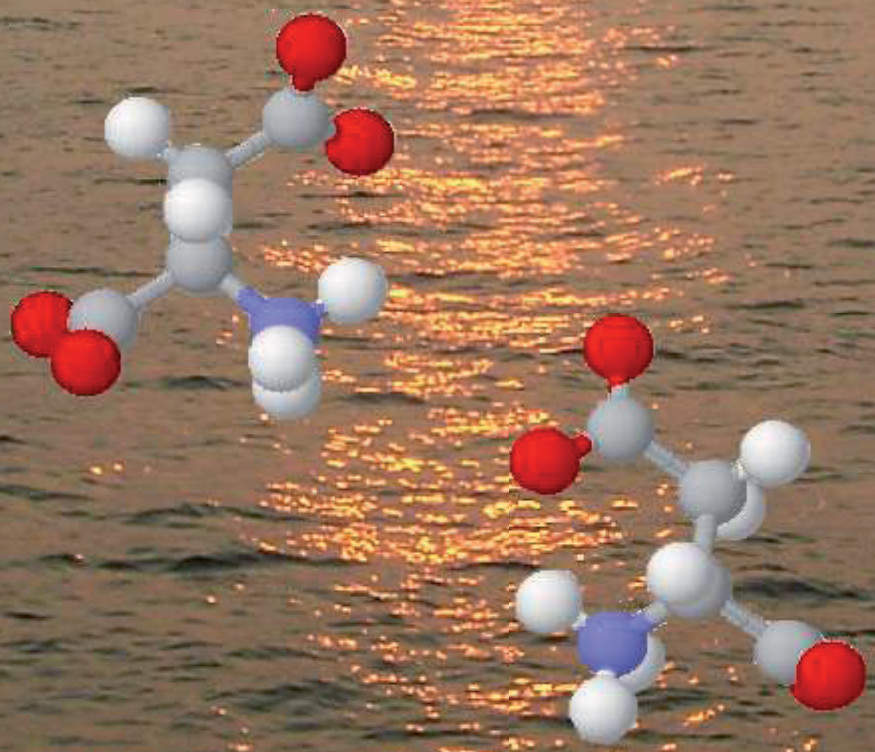
Wessex Archaeology

Lynn and Inner Dowsing Offshore Wind Farms

Geoarchaeological Assessment and Analysis
Final Report (Stages 1-4)



Ref: 59096.01

March 2009

LYNN AND INNER DOWSING OFFSHORE WINDFARMS

GEOARCHAEOLOGICAL ASSESSMENT AND ANALYSIS FINAL REPORT (STAGES 1-4)

Prepared by:

Wessex Archaeology
Portway House
Old Sarum Park
Salisbury
WILTSHIRE
SP4 6EB

Prepared for:

RPS Group Plc
Irwin House
118 Southwark Street
London
SE1 0SW

On behalf of:

Centrica Renewable Energy Limited

Ref: 59096.02

March 2009

LYNN AND INNER DOWSING OFFSHORE WINDFARMS

GEOARCHAEOLOGICAL ASSESSMENT AND ANALYSIS FINAL REPORT (STAGES 1-4)

Ref: 59096.02

Title:	Lynn and Inner Dowsing Offshore Windfarms - Geoarchaeological Assessment and Analysis: Final Report (Stages 1-4)
Principal Author(s):	Jack Russell
Managed by:	John Gribble
Origination date:	March 2009
Date of last revision:	March 2009
Version:	59096.02
Wessex Archaeology QA:	Euan McNeill
Status:	Final
Summary of changes:	Clarification regarding borehole of primary interest; Correction of a number of typographical errors; Inclusion of difference between OD and CD; Changes to figures; Clarification regarding further AAR work by Dr Penkman
Associated reports:	59091.01, 59092.01, 59093.03, 59094.01, 59095.01
Client Approval:	Chris Jenner and Ed Frost

LYNN AND INNER DOWSING OFFSHORE WINDFARMS

GEOARCHAEOLOGICAL ASSESSMENT AND ANALYSIS FINAL REPORT (STAGES 1-4)

Ref: 59096.02

Acknowledgements

This geoarchaeological assessment was commissioned by RPS Group plc on behalf of Centrica. Wessex Archaeology would like to thank James Sandon and John Ashworth for their co-operation.

The sample assessments and analyses were carried out by, Jack Russell and Dr Robert Scaife. Dr Kirsty Penkman undertook the amino acid racemisation (AAR) dating. This report was written by Jack Russell and figures were prepared by Kitty Brandon. John Gribble managed the project and edited the report.

LYNN AND INNER DOWSING OFFSHORE WINDFARMS

GEOARCHAEOLOGICAL ASSESSMENT AND ANALYSIS FINAL REPORT (STAGES 1-4)

REF: 59096.02

Contents

Figures:

LYNN AND INNER DOWSING OFFSHORE WINDFARMS

GEOARCHAEOLOGICAL ASSESSMENT AND ANALYSIS FINAL REPORT (STAGES 1-4)

REF: 59096.02

1. INTRODUCTION

1.1. PROJECT BACKGROUND

1.1.1. Wessex Archaeology (WA) was commissioned by RPS Group plc, on behalf of Centrica Renewable Energy Limited, to undertake Stage 4 ostracod and pollen analyses and amino acid racemisation (AAR) dating of samples taken from borehole **BHID25**, collected during the geotechnical surveys for the Lynn and Inner Dowsing Offshore Wind Farms. This report is the Stage 5 or final report detailing the results of the Stage 4 analyses and dating and summarises the earlier Stage 1 to 3 assessments and geoarchaeological recording (WA 2005, 2006 and 2007).

1.1.2. The Stage 1 assessment comprised a review of vibrocore and borehole logs generated by the geotechnical contractors which were assessed by WA in 2005. Stage 1 established the likely presence of horizons of archaeological interest within the cores, broadly characterised them and recommended that Stage 2 archaeological recording was required (WA 2005).

1.1.3. During Stage 2 geoarchaeological recording was undertaken upon available selected cores. This entailed the splitting of the cores, with half of each core being cleaned and recorded. The Stage 2 report described the results of the geoarchaeological recording and indicated that Stage 3 work upon core samples from borehole **BHID25** was warranted (WA 2006).

1.1.4. The Stage 3 sample assessment comprised laboratory assessments of sediment subsamples from **BHID25** (**Figure 1**). The subsamples were assessed for pollen, diatoms, ostracods and foraminifera. The results of these assessments indicated the presence of pollen and ostracods in sufficient numbers to warrant Stage 4 analysis (WA 2007).

1.1.5. The method and results of the Stage 4 analyses (pollen and ostracod) and dating (AAR) are presented in full in **Appendices 1**, **2** and **3**.

1.2. SUMMARY OF STAGES 1 TO 3

1.2.1. The Stage 1 assessment of geotechnical logs comprised the geoarchaeological review of 29 borehole logs and 22 vibrocore logs (Fugro 2004). Of the boreholes, 15 were from the proposed Lynn windfarm area and 14 were from the Inner Dowsing windfarm area (see table below and **Figure 1 (inset location map)**). The 22 vibrocores were associated with the export cable route areas.

Area	Borehole / Vibrocore numbers
Lynn OWF	**BHL2**, **BHL4**, **BHL6**, **BHL8**, **BHL10**, **BHL11**, **BHL13**, **BHL15**,

	BHL17, **BHL19**, **BHL21**, **BHL24**, **BHL26**, **BHL28, BHL30**
Inner Dowsing OWF	**BHID1**, **BHID3**, **BHID6**, **BHID8**, **BHID10**, **BHID11**, **BHID13**, **BHID15**, **BHID18**, **BHID21**, **BHID23**, **BHID25**, **BHID27, BHID30**
OWF export cable route	**TB05-02A**, **TB05-04**, **TB05-05**, **TB05-06**, **TB05-06A**, **TB05-07**, **TB05-08**, **TB05-09**, **TB05-10**, **TB05-11A**, **TB10-02**, **TB10-03**, **TB10-04**, **TB10-05**, **TB10-06**, **TB10-07**, **TB10-07A**, **TB10-08**, **TB10-09**, **TB10-10**, **TB10-11**, **TB10-12**

1.2.2. The Stage 1 study identified sedimentary units of potential archaeological importance based on their lithology and the possible presence of organic remains in the sediments which can provide both dating and palaeoenvironmental information. Undisturbed core samples were requested from the following boreholes and vibrocores: **BHL2**, **BHL17**, **BHL21**, **BHL28**, **BHID6**, **BHID13**, **BHID25**, **TB10-02** and **TB10-10** (WA 2005).

1.2.3. Ten short sections of undisturbed core samples from boreholes were available for Stage 2 recording. Two of the boreholes - **BHL21** and **BHL28** – where from the Lynn Wind Farm area where water depths range from six to 13 metres below Lowest Astronomical Tide (LAT). The third, **BHID25**, was located in the Inner Dowsing Wind Farm area where water depths range from six to nine metres below LAT (see **Figure 1 (inset location map)**). In this area, LAT and Chart Datum (CD) are considered to be the same (UKHO Chart 108). CD is approximately 3.75m below Ordinance Datum (OD) at Skegness (UKHO Chart 108).

1.2.4. These samples were assigned WA Identification Numbers (**WAID**) and their depths below OD and the geoarchaeological descriptions generated by the Stage 2 recording are detailed in the table below:

WA ID	Borehole	Section below OD* (m)	Description
1	**BHL21**	14.50 - 14.67	10YR 3/4 Dark yellowish brown coarse sand with small shell and gravel inclusions (<5mm). Very loose, very probably contamination consisting of recent seabed deposits.
2		14.67 - 14.78	2.5Y 4/1 Dark grey clay, very firm, stiff, with frequent big chalk inclusions (10-25mm), patch with sand and shell inclusions (<5mm) running from the top corner, probably intrusion from above.
3		14.78 - 14.86	5Y 4/4 Olive coarse sand and gravel (10-65mm), firm and stiff, one black fleck visible at c. 14.79m (organic/mineral?).
4	**BHID25**	12.20 - 12.45	10YR 3/2 Very dark greyish brown clay, firm and stiff, with frequent chalk (2-10mm) and occasional flint inclusions (10-20mm). Big patch of white chalk at 12.28-12.39, firm and stiff. Big patch of yellowish brown, loose medium sand with big gravel inclusions (40mm) at 12.37-12.45.
5		13.20 - 13.63	10YR 3/2 Very dark greyish brown clay, firm and stiff, occasionally slightly sandy, with frequent subrounded gravel inclusions (chalk, flint, red sandstone etc., 4-40mm) and rare tiny black (mineral?) flecks.
6		14.20 - 14.59	10YR 3/2 Very dark greyish brown clay, firm and stiff, frequent subrounded gravel inclusions (chalk, flint etc., 5-45mm), rare small black (mineral?) flecks.
7		17.70 - 17.93	2.5Y 3/2 Very dark greyish brown sandy silty clay, firm and stiff, well sorted. No inclusions (apart from intrusive small chalk and flint particles at the sides). One brownish sandy band at 17.83-17.84.
8		18.70 - 19.05	2.5Y 3/1 Very dark grey sandy silty clay, completely crossed by slightly arched horizontal black organic(?) bands (c.3mm wide), especially dense between 18.95 and 19.05. Well sorted, firm and stiff, no visible inclusions.

WA ID	Borehole	Section below OD* (m)	Description
9	**BHL28**	17.95 - 18.14	2.5Y 4/1 Dark grey sandy clay, firm and stiff, medium to coarse sandy patches especially along the sides (intrusive contamination?), frequent gravel inclusions (chalk and flint, 10-50mm), rare very small shell fragments (<3mm).
10		18.95 - 19.30	5Y 4/1 Dark grey sandy clay, firm and stiff, with rare small shell inclusions (<3mm). Occasionally brownish sand bands, especially at 19.13, and between 19.20 and 19.30. These sand bands are 2-3cm wide and irregular. They contain frequent small chalk (<6mm) and bigger flint (30mm) inclusions.

Note: * - OD is approximately 3.75m above Chart Datum (Skegness)

1.2.5. It was proposed that sediment subsamples from **BHID25** should be subject to Stage 3 further assessment because the black, possibly organic bands crossing the sandy silty clay sediment noted in Stage 2 are an unusual phenomenon within the general sedimentary sequence of the area. The preliminary suggestion that these sediments represented varves implied they were laid down in a freshwater, pro-glacial lake in a terrestrial environment, which in turn suggested the potential for human occupation of this environment (WA 2006). The Stage 3 assessment comprised assessment of sediment subsamples for diatoms, pollen, foraminifera and ostracods. The results of the Stage 3 assessment showed the presence of pollen and ostracods in sufficient numbers to warrant a more detailed Stage 4 analysis. The ostracods recovered were also considered suitable for scientific (AAR) dating (WA 2007)

1.3. GEOARCHAEOLOGICAL INTERPRETATION OF THE AREA

1.3.1. The sedimentary sequence was interpreted from the Stage 1 assessment (WA 2005) of geotechnical logs (Fugro 2004) and the Stage 2 geoarchaeological recording (WA 2006). It can be summarised as follows:

- **Unit 1**: Recent seabed sediments; brown gravelly sand or sandy gravel, with shell inclusions and flint content.
- **Unit 2iii**: Glacial till: firm to stiff brown; sometimes speckled white, slightly sandy or gravelly clay; silty lenses.
- **Unit 2ii**: Glaciolacustrine sediments;
- **Unit 2i**: Glaciolacustrine sediments;
- **Unit 3**: Gravel: including a variation of sometimes clayey, sometimes silty sand and gravel layers.
- **Unit 4**: Bedrock: Upper Cretaceous Chalk.

