

## **Petrography, Stable isotope chemistry and U-series chronology of the Easington Raised Beach, N.E. England**

**Ian Candy**

Royal Holloway, University of London

### **Geological Context**

The Easington Formation (Thomas, 1999) consists of a well-cemented fine-gravel and sand with a temperate molluscan fauna. This unit has an erosional contact with the underlying limestone bedrock and this contact is found at 32m O.D. The unit has been interpreted as a raised beach but uncertainty exists about the age of the highstand that this deposit represents. Smith and Francis (1967) have radiocarbon dated the molluscan fauna indicating that it is >38,000yrs in age, whereas amino acid racemisation (AAR) work by Bowen et al. (1991) has indicated that the molluscan assemblage is primarily MIS 7 in age with a reworked MIS 9 component. Although the raised beach contains a densely-cemented calcite matrix suitable for  $^{230}\text{Th}/\text{U}$  dating there has been no previous attempt at producing a radiometric age for the formation of this precipitate which could provide a minimum age for the formation of the raised beach and, therefore, for the highstand event.

### **Carbonate cement from the Easington Raised Beach**

Densely cemented samples were taken from representative sediment fabrics within the raised beach sequence, these were; 1) well-sorted medium sands, 2) pebble gravels with a medium sand matrix, and 3) open-framework pebble gravels. Thin sections were made from these materials, using the crystic resin impregnation technique of Lee and Kemp (1991). Under thin section the petrography of the carbonate cement matrix is dominated by secondary calcite spar (Fig. 1), however, the size, morphology and geometry of the spar crystals is dictated by the sedimentology of the host sediment. Within sediments dominated by sand the small size of the pore space means that there is minimal room for cement crystal growth, consequently the cement is characterised by small (10 $\mu\text{m}$ ) spar crystals. Within the open-fabric gravels the calcite crystals are larger (300  $\mu\text{m}$  in length) and elongate in form. In both the sand dominated and open-framework sediments the calcite crystals are fibrous in form and exhibit an isopachous arrangement (Tucker, 1991), with cements of consistent thickness growing around the pore rim.

### **Stable oxygen and carbon isotopic composition of the Easington carbonate cement**

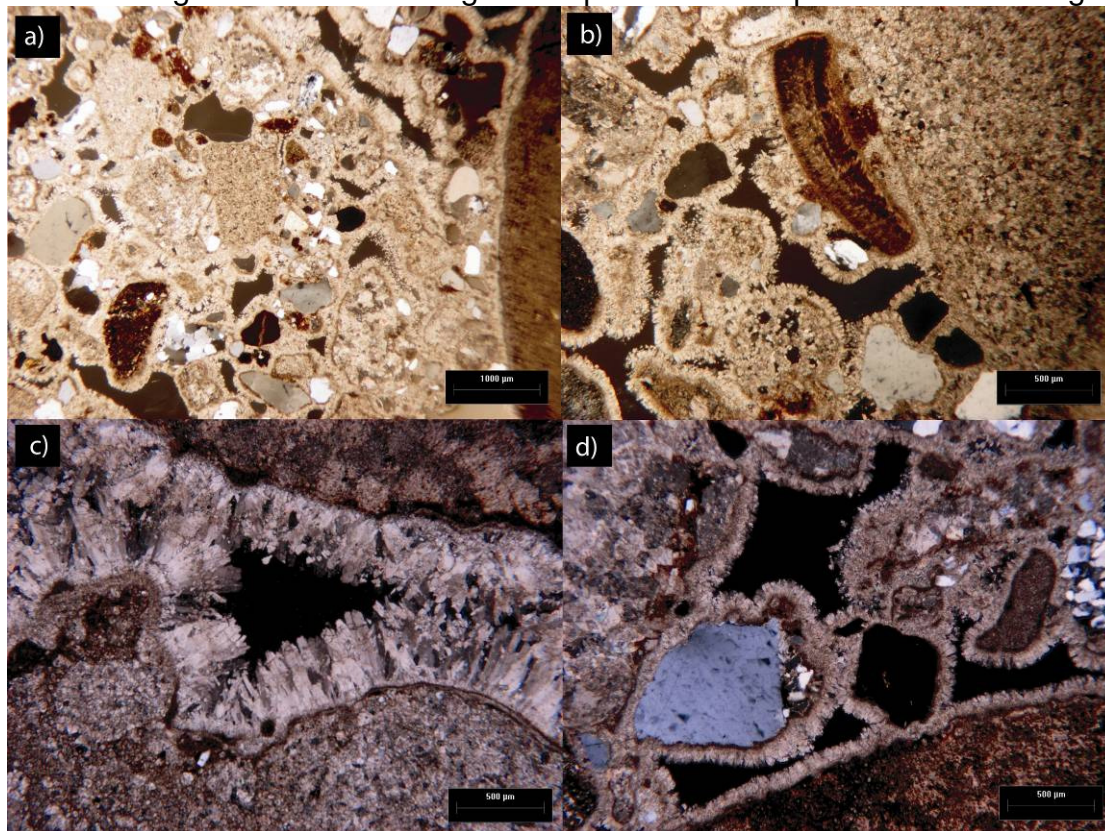
6 samples were taken from the Easington beach cement for stable isotopic analysis. This material was taken from the cements found in the three fabric types outlined above. Samples were picked from fractured blocks of the sampled cements and powdered using an agate pestle and mortar. Powdered samples were left to dry overnight at 65°C and then weighed into steel crucibles for analysis. The stable  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  isotopic composition was established by analysing  $\text{CO}_2$  liberated from sample reaction with phosphoric acid at 90°C. Internal (RHBNC-PRISM) and external (NBS-19) standards were analysed after every 10 samples. Carbonate stable isotopes were analysed using a VG PRISM Series 2 mass spectrometer. All isotopic data presented here are quoted in reference to PDB. Mean  $\delta^{18}\text{O}$  values from the Easington beach sediments were -4.94‰ (STDEV 0.19), whilst mean  $\delta^{13}\text{C}$  values from the Easington beach sediments were -8.52‰ (STDEV 0.84).

