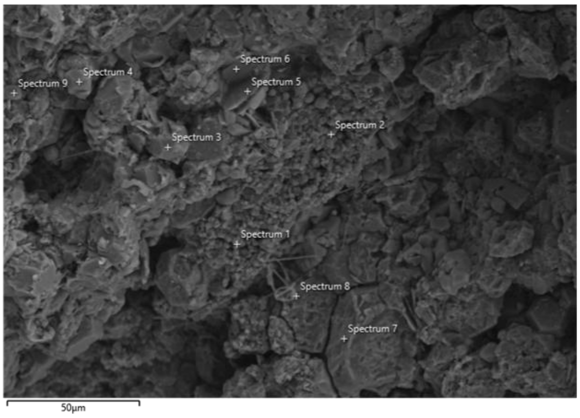


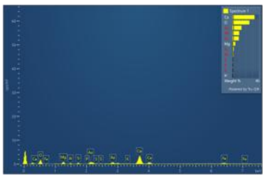


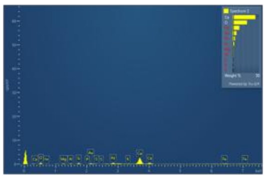


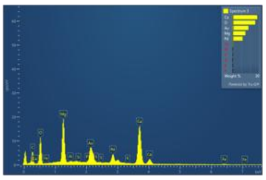
DM3_Claxheugh Rocks

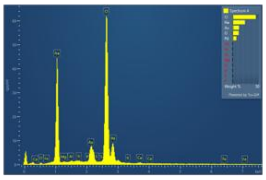
Site 1

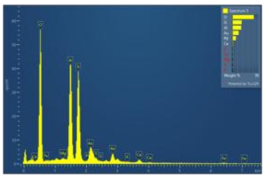


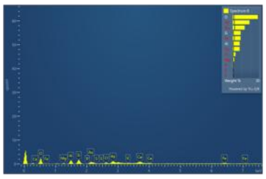


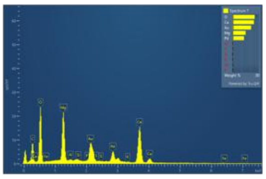


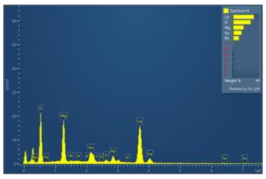


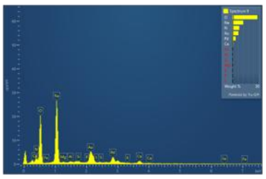




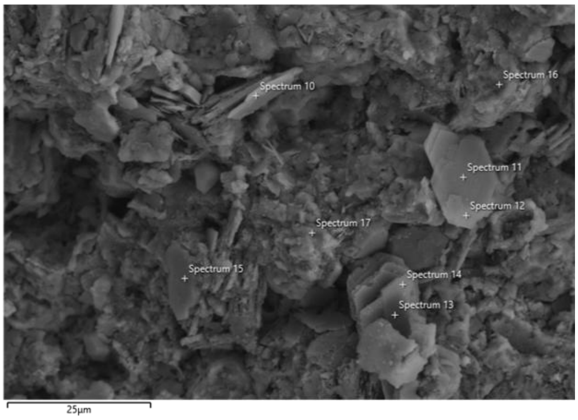


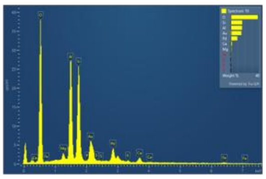


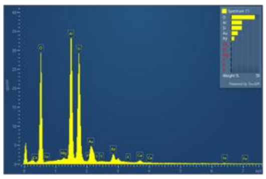


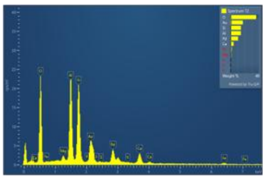


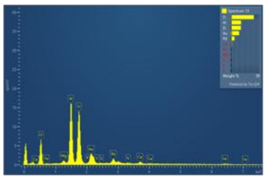
Site 2

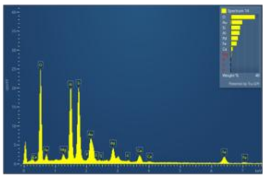


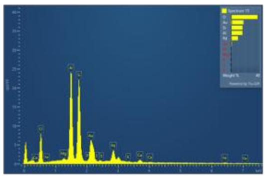


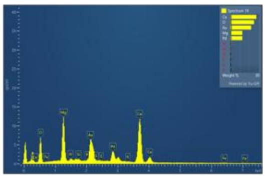


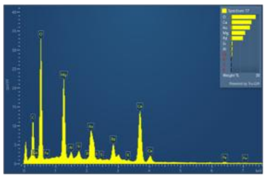






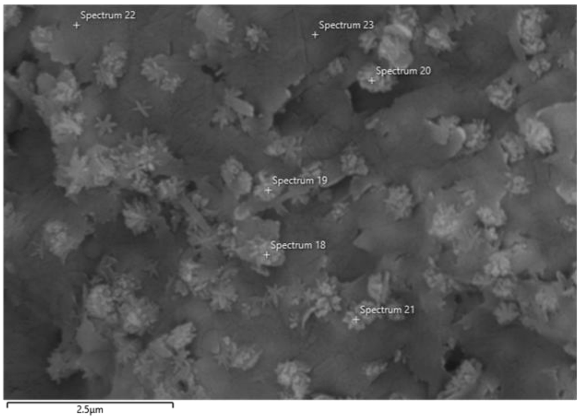


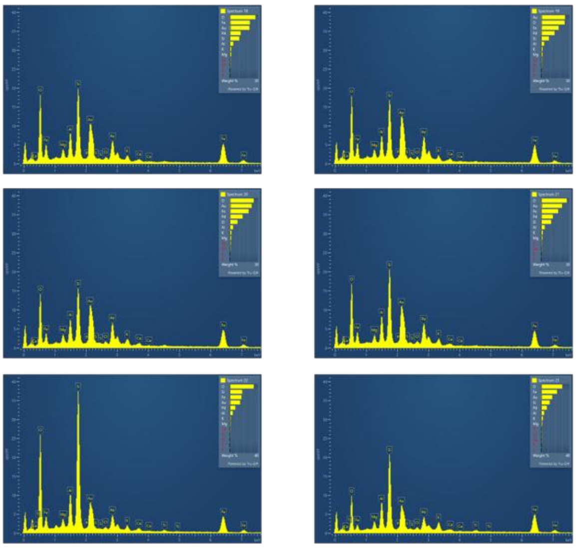




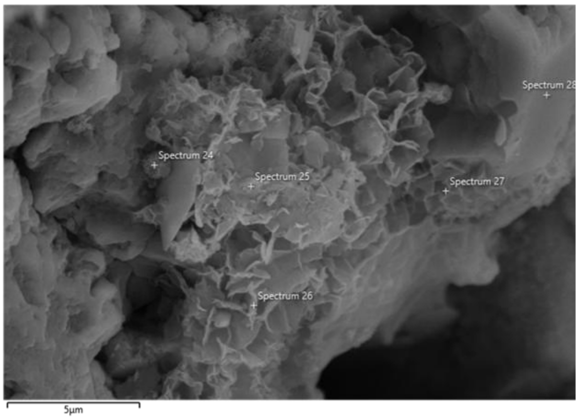
DM3_Claxheugh Rocks

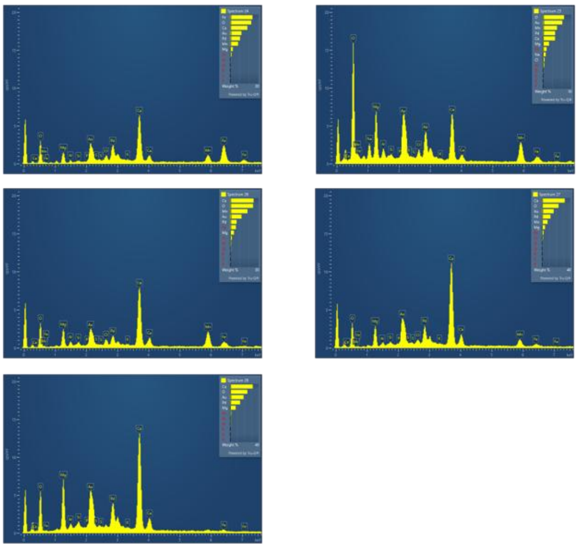
Site 3



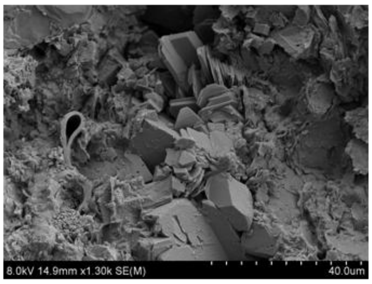


Site 4

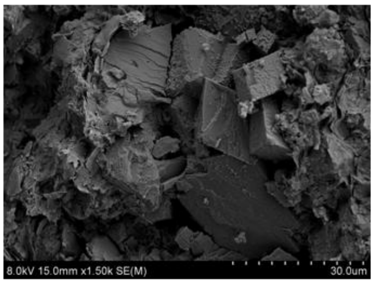




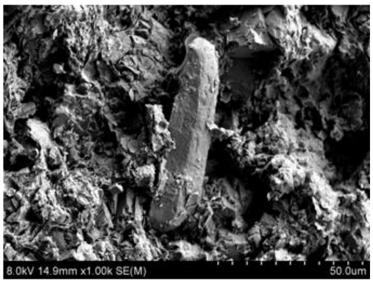
DM2 Equivalent_Middridge Quarry



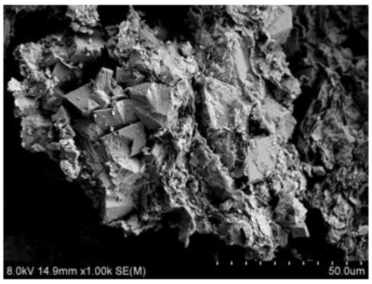
001



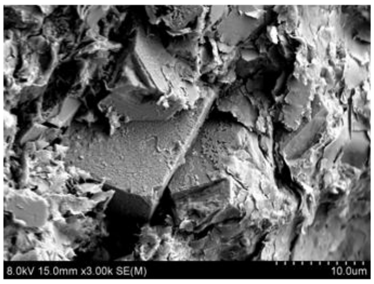
002



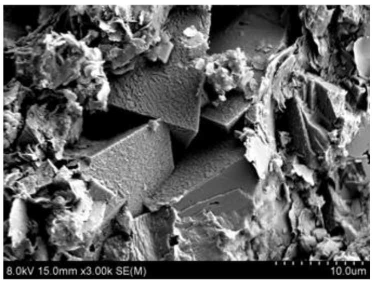
003



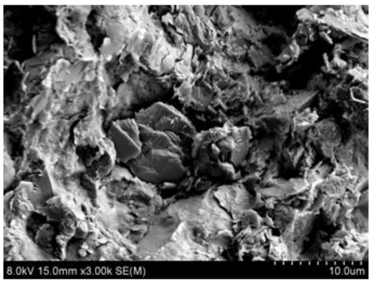
004_Dolomites



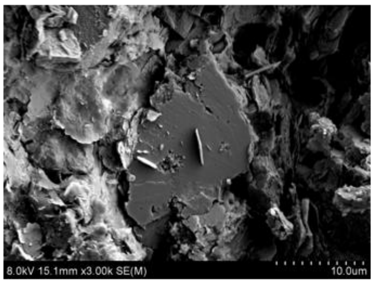
005_Dolomites



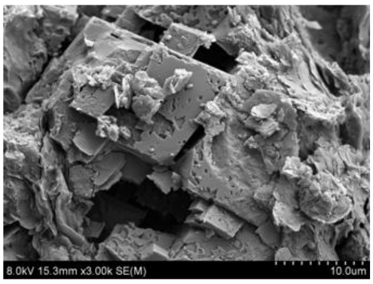
006_Dolomites



007_Smectite-Illite



008_Dolomite



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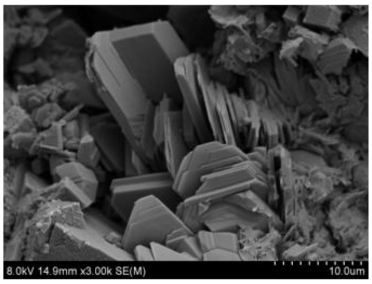

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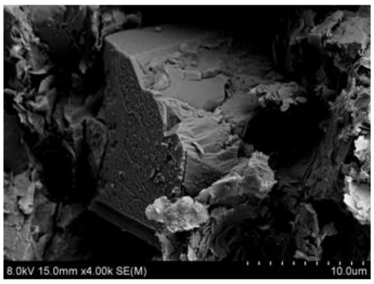
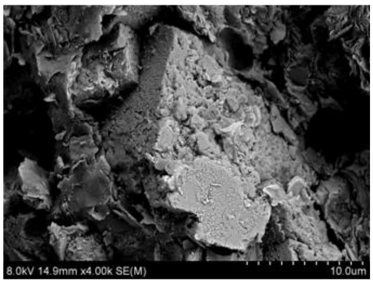
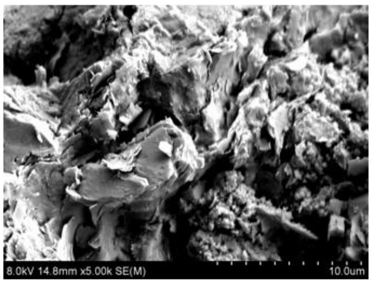


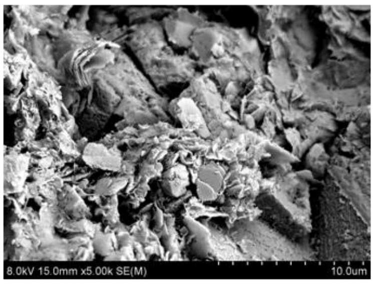
011_Dolomite



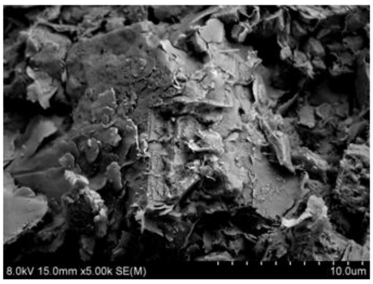
012_Dolomite



013_Smectite-Illite

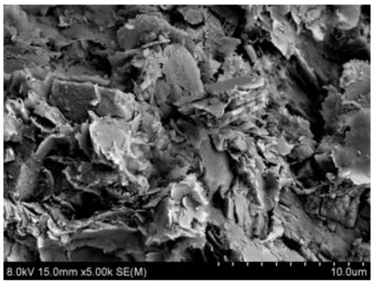


014_Illite

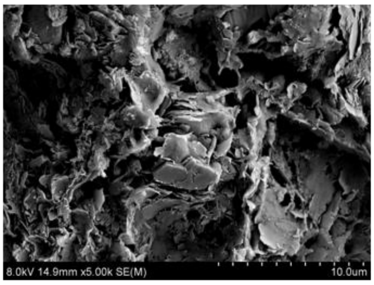


015_Smectite-Illite

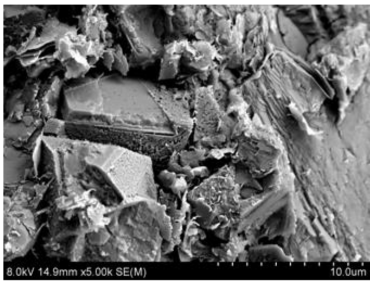
DM2 Equivalent_Middridge Quarry



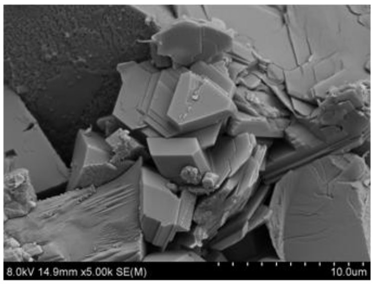
016_Smectite-Illite



017_Illite



018_Illite_Dolomites



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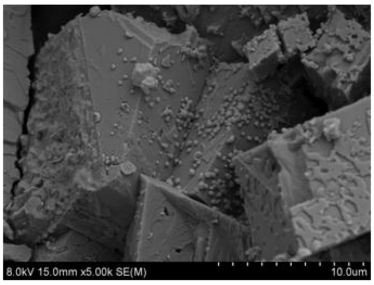
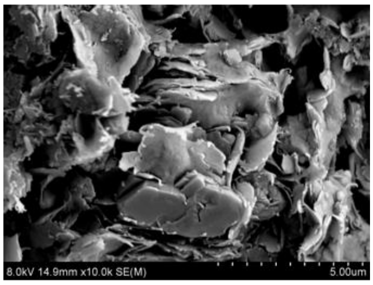
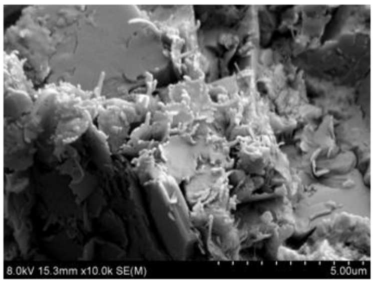


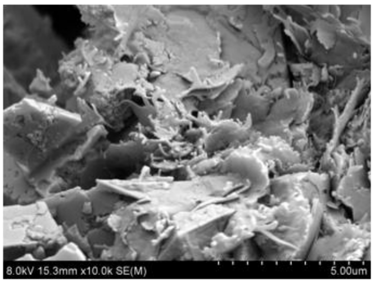
020_Pyrite_Dolomites



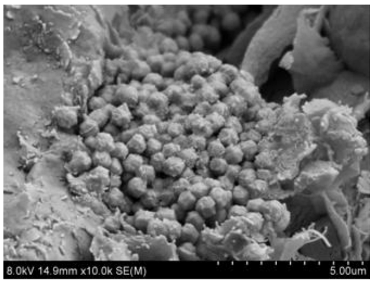
021_Illite



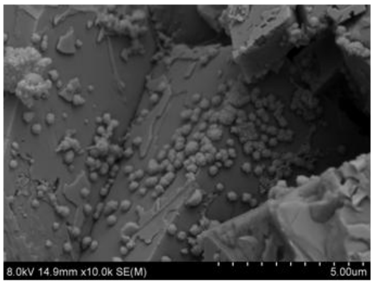
022_Smectite-Illite



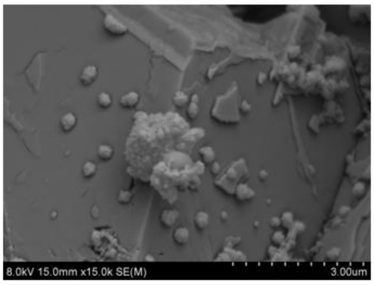
023_Smectite-Illite



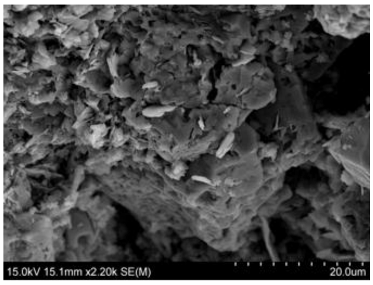
024_PyriteFramboids



025_Pyrite_Dolomites



026_Pyrite_Dolomites

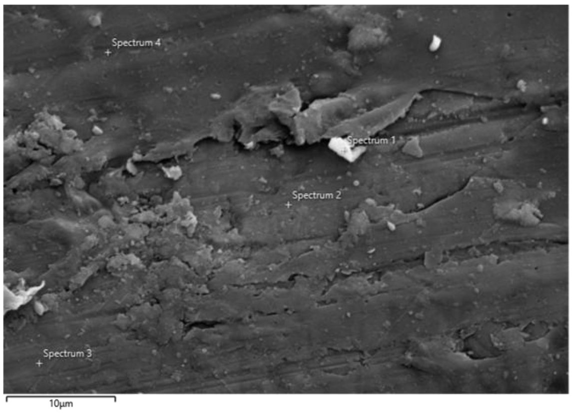


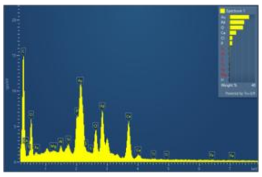
027_Smectite

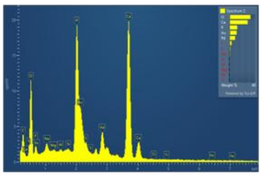
Appendix D: Fossiliferous Rock Chips

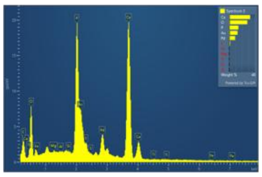
Specimen 34_Scale

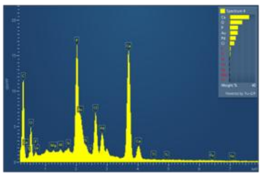
Site 1



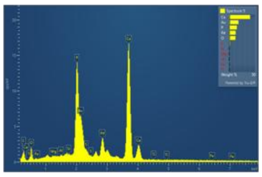


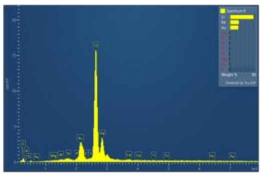


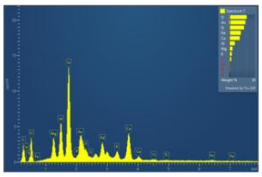




Site 2







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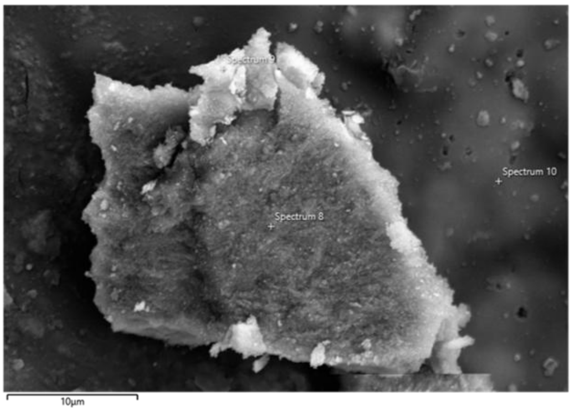
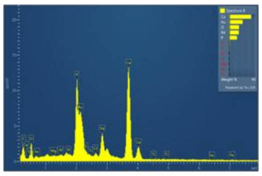
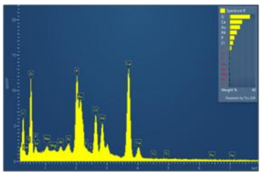
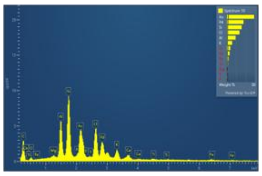