1.3.2. **Unit 4**, Upper Cretaceous Chalk bedrock was encountered at the base of the boreholes. Overlying **Unit 4**, **Unit 3** comprised occasionally clayey, silty sand and gravel. Within borehole **BHID25, Unit 3** comprised flint gravel, according to the geotechnical logs (Fugro 2004, WA 2005). It is interesting to note that Hey (1982) suggests the Early Pleistocene gravels of the Norwick Crag group are comprised solely of flint. From the geotechnical descriptions alone it is not possible to date **Unit 3**.

1.3.3. Within borehole **BHID25 Unit 2iii** is most likely to be a Bolders Bank Formation deposit of Devensian till, which appears from available data to be the prevailing sediment near the seabed surface within the Lynn and Inner Dowsing OWF areas. The formation is internally largely structureless on seismic profiles and consists of red-brown, calcareous, gravelly, sandy clay with erratics which are predominantly of

chalk, red-brown sandstone and grey mudstone. The formation is up to 25m thick (BGS 1991).

1.3.4. Interpretation of seismic profiles and micromorphological studies imply that the Bolders Bank Formation is a composite of subglacial and supraglacial deposits. It appears to be the lateral equivalent of the Hunstanton Till of East Anglia and the tills of Holderness, north of Spurn Point, both of which it resembles lithologically (Cameron *et al*. 1992; BGS1991).

1.3.5. It was clear that **Units 2ii** and **2i**, containing sandy silty clays with laminations and organic streaks, were clearly different from the overlying till (**Unit 2iii**). The results of Stages 1, 2 and 3 (WA 2005, 2006 and 2007) indicate that they are sediments from a glaciolacustrine deposit.

1.3.6. **Unit 1** was interpreted as Holocene seabed sediments, likely to have formed originally as a transgressive beach deposit during rising sea levels. Comparison of the depth of **Unit 1** in borehole **BHID25** with sea level data from the southern North Sea suggests this unit would have originally formed at around 8,000BP (Jelgersma 1979). Much of the seabed sediment in this area is, however, presently mobile (Cameron *et al*. 1992).

2. METHOD

2.1. INTRODUCTION

2.1.1. The subsamples submitted for assessment, analyses and dating are from sedimentary **Unit 2** within borehole **BHID25**. This unit has been further subdivided into three subunits on the basis of the original borehole descriptions (Fugro 2004) and the archaeological descriptions (WA 2006):

2.1.2. Comprising grey sandy silty clay **Unit 2i** was elevated between 18.5m and 19.05m below OD. From the geotechnical description this unit would appear to be 0.55m in thickness and forms the base of **Unit 2**. A small section of **Unit 2i** (18.70m to 19.05m below OD) was archaeologically recorded (WA 2006). It is distinguished from **Unit 2ii** by the presence of dark, possibly organic bands (**Figure 1**).

2.1.3. Comprising greyish brown sandy silty clay **Unit 2ii** was elevated between 17.10m and 18.50m below OD. From the geotechnical descriptions (Fugro 2004) this unit would appear to be 1.4m thick within borehole **BHID25**. A short section of the unit (17.70m to 17.93m below OD) was available for archaeological recording (WA 2006). This unit is stratigraphically above **Unit 2i** and is sedimentologically distinct from **Unit 2i** in that it lacks the dark, possibly organic bands and contains occasional chalk and flint inclusions (**Figure 1**).

2.1.4. Comprising very dark greyish brown clay **Unit 2iii** was elevated between 11.90m and 17.10m below OD. From the geotechnical descriptions (Fugro 2004) this unit would appear to have a thickness of 5.2 metres within **BHID25**. Three short sections (12.20m to 12.45m, 13.20m to 13.69m and 14.70m to 14.59m below OD) of this unit were geoarchaeologically recorded (WA 2006). The unit differs from **Units 2i** and **2ii** in its stiff, massive structure and the lack of laminations and dark organic bands of **Units 2i** and **2ii** is stratigraphically above **Unit 2ii** and below **Unit 1** (**Figure 1**).

2.1.5. The further sampling and assessment aimed to confirm the freshwater glaciolacustrine interpretation suggested in Stage 3, and together with the AAR dating attempt to place this core sample in the archaeological sequence of the UK: either during the late Devensian, Early Upper Palaeolithic which would imply deposition in a period when the UK was probably virtually unoccupied by humans; or, if older, somewhere during the long period of the Lower, Middle and Early Upper Palaeolithic of the UK, which saw the arrival of early hominids, Neanderthals and modern humans.

2.1.6. The table below presents the depths and sedimentary units from which the diatom, foraminifera, pollen, ostracod and AAR samples were taken for Stage 3 assessment and subsequent Stage 4 analysis, from within units **Unit 2i**, **Unit 2ii** and **Unit 2iii** in borehole **BHID25**:

Section of borehole (m below OD*) Stage 2 recorded	Subsample depth (m below OD*)	Stage 3 assessed subsample diatom (d), foraminifera (f) ostracod (o), pollen (p)	Stage 4 subsample analysis AAR (a), ostracod (o), pollen (p)	Description of sediments (WA 2006)
12.20 - 12.45	12.24	d,p		10YR 3/2 Very dark greyish brown clay, firm and stiff, with frequent chalk (2-10mm) and occasional flint inclusions (10-20mm). Big patch of white chalk at 12.28-12.39, firm and stiff. Big patch of yellowish brown, loose medium sand with big gravel inclusions (40mm) at 12.37-12.45. **Unit 2iii**
13.20 - 13.63	13.59	d,p		10YR 3/2 Very dark greyish brown clay, firm and stiff, occasionally slightly sandy, with frequent subrounded gravel inclusions (chalk, flint, red sandstone etc., 4-40mm) and rare tiny black (mineral?) flecks. **Unit 2iii**
14.20 - 14.59	14.3	d,p		10YR 3/2 Very dark greyish brown clay, firm and stiff, frequent subrounded gravel inclusions (chalk, flint etc., 5-45mm), rare small black (mineral?) flecks. **Unit 2iii**
17.70 - 17.93	17.74		o,p	2.5Y 3/2 Very dark greyish brown sandy silty clay, firm and stiff, well sorted. No inclusions (apart from intrusive small chalk and flint particles at the sides). One brownish sandy band at 17.83-17.84. **Unit 2ii**
	17.77		a,o	
	17.78	d,f,o,p	o,p	
	17.81		o,p	
	17.83	d,f,o,p	o,p	
	17.87		a,o,p	
	17.88	d,p	o,p	
18.70 - 19.05	18.74		a,o	2.5Y 3/1 Very dark grey sandy silty clay, completely crossed by slightly arched horizontal black organic (?) bands (c.3mm wide), especially dense between 18.95 and 19.05. Well sorted, firm. **Unit 2i**
	18.75	d,f,o,p	p,o	
	18.81		o,p	
	18.87	d,f,o,p	o,p	
	18.93		o,p	
	19	f,o	O	
	19.04		a,o,p	

Note: * - OD is approximately 3.75m above Chart Datum (Skegness)

2.2. STAGE 4 SAMPLING

2.2.1. Six pollen samples were processed using standard palynological processing techniques. The full sample processing method is described in **Appendix 1**. Once processed the pollen and spores were identified and counted in conjunction with the samples already assessed during Stage 3 (Scaife 2007). The depths of the pollen samples are shown in **Appendix 1** and **Figures 2, 3a** and **3b**.

2.2.2. Eight ostracod samples were processed using a technique modified for the submission of ostracod valves for AAR dating. Care was taken not to heat the samples in the drying process in order not to affect the AAR results. The full processing method is described in **Appendix 2**. Ostracods were identified and kept in card slides. The depths of the ostracod samples is given in **Appendix 2** and shown on **Figure 2**.

2.2.3. Four amino acid racemisation (AAR) dating samples were processed. The material submitted for AAR dating was ostracod valves of the species *Candona neglecta*. The processing technique is detailed in **Appendix 3**. The depths of the four AAR samples is shown in **Figure 2**.

3. RESULTS

3.1.1. This section summarises the results of the sample analyses. The full reports of the individual assessments, containing more detailed methodologies and discussions of results can be found in **Appendices 1-3**.

3.2. INTRODUCTION

3.2.1. The following environmental analyses were undertaken:

- Pollen (**Appendix I**)
- Ostracods (**Appendix 2**)
- Amino Acid Racemisation (**Appendix 3**)

3.2.2. A further six pollen samples were processed to supplement the eight already assessed (WA 2007). These samples were all taken from the base of **Unit 2** (**Unit 2i** and **Unit 2ii**) (**Figures 2, 3a** and **3b**, **Appendix I**). The pollen assemblages are low in abundance and are homogenous. The samples include pine (*Pinus*), birch (*Betula*), grasses (Poaceae), sedges (Cyperaceae) ferns (*Dryopteris/Pteridium*) and freshwater algal cysts (*Pediastrum*). These are indicative of an open herbaceous environment surrounding a depositional environment of standing or slow flowing freshwater. They are indicative of a cold stage within the Pleistocene, with the presence of spruce (*Picea*) suggesting an earlier Devensian (Marine Isotope Stage (MIS) 5a and 5c) age at the latest (**Appendix I**).

3.2.3. A further eight ostracod samples were processed in addition to the five samples assesed during the Stage 3 assessment (Russell 2007). Four of the samples were carefully processed to provide ostracods suitable for AAR dating (**Appendix 3**). All of the samples were taken from **Unit 2** (**Unit 2i** and **Unit 2ii**; **Figure 2, Appendix 2**) and were indicative of cold freshwater habitats. Together they are indicative of a depositional environment on the margins of a glacial lake (**Appendix 2**). The

occurrence of "*Leucocythere batesi*" and *Limnocythere falcata* are of biostratigraphic value and indicate that the sediments date from a cold period from the Hoxnian (Marine Isotope Stage (MIS) 11) to Devensian (MIS 3) *c*.380,000 to 43,000BP (see **Figure 2**).

3.2.4. Amino Acid Racemisation (AAR) dating was undertaken on ostracods (*Candona neglecta)* retrieved from four samples from depths of 17.77, 17.88, 18.74 and 19.04m below OD (**Figure 2**, **Appendix 3**). The results of the dating indicate that the ostracods are probably younger than MIS7-6 or *c*.185,000BP (**Figure 2**, **Appendix 3**).

4. DISCUSSION

4.1. SEDIMENTS

4.1.1. Earlier discussions about the black, possibly organic bands within in the lower part of **Unit 2** (**Unit 2i**) suggested that they were varves, which are described as: "*annual sediments deposited in glacial melt water lakes. These consist of a coarser layer, representing summer deposition, and a finer layer, representing winter deposition*." (Whitten & Brooks 1972).

4.1.2. The sediments described by Wessex Archaeology 2006 are not varves in that they do not comprise a coarser and finer layer of deposition. Given the sedimentary descriptions and pollen and ostracod content of the sediments they are better described as glacial lacustrine sediments. It is interesting to note that the ostracod and pollen assemblages are no different in the sediments with darker organic bands (**Unit 2i**) and those without (**Unit 2ii**). **Unit 2ii** therefore also comprises glacial lacustrine sediments. Organic material was noted in the foraminifera/ostracod samples in both **Unit 2i** and **Unit 2ii**.

4.1.3. The bands within **Unit 2i** were also noted not to cross the sediment in an unbroken line across the width of the borehole and had a somewhat broken, lenticular and mottled appearance. This may be due to the influence of post-depositional freezing on the sediments.

4.1.4. The main component of **Unit 2** is **Unit 2iii,** a glacial till, which represents the advance of an ice sheet. The description of this unit and comparison with the described offshore geology suggests that it is part of the Bolders Bank Formation (WA 2006; BGS 1991; Cameron *et al*. 1992) which has been ascribed a Devensian date (Cameron *et al*. 1992).

4.2. DATING

4.2.1. Using specific ostracod taxa ("*Leucocythere batesi*" and *Limnocythere falcata*) as markers, the glacial lacustrine sediments at the base of **Unit 2** (**Unit 2i** and **Unit 2ii**) biostratigraphically correlate to a cold stage between the Hoxnian (MIS 11) *c*.380,000BP to early Devensian (MIS 5 - 3) *c*.50,000BP date (**Figure 2**, **Appendix 2**).

4.2.2. The open herbaceous environment indicated by the pollen analysis is suggestive of deposition within a cold stage. The presence of spruce (*Picea*), not a native of the Holocene and given the stratigraphic position of the sediments (overlain by glacial till) **Unit 2i** and **Unit 2ii** were probably deposited no later than the earlier part of the Devensian *c*.60,000BP (MIS 5c or 5a).

4.2.3. The results of the AAR dating so far suggest that the sediments were deposited after MIS 7-6. This suggests that the deposition of **Unit 2i** and **Unit 2ii** occurred during the latter part of the Wolstonian glacial (MIS 6 / *c.*200,000–130,000BP) and prior to the Ipswitchian interglacial (MIS 5 / *c.*130,000-110,000BP). **Units 2i** and **2ii** would thus be comparable to the offshore geological formation known as Brown Bank which is not at present mapped in the area of **BHID25** (Cameron *et al.* 1992 and BGS 1991).

4.2.4. The till recorded as **Unit 2iii** is known offshore as the Bolders Bank formation and is equivalent to the onshore formations known as Hunstanton till in East Anglia and the Holderness tills north of Spurn point. These are thought to have been deposited in this area during the Devensian glacial maximum, MIS 2, *c.*18,000BP (Cameron *et al*. 1991).

4.3. ENVIRONMENT

4.3.1. Ostracods recovered from **Units 2i** and **2ii** are clearly indicative of deposition on the fringes of a cold glacial lake. The frequent cysts of algal *Pediastrum* and occasional aquatic plants including *Potomageton* and *Myriophyllum* support this interpretation.

