New constraints upon isotope variation during the early Cretaceous (Barremian–Cenomanian) from the Pacific Ocean

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Abstract – Carbon and oxygen isotope data from a succession of Cretaceous (Barremian–Cenomanian) age recovered from the Pacific Ocean (DSDP site 463) are presented. The carbon isotope curve reveals a large isotope excursion within the early Aptian where $\delta^{13}C$ values reach ~4.8‰ in the *L. cabri–G. ferreolensis* foraminifera zone. A decrease in $\delta^{13}C$ values is observed at the base *G. algerianus* zone, before a return to more positive values at the top of the *G. algerianus–T. bejaouaensis* zone. The pronounced early Aptian positive event is preceded by a large negative isotope excursion, confined to the *G. blowi* zone. Synchronous with this excursion are increased total organic carbon values and increases in Mn and Fe concentrations. Integrated biostratigraphic and magnetostratigraphic data, together with the carbon isotope profile, suggest that the organic-rich units of site 463 are correlatable with Oceanic Anoxic Event 1a. The input of isotopically light volcanic CO_2 in concert with the intensification and upwelling of intermediate water enriched in ^{12}C could account for the observed trends. A potential trigger may have been the destabilization of the water column and the prodigious CO_2 emissions associated with hydrothermal activity and the emplacement of the Ontong Java Plateau. Coupled with faunal evidence, the subsequent positive carbon isotope excursion is interpreted to be resulting from high, but decreasing, productivity and possibly increasing ocean stratification resulting in strong carbon isotopic gradients and ^{13}C-enriched surface waters. The decrease in $\delta^{13}C$ within the *G. algerianus* zone is coincident with more positive $\delta^{18}O$ values. If these are interpreted in terms of temperature this interval may be characterized by a period of cooling and possibly a waning of C_{org} cycling. A return to lower $\delta^{13}C$ values during the middle Albian is considered to be related to the increased influence of upwelling, as opposed to a waning of C_{org} cycling. Upwelling introduced isotopically light carbon to the surface, arresting the stratified oceanic conditions.

Keywords: Cretaceous, Aptian, oxygen, carbon, isotopes.

1. Introduction

Major episodes of organic carbon-rich black shale deposition of Cretaceous age, corresponding to the Oceanic Anoxic Events OAE1 (Aptian) and OAE2 (Cenomanian–Turonian boundary), have been described (Schlanger & Jenkyns, 1976). As organic carbon is preferentially enriched in the lighter isotope ^{12}C, its removal from the oceanic reservoir renders global sea waters relatively enriched in ^{13}C (Berger & Vincent, 1986; Marshall, 1992). Hence, positive carbon-isotope compositions of carbonate rocks and fossils have been interpreted in terms of increased burial of organic carbon attributed to enhanced preservation under reduced O_2 conditions (e.g. Bralower & Thierstein, 1984; Bralower *et al.* 1994) or driven by changes in surface water productivity (delivering more organic carbon to the sea-floor: e.g. Weissert, 1989; Weissert & Lini, 1991; Erba, 1994; Hochuli *et al.* 1999). It has been observed, however, that positive $\delta^{13}C$ excursions sometimes post-date black shale deposition (e.g. Bralower *et al.* 1994; Erba *et al.* 1999) and hence,

positive excursions may not be simply driven by increased carbon burial (Menegatti *et al.* 1998). A number of studies (e.g. Kerr, 1998; Larson & Erba, 1999; Jones & Jenkyns, 2001; Sinton & Duncan, 1997) have evaluated the effect of hydrothermalism and associated volcanism upon consumption of seawater O_2 and the stimulation of the organic carbon flux to the sea-floor during the early Aptian and Cenomanian–Turonian boundary interval. These latter authors suggest that the oxidation of reduced material in hydrothermal effluents and the stimulation of primary productivity owing to the injection of hydrothermal Fe into surface waters are both potential O_2-reducing mechanisms. Such fluctuations in oxygen depletion and eutrophication within oceans of Cretaceous age, in concert with temperature and sea-level variation, have been linked to dramatic changes in faunal assemblage compositions (e.g. Leckie, 1989; Coccioni, Erba & Premoli Silva, 1992; Bralower *et al.* 1994; Erba, 1994; Erbacher, Thurow & Littke, 1996; Bischoff & Mutterlose, 1998; Hart, 1999; Premoli Silva & Sliter, 1999).

Recently it has been demonstrated that a negative carbon isotope excursion precedes the positive early Aptian excursion OAE1a (equivalent to the Selli level)
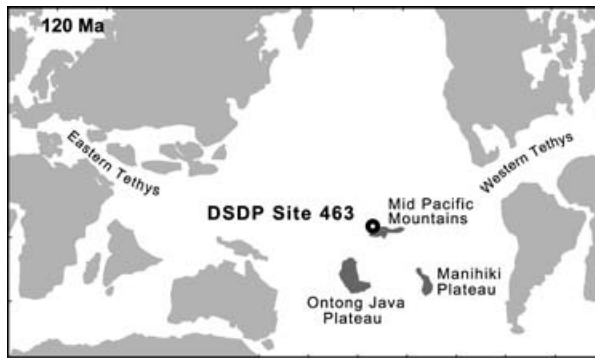
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Figure 1. Palaeogeographic reconstruction at ~120 Ma showing superplume eruption area and location of DSDP site 463 (modified from Larson & Erba, 1999).

(Bralower *et al.* 1999; Jenkyns, 1995; Menegatti *et al.* 1998; Gröcke, Hesselbo & Jenkyns, 1999; Ando *et al.* 2002). The brevity and magnitude of the early Aptian negative excursion has been compared to the late Paleocene negative excursion (Dickens *et al.* 1995) and hence linked to the voluminous release of methane from gas hydrates contained in marine continental-margin sediments (Opdyke *et al.* 2001; Jahren *et al.* 2001; Jenkyns & Wilson, 1999; Beerling, Lomas & Gröcke, 2002; Jahren, 2002). Negative isotope excursions in the Early Toarcian (Hesselbo *et al.* 2000) and Late Jurassic (Padden, Weissert & de Rafelis, 2001) have also been attributed to methane release. A combination of increased volcanic activity leading to enhanced CO_2 emissions and intensified recycling and upwelling of intermediate water enriched in ^{12}C (Menegatti *et al.* 1998; Bralower *et al.* 1994, 1999; Larson & Erba, 1999) has also been considered as a mechanism to account for the early Aptian excursion. It is the purpose of this paper to explore in detail the Aptian–Albian interval from DSDP site 463 using isotopic analyses coupled with geochemical data, in order to assess the sequence of geological events and their timing, in addition to understanding any causal linkages.

2. Materials and methods

Samples were selected from DSDP site 463 (Thiede *et al.* 1981), located southwest of the Hawaiian Ridge on the Western Mid-Pacific Mountains (21°21.01′ N; 174°40.07′ E) (Fig. 1). The lithology of site 463 consists largely of foraminiferal and nannofossil chalk ooze. From 626 to 615 mbsf the succession is characterized by white to black carbonaceous sediments containing up to 7.5 wt% total organic carbon (TOC) and siliceous limestones and tuffs. In the lower parts of the section the sediment is slightly more lithified (see Thiede *et al.* 1981). Black and dark grey chert fragments are recorded throughout. During mid-Cretaceous times site 463 was located close to the palaeoequator and moved from ~20° S in the Aptian northwards to ~5° S in the

Cenomanian, as a result of the motion of the Pacific Plate (Tarduno *et al.* 1989; Erba, 1992).

Bulk carbonate samples were isotopically analysed using conventional stable isotope techniques on a Micromass Prism III Isotope Ratio Mass Spectrometer. The $\delta^{18}O$ and $\delta^{13}C$ compositions are reported in per mil (‰) notation with respect to the V-PDB (Vienna Peedee Belemnite) international standard. Reproducibility of replicate analyses of standards, for both $\delta^{18}O$ and $\delta^{13}C$, was generally better than 0.1‰. Elemental concentrations (Mn and Fe) were analysed using a Perkin Elmer 3100 Atomic Absorption Spectrometer. Analyses were performed on bulk powders after sample digestion with 10 ml of concentrated of HCl, added in stages allowing for any effusive reaction to take place, on 0.2–0.5 g subsamples. The solution was then filtered and the insoluble residue left on the filter paper was weighed and subtracted from the original sample weight. This method provides an assessment of the elemental concentration of the carbonate fraction and is hence comparable with the isotopic analyses and is a similar approach to that of Pomerol (1983). Although some exchange with the insoluble clay fraction is to be anticipated, the obtained trends are essentially identical to the whole rock data obtained by Dean (1981*a*). The insoluble concentrations generally ranged from 1 to 40 % (see also Dean, 1981*a*), although from the succession characterized by carbonaceous sediments and siliceous limestones and tuffs (626–615 mbsf), typically the insoluble concentration was larger (50–90 %). Based upon replicate analysis, analytical precision was estimated to be less than ±5 % of the measured concentration of each element.

Stratigraphic control of the studied section is based upon integrated nannofossil (Cepek, 1981; Roth, 1981; Erba, 1994) and foraminiferal biostratigraphy (Boersma, 1981; Sliter, 1989, 1992) and magnetostratigraphy (Tarduno *et al.* 1989). These data indicate that a complete Aptian–early Albian succession was present. Particularly poor core recovery is evident for the Barremian part of the succession and around the Albian–Cenomanian boundary.

3. Results

The isotope and trace element data are presented in Figures 2–4. The lightest oxygen isotope values are observed in the lowest, Barremian, parts of the site, before increasing towards the Barremian–Aptian boundary. Low $\delta^{18}O$ values are also seen within the *G. blowi* foraminifera zone, and although showing a degree of scatter, isotope values become increasingly more positive, reaching a value of −0.14‰ towards the top of the *G. algerianus* foraminifera zone. The $\delta^{18}O$ values then gradually decrease upwards through into the Albian sediments.

The carbon isotope curve (Fig. 2) reveals a pronounced negative isotope excursion, occurring entirely
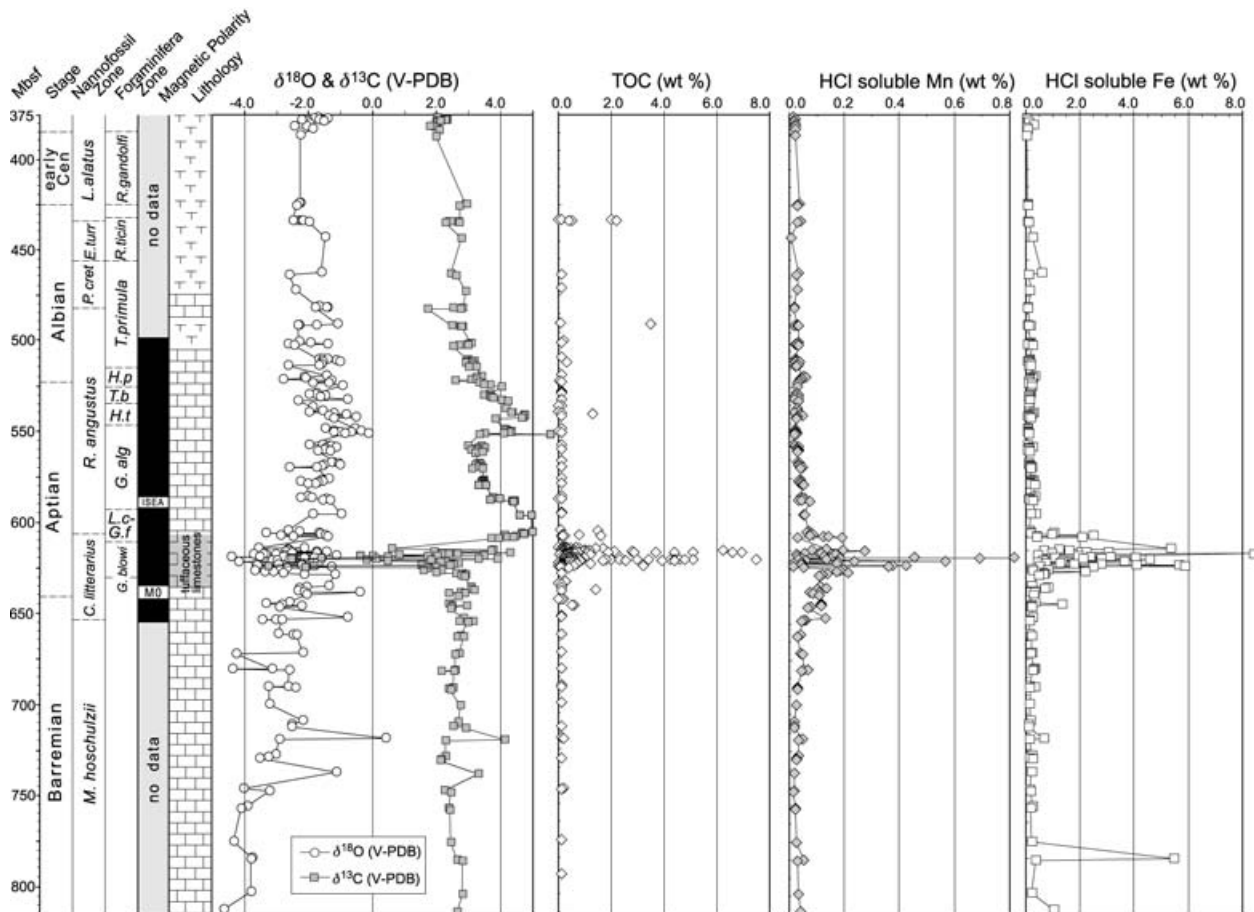
Figure 2. Oxygen and carbon isotope stratigraphy of the Barremian–Cenomanian of site 463 showing HCl-soluble Mn and Fe variation (this study) and total organic carbon data (from Dean, 1981*b*; Mélières, Deroo & Herbin, 1981). Lithology is from Thiede *et al.* (1981), nannofossil biostratigraphy from Cepek (1981), Roth (1981) and Erba (1994), and the foraminiferal biostratigraphy is from Sliter (1989, 1992) and Boersma (1981). The magnetostratigraphy data are from Tarduno *et al.* (1989), showing Chrons M0 and ISEA, the latter of which is an alternative name of the reversed interval M " − 1r". The following abbreviations are used: *M. hoschulzii = Micrantholithus hoschulzii*; *C. litterarius = Chiastozygus litterarius*; *R. angustus = Rhagodiscus angustus*; *P. cret = Prediscosphaera cretacea*; *E. turr = Eiffellithus turriselffeli*; *L. alatus = Lithraphidites alatus*; *G. blowi = Globigerinelloides blowi*; *L.c = Leupoldina cabri*; *G.f = Globigerinelloides ferreolensis*; *G. alg = Globigerinelloides algerianus*; *H. t = Hedbergella trocoidea*; *T. b = Ticinella bejaouaensis*; *H. p = Hedbergella planispira*; *T. primula = Ticinella primula*; *R. ticin = Rotalipora ticinensis* and *R. gandolfi = Rotalipora gandolfi*.

within the *G. blowi* zone (*C. litterarius* nannofossil zone). Synchronous with this negative excursion are increased TOC values, in addition to large increases in Mn and Fe (Fig. 2). The TOC data are derived from the study of Mélières, Deroo & Herbin (1981), who undertook standard Rock-Eval pyrolysis. Where the TOC contents reach maximum values (up to 7.5 wt%) they contain predominantly organic carbon of marine origin, whilst background values are considered to have been derived from mixed marine and continental sources (Mélières, Deroo & Herbin, 1981). Given the integrated biostratigraphic (Sliter, 1992; Erba, 1994) and magnetostratigraphic data (Tarduno *et al.* 1989), together with the carbon isotope profile, the organic-rich units of site 463 are interpreted as correlatable with OAE1a. Following the negative excursion, $\delta^{13}C$ values within the Aptian increase to ~4.8‰ in the *L. cabri–*

G. ferreolensis foraminifera zone. A late Aptian decrease in $\delta^{13}C$ is observed within the *G. algerianus* zone. The $\delta^{13}C$ curve then shifts back again to more positive values (~4.6‰) at the top of the *G. algerianus* zone. $\delta^{13}C$ values return to pre-excursion values of around +2.4‰ within the Albian and Cenomanian (see also Price *et al.* 1998).

Examination of this section in detail (Fig. 3) shows that the excursion is in fact composed of a series of events varying in scale from a 2‰ shift up to a shift of ~6‰. Increases in Mn are also coincident with the most negative carbon isotope values, whereas the highest TOC values appear between the negative peaks. Iron displays a more variable distribution and shows an increase in concentration before, during and after the isotope excursion (Fig. 3). The smectite data, also shown in Figure 3, are derived from Mélières, Deroo &
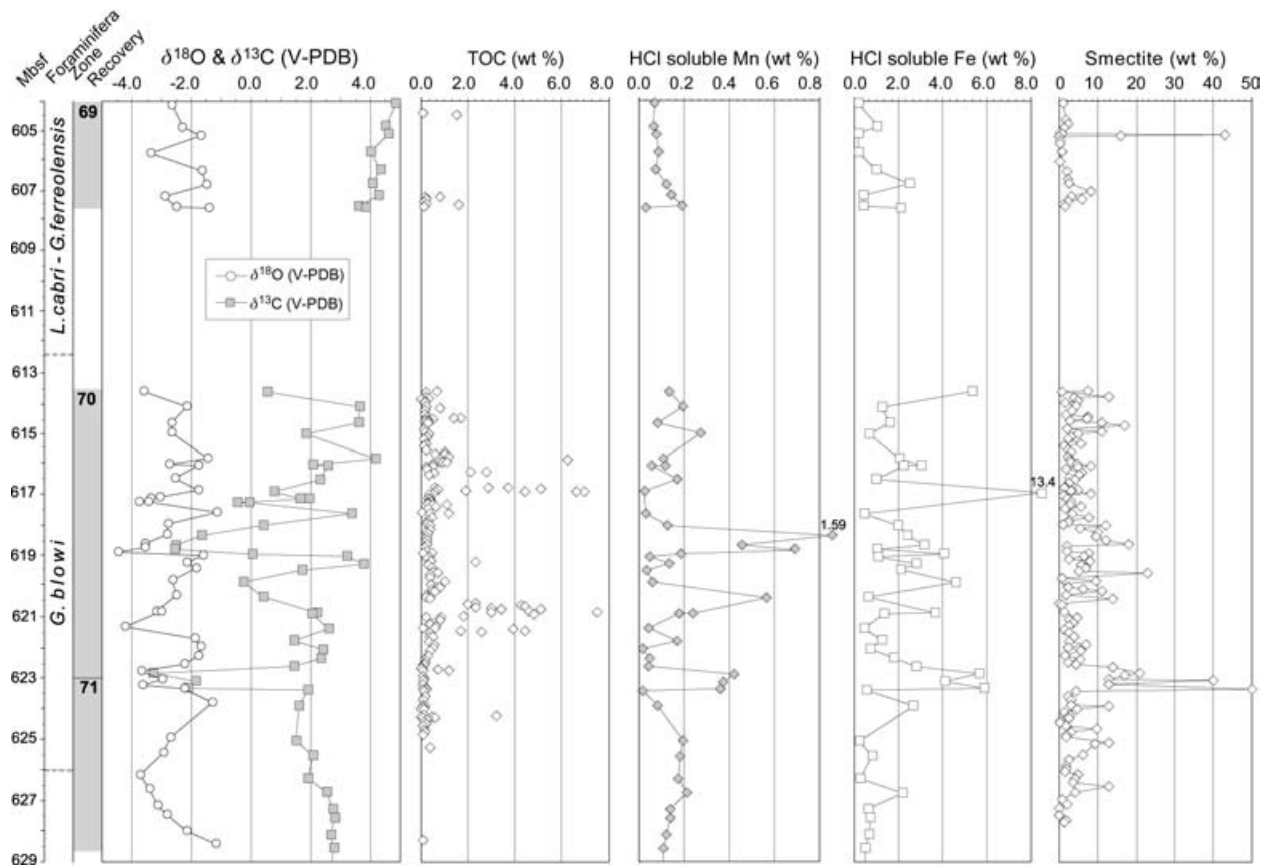
Figure 3. Detail of the $\delta^{18}O$ and $\delta^{13}C$ stratigraphy, TOC, smectite and trace element variation from the early Aptian *G. blowi* zone, DSDP site 463. The smectite data are from Mélières, Deroo & Herbin (1981).
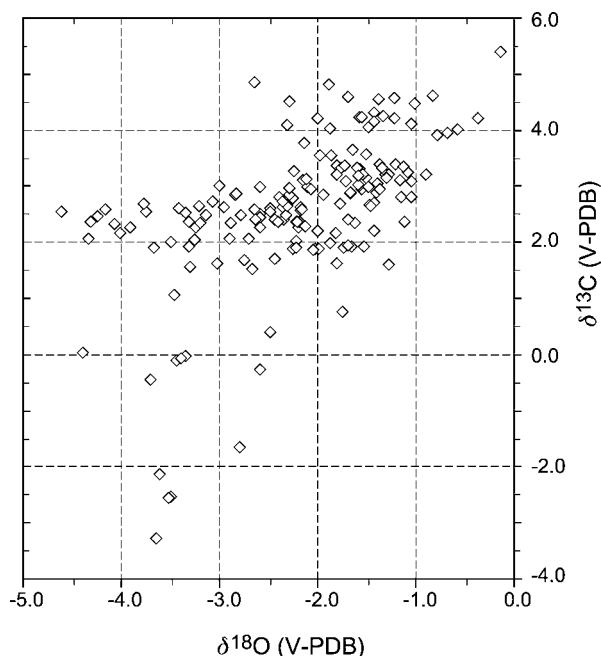

Figure 4. $\delta^{18}O$ and $\delta^{13}C$ cross-plot of carbonate samples from DSDP Site 463.

Herbin (1981). These data were produced by standard X-ray diffraction methods and represent the percentage of the total sediment rather than the clay fraction alone.

4. Diagenesis and isotope signatures

Diagenetic alteration causes a masking of any primary palaeoecological and/or palaeoceanographic signal. During diagenesis the primary calcite dissolves and is replaced by calcite that precipitates in isotopic equilibrium with the sediment column. As the carbonate at site 463 was formed in low latitudes, according to the model of Schrag, Depaolo & Richter (1995), it is likely to be highly susceptible to diagenesis as the oxygen isotopic composition of the primary biogenic calcite is likely to be far from equilibrium with the cold seawater encountered during early burial. Increasing temperatures, resulting from continued burial and further recrystallization, then cause the $\delta^{18}O$ value of the carbonate to drop below the $\delta^{18}O$ of the total carbonate. Temperatures measured in the lowermost part of the site were up to 49 °C (Theide *et al.* 1981). The measured $\delta^{18}O$ profile from site 463 is generally consistent with the model of Schrag, Depaolo & Richter (1995), whereby increasingly light oxygen isotope values in concert with increases in Mn and Fe, are observed in the lowest, Barremian, parts of the site. This is consistent with downhole deterioration of the state of preservation of the calcareous nannofossils and the progressive increase in the development of calcite cement (Thiede *et al.* 1981; Price & Hart, 2002). Thus, the sediments undoubtedly contain a

component emanating from diagenetic processes, and rather than absolute palaeotemperature determination, it is only the trends are considered herein (e.g. Clarke & Jenkyns, 1999), particularly as recent research on glassy foraminiferal calcite (Wilson, Norris & Cooper, 2002) has demonstrated that diagenetically compromised material can be wholly misleading (see also Pearson *et al.* 2001). Certainly reproducible trends have been recorded in sediments considerably more modified by diagenetic alteration (e.g. Jenkyns, Gale & Corfield, 1994; Hochuli *et al.* 1999). Similar trends to those seen in this study have been recorded from other successions which were derived from contrasting depositional and diagenetic settings (e.g. Bralower *et al.* 1999; Menegatti *et al.* 1998). The retention of primary δ^{13}C values is, however, more likely due to the buffering effect of carbonate carbon on the diagenetic system as this is the largest carbon reservoir (e.g. Scholle & Arthur, 1980).

As noted above, coincident with the siliceous limestones and tuffs, extremely light isotope values are recorded (Fig. 3). Pore waters within volcaniclastic-rich sediments have been shown to display a progressive decrease in δ^{18}O with burial depth, as a result of alteration of volcanic glass to smectite and zeolite (Aagard, Egberg & Smalley, 1989). This alteration process will provide an abundance of metals that would then be available to be incorporated into the carbonate. Within the studied interval siderite is common and considered by Mélières, Deroo & Herbin (1981) to be of diagenetic origin. As seen in Figure 3, the most negative δ^{18}O and δ^{13}C values coincide with smectite peaks. The smectite is related to the breakdown of volcanogenic material (Mélières, Deroo & Herbin, 1981). Alteration of volcaniclastic sediments does not, however, produce negative δ^{13}C porewaters. Both negative δ^{18}O and δ^{13}C porewaters can be generated by organic matter degradation by sulphate reduction (Sass, Bein & Almogi-Labin, 1991; Marshall, 1992). Nevertheless, within the model of Sass, Bein & Almogi-Labin (1991), organic matter concentrations were considerably higher and their model was based upon a closed diagenetic system. Given the global nature of the carbon isotope excursion and that a synchronous negative event is also recorded in organic carbon at site 463 (e.g. Bralower *et al.* 1999), it seems unlikely that local diagenetic alteration of the earliest Aptian sediments is the single mechanism accounting for the negative isotopic trends.

5. Discussion

The early Aptian positive carbon-isotope excursion has been linked directly with episodes of increased organic carbon burial (e.g. Weissert, 1989; Weissert & Lini, 1991). Models have been presented whereby the leaching of nutrients on coastal lowlands during a rise in sea-level (e.g. Haq, Hardenbol & Vail, 1988), possibly triggered by globally warmer temperatures,

resulted in increased ocean fertilization, productivity and an expansion of the oxygen minimum zone (e.g. Weissert, 1989; Leckie, 1989; Erbacher & Thurow, 1997; Erbacher *et al.* 2001). This in turn leads to both organic matter preservation and global sea-waters enriched in ^{13}C, habitat reduction and hence radiolarian extinction (Erbacher, Thurow & Littke, 1996) and decreases in planktonic foraminiferal diversity (Leckie, 1989; Premoli Silva & Sliter, 1999). Such faunal events are therefore synchronous with early Aptian organic-rich black shale deposition. A number of recent investigations have, however, demonstrated that the organic-rich units fall only partly (e.g. Luciani, Cobianchi & Jenkyns, 2001; Strasser, Caron & Gjermeni, 2001) or before (e.g. Bralower *et al.* 1994; Menegatti *et al.* 1998; Erba *et al.* 1999) the main positive segment of the δ^{13}C curve. Such an observation may simply reflect the fact that the δ^{13}C record is a global signal, whilst the black shale deposition is a local phenomenon. The early Aptian positive δ^{13}C excursion recorded in this study (Figs 2, 3) also clearly post-dates the peaks of total organic carbon. Menegatti *et al.* (1998), in a study of the Livello Selli, thus note that the positive δ^{13}C excursion cannot be simply driven by increased carbon burial, but instead propose that the preferential extraction of ^{12}C into the sedimentary carbon sink must be balanced by a flux of ^{12}C to the surface waters (Bralower *et al.* 1994). Sources of ^{12}C-enriched waters could be derived from the intensification and upwelling of intermediate water (e.g. Menegatti *et al.* 1998), an intensified flux of ^{12}C-rich riverine dissolved inorganic carbon (Weissert, 1989), or an increase in hydrothermal activity (e.g. Arthur *et al.* 1991; Bralower *et al.* 1994, 1999). Such a situation could therefore provide steady state conditions for deposition of the organic-rich levels, without a marked positive carbon isotope excursion.

Two pronounced negative carbon isotope excursions are observed immediately prior to the positive event at site 463 (Fig. 3). A single negative carbon isotope excursion has been observed prior to the OAE1a positive event from shallow water and pelagic limestones from the Pacific (Jenkyns, 1995), various Tethyan limestones (Menegatti *et al.* 1998; Luciani, Cobianchi & Jenkyns, 2001; Strasser, Caron & Gjermeni, 2001), including the Cismon reference section (Erba *et al.* 1999), and by Bralower *et al.* (1999) in Mexico. This negative carbon isotope excursion observed at site 463 is similar in scale to the coeval excursions recorded by Jenkyns (1995) and Jones & Jenkyns (2001) in pelagic carbonate, although not as great as that recorded in organic carbon (e.g. Gröcke, Hesselbo & Jenkyns, 1999). The brevity and magnitude of this negative carbon isotope excursion has been accounted for by an extremely voluminous rapid release of methane from gas hydrate (e.g. Opdyke *et al.* 2001; Jahren *et al.* 2001; Beerling, Lomas & Gröcke, 2002). Given that most CH$_4$ in these deposits is formed through bacterial

methanogenesis, it is extremely enriched in ^{12}C (δ^{13}C of $\sim -60‰$: Kvenvolden, 1998) and therefore provides a conceivable mechanism from a volumetric viewpoint.

The construction of a precise chronology is crucial in the determination of whether the release of methane from gas hydrate is a factor in accounting for the negative carbon isotope excursion. Based on both cyclostratigraphy and isotope stratigraphy, Opdyke *et al.* (2001) suggest that the negative perturbation recorded within the Cismon Apticore from Northern Italy (Erba *et al.* 1999) lasts approximately 140 000 years, certainly within limits described for other possible methane events (e.g. Hesselbo *et al.* 2000; Beerling, Lomas & Gröcke, 2002). The whole Selli interval, having a thickness of 5 m, lasts 700 000 years (Opdyke *et al.* 2001). Such a duration would not be inconsistent with the age constraints provided by the magneto-stratigraphic data of site 463 (Tarduno *et al.* 1989), whereby ~57 m of sediments are bracketed by Chrons M0 and ISEA, spanning 5.5 Myr (Channell *et al.* 1995). If methane is a causal mechanism, the repetition of the negative carbon excursions could be accounted for by multiple releases of methane. The intervening positive plateaus in δ^{13}C values could either reflect an interim cessation of methane outgassing or a balance between the input of methane and burial of ^{12}C-rich organic matter. The enrichment of Mn and Fe (Fig. 3) at this level, by dissociation of methane hydrate alone is, however, more difficult to explain.

Negative carbon isotope excursions have also been explained by the input of isotopically light (−6 to −7‰) volcanic CO_2 (e.g. Bralower *et al.* 1994; 1999). The data of Larson (1991) and Larson & Erba (1999) indicate an abrupt increase in spreading rates and increased mid-plate volcanism in the latest Barremian–early Aptian (*c.* 125–120 Ma). Most of the radiometric dates on the Ontong Java Plateau pre-date the base of the Selli level by about 2 Myr (Larson & Erba, 1999). However, basalts sampled from ODP Hole 807C from the Ontong Java Plateau and the tuffaceous limestones of site 463, both occurring within the *C. litterarius* nannofossil zone (e.g. Erba, 1994), attest to some volcanic activity continuing during this period.

The construction of the Ontong Java Plateau and other ocean plateaus certainly led to an increase in hydrothermal activity and an increase in CO_2 outgassing (Larson & Erba, 1999). Hydrothermal activity could conceivably account for the enrichment of the metals seen in Figures 2 and 3. Dispersion of metals into the ocean water–sediment system up to several thousands of kilometres from the hydrothermal vents has been observed in the modern ocean (e.g. Klinkhammer & Hudson, 1986; Roy, 1992; Sinton & Duncan, 1997). The coincidence of the negative δ^{13}C excursions and smectite peaks (the latter derived from the breakdown of volcanogenic material: Mélières, Deroo & Herbin, 1981), suggests a close relationship

between these two variables. Furthermore, Sinton & Duncan (1997) suggest that both the consumption of dissolved O_2 in seawater by oxidation of reduced metals during hydrothermal processes, as well as increased fluxes of particulate (biolimiting) metals inducing large fluctuations in primary productivity, could stimulate organic carbon fluxes and preservation on the seafloor. Moreover, Vogt (1989) postulated that massive outpourings of basalt, associated with increases in heat flow, could destabilize the water column, causing mixing of nutrient-rich deep waters to the surface, promoting high productivity and high C_{org} fluxes to the seafloor. Larson & Erba (1999) and Jones & Jenkyns (2001) also note a negative seawater strontium excursion beginning in the earliest Aptian, coincident with OAE1a. This negative Sr isotope excursion is interpreted to be related to increased hydrothermal activity associated with ocean-crust production at the mid-ocean ridges, although not necessarily plateau basalts (Jones & Jenkyns, 2001).

Further evidence of the influence of volcanic activity is also recorded by Erba (1994), who documents a widespread decline in nannoconids during the early Aptian, *G. blowi* foraminifera zone. Although the palaeoecological significance of nannoconids is not fully understood, a number of authors (e.g. Coccioni, Erba & Premoli Silva, 1992; Erba, 1994) have suggested that in comparison with modern nannoplankton, nannoconids may have been oligotrophic forms, inhabiting the lower photic zone. Erba (1994) suggests that during the early Aptian, a decrease in nannoconids, paralleled by accelerated rates in diversification of other forms of calcareous nannoplankton, stemmed from increased nutrient availability in surface waters inducing blooms of coccolithiphores at the expense of nannoconids. At site 463, a decline in nannoconids occurs within core 71 (Erba, 1994), immediately prior to the lowermost negative carbon isotope excursion. The overlying tuffaceous and organic-rich limestones are virtually barren of nannoconids (Erba, 1994), and similarly timed events are also recorded elsewhere in Pacific and Tethyan limestones. The synchroneity of the 'nannoconid crisis' suggests that the event was the result of a rapid turnover and increased nutrients in surface waters caused by the superplume eruptions (Erba, 1994).

Given the above arguments it is conceivable that the input of isotopically light volcanic CO_2, in concert with the intensification and upwelling of intermediate water enriched in ^{12}C (e.g. Menegatti *et al.* 1998) induced by volcanism (Vogt, 1989), could account for the negative carbon isotope excursions. Furthermore, both mechanisms have the potential to stimulate primary productivity. Such a model fits with the observation that the two largest negative δ^{13}C excursions are concomitant with increases in smectite and Mn concentrations and are succeeded by each of the two C_{org} peaks (Fig. 3). As noted above, coincident with these organic carbon-rich levels, δ^{13}C values become

more positive, possibly attesting to increased ^{12}C extraction from surface waters. Hence, in this section of the succession it certainly appears that positive carbon-isotope excursions can be linked directly with episodes of increased organic carbon burial. Aside from isotopic and modelling data, empirical evidence for methane input as a causal factor remains elusive and hence is more difficult to discount unconditionally.

The return to more positive carbon isotope values within the *L. cabri–G. ferreolensis* zone (Fig. 2) may reflect a cessation and/or reduction of ^{12}C input or increased extraction of ^{12}C from surface waters resulting in stronger carbon isotope gradients (e.g. Bralower *et al.* 1994). This positive segment of the $\delta^{13}C$ curve also appears to be coincident with radiolarian radiation (Erbacher, Thurow & Littke, 1996) and increases in planktonic foraminiferal diversity (Leckie, 1989; Premoli Silva & Sliter, 1999). Erbacher & Thurow (1997) and Leckie (1989) suggest that such a trend stems from initially high, but decreasing, nutrient leaching and productivity during the sea-level high stand (e.g. Haq, Hardenbol & Vail, 1988) and subsequent fall. These changes in sea-level lead to the development of new habitats through a reduction of the oxygen minimum zone and provide further evidence of increasing water column stratification during this interval.

The intervening low $\delta^{13}C$ values of the *G. algerianus* zone are also coincident with a shift in $\delta^{18}O$ values which decrease from $\sim -3.5‰$ in the *G. blowi* foraminifera zone to a minimum of -0.14 in the *G. algerianus* foraminifera zone (Fig. 2). This pattern is consistent with waters becoming cooler (a decrease of $\sim 10°C$) (or becoming more saline) from the early through to the late Aptian (Fig. 2). A similar pattern has been observed from the Aptian of the western Tethys (Hochuli *et al.* 1999). The decrease in $\delta^{13}C$ within the *G. algerianus* zone has also been recorded within Tethyan limestone successions and interpreted as an interval of cooling and a waning of C_{org} cycling (e.g. Weissert & Lini, 1991) and is thus in agreement with this study. The low $\delta^{18}O$ values of the *G. blowi* zone, if interpreted in terms of temperature, might be a response to enhanced CO_2 outgassing, whilst the cause of cooling may be related to a waning of outgassing coupled with enhanced organic-matter production and burial in the oceans, leading to a reduction in CO_2 levels (cf. Kuypers, Pancost & Sinninghe Damsté, 1999). Complexity is provided, however, by Bralower *et al.* (1999), who in a study of the late Aptian in Mexico, report a C_{org}-rich horizon, coincident with low $\delta^{13}C$ values of the *G. algerianus* foraminifera zone.

Following the late Aptian positive excursion, the observed $\delta^{13}C$ decrease may be related to the movement northwards of site 463 and consequent increased influence of upwelling, as opposed to a decrease in C_{org} cycling. As a result of the motion of the Pacific Plate during Albian times, site 463 was located at the edge of the equatorial palaeo-upwelling belt, indicated

by an increase of nannofossil indices of high fertility (Roth, 1981; Erba, 1992), notably absent from the Aptian part of the succession. The analysis of foraminiferal assemblages by Premoli Silva & Sliter (1999) also suggests a relatively weak or a completely disrupted thermocline during the middle Albian, an observation also made by Wilson & