

## ISOTOPIC VARIATION IN LATE CENOMANIAN TO EARLY TURONIAN FORAMINIFERA AND MATRIX FROM DSDP SITE 551 (GOBAN SPUR, NORTHEAST ATLANTIC)



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Stable isotopic measurements have been made on both planktonic foraminifera and coccolith-rich matrix of Cretaceous (latest Cenomanian-early Turonian) age from DSDP site 551 (Goban Spur, Northeast Atlantic). The foraminifera display a  $\delta^{18}\text{O}$  range of -1.1 to -2.2 ‰ (PDB) whilst the  $\delta^{13}\text{C}$  values are confined to a narrower range of 2.0 to 2.1 ‰ (PDB). The preservation of the foraminifera has been assessed through geochemistry and scanning electron microscopy and indicates that they show evidence of some diagenetic alteration. Consequently palaeotemperature estimates using these values are deemed to be in general unreliable. The  $\delta^{13}\text{C}$  of the matrix (in conjunction with published data) show heaviest values during the latest Cenomanian. The data are thus consistent with the widely observed positive carbon isotope excursion associated with the latest Cenomanian oceanic anoxic event.

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### INTRODUCTION

The latest Cenomanian Oceanic Anoxic Event (OAE), frequently represented by deposition of organic rich sediments (e.g. the Plenus Marl Formation), is in turn characterised by a positive carbon isotope excursion (e.g. Schlanger and Jenkyns 1976; Hart 1985). The positive shift in carbon isotope values for this interval is conventionally interpreted in terms of regional burial of organic carbon, causing drawdown of  $\text{CO}_2$  and initiating climatic deterioration thereafter (Jenkyns *et al.* 1994). The present study focuses upon isotopic analyses of planktonic foraminifera and matrix derived from late Cenomanian-early Turonian nannofossil chalks from Deep Sea Drilling Project (DSDP) site 551. The aims of this paper are to identify whether the foraminifera and matrix have retained their primary isotopic signal and to establish whether a positive carbon isotope excursion is observed. Scanning electron microscopy (SEM) and trace element analysis has been employed to distinguish any trends originating from diagenetic overprinting.

### GEOLOGICAL SETTING AND SAMPLING

DSDP Site 551, located on Goban Spur, Western Approaches (48° 54.64' N; 13° 30.09' W), 424 km southwest of Ireland (Figure 1) penetrated post-Aptian Mesozoic and Tertiary sediments (Graciansky *et al.* 1985). Seven samples were obtained from this site which are of late Cenomanian to early Turonian age (*Rotalipora cushmani* to *Whiteinella archaeocretacea* foraminifera zones). The lithology of studied section consisted of bioturbated white-grey nanno-chalk, overlain by massive to a faintly laminated organic-rich black shale (Figure 2). Mineralogically the nanno-chalks are largely calcite, with minor amounts of clay minerals (smectite and illite) and quartz (Thiry and Pascal 1985). Rotaliporid foraminifera and praeglobotruncanids are most abundant in the 211-425 mm size fraction in all samples, together with a few species of *Hedbergella* sp. The assemblage thus represents an unrestricted open ocean assemblage, deeper than coeval assemblages from onshore sections of southern England (Leary and Hart 1988).

*Rotaliporids* (including *R. cushmani* and *R. greenhornensis*) and *globotruncanids*, were picked for isotope analysis from the 211-

425 $\mu\text{m}$  size fraction. Additionally the surrounding matrix was isotopically analysed and combined with data from Cunningham and Kroopnick (1985).

### ANALYTICAL PROCEDURES

The generally unconsolidated nature of the sediments permitted relatively easy sample diasaggregation using an ultrasonic bath.

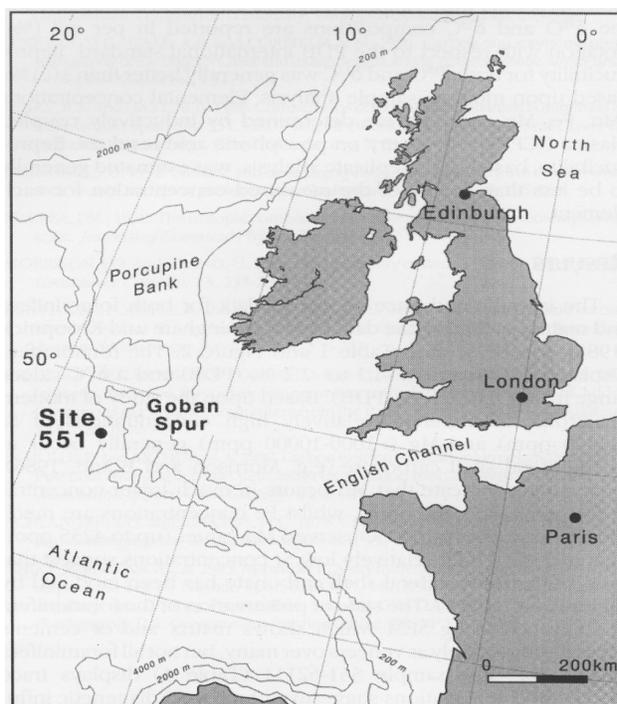


Figure 1. Location map of DSDP Site 551, Goban Spur, Western Approaches.