4.3.2. The surrounding environment indicated by pollen anlaysis is of an open habitat dominated by grasses and sedges. A periglacial, freeze/thaw environment is indicated by the presence of *Plantago major* type (greater plantain), Chenopodiaceae (goosefoots and oraches) and *Artemisia* (mugwort). The latter are also diagnostic plants of steppe.

4.4. ARCHAEOLOGICAL POTENTIAL

4.4.1. As described above, the results of this assessment suggest that the **Units 2i** and **2ii** were deposited during the latter part of the Wolstonian glacial (MIS 6 / *c.*200,000–130,000BP). Although this corresponds with the Middle Palaeolithic in the UK and Europe, there is currently no archaeological evidence for the presence of humans in the UK during this period. The harsh environmental conditions are likely to have made the area unattractive for human occupation.

5. FURTHER WORK

5.1.1. Further bulked ostracod samples are being processed as part of ongoing research by Dr Penkman to refine the AAR dating. This work will be funded by Dr Penkman / University of York.

5.1.2. Some ostracod taxa have been submitted for photography by Scanning Electron Micrograph (SEM).

5.1.3. Subject to the approval of Centrica Renewable Energy Limited, the results of the Stage 1-4 assessment should be published in a suitable scientific journal.

6. REFERENCES

BGS, 1991, *Spurn Sheet 53˚N - 00˚*, British Geological Society, 1:250,000 Series, Quaternary Geology, Offshore Geology.

Cameron, T.D.J., Crosby, A., Balson, P.S., Jeffery, D.H., Lott, G.K., Bulat, J. and Harrison, D.J., 1992, *The geology of the Southern North Sea*. British Geological Survey, United Kingdom Offshore Report 7, London: HMSO.

Fugro Engineering Services Ltd., 2004, 'Lynn And Inner Dowsing Wind Farm Developments. Geotechnical Investigations. Final Report on Ground Investigation'. Unpublished report ref NEA04/005.

Hey, R.W. 1982. Composition of pre-Anglian gravels inNorfolk. *Bulletin of the Geological Society of Norfolk*. 32. 51-59

Jelgersma, S., 1979, 'Sea-level changes in the North Sea Basin', in Oele, E., Schüttenhelm, R.T.E. and Wiggers, A.J. (eds.), *The Quaternary History of the North Sea*, Acta Univeritatis Upsaliensis: Symposium Universitatis Upsaliensis Annum Quingentesimum Celebrantis 2

Wessex Archaeology, 2005, 'Lynn and Inner Dowsing Offshore Wind Farms: Stage 1 Borehole Assessment'. Unpublished report ref. 59091.01.

Wessex Archaeology, 2006, 'Lynn and Inner Dowsing Offshore Wind Farms: Stage 2 Archaeological recording of cores'. Unpublished report ref. 59093.01.

Weseex Archaeology 2007, 'Lynn and Inner Dowsing Offshore Wind Farms: Stage 3 Archaeological recording of cores'. Unpublished report ref. 59094.01

Whitten, D.G.A. and Brooks, J.R.V., 1972, *The penguin dictionary of Geology*. Harmondsworth: Penguin Books

APPENDIX 1: POLLEN ANALYSIS

Pollen analysis of sediments from the site of the Lynn and Inner Dowsing Offshore Windfarms

Rob Scaife

Visiting Reader in Palaeoecology
School of Geography
University of Southampton
Highfield
Southampton
SO17 1BJ
2009

INTRODUCTION

The fine grained and possibly varved sediments offered potential for pollen and diatom analysis and thus, reconstruction of the prehistoric environment prior to marine submergence. A preliminary analysis of pollen samples previously carried out by the author (Scaife 2006) demonstrated that sub-fossil pollen and spores are present in these sediments. Because of the dominance of herb pollen and the impoverished arboreal flora, it was suggested that the sediments are of glacial age. That is, possibly the last (Devensian) glacial although possibly the preceding Wolstonian as the sediments analysed are overlain by till. Additional samples and pollen totals have now been fully analysed which confirms the view that the sequence relates to a major cold stage where the habitat was open and comprised grass and sedge dominated herbaceous communities. Pollen was found to be generally well preserved in the finer grained sediments but, however, absolute numbers present were small.

POLLEN METHOD

Undisturbed core samples from this offshore site have been described and sampled for pollen in the laboratory (Dr D. Paddenberg, Wessex Archaeology). Sub-samples of 2ml were processed using standard techniques for the extraction of the sub-fossil pollen and spores (Moore and Webb 1978; Moore *et al.* 1992). Micromesh sieving (10u) was also used to aid with removal of the clay fraction from these largely minerogenic sediments. The pollen and spores were identified and counted using an Olympus biological research microscope fitted with Leitz optics. A pollen sum of up to 400 grains per sample level was counted where preservation allowed. Other, miscellaneous microfossils including substantial numbers of algal *Pediastrum* and pre-Quaternary palynomorphs were also recorded. Data are presented in pollen diagram form (**Figures 3a** and **3b**) and where appropriate, in tables. The former have been plotted using Tilia and Tilia Graph. Where percentages are given, these have been calculated as follows:

Sum =	% total pollen.
Spores =	% total pollen + sum of spores.
Miscellaneous =	% total pollen + sum of misc. taxa.

Taxonomy, in general, follows that of Moore and Webb (1978) modified according to Bennett *et al.* (1994) for pollen types and Stace (1992) for plant descriptions. These procedures were

carried out in the Palaeoecology Laboratory of the School of Geography, University of Southampton.

THE POLLEN DATA

Eleven samples contained pollen and spores. These samples, as anticipated, come from the laminated (possibly varved) sediments only and not from the under and overlying glacial till. Overall, the pollen assemblages are herb dominated but with a moderate taxonomic diversity. There are correspondingly few trees and shrubs.

Trees and shrubs: There are few tree and shrub pollen. *Pinus* (Pine) and *Betula* (birch) are most consistent with values to 2% and 5% respectively in the upper sequence. Of note are occasional records of *Picea* (spruce). Occasional thermophiles include sporadic occurrences of *Quercus* (oak), *Alnus* (alder) and *Corylus* avellana type (hazel). In some case these pollen grains are darker and degraded and may be derived from earlier (interglacial) sediments.

Dwarf Shrubs; There are small numbers of *Empetrum nigrum* (crowberry), *Erica* (heather) and tentative identification (based on small size) of *Betula nana* (dwarf birch). *Salix* (willow) is also present and it is most probable that this was also a dwarf shrub form given the cold environment which existed at the time of sediment deposition.

Herbs; Poaceae (Grasses; to 60%) and Cyperaceae (sedges; to 60%) are dominant in all samples from both the upper and lower sequences. Overall there is a moderate herb diversity which includes plants which are typical/diagnostic of grassland. These include Ranunculaceae (buttercup family) with *Ranunculus* type (buttercups), *Caltha* type (marsh marigold), *Thalictrum* (meadow rue) and *Anemone* type. Also present are Asteraceae types (daisy family), *Plantago lanceolata* (ribwort plantain), Caryophyllaceae (pinks) including *Dianthus* type, *Stellaria* type and *Cerastium* type. Plants of disturbed ground are also represented with *Plantago major* type (probably greater plantain), *Artemisia* (mugwort), Chenopodiaceae (goosefoots and oraches), Brassicaceae (charlocks) and *Spergula* (spurrey).

Marsh and aquatic: Cyperaceae as noted are the dominant marsh plants with percentages to 65%. Aquatic plants are present with *Potamogeton* type (pondweed) and *Myriophyllum spicatum* (water milfoil). Other wetland plants are present with *Caltha* type (marsh marigold), T*halictrum* (meadow rue) and *Valeriana officinalis* (valerian). Aquatic algal *Pediastrum* attains high values in both sections.

Spores: There are small numbers only of monolete spores forms - *Dryopteris* type (ferns) and *Pteridium* (bracken) in the basal level. *Botrychium lunaria* (moonwort) is the most diagnostic taxon present, being a plant of short turf grassland. There are occasional Sphagnum spores (bog moss).

Miscellaneous: Of specific note (as noted above), are the substantial numbers of freshwater algal *Pediastrum* cysts (to 65% sum + misc.). Values of these are higher in the upper profile. Pre-Quaternary palynomorphs are more abundant throughout and as might be expected in the under and overlying till.

INTERPRETATION AND DISCUSSION

The climatic and dating context

The small absolute numbers of pollen present, the paucity of trees and shrubs and the dominance of herbs are diagnostic of cold stage environments. Steppe habitats may have overall pollen production, which is many orders of magnitude less than tree, and shrub dominated interglacial periods. The pollen spectra, portraying an open herbaceous

environment, suggests that deposition occurred during a cold (glacial) stage. However, dating to a specific cold stage may be problematic unless the age of the overlying till can be ascertained. A Devensian (last glacial), age is perhaps unlikely given the fact that there is till overlying these fine-grained sediments. Given dating from the ostracods, an earlier Wolstonian age may be possible. The pollen does not offer any dating solutions and only the character of the environment of deposition can be deduced from the data obtained.

The environment
The pollen data clearly demonstrate a very open, herb-dominated environment. A number of different habitats are evidenced which include grassland, disturbed ground and marsh and aquatic habitats. The pollen assemblages are dominated by Poaceae (grasses) which may be constituents of all of these habitats. Pollen morphology does not allow separation to a lower taxonomic level.

The depositional habitat
Cyperaceae (sedges) are also extremely important growing in areas of nearby fen and perhaps adjacent to the freshwater depositional hollow. The depositional habitat was one of standing or very slow flowing freshwater. The presence of varves, as well as being indicative of a cold stage environment with seasonal freeze and thaw, also suggests a water filled depression (lake?). Palynologically this is evidence by substantial numbers of cyst of algal *Pediastrum* and occasional aquatic plants (*Potamogeton* and *Myriophyllum*). A wet, grass-sedge community fringed this sedimentary basin, possibly with Cyperaceae, *Caltha palustris* (marsh marigold), *Thalictrum* (meadow rue) and *Valeriana officinalis* (valerian).

Other vegetation communities/habitats.
Typical of such open cold stage, periglacial environments, is evidence of a range of different plant communities that occupy specific ecological niches (Moore 1980). This is the case here although vegetation diversity is not as great as may be encountered in late Devensian.

Apart from the clear importance of Poaceae, there are a number of other herbs which may derive from the grassland. These include the diagnostic, low growing fern, *Botrychium lunaria* (moonwort), *Ranunculaceae (*buttercups*), Plantago lanceolata* (ribwort plantain), Asteraceae types (dandelion and daisy family).

Typical of periglacial habitats are areas of disturbed ground due to cryogenic (freeze/thaw) action. Indications of this come from pollen of *Plantago major* type (greater plantain), Chenopodiaceae (goosefoots and oraches) and *Artemisia* (mugwort). The latter are also diagnostic plants of steppe. Other herb pollen taxa are less diagnostic but may include *Cerastium* type (mouse ears), *Spergula* (spurrey), *Sinapis* type (charlocks).

Throughout the sequence, there are a small number of tree pollen present. These comprise the typical glacial-Boreal taxa, *Pinus* (pine) and *Betula* (tree birch). These are anemophilous and high pollen producers and as such, are thought to be of long distance, extra-regional origin. *Picea* (spruce) is occasionally present and is diagnostic of earlier interglacial periods and from interstadial periods within glacial periods. Not a native of the Holocene, the most recent occurrences of this conifer are from the earlier part of the Devensian, interstadial periods (OI 5a. and 5c.) from South Oxfordshire and the Midlands. It is not thought that trees were present in the local environment during the period of sediment accretion. Occasional thermophilous trees (*Quercus, Alnus* and *Corylus avellana* type) have poorer preservation and are thought to be reworked from earlier interglacial sediments.

Small numbers of dwarf shrubs including *Empetrum* (crowberry) and *Erica* (heather) are evidence of localised heath on better drained (?sandy) substrates. These taxa are poorly represented in pollen assemblages/spectra but are also diagnostic of such cold stage habitats.

SUMMARY AND CONCLUSIONS

The following principal points have been obtained from this study.

* Pollen is present in the laminated ?varved sediments but not, unexpectedly, in the over and underlying till, except for derived geological palynomorphs.

* The pollen is well preserved but with small numbers of pollen present.

* The pollen assemblages are dominated by herbs, predominantly grasses and sedges with a moderate taxonomic diversity. An open herbaceous environment is thus demonstrated.

* There is evidence of a diversity of vegetation communities including grassland, disturbed ground, dwarf shrub/heath elements, fen and aquatic habitats.

* There are small numbers of birch and pine and occasional spruce pollen which are considered to be from extra regional sources (that is, a long distance transport component).

* The above palynological features clearly demonstrate that the sediments were deposited in a cold stage. The small species diversity indicates an extreme cold, arctic environment. This is in accord with the stratigraphical location of these fine sediments intercalated between till. The laminated/varved nature of these sediments also implies a seasonal, but harsh freeze thaw, periglacial, permafrost environment.

* The presence of algal *Pediastrum* and the lamination of the sediments suggest a low energy, freshwater environment of deposition. This may have been a small lake or water filling a glacially scoured topographic hollow or other feature.

* It has not been possible to suggest an age for the sediments based on these pollen assemblages. This may be achieved by more accurate characterisation of the associated till deposits. Presence of spruce (*Picea*) suggests an early Devensian age at the latest, although an earlier glacial phase is readily possible (? Wolstonian).

