1  **Tracking Holocene palaeostratification and productivity changes in the**

2  **Western Irish Sea: A multi-proxy record**

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18  **Abstract**

19  The Western Irish Sea preserves an exceptionally thick (ca. 40 m) Holocene

20  succession that is ideally suited to understanding the pattern of palaeostratification

21  and water mass productivity changes in the region, and their relationship with sea

22  level, sedimentation, and biota. Additionally, the presence of shallow-buried methane

23  provides an opportunity to explore its potential impact on the local pattern of

24  Holocene marine environmental change. Multi-proxy investigation of a cored

25  borehole succession through the Holocene interval tracks changes from mixed to

26  seasonally stratified conditions. In the earliest Holocene (11.2–10 ka), high

27  productivity, mixed water conditions prevailed, with abundant and diverse

28  foraminifera and dominant heterotrophic dinoflagellate cysts. Productivity was

29  probably driven by high nutrient fluxes related to high rates of sedimentation (>1600

30  cm/kyr), in turn influenced by relatively low sea level and restricted sediment

31  accommodation space across shelf areas to the east of the borehole site (eastern

32  Irish Sea Basin). With rising sea level in the later part of the Early Holocene, the

33  region evolved into a relatively lower productivity mixed water mass system, with

34  significant changes in ecology revealed by dinoflagellate cysts and foraminifera. In

35  the latest Early Holocene and earliest Mid Holocene (ca. 8.4–8.2 ka) a return to

36  higher productivity is signalled by dinoflagellate cyst data; a result of seasonal

37  stratification becoming established, evidenced by sharply increased summer sea

38  surface temperature estimates (typically 16–17$^{\circ}$C) that contrast with an opposite

39  (more positive) trend in $\delta^{18}O$ values for benthic foraminifera. Reductions in turbulent

40  mixing associated with stratification might have exacerbated the palaeoecological

41  impact of shallow-buried methane associated with the borehole site, potentially

42  evidenced by a significant change in dominant benthic foraminifera and strong,

43  localised excursions in the benthic $\delta^{13}C$/ $\delta^{18}O$ record.

44  **Keywords**

45  microfossils , stable isotopes, Rock-Eval, sea surface temperature, methane,

46  palaeotidal modelling

47  **1.    Introduction**

48    Detailed evidence of relative sea level change in the Holocene has been

49  assembled from an array of sites around the margin of the Irish Sea Basin, combined

50  with modelling of glacial isostatic adjustment (GIA) response following the collapse of

51  Late Devensian ice sheets (Lambeck, 1995; Lambeck and Purcell, 2001; Shennan

52  and Horton, 2002; Roberts et al., 2006; Brooks et al., 2008; Bradley et al., 2011;

53  Smith et al., 2012). Yet little is known about the pattern of Holocene environmental

54  change in deeper parts of this basin; a region that hosts shallow-buried methane and

55  related gas-escape structures (Crocker et al., 2005; Judd, 2005; Figure 1), and

56  where localised seasonal water-mass stratification is important for marine

57  productivity today (Gowen et al., 1998).

58    Seasonal water-mass stratification currently develops in an isolated part of the

59  Western Irish Sea (WIS), where tides entering from the south (St George's Channel)

60  and from the north (North Channel) meet to create a region of permanent slack water

61  south-west of the Isle of Man (Dabrowski et al., 2010; Figure 1). In late spring and

62  summer, weak tidal mixing combines with reduced wind shear and increased solar

63  insolation, allowing thermal/density stratification to develop (Hill et al., 1996;

64  Howarth, 2005; Dabrowski et al., 2010; Williams et al., 2013). Short-lived

65  phytoplankton blooms develop in near-surface waters across the stratified region in

66  the spring, exploiting enhanced water clarity and consuming nutrient residues stirred

67  up by the winter storms (Sharples et al., 2010). At the margins of the stratified water

68  mass, deeper water nutrient flows are concentrated at mixing fronts, boosting marine

69  productivity in these regions (Austin and Scourse, 1997; Sharples, 2008). Nutrients

70  are also harvested by a narrow, concentrated band of phytoplankton (Sub

71  Chlorophyll Maximum) developed at the density gradient (pycnocline) between warm

72  (near-surface) and cool (deeper) water masses across stratified regions, sustaining

73  organic fluxes to the seabed and depressing dissolved oxygen concentrations

74  (Scourse et al., 2002; Greenwood et al., 2010; Sharples et al., 2010; Williams et al.,

75  2013). These processes underpin economically important marine fisheries (e.g. Hill

76  et al., 1996), and more generally disproportionately boost the contribution of shelf

77  seas to total global oceanic primary production (15–30%; Wollast, 1998) and the

78  marine storage of carbon dioxide (20–50%) through the mechanism referred to as

79  the 'shelf sea pump' (Rippeth, 2005).

80      Here we present a multidisciplinary study of a thick (ca. 40 m) Holocene cored

81  borehole succession in the WIS (Figure 1), located within the region of present-day

82  seasonal water-mass stratification and shallow-buried methane. The borehole is

83  ideally positioned to explore the impact of sea-level change on the deep marine

84  shelf, and to reveal the Holocene record of changes in water-mass productivity in an

85  unusually expanded succession compared to that previously reported in the Celtic

86  Sea (Austin and Scourse, 1997; Scourse et al., 2002). The potential influence of

87  changes in water-column circulation on methane accumulation and seepage at the

88  borehole site (Judd, 2005), and the extent to which this has impacted the marine

89  ecology of the region, are significant further objectives of this work.

90  **2.      Material and previous research**

91      The borehole (BGS index 89/15; $54.0360^0$N, $5.3458^0$W), drilled in 1989 to a

92  total depth of 85 m, is located in a narrow deep water region in the central part of the

93  WIS forming part of the Manx Depression. Southwards this region forms the Western

94  Trough, between 80 and 120 m water depth, whilst northwards there is further

95  deepening (below 140 m) into the North Channel, linking the Irish Sea with the

96  Atlantic (Figure1). The cored succession comprises 39.3 m of Holocene sediments,

97  unconformably overlying 45.7 m of Pleistocene deposits (including at 40.05–44.15 m

98  depth foraminifera, ostracods and dinoflagellate cysts indicative of cold Late

99  Devensian climate conditions; Riding, 1995; Wilkinson, 1995; Dickson, 1995),

100  collectively forming part of the Western Irish Sea Formation (Chesher and Wingfield,

101  1990; Jackson et al., 1995). The Holocene strata, predominantly comprise pale grey-

102  coloured clay and silty clay, becoming increasingly micaceous below 20 m, with shell

103  and sand-rich intervals towards the base of the succession (Figure 2A). A sharp

104  erosional contact and pebble bed occurs at 39.3 m, marking the base of the

105  Holocene (Wilkinson, 1995) and a rapid downward transition to pale red-coloured

106  glaciomarine sediments (Chesher and Wingfield, 1990). Below the Quaternary

107  succession at the borehole site, regional geophysical data indicate the presence of a

108  thick (+1000 m) succession of Permo-Triassic rocks occupying a structurally

109  complex fault-bounded basin (Peel Basin) west and southwest of the Isle of Man

110  (Chadwick et al., 2001). Apart from limited sampling of the core to establish broad

111  biostratigraphical and palaeoecological interpretations (Dickson, 1995; Riding, 1995;

112  Wilkinson, 1995), and reference to the presence of shallow-buried methane at the

113  borehole site (Judd, 2005), no detailed work has been carried out on this uniquely

114  thick Irish Sea Holocene succession.

115  References to subdivisions of the Holocene (Early/Mid/Late) follow Walker et

116  al. (2012, 2018). All borehole depths are metres below top of core. All ages reported

117  in this article are calibrated radiocarbon years (cal BP). Author citations for taxa

118  follow the Ellis and Messina Catalogue of Foraminifera (ISBN 978-0-913424-34-6),

119  and Williams et al. (2017) for dinoflagellate cysts.