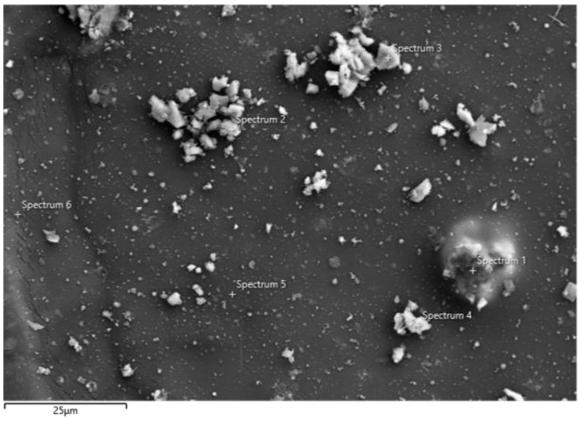


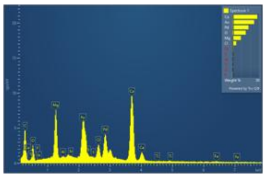


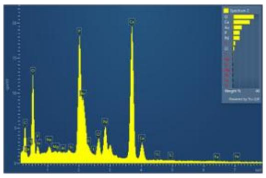


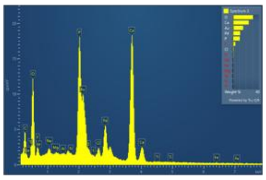
Specimen 39_Scale

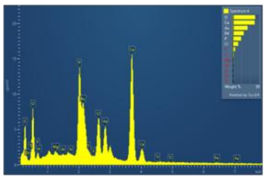
Site 1

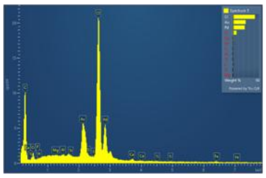


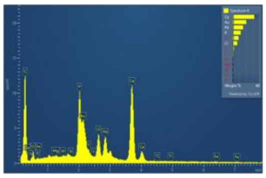




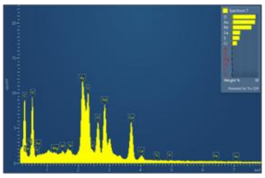


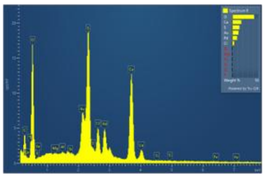


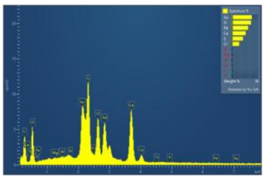


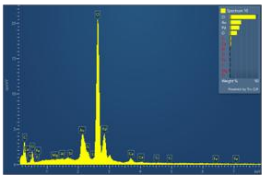


Site 2



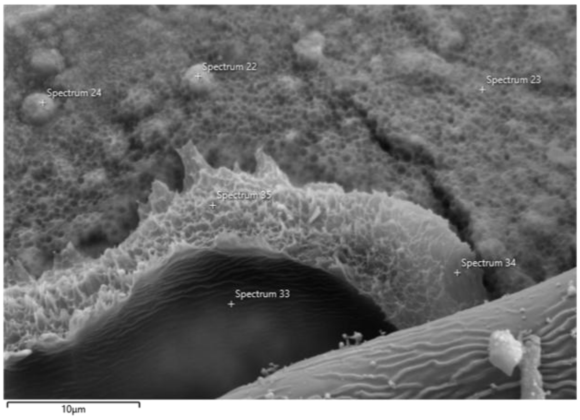






Specimen 39_Scale

Site 3



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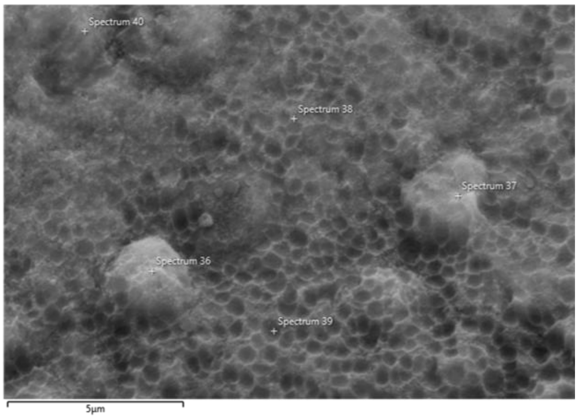
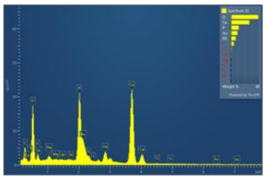
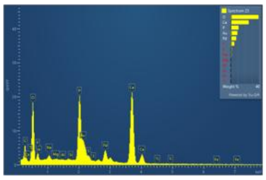
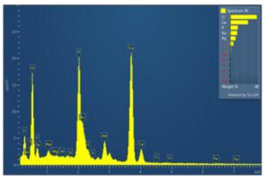
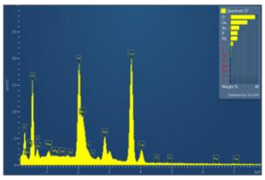
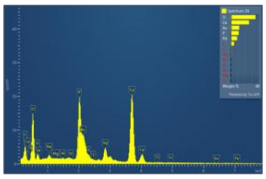
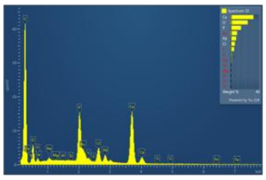
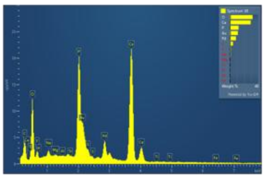
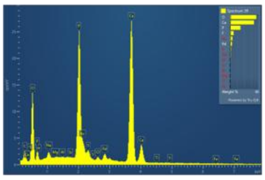
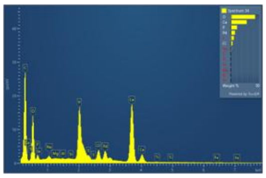
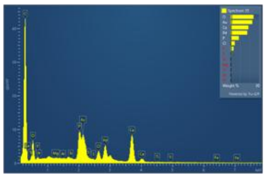
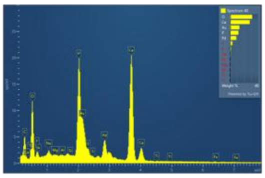
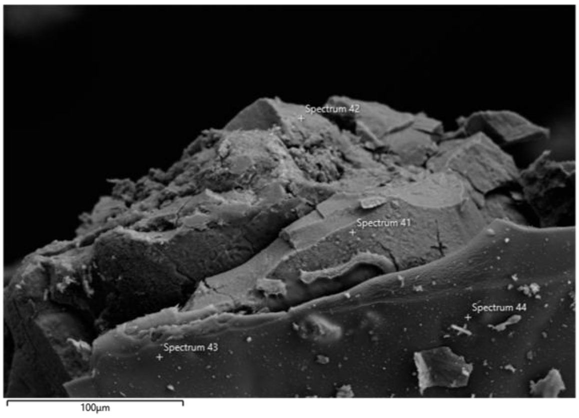
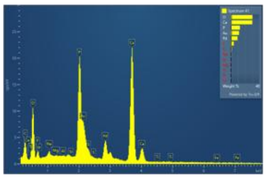


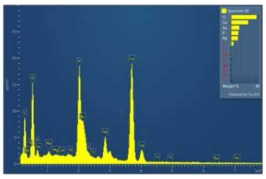












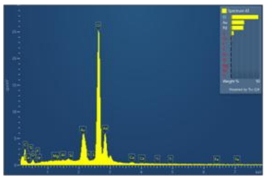
Specimen 39_Scale

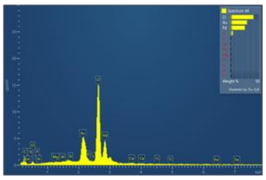
Site 5





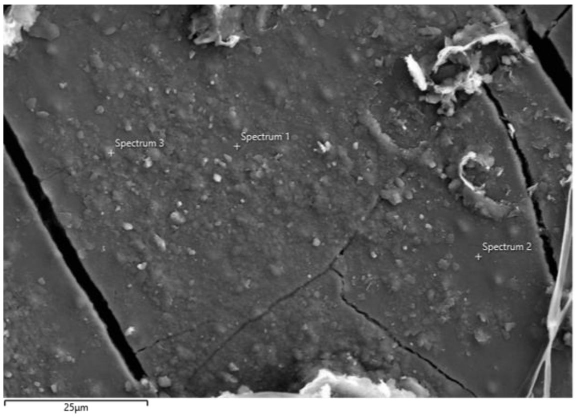


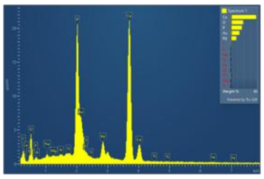


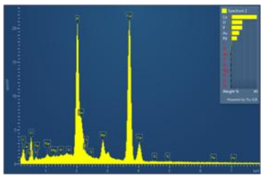


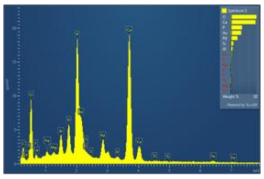
Specimen P.478_Scale

Site 1

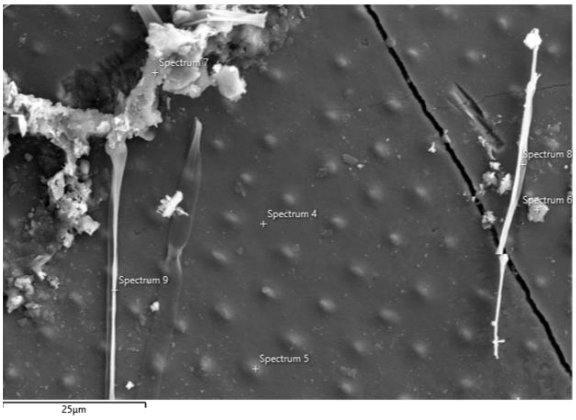


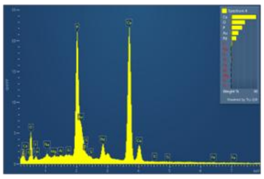


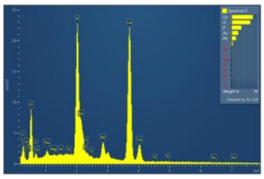


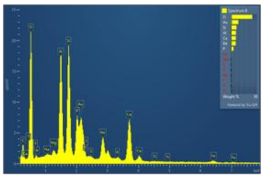


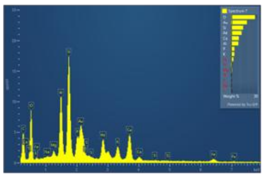
Site 2

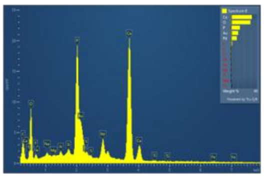


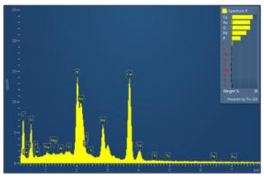






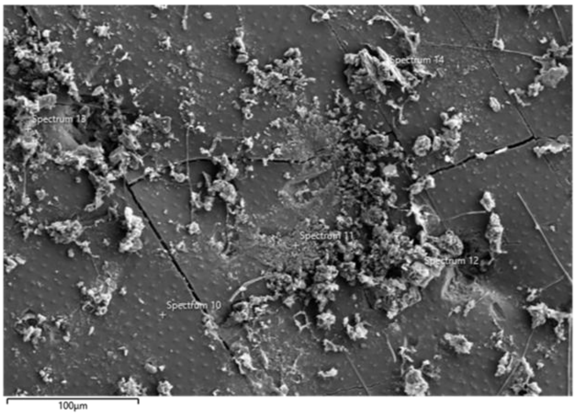


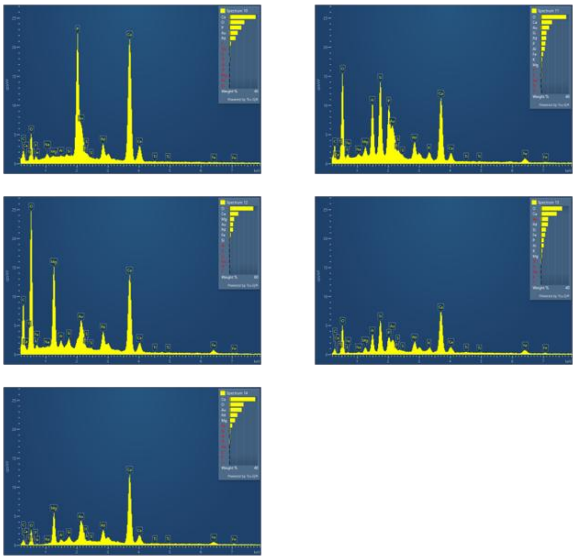




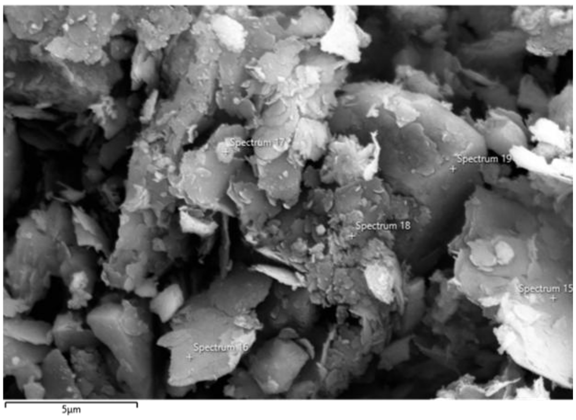
Specimen P.478_Scale

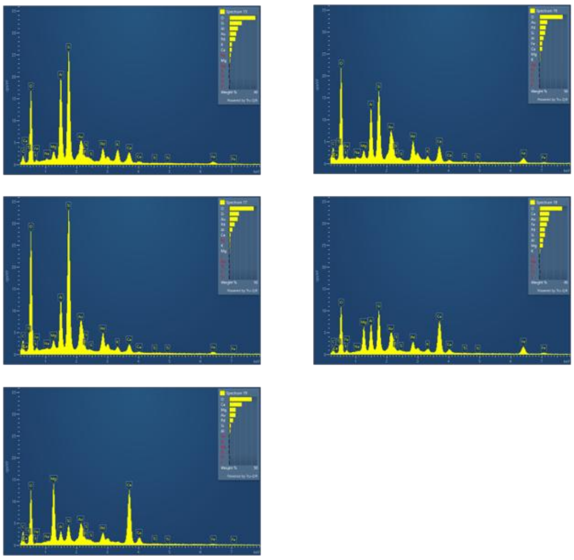
Site 3





Site 4





Specimen P.8114_Scale/Chip

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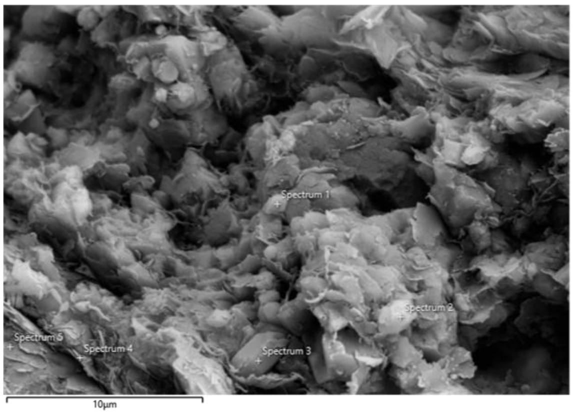

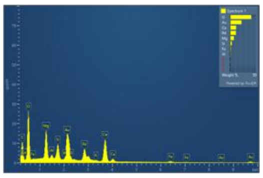

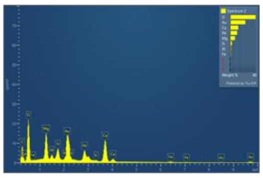

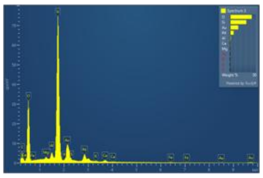

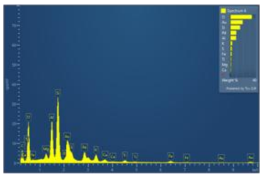

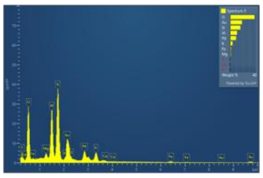

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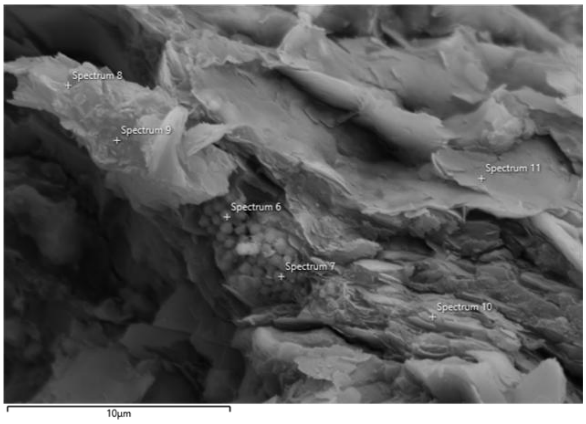
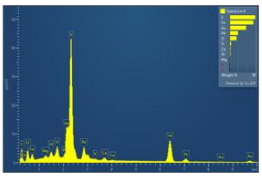
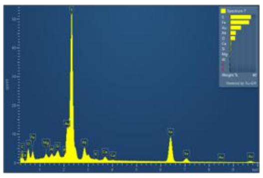
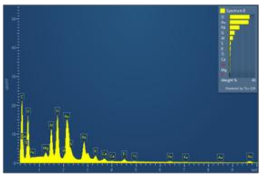
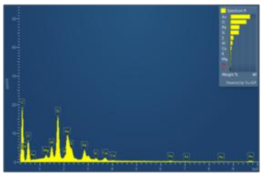
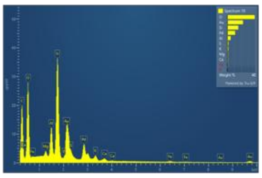