### **Origin of the cements in the Easington Raised Beach sediments**

Both the petrography and stable isotopic composition of the Easington cements are characteristic of carbonate precipitation by phreatic (groundwater) processes. The coarse-spar cements are

U-series dating of the calcite cement matrix in the Easington Raised Beach, N.E.  
England

indicative of calcite precipitation in association with regularly recharging waters, whilst their isopachous arrangement implies that the pores were permanently filled with water. The isotopic composition is also typical of carbonates that have precipitated in association with groundwater processes under interglacial conditions. Fig. 2 compares the isotopic data from Easington with



*Figure 1 – Photomicrographs of the microstructure of the Easington beach cement. a) low power view of the sediment and cement matrix. b) carbonate cements within the sandy fabric, fibrous calcite crystals in an isopachous arrangement. c) carbonate cements within the open-framework gravels. D) carbonate cements within the pebble-gravel with sandy matrix. All photo-micrographs are shown in cross-polarised light.*

British interglacial carbonates that have precipitated in association with water tables (typically groundwater carbonate nodules) and at spring lines (tufa precipitates). Both the oxygen and carbon isotopic values of the Easington cements are consistent with those of interglacial 'groundwater' carbonates. In Britain the oxygen isotopic composition of groundwater carbonates will be primarily controlled by the  $\delta^{18}\text{O}$  composition of the groundwater. The oxygen isotopic composition of groundwater is typically a mean of the  $\delta^{18}\text{O}$  composition of rainfall which is, in turn, controlled by air temperature (Rozanski et al., 1993; Darling and Talbot, 2003; Darling, 2004). Warmer air temperatures would typically generate a more enriched  $\delta^{18}\text{O}$  signal than colder air temperatures. The consistency between the  $\delta^{18}\text{O}$  of the Easington cements and the  $\delta^{18}\text{O}$  of interglacial groundwater carbonates implies that; 1) they have precipitated from groundwaters of broadly similar  $\delta^{18}\text{O}$ , and 2) they have precipitated under broadly similar climatic regimes (i.e. interglacials).

The carbon isotopic composition is relatively depleted with respect to  $^{13}\text{C}$  and this is very common for interglacial groundwater carbonates in British Quaternary deposits. Recharging waters percolate through the soil zone, uptaking  $\text{CO}_2$  from the soil atmosphere as percolation occurs. Soil zone  $\text{CO}_2$  is typically depleted with respect to  $^{13}\text{C}$ , because of the fractionation of carbon isotopes and the selective uptake of  $^{12}\text{C}$  which occurs during photosynthesis (Cerling et al., 1989; Quade et

## U-series dating of the calcite cement matrix in the Easington Raised Beach, N.E. England

al., 1989; Cerling and Quade, 1993). The negative  $\delta^{13}\text{C}$  values of the Easington cements, therefore, implies that the landscape under which they have formed must have been well-vegetated, allowing soil-zone  $\text{CO}_2$  to have had a significant impact on the groundwater signature.

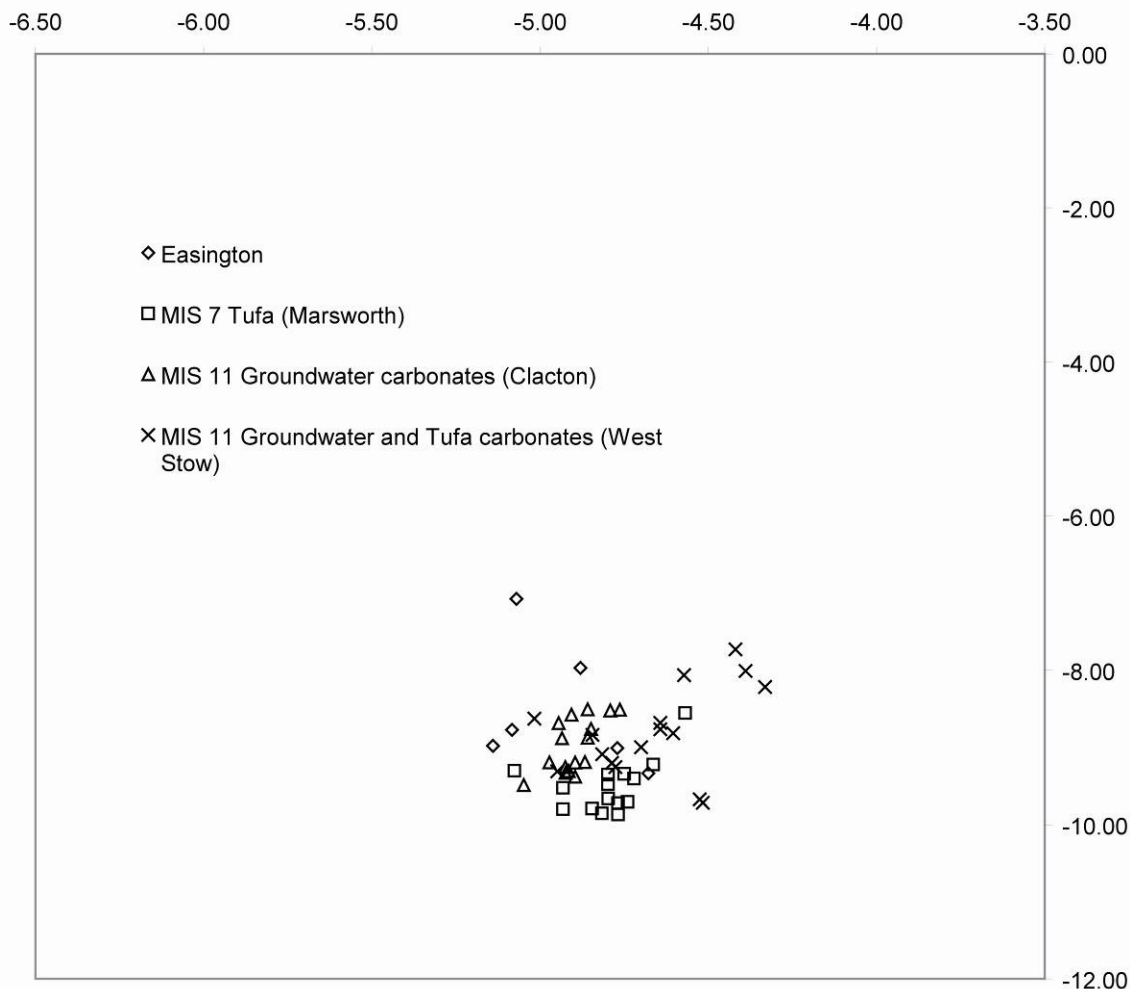


Figure 2 – Comparison of the stable oxygen and carbon isotopic composition of the Easington raised beach cements with groundwater and Tufa cements from British interglacial deposits (MIS 7 and MIS 11).

The petrography and chemistry of these cements are typical of terrestrial carbonates with no indication of any precipitation under marine conditions.

### **U/Th analysis of the Easington Raised Beach cements**

In an attempt to constrain the age of the raised beach deposits, samples of the carbonate cements were taken for  $^{230}\text{Th}/\text{U}$  dating. The most suitable material for dating was considered to be the large spar cement accumulations that have developed in the open-framework gravels. These materials were selected because; 1) cements in these contexts can grow into open pores, resulting in low amounts of detrital contamination with the cement lattice, and 2) the relatively thick accumulations of cements means that any cement surfaces that have undergone weathering can be removed before analysis. 5 samples of between 0.30 and 0.45g in mass were taken for U/Th analysis.

U-series sample preparation, separation geochemistry and mass spectrometry techniques follow the procedure of Seth et al. (2003). 300 to 400 mg of each sub-sample were weighed into PTFE

# U-series dating of the calcite cement matrix in the Easington Raised Beach, N.E. England

beakers and wetted using >18.2 MΩ H<sub>2</sub>O from a Millipore Element plant. The carbonate was dissolved by the drop wise addition of sub-boiled ~16 M HNO<sub>3</sub>. The samples were then spiked with a mixed <sup>229</sup>Th-<sup>236</sup>U spike solution, sealed and left to equilibrate overnight on a hot plate. U and Th separation was carried out following the procedure set out by Seth et al., 2003 (after Luo et al., 1997, and Pin and Joannon, 2001). This procedure uses the chelating TRU.Spec resin and a HNO<sub>3</sub>-HCl-HF chemistry, with Th (3 ml 0.5 M HCl) and U (3ml 0.1 M HCl-1 M HF) collected separately. Collections were evaporated to dryness and then converted to nitrate by evaporating with HNO<sub>3</sub>. For measurement, samples were dissolved in 2% HNO<sub>3</sub>-0.1% HF.

The U/Th isotopic ratios of the raised beach carbonate samples were analysed on a IsoProbe® multicollector ICP-MS in the Department of Geology, Royal Holloway University of London (see Seth et al., 2003 for details and operating parameters), using static mode on Faraday collectors and the ion-counting Daly detector in the axial position. Th and U analysis was carried out for a mass range from mass 228 to mass 238. Th and U were analysed separately, with mass <sup>230</sup>Th on the Daly detector for measuring Th isotope ratios and with mass <sup>234</sup>U on the Daly detector for measuring U isotope ratios. The samples were run in conjunction with total procedural blanks and rock standards (Table Mountain Latite and OU Young Speleothem).

The U/Th geochemistry of the five cement samples are shown in Table 1 and the derived ages scatter between 7,470 yrs (+/-120) and 39,360 yrs (+/-450). Interpreting the ages of the Easington Raised Beach cements is not straight forward as the U/Th chemistry suggests that there is detrital contamination present which make these ages unreliable age estimates (Ivanovich et al., 1992; Candy et al., 2005). Importantly, the concentration of <sup>232</sup>Th (80-250ppb) and the <sup>230</sup>Th/<sup>232</sup>Th activity ratio (1 to 6.8) would both suggest detrital contamination (NB a detritally contaminated carbonate has <sup>232</sup>Th concentrations of >10ppb and a <sup>230</sup>Th/<sup>232</sup>Th activity ratio of <20). Although this would typically suggest that these age estimates are unreliable they can still provide important geochronological information, this is suggested for two reasons. Firstly, the effect of detrital contamination is always to over estimate the true age of the carbonate cement, therefore, the derived ages can act as maximum ages for the true cement age.

Sample	U (ppb)	Th (ppb)	<sup>(230</sup> Th/ <sup>238</sup> U) 2σ		<sup>(234</sup> U/ <sup>238</sup> U) 2σ		<sup>(230</sup> Th/ <sup>232</sup> Th) 2σ		Age	+/-
EAS1	853	243	0.305	(0.003)	1.104	(0.007)	3.582	(0.015)	39,360	450
EAS2	834	125	0.066	(0.001)	1.150	(0.005)	1.543	(0.022)	7,470	120
EAS3	900	250	0.096	(0.003)	1.149	(0.006)	1.202	(0.021)	10,940	310
EAS4	1029	82	0.155	(0.002)	1.157	(0.006)	6.831	(0.068)	18,300	260
EAS5	925	169	0.080	(0.001)	1.158	(0.006)	1.538	(0.022)	9,070	160