REFERENCES

Bennett, K.D., Whittington, G. and Edwards, K.J. 1994 'Recent plant nomenclatural changes and pollen morphology in the British Isles'. ***Quaternary Newsletter*** 73, 1-6

Moore, P.D. 1980 'The reconstruction of the late glacial environment: some problems associated with the interpretation of pollen data'. pp. 151-155 in Lowe, J.J., Gray, J.M. and Robinson, J.E. (eds.) ***Studies in the Late Glacial of North-West Europe.*** Oxford: Pergamon Press.

Moore, P.D. and Webb, J.A. 1978 ***An illustrated Guide to Pollen Analysis***. London: Hodder and Stoughton.

Moore, P.D., Webb, J.A. and Collinson, M.E. 1991 ***Pollen Analysis*** Second edition. Oxford: Blackwell Scientific.

Stace, C. 1991 ***New Flora of the British Isles***. Cambridge: Cambridge University Press.

APPENDIX 2: OSTRACOD ANALYSIS

Jack Russell
Wessex Archaeology

INTRODUCTION

Eight subsamples taken from vibrocore BHID25 have been analysed for their of ostracod content in addition to the five samples already assessed as part of the Stage 3 asessment (Russell 2007). The sediments are glacilacustrine sandy silty clays.

METHOD

Sediment was wet sieved through a 63µm sieve to extract the coarser fraction. The fine sediment was dried and then sieved through 500µm, 250µm, 125µm sieves. Care was taken not to heat the samples during this process as specimens were sent for Amino Acis Racemisation (AAR) dating (see **Appendix 3**). Ostracods were picked out under 10-60x magnification and transmitted and incident light using a Vickers microscope. All of the taxa in the sample were picked out and kept in card slides. Identification, ecological interpretation and biostratigraphic inference follows Meisch (2000) and Hart and Whittaker (2009).

RESULTS

Ostracods were present in all of the samples. Abundance of ostracods per sample from borehole BHID25 is summarised in **Table 1**. Abundance of ostracods was medium to high, and preservation was moderate.

At 17.74 abundance of ostracods was high. The assemblage is dominated by *Candona candida* and *Candona neglecta*. *Limnocythere falcata, Lymnocytherina sanctipatricii* and *"Leucocythere batesi"* were also occasionally present. Both adults and instars of *Candona candida* and *Candona neglecta* were recovered indicative of a thanatocenosis. One charophyte oogonia was recovered from this sample.

At 17.77 abundance of ostracods was moderate. The assemblage is dominated by *Candona candida* and *Candona neglecta*. *Limnocythere falcata, Lymnocytherina sanctipatricii* and *"Leucocythere batesi"* were also present. Most of the ostracods recovered were adult however there were significant numbers of instars of *Candona candida* and *Candona neglecta.*

At 17.78m abundance of ostracods was high and preservation was moderate. The assemblage is dominated by *Limnocytherina sanctipatricii* and *"Leucocythere batesi", Limnocythere falcata* and *Eucypris* sp. were also present. Many broken specimens were recovered. There was a notable lack of instar stages and most valves recovered were adult forms.

At 17.81 abundance of ostracods was moderate. The assemblage is dominated by *Candona candida* and *Candona neglecta*. *Limnocythere falcata* and *"Leucocythere batesi"* were also present. Most of the ostracods recovered were adult forms. Plant remains including seeds were conspicous within this sample.

At 17.83m abundance of ostracods was moderate to high. The most abundant taxon was *Limnocytherina sanctipatricii*. "Leucocythere batesi" and *Candona neglecta* were also

present. The majority of the valves were broken and of those identified were mostly adult forms.

At 17.88 abundance of ostracods was high. The assemblage is dominated by *Candona candida* and *Candona neglecta*. *Limnocythere falcata, Lymnocytherina sanctipatricii* and *"Leucocythere batesi"* were also present. Most of the ostracods recovered were adult however there were significant numbers of intars of *Candona candida* and *Candona neglecta.* Three charophyte oogonia were recoverd from this sample.

At 18.74m abundance of ostracods was low to moderate. The assemblage is dominated by *Candona candida* and *Candona neglecta*. *Limnocythere falcata* and *Lymnocytherina sanctipatricii* were also present. One broken *Ilyocypris papillata* was recovered. The majority of the ostracods recovered were adult forms.

At 18.75m abundance of ostracods was moderate. The assemblage contained adult forms of *Limnocytherina sanctipatricii*, *"Leucocythere batesi"* and *Cytherissa lacustris*. 26 broken and unidentified specimens were recovered.

18.81m abundance of ostracods was low. The assemblage was dominated by *Candona candida* and also contained *Candona neglecta, Limnocytherina sanctipatricii*, *"Leucocythere batesi" and Eucypris* sp..

At 18.87m abundance of ostracods was moderate. The assemblage was dominated by adult forms of *Limnocytherina sanctipatricii*, and also contained *Cytherissa lacustris* and *Candona candida.*

At 18.93m abundance of ostracods was low. The assemblage was dominated by *Candona candida* and also contained *Candona neglecta, Limnocytherina sanctipatricii*, *"Leucocythere batesi" and Ilyocypris* sp..

At 19.00m abundance of ostracods was moderate The assemblage was dominated by *Candona candida* and also contained *Candona neglecta, Limnocytherina sanctipatricii* and *"Leucocythere batesi"*.

19.04m abundance of ostracods was low. The assemblage was dominated by *Candona neglecta and also contained Limnocytherina sanctipatricii*, *"Leucocythere batesi" and Limnocythere falcata.*

Organic plant macrofossils including Charophyte oogonia, *Potomageton,* seeds and twigs were recovered from 17.74, 17.77, 17.78, 17.81, 17.88, and 18.75m.

DISCUSSION

The assemblages are very similar in nature, with many broken specimens and mostly dominated by *Candona neglecta*, *Candona candida* and *Limnocytherina sanctipatricii.* All of the species recovered are non-marine and are known to inhabit freshwater.

The samples recovered from 17.74 and 17.88m and 18.74 to 19.04m differed sedimentologically by the presence of lenticular organic laminae in the lower samples. It is interesting to note that the highest proportion of identifiable plant remains recovered from the ostracod samples occurred in the sediments from 6.04 to 17.88m. The ostracod faunas generally contained the same taxa however the presence of high numbers of both adults and instars of *Candona candida* and *Candona neglecta* and an increase in total abundance of ostracods was noticeable in the upper samples (6.04 to 17.88m).

Candona neglecta was the most numerically dominant taxon recovered with both adults and (assumed) instars present. Due to the genetic variability and carapace shape which differs little from other species within the genera it is assumed that the juveniles are also *Candona neglecta,* as they were found in association with the adult forms which displayed dorsal margins of characteristically neglectoid form. The species prefers cold freshwaters but can tolerate temperature increases up to 20ºC. Although covering a wide ecological range, *Candona neglecta* is often found in large numbers in cold, slow flowing or still fresh waterbodies). *Candona candida* has also a wide ecological tolerance, but is more commonly found in fresh waterodies. Within lakes *Candona candida* is known to prefer the littoral zone *Limnocythere sanctipatricii* is known from still, permanent freshwater bodies and is often, but not exclusively associated with cold freshwater lakes Of the other less abundant taxa, *Cytherissa lacustris* is known from the profundal and littoral zones of cold freshwater lakes (Meisch 2000).

Three of the taxa recovered, two of which are now extinct, known from Quaternary glacial sediments also have some biostratigraphic value. *Limnocythere sanctipatricii has* a range from Cromerian (MIS 15-13) to Recent. Of greater biostratigraphic value is the presence of "*Leucocythere batesi*", another cold freshwater indicator with a known range from the Hoxnian (MIS 11) to Devensian (MIS 5-3) periods. *Limnocythere falcata* also has a known range from the Hoxnian (MIS 11) to Devensian (MIS 3) periods (Hart and Whittaker 2009).

The facts that many of the valves were broken, no united carapaces were recovered and the predominance of adult forms of some taxa suggests that many of the low abundance assemblages and singular valves are likely to be allochthonous. The generally good preservation would seem to suggest however that these assemblages have not travelled far. The valves of freshwater ostacoda are also notoriously weak and may have been broken in part by any associated freeze/thaw processes upon the sediment. In summary, it would be reasonable to assume that these faunas have originated from the margins of a glacial lake of any cold period between the Hoxnian (MIS 11) to Devensian (MIS 3 periods).

FURTHER WORK

The results of this ostracod analysis should be published in conjunction with the sedimentary, palynological and scientific dating (AAR) evidence.

REFERENCES

Hart, M.B. and Whittaker, J.E., (eds.) 2009. In press. *Stratigraphic Index of Ostracoda*. Second Edition. Special Publication of the Micropalaeontological Society, London (in association with the Geological Society Publishing House, Bath)

Meisch, C., 2000. *Freshwater Ostracoda of Western and Central Europe*. In: J. Schwoerbel and P. Zwick, editors: Suesswasserfauna von Mitteleuropa 8/3. Spektrum Akademischer Verlag, Heidelberg, Berlin. 522pp

Russell 2007. Ostracod Assessment in: Weseex Archaeology 2007, 'Lynn and Inner Dowsing Offshore Wind Farms: Stage 3 Archaeological recording of cores'. Unpublished report ref. 59094.01

Table 1: Ostracods per sample in borehole BHID25

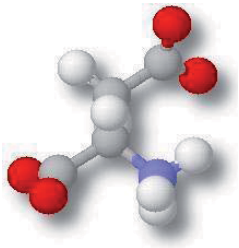
BHID25 Depth m below OD	*Candona sp.*	*Candona candidia*	*Candona neglecta*	*Cytherissa lacustris*	*Eucypris* sp.	*Ilyocypris* sp	*Ilyocypris papillata.*	*"Leucocythere batesi"*	*Limnocythere falcata*	*Limnocytherina sanctipatricii*	Charophyte oogonia	Plant remains
17.74		++	++					+	++	+		+
17.77		+	++					+				
17.78					+			++	+	++		+
17.81		+	++					+	+			+
17.83			+					+		++		
17.88		++	+++					+	+	+	+	+
18.74		+	++				+		+	+		
18.75				+				+	+			+
18.81		+	+						+	+		
18.87		+		+						+		
18.93		+	+			+			+	+		
19.00		++	+						+	+		+
19.04			+					+	+	+		

+ – 1-9 valves
++ – 10-50 valves
+++ - greater than 50 valves

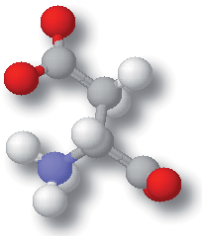
APPENDIX 3: AMINO ACID RACEMIZATION

Dr Kirsty Penkman
NEaar
BioArch
Biology S Block
Department of Biology
University of York
PO Box 373
York
YO10 5YW

neaar.co.uk



L-Asp



D-Asp

SUMMARY

This report documents the preliminary attempts to conduct amino acid racemization analysis for age estimation on the intra-crystalline protein fraction of *Candona neglecta* ostracod carapaces as part of the Lynn and Inner Dowsing Offshore Wind Farms project. It is concluded that the samples showed lower levels of protein degradation than other *Candona neglecta* samples from the UK, the youngest of which have been correlated with MIS 6-7. Therefore these ostracod samples are likely to be younger than MIS 7. However, the concentrations of the samples were near the limit of detection of the technique, and therefore further analyses of bulked samples will help resolve the amino acid age determinations further.

INTRODUCTION

On behalf of Centric Renewable Energy Limited, Wessex Archaeology undertook a Stage 3 subsample assessment of samples taken from borehole BHID25 for the Lynn and Inner Dowsing Offshore Wind Farms. Pollen and ostracods were recovered in sufficient numbers for assessment, which indicates that the depositional environment was on the fringes of a glacial lake. The biostratigraphic marker species of ostracods suggested the deposition of the lowest part of Unit 2 during a cold stage between the Hoxnian and Devensian periods, i.e. between MIS 11 and MIS 4. The presence of *Picea* (spruce) may indicate that the sediments are no younger than the earlier part of the Devensian.

Although amino acid dating of ostracods is a technique that is currently under development, it has the potential to narrow down the time frame of the date of deposition. Amino acid analyses were therefore undertaken at the York Laboratory (NEaar) from four horizons. This involves isolating the intra-crystalline protein fraction of the ostracod shells.

This report details attempts to obtain age estimates on the Lynn and Inner Dowsing Offshore Wind Farms material using amino acid racemization (AAR).

Amino Acid Racemization Geochronology

A new technique of amino acid analysis has been developed for geochronological purposes (Penkman, 2005; Penkman *et al*., 2007; 2008), combining a new Reverse-Phase High Pressure Liquid Chromatography method of analysis (Kaufman & Manley, 1998) with the isolation of an "intra-crystalline" fraction of amino acids by bleach treatment (Sykes *et al.,* 1995). This combination of techniques results in the analysis of D/L values of multiple amino acids from the chemically-protected protein within the biomineral; enabling both decreased sample sizes and increased reliability of the analysis.

Theory

Amino acids, the building blocks of proteins, occur as two isomers that are chemically identical, but optically different. These isomers were designated as either D (dextro-rotary) or L (laevo-rotary) depending upon whether they rotate plane polarised light to the right or left respectively (Fig. 1). In living organisms the amino acids in protein are almost exclusively L and the D/L value approaches zero[1]. The potential application to geochronology arises from the fact that after death amino acid isomers start to interconvert. This process is commonly termed racemization. In time the D/L value approaches one. The proportion of D to L amino acids is therefore an estimate of the extent of protein degradation, and if this is assumed to be predictable over time can be used to estimate age. Other indications of protein decomposition, such as the degradation of unstable amino acids, can also be used to estimate the age of a sample.

[1] D-amino acids are synthesised by some organisms; they are found free in invertebrate body fluids where they play a role in osmoregulation and can occur peptide bound in bacterial peptidoglycan, where part of their function is resistance to proteases.

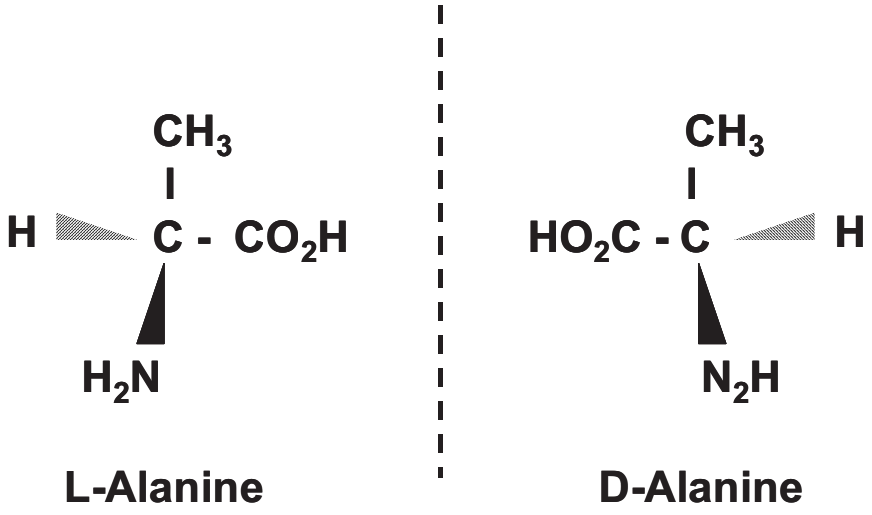


Figure 1: L- and D- amino acid structure

Mechanisms of racemization

The rate of racemization is governed by a variety of factors, most of which have been studied in detail only for free amino acids. North East amino acid racemization (NEaar) analyse the intra-crystalline amino acid fraction and in this way, within a closed environment in which other factors (water content, concentration of cations, pH) are constant, the extent of racemization is a function of time and temperature. Over a small geographical area, such as that represented in this study, it can be assumed that the integrated temperature histories are effectively the same. Any differences in the extent of decomposition of protein within the sample are therefore age-dependent.

Intra-crystalline protein decomposition

The organic matter existing within individual crystals (intra-crystalline fraction) is believed to be a more reliable substrate for analysis than the whole shell (Sykes *et al.*, 1995; Penkman, 2005; Penkman *et al*., 2007, 2008). The initial bleaching step in the recovery of the intra-crystalline fraction removes both secondary contamination and the organic matrix of the shell. This organic matrix degrades and leaches at an unpredictable rate over time, leading to variation in the concentration and D/L of the amino acids. Thus, as appears to be the case in ostrich eggshell (Miller *et al.*, 2000), the D/L values of amino acids in the intra-crystalline fraction of shells have been analysed; in the case of ostrich eggshell no bleaching step was used. The racemisation data reported therefore contrasts with previous work that examined D/L values from whole shells containing both intra- and inter-crystalline material.

This isolation of the intra-crystalline fraction is believed to provide a closed system repository for the amino acids during the burial history of the shell. Only the amino acids within this fraction are protected from the action of external rate-affecting factors (except temperature), contamination by exogenous amino acids and leaching. Amino acids within the whole shell are not protected and can be leached out into the environment. Figure 2 shows a schematic of the intra-crystalline fraction with respect to the whole shell. The low level of Free amino acids observed in the inter-crystalline fraction of unbleached samples (Penkman, 2005; Penkman *et al*., 2007, 2008) indicates that these have been lost through diagenesis, and as these tend to be more highly racemised than the Total fraction, this loss would lead to a lower than expected D/L for the Total fraction of the whole shell.

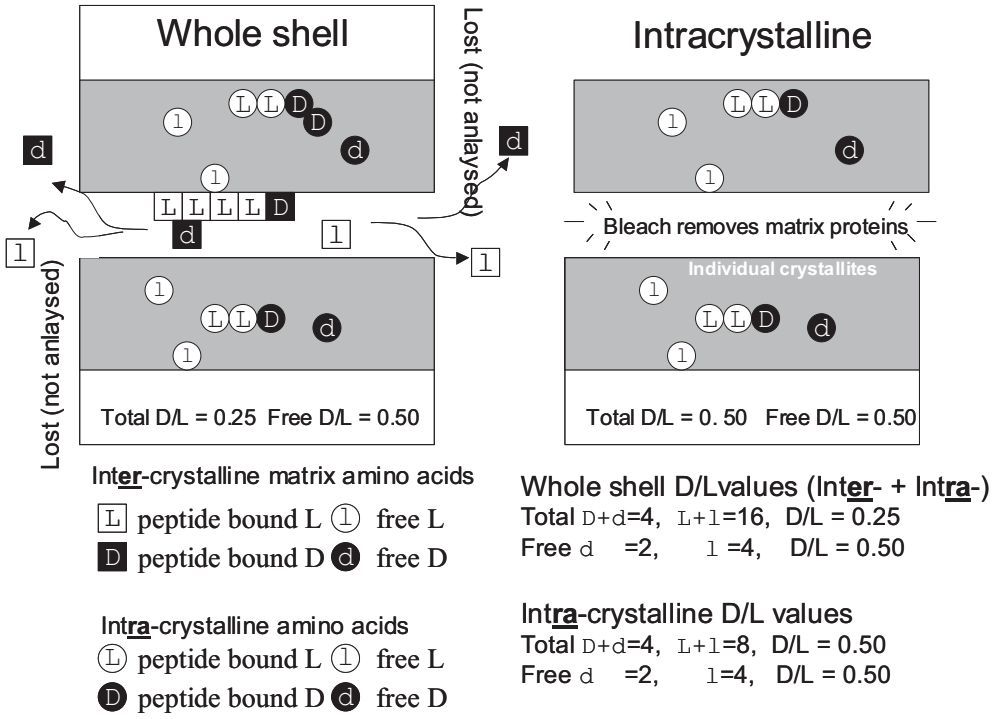


Figure 2: Schematic of intra-crystalline amino acids entrapped within carbonate crystallites. Unlike the proteins of the organic matrix between the crystallites, which leach from the shell with time, in a closed "intra-crystalline" system the amino acids are entrapped. Thus the relationship between the DL ratios of different amino acids and between free (non-protein bound) and total (both free and originally protein-bound amino acids, released by acid hydrolysis) amino acids is predictable. Analysis of the whole shell would result in lower than expected D/L for the total fraction, due to the loss of the more highly racemised frees.

Once a closed system inside shells has been isolated, then the kinetics of protein decomposition are much simpler to predict. In this laboratory the concept of age estimation using the extent of overall Intra-crystalline Protein Degradation (IcPD) has been devised, which links the hydrolysis, racemisation and decomposition of all the amino acids isolated by this method. The concept behind the IcPD is to combine multiple information from a single sample to derive an overall measure of the extent of diagenesis of the protein in that fossil. Similar ideas have been used before, although not in such a comprehensive way. Divergence from the normal in a plot of A/I vs Gly/Ala is thought to indicate leaching in molluscs (Murray-Wallace and Kimber, 1987). Kaufman (2000) used ratios of Asx to Glx to screen out ostracod samples with any unusual values.

Traditionally AAR studies targeted a single amino acid racemisation reaction, that of L-isoleucine to D-alloisoleucine (A/I), due to the technical ease of separation and its slow rate of racemisation. The approach used in this study diverges from this, as dates are derived from the analysis of multiple amino acids. Whilst racemisation rates differ between individual amino acids, they should be highly correlated in a closed system. By linking together different amino acids, and then linking this to a temperature driven model of decay, which includes hydrolysis, racemisation and degradation, the extent of protein degradation can be derived. The pattern of decomposition appears to be different between mollusc genera, requiring separate models for each genus or species studied.

If a closed system is isolated, it should be possible to predict the relationship between geological time and IcPD increase, using not just racemisation but other measures of protein decomposition, such as total and relative concentrations. It follows from the innovations above that, assuming sampling is from an idealised closed system, the pattern of protein decomposition governs the observed racemisation of (a) free amino acids and (b) the total system, (c) the percentage of free amino acids and (d) the total concentration of amino acids.

This model can also be used as a method of assessing the internal reliability of each biomineral used and to determine how closely these substrates approximate to a closed system. Subsequently palaeotemperature information can be included and estimates made of the link between degradation and absolute age in environments with fluctuating temperatures. If an accurate temperature model is used, then age estimates can be derived directly from the IcPD data, although the results presented here do not incorporate any palaeotemperature information and are presented simply as a relative dating tool.

MATERIALS AND METHOD

Materials

Ostracod samples were supplied by Jack Russell, consisting of 4 horizons from the BHID25 borehole. Amino acid racemization (AAR) analyses were undertaken on 25 individual *Candona neglecta* carapaces from 4 horizons:
6 from 17.77 m (NEaar 5588; LyCnA1);
6 from 17.88 m (NEaar 5589; LyCnB1);
both from Unit 2ii; and
6 from 18.74 m (NEaar 5590; LyCnC1);
6 from 19.04 m (NEaar 5591; LyCnD1),
both from Unit 2i.
The samples come from Unit 2 within borehole BHID25, sitecode 59096. The sediment description is “glacial lake sediments, sandy silty clays”.

Sample Preparation

Shells were examined under a low powered microscope, and 6 individual ostracod carapaces selected for each horizon: 3 for the Free fraction and 3 for the Total fraction.

Bleaching

20 µl of 12% solution of sodium hypochlorite at room temperature was added to each set of 3 carapaces and the caps retightened. The carapaces were bleached for 48 hours with a shake at 24 hours. The bleach was pipetted off and the carapaces were then rinsed five times in HPLC-grade water and a final rinse in HPLC-grade methanol (MeOH) to destroy any residual oxidant by reaction with the MeOH. The bulk of the MeOH was pippetted off and the remainder left to evaporate to dryness.

Hydrolysis

Protein bound amino acids are released by adding an excess of 7 M HCl to the bleached carapaces and hydrolysing at 110^{o}C for 24 hours (H*).

10 µl of sample of 7 M Hydrochloric Acid (HCl) was added to each Hydrolysis (“Hyd”, H*, THAA) sample in sterile 0.5 ml tapered glass vials, were flushed with nitrogen for 20 seconds to prevent oxidation of the amino acids, and were then placed in an oven at 110°C for 24 hours. After 10 minutes in the oven, the caps of the glass vials were re-tightened to prevent the samples drying out.

After 24 hours, the samples were dried in a centrifugal evaporator overnight.

Demineralisation

Free amino-acid samples ("Free", F, FAA) were demineralised in cold 2 M HCl, which dissolves the carbonate but minimises the hydrolysis of peptide bonds, and then dried in the centrifugal evaporator overnight.

Rehydration

When completely dry, samples were rehydrated with 8 µl of Rehydration Fluid: a solution containing 0.01 mM HCl, 0.01 mM L-homo arginine internal standard, and 0.77 mM sodium azide at a pH of 2. Each vial was vortexed for 20 seconds to ensure complete dissolution, and checked visually for undissolved particles. The supernatant liquid was then placed in a sterile, labelled 2 ml autosampler vial containing a glass insert, capped and then placed on the autosampler tray of the HPLC.

For each set of sub-samples a blank vial was included at each stage to account for any background interference from the bleach, acid, or rehydration fluid added to the samples.

Analysis of Free and Hydrolysed Amino Acids

Amino acid enantiomers were separated by Reverse Phase High Pressure Liquid Chromatography (RP-HPLC). NEaar uses the method of Kaufman and Manley (1998) using an automated RP-HPLC system. This method achieves separation and detection of L and D isomers in the sub- picomole range.

Samples (2 µl) were derivitised with 2.2 µl *o*-phthaldialdehyde and thiol *N*-isobutyryl-L-cysteine automatically prior to injection. The resulting diastereomeric derivatives were then separated on Hypersil C_{18} BDS column (sphere d. 5 µm; 250 x 3 mm) using a linear gradient of a sodium acetate buffer (23 mM sodium acetate, 1.3 mM Na_2EDTA; pH6), methanol, and acetonitrile on an integrated HP1100 liquid chromatograph (Hewlett-Packard, USA).

Individual amino-acids are separated on a non-polar stationary phase according to their varied retention times: a function of their mass, structure, and hydrophobicity. A fluorescence detector is used to determine the concentrations of each amino-acid and record them as separate peaks on a chromatogram. A gradient elution programme was used to keep the retention time to below 120 minutes.

The fluorescence intensity of derivitised amino acids was measured (Ex = 230 nm, Em = 445 nm) in each sample and normalised to the internal standard. Quantification of individual amino acids was achieved by comparison with the standard amino acid mixture.

External standards containing a variety of D- and L- amino acids, allowing calibration with the analyte samples, were analyzed at the beginning and end of every run, and one standard was analyzed every ten samples. Blanks were randomly interspersed amongst the standards.

The L and D isomers of 10 amino acids were routinely analysed. During preparative hydrolysis both asparagine and glutamine undergo rapid irreversible deamination to aspartic acid and glutamic acid respectively (Hill, 1965). It is therefore not possible to distinguish between the acidic amino acids and their derivatives and they are reported together as Asx and Glx.

RESULTS AND DISCUSSION

In total we conducted 7 analyses, as the Free sample for 18.74 m was contaminated during preparation. Whilst amino acid analyses of the whole protein within single ostracods can be undertaken (e.g. Kaufman, 2000), bleaching to isolate the 'closed-system' intracrystalline fraction reduces the concentration by as much as 90%. Despite bulking three carapaces per

analysis, amino acid concentrations were low, nearing our limit of detection, particularly for the Free samples, and so the data should be treated with caution.