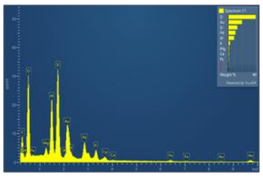






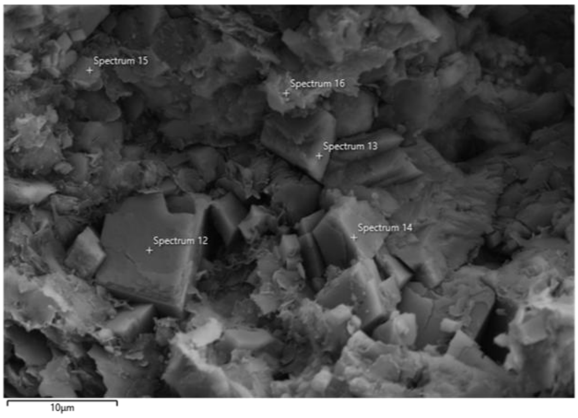


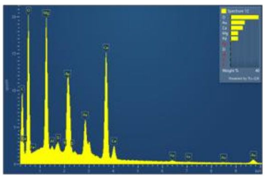


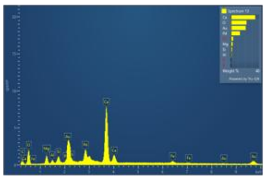


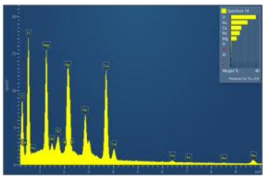
Specimen P.8114_Scale/Chip

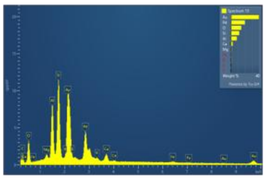
Site 3

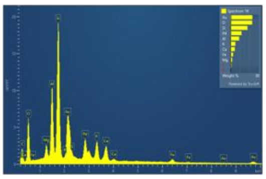




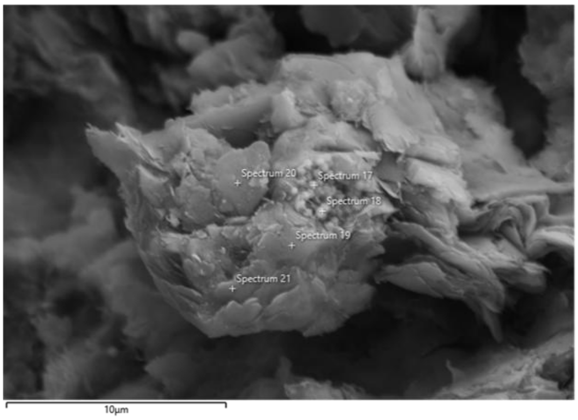


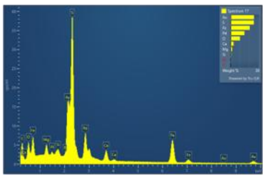


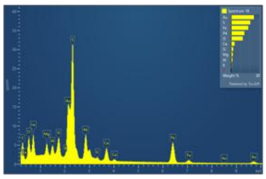


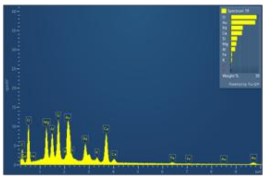


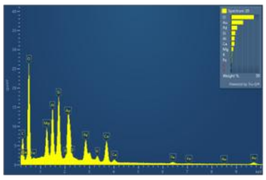
Site 4

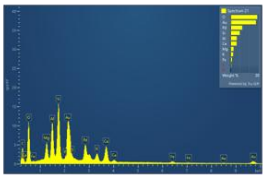






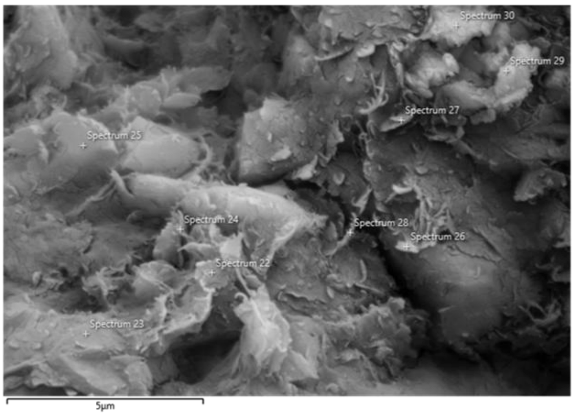


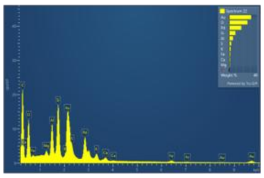


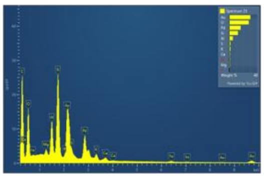


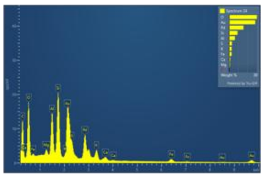
Specimen P.8114_Scale/Chip

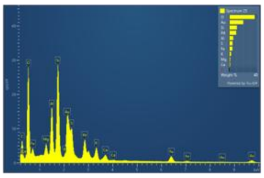
Site 5

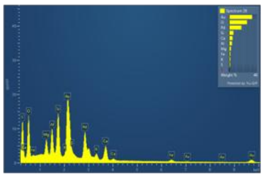


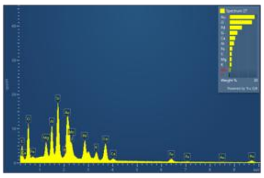


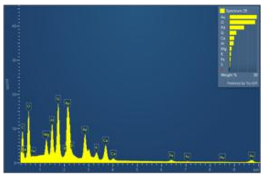


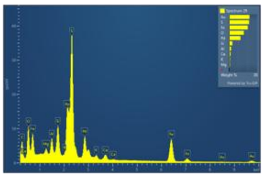


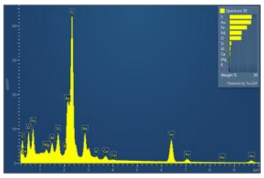




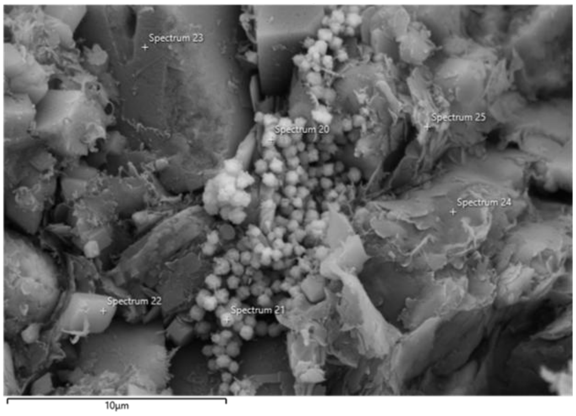


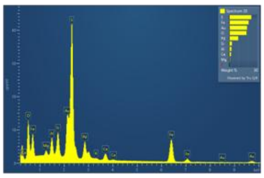


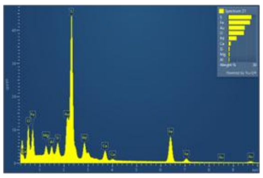


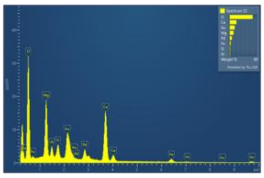


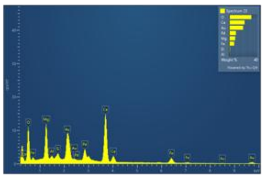
Site 6

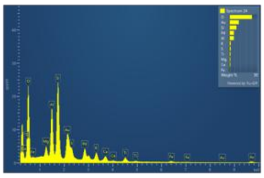


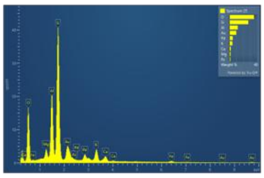






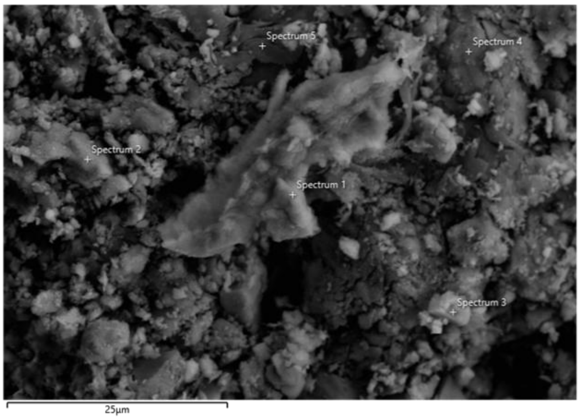




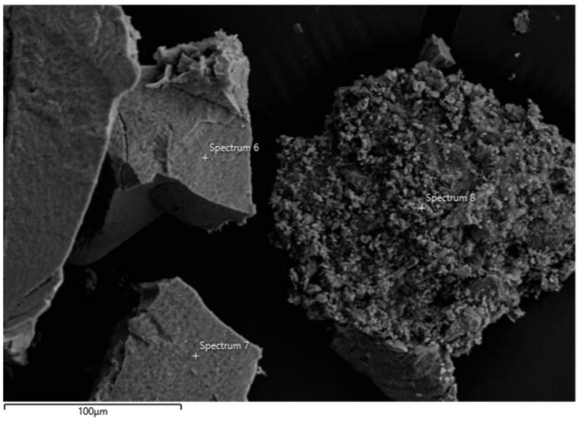


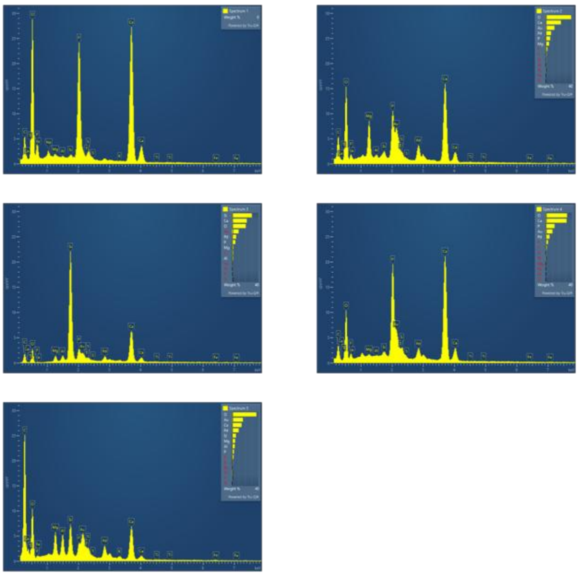
Specimen P.8795_Scale/Chip

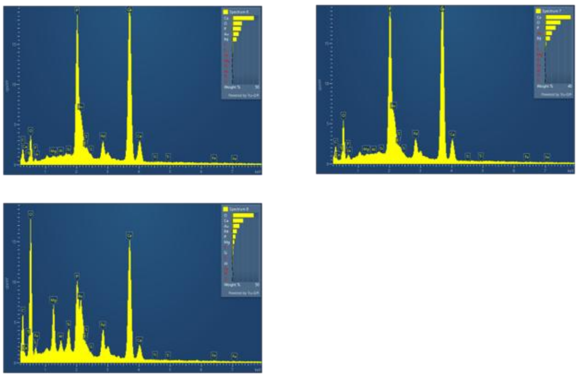
Site 1



Site 2

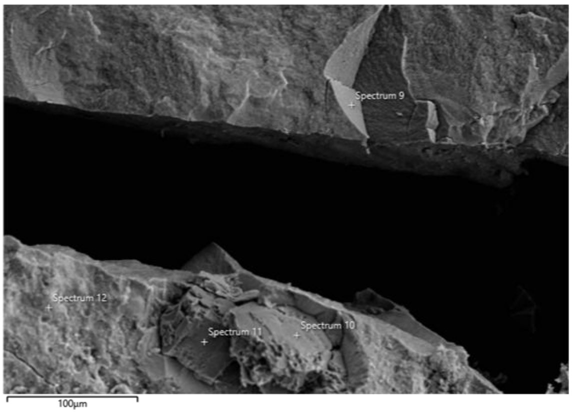


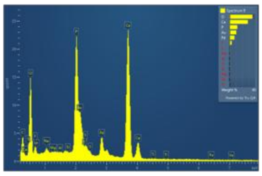


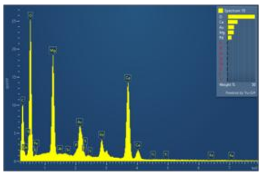


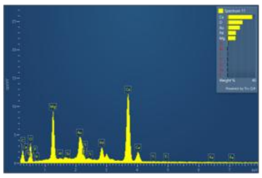
Specimen P.8795_Scale/Chip

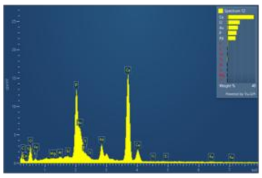
Site 3



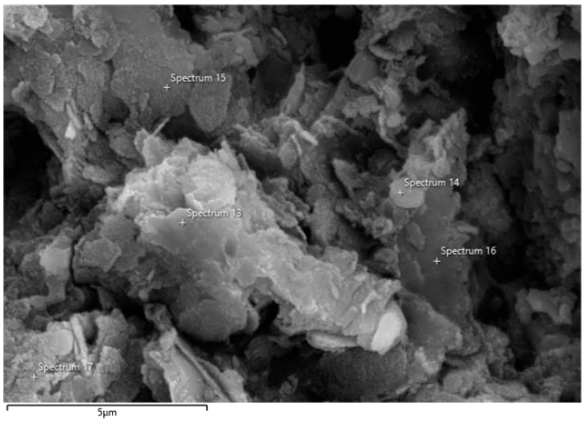


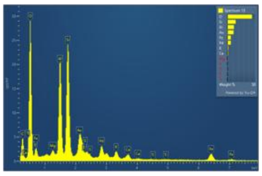


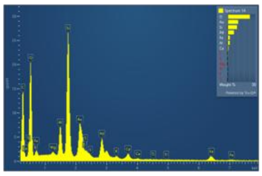


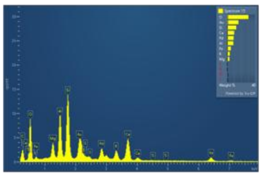


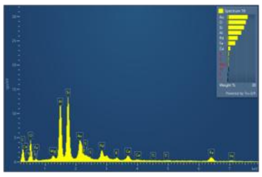
Site 4

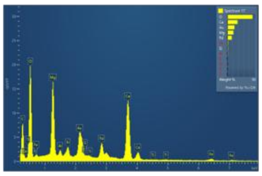






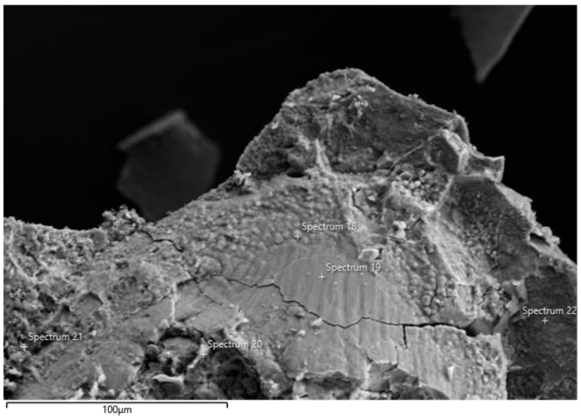




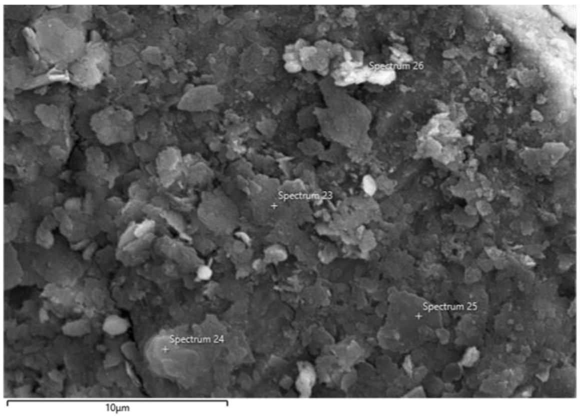


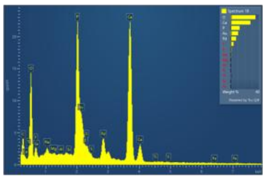
Specimen P.8795_Scale/Chip

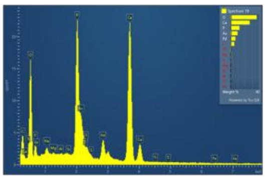
Site 5

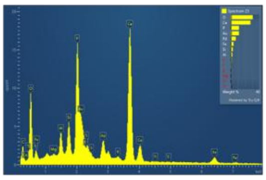


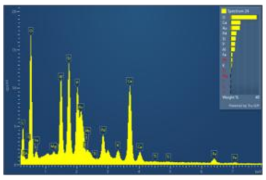
Site 6

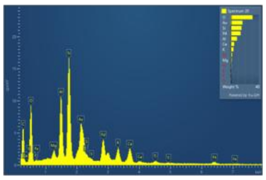


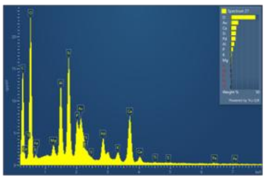


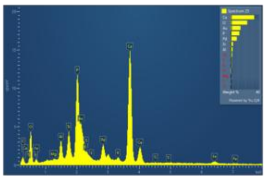


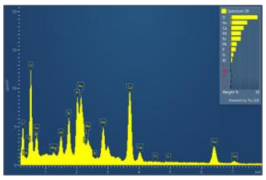


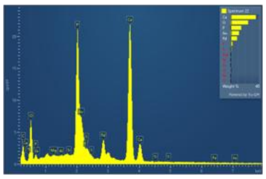






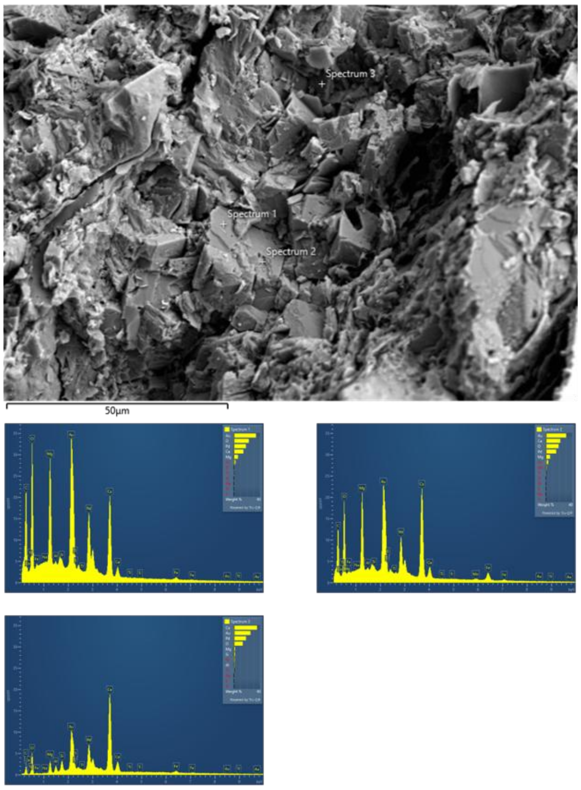




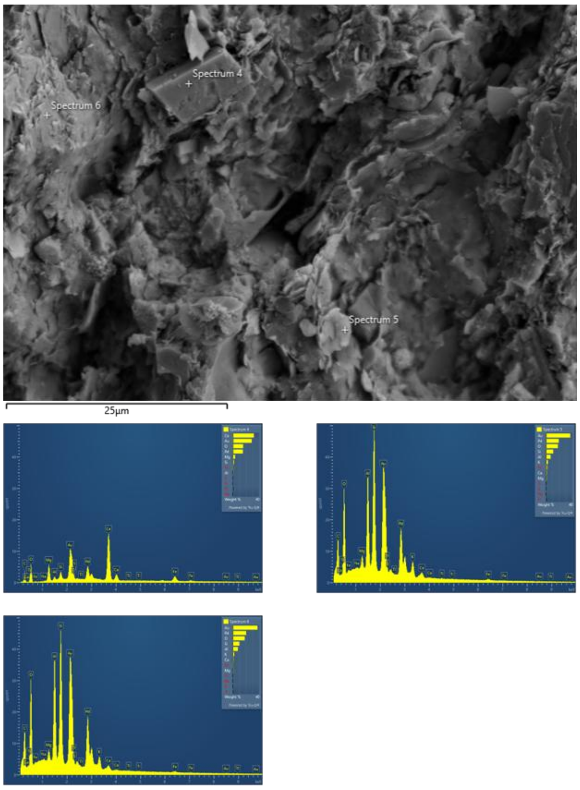


Specimen P.9143_Scale/Chip

Site 1



Site 2



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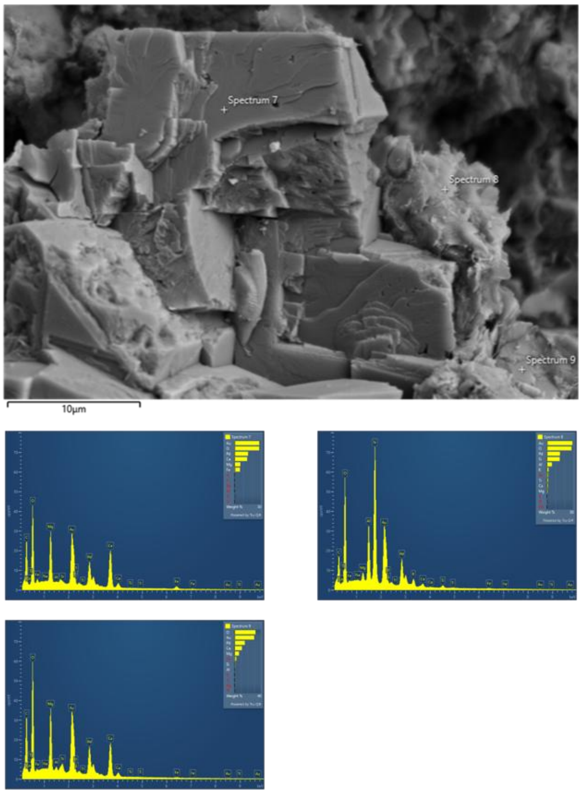

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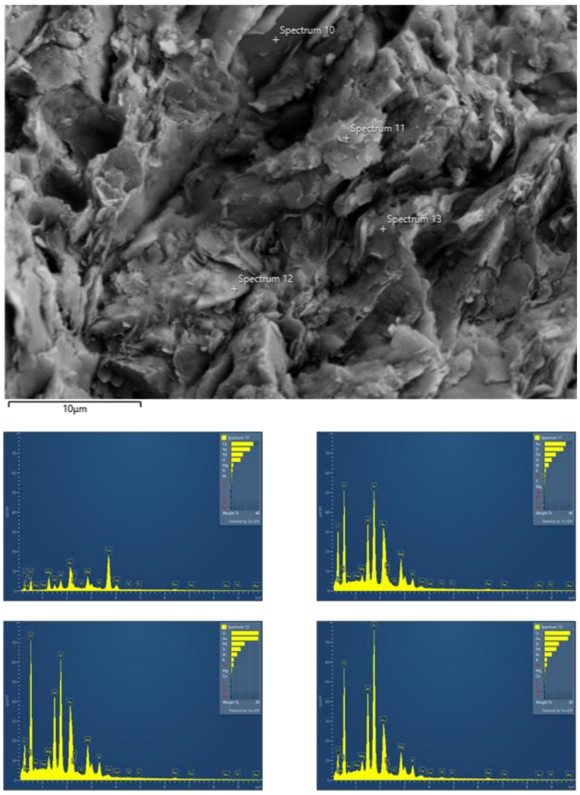
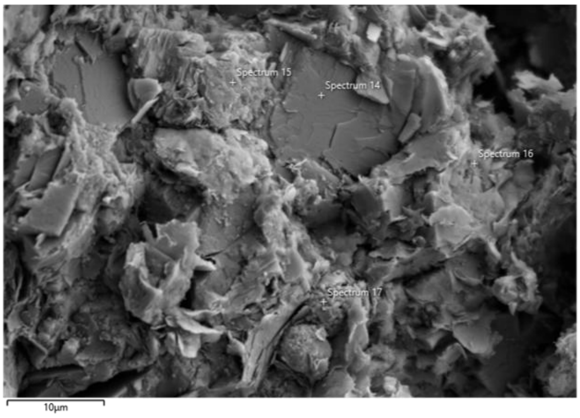
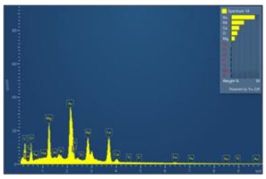
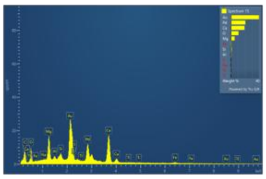


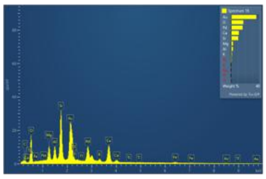
Specimen P.9143_Scale/Chip

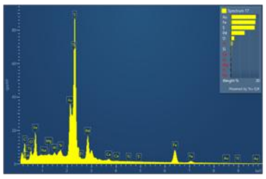
Site 5



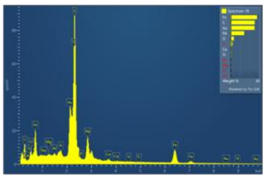


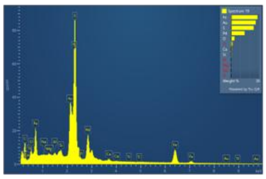


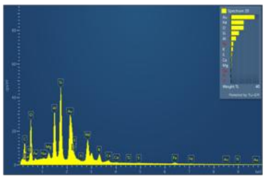


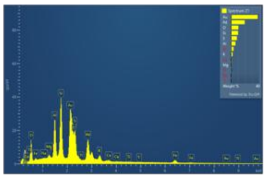


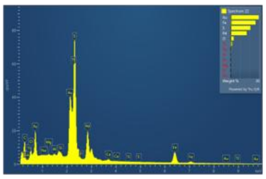
Site 6





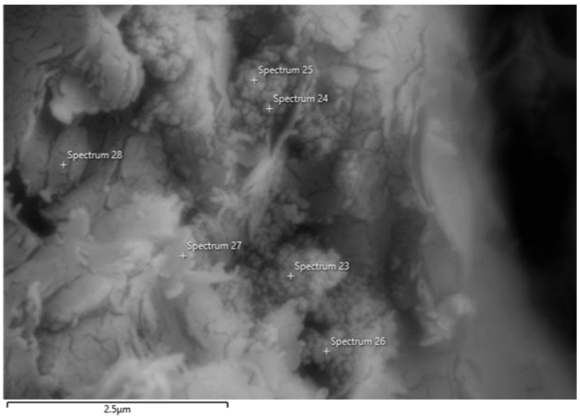


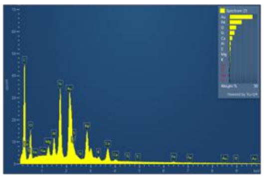
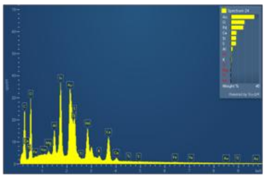
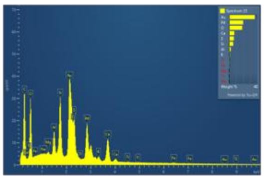
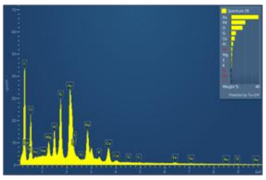
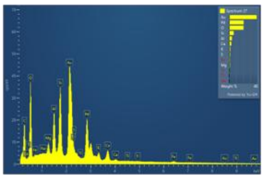
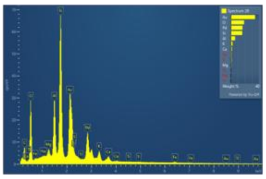




Specimen P.9143_Scale/Chip

Site 7



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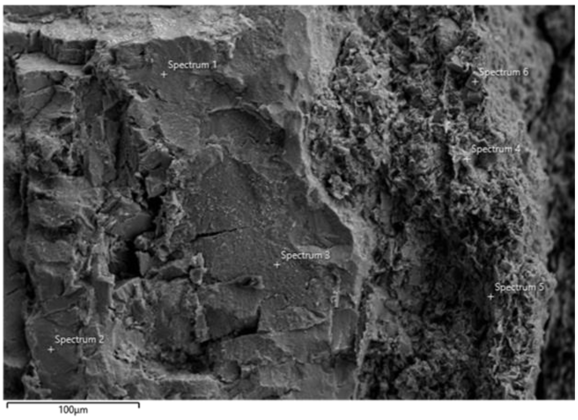
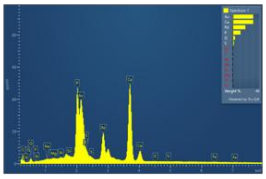
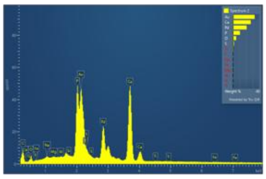
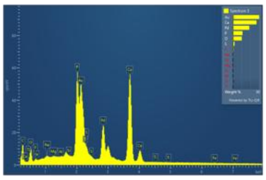
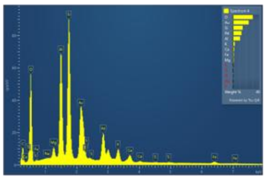
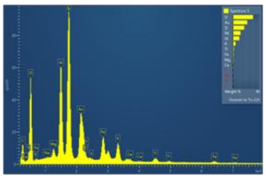
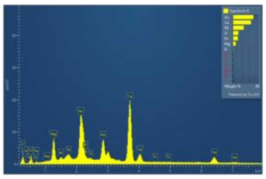
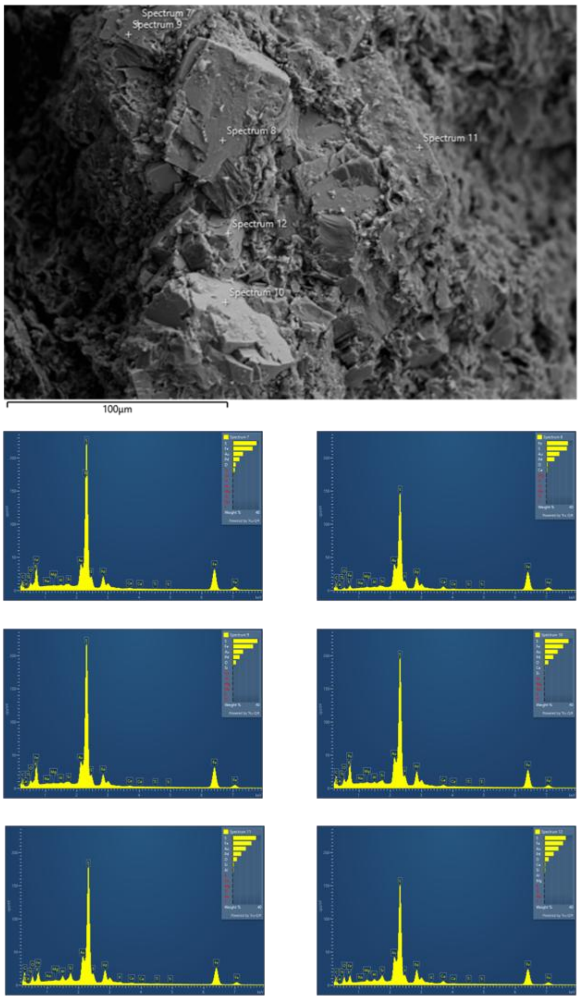


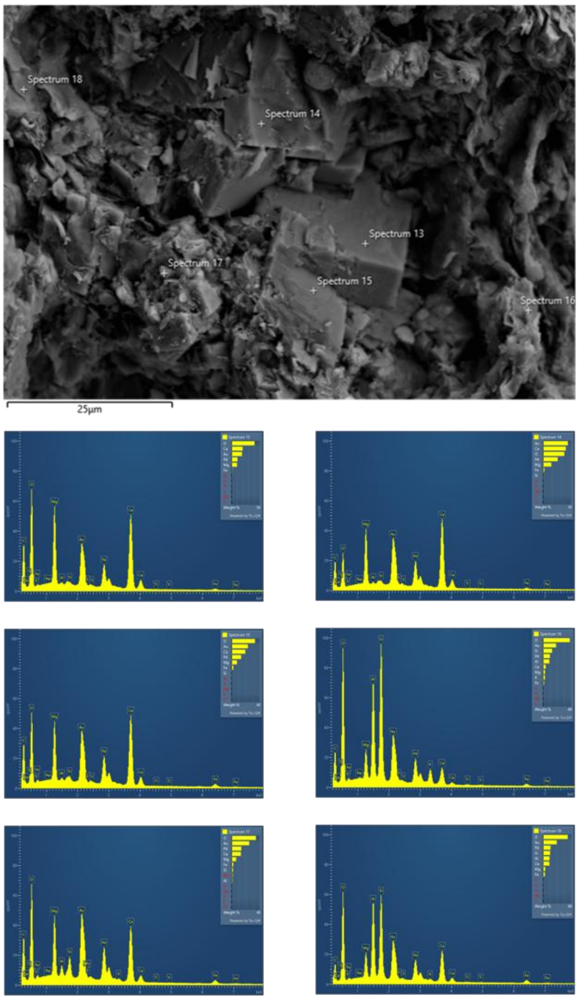







Specimen P.9143_Scale/Chip

Site 9

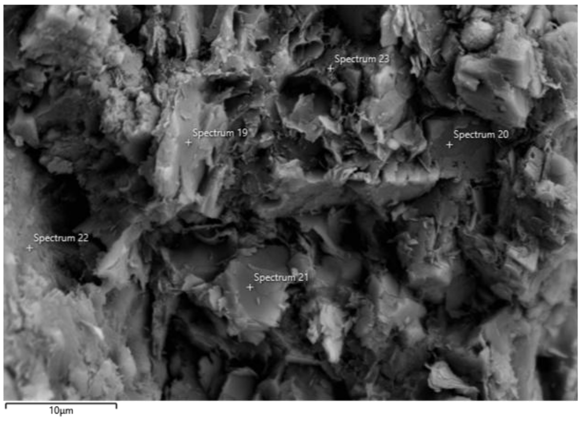


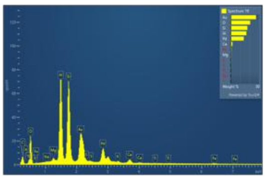
Site 10

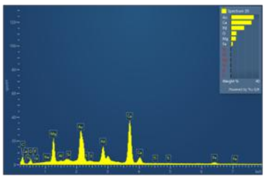


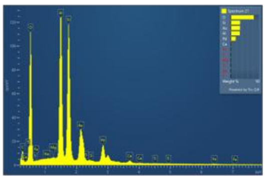
Specimen P.9143_Scale/Chip

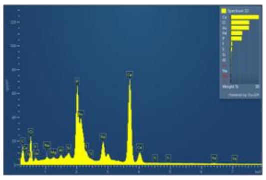
Site 11

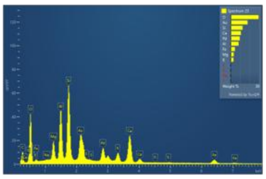










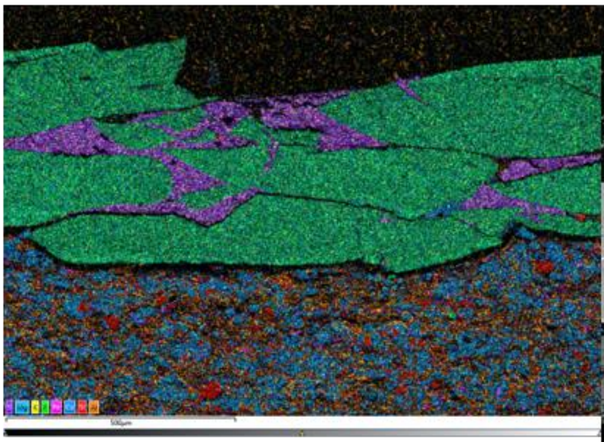


Appendix E: P.8114 Thin Sections

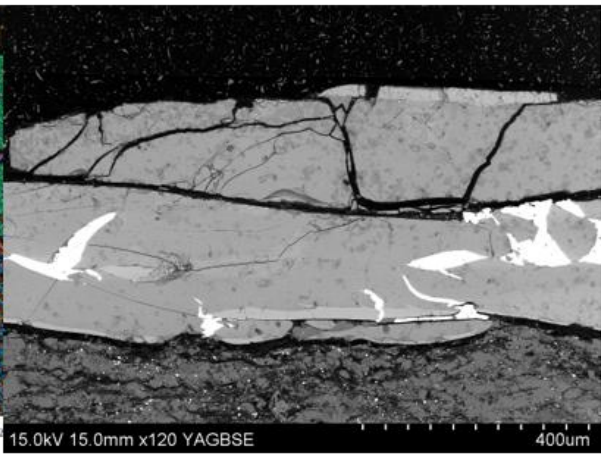
Specimen P.8114_Body

Location 1

EDS

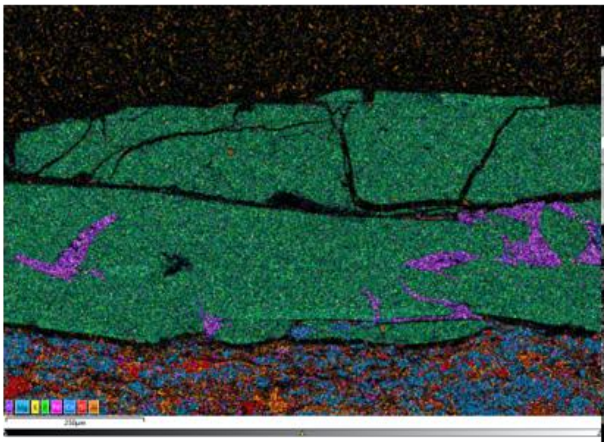


Electron Image

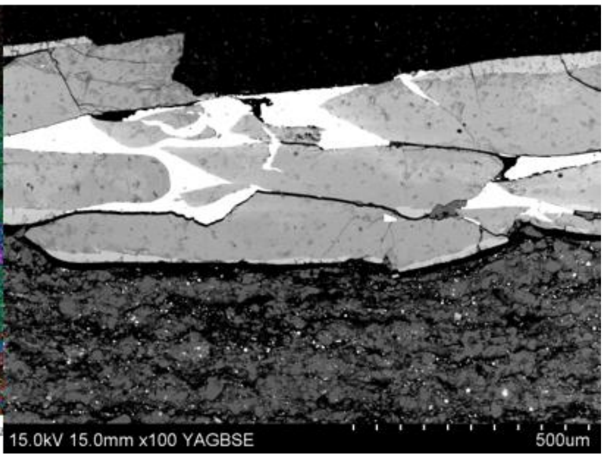


Location 2a

EDS



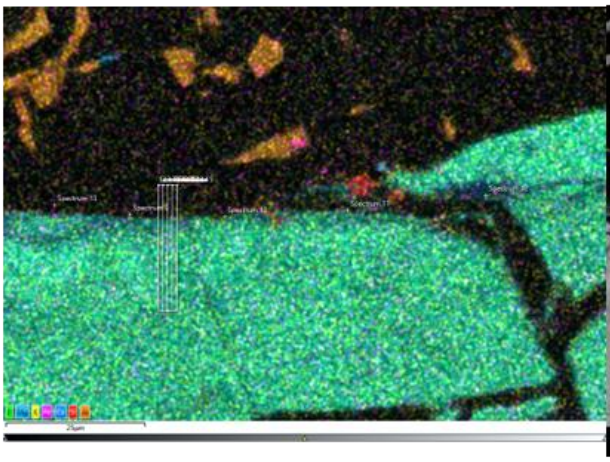
Electron Image



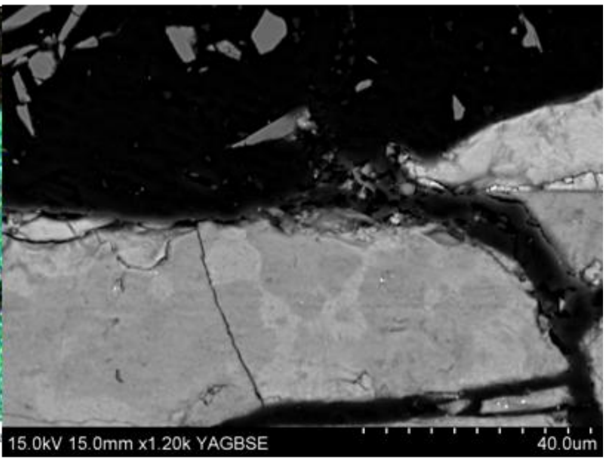
Specimen P.8114_Body

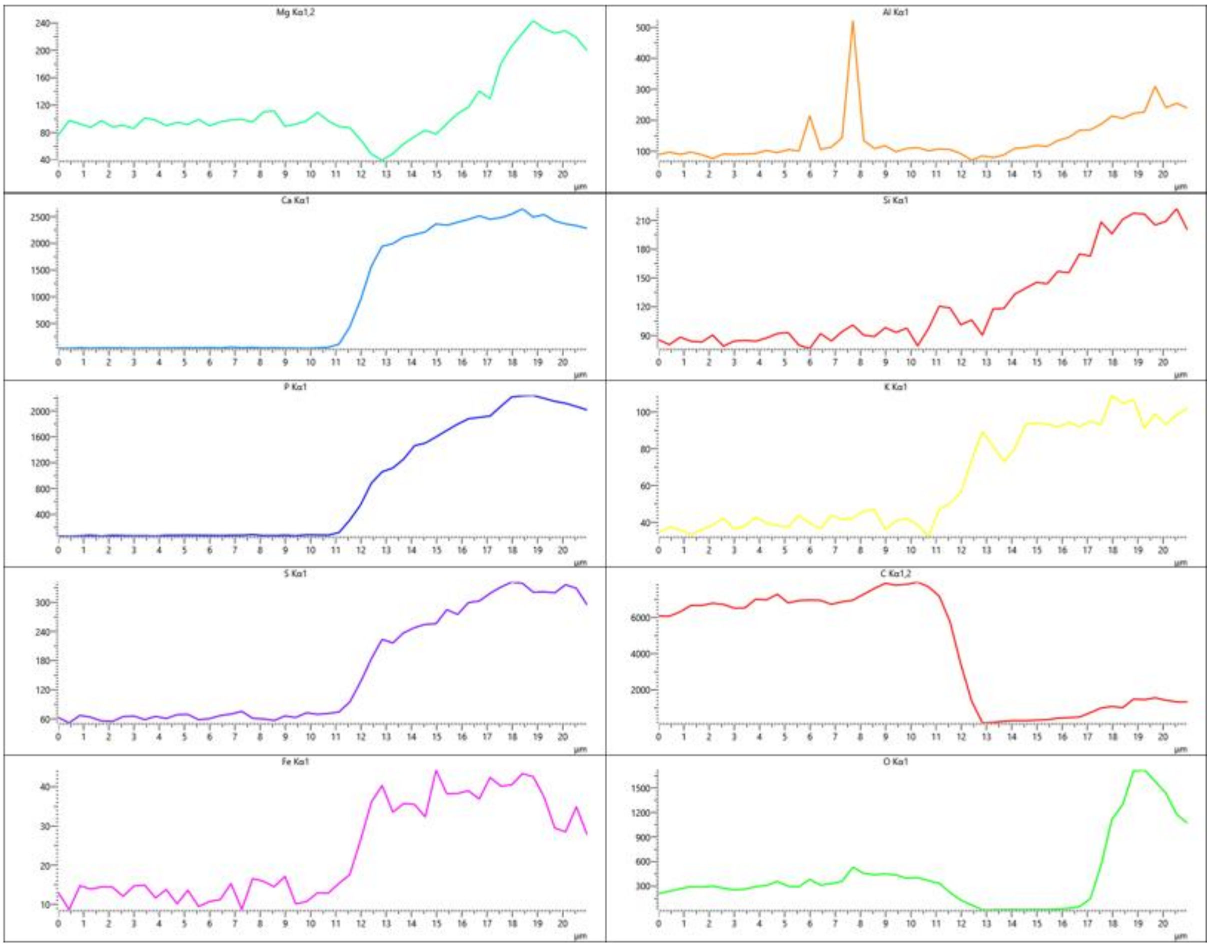
Location 2b

EDS



Electron Image

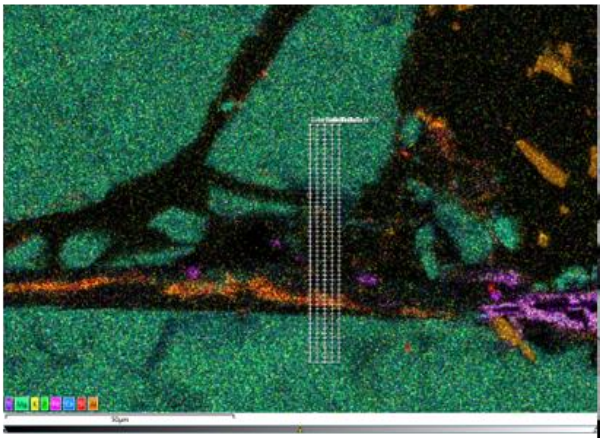




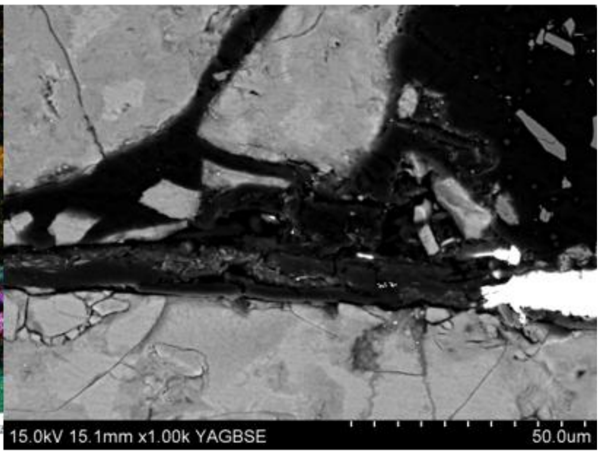
Specimen P.8114_Body

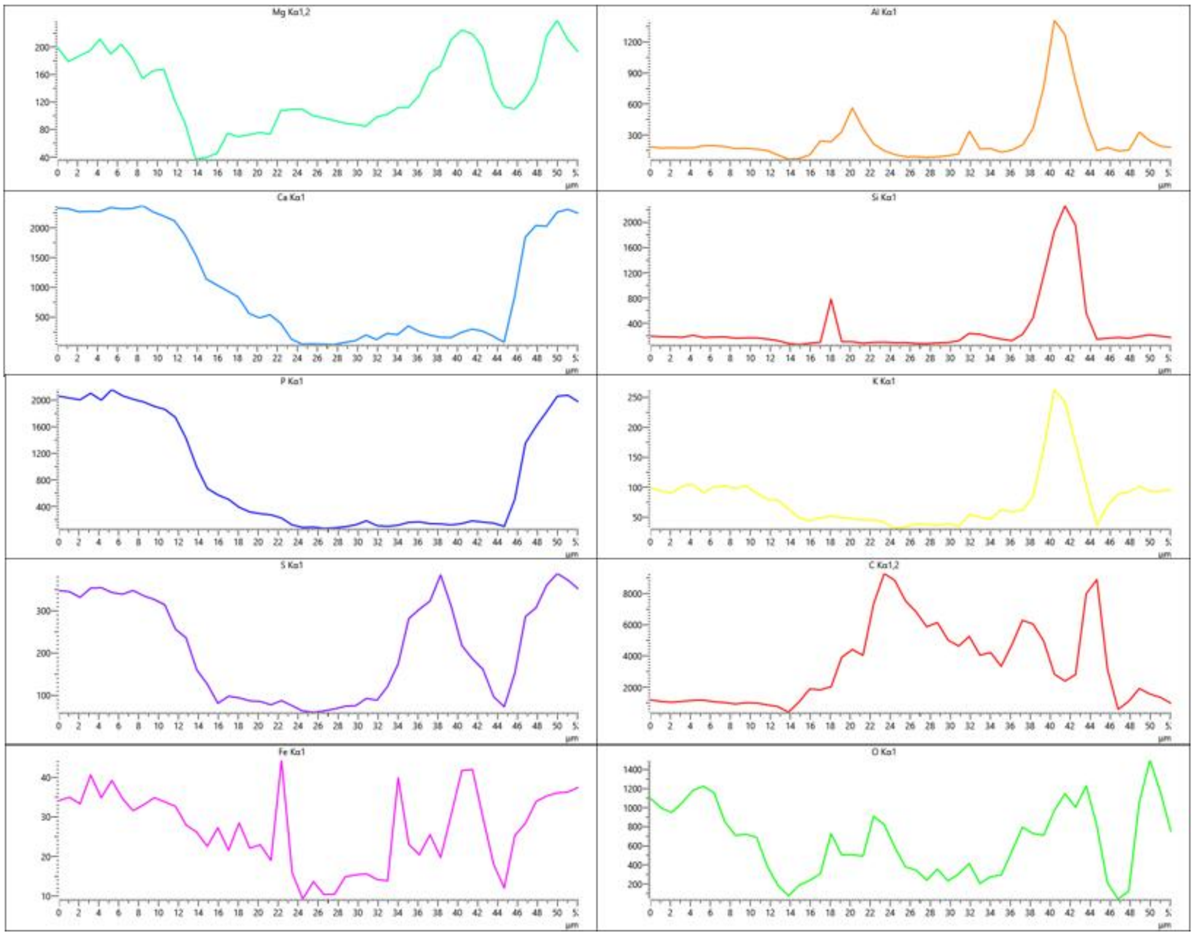
Location 3

EDS



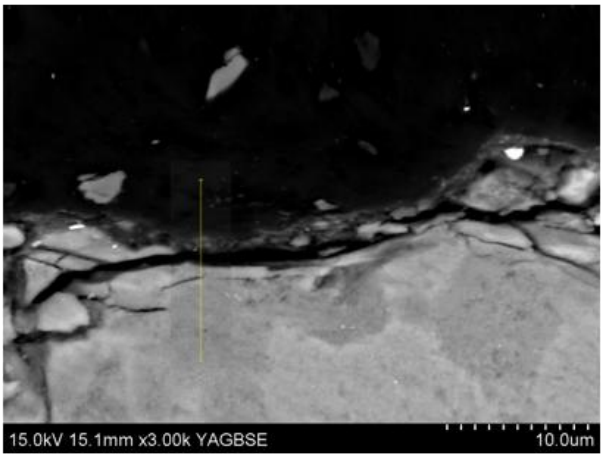
Electron Image

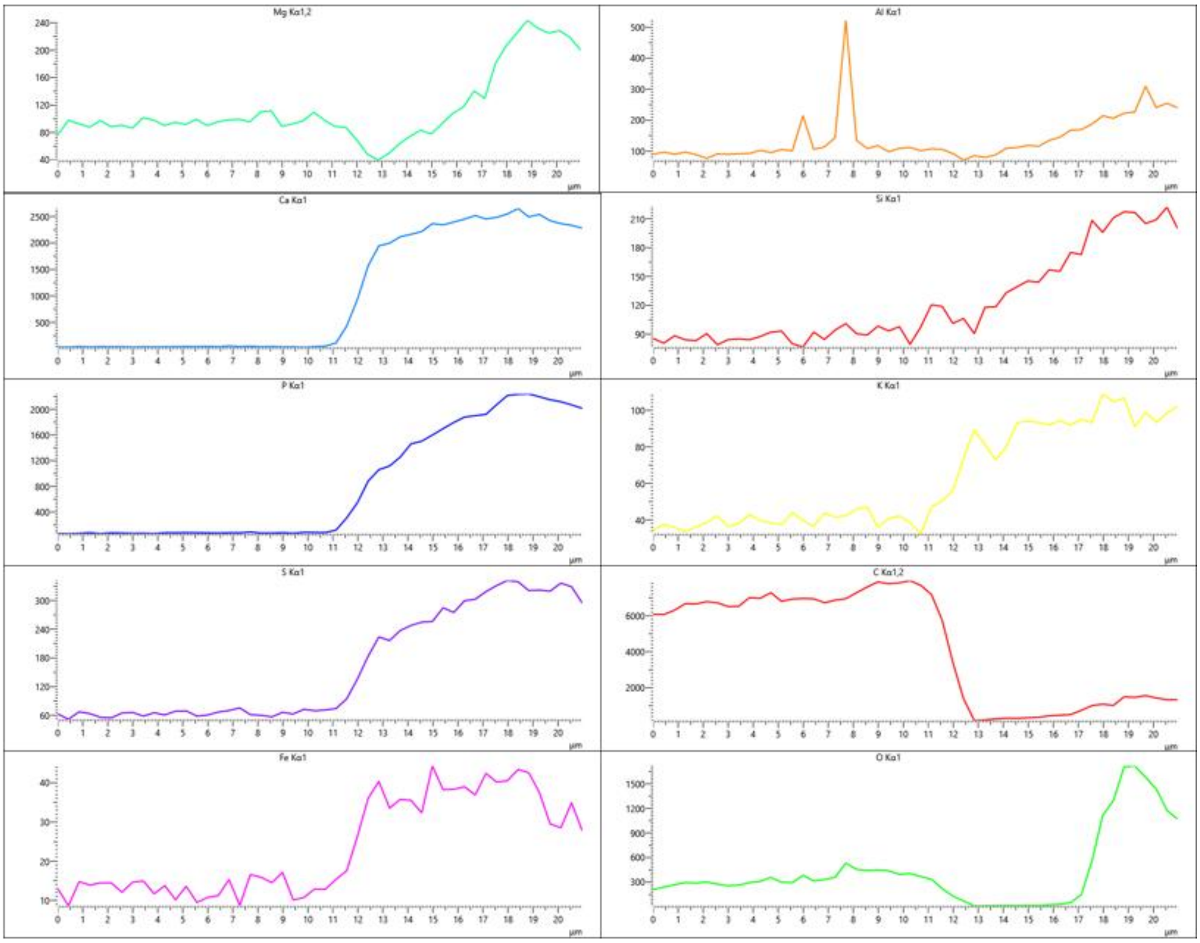




Specimen P.8114_BodyAdditional

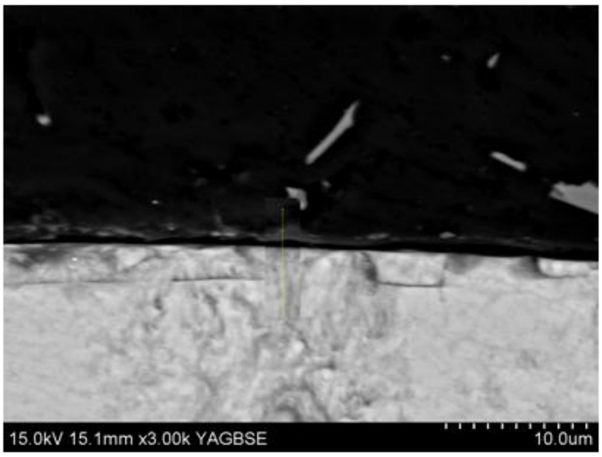
Location 4

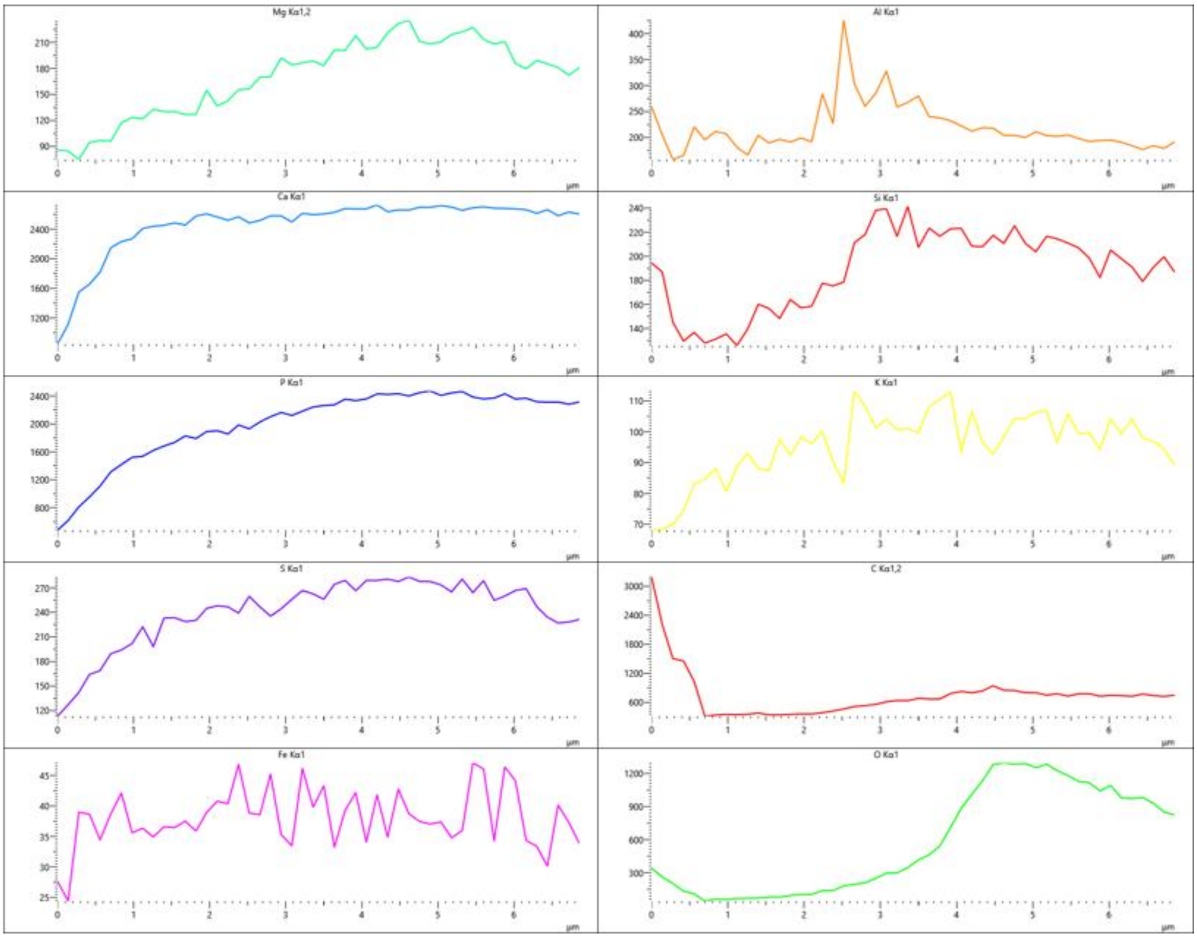




Specimen P.8114_BodyAdditional

Location 5

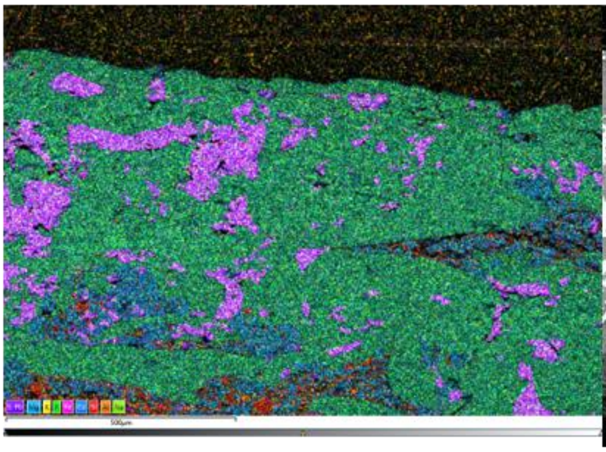




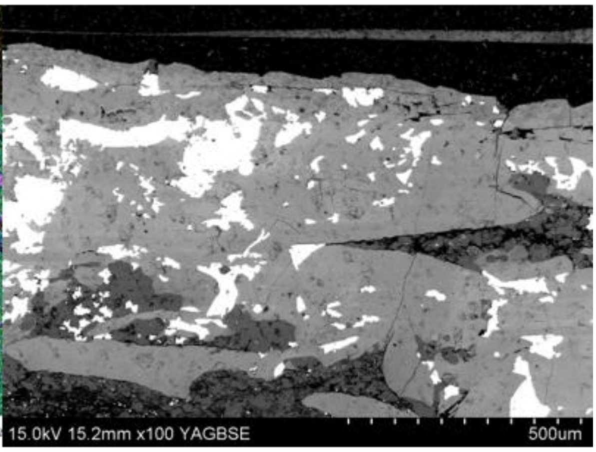
Specimen P.8114_Head

Location 1

EDS

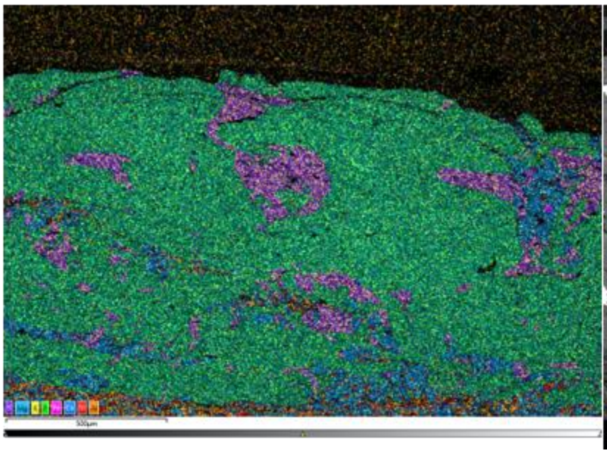


Electron Image

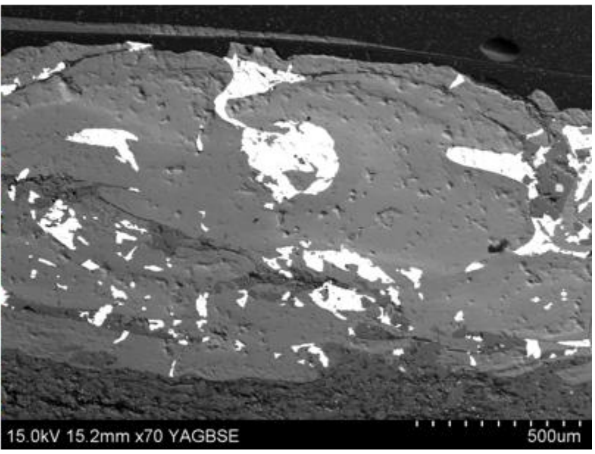


Location 2

EDS



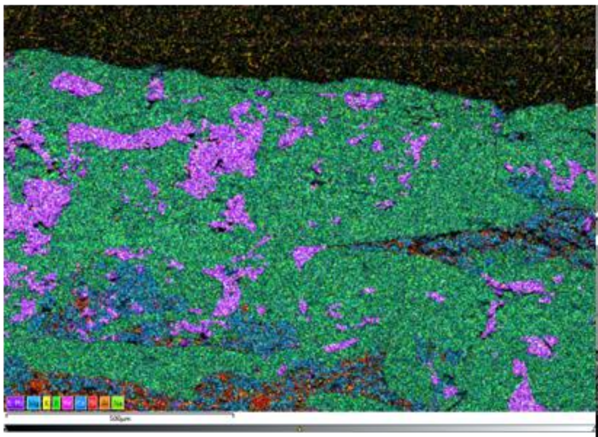
Electron Image



Specimen P.8114_Head

Location 3

EDS



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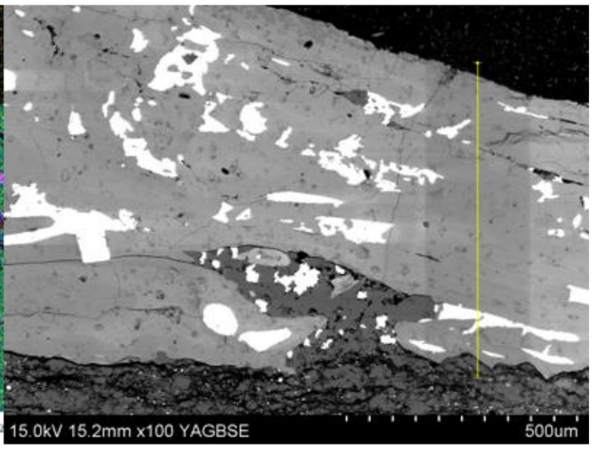
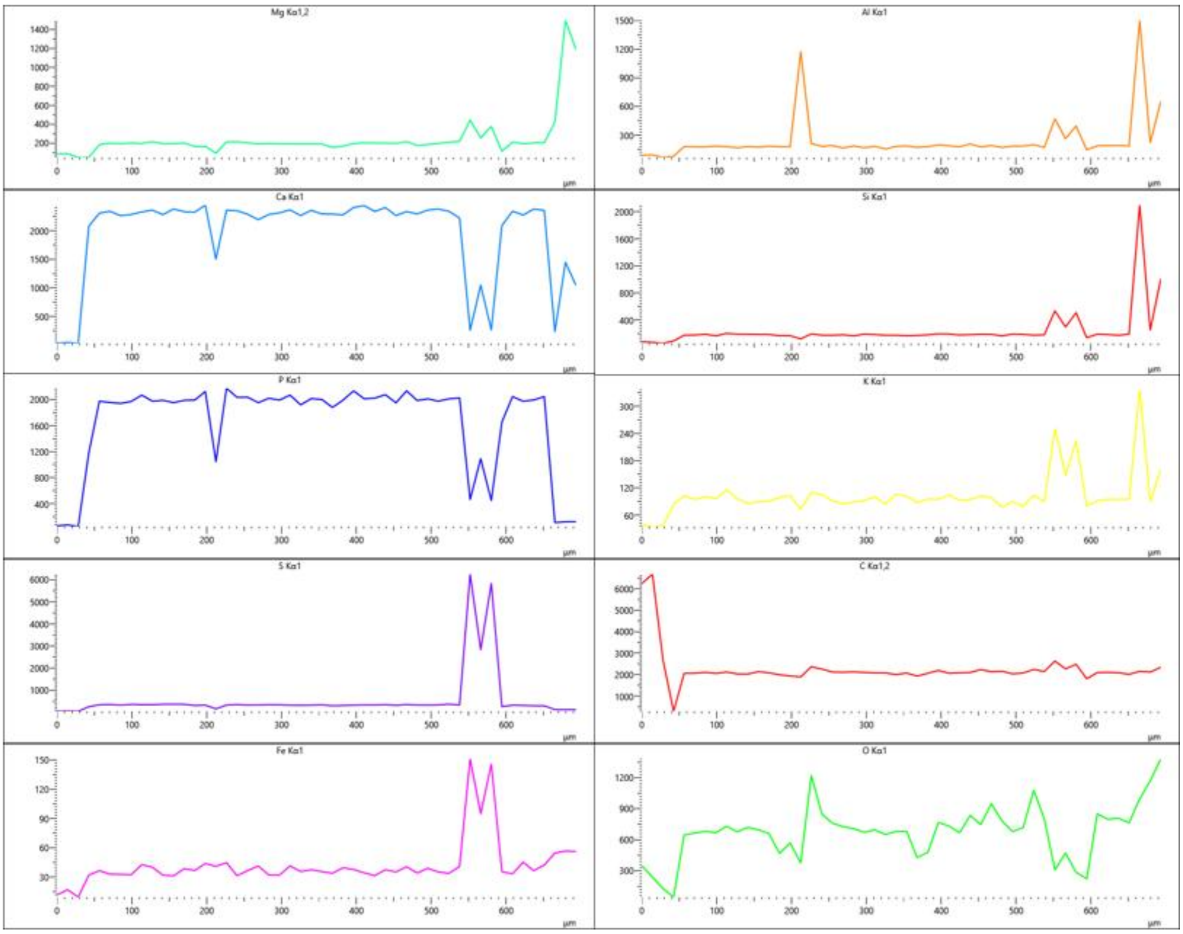
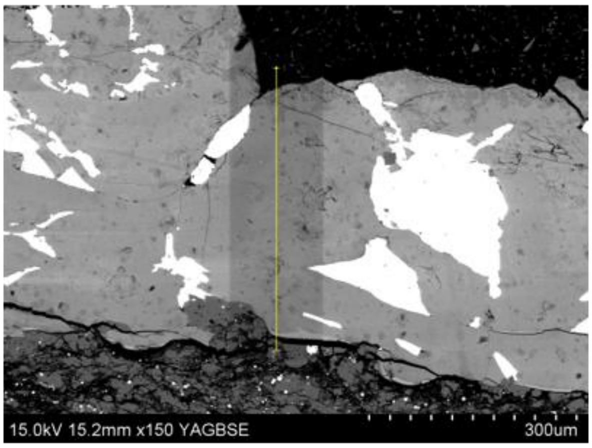
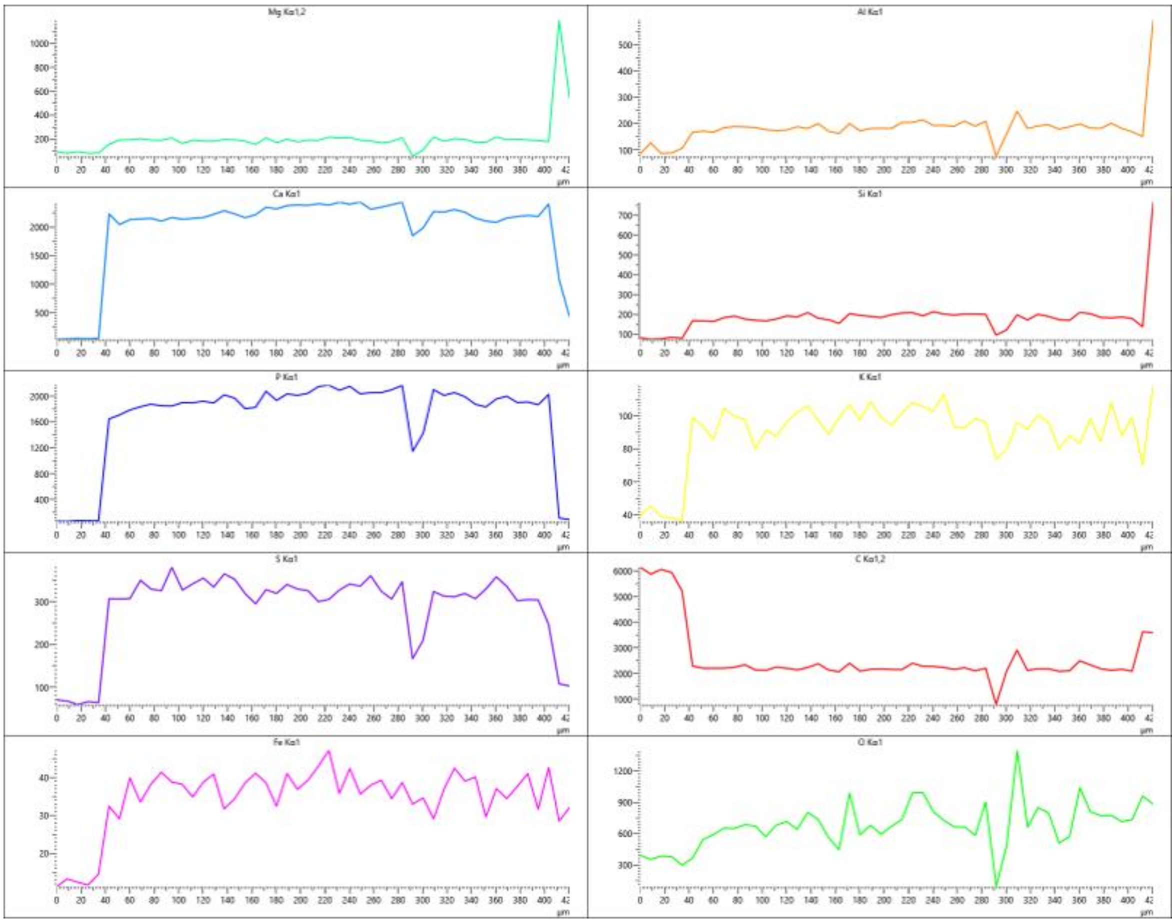




Specimen P.8114_HeadAdditional

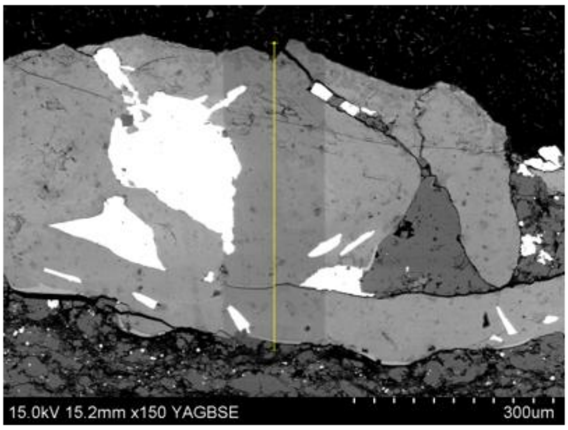
Location 4

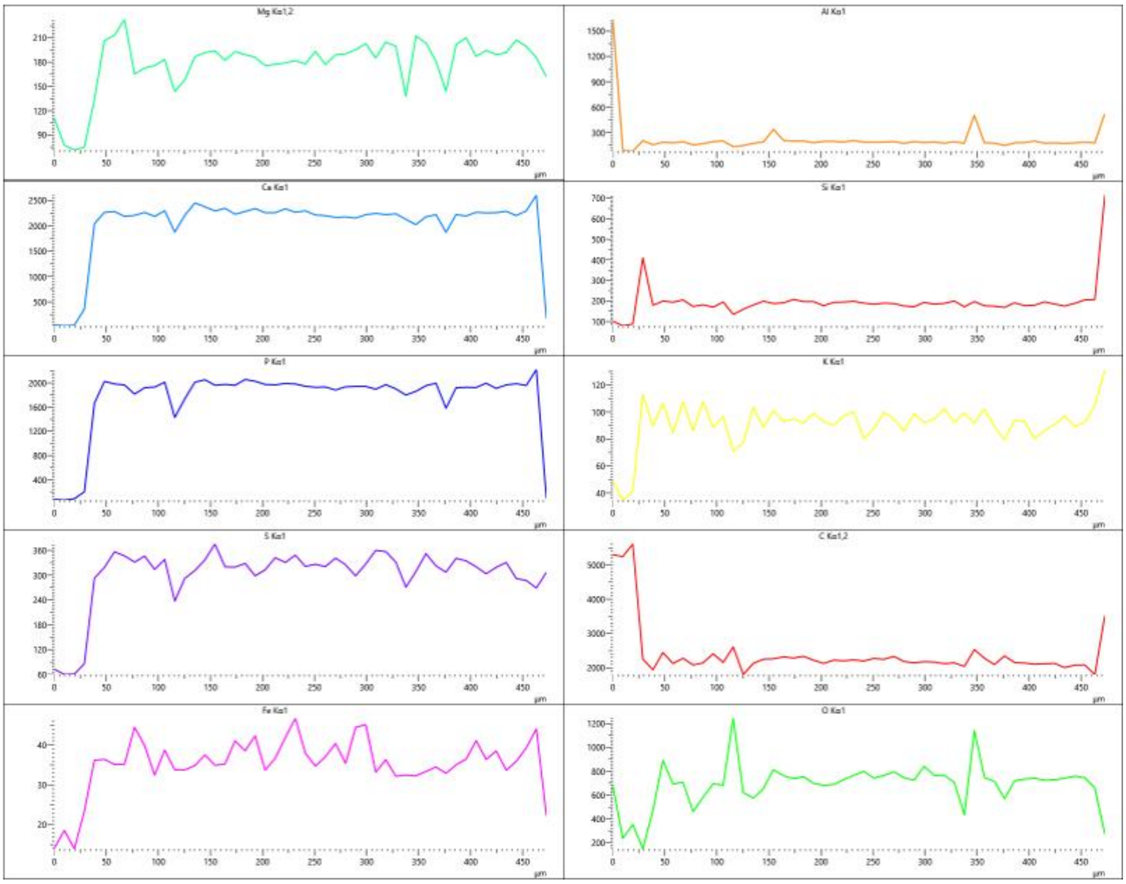




Specimen P.8114_HeadAdditional

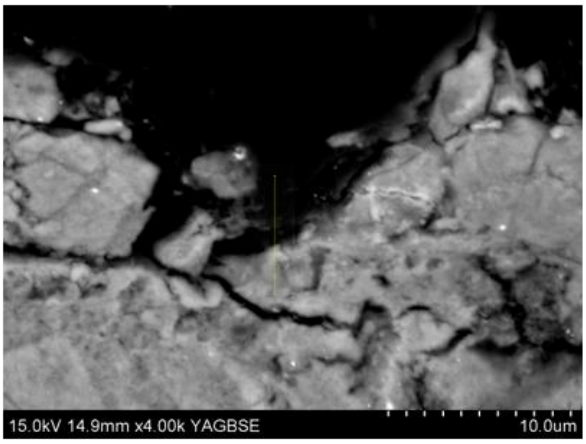
Location 5

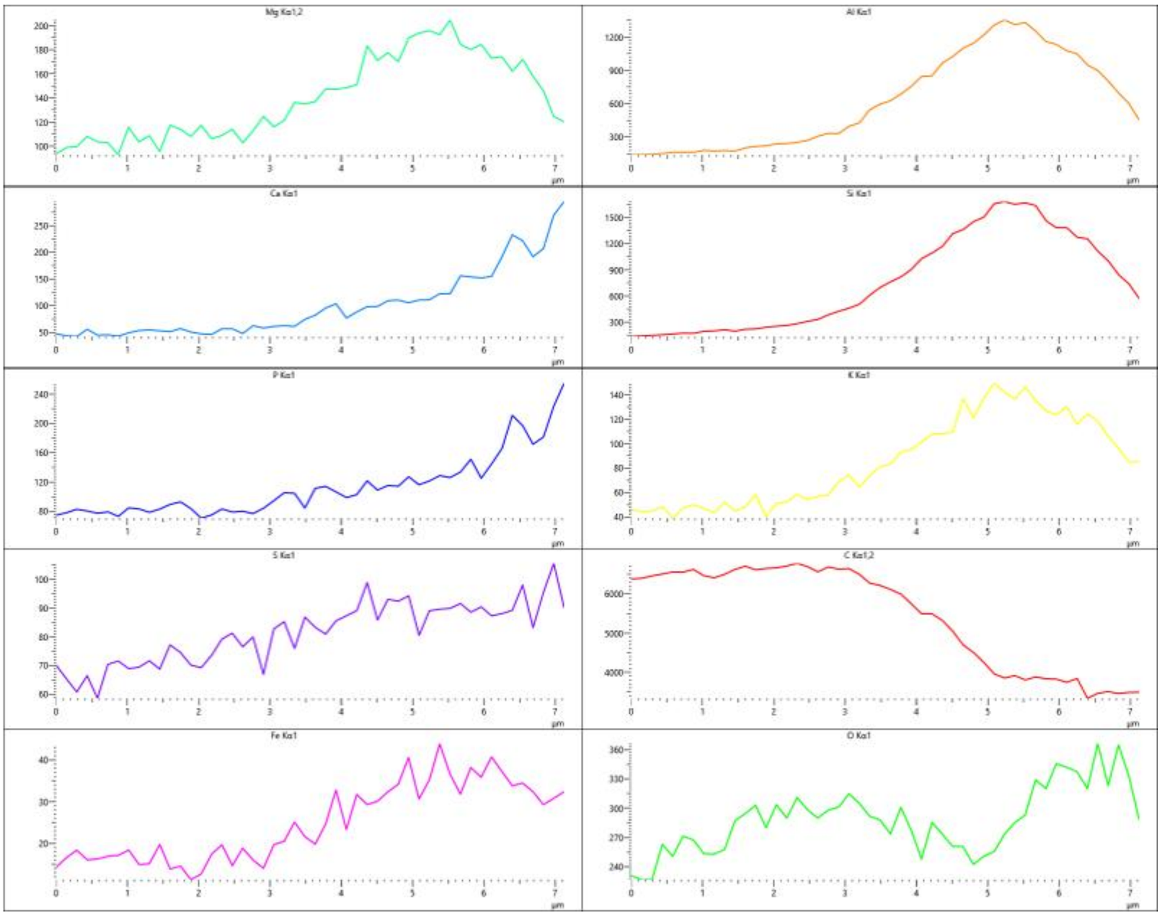




Specimen P.8114_HeadAdditional

Location 6

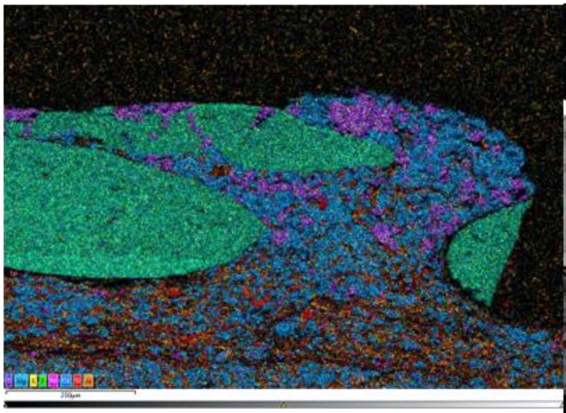




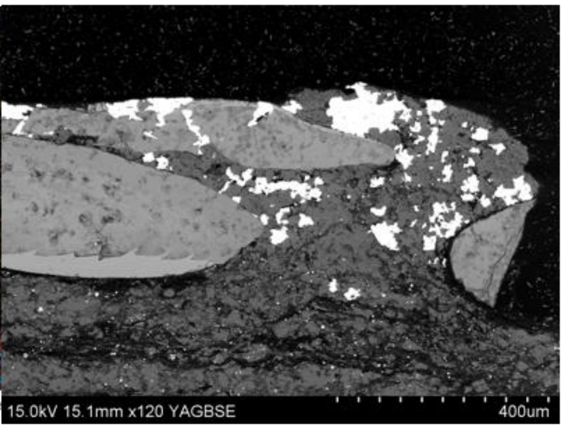
Specimen P.8114_Tail

Location 1

EDS

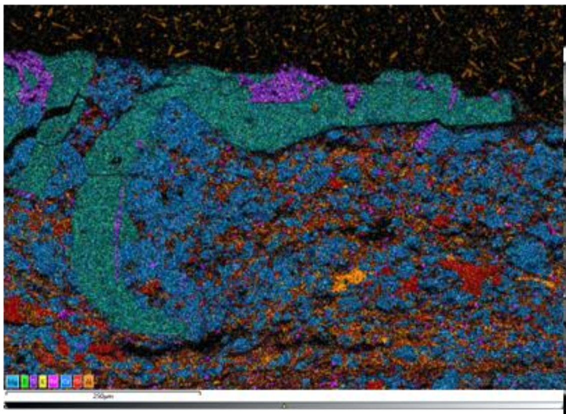


Electron Image

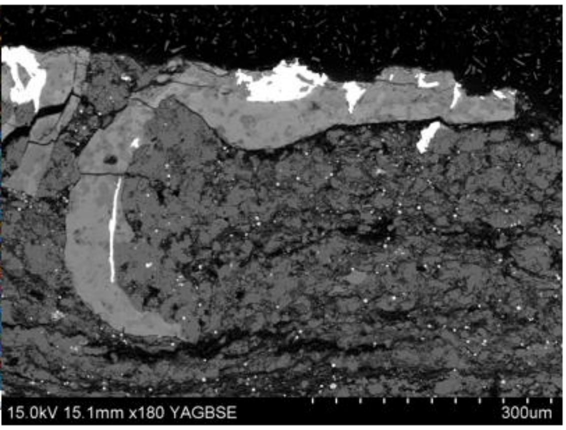


Location 2

EDS

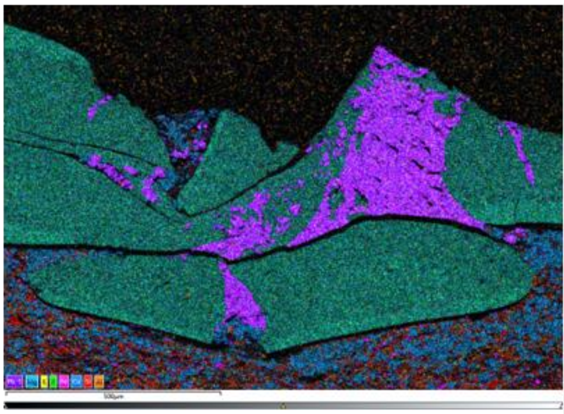


Electron Image



Location 3

EDS



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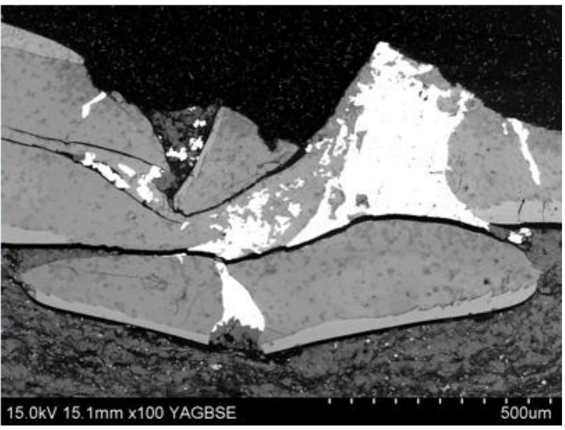
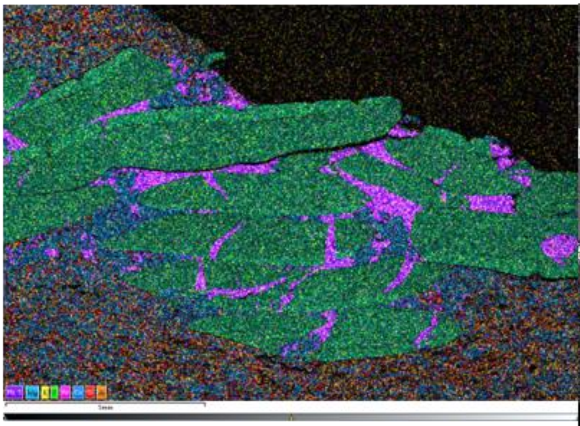


Specimen P.8114_Tail

Location 4

EDS



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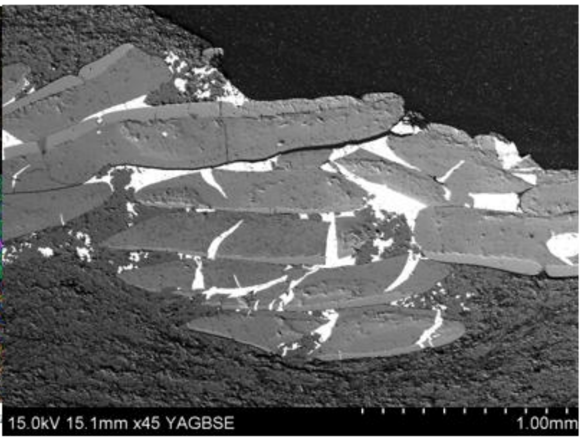
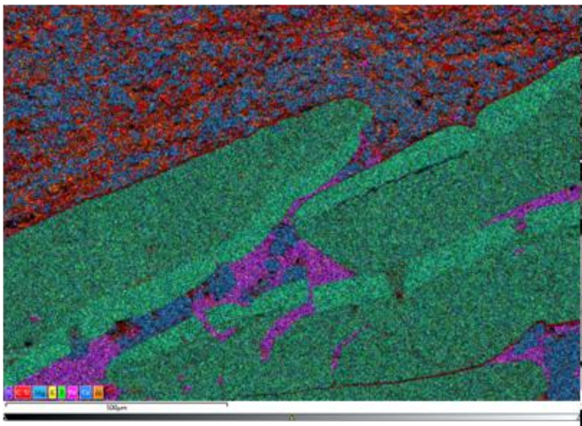


Location 5

EDS



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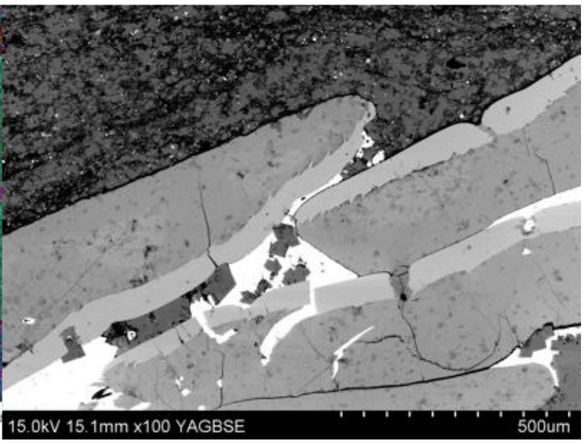
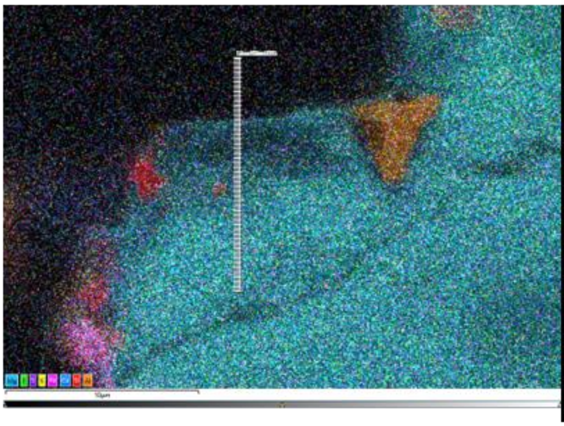


Specimen P.8114_Tail

Location 6

EDS



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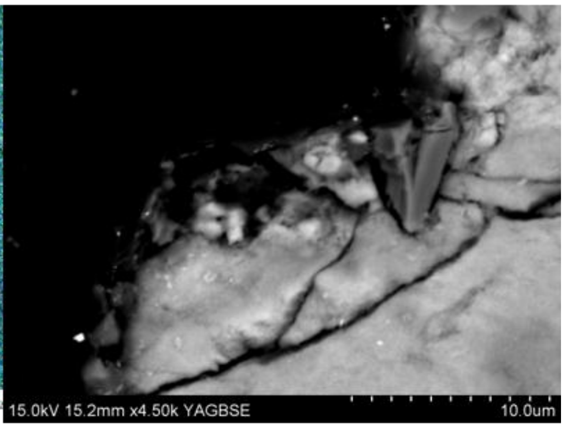

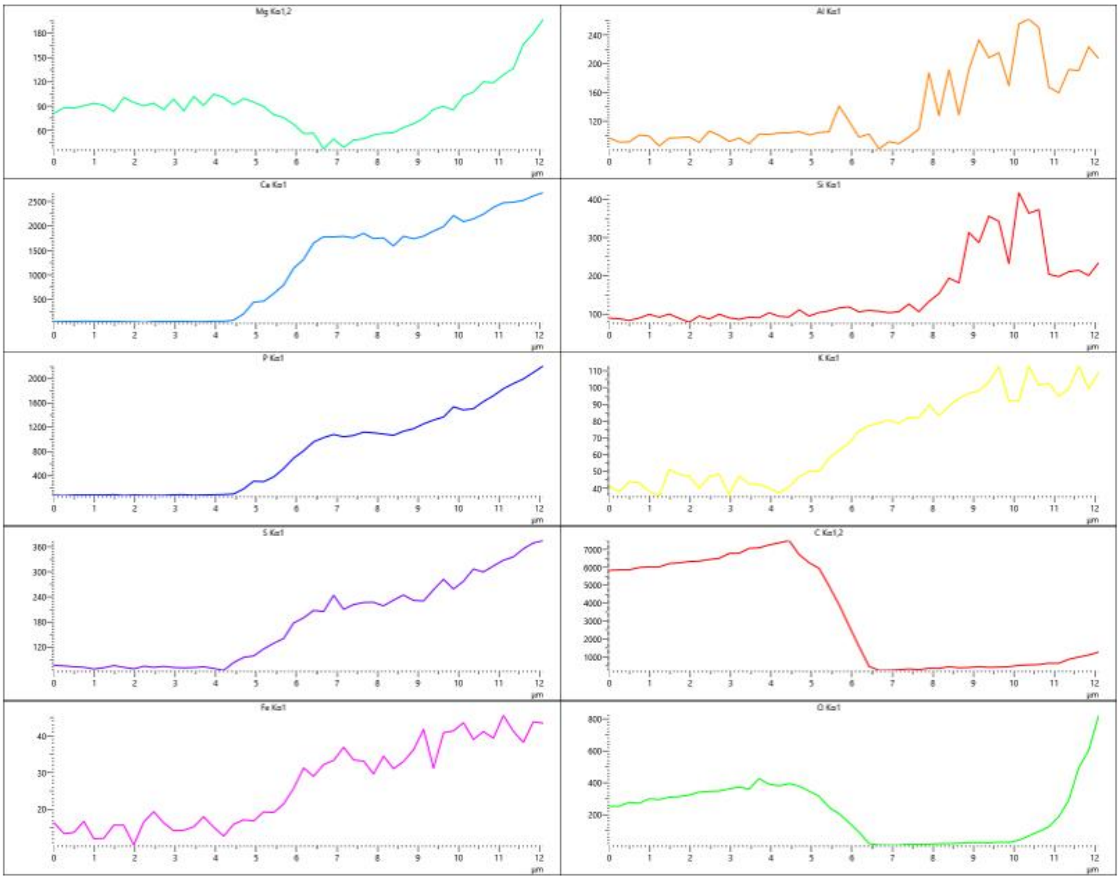

Specimen P.8114_TailAdditional

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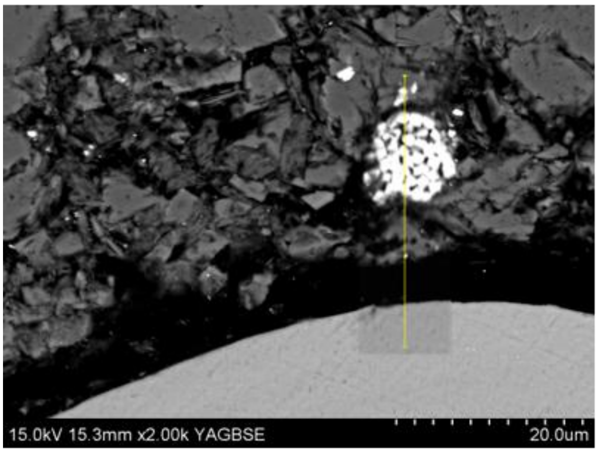

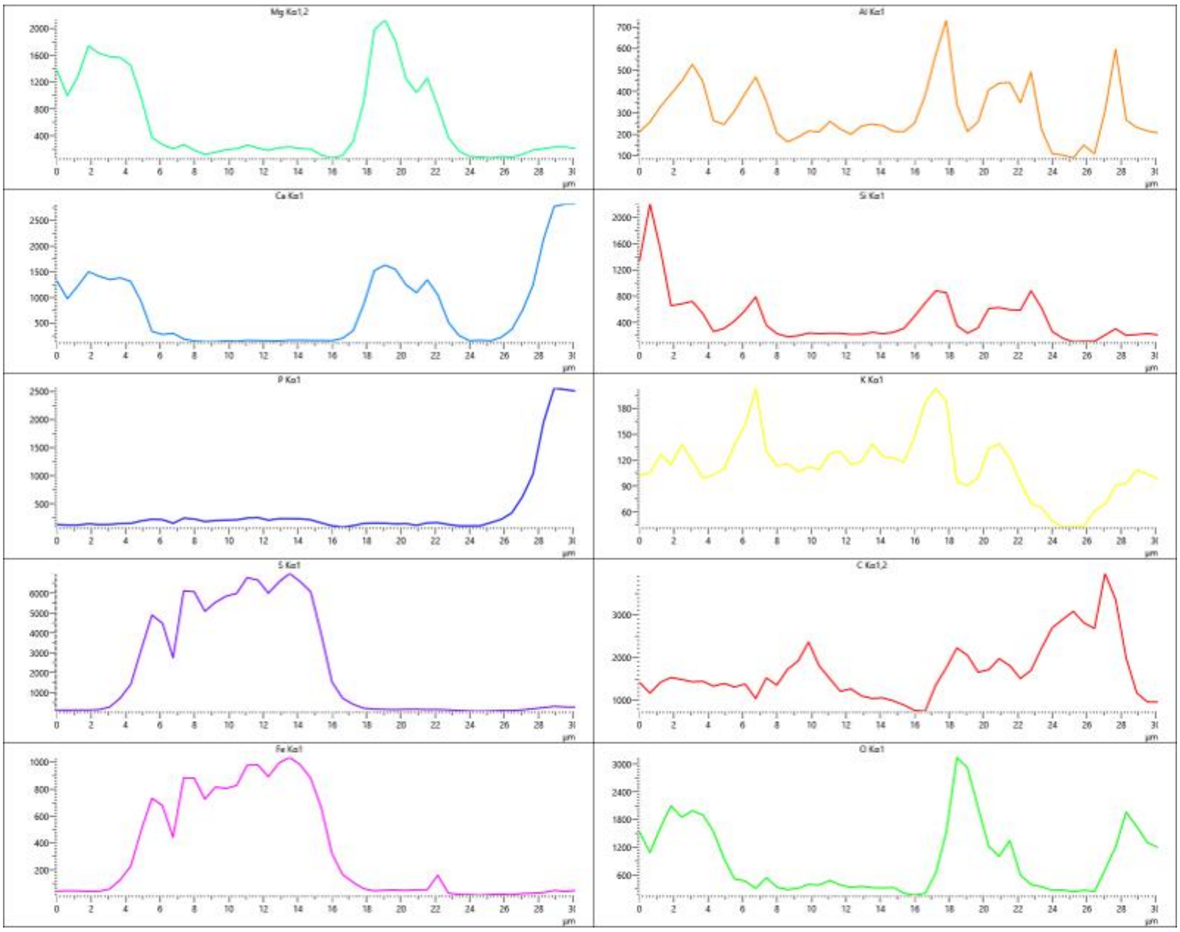

Specimen P.8114_TailAdditional

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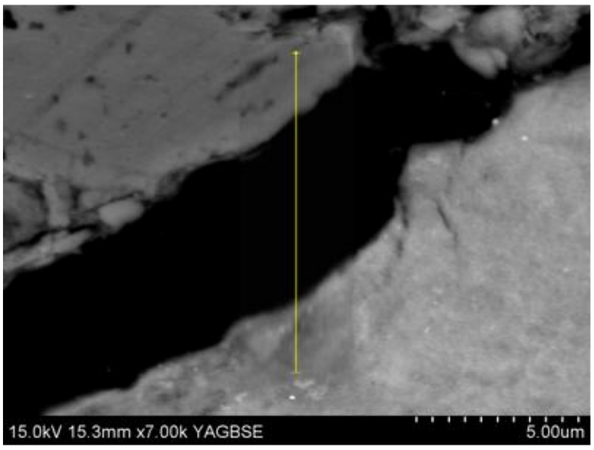
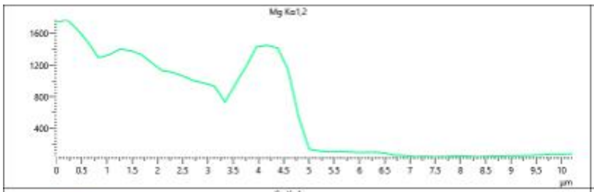
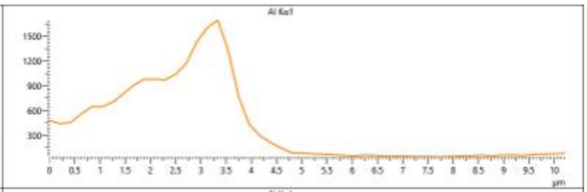
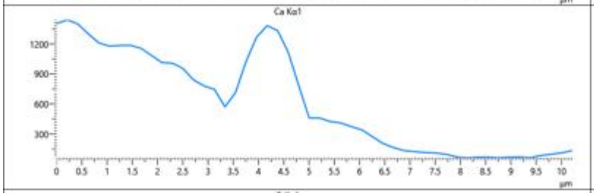
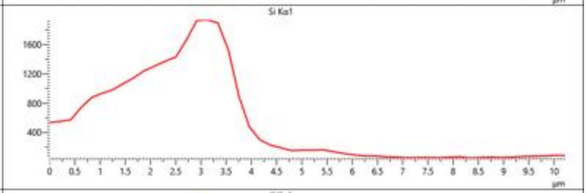
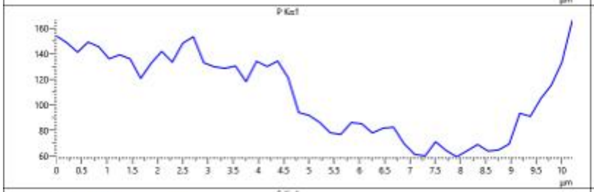


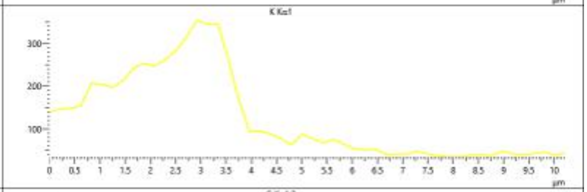


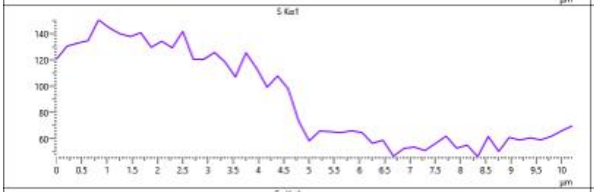


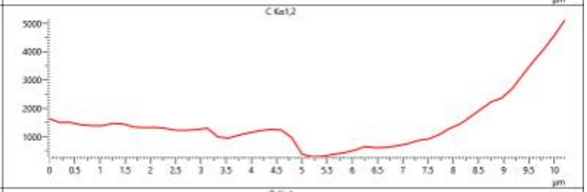


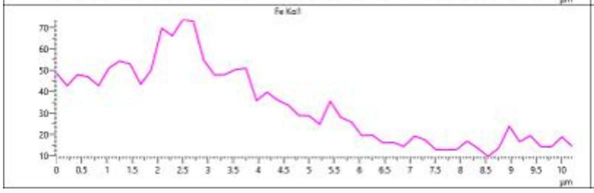


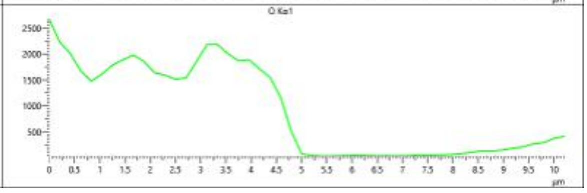






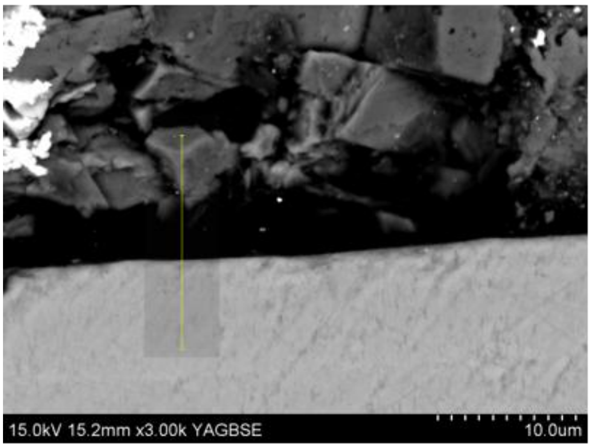


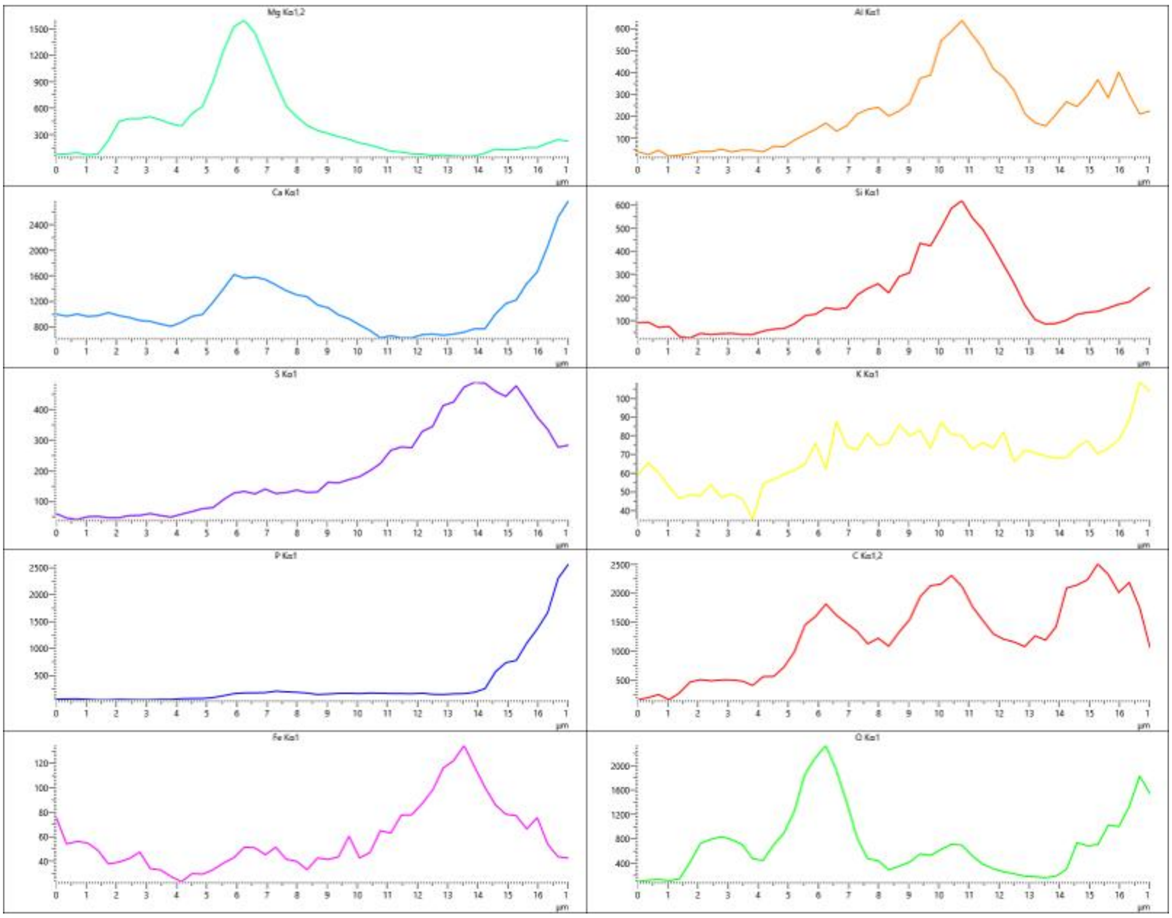




Specimen P.8114_TailAdditional

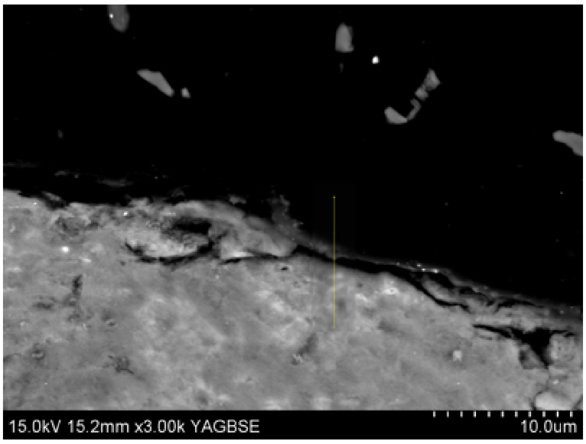
Location 9

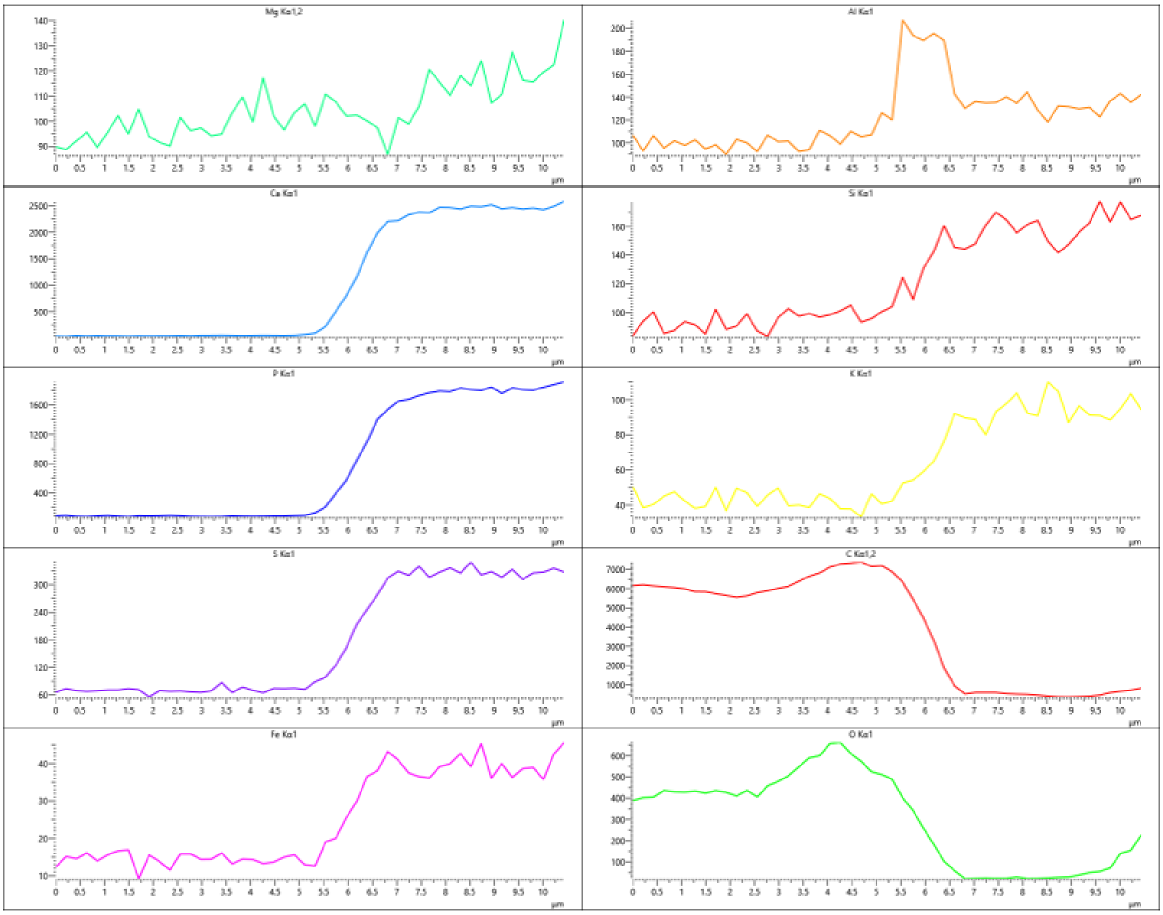




Specimen P.8114_TailAdditional

Location 10





Appendix F: Conodonts and Fish Scales/Teeth, C.M Henderson, Calgary

Report on the Marl Slate in Durham County, UK

Charles M. Henderson

Department of Earth, Energy, and Environment

University of Calgary, Calgary, Alberta CANADA

Samples:

All lower/bottom Marl Slate samples have been processed completely and picked. Three samples have yielded very nice fish teeth and scales, but no conodonts. The list of samples and locations is provided in Appendix 1.

Sample Processing:

I was able to dissolve and disaggregate the samples almost completely. The samples were slightly calcareous and were placed in buckets with a 10% acetic acid solution for up to a week. This dissolved some of the sample material and essentially softened the remainder. Residues were sieved and the coarser fraction was boiled in pots filled with Quaternary O solution – a detergent to deflocculate the clays. This was repeated given the muddiness of the samples. Washing to recover the insoluble residue took time because the mud regularly clogged the lower sieve. The upper sieve is mesh 16 (1.18 mm) and lower is mesh 200 (75 µm) meaning that the clay portion is washed down the sink. There was a lot of clay, which might account for the lack of conodonts so far in our samples. The sand sized material in the lower sieve is then bleached (boiled in a pot with household javex bleach) to remove organics, washed again, and then dried in a low temperature oven. Finally, the dried insoluble residue is separated in a heavy liquid at specific gravity of 2.86 – fish teeth, conodonts, pyrite etc. will sink and quartz etc. will float. The heavy fraction is then picked with a fine (000) liner paint brush that is dipped in water in order to pick up individual particles using the cohesion properties of water. The residue is spread evenly on a plate and then examined systematically under a binocular microscope. Later individual grains (fish teeth and/or conodonts) are selected and mounted on SEM stubs for photography.

Results:

To date no conodonts have been recovered. I chose to work on the basal Marl first because Swift (1995) found it to be most productive. His largest recovery came from DHQ1 (basal Marl Slate immediately above Yellow Sands at Downhill Quarry in Sunderland) in which he recovered 22 complete platform specimens of *Mesogondolella britannica* (his *M. phosphoriensis* – see below) and 76 fragmented specimens within a 21.5 kg sample (1 complete and 3.5 fragments per kilogram). His best productivity was in EH6 from the upper Marl at Eldon Quarry with 4 complete and 40 fragments of *M. phosphoriensis* within a 2.0 kg sample (2 complete and 20 fragments per kg). Many of his samples were barren. I remain optimistic I will recover a few specimens (but not in time for MSc completion), but obviously this is not an ideal setting for conodonts. This is likely a result of turbidity as it has often been noted that conodonts are rare or absent in samples with abundant mud and silt (mentioned briefly in Corradini et al., 2024). However, the Marl Slate must have been open marine at times since *Mesogondolella* only occurs in offshore normal marine settings. Their relative rarity might be related to turbidity, but also could be a function of fluctuations between open marine and more restricted conditions. Anoxia near the sea-floor would normally not be an issue since conodonts were nektic organisms. The climate during the Middle and early Late Permian was likely relatively arid in this part of NE England, but with probable significant cyclic variation. I suspect you might have some sort of estuarine circulation conditions that fluctuated with some cyclicity. Maybe similar to around the North Sea today, but a little warmer and dryer. It seems likely that this circulation and associated turbidity allowed some fish to migrate into the area (and a few conodonts as well) but seemed to preclude most benthic organisms. I didn't see other fossils in the sample residues. I have a local Lower Permian deposit that I similarly interpret with the only benthic organisms being demosponges. It is cyclic and silty levels have conodonts, fish bits, and sponge spicules followed by evaporate nodular dolostone with only some sponge spicules.

However, three samples (1433-1, Crime Rigg Quarry, Marl Slate bottom, sample #17; 1433-2, Crime Rigg Quarry, Marl Slate bottom, #18; 1436-1, Middridge Quarry, Marl Slate lower, #16) so far have yielded fish-teeth (most 1-2 mm long), fish scales, and a few shark dermal denticles. The fish remains are dominated by ray-finned (actinopterygian) fishes and sharks (chondrichthyans) are rare (Dankina et al., 2021a, 2021b). The preservation of micro-ornament is exceptional. Note that magnification factors differ somewhat in the SEM material (all from 1433-1), but most are 100 or 200 times. I tend to simplify magnification variability to make it easier to develop plates with same magnification. Also note that there are two pictures of each (created simultaneously) - one from the back-scatter electron (BSE) detector (gives a semi-quantitative impression of composition) and the other from the ETD detector, which records secondary electrons and creates the best image of the surface. There are a few thin cemented laminae with lots of fish bits embedded in and on the matrix suggesting that these may thin lags on the seafloor. For example, 1433-1-3 had a dermal denticle in lateral profile and I thought it would show in contrast to matrix on BSE, but it does not, suggesting that the matrix and fish scale are both phosphatic. See also 1433-1-4, which has a rhomboid scale in relief, but little BSE difference. Werynski et al. (2023) provides detailed images that identify features like the acrodin cap (compare to 1433-1-8&14&15) on many of the teeth. McCurry et al. (2019) describe the apicobasal ridges that are well preserved on many of our teeth. The micro-ornament or apicobasal enameloid ridges are interpreted as a typical feature of aquatic amniotes (marine reptiles and mammals) as well as some fishes. In all cases, these organisms are predators of fish and the ridges increase the ability to catch and hold onto their squishy slippery prey (for example a conodont animal or another juvenile fish). It seems that the fishes in this sample are dominated by predator life mode, a few teeth may be more typical of durophagous trophic habit (ie. fish that eat hard shells like brachiopods, but there seems little to eat in the Marl Slate save for a few "inarticulates" like *Lingula* and *Discina* identified by King, 1850 from the Marl Slate). Durophagous fish teeth could be viewed for microwear to possibly determine diet (Purnell and Darras, 2016). The bumps on the rhomboid scales are likely an adaptation for generating or controlling turbulence that decrease drag on the fish body. Something similar was adapted into sharkskin swimwear - it was so effective that it is now banned from Olympic competition.

Age:

We have not yet recovered conodonts, but a review of the material Swift (1995) illustrated provides new insights as to age of these samples. His conodonts are all well preserved – many are fragmented, but this is typical for specimens buried in fine-grained lithologies. The standard correlation for the initial Zechstein transgression is Wuchiapingian and younger than 257.6 Ma (Menning et al., 2006; Menning, 2022). The conodonts in Durham and Yorkshire counties include *Mesogondolella phosphoriensis* (sensu Swift, 1995; later named by Kozur 1998 as *M. britannica*) from the Marl Slate and *Merrillina divergens* from the Raisby/Ford/Cadeby formations. These two taxa do not overlap in any sample reported by Swift (1995), nor do they overlap in the Phosphoria Basin of western USA

(Wardlaw and Collinson, 1984, 1986). In fact, they are separated by a major lowstand of sealevel and subsequent early Wuchiapingian global transgression. In my view, there is a high probability that these two different conodonts reflect two different times within the Permian. Legler et al. (2005) and Legler and Schneider (2008) also point out three pre-Zechstein ingressions, in addition to T1 with Kupferschiefer equivalent (also with *Mesogondolella britannica*) and a Zechstein Ca1 phase with *Merrillina divergens*; the upper Rotliegend II transgressions would date to 266-257.6 Ma (Menning, 2022).

There is a long history to the naming of the *Mesogondolella* taxon. Swift (1995) identified it as *Mesogondolella phosphoriensis*, which is more or less correlative with the Wordian Stage. The specimens illustrated by Swift (1995) are indeed very similar. Kozur (1998) renamed the taxon as *Mesogondolella britannica* (perhaps motivated by the fact that this taxon was presumed to be Wuchiapingian) and said it was the ultimate species of a cool-water lineage from *M. idahoensis* to *M. phosphoriensis* to *M. rosenkrantzi* (2 subspp.) to *M. britannica*. However, *M. rosenkrantzi* is the youngest member of this lineage (see Beauchamp et al., 2009). The "Kozur" lineage is repeated in Legler and Schneider (2008; p. 112) and this should be corrected. Kozur (1998) compared *M. britannica* to *M. phosphoriensis* and said it was most like *M. rosenkrantzi* n.subsp. (not published), which was found in the Retort Shale Member of the Phosphoria Formation. Kozur and Wardlaw (2010) next contrasted this taxon (as *Mesogondolella* n.sp. from the Retort and descended from *M. phosphoriensis*) from a new and slightly older species from Oman they called *Mesogondolella omanensis*. They did not mention, nor cite Kozur's 1998 paper naming *M. britannica*. Finally, Wardlaw (2015) named this taxon as *M. retortensis* and cites only Kozur and Wardlaw (2010) and makes no mention of *M. britannica*. If *M. retortensis* and *M. britannica* are synonymous, as seems most likely to me, then priority goes to *M. britannica* with the holotype in Swift (1995; pl. 3, fig. 2). Based on an updated integrated brachiopod-conodont biostratigraphy (Wardlaw and Collinson, 1979, 1984, 1986), *M. britannica* would correlate with the Capitanian. The GSSP for the Capitanian (Shen et al., 2022) occurs in a transgressive interval within the Pinery Member of the Bell Canyon Formation (age ~264 Ma).

The taxon *Merrillina divergens* has a long history regarding its apparatus (not pertinent to this age discussion), since the genus was named by Kozur (1975), but the age is normally considered early Wuchiapingian (Henderson, 2018; fig. 4). This species may range from upper Capitanian to mid-Wuchiapingian. It has been recovered from central East Greenland (Ravnefjeld Formation) in association with *Mesogondolella rosenkrantzi* (Rasmussen et al., 1990), and occurs in the Raisby/Ford/Cadeby formations above the Marl Slate in Durham, Tyne and Wear, and north Yorkshire (Swift and Aldridge, 1982; Swift, 1986; Swift, 1995). It also occurs in the lower Zechstein (cycle Ca1) in many localities in Germany (Bender and Stoppel, 1965 originally named as *Spathognathodus divergens*) and Poland (Szaniawski, 1969). Stephenson and McLean (2023) describe Lopingian palynomorphs from the Cadeby Formation, Cadeby Quarry, Yorkshire. In North America, it has been recovered from the Ervay and Gerster formations (Wardlaw and Collinson, 1984, 1986), which correlate with the Capitanian to Wuchiapingian.

The Marl Slate best correlates with upper Capitanian based on conodont biostratigraphy, but there are always issues when making such long-distance correlations, especially within what Mei and Henderson (2001) called the North cool-water province. If so, then we can expect a major lowstand at the top followed by a Wuchiapingian transgression, assuming that global eustacy was the primary cause of the ingressions into the Southern Permian Basin. However, tectonic controls might overprint this global signature. Clearly, the units above the Marl Slate are more open marine and less turbid. It will be interesting to see whether David Selby can obtain a Re-Os age. The Marl Slate is obviously important to understand the Permian near the Middle-Upper Permian boundary and there is a lot to learn yet.

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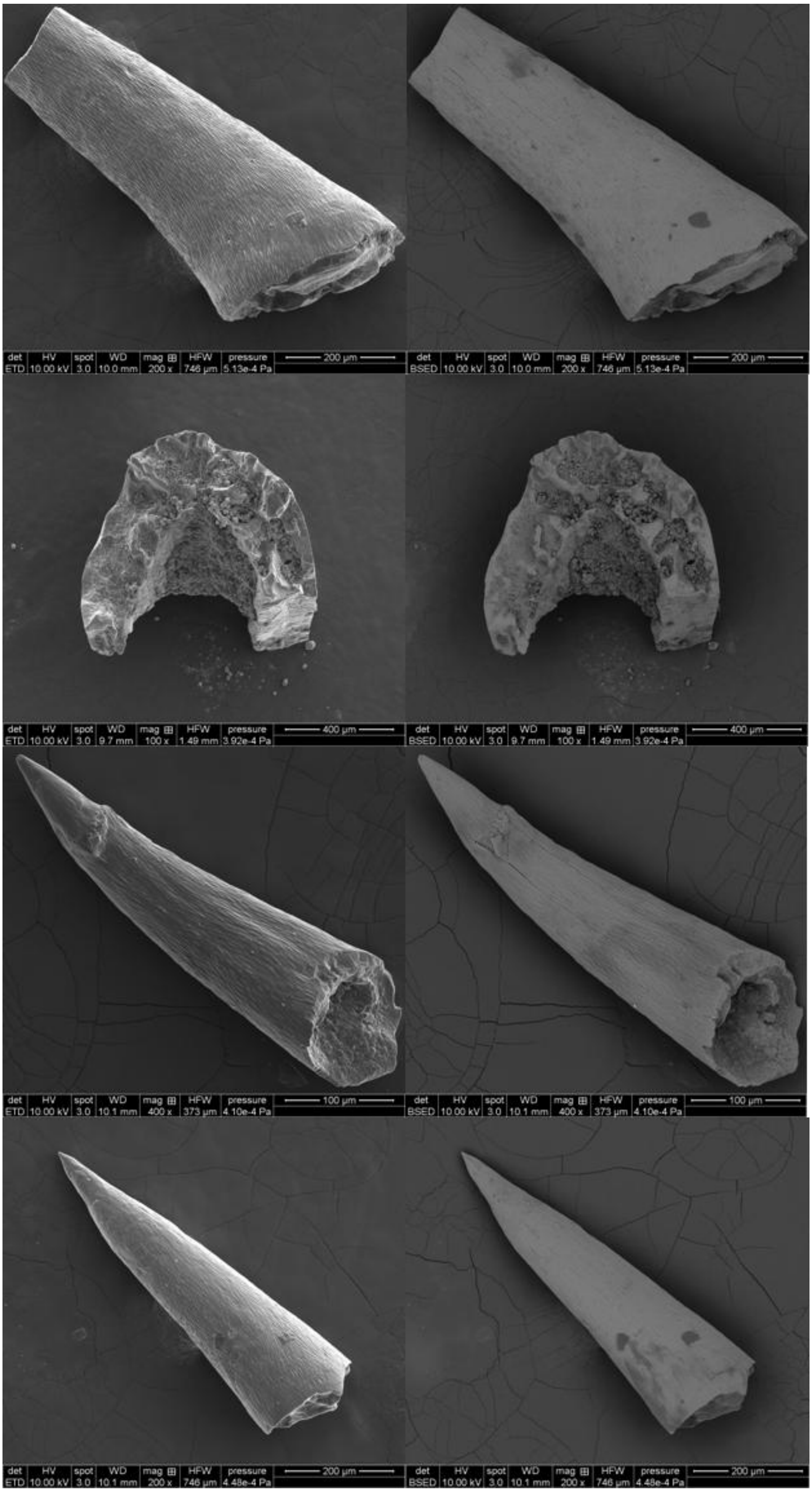
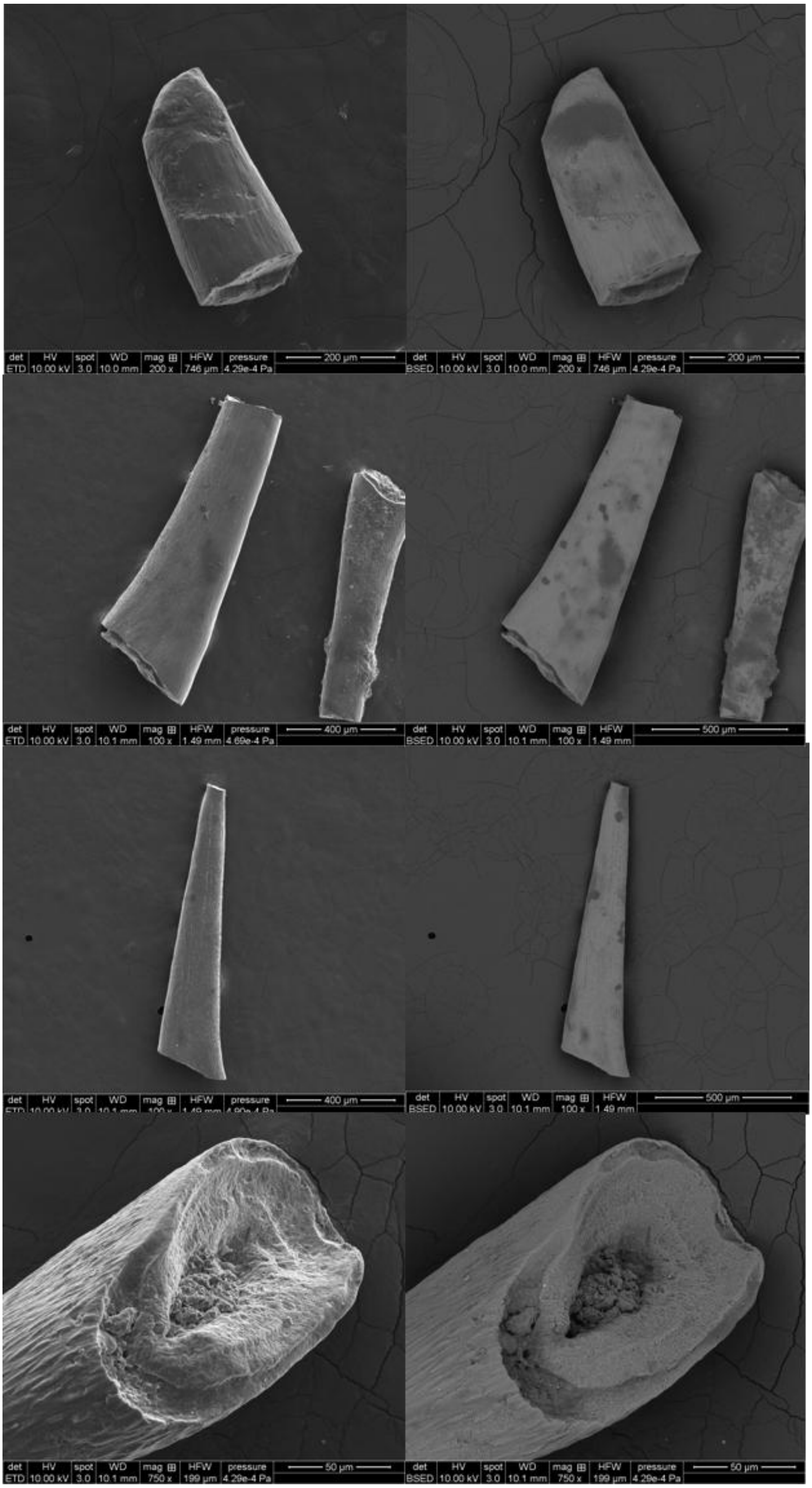
Appendix 1

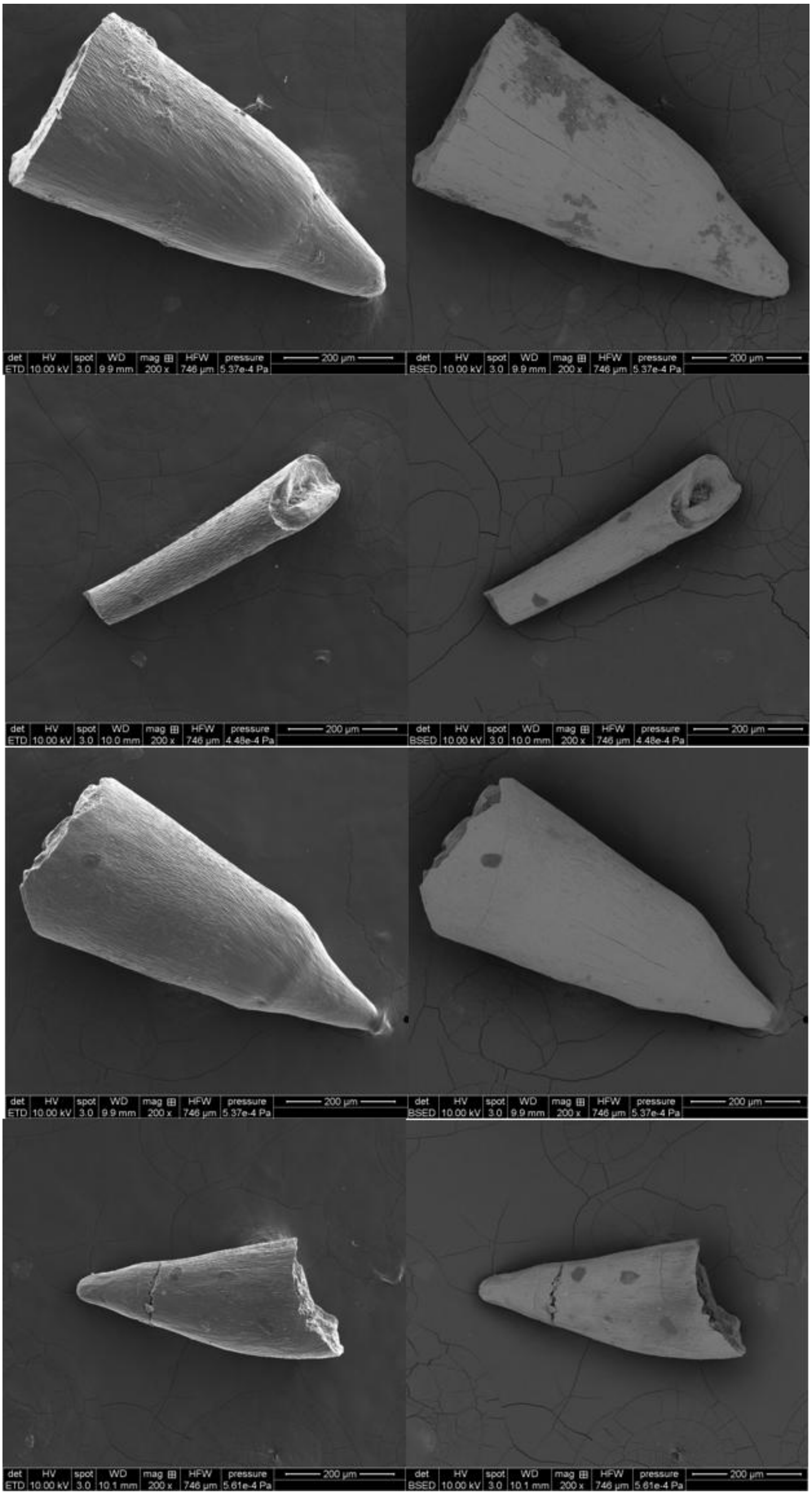
Marl Slate Conodonts

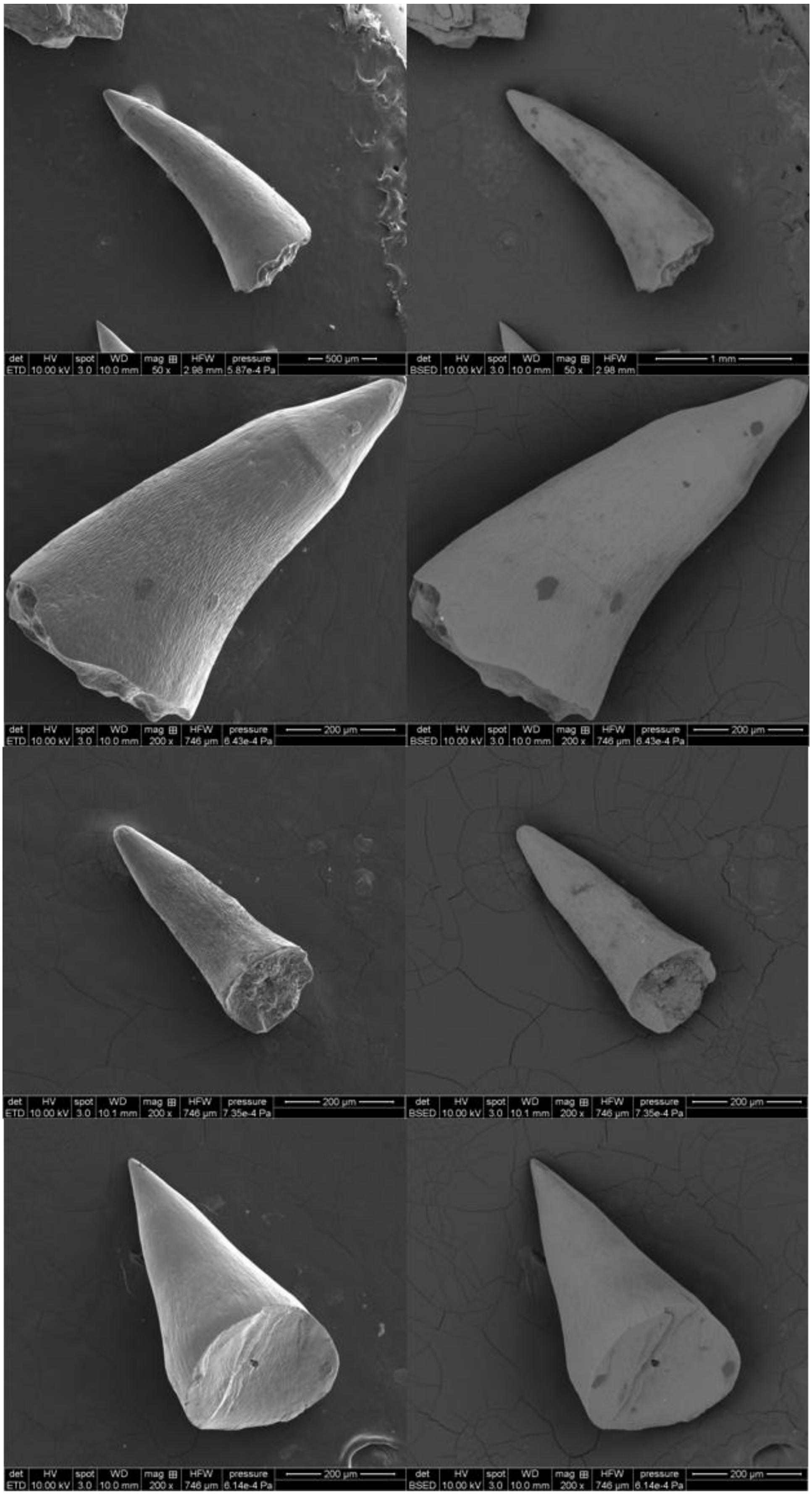
Sample No.	Collection Area	GPS Coordinates	Unit - Location	Weight (kg)
1	Crime Rigg Qy	54°46'07.30"N / 1°27'24.90"W	Marl Slate - Top	2.78
2	Crime Rigg Qy	54°46'07.30"N / 1°27'24.90"W	Marl Slate - Top	2.83
3	Crime Rigg Qy	54°46'07.30"N / 1°27'24.90"W	Marl Slate - Top	2.98
4	Crime Rigg Qy	54°46'07.30"N / 1°27'24.90"W	Marl Slate - Top	3.1
5	Crime Rigg Qy	54°46'07.30"N / 1°27'24.90"W	Marl Slate - Upper	0.74
6	Claxheugh Rocks	54°54'38.75"N / 1°26'09.92"W	Marl Slate - Upper	1.63
7	Claxheugh Rocks	54°54'38.75"N / 1°26'09.92"W	Marl Slate - Upper	2.54
8	Claxheugh Rocks	54°54'38.75"N / 1°26'09.92"W	Marl Slate - Upper	1.46
9	Crime Rigg Qy	54°46'07.30"N / 1°27'24.90"W	Marl Slate - Middle	1.93
10	Crime Rigg Qy	54°46'07.30"N / 1°27'24.90"W	Marl Slate - Middle	1.52
11	Crime Rigg Qy	54°46'07.30"N / 1°27'24.90"W	Marl Slate - Middle	2.55
12	Crime Rigg Qy	54°46'07.30"N / 1°27'24.90"W	Marl Slate - Middle	1.78
13	Crime Rigg Qy	54°46'07.30"N / 1°27'24.90"W	Marl Slate - Middle	1.91
14	Claxheugh Rocks	54°54'38.75"N / 1°26'09.92"W	Marl Slate - Middle	2.55
15	Claxheugh Rocks	54°54'38.75"N / 1°26'09.92"W	Marl Slate - Lower	0.5
16	Middridge Qy	54°37'21.78"N / 1°36'55.99"W	Marl Slate - Lower	1.44
17	Crime Rigg Qy	54°46'07.30"N / 1°27'24.90"W	Marl Slate - Bottom	2.68
18	Crime Rigg Qy	54°46'07.30"N / 1°27'24.90"W	Marl Slate - Bottom	0.88
19	Crime Rigg Qy	54°46'07.30"N / 1°27'24.90"W	Permian Yellow Sands - Top	0.94
20	Claxheugh Rocks	54°54'38.75"N / 1°26'09.92"W	Marl Slate - Lower	4.66
21	Claxheugh Rocks	54°54'38.75"N / 1°26'09.92"W	Marl Slate - Lower	7.3