*Table 1 – U-series chemistry and derived age estimates of the five carbonate samples taken from the Easington Raised Beach cement matrix.*

Secondly, that although the cements appear to be detritally contaminated it is here suggested that the effect of the detrital contamination on these ages is actually minimal. Although concentrations of Th are high in these samples they are relatively low compared to the concentrations of U (850-1000ppb). In many carbonate systems such a high level of U relative to Th would mean that the effect of detrital contamination should actually be minimal and the <sup>230</sup>Th/<sup>232</sup>Th activity ratio should be >>20. That this is not the case in the Easington samples is likely to be a function of the very young age of the cement. In a sample which contains some detrital contamination, but not enough to effect the age, when the sample is young very little <sup>230</sup>Th will have accumulated through radioactive decay and, as a consequence, the <sup>230</sup>Th/<sup>232</sup>Th will be relatively low making the

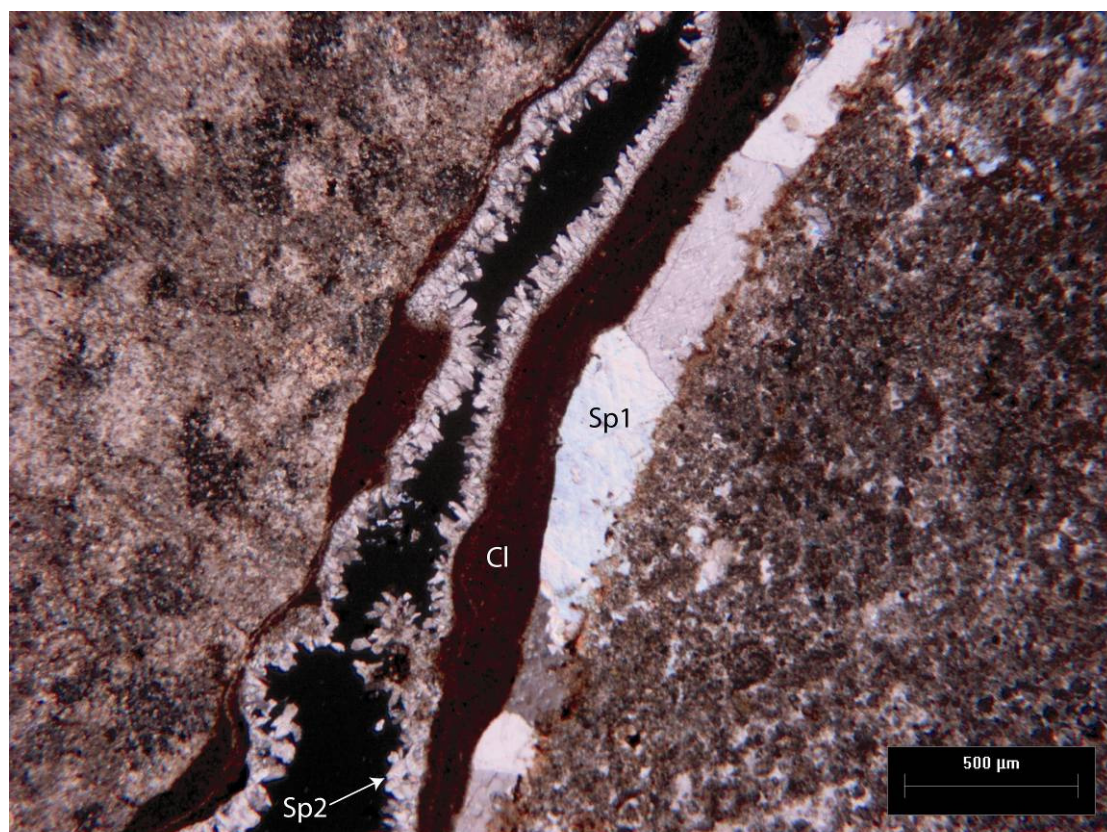


## U-series dating of the calcite cement matrix in the Easington Raised Beach, N.E. England

samples appear heavily contaminated. Applying a detrital correction to this data set (following the procedure of Ludwig and Paces (2002) and Sharp et al., (2003) and assuming that the detritus has an isotopic composition of  $^{232}\text{Th}/^{238}\text{U} = 1.2 \pm 0.6$  and  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U} = 1 \pm 0.1$ ) does alter the ages slightly but does not change their stratigraphic distribution (i.e. the three Holocene ages remain Holocene, whilst the two Late Devensian ages remain Late Devensian).

### **Discussion**

Despite the issues with the dataset, the U/Th data derived from the raised beach cement indicates that carbonate precipitation within this deposit is primarily a Late Quaternary phenomenon with evidence for cementation occurring primarily during the Holocene. There is, however, a discrepancy between the petrography/stable isotope geochemistry and some of the U/Th age estimates. The isotope geochemistry suggests that cement precipitation is an interglacial phenomenon, an idea also supported by the fact that the cement petrography suggests the necessity of a constant and persistent water table (a feature more likely to occur during an interglacial than a glacial stage), however, two of the derived ages place periods of cementation into a glacial stage. There is, therefore, the possibility that cementation spans the last 40,000 years and that the groundwater processes responsible for cementation are only weakly related to the nature of the prevailing climate. However, it is also possible that cementation could be multi-phase and that although the main phase of cementation was during the Holocene, earlier phases of carbonate precipitation may have occurred during previous interglacials. In this scenario the glacial ages would be averages of Holocene and, potentially, Ipswichian ages, however, in the ages reported here Holocene cements would have to be dominant to account for the Late Devensian ages. Whether some of the ages are averaged or whether there are genuine glacial stage cements within the raised beach sequence is difficult to prove, however, at localised points within the cement there is evidence that carbonate was precipitated during multiple phases and does not represent a single phase of carbonate precipitation (Fig. 3).



## U-series dating of the calcite cement matrix in the Easington Raised Beach, N.E. England

*Figure 3 – Photomicrograph illustrating the complexity of cement stratigraphy within the cemented raised beach. Two phases of calcite spar precipitation (Sp1 and Sp2) separated by a period of clastic sediment (clay and silt) accumulation.*

If it is accepted that the beach represents a pre-Holocene highstand then there is the question of why the beach deposits only become widely cemented during the Holocene, at least 120,000 yrs after the sediments were deposited. It is here argued that in order to generate the cements found within the raised beach sediments two major conditions are required; 1) the dissolution of significant amounts of carbonate from somewhere in the hydrological system, and 2) the re-precipitation of carbonate within the beach gravels as a results of a change in carbonate solubility. Crucial to this suggestion is the sub-glacial till which overlies the raised beach deposits. During an interglacial the expansion of vegetation and development of soil processes across the surface of the till would lead to dissolution of detrital carbonate due to; 1) the presence of organic acids and 2) the high partial pressure of CO<sub>2</sub> in the soil atmosphere which causes it to be uptaken into solution as carbonic acid. Downward percolation of waters through this till is slow due to the low permeability of this deposit. As these vadose waters enter the phreatic groundwater zone, within the highly permeable raised beach deposits, the increased rate of water flow, increased pore size and increased pH are more conducive to carbonate precipitation. Consequently carbonate comes out of solution and precipitates in the form of the dense spar crystals, observable in thin section. In this model the emplacement of the overlying till is essential to the precipitation of the raised beach cement matrix and it is likely that widespread cementation of the raised beach was not possible until after the LGM and the deposition of this till.

### **Conclusions**

1. The carbonate cement within the Easington raised beach sediments are precipitated from terrestrial groundwaters, probably operating under interglacial climatic conditions.
2. The U/Th ages of the cement are problematic, because of detrital contamination, however, they imply carbonate precipitation during the Late Quaternary, most probably during the Holocene.
3. Cementation of these deposits is late relative to the age of the raised beach sediments. It is Likely that the emplacement of an overlying, fine-grained, carbonate-rich sediment and the onset of interglacial soil processes was necessary before these cements could be formed. Intense cementation of the raised beach is, therefore, likely to be a post LGM (i.e. Holocene) process, regardless of the true age of the highstand responsible for the deposition of the Easington Formation.
4. The precipitation of a dense, widespread carbonate cement in the Easington raised beach sediment is not an important control in the preservation of this feature. For most of its geological history it is likely to have had only a weak or incipient cement content.

U-series dating of the calcite cement matrix in the Easington Raised Beach, N.E.  
England

*References*

- Bowen, D.Q., Smith, D.B., Sykes, G.A., 1991. The age of the Easington Raised Beach, County Durham. *Proceedings of the Yorkshire Geological Society*, 48, 415-420.
- Candy, I., Black, S., Sellwood, B.W., 2005. U-series isochron dating of immature and mature calcretes as a basis for constructing Quaternary landform chronologies; Examples from the Sorbas basin, southeast Spain. *Quaternary Research*, 64, 100-111.
- Cerling, T.E., Quade, J., 1993. Stable carbon and oxygen isotopes in soil carbonates. In: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S., (eds). *Climate Change in Continental Isotopic Records*. Geophysical Monograph 78, 217-231. American Geophysical Union, Washington.
- Cerling, T.E., Quade, J., Wang, Y., Bowman, J.R., 1989. Carbon isotopes in soils and palaeosols as palaeoecologic indicators, *Nature* 341, 138–139.
- Darling, W.G., 2004. Hydrological factors in the interpretation of stable isotopic proxy data present and past: a European perspective. *Quaternary Science Reviews* 23, 743-770.
- Darling, W.G., Talbot, J.C., 2003. The O and H stable isotopic composition of fresh waters in the British Isles. 1. Rainfall. *Hydrology and Earth System Sciences* 7, 163–181.
- Ivanovich, M., Latham, A.G. and Ku, T.L., 1992. Uranium-series disequilibrium applications in geochronology. In: Ivanovich, M. and Harmon, R.S. (eds.) *Uranium-series disequilibrium: applications to earth, marine and environmental science* (2<sup>nd</sup> edition), Oxford University Press, Oxford, 62-94.
- Lee, J., Kemp, R., 1994. Thin sections of unconsolidated sediments and soils: a recipe. Royal Holloway, University of London, Egham. 45 pp.
- Ludwig, K.R., Paces, J.B., 2002. Uranium-series dating of pedogenic silica and carbonate, Crater Flat, Nevada, *Geochimica et Cosmochimica Acta*, 66, 487-506.
- Luo, X., Rehkämper, M., Lee, D.-C., Halliday, A.N., 1997. High precision (230)Th/(232)Th and (234)U/(238)U measurements using energy-filtered ICP magnetic sector multiple collector mass spectrometry. *International Journal of Mass Spectrometry Ion Processes* 171, 105-117.
- Pin, C., Joannon, S., 2001. Isotope dilution-chemical separation: a powerful combination for high precision analysis at the ultra-trace level using ICP mass spectrometry; example of U and Th determination in silicate rocks. *Journal of Analytical Atomic Spectrometry* 16, 739-743.
- Quade, J., Cerling, T.E., Bowman, J.R., 1989. Systematic variation in the carbon and oxygen isotopic composition of Holocene soil carbonate along elevation transects in the southern Great Basin, USA: *Geological Society of America Bulletin* 101, 464-475.
- Rozanski, K., Araguas-Araguas, L., Gonfiantini, R., 1993. Isotopic Patterns in Modern Global Precipitation In: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S. (Eds), *Climate Change in Continental Isotopic Records*. Geophysical Monograph 78, American Geophysical Union, pp 1 - 36.

U-series dating of the calcite cement matrix in the Easington Raised Beach, N.E.  
England

Seth, B., Thirlwall, M.F., Houghton, S.L., Craig, C.A., 2003. Accurate measurements of Th-U isotope ratios for carbonate geochronology using MC-ICP-MS. *Journal of Analytical Atomic Spectrometry* 18, 1323-1330.

Sharp, W.D., Ludwig, K.R., Chadwick, O.A., Amundson, R., Glaser, L.L., 2003. Dating fluvial terraces by  $^{230}\text{Th}/\text{U}$  on pedogenic carbonate, Wind River Basin, Wyoming. *Quaternary Research*, 59, p. 139-150.

Smith, D.B., Francis, E.A., 1967. *Geology of the country between Durham and West Hartlepool*. Memoir of the Geological Survey.

Thomas, G.S.P., 1999. Northern England. In D.Q. Bowen (ed.) *A revised correlation of Quaternary deposits in the British Isles*. Geological Society Special Report, 23, 91-98.

Tucker, M.E., 1991. *Sedimentary Petrology*. Blackwell Science, Oxford.