The analysis of intra-crystalline amino acids from ostracods is at a very early stage of research, but a test suite of *Candona neglecta* samples, ranging from sites correlating with MIS 6-7 age to the Cromerian (MIS 15-19) has shown a predictable increase in the extent of protein breakdown with time, enabling different interglacial episodes to be distinguished.

All of the ostracod data from BHID25 show lower levels of racemization than that seen in the test samples, indicating that the samples are younger than MIS 7 in age, given a similar temperature history. However, the data is surprisingly variable, probably due to the low concentrations, and further analyses will be undertaken with larger sample sizes.

For example, the extent of racemization in Asx in the Free fraction was lower than 0.6, the expected range for an MIS 6-7 sample, for the 17.77 m and 17.88 m samples. However, the size of the D-peaks were so small that it was difficult to measure them accurately, and in the case of 18.74 m sample, too low to measure at all. The individual peaks in the THAA fraction showed greater concentrations, and values lower than 0.3, consistent with an age younger than MIS 6-7. Asx is one of the fastest racemizing of the amino acids discussed here (due to the fact that it can racemize whilst still peptide bound; Collins *et al.,* 1999). This should enable good levels of resolution at younger age sites. However, the variability within these sampes was too high to yield a consistent stratigraphic order.

Glx is one of the slower racemizing amino acids and so the level of resolution from young sites is less than that seen with faster racemizing amino acids such as Asx. It is noteworthy that Glx has a slightly unusual pattern of racemization in the free form, due to the formation of a lactam (see Walton, 1998). This results in difficulties in measuring Glx in the Free form, as the lactam cannot be derivitized and is therefore unavailable for analysis.
The D/L of Glx in the THAA form yielded values less than 0.13, again consistent with an age of younger than MIS 7, but in consistent stratigraphical order.

Alanine (Ala) is a more hydrophobic amino acid, whose concentration is partly contributed from the decomposition of other amino acids (notably Serine). Ala racemises at an intermediate rate, and the samples all show levels of racemisation < 0.45 in the FAA fraction and ≤ 0.33 in the THAA fraction, consistent again with an age of younger than MIS 7.

If the amino acids were contained within a closed system, the relationship between the Free and the Hyd fractions should be highly correlated, with non-concordance enabling the recognition of compromised samples (Preece & Penkman, 2005). The limited dataset on ostracods precludes any distinction at this point, but with further data this will be possible.

CONCLUSIONS

In this study the amino acids have been analysed in order to test the potential for AAR to be used as a relative dating technique for the area in question. The conversion of relative sequences into absolute dates and accurate correlation between different areas will require further work.

The samples showed lower levels of protein degradation than other *Candona neglecta* samples from the UK of MIS 6-7 age, therefore significantly narrowing down the time frame of deposition. Further analyses of samples and information on the site under study will help resolve the amino acid age determinations further.

GLOSSARY

18MΩ water: The water has a resistivity of 18MΩ/cm, indicating a lack of ions.

HPLC grade water: In addition to low ion content, HPLC grade water has a low organic content (typically < 2 ppb).

Amino acids: the building blocks of proteins and consist of an alpha carbon atom (C_α) which has four different groups bonded to it: an amino group ($-NH_2$), a carboxyl group (-COOH), a hydrogen atom (-H), and a side chain, (often called an R group). About 20 amino acids normally occur in nature and some of these can undergo further modification (eg the hydroxylation of proline to hydroxyproline). The amino acids are commonly known by three letter codes (see Appendix 3: Abbreviations). They exist free in the cell, but are more commonly linked together by **peptide bonds** to form proteins, peptides, and sub-components of some other macromolecules (eg bacterial peptidoglycan).

Amino acid isomers: amino acids occur as two stereoisomers that are chemically identical, but optically different. These isomers are designated as either D (dextro-rotary) or L (laevo-rotary) depending upon whether they rotate plane polarised light to the right or left respectively (Fig 6). In living organisms the amino acids in protein are almost exclusively L and the D/L ratio approaches zero. Two amino acids, isoleucine and threonine, have two chiral carbon atoms and therefore have four stereoisomers each. As well as racemization, these two amino acids can undergo a process known as epimerization. The detection of the L-alloisoleucine epimer (derived from L-isoleucine) is possible by conventional ion-exchange chromatography, and was thus the most commonly used reaction pathway in geochronology.

Asx: Measurements of aspartic acid following hydrolysis also include asparagines, which decomposes to Asx. This combined signal of aspartic acid plus asparagine (Asp +Asn) is referred to as Asx (Hill, 1965).

D-amino acid: dextrorotary amino acid, formed following synthesis of the protein as it degrades over time (remember as “dead amino acid”).

IcPD: Intra-crystalline Protein Degradation. This is the measure of the overall extent of protein breakdown in the closed system of the intra-crystalline fraction of a shell. Conventional racemization analysis tends to report an allosioleucine / isoleucine (A/I or D/L ratio). This amino acid ratio has the advantage of being relative easy to measure and also sufficiently slow to be used to “date” sediments in the European Quaternary.

Our IcPD approach utilises multiple amino acids. However we have avoided trying to give a whole series of D/L values for each amino acid in each sample. Instead we are using a theoretical model of protein degradation. The model outputs are then used to compare observed D/L values of any amino acid against the A/I value at the same stage of protein decomposition. The relative rate of racemization of any amino acid (its DL ratio) is then reported as an A/I equivalent - which as a working title we have named the Intra-crystalline Protein Degradation value (or IcPD) (Collins Penkman and Kaufman in prep).

Instead of getting a single A/I ratio we obtain a series of (IcPD) values, currently $IcPD_{Asx}$, $IcPD_{Glu}$, $IcPD_{Phe}$, $IcPD_{Ala}$, $IcPD_{Val}$. Other ratios, notably $IcPD_{Ser}$, are not currently of implemented in the model – ie we don’t have a good degradation model for this amino acid yet.

Because each amino acid has its own particular characteristics, only in a well behaved system will $IcPD_{Asx} = IcPD_{Glu} = IcPD_{Phe} = IcPD_{Ala} = IcPD_{Val}$. If an amino acid has an unusually low ratio (due to modern contamination) or unusually high racemization (due to

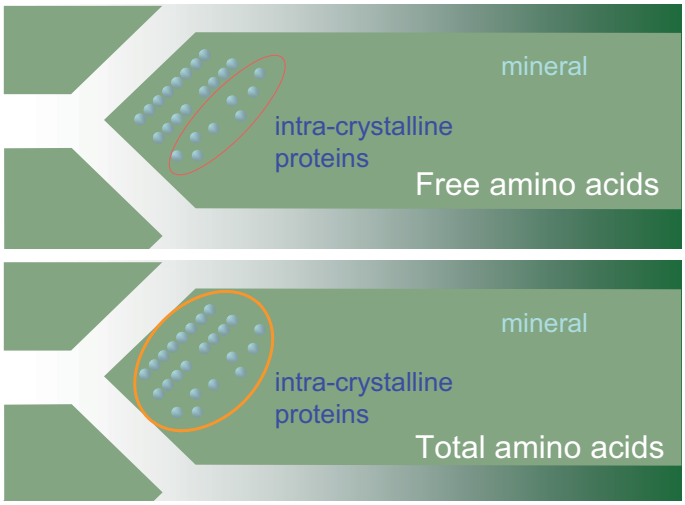
inclusion of bacterial cell wall contaminants) either some or all of the amino acids will no longer fit to the idealized degradation model. Indeed we can use elevation of $IcPD_{Asx}$ = $IcPD_{Glu}$ and = $IcPD_{Ala}$ to provide a bacterial contamination index. We have not done so in this case as there was no evidence of contamination.

IcPD values: Intra-crystalline Protein Degradation value, a summary value obtained from multiple amino acid D/L values from a single sample all normalised to a common model of protein degradation and racemization.

Enantiomers / optical isomers: mirror image forms of the same compound that cannot be superimposed on one another.

Epimerisation: the inversion of the chiral α-carbon atom.

Free amino acid fraction: The fraction of amino acids directly amenable to racemization analysis. Only amino acids which have already been naturally hydrolysed (over time) are measured. These are the most highly racemized amino acids.



Hydrolysis: A chemical reaction involving water leading to the breaking apart of a compound (in this case the breaking of peptide bonds to release amino acids).

L-amino acid: laevorotary amino acid, the constituent form of proteins (remember as “living amino acid”).

Peptide bond: an amide linkage between the carboxyl group of one amino acid and the amino group of another.

Racemization: the inversion of all chiral carbon atoms, leading to the decrease in specific optical rotation. When the optical rotation is reduced to zero, the mixture is said to be racemized.

Stereoisomers: molecules of the same compound that have their atoms arranged differently in space.

Total amino acid fraction: The extent of racemization of all amino acids in a sample, determined following aggressive high temperature hydrolysis with strong mineral acid, which has the effect of breaking apart all peptide bonds so that the total extent of racemization in all amino acids both free and peptide bound are measured.

Zwitterion: A dipolar ion containing ionic groups of opposite charge. At neutral pH the ionic form of amino acids which predominates is the zwitterions

What does the date estimated from IcPD mean?
The date is our best estimate based upon the temperature history of the site. If we wanted to constrain this further we would need reliable independent dates. There are considerable differences in racemization rates between different molluscs. This reflects differences in rates of decomposition of proteins within the shell – the so-called species effects (Lajoie *et al*, 1980).

PAST USE OF AMINO ACID RACEMIZATION DATING

The presence of proteins in archaeological remains has been known for some time. Nearly fifty years ago Abelson (1954) separated amino acids from subfossil shell. He suggested the possibility of using the kinetics of the degradation of amino acids as the basis for a dating method (Abelson, 1955). In 1967 Hare and Abelson measured the extent of racemization of amino acids extracted from modern and sub-fossil *Mercenaria mercenaria* shells (edible clam). They found that the total amount of amino acids present in shell decreased with the age of the shell. The amino acids in recent shell were all in the L configuration and over time the amount of D configuration amino acid increased (Hare and Abelson, 1967). However, even after 35 years this method of dating is still subject to vigorous debate, with the application of AAR to date bone being particularly controversial (Bada 1990; Marshall 1990). Major reviews of AAR include: Johnson and Miller (1997), Hare, von Endt, and Kokis (1997), Rutter and Blackwell (1995), Murray-Wallace (1993), Bada (1991) and Schroeder and Bada (1976). Racemization is a chemical reaction and a number of factors influence its rate (Rutter and Blackwell, 1995). These include: amino acid structure, the sequence of amino acids in peptides, pH, buffering effects, metallic cations, the presence of water and temperature. To establish a dating method the kinetics and mechanisms of the racemization (and epimerization) reaction of free and peptide bound amino acids need to be established. To this end various workers in the late 1960s and the 1970s studied free amino acids in solution and carried out laboratory simulations of post mortem changes in the amino acids in bone (Bada, 1972) and shell (Hare and Abelson, 1967; Hare and Mitterer, 1969). Attempts have also been made to relate the kinetics of free amino acids, with those in short polypeptides and the proteins in various archaeological samples (Bada, 1982; Smith and Evans, 1980).

The ability of this technique to be used as a geochronological and geothermometry tool has led to its use in many environmental studies, with research into AAR in terrestrial gastropods (Goodfriend, 1991; 1992), bivalves (Goodfriend and Stanley, 1996), foraminifera (Harada *et al*, 1996), ostrich egg shells (Miller *et al*, 1992; 1997) and speleothems (Lauritzen, 1994). Studies within UK deposits have been based on early methods of chemical separation, using Ion-Exchange liquid chromatography, able to separate the enantiomers of one amino acid found in proteins, L-isoleucine (L-Ile, I), from its most stable diastereoisomer alloisoleucine (D-aile, A). By analysing the total protein content within marine (Bowen & Sykes, 1988) and non-marine mollusc shells (Bowen *et al.,* 1989) from UK interglacial sites, an amino acid geochronology was developed using the increase in A/I, correlating with the marine oxygen isotope warm stages.

ABBREVIATIONS USED IN THIS REPORT

Abbrev	1-letter code	number of chiral centres	
Ala	A	1	Alanine
Arg	R	1	Arginine
Acn			acetonitrile
AA			Amino acid(n)
Asn	N	1	Asparagine
Asp	D	1	Aspartic acid
Asx			Asparagine + Aspartic acid + succinimide
Asu			Succinimide
Cys	C	1	Cysteine
DCM			Dichlormethane
GABA			γ-Aminobutyric acid
Gln	Q	1	Glutamine
Glu	E	1	Glutamic acid
Gly	G	0	Glycine
His	H	1	Histidine
HPLC			High-Performance Liquid Chromatography
Hyp			Hydroxyproline
IBD(L)C			N-Isobutyryl-D(L)-Cysteine
Ile	I	2	Isoleucine
Leu	L	1	Leucine
Lys	K	1	Lysine
MeOH			Methanol
Met	M	1	Methionine
Nle			Norleucine
OPA			ortho-Phthaldialdehyde
Orn			Ornithine
Phe	F	1	Phenylalanine
Pro	P	1	Proline
Ser	S	1	Serine
Thr	T	2	Threonine
Trp	W	1	Tryptophan
Tyr	Y	1	Tyrosine
Val	V	1	Valine

LYNN AND INNER DOWSING OFFSHORE WIND FARMS DATASHEETS

					FAA			THAA		
Neaar no.	Sample name	Species	depth (m)	NI	Asx D/L	Glx D/L	Ala D/L	Asx D/L	Glx D/L	Ala D/L
5588	LyCnA1	*Candona neglecta*	6.07	3	0.44	0.69	0.37	0.27	0.00	0.33
5589	LyCnB1	*Candona neglecta*	6.18	3	0.36	0.80	0.32	0.24	0.11	0.21
5590	LyCnC1	*Candona neglecta*	7.04	3	0.00	0.00	0.33	0.16	0.11	0.11
5591	LyCnD1	*Candona neglecta*	7.34	3	ND	ND	ND	0.24	0.13	0.19

WORKS CITED IN TEXT

Abelson, P H, 1954 Amino acids in fossils, *Science,* **119**, 576

Abelson, P H, 1955 Organic constituents of fossils, *Carnegie Institution of Washington Year Book*, **54**, 107-9

Augustin L, *et al*, 2004 Eight glacial cycles from an Antarctic ice core, *Nature* **429** (6992), 623-628

Bada, J L, 1972 The dating of fossil bones using the racemization of isoleucine, *Earth and Planetary Science Letters,* **15**, 223-31

Bada, J L, 1982 Racemization of amino acids in nature, *Interdisciplinary Science Reviews,* **7**(1), 30-46

Bada, J L, 1990 Racemization dating, *Science,* **248**, 539-40

Bada, J L, 1991 Amino acid cosmogeochemistry, *Philosophical Transactions of the Royal Society, London*, Series B*,* **333**, 349-58

Bada J L, Shou M-Y, Man E H and Schroeder R A, 1978 Decomposition of hydroxy amino acids in foraminiferal tests: Kinetics, mechanism and geochronological implications, *Earth and Planetary Science Letters* **41**, 67-76.

Bowen, D Q, and Sykes G A, 1988 Correlation of marine events and glaciations on the Northeast Atlantic Margin, *Philosophical Transactions of the Royal Society, London*, Series B, **318**, 619-35

Bowen, D Q, Hughes, S, Sykes, G A and Miller, G H, 1989 Land-sea correlations in the Pleistocene based on isoleucine epimerization in non-marine mollusks, *Nature* **340**, 49-51

Bridgland, D R, Currant, A P and Preece, R C, 1995 East Mersea Restaurant Site, In *The Quaternary of the Lower Reaches of the Thames: Field Guide* (Ed. Bridgland, D R, Allen, P A & Haggart, B A) Quaternary Research Association, London, 271-274

Bridgland, D R, Field, M H, Holmes, J A, McNabb, J, Preece, R C, Selby, I, Wymer, J J, Boreham, S, Irving, B G, Parfitt, S A & Stuart, A J, 1999 Middle Pleistocene interglacial Thames-Medway deposits at Clacton-on-Sea, England: Reconsideration of the biostratigraphical and environmental context of the type Clactonian Palaeolithic industry, *Quaternary Science Reviews* **18**, 109-146.

Bridgland, D R, Preece, R C, Roe, H M, Tipping, R M, Coope, G R, Field, M H, Robinson, J E, Schreve, D C and Crowe, K, 2001 Middle Pleistocene interglacial deposits at Barling, Essex, England: evidence for a longer chronology for the Thames terrace sequence, *Journal of Quaternary Science*, **16**, 813-840.

Collins, M J, and Riley M S, 2000 Amino acid racemization in biominerals, the impact of protein degradation and loss. In Perspectives in Amino Acid and Protein Geochemistry (ed. Goodfriend, G A, Collins, M J, Fogel, M L, Macko, S A and Wehmiller, J F), pp. 120-142. Oxford University Press

Collins, M J, Waite, E R, and van Duin, E C T, 1999 Predicting protein decomposition: the case of aspartic-acid racemization kinetics, *Philosophical Transactions of the Royal Society, London*, Series B, **354**(1379), 51-64

Gibbard, P L, Boreham, S, Burger, A W and Roe, H M, 1996 Middle Pleistocene lacustrine deposits in eastern Essex, England and their palaeogeographical implications, *Journal of Quaternary Science*, **11,** 281–298.

Goodfriend, G A, 1991 Patterns of racemization and epimerization of amino acids in land snail shells over the course of the Holocene, *Geochimica et Cosmochimica Acta*, **55**, 293-302

Goodfriend, G A, 1992 Rapid racemization of aspartic acid in mollusc shells and potential for dating over recent centuries, *Nature*, **357**, 399-401.

Goodfriend, G A, and Stanley, D J, 1996 Reworking and discontinuities in Holocene sedimentation in the Nile Delta - documentation from amino-acid racemization and stable isotopes in mollusk shells, *Marine Geology,* **129,** 271-83.

Harada, N, Handa, N, Ito, M, Oba, T, and Matsumoto, E, 1996 Chronology of marine sediments by the racemization reaction of aspartic acid in planktonic foraminifera, *Organic Geochemistry,* **24**, 921-30.

Hare, P E, and Abelson, P H, 1967 Racemization of amino acids in fossil shells, *Carnegie Institution of Washington Year Book*, **66**, 526-8

Hare, P E, and Mitterer, R M, 1969 Laboratory simulation of amino-acid diagenesis in fossils, *Carnegie Institution of Washington Year Book*, **67**, 205-8

Hare, P E, von Endt, D W, and Kokis, J E, 1997 Protein and amino acid diagenesis dating, in *Chronometric Dating in Archaeology* (eds R E Taylor and M J Aitken), 1st edn, Advances in Archaeological and Museum Science, **2**, 261-96, New York (Plenum Press)

Hill, R L, 1965 Hydrolysis of proteins, *Advances in Protein Chemistry,* **20**, 37-107

Johnson, B J, and Miller, G H, 1997 Archaeological applications of amino acid racemization, *Archaeometry*, **39**(2), 265-87

Karner, D B, Levine, J, Medeiros, B P and Muller, R A, 2002 Constructing a Stacked Benthic $\delta^{18}O$ Record, Paleoceanography, 17 (3), 1030

Kaufman D S and Manley W F, 1998 A new procedure for determining DL amino acid ratios in fossils using Reverse Phase Liquid Chromatography, *Quaternary Science Reviews* **17** 987-1000

Kaufman, D S, 2000 Amino Acid Racemization in Ostracodes, In *Perspectives in Amino Acid and Protein Geochemistry* (Ed. Goodfriend, G.A., Collins, M.J., Fogel, M.L., Macko, S.A. & Wehmiller, J.F.), Oxford University Press 145-160

Lauritzen, S E, Haugen, J E, Lovlie, R, and Giljenielsen, H, 1994 Geochronological Potential of Isoleucine Epimerization in Calcite Speleothems, *Quaternary Research,* **41**(1), 52-8

Lajoie, K R, Peterson, E, and Gerow, B A, 1980 Amino acid bone dating: a feasibility study, South San Francisco Bay region, California. In *Biogeochemistry of amino acids* (ed. P E Hare, T C Hoering, and K J King), 477-89, New York (John Wiley and Sons)

Marshall, E, 1990 Racemization dating: great expectations, *Science*, **247**, 799

Miller, G H, Beaumont, P B, Jull, A J T, and Johnson, B, 1992 Pleistocene geochronology and palaeothermometry from protein diagenesis in ostrich eggshells: implications for the evolution of modern humans, *Philosophical Transactions of the Royal Society, London*, Series B

Miller, G H, Magee, J W, and Jull, A J T, 1997 Low-latitude glacial cooling in the Southern Hemisphere from amino acid racemization in emu eggshells, *Nature*, **385**, 241-4

Miller, G H, Hart, C P, Roark, E B, and Johnson, B J, 2000 Isoleucine epimerization in eggshells of the flightless Australian birds Genyornis and Dromaius, *Perspectives in Amino Acid and Protein Geochemistry* (Ed. Goodfriend, G. A., Collins, M.J., Fogel, M.L., Macko, S.A. & Wehmiller, J.F.), Oxford University Press 161-181

Murray-Wallace, C V, 1993 A review of the application of the amino acid racemisation reaction to archaeological dating, *The Artefact*, **16**, 19-26

Murray-Wallace, C V and Kimber, R W L, 1987 Evaluation of the amino acid racemization reaction in studies of Quaternary marine sediments in South Australia, *Australian Journal of Earth Sciences,* **34**, 279-292

Penkman K E H, 2005 Amino acid geochronology: a closed system approach to test and refine the UK model, Unpublished PhD thesis, University of Newcastle.

Penkman, K E H, Preece, R C, Keen, D H, Maddy, D, Schreve, D C & Collins, M J, 2007. Testing the aminostratigraphy of fluvial archives: the evidence from intra-crystalline proteins within freshwater shells. *Quaternary Science Reviews,* **26**, 2958-2969

Penkman, K E H, Kaufman, D S, Maddy, D and Collins, M J, 2008. Closed-system behaviour of the intra-crystalline fraction of amino acids in mollusc shells. *Quaternary Geochronology,* **3**, 2-25

Preece, R C and Penkman, K E H, 2005 Molluscan assemblages and amino acid dating of the Lower Palaeolithic site at East Farm, Barnham, Suffolk, *Proceedings of the Geologists' Association* **116**, 363-377

Roe, H M, 1994 Pleistocene buried channels in eastern Essex, Unpublished PhD thesis, University of Cambridge

Roe, H M, 1999 Late Middle Pleistocene sea-level change in the southern North Sea: the record from eastern Essex, UK, *Quaternary International*, **55**, 115–128

Roe, H M, 2001 The late Middle Pleistocene biostratigraphy of the Thames valley, England: new data from eastern Essex, *Quaternary Science Reviews*, **20**, 1603–1619

Rutter, N W, and Blackwell, B, 1995 Amino acid racemization dating, in *Dating methods for Quaternary deposits* (eds N W Rutter and N R Catto), 125-64, St John's, Newfoundland (Geological Association of Canada)

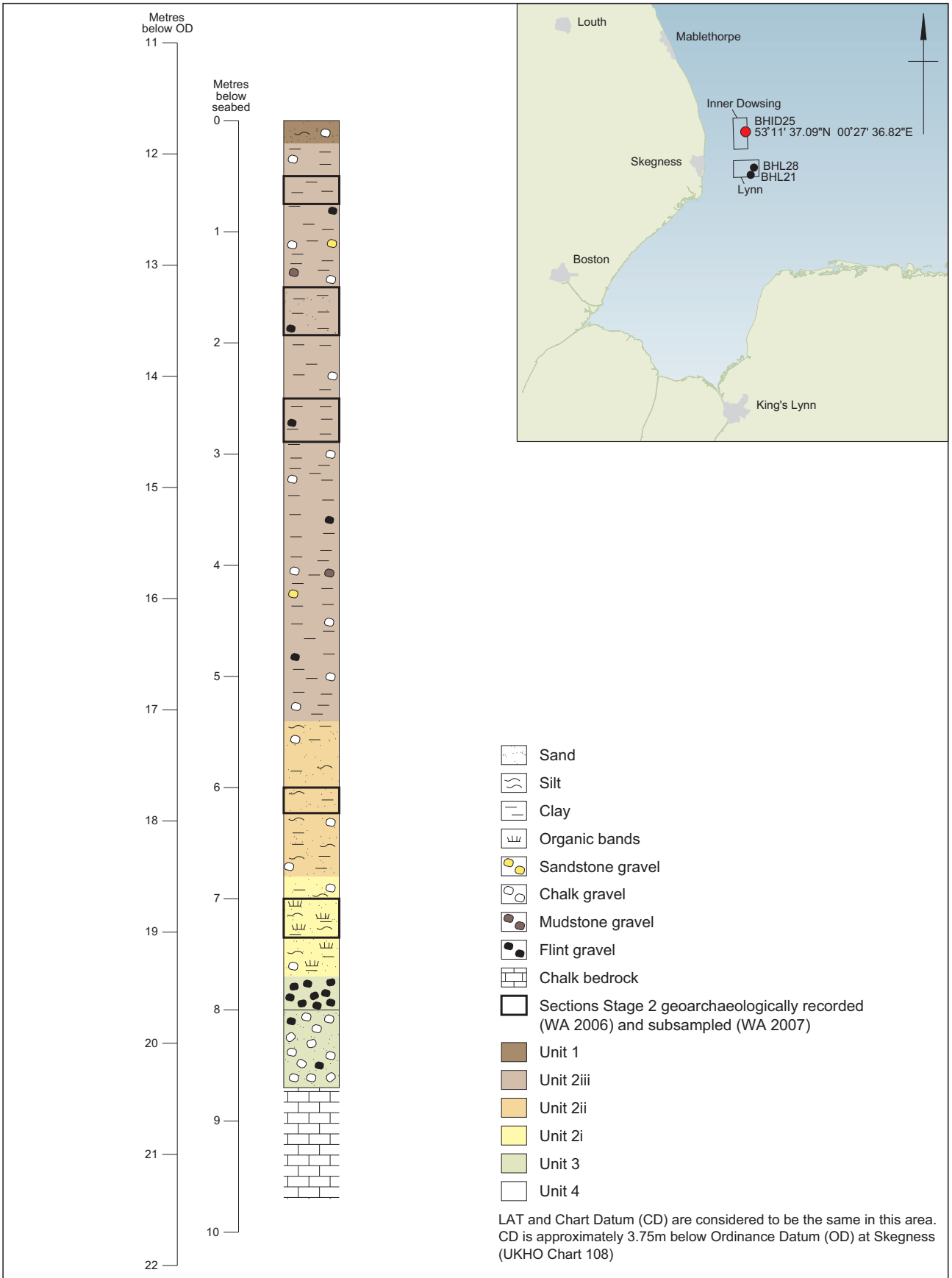
Schroeder, R A, and Bada, J L, 1976 A review of the geochemical applications of the amino acid racemization reaction, *Earth-Science Reviews*, **12**, 347-91

Smith, G G, and Evans, R C, 1980 The effect of structure and conditions on the rate of racemization of free and bound amino acids. In *Biogeochemistry of amino acids* (eds P E Hare, T C Hoering, and J King), 257-82, New York (John Wiley and Sons)

Sykes, G A, Collins, M J & Walton, D I, 1995. The significance of a geochemically isolated intracrystalline organic fraction within biominerals, *Organic Geochemistry* **23** (11/12) 1039-1065

Walton D, 1998 Degradation of intracrystalline proteins and amino acids in fossil brachiopods, *Organic Geochemistry,* **28**, 389-410

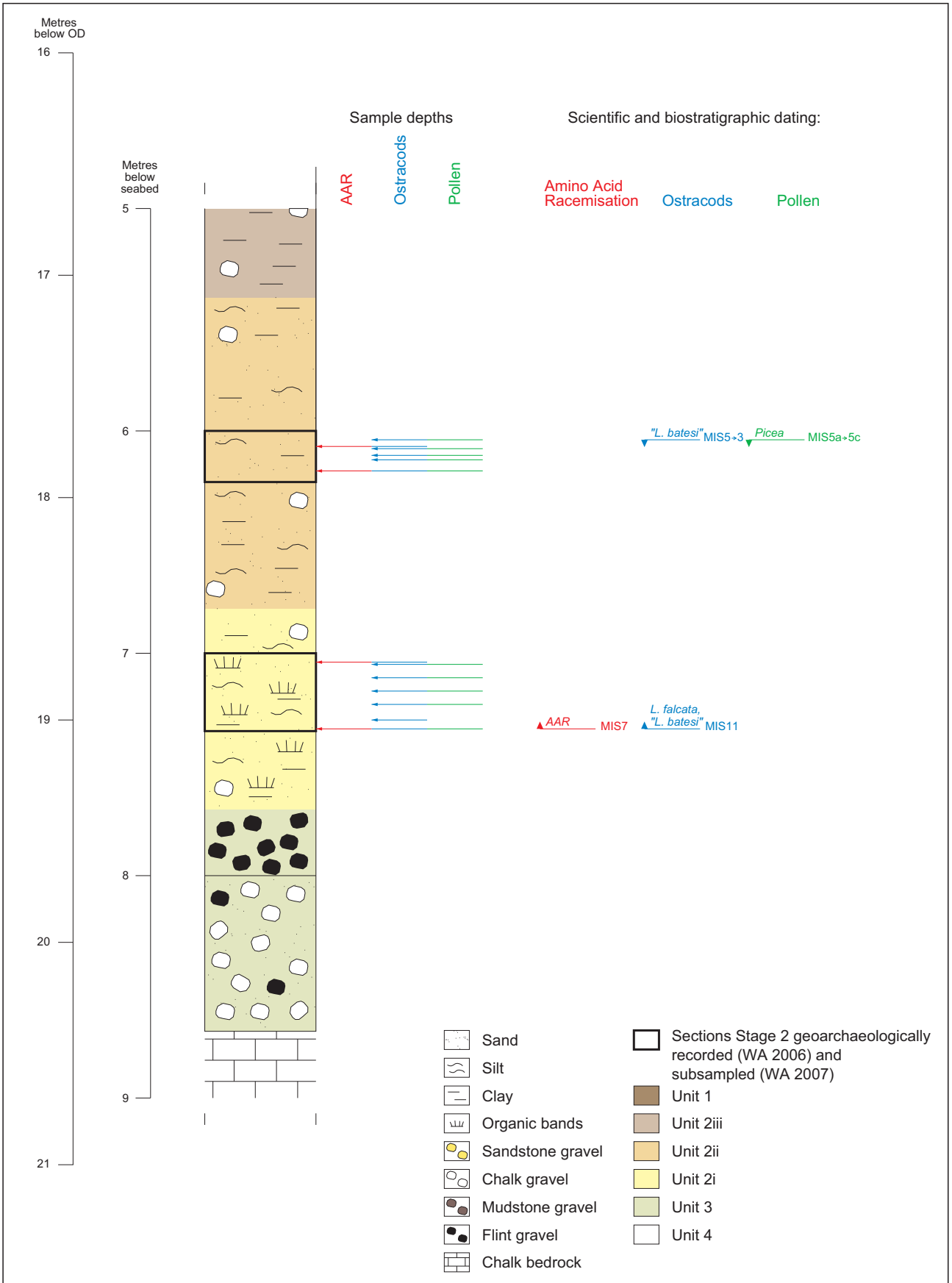
Warren, S H, 1955 The Clacton (Essex) Channel deposits, *Quarterly Journal of the Geological Society of London* **111** 283-387



Date:	16/03/09	Revision Number:	0
Scale:	1:50 vertical	Illustrator:	KJB
Path:	W:\Projects\59096\Drawing Office\Report Figures\Analysis\09-03-16		

Wessex Archaeology

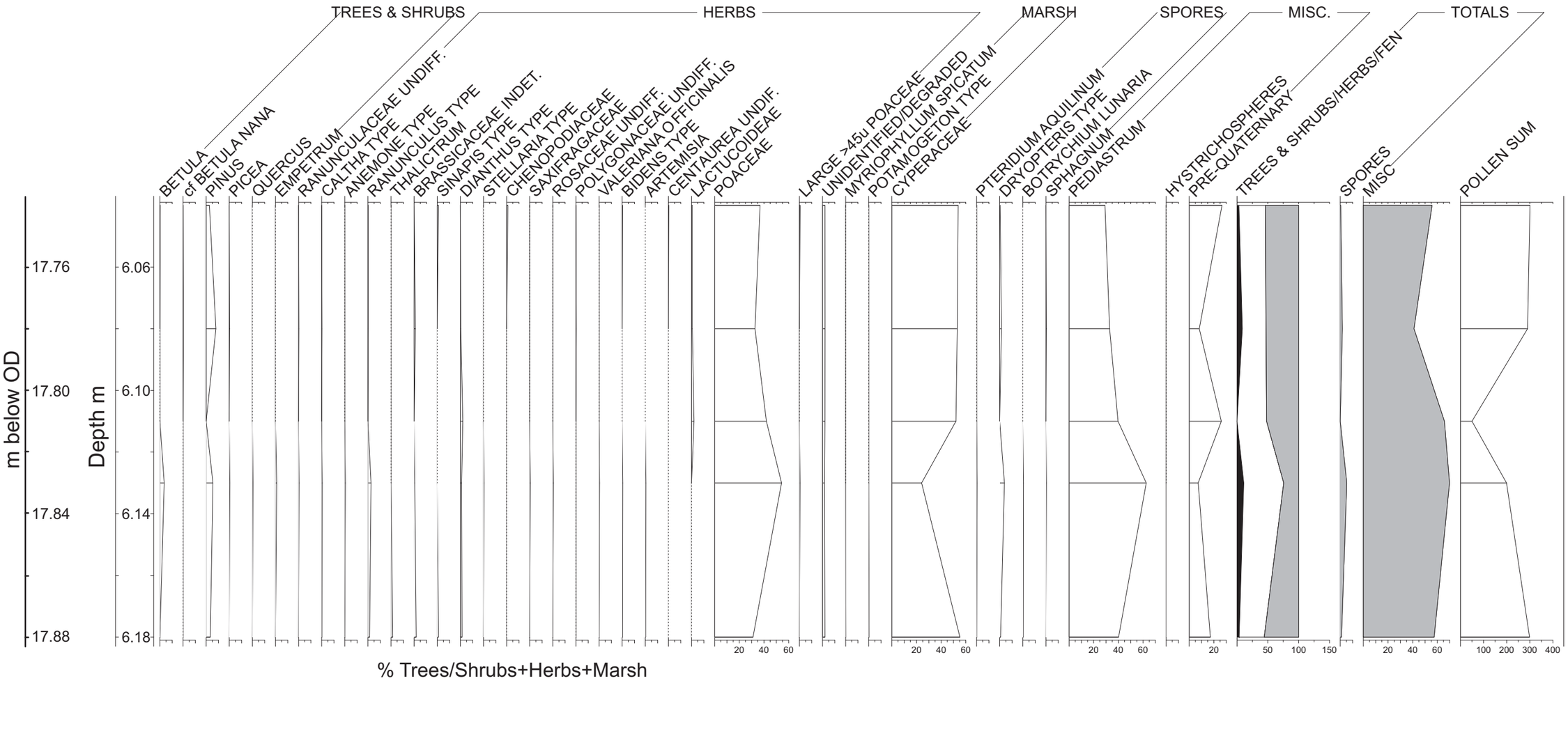
Borehole BHID25 Location and stratigraphy



Date:	16/03/09	Revision Number:	0
Scale:	1:25 vertical	Illustrator:	KJB
Path:	W:\Projects\59096\Drawing Office\Report Figures\Analysis\09-03-16		

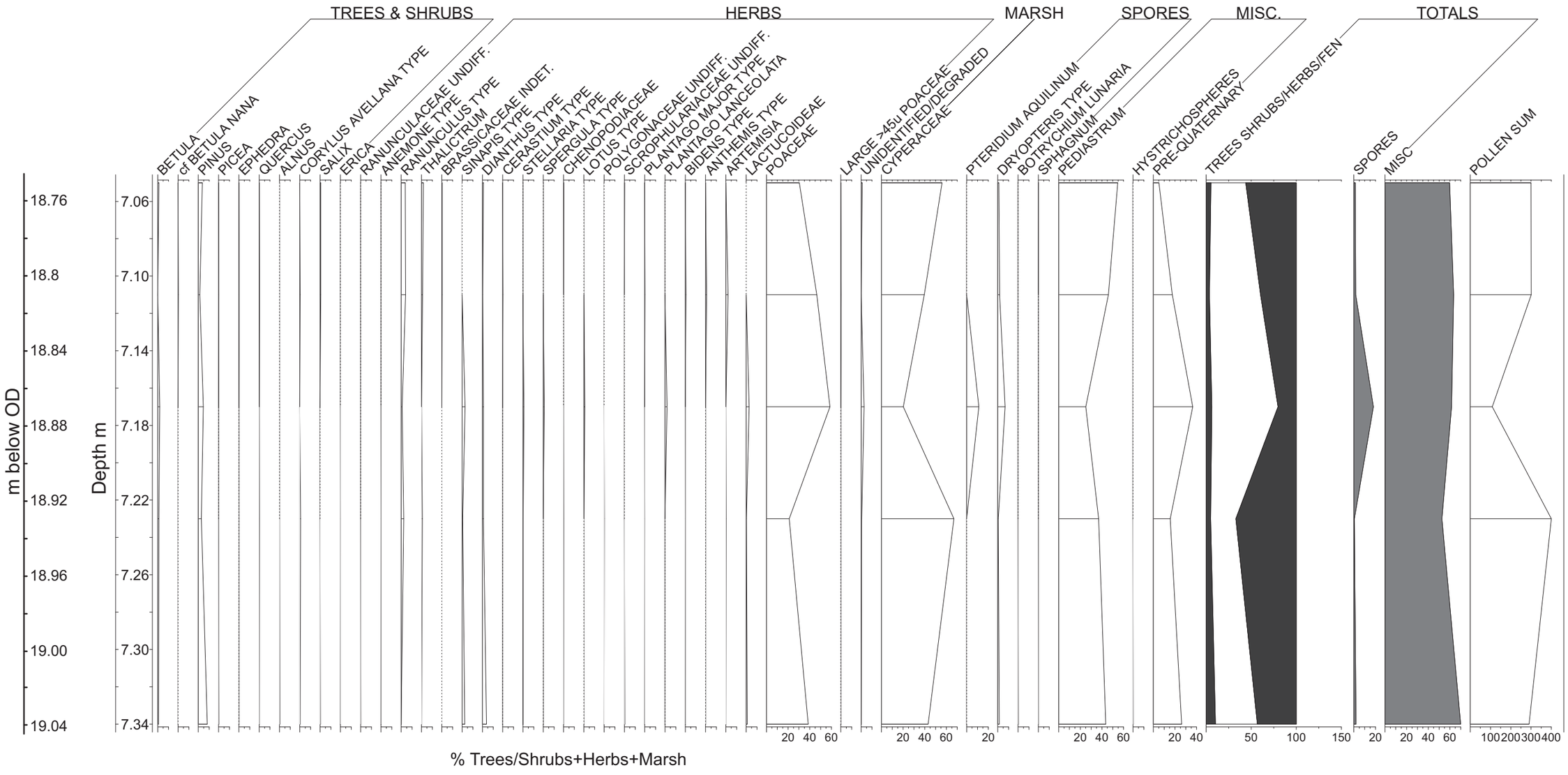
Wessex Archaeology

Sample depths and dating from borehole BHID25



Date:	16/03/09	Revision Number:	0
Scale:	N/A	Illustrator:	KJB
Path:	W:\Projects\59096\Drawing Office\Report Figures\Analysis\09-03-16		

Percentage pollen diagram from BHID25, unit 2ii



Wessex Archaeology

Date:	16/03/09	Revision Number:	0
Scale:	N/A	Illustrator:	KJB
Path:	W:\Projects\59096\Drawing Office\Report Figures\Analysis\09-03-16		

Percentage pollen diagram from BHID25, unit 2i

WESSEX ARCHAEOLOGY LIMITED.
Head Office: Portway House, Old Sarum Park, Salisbury, Wiltshire SP4 6EB.
Tel: 01722 326867 Fax: 01722 337562 info@wessexarch.co.uk www.wessexarch.co.uk
London Office: Unit 113, The Chandlery, 50 Westminster Bridge Road, London SE1 7QY.
Tel: 020 7953 7494 Fax: 020 7953 7499 london-info@wessexarch.co.uk www.wessexarch.co.uk