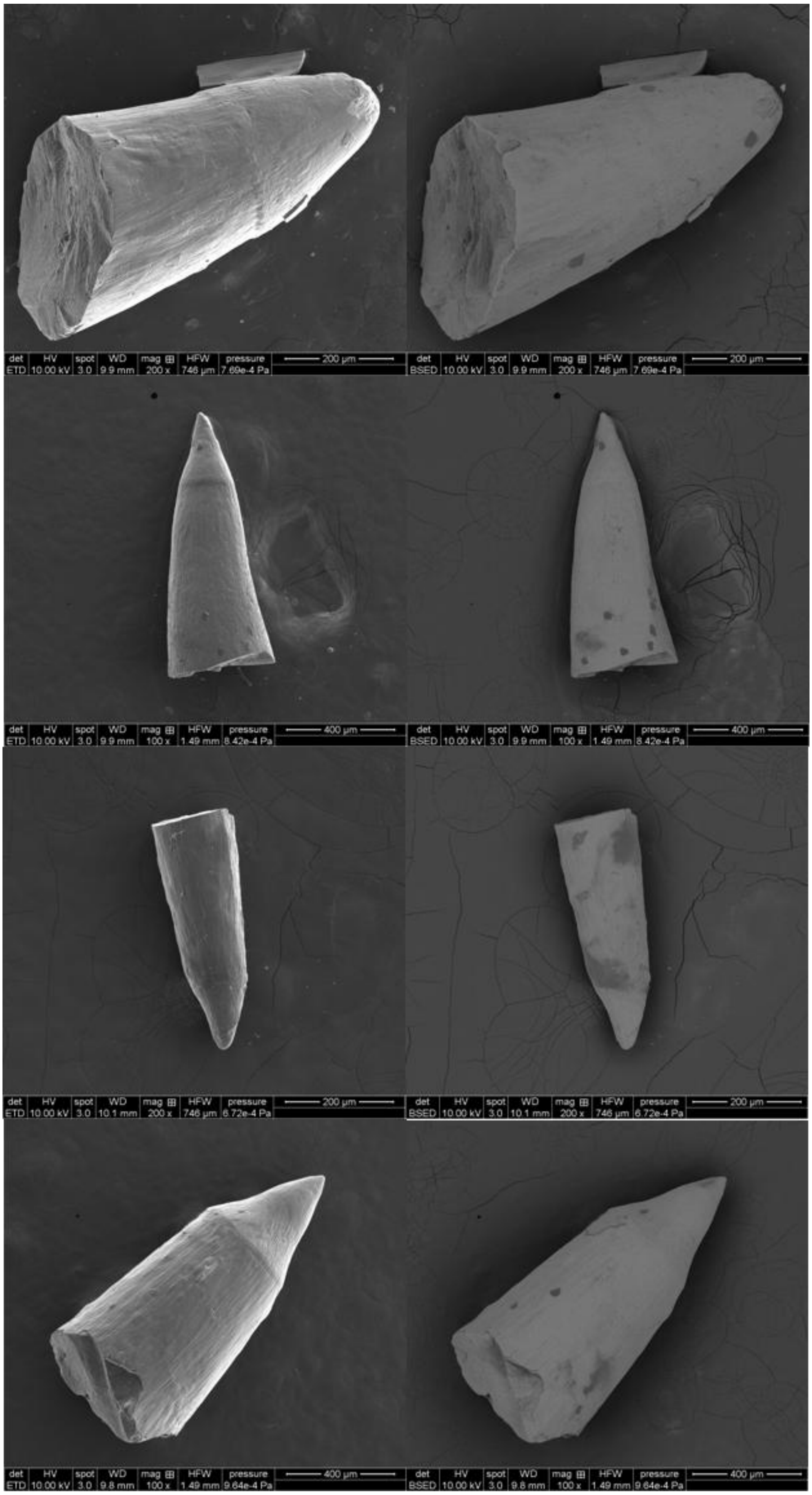
Fish Teeth

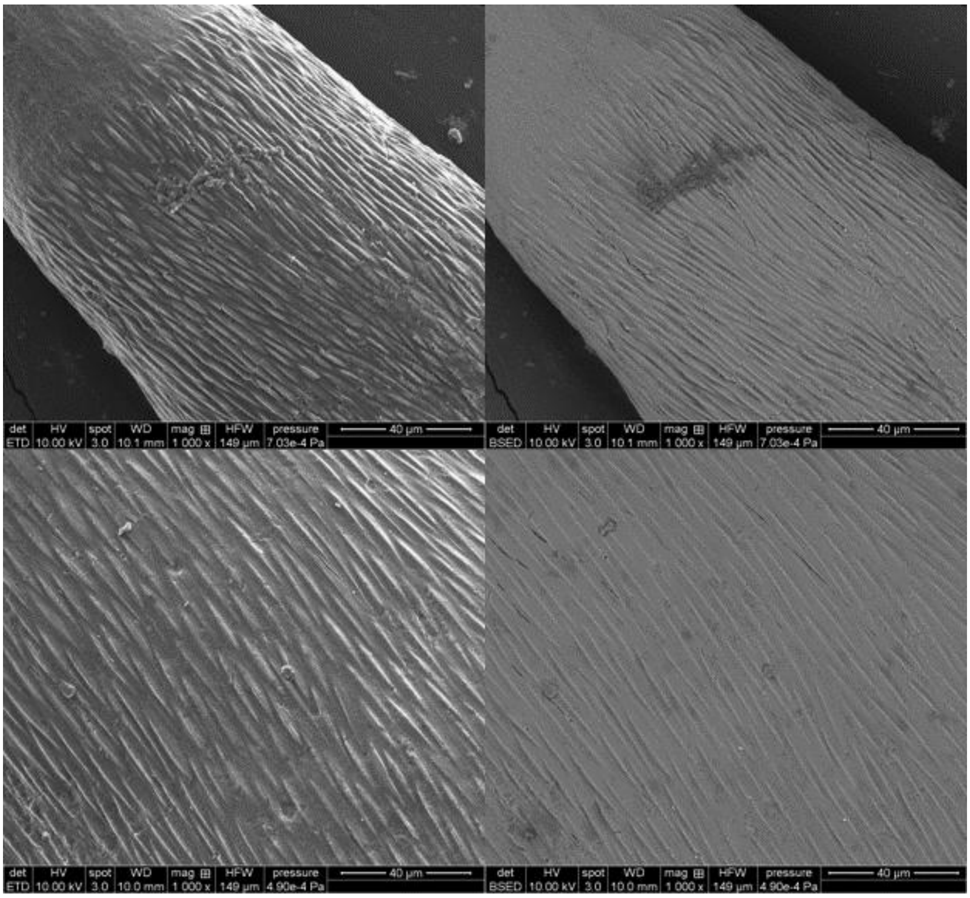

det | HV | spot | WD | mag | HFW | pressure | 200 µm
ETD | 10.00 kV | 3.0 | 10.0 mm | 200 x | 746 µm | 5.13e-4 Pa
det | HV | spot | WD | mag | HFW | pressure | 200 µm
BSED | 10.00 kV | 3.0 | 10.0 mm | 200 x | 746 µm | 5.13e-4 Pa
det | HV | spot | WD | mag | HFW | pressure | 400 µm
ETD | 10.00 kV | 3.0 | 9.7 mm | 100 x | 1.49 mm | 3.92e-4 Pa
det | HV | spot | WD | mag | HFW | pressure | 400 µm
BSED | 10.00 kV | 3.0 | 9.7 mm | 100 x | 1.49 mm | 3.92e-4 Pa
det | HV | spot | WD | mag | HFW | pressure | 100 µm
ETD | 10.00 kV | 3.0 | 10.1 mm | 400 x | 373 µm | 4.10e-4 Pa
det | HV | spot | WD | mag | HFW | pressure | 100 µm
BSED | 10.00 kV | 3.0 | 10.1 mm | 400 x | 373 µm | 4.10e-4 Pa
det | HV | spot | WD | mag | HFW | pressure | 200 µm
ETD | 10.00 kV | 3.0 | 10.1 mm | 200 x | 746 µm | 4.48e-4 Pa
det | HV | spot | WD | mag | HFW | pressure | 200 µm
BSED | 10.00 kV | 3.0 | 10.1 mm | 200 x | 746 µm | 4.48e-4 Pa


det HV spot WD mag HFW pressure 200 µm
ETD 10.00 kV 3.0 10.0 mm 200 x 746 µm 4.29e-4 Pa
det HV spot WD mag HFW pressure 200 µm
BSED 10.00 kV 3.0 10.0 mm 200 x 746 µm 4.29e-4 Pa
det HV spot WD mag HFW pressure 400 µm
ETD 10.00 kV 3.0 10.1 mm 100 x 1.49 mm 4.69e-4 Pa
det HV spot WD mag HFW 500 µm
BSED 10.00 kV 3.0 10.1 mm 100 x 1.49 mm
det HV spot WD mag HFW pressure 400 µm
det HV spot WD mag HFW 500 µm
BSED 10.00 kV 3.0 10.1 mm 100 x 1.49 mm
det HV spot WD mag HFW pressure 50 µm
ETD 10.00 kV 3.0 10.1 mm 750 x 199 µm 4.29e-4 Pa
det HV spot WD mag HFW pressure 50 µm
BSED 10.00 kV 3.0 10.1 mm 750 x 199 µm 4.29e-4 Pa

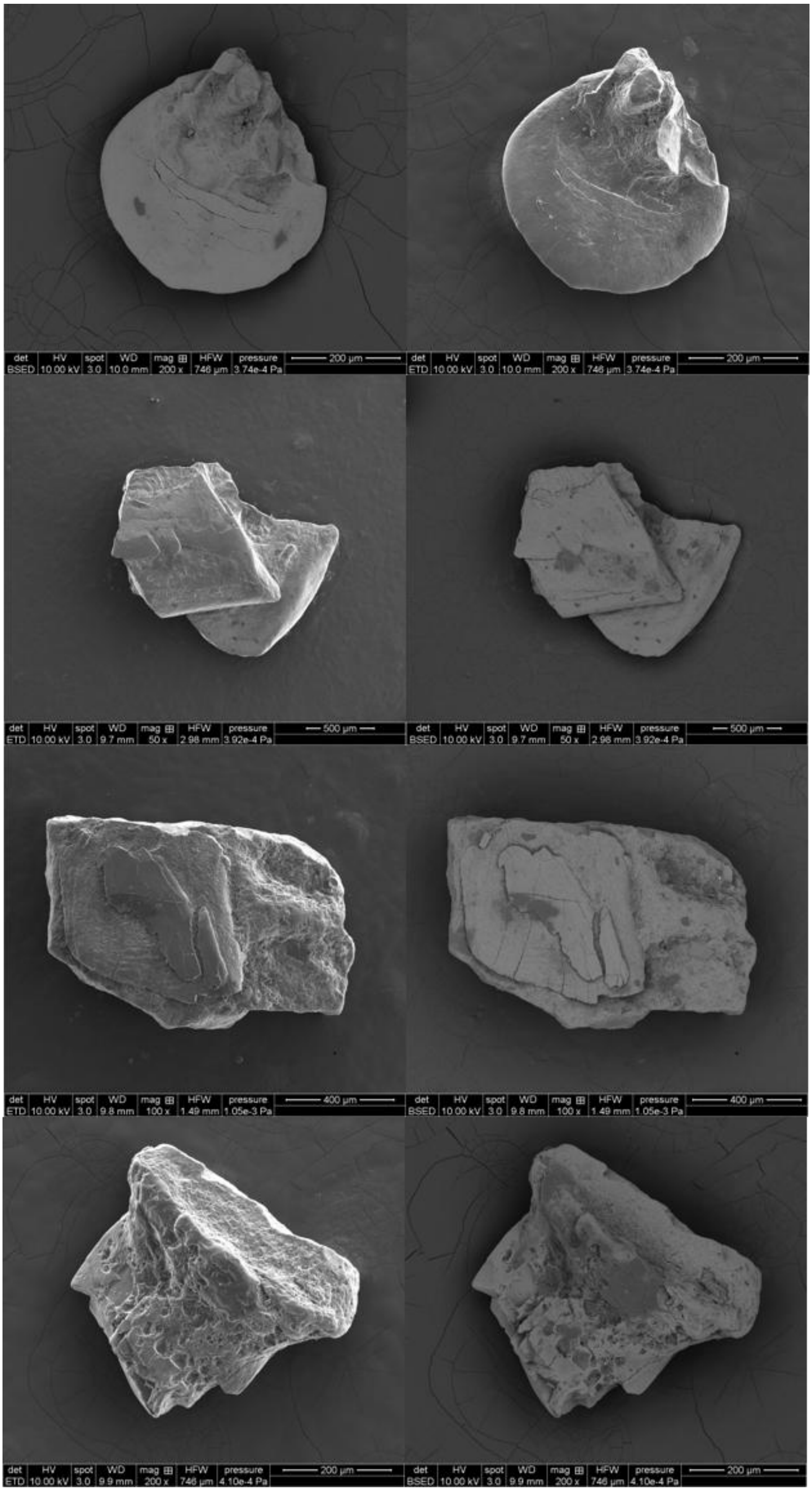

det HV spot WD mag HFW pressure 200 µm
ETD 10.00 kV 3.0 9.9 mm 200 x 746 µm 5.37e-4 Pa
det HV spot WD mag HFW pressure 200 µm
BSED 10.00 kV 3.0 9.9 mm 200 x 746 µm 5.37e-4 Pa
det HV spot WD mag HFW pressure 200 µm
ETD 10.00 kV 3.0 10.0 mm 200 x 746 µm 4.48e-4 Pa
det HV spot WD mag HFW pressure 200 µm
BSED 10.00 kV 3.0 10.0 mm 200 x 746 µm 4.48e-4 Pa
det HV spot WD mag HFW pressure 200 µm
ETD 10.00 kV 3.0 9.9 mm 200 x 746 µm 5.37e-4 Pa
det HV spot WD mag HFW pressure 200 µm
BSED 10.00 kV 3.0 9.9 mm 200 x 746 µm 5.37e-4 Pa
det HV spot WD mag HFW pressure 200 µm
ETD 10.00 kV 3.0 10.1 mm 200 x 746 µm 5.61e-4 Pa
det HV spot WD mag HFW pressure 200 µm
BSED 10.00 kV 3.0 10.1 mm 200 x 746 µm 5.61e-4 Pa

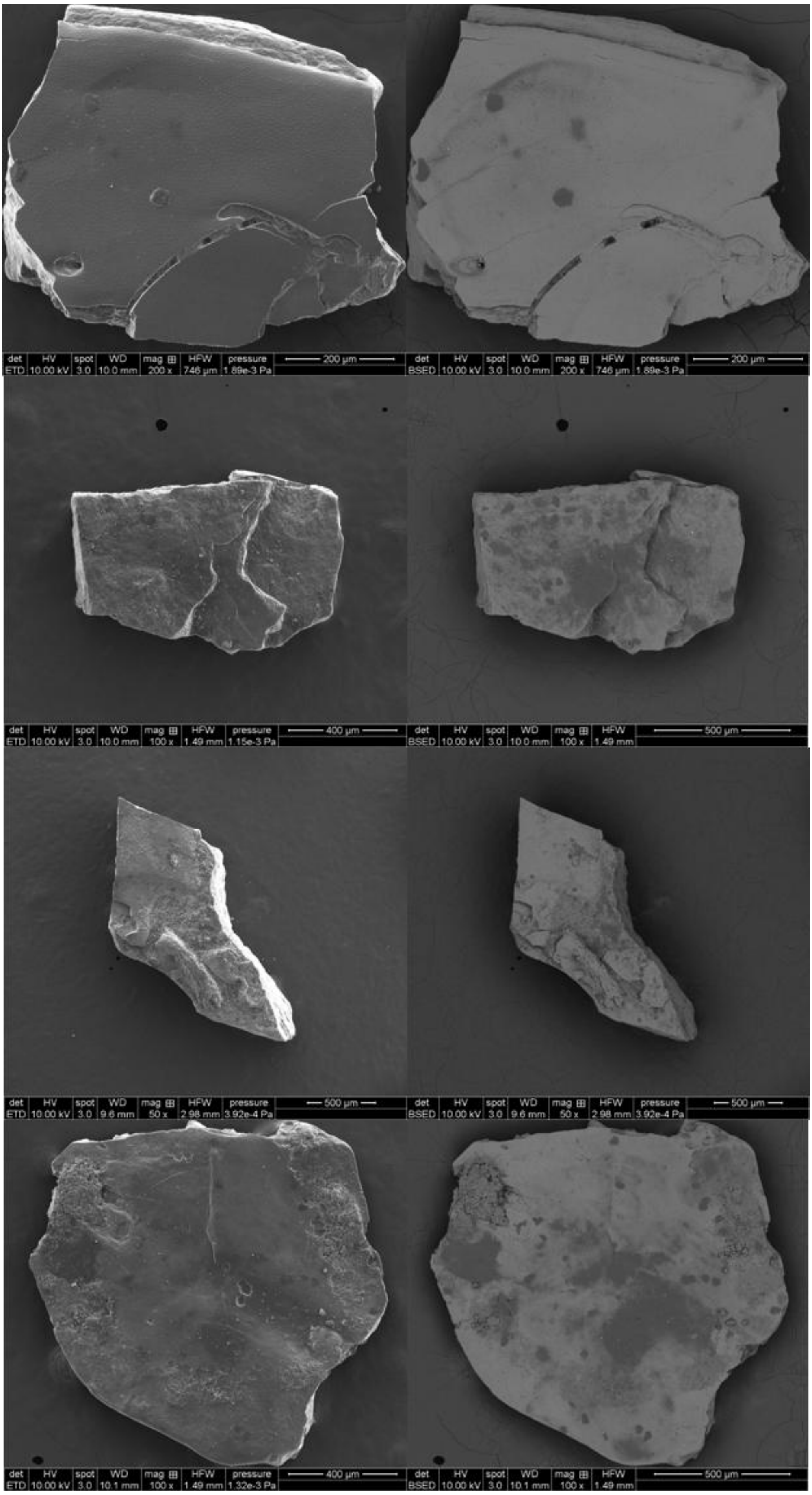

det HV spot WD mag HFW pressure 500 µm
ETD 10.00 kV 3.0 10.0 mm 50 x 2.98 mm 5.87e-4 Pa
det HV spot WD mag HFW 1 mm
BSED 10.00 kV 3.0 10.0 mm 50 x 2.98 mm
det HV spot WD mag HFW pressure 200 µm
ETD 10.00 kV 3.0 10.0 mm 200 x 746 µm 6.43e-4 Pa
det HV spot WD mag HFW pressure 200 µm
BSED 10.00 kV 3.0 10.0 mm 200 x 746 µm 6.43e-4 Pa
det HV spot WD mag HFW pressure 200 µm
ETD 10.00 kV 3.0 10.1 mm 200 x 746 µm 7.35e-4 Pa
det HV spot WD mag HFW pressure 200 µm
BSED 10.00 kV 3.0 10.1 mm 200 x 746 µm 7.35e-4 Pa
det HV spot WD mag HFW pressure 200 µm
ETD 10.00 kV 3.0 10.0 mm 200 x 746 µm 6.14e-4 Pa
det HV spot WD mag HFW pressure 200 µm
BSED 10.00 kV 3.0 10.0 mm 200 x 746 µm 6.14e-4 Pa


det HV spot WD mag HFW pressure 200 µm
ETD 10.00 kV 3.0 9.9 mm 200 x 746 µm 7.69e-4 Pa
det HV spot WD mag HFW pressure 200 µm
BSED 10.00 kV 3.0 9.9 mm 200 x 746 µm 7.69e-4 Pa
det HV spot WD mag HFW pressure 400 µm
ETD 10.00 kV 3.0 9.9 mm 100 x 1.49 mm 8.42e-4 Pa
det HV spot WD mag HFW pressure 400 µm
BSED 10.00 kV 3.0 9.9 mm 100 x 1.49 mm 8.42e-4 Pa
det HV spot WD mag HFW pressure 200 µm
ETD 10.00 kV 3.0 10.1 mm 200 x 746 µm 6.72e-4 Pa
det HV spot WD mag HFW pressure 200 µm
BSED 10.00 kV 3.0 10.1 mm 200 x 746 µm 6.72e-4 Pa
det HV spot WD mag HFW pressure 400 µm
ETD 10.00 kV 3.0 9.8 mm 100 x 1.49 mm 9.64e-4 Pa
det HV spot WD mag HFW pressure 400 µm
BSED 10.00 kV 3.0 9.8 mm 100 x 1.49 mm 9.64e-4 Pa


det HV spot WD mag ⊞ HFW pressure 40 µm
ETD 10.00 kV 3.0 10.1 mm 1 000 x 149 µm 7.03e-4 Pa
det HV spot WD mag ⊞ HFW pressure 40 µm
BSED 10.00 kV 3.0 10.1 mm 1 000 x 149 µm 7.03e-4 Pa
det HV spot WD mag ⊞ HFW pressure 40 µm
ETD 10.00 kV 3.0 10.0 mm 1 000 x 149 µm 4.90e-4 Pa
det HV spot WD mag ⊞ HFW pressure 40 µm
BSED 10.00 kV 3.0 10.0 mm 1 000 x 149 µm 4.90e-4 Pa

Fish Scales


det HV spot WD mag HFW pressure 200 µm
BSED 10.00 kV 3.0 10.0 mm 200 x 746 µm 3.74e-4 Pa
det HV spot WD mag HFW pressure 200 µm
ETD 10.00 kV 3.0 10.0 mm 200 x 746 µm 3.74e-4 Pa
det HV spot WD mag HFW pressure 500 µm
ETD 10.00 kV 3.0 9.7 mm 50 x 2.98 mm 3.92e-4 Pa
det HV spot WD mag HFW pressure 500 µm
BSED 10.00 kV 3.0 9.7 mm 50 x 2.98 mm 3.92e-4 Pa
det HV spot WD mag HFW pressure 400 µm
ETD 10.00 kV 3.0 9.8 mm 100 x 1.49 mm 1.05e-3 Pa
det HV spot WD mag HFW pressure 400 µm
BSED 10.00 kV 3.0 9.8 mm 100 x 1.49 mm 1.05e-3 Pa
det HV spot WD mag HFW pressure 200 µm
ETD 10.00 kV 3.0 9.9 mm 200 x 746 µm 4.10e-4 Pa
det HV spot WD mag HFW pressure 200 µm
BSED 10.00 kV 3.0 9.9 mm 200 x 746 µm 4.10e-4 Pa


det HV spot WD mag HFW pressure 200 µm
ETD 10.00 kV 3.0 10.0 mm 200 x 746 µm 1.89e-3 Pa
det HV spot WD mag HFW pressure 200 µm
BSED 10.00 kV 3.0 10.0 mm 200 x 746 µm 1.89e-3 Pa
det HV spot WD mag HFW pressure 400 µm
ETD 10.00 kV 3.0 10.0 mm 100 x 1.49 mm 1.15e-3 Pa
det HV spot WD mag HFW 500 µm
BSED 10.00 kV 3.0 10.0 mm 100 x 1.49 mm
det HV spot WD mag HFW pressure 500 µm
ETD 10.00 kV 3.0 9.6 mm 50 x 2.98 mm 3.92e-4 Pa
det HV spot WD mag HFW pressure 500 µm
BSED 10.00 kV 3.0 9.6 mm 50 x 2.98 mm 3.92e-4 Pa
det HV spot WD mag HFW pressure 400 µm
ETD 10.00 kV 3.0 10.1 mm 100 x 1.49 mm 1.32e-3 Pa
det HV spot WD mag HFW 500 µm
BSED 10.00 kV 3.0 10.1 mm 100 x 1.49 mm