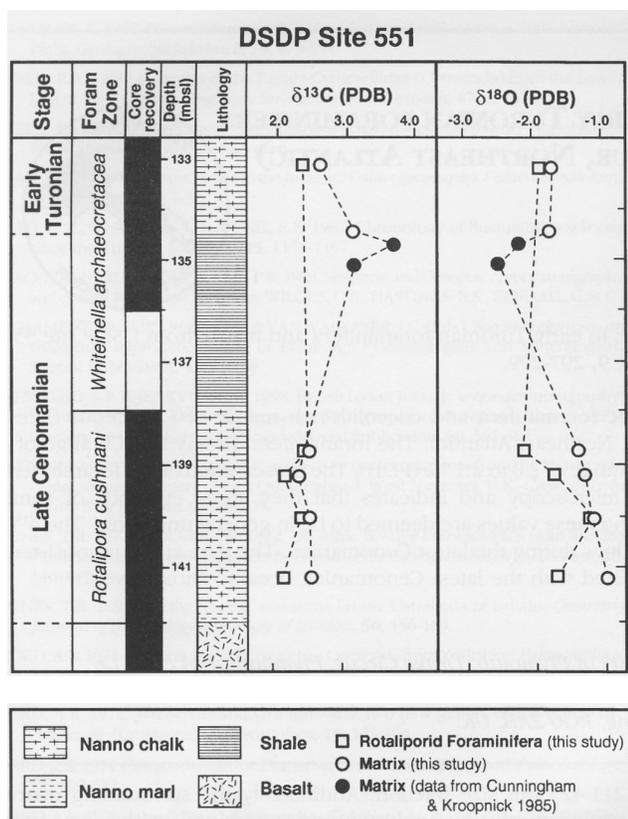


Figure 2. Lithology and isotopic composition of sediments plotted against depth (metres below sea floor) from Site 551.

2 mg foraminiferal and 10 mg matrix samples were analysed for stable isotopes using standard methods on a VG Sira series II mass spectrometer, following the method of McCrea (1950) and the correction procedures of Craig (1957) were applied. Isotopic results were calibrated against an in-house standard and the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  compositions are reported in per mil (‰) notation with respect to the PDB international standard. Reproducibility for both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  was generally better than  $\pm 0.1\%$ , based upon multiple sample analysis. Elemental concentrations (Mn, Fe, Mg and Sr) were determined by inductively coupled plasma (ICP) spectrometry on phosphoric acid residues. Reproducibility, based upon replicate analysis, was estimated generally to be less than  $\pm 15\%$  of the measured concentration for each element.

## RESULTS

The isotopic and trace elemental data for both foraminifera and matrix, including the data from Cunningham and Kroopnick (1985), can be seen in Table 1 and Figure 2. The foraminifera display a  $\delta^{18}\text{O}$  range of  $-1.1$  to  $-2.2$  ‰ (PDB) and a  $\delta^{13}\text{C}$  values range from  $2.0$  to  $2.1$  ‰ (PDB). Based upon the study of modern planktonic foraminifera, relatively high concentrations of Sr ( $\sim 1000$  ppm) and Mg ( $\sim 1000$ – $10000$  ppm) generally occur in foraminiferal shell carbonate (e.g. Morrison and Brand, 1986). Such studies indicate that Mn occurs in much lower concentrations (generally  $< 200$  ppm), whilst Fe concentrations are much more poorly constrained. Observed Mn values (up to  $4235$  ppm) in conjunction with relatively low Sr concentrations suggest that most of the foraminiferal shell carbonate has been modified by diagenesis (Table 1). The state of preservation of the foraminifera is confirmed using SEM which shows matrix and/or cements occurring commonly as veneers over many, but not all foraminifera (Figure 3). Only sample 551-62111 (Table 1) displays trace elemental concentrations suggestive of minimal diagenetic influence.

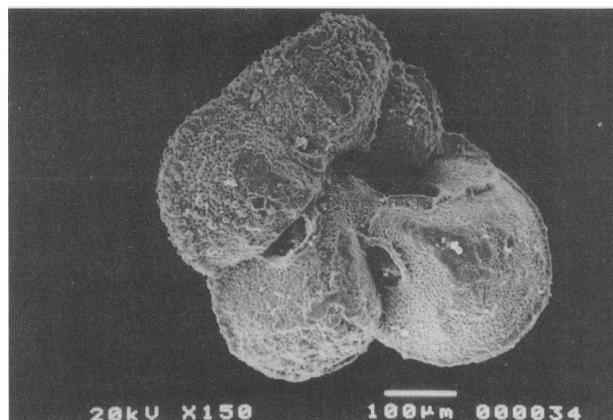


Figure 3 SEM photomicrograph of a Rotaliporid foraminifera, with surface features partially masked by coating of matrix (sample 551-61147).

SEM analysis confirms that the matrix is dominated by coccoliths and reveals the presence of limited calcite cements and overgrowths. Despite this diagenetic influence, the carbon isotope data demonstrates a positive excursion associated with the organic rich shales (Figure 2). The oxygen isotope values derived from the matrix for this interval are lightest and show a sharp shift towards more positive values in the early Turonian.

## DISCUSSION AND CONCLUSIONS

Despite the apparent diagenetic influence a number of oceanographic and climatic inferences may be drawn from the data. The matrix, dominated by surface dwelling coccoliths, display more positive  $\delta^{13}\text{C}$  values than the rotaliporid foraminifera (Figure 2). Such a trend is consistent with ocean surface waters being relatively enriched in the heavy carbon isotope ( $^{13}\text{C}$ ) and with previous concepts of foraminiferal depth stratification (e.g. Hart 1985; Leary and Hart 1988).

The dark organic shale (Figure 2) is thought to be the local representation of the late Cenomanian OAE of Schlanger and Jenkyns (1976) (e.g. Hart 1985). A positive carbon excursion, a characteristic of the OAE, is well documented for coeval strata (e.g. Scholle and Arthur 1980) and is interpreted as a record of enhanced preservation and burial of organic matter in marine sediments (Pratt *et al.* 1990; Jenkyns *et al.* 1994), causing drawdown of  $\text{CO}_2$  and initiating climatic cooling (inverse greenhouse effect). Palaeotemperature trends derived from the analysis of matrix remain problematic because of the incorporation of a biogenic mixture and variable diagenetic component (see Jenkyns *et al.* 1994). Isotopic data from such media may not therefore reveal absolute temperature values but importantly short and longer term trends may be revealed (Marshall 1992). In a detailed study of the English Chalk Jenkyns *et al.* (1994) record warmest palaeotemperatures at the Cenomanian-Turonian boundary associated with the most positive carbon isotope values and a subsequent decrease in carbon isotope values correlated with inferred climatic cooling. The oxygen isotope data from the matrix, in this study, if interpreted in terms of temperature tends, suggests warming through the late Cenomanian (a pattern consistent with other studies e.g. Douglas and Savin 1975; Price *et al.* 1998) and possibly cooling before the peak of the carbon isotope excursion. Thus cooling could have been initiated before deposition of carbon-rich sediments ceased. Alternatively Jarvis *et al.* (1988), who recorded a small  $\delta^{18}\text{O}$  heavy event associated with the positive  $\delta^{13}\text{C}$  excursion infer cooling related to possible upwelling of colder (and nutrient rich) waters on to the European shelf or southward invasion of a cooler water mass. More controversially Jeans *et al.* (1991) propose that the whole of the late Cenomanian OAE is associated with cool (possibly glacial conditions), a conclusion not justified by the results shown in Figure 2, although more detailed analysis is ultimately required.

Sample	Depth	Sample (mbsf)	$\delta^{13}\text{C}$ (PDB)	$\delta^{18}\text{C}$ (PDB)	Fe, (ppm)	Mg, (ppm)	Mn, (ppm)	Sr, (ppm)
551-5168	133.18	<i>Globotruncana sp.</i>	2.4	-1.9	<1	1467	608	670
551-6117	142.17	<i>Rotalipora sp.</i>	2.4	-2.2	<1	578	5170	633
551-6167	142.67	<i>Rotalipora sp.</i>	2	-1.7	<1	2396	464	664
551-61147	143.47	<i>Rotalipora sp.</i>	2.3	-1.1	<1	2523	2581	792
551-62111	144.61	<i>Rotalipora sp.</i>	2	-1.7	11362	1385	246	505
551-5168	133.18	Matrix	2.6	-1.7	5156	3311	710	502
551-5244	134.44	Matrix	3.1	-1.8	8069	3767	402	443
551-5269*	134.69	Matrix	3.7	-2.2				
551-52108*	135.08	Matrix	3.1	-2.5				
551-6117A	138.67	Matrix	2.3	-1.3	2753	2465	7102	570
551-6117B	138.67	Matrix	2.4	-1.4	2609	2347	6982	566
551-6167	139.17	Matrix	2.3	-1.2	621	1825	667	417
551-61147	139.97	Matrix	2.4	-1.1	5336	3576	978	602
551-62111	141.11	Matrix	2.5	-0.9	4913	3020	263	483

\* data from Cunningham and Kroopnick (1985)

Table 1. Elemental and Isotopic compositions of fossils and matrix from Site 551.

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