120  **3.    Methodology**

121  For this study we focus on the Holocene succession, integrating a $^{14}$C

122  age/depth model with a range of environmental proxies to track changes in marine

123    mixing ($U^{K'}_{37}$, $\delta^{13}C$, $\delta^{18}O$), water mass productivity (foraminifera, dinoflagellate cysts,

124    Rock-Eval) and sediment characteristics (XRFS).

125        The stratigraphical distributions and relative abundances of foraminifera (M1–

126    29; Figure 2A) and dinoflagellate cysts (P1–31; Figure 2A) were analysed in the

127    upper 39.3 m of the core. Calcareous micropalaeontology samples were prepared

128    from air-dried residues of core samples washed through a 63 µm sieve with de-

129    ionised water, and taxa counts based on the 125–1000 µm size fraction. Slides for

130    palynological analysis were prepared using a standard processing technique (Wood

131    et al., 1996). Systematic abundance counts were made for all the samples, with

132    correspondence analysis used to explore their taxonomic similarity.

133        Bulk sediment geochemistry was measured for 204 samples using a portable

134    Niton XLt 793 X-Ray Fluorescence Spectrometer (XRFS), fitted with a 40kV Ag

135    anode X-ray tube. Samples were milled to <32 micron powders using agate

136    planetary ball mills and analysed for 120 seconds using the XRFS in a static semi-

137    automated configuration with 'Standard Soil Mode' selected. A subset of 13 samples

138    was selected for laboratory XRFS analysis (using PANalytical Axios sequential,

139    wavelength-dispersive X-ray fluorescence spectrometer, fitted with a 60 kV

140    generator and 4 kW rhodium (Super Sharp) end–window X-ray tube) to permit data

141    calibration.

142        The type, quantity and maturity of sedimentary organic matter, and its

143    variation through the succession, was assessed by Rock-Eval pyrolysis using a

144    Rock-Eval 6 analyser configured in standard mode (pyrolysis and oxidation as a

145    serial process) following the methodology of Slowakiewicz et al. (2015). Rock-Eval

146    parameters were calculated by integration of the amounts of HC (thermally-

147    vaporized free hydrocarbons) expressed in mgHC/g rock (S1) and hydrocarbons

148    released from cracking of bound organic matter (OM) expressed in mgHC/g rock

149    (S2). The Hydrogen Index (HI) was calculated from S2 x 100/Total Organic Carbon

150    (TOC) and the Oxygen Index (OI) from S3 x 100/TOC.

151           Age data were obtained by $^{14}$C analysis of 35 samples of mixed shell material

152    (samples individually comprising either echinoderm or mollusc shell, or ostracods

153    and foraminifera, or a combination of these components), between the top of the

154    core and 37.9 m depth, using the Natural Environment Research Council (NERC)

155    Radiocarbon Facility (East Kilbride) and the Keck C Cycle AMS Laboratory,

156    University of California (Irvine). A preliminary set of 10 bulk sediment radiocarbon

157    ages was used to guide borehole sampling. These bulk samples showed that the 0–

158    20 m core interval age range is much greater than the 20–37.9 m interval, and

159    sample frequency, for both detailed age ($^{14}$C) – depth modelling and other analyses,

160    was adjusted accordingly. Monospecific dating of shell samples was not attempted

161    because sample weights were consistently below the critical weight for accurate age

162    determination, even when the depth ranges of samples was increased. Although use

163    of mixed shell material may potentially lead to lower age precision because of

164    different ecological factors associated with different taxa, analysis of archaeological

165    samples has shown that for molluscs at least, $^{14}$C measurements from a range of

166    taxa sampled from well-constrained horizons show no significant age variation

167    (Ascough et al., 2005). Other work (Heier-Nielsen et al., 1995; Barker et al., 2007)

168    suggests that our inclusion of marine macrofossil shell for dating may have

169    significant advantages for age reliability compared to dates based on foraminifera

170    alone. In all cases, pristine shell material was selected to reduce potential error

171    caused by reworking.

172     Calibrated radiocarbon ($^{14}$C) ages for shell samples were converted into an

173     age-depth profile using CLAM (Version 2.2) (Blaauw, 2010;

174     http://chrono.qub.ac.uk/blaauw/clam.html) using the Intcal calibration curve and

175     applying an average reservoir correction of -62 $^{14}$C yrs (Butler et al., 2009). No

176     correction was made for methane, which is probably thermogenic in the WIS

177     (Crocker, 1995) with negligible radiogenic carbon (Winckler et al., 2002). Nor are age

178     data likely to be significantly compromised by the dead carbon content of methane,

179     based on recent data from cold seep sites in Japan (Yakasaki et al., 2016).

180     Age/depth reversals shown by preliminary results are evident in replicate

181     analyses and bulk samples, suggesting they are real features of the succession and

182     not sampling/analytical errors. The age reversals are associated with an interval of

183     the borehole containing units of core loss (Figure 2A) and most of the units of core

184     loss are associated with units of vesicular textured sediment above or below them

185     (Figure 2A, 2B). This texture is probably associated with methane-rich intervals in

186     the borehole succession, noted by Judd (2005) as occurring in Borehole 89/15 at

187     depths down to 36 m. High gas content is likely to have reduced sediment cohesion

188     during drilling, causing local collapse as confining pressure is reduced, or allowing

189     sediment to become entrained in the circulating drilling lubricant or mixed with

190     adjacent sediment. The archive copy of the borehole log at 31–32 m depth, just

191     above an interval of core loss, records additional drilling weight required to

192     compensate for gas back-pressure.

193     To mitigate the effects of age reversals on age-depth modelling, selection of

194     the most reliable data points for detailed model calculation (Figure 2A) was guided

195     by the general trend of bulk sediment age data, ignoring the age-reversals. This

196 trend closely matches that of dated shell material, but is consistently older, probably

197 indicating significant 'dead' carbon (Figure 2C) fed from the source areas for

198 Holocene sediment. In our Rock-Eval data, this is represented by values for non-

199 pyrolisable carbon (RC(%)), which locally exceeds 90% of TOC in the lower part of

200 the borehole, and remains greater than 70% near the top of the succession.

201       A further series of 210 samples of the two long-ranging and numerically

202 dominant benthonic foraminifera *Quinqueloculina seminula* and *Ammonia beccarii*

203 provided calcite for stable isotope analysis ($\delta^{13}C$, $\delta^{18}O$), with representative

204 specimens from a range of depths assessed for diagenetic alteration using SEM

205 imagery (BSEM and EDX) and optical cathodoluminescence (CL). In the context of

206 the previously recorded presence of shallow-buried methane at the study site (Judd,

207 2005), and the potential of this to produce methane derived authigenic carbonate

208 (MDAC), CL analysis was considered a useful cross-check on the extent of any

209 diagenetic alteration that might not immediately be apparent from visual

210 observations. Isotope analyses were performed at BGS with an Isoprime dual inlet

211 mass spectrometer plus Multiprep device, using 30–100 μg of calcite. Isotope values

212 ($\delta^{13}C$, $\delta^{18}O$) are reported as per mille (‰) deviations of the isotopic ratios ($^{13}C/^{12}C$,

213 $^{18}O/^{16}O$) calculated to the VPDB scale using a within-run laboratory standard

214 calibrated against NBS-19 ($\delta^{13}C$= +1.95‰ and $\delta^{18}O$= -2.20‰ as defined by IAEA).

215 Analytical reproducibility of the standard Carrara marble ($\delta^{13}C$= +2.00‰ and $\delta^{18}O$= -

216 1.73‰) is 0.03‰ for $\delta^{13}C$ and 0.06‰ for $\delta^{18}O$ (n=27). Craig correction is also

217 applied to account for $^{17}O$ (Craig, 1957).

218       Finally, alkenone-based estimates of Holocene sea surface temperatures

219 (SSTs) were calculated for 26 sediment samples spanning the Holocene interval

220  based on lipids extracted using an accelerated solvent extractor (ASE 200, Dionex)

221  and gas chromatography analysis (Hewlett Packard 6890 equipped with flame

222  ionization detection (FID) and an Agilent DB-1 ms UI column). $U^{K'}_{37}$ values were

223  calculated using the equation of Prahl and Wakeham (1987), and SST values

224  estimated using the global core top calibration of Müller et al. (1998).

225  **4.    Results**

226       All raw and calibrated data relating to this study are provided as a data

227  appendix, and also deposited at the National Geoscience Data Centre, British

228  Geological Survey, Keyworth, Nottingham (DOI: 10.5285/d959d29f-7660-4acc-82e2-

229  2ef2203adb70), where all core and sample materials can be examined.

230  *4.1 Radiocarbon ($^{14}$C) dating*

231       The best-fit age-depth model shows very high rates of sedimentation in the

232  lower part of the borehole (below 12 m), rapidly declining upwards, particularly above

233  2 m depth (Figure 2A). Ages for small intervals of the borehole (highest 0.05 m and

234  lowest 1.4 m) not covered by the age-depth model are derived by extrapolation from

235  the immediately adjacent age-depth trends. This suggests an age of ca. 11.2 ka for

236  the unconformity surface inferred to mark the base of the Holocene at 39.3 m.

237  *4.2 Foraminifera*

238       The Holocene succession contains three stratigraphically distinct foraminiferal

239  associations (F1 to F3; Figure 3) that allow subdivision as follows (Figure 4):

240  F1:    *Ammonia beccarii* association (39–39.1 m; ca. 11.17 ka): Flood abundance

241        of *A. beccarii* and subordinate *Quinqueloculina seminula*.

242   F2:    *Quinqueloculina seminula – Pyrgo williamsoni* association (11.6 m–38.3 m;

243         8.7–11.1 ka): Dominated by miliolid taxa and "species of southern origin"

244         *sensu* Murray (1971, 1973, 1991) including *Rosalina praegeri, Bulimina*

245         *elongata, B. marginata, Asterigerina mamillata* and *Bolivina pseudoplicata*.

246         Rare *Virgulina* (= *Stainforthia* of Scott et al., 2003).

247   F3:    *Spiroplectammina wrighti - A. beccarrii* association (0–10.56 m; 0–8.5 ka):

248         Numerically dominated by *A. beccarrii*, but uniquely characterised by *S.*

249         *wrighti*. This assemblage is also characterised by agglutinated taxa including

250         *Textularia sagittula. Bulimina* is more numerous and consistent in its

251         occurrence compared to underlying units, with peak abundance at 6.88 –

252         6.95 m (ca.7.5 ka).

253         Correspondence analysis of the foraminifer assemblages (Figure 5) reveals

254   that samples belonging to F2 and F3 define clusters of points, and that F2 can be

255   subdivided into a more diverse lower part (F2a; ca. 38.3–21.2 m, 11.1–9.9 ka), and

256   an upper part (F2b; ca. 21.2–10.56 m, 9.9–8.7 ka ) with markedly reduced diversity

257   resulting from a loss of hyaline taxa. Sample M28 is closely associated with points

258   defining F2b, but is unrelated stratigraphically, occurring close to the base of the

259   Holocene. The unusual low diversity of this sample may be influenced by rapidly

260   transitioning Early Holocene environmental conditions. Sample M29 stratigraphically

261   defines F1, but plots with points defining F3. This reflects the high abundance of

262   *Ammonia* in this Early Holocene sample.

263         With the exception of the occurrence of *Ammonia* in F1, one of the most

264   striking features in Borehole 89/15 is the general dominance of *Quinqueloculina*

265  *seminula* in the older parts of the succession (ca. 11–8 ka) and *Ammonia beccarii* in

266  the younger part (post 8 ka) (Figures 3 and 4).

267  *4.3 Palynology*

268  Three broad assemblages can be recognised in the stratigraphical distribution

269  of dinoflagellate cysts (Figure 6). The oldest (D1; 38.69–26.66 m; ca. 11.15–10.3 ka)

270  assemblage is dominated by heterotrophic cysts (e.g. *Brigantedinium*), with relatively

271  low proportions of *Spiniferites* and no *Operculodinium centrocarpum*. *Lingulodinium*

272  *machaerophorum* is abundant in one sample (ca. 10.5 ka). Above this, assemblage

273  D2 (26.41–9.27 m; ca. 10.3–8.3 ka) contains a higher number of taxa, with a higher

274  and frequently dominant proportion of autotrophic taxa, including significant

275  increases in the relative abundance of the genus *Spiniferites*. Also *Operculodinium*

276  *centrocarpum* sensu Wall and Dale (1966), *Selenopemphix nephroides* and

277  *Spiniferites membranaceus* appear in the record from around 10.3 ka. The youngest

278  (D3; 7.29–0.07 m; ca. 7.7–0.6 ka) assemblage sees a return of a higher proportion of

279  heterotrophic taxa (particularly *Brigantedinium*) that become dominant over

280  autotrophic taxa. With the exception of a single occurrence in D2, *Bitectatodinium*

281  *tepikiense* is only recorded in the D3 assemblage. There is also a gradual shift to

282  higher average cyst concentrations in the younger sediments.

283  Detrended correspondence analysis (Figure 7) reveals a strong distinction

284  between samples comprising the D1 and D2 assemblages. The D3 assemblage

285  occupies an intermediate region of the DCA plot, with the youngest samples from D3

286  showing increased similarity with D1.

287  *4.4 Bulk geochemistry*

288       Laboratory-calibrated bulk sediment XRFS analyses of selected elements (K,

289    Ca, Ti, Fe, Rb, Sr) are plotted in Figure 8, with element concentrations also

290    presented as log ratios normalised to K (a proxy for clay in the absence of data for

291    Al).

292       Plots of absolute and normalised Ca and Sr are very similar and show strong

293    shifts in their relative concentration; high values at and near the base of the

294    succession decline sharply towards 8 ka, and then increase progressively and more

295    gradually above this to 3.1 ka. Sediment residues prepared for microfossil extraction

296    suggest that the main contributors to the Ca and Sr plots are biogenic shell material

297    and locally voluminous crystalline gypsum (Figure 8), occurring as euhedral twinned

298    crystals and inter-grown crystal rosettes. This gypsum does not have the typical

299    crystal habit of 'gypsum spotting' that develops during storage and drying of borehole

300    core. SEM analysis reveals clear signs of multi-stage growth of gypsum crystals (J C

301    Rushton, BGS, pers. comm., 2015), and preliminary Sulphur isotope analysis ($\delta$ $^{34}$S)

302    indicates a significant contrast with modern seawater, and suggests the potential for

303    a pre-Holocene source (T E Heaton, BGS, pers. comm., 2015) or growth from

304    sulphide oxidation. Sulphide oxidation could include in-situ alteration of pyrite, but

305    the observation of pristine pyrite enclosed in gypsum crystals makes this origin seem

306    unlikely, potentially favouring a relationship with shallow-buried methane and

307    associated hydrogen sulphide (recorded on borehole drill logs).

308       Both Fe and K have a strong correlation with Ti ($R^2$ = 0.88 for Fe and 0.94 for

309    K), and all have similar overall trends, with well-defined and coincident maxima

310    around 8 ka. These similar trends suggest a common link to sediment input, with the

311    Fe predominantly in the form of oxy-hydroxide rich particulates. The trend in Ti

312    concentration is approximately inverse to those of Ca and Sr, and also to sediment

313    accumulation rate prior to 8 ka. This somewhat counter-intuitive relationship is

314    probably a dilution effect, largely driven by high concentrations of gypsum judging by

315    records of sample residues (Figure 8). In contrast, the normalised plot of Ti reveals

316    peak values below 10 ka, and only modest changes in overall values at 10–8 ka

317    (Figure 8). Sharp peaks in the plots of total and normalised concentrations of Fe,

318    occurring around 8.6 ka and 4.4 ka, correspond to thin, highly cemented, iron-

319    stained horizons in the core (Figure 8), and it is noticeable that unlike Ti, the

320    normalised Fe plot shows a trend to lower values below 8 ka.  In combination, these

321    characteristics suggest that Fe concentration is somewhat independent of the

322    dilution effects, and reflects its susceptibility to remobilisation in the sediment in

323    response to changes in redox conditions.

324    *4.5 Stable isotope composition ($\delta^{13}C$, $\delta^{18}O$)*

325        The plot of $\delta^{18}O$ (Figure 3) shows a strongly fluctuating pattern for

326    *Quinqueloculina*, with the bulk of the data ranging between -0.25‰ and +1.5‰.

327    There are two points on the curve where values for $\delta^{18}O$ are significantly more

328    negative ('M' on Figure 3), where values for *Quinqueloculina* are between -0.5 and -

329    1.5‰. The $\delta^{18}O$ plot for *Ammonia* is much less variable (<1‰), and values are

330    consistently more positive. The  $\delta^{13}C$  plot shows that whilst there is less separation

331    in the isotopic values of *Quinqueloculina* and *Ammonia* (compared to $\delta^{18}O$), values

332    for *Quinqueloculina* show a much greater range of variation (+0.4 to -6.3‰). Values

333    for *Ammonia* vary by less than 1‰, and are generally more positive than

334    *Quinqueloculina* above 8 ka, and more negative below this level. Two intervals

335    marked by more strongly negative $\delta^{13}C$ ('M' peaks on Figure 3) occur after 8 ka, and

336  values for *Quinqueloculina* above 8 ka appear to be consistently more negative by at

337  least 1‰ ('A' on Figure 3). Previous work has shown that separation of the isotopic

338  signatures of *Ammonia* and *Quinqueloculina* is likely a combination of vital effects

339  and seasonal differences in the timing of shell calcification (Austin and Scourse,

340  1997; Scourse et al., 2002, 2004).

341      Whilst SEM images show no significant diagenetic carbonate

342  overgrowths/infills of foraminifera, and excellent preservation (with sub-micron scale

343  morphological detail and no conspicuous physical alteration of the skeletal micro-

344  fabrics present), CL analysis revealed extensive luminescence (Figure 9).

345  Conventionally, luminescence is taken to signal diagenetic alteration, although it can

346  also reflect variation in original environmental geochemistry influencing skeletal

347  growth in foraminifera (Barbin, 2013). If diagenetic alteration is present, despite the

348  seemingly exquisite preservation, then the broadly consistent pattern of variation

349  between $\delta^{18}O$ and SST values (see Discussion; Figure 3) suggests that it has not

350  over-printed environmental signals, and that the broad trends shown by the stable

351  isotope data are valid.

352  *4.6 Rock-Eval*

353      Organic matter (OM) in coastal and marine sediments may be characterised

354  by hydrogen index (HI) values, which provide a measure of the extent of organic

355  matter hydrogenation as well as an indication of pre- and post-depositional alteration

356  effects (Lacey et al., 2014; Slowakiewicz et al., 2015). The HI profile for Borehole

357  89/15 suggests that the source of organic matter began to change after 8 ka (Figure

358  3). The overall trend of increasing HI values after 8 ka suggests increasing amounts

359  of marine/aquatic derived organic matter (Stephenson et al., 2005). The method of

360 calculating HI, which is normalised to the Total Organic Content (TOC), means that

361 unlike the latter, HI is unaffected by changes in sediment accumulation rate.

362 *4.7 Sea surface temperatures (SST)*

363 The results of alkenone-based SST estimates (Figure 3) show that the interval

364 11.2–8.6 ka is characterised by values between 13.7 and 15.1°C. Above this, there

365 is a pronounced and sharply defined increase, with SST varying between 15.6 and

366 17.2 °C, continuing into the youngest analysed part of the succession.

367 The above SST estimates are comparable to the current (observed) summer

368 SST values for the Irish Sea (Howarth, 2005), and are consistent with the current

369 May and June blooming in the Irish Sea of haptophytes (Kennington and Rowlands,

370 2005), algae that include the source organisms of alkenones. These observations

371 appear to suggest that $U^{K'}_{37}$ is recording summer SST in the Irish Sea. More

372 generally, it has been suggested that the record of variation in $U^{K'}_{37}$ reflects the

373 timing of the spring bloom and the intensity of this bloom compared to production

374 throughout the rest of the year, with a significant summer bias in some settings

375 (Jonas et al., 2017), particularly where environmental factors (e.g. insolation) limit

376 winter productivity (Bachem et al., 2016).

377 **5.    Discussion**

378 Comparison of the broad range of environmental proxy data assembled for

379 this study (Figure 3) reveals fundamental changes in micro-biota, water temperature

380 structure and sediment supply, allowing evaluation of the development,

381 palaeoecological impact and long-term stability of seasonal stratification in the WIS.

382 Today the WIS is a relatively deep water, open marine setting, characterised by a

383 low-gradient salinity:$\delta^{18}O_{water}$ mixing-line (Austin et al., 2006, fig. 5), that in common

384　with much of the north-west European shelf, allows the seasonal impact of changes

385　in salinity on $\delta^{18}O_{water}$ to be ignored (Austin et al., 2006). Furthermore, the near

386　ubiquitous presence of the remains of echinoderms (almost exclusively stenohaline;

387　Smith, 1984) in our calcareous micro-fossil sample residues, including cidarid

388　echinoids from close to the base of the Holocene succession (39.15–39.17 m),

389　suggests that normal salinity conditions have existed at the borehole site even at

390　times of significantly lowered sea level. On this basis, the following discussion

391　interprets changes in $\delta^{18}O$ values derived from benthic foraminifera as most probably

392　reflecting changes in water temperature. Salinity effects may form components of

393　anomalies on our stable isotope plots that are potentially associated with methane

394　release and brine migration (see below), but these anomalies do not form part of the

395　general trends in isotope data that we discuss. Furthermore, the impact of these

396　potential brines is likely to be minor in terms of their stable isotope chemistry, and

397　their ionic content significantly reduced by dilution.

398　*5.1 Early Holocene (11.2–8.2 ka)*

399　　　Two distinct environmental states are discernible in the Early Holocene record

400　of the WIS: an early, 'high-productivity mixed water-mass state' (11.2–10 ka), and a

401　later 'lower productivity mixed water-mass state' (10–8.2 ka) (Figure 3). The first is

402　characterised by a diverse assemblage of benthic foraminifera and ostracods

403　(Dickson, 1995) and a predominance of heterotrophic dinoflagellate cysts (Figures 3

404　and 6), reflected by D1 assemblage dinoflagellate cyst samples occupying a

405　distinctly separate region of the DCA plot on Figure 7. Abundant shelly macrofossils

406　(e.g. oysters, cidarid echinoids) suggest relatively shallow, marine conditions, as do

407　rare occurrences of the foraminifer *Elphidium macellum* and low relative abundances

408　of *Spiniferites* and occasional high abundance of the coastal species *Votadinium*

409  *calvum* (Zonneveld et al., 2013). Low dinoflagellate cyst concentrations (Figure 3)

410  are probably affected by very high sedimentation rate through this interval and

411  relatively high tidal currents causing winnowing of silt-grade material. *Ammonia*

412  *beccarii* is a highly adaptable and opportunistic species, surviving in regions affected

413  by low oxygen levels, high inputs of nutrients and trace metals, and variable depth,

414  temperature and salinity (Alve and Murray, 1999; Nikulina et al., 2008; Polovodova et

415  al., 2009). Its sudden and short-lived abundance also at the base of the Holocene

416  (F1 association) is probably an opportunistic response to a newly created habitat.

417  Above this, *Pyrgo williamsoni* is a marker for the F2a assemblage, with two distinct

418  abundance peaks (Figure 4). This foraminifer is characteristic of shelfal

419  environments (Murray, 2013), and in Arctic deglacial successions Cronin et al.

420  (2017) assigned it to their "river-intermediate" assemblage (as distinct from "river

421  proximal" and "river distal" associations) following Polyak et al (2002). This

422  ecological interpretation broadly fits with its occurrence in the WIS during the Early

423  Holocene, when lowered sea level would have increased the impact of terrestrial

424  sediment sources across the Irish Sea Basin (see below). The peaks in *P.*

425  *williamsoni* may be related to changes in seabed conditions, as Novak (2017)

426  reported a preference of this foraminifer for muddy substrates. If correct, these peaks

427  potentially demonstrate cyclicity in the mud/sand ratio at the borehole site, and are

428  possibly evidence of fine-scale lithological change in response to variation in the rate

429  of sea level rise.

430  Summer SST values increase through the Early Holocene, peaking around

431  15°C at 10.2 ka, and are mirrored by lower $\delta^{18}O$ values of benthic *Quinqueloculina*,

432  suggesting that warming affected the whole water column and that the system was

433  fully mixed. More generally, warming of the Early Holocene climate is marked across

434    NW Europe by the rapid spread/appearance of hazel (*Corylus*) pollen (Tallantire,

435    2002; Theuerkauf et al., 2014), which in Borehole 89/15 was noted as reaching its

436    acme in this interval. High sedimentation rates (1200–1600 cm/kyr) are associated

437    with peak values in the Ti/K ratio, suggesting proportionately greater input of

438    hydrodynamically heavy (i.e. coarse-grained) detrital sediment at this time. Although

439    the concentrations of Rb are low, there is a suggestion in our Rb/K plot that the

440    sediment deposited prior to 8 ka is geochemically contrasting to that deposited after

441    8 ka. Voluminous sediment supply, perhaps partly reflecting the availability of easily

442    remobilised glacigenic sediment, could have boosted productivity through the supply

443    of bio-limiting nutrients, explaining the abundance of heterotrophic dinoflagellate

444    cysts and diverse and abundant benthic foraminifera. The high abundance of

445    *Lingulodinium machaerophorum* in one sample could be interpreted as evidence for

446    increased mixing (cf. Marret et al., 2002) or is consistent with increased riverine input

447    (e.g. Zonneveld et al., 2013).

448        Inferred lower sea-level (20–40 m below present level) across the Irish Sea

449    basin during the Early Holocene (Stone et al., 2010; Smith et al., 2012), consistent

450    with the dinoflagellate cyst record of this work, would have focused sedimentation

451    towards the deeper WIS region, following a typical Low Stand Systems Tract pattern

452    of deposition (Van Wagoner et al., 1988; Catuneanu et al., 2011). Amplification of

453    this effect in the Irish Sea is likely to have been driven by: 1) unusual geometry of the

454    Irish Sea basin, with a restricted deep water region to the west, and extensive, much

455    shallower shelf to the east; 2) patterns of Early Holocene isostatic uplift across

456    northern Britain that initially outpaced rates of sea-level rise (Smith et al., 2012),

457    probably driving high sediment fluxes to adjoining depositional basins. In effect, the

458 WIS basin probably acted as a sediment sink for material that was unable to be

459 stored on the eastern shelf.

460     In the later part of the Early Holocene, a modest stepped phase of cooling in

461 summer SSTs around 10 ka is matched by shifts to more positive $\delta^{18}O$ values of

462 *Quinqueloculina*, marking the onset of a 'lower productivity mixed water state'

463 (Figure 3). The micro-biota is characterised by low diversity benthic foraminifera

464 (particularly hyaline taxa) overwhelmingly dominated by *Quinqueloculina seminula*,

465 lower abundances of heterotrophic dinoflagellate cysts and increasing dominance of

466 the autotrophic genus *Spiniferites*. Compared to the D1 dinoflagellate cyst

467 assemblage, samples comprising the D2 assemblage occupy a separate and non-

468 overlapping region of the DCA plot, but have a broad spread, consistent with a shift

469 to a distinctly different and/or more complex/rapidly varying environment. Coincident

470 with this is a rise in Holocene sea-level, modest initially, culminating in a rapid phase

471 of increase beginning around 8.8 ka (Figure 3). The first appearance of

472 *Operculodinium centrocarpum* sensu Wall and Dale (1966) and *S. membranaceus*

473 represent an important shift in the dinoflagellate cyst record, reflecting a deeper

474 environment with mostly mixed water conditions, and some influence of frontal zones

475 (*S. quanta*, *S. ramosus*, cysts of *P. schwartzii*).

476     An interval dominated by *Quinqueloculina seminula* is recorded by Scourse et

477 al. (2002) in the Holocene succession in the Celtic Sea between ca. 10.5 and 9 ka,

478 interpreted to represent a high energy, shallow marine setting. This foraminifer is an

479 active coloniser that is often associated with coarser-grained sediment substrates

480 (Murray, 2006), and *Quinqueloculina* spp. in general show a preference for regions

481 experiencing high velocity currents and low flux of organic carbon (Martins et al.,

482 2006). Cearreta et al (2002) also note that in settings where connections with

483    oceanic waters are restricted, increasing that connectivity favours increasing

484    abundance of *Q. seminula*.

485        Between 11 and 10 ka sediment accumulation rates are very high (ca. 1600 –

486    1200 cm/kyr) and are matched by peak values in Ti/K, before steadily declining. Ti/K

487    values build again around 8 ka, although this is not matched by an increase in

488    sedimentation rate. In situ sediment reworking is one possible explanation of the

489    latter trend, although no complimentary macro-sedimentary features were noted in

490    the core. Alternatively, rising concentration of Ti and declining sediment

491    accumulation could indicate proportionately coarser sediment being moved across

492    the borehole site because of lack of effective storage. This process of 'normal

493    regression' (sensu Catuneanu et al., 2011) occurs when newly flooded basin

494    margins are not initially able to store the sediment volumes they receive. In the

495    eastern Irish Sea basin, this might also reflect strong tidal/storm scour, and possibly

496    remobilisation of newly flooded and poorly consolidated sediment. This environment

497    may have favoured the robust, heavily calcified *Quinqueloculina*, and perhaps more

498    generally the distinct shell calcification mechanism adopted by milliolid taxa which

499    avoids the need for an organic template to control shell growth (de Nooijer et al.,

500    2009).

501        The latest part of the Early Holocene (8.6 to 8.2 ka) in the WIS is marked by a

502    dramatic warming of summer SST values, inferred to represent the establishment of

503    seasonal stratification (see below). There is no evidence of the widely recognised

504    globally cooler climate conditions around 8.2 ka, particularly affecting the North

505    Atlantic region (Alley et al., 1997). Its absence in the WIS might be similar to other

506    Atlantic sites where this event is undetected by SST data, possibly because of

507    decoupling of surface and subsurface marine temperature records (Moros et al.,

508    2004), or reflect the influence of local conditions (e.g. erosion/ environmental over-

509    printing) and/or low sample resolution.

510    *5.2 Mid and Late Holocene (post 8.2 ka)*

511    In the latest Early Holocene, the development of persistently higher average

512    summer SST values coincides with a change from rapid to more gradually rising sea-

513    level that continues through the Mid and Late Holocene (Figure 3). Warming is not

514    suggested by the $\delta^{18}O$ record of benthic *Quinqueloculina*, which (apart from some

515    anomalously negative values; see below) generally shows a trend to more positive

516    (i.e. cooler) values above the base of the Mid Holocene, at least until this foraminifer

517    disappears from the WIS succession around 5.6 ka (Figure 3).  The Mid Holocene

518    $\delta^{18}O$ record of *Quinqueloculina* with respect to *Ammonia* in the WIS is similar to the

519    trend of these foraminifera from the Celtic Sea reported by Scourse et al. (2004).

520    Austin and Scourse (1997) and Scourse et al. (2002, 2004) discussed seasonal

521    differences in calcification that contribute (with vital effects) to an offset in the $\delta^{18}O$

522    records of *Quinqueloculina* and *Ammonia*. In this context, the apparent convergence

523    of the trend of *Quinqueloculina* with the $\delta^{18}O$ record of *Ammonia* (Figure 3) in both

524    the Celtic Sea and WIS is plausible evidence for progressive reduction of this

525    seasonal effect with the onset of stratification.  Scourse et al. (2004) reported that in

526    stratified settings, both *Ammonia* and *Quinqueloculina* select the same season

527    (typically September) for calcification, when peak bottom water temperatures are

528    achieved. The contrasting trends in SST and the $\delta^{18}O$ record of benthic

529    *Quinqueloculina* described above and shown on Figure 3 suggest the relatively rapid

530    establishment of seasonal water-mass stratification around 8.4–8.2 ka that persists

531    to the present day.

532   Negative shifts of $\delta^{13}C$ can also be used to recognise seasonal water-mass

533 stratification, reflecting increased preservation of light organic carbon beneath the

534 pycnocline (Austin and Scourse, 1997; Scourse et al., 2002; 2004). Understanding

535 the $\delta^{13}C$ record for the WIS is complicated by some unusually negative values (see

536 below), generally corresponding with intervals that also show abnormally negative

537 $\delta^{18}O$. However, by considering only the difference between the maximum positive

538 values of $\delta^{13}C$ for *Quinqueloculina* observed before and after the inflection in SST

539 values ('A' on Figure 3), there appears to be a small negative shift of about 1‰,

540 similar to that associated with stratification in the Celtic Sea during the Holocene

541 (Scourse et al. 2002). Large, short lived negative excursions in the $\delta^{13}C$ (>-6‰) and

542 $\delta^{18}O$ data for *Quinqueloculina* ('M' on Figure 3) depart significantly from the expected

543 response to stratification (Austin and Scourse, 1997; Scourse et al., 2002).

544 Geophysical data show the borehole site coincides with a significant area of

545 shallowly-buried methane, with active seepage indicated by pockmarks (Crocker et

546 al., 2005). By analogy with work elsewhere (Rathburn et al., 2003; Torres, et al.,

547 2003; Consolaro et al., 2015), the negative excursions in $\delta^{13}C$ (and presumably also

548 $\delta^{18}O$) may document the influence of methane seeps in the WIS on the Mid and Late

549 Holocene marine environment. The WIS material appears to show the typical

550 variability of (amplified) negative $\delta^{13}C$ values within species and between species,

551 indicative of a primary (and not diagenetic) signal, with marked disequilibrium with

552 the strongly negative $\delta^{13}C$ of methane (Rathburn et al., 2003; Hill et al., 2004; Panieri

553 et al., 2012; Consolaro et al., 2015). Temporal variability of methane seepage might

554 explain the absence of isotope evidence for this feature in the Early Holocene, or the

555 development of stratification could have boosted methane concentration in benthic

556 settings by reducing turbulent mixing, a feature observed at North Sea methane

557 seep sites (Mau et al., 2015).

558 　　　　Dinoflagellate cysts respond to the onset of stratification in the WIS by a

559 progressive increase in the relative proportion of heterotrophic forms (especially

560 *Brigantedinium* and *Votadinium*), and they largely dominate over autotrophic forms

561 after 7.5 ka (Figure 3), indicating greater primary productivity (Bringué et al., 2014).

562 *Bitectatodinium tepikiense*, *Selenopemphix quanta* and *Spiniferites elongatus*,

563 present in the D3 assemblage, associated with low abundance of *Spiniferites*

564 *membranaceus*, characterise regions in the Celtic Sea associated with seasonal

565 stratification, with *B. tepikiense* particularly favouring geographical regions where

566 there is high seasonal temperature range (Marret et al., 2004). *Spiniferites lazus* was

567 discussed extensively by Marret et al (2004), who suggested that high relative

568 abundances of this taxon might be related to warm temperatures and/or relatively

569 lower sea level. In Borehole 89/15, this taxon builds to a peak of 30% abundance

570 around the D2/D3 boundary, and then declines in abundance higher in the

571 succession. Since the D2/D3 boundary is a time of rapidly rising sea level (Figure 3),

572 abundance of *S. lazus* might be a response to the onset of warmer surface water

573 conditions created at the inception of seasonal stratification. Whilst potentially

574 favourable for *S. lazus* initially, stabilisation of this higher productivity environment

575 would have made it a niche with increasing competition and predation that might

576 explain its subsequent progressive decline. Increasing influence of frontal conditions

577 in the youngest part of the D3 succession (post-dating 3 ka), perhaps reflecting

578 changing extent and pattern of the area of WIS seasonal stratification, is potentially

579 signalled by increasing abundance of *S. ramosus* based on comparison with the

580 Celtic Sea dinoflagellate cyst distributions (Marret et al., 2004).

581     The change in the character of the dinoflagellate cyst assemblage is clearly

582     seen on the DCA plot, with D3 assemblage samples plotting between D1 and D2

583     samples, and younger samples in D3 tracking closer to the high productivity Early

584     Holocene D1 assemblage. The persistent separation of the two high productivity

585     assemblages on the DCA plot supports the view that these similar trophic strategies

586     are a response to distinctly different environmental settings. The increase in

587     heterotrophic cysts appears to track increasing HI. This, and the tendency in

588     correspondence analysis (Figure 7) for the youngest components of the D3

589     assemblage to track towards the D1 assemblage, suggests a trend of increasing

590     productivity associated with increasing deposition of marine derived organic matter.

591     This might indicate intensification of the thermocline during seasonal stratification

592     (which in the WIS is sensitive to long-term variation in summer air temperatures and

593     wind speeds; Olbert et al., 2011), or perhaps progressive growth in the nutrient

594     content of water beneath the pycnocline as stratification became established;

595     nutrients that amplify productivity at mixing fronts and across the Sub Chlorophyll

596     Maximum, and contribute to increasing fluxes of heterotrophic cysts. However, the

597     apparent stabilisation in the relative abundance of heterotrophic cysts after 5 ka

598     probably shows that factors such as winter mixing and bioturbation (Austin and

599     Scourse, 1997; Scourse et al., 2002, 2004) may ultimately limit the capacity of the

600     WIS to progressively enhance the organic content of sediments through seasonal

601     stratification.

602     Although numerically dominated by *Ammonia beccarii*, the F3 foraminiferal

603     assemblage is uniquely distinguished by the record of *Spiroplectammina wrightii* ,

604     which appears to have a broad environmental tolerance, being recorded on sand

605     and mud substrates in fully marine salinities (Murray, 1991 and references therein),

606    and a component of both the mixed water assemblage (Scott *et al*., 2003, p. 46) as

607    well as the fully stratified setting well away from frontal regions (ibidum, Appendix III)

608    in the Celtic Sea. The relatively sudden appearance of this Mediterranean to

609    Lusitanian species (Haynes, 1973, 1981) in the WIS around 8 ka, approximately

610    coincident with the onset of seasonal stratification, probably reflects a broader

611    pattern of migration in response to improving marine conditions between the Early

612    and Mid Holocene (e.g. Andersson et al., 2010 and references therein). The F3

613    assemblage includes forms (*Nonionella turgida*, *Bulimina marginata*) that are

614    characteristic of Recent sediments in the Celtic Sea associated with seasonal

615    stratification and mixing fronts (Scott et al., 2003), with even low abundances of *N.*

616    *turgida* (spiking at 18% in Borehole 89/15; Figure 4) significant for interpretation of

617    these environments (Scott et al., 2003).

618         The switch in the dominant benthic foraminifer, from *Quinqueloculina*

619    *seminula* below the SST inflection, to *Ammonia beccarii* above, is remarkably sharp,

620    and a feature seen in both absolute and relative abundance data (Figure 4).

621    *Quinqueloculina* spp. like *Ammonia* are opportunistic (Langlet et al., 2014 and

622    references therein) with broad environmental tolerance, inhabiting lagoons, marshes

623    and deeper inner shelf environments (Murray, 2006) with some ability to withstand

624    low oxygen concentration (Langlet et al., 2014). Opportunistic behaviour of these

625    taxa in Borehole 89/15 is suggested by the coincident peaks in absolute abundance

626    at the approximate onset of seasonal stratification (Figure 4). The subsequent

627    decline in *Quinqueloculina* and dominance of *A. beccarii* suggests a pattern of

628    environmental change that *Q. seminula* was less well adapted to over the longer

629    term. The pattern of decline in *Q. seminula* is similar to that seen in the Celtic Sea

630    (Austin and Scourse, 1997, fig. 5), but the dominance of *Ammonia* is distinctive of

631 the WIS record. Experimental data suggests that *Q. seminula* is sensitive to

632 prolonged deterioration in seabed oxygenation, although it might initially respond

633 opportunistically if this is associated with greater availability of organic matter

634 (Langlet et al., 2014), both factors associated with the onset of seasonal stratification

635 in the Celtic Sea and WIS. The strongly contrasting record of *Ammonia* with respect

636 to this event in the WIS suggests that it is responding to local environmental factors

637 that favoured its abundance in the WIS following the onset of seasonal stratification.

638 One possibility is that the WIS site provides a record of seasonal stratification that

639 was sustained without interruption from the influence of a tidal mixing front. In the

640 Celtic Sea, dinoflagellate cysts (Marret et al., 2004) provide some evidence for the

641 migration of frontal conditions towards the site described by Austin and Scourse

642 (1997) and Scourse et al. (2002). Alternatively, the presence of shallow-buried

643 methane in the WIS may have tipped the ecological balance in favour of *Ammonia*,

644 species of which are tolerant of a broad range of environmental disturbance (Alve

645 and Murray, 1999; Nikulina et al., 2008; Polovodova et al., 2009; Gooday et al.,

646 2009). This potentially includes a range of environmental factors associated with the

647 presence of methane, for example hydrogen sulphide (noted on drilling logs of

648 Borehole 89/15) and mineral-enriched fluids associated with gas emplacement

649 (gypsum in the Holocene succession possibly remobilised from the thick underlying

650 Permo-Triassic succession; Figure 8). Although methane and associated fluid/gas

651 release at the site is likely to have a long geological history in the WIS, the reduced

652 water column mixing associated with seasonal stratification could have emphasised

653 its ecological impact. Similarly, changes in sediment characteristics and diagenetic

654 environment associated with the onset of stratification may explain why the upper

655  limit of maximum gypsum concentration in Borehole 89/15 (Figure 8) is

656  approximately coincident with the horizon of SST inflection.

657      Since the current pattern of stratification in the WIS can be understood both in

658  terms of water depth and low tidal energy (Howarth, 2005; Dabrowski et al., 2010),

659  the significant rise in sea-level at the end of the Early Holocene was likely critical to

660  establishing threshold values of these parameters for stratification to develop.

661  Palaeotidal modelling (e.g. Scourse and Austin, 1995; Uehara et al., 2006; Ward et

662  al., 2016) reconstructs the spatial and temporal changes of tidal dynamics through

663  the Holocene for north-west European shelf seas, and can be used to predict the

664  timing of onset of seasonal marine stratification. Using outputs from the Ward et al.

665  (2016) palaeotidal simulations, the predicted timing for the onset of seasonal

666  stratification at the site of Borehole 89/15 is around 10–9 ka, compared with the 8.4–

667  8.2 ka indicated by this study. There are several reasons why these values might

668  differ. Firstly, errors and assumptions in the age/depth model derived for Borehole

669  89/15 could cause differences between the modelled and observed timing of

670  seasonal stratification. Secondly, palaeotidal models are highly sensitive to GIA

671  effects (Uehara et al., 2006; Ward et al., 2016), and modelling of these in turn

672  depends on assumptions on the rheology of the mantle and crust. Palaeotidal

673  models are underpinned by an elastic density structure taken from an average-Earth

674  seismic model by Dziewonski and Anderson (1981). This model uses a simple 3-

675  layer earth model each with different viscosity values (Bradley et al., 2011), but

676  Dziewonski and Anderson (1981) acknowledged that their average Earth Model does

677  not take account of the very large lateral variations in the first few 10s km of the

678  Earth's crust. New evidence for the crustal structure of the Irish Sea and wider north-

679  west European region shows significant laterally heterogeneity, with fingers of low

680    density rock radiating from a plume beneath Iceland; one such feature extends down

681    the Irish Sea region (Schoonman et al., 2017, fig. 4). Bradley et al. (2011) refer to

682    data-model misfit relating to "the lateral variations in earth properties", shown to

683    particularly affect Fennoscandia, which is also the site of one of the crustal

684    anomalies identified by Schoonman et al. (2017). Until Earth models are developed

685    that can fully reflect lateral and vertical heterogeneities in crustal structure, it is not

686    possible to reach any firm conclusion about the source of misfit between modelled

687    and observed data for the timing of marine stratification in the WIS area. Recent

688    palaeotidal models of the region are dependent on a single ground-truth point in the

689    Celtic Sea based on work by Austin and Scourse (1997) and Scourse et al. (2002)

690    (Uehara et al., 2006; Neill et al., 2010; Ward et al., 2016), so in this context our data

691    misfit with the timing of stratification predicted by palaeotidal models is potentially

692    significant in providing a much-needed control point for validating/constraining

693    palaeotidal model outputs.

694        As well as influencing marine stratification, rising sea-level through the

695    Holocene also explains the sharp decline in sediment accumulation rate (to less than

696    100 cm/kyr) in the Late Holocene. During high/maximum sea-level, detrital loads of

697    riverine sources are easily trapped in the increased accommodation space at the

698    basin margin.  In the case of the Irish Sea Basin, small rises in sea-level across the

699    expansive low relief of the eastern part of the basin would have added

700    disproportionately to the capacity of this area to store sediment, evidenced by

701    extensive modern sand and mud banks fringing the Lancashire coast. Higher

702    residual sedimentation in the early part of the Mid Holocene (7.5–5.5 ka), and minor

703    peaks between 6.1 and 5.8 ka (matched by peaks in Ti/K and Rb/K ratios) could

704    reflect short-lived overspill from small infilled depo-centres on the Eastern Irish Sea

705    Shelf, before later Holocene sea-level rise created additional sediment-storage

706    capacity across this region.

707        Although summer SST values are generally elevated in the WIS through the

708    Mid and Late Holocene, there is a fluctuation between relatively warmer and cooler

709    intervals. At least three of these fluctuations match warm/cold events recognised in

710    the wider Northern Hemisphere Holocene climate (7.5, 4, and 3 ka; Wanner et al.,

711    2014). The extent to which peaks in SST values in the WIS can be linked to solar

712    variability is difficult to assess. Problems exist with the age calibration of different

713    proxy data, but broadly, peaks in solar activity at 4.4 ka and 2.7 ka (Charman, 2010)

714    correspond with times of elevated SST in the WIS. The sustained fall in summer SST

715    values since 3 ka suggests a progressive weakening of the stratification in the WIS.

716    This period includes significant cool phases and is part of a longer term, probably

717    orbitally-driven Northern Hemisphere pre-industrial cooling trend, perhaps

718    additionally influenced in the last 2000 years by groups of major volcanic eruptions,

719    both acting to reduce summer insolation (Wanner et al., 2008; Charman, 2010;

720    Wanner et al., 2014).

721    **6.    Conclusions**

722        Seasonal stratification boosts modern day marine productivity in the WIS

723    region, and based on the evidence of multi-proxy data from Borehole 89/15, became

724    established around the transition from Early to Mid Holocene (ca. 8.4–8.2 ka). This is

725    slightly younger compared to the Celtic Sea (8.99 to 8.44 ka) but overlaps with

726    palaeotidal model simulations of stratification onset (ca. 10–8 ka). In the WIS,

727    seasonal stratification was preceded by two distinct Early Holocene mixed-water

728    marine settings, a high productivity mixed water-mass state between 11.2 and 10 ka,

729    and a period of lower productivity between 10 and 8.2 ka. In the Mid and Late

730 Holocene (post 8.2 ka), rapid warming of summer SSTs (typically 16 to 17$^0$C) is

731 associated with a trend of more positive $\delta^{18}$O in benthic foraminiferal, suggesting a

732 cooling of deeper water and the establishment of seasonal stratification. This change

733 is associated with an increase in the burial of marine-derived organic matter

734 (increasing HI) and long term increase and eventual dominance of heterotrophic

735 dinoflagellate cysts.

736 The strong temporal association of increase in summer SSTs and maximum

737 rate of sea-level rise suggests that threshold values in bathymetry and tidal energy

738 are the main factors driving stratification in the WIS. Higher sediment supply to the

739 WIS during lowered sea-level in the Early Holocene may have helped to sustain high

740 productivity. Later rises in sea-level are associated with a decline in productivity and

741 reduced sediment accumulation rate. Flooding and deepening across the eastern

742 Irish Sea shelf likely increased the sediment storage potential of the shelf and

743 restricted sediment fluxes to deeper regions westwards. Resurgence in WIS

744 productivity occurred once sea-level rise was sufficient to allow seasonal

745 stratification to become established. The effect of a reduction in turbulent mixing

746 caused by stratification may have amplified the effects of local seabed methane

747 seepage, by producing anomalously negative values of $\delta^{13}$C/ $\delta^{18}$O in benthic

748 foraminifera and favouring the highly adaptable *Ammonia beccarri* as the dominant

749 foraminifer species. Despite short term fluctuation in summer SSTs, after 8.2 ka

750 there is no return to the values associated with the inferred mixed marine settings of

751 the Early Holocene. A sustained decline in summer SSTs between ca. 3 ka and the

752 end of our SST record at ca. 1.4 ka, suggests progressive weakening in the

753 magnitude of the summer thermocline over this period.

754 **Acknowledgements**

766

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1067

**FIGURE CAPTIONS**:

**Figure 1.** Geography and bathymetry of the Irish Sea, showing location of Borehole 89/15 and approximate extents of present-day seasonal water mass stratification and shallow-buried gas deposits in the Western Irish Sea. Bathymetry (in metres) from DigBath250 digital data (British Geological Survey © NERC). Derived in part from data provided by Vlaamse Hydrografie (Belgium), Bundesamt för Seeschifffahrt und Hydrographie (BSH - Germany), Bureau Hydrografie (Netherlands), Statens Kartverk (Norway), Farvandsvæsenet (Denmark) and United Kingdom Hydrographic Office). Stratification extent based on Howarth (2005) and gas data based on Crocker et al. (2005). <mark>(1.5 COLUMN WIDTH FIGURE)</mark>

**Figure 2.** (**A**) Stratigraphy, borehole core log, micro-fossil sampling and age-depth model for Borehole 89/15. Age-depth model (solid line) calculated from CLAM 2.2 (Blaauw, 2010) using calibrated radiocarbon ages for samples of shell material. (**B**) Image of 'vesicular texture' representing core intervals that were methane-bearing when drilled. (**C**) SEM images of woody plant fragments in Holocene sediment residues from Borehole 89/15. This 'old' carbon helps explain the relatively greater $^{14}$C age of the bulk sediment compared to that determined for individual foraminifera. Scale bar = 10 mm; Pleist = Pleistocene. <mark>(2 COLUMN WIDTH FIGURE)</mark>

**Figure 3.** Comparison of selected data for the Holocene succession in Borehole 89/15 plotted against age and interpretations of biostratigraphical (dinoflagellate cysts, foraminifera) and palaeoecological subdivisions. (1) Relative sea level data for Morecambe Bay UK (Smith et al., 2012, fig. 1) and summer SST (* = typical current summer SST range for Irish Sea measured at Cypris Station, Isle of Man between

1092 1904 and 2004 (Evans et al., 2003); (2) δ$^{18}$O for benthic foraminifera

1093 (*Quinqueloculina*, *Ammonia*) with general trends highlighted by grey shading.

1094 Aberrant peaks labelled 'M' may indicate the influence of seafloor methane seepage

1095 on isotope values; (3) δ$^{13}$C for benthic foraminifera (*Quinqueloculina*, *Ammonia*), with

1096 peaks ('M') potentially influenced by seafloor methane seepage. Difference between

1097 maximum δ$^{13}$C for *Quinqueloculina* before and after stratification indicated by 'A'; (4)

1098 Sediment accumulation compared with total concentration of Ti and Log Ti/K; (5)

1099 Hydrogen index (HI) compared with Total Organic Carbon (TOC) determined from

1100 Rock-Eval analysis; (6) Percentage spores and pollen; (7) Percentage autotrophic

1101 and heterotrophic dinoflagellate cysts; (8) Foraminifera diversity and abundance

1102 distribution of *Quinqueloculina* and *Ammonia*; (9) Frequency of warm/cold and

1103 wet/dry Holocene climate events of Wanner et al. (2014), with grey highlight

1104 indicating events that align with SST inflections.

1105 Water mass productivity state: 1= Mixed marine, high productivity; 2= Mixed marine,

1106 low productivity; 3= Seasonally stratified, high productivity. (FULL PAGE

1107 LANDSCAPE FIGURE, COLOUR IN PRINT)

1108 **Figure 4.** Relative abundance of selected foraminifera in the Holocene succession of

1109 Borehole 89/15 with respect to subdivisions based on foraminifera associations, total

1110 foraminifera diversity, total foraminifera abundance and onset of seasonal

1111 stratification. Excludes taxa where the sum of percentage abundances in all samples

1112 is low (<15%). The numerical dominance of *Quinqueloculina* in most Early Holocene

1113 assemblages is rapidly replaced by *Ammonia*, *Bulimina* and *Spiroplectammina* in the

1114 Mid and Late Holocene. A complete listing of all the foraminifera taxa identified in the

1115 samples, and their raw abundances, is provided in Supplementary Data. (FULL

1116 PAGE LANDSCAPE FIGURE)

1117 **Figure 5.** Correspondence analysis of foraminifera samples (M1 (youngest) - M29

1118 (oldest)) shaded to show relationship to stratigraphically constrained associations

1119 (F1, F2 & F3). The analysis allows subdivision of F2 into an early high diversity part

1120 (F2a) and a later low diversity interval (F2b). M28 and M29 have unusual taxonomic

1121 features (probably influenced by Early Holocene environmental conditions) that

1122 distort their positions on this plot (see text for details). DCA sample scores and eigen

1123 values are detailed in Supplementary Data. (1.5 COLUMN WIDTH FIGURE)

1124 **Figure 6.** Relative abundances of selected dinoflagellate cyst taxa for the Holocene

1125 succession of Borehole 89/15, and its subdivision based on dinoflagellate cyst

1126 assemblages. P=Peridinalid taxa, G=Gonyaulacid taxa. **6A**: Relative abundances of

1127 taxa excluding *Spiniferites*; **6B**: Relative abundances of species of *Spiniferites*.

1128 Heterotrophic taxa dominate in D1, reduce in their relative proportion in D2, and

1129 show progressive increase and return to dominance in D3. (FIG 6A: FULL PAGE

1130 LANDSCAPE FIGURE; FIG 6B: 1.5 COLUMN WIDTH FIGURE)

1131 **Figure 7.** Correspondence analysis of dinoflagellate cyst samples. Analysis excludes

1132 samples P24 and P26 which both have low cyst counts and have dominant

1133 occurrences of single taxa (*Lingulodinium machaerophorum* in P24 and

1134 *Xandarodinium xanthum* in P26). The plot shows a strong distinction between the D1

1135 and D2 assemblages, with the D3 assemblage occupying an intermediate position.

1136 Younger parts of the D3 assemblage appear to show a trend of increasing similarity

1137 with the D1 assemblage (indicative of high productivity). DCA sample scores and

1138 eigen values are detailed in Supplementary Data. (1.5 COLUMN WIDTH FIGURE)

1139 **Figure 8.** Total concentration (ppm) and log ratio plots (normalised to K) of selected

1140 elements based on laboratory calibrated bulk sediment XRFS analysis of 204

1141    samples from the Holocene succession in Borehole 89/15. Log ratio plots are

1142    normalised to potassium (K) and compared with sedimentation rate and composition

1143    of sediment residues prepared for stable isotope analysis. Plots of Fe, K, Ti and Rb

1144    predominantly record the type and quantity of sediment, although sharp peaks in Fe

1145    around 8.6 ka and 4.4 ka may be a response to local changes in redox state related

1146    to changes in seafloor methane seepage. Ca and Sr predominantly respond to the

1147    amount of bioclastic shell and gypsum in the succession, with the latter probably

1148    being the dominant influence in the lower part of the succession. (LANDSCAPE 2

1149    COLUMN WIDTH FIGURE)

1150    **Figure 9.** Transmitted light SEM and CL imagery of polished thin sections of

1151    *Ammonia beccarii* (a, c) and *Quinqueloculina seminula* (b, d). The imagery shows

1152    good preservation of *Ammonia* (including spines) and *Quinqueloculina*, but

1153    luminesence of CL images suggests varying degrees of diagenetic alteration.

1154    (SINGLE COLUMN WIDTH FIGURE, COLOUR IN PRINT)

1155

Map showing the Irish Sea region. Labels include: 55°N, 54°N at left; 6°W, 5°W, 4°W, 3°W along the top. N (north arrow). 50 km scale bar. Place names: Belfast, Stranraer, Dundalk, Dublin, Isle of Man, Morecambe Bay, Liverpool. North Channel, Manx Depression, Western Trough, IRISH SEA, BH89/15. Depth contours: -20, -30, -40, -50, -70, -80, -120. Maximum extent of Western Irish Sea Seasonal Stratification. Potential extent of shallow-buried gas. Inset map: Ireland, UK, St George's Channel, Celtic Sea.

(A)

Dated shell-samples with error bars(solid fill where excluded from age-depth model)

**Key to core log and sampling symbols**

Silty mudstone

CL  Core loss

Iron-stained cemented horizon

Bioclastic material

Sandy

Pebble

V  Vesicular texture

▲  Foraminifera samples (M1 - 29)

●  Palynology samples (P1 - 31)

Bulk Sediment ages

Data excluded from CLAM calculation of age-depth curve

Modelled age-depth curve and error (grey-shading)

Extrapolated age-depth trend

Age (kyr B.P.)

Depth (m)

Core Log

Micropalaeontology samples

Stratigraphy

M1  P1

CL

V  V  V

CL

V  V  V

CL

V  V  V

V

CL

V

CL

V  V  V

V  V  V

CL

V  V  V

V  V  V

M29  P31

Borehole Total Depth = 85 m

Micaceous

Western Irish Sea Formation

HOLOCENE

PLEIST.

(B)

(C)

100 μm

100 μm

See Figure 6b for data relating to *Spiniferites*   ● present but not forming part of abundance count

present but not forming part of abundance count

(a)

Spines

(b)

(c)

200 µm

(d)

200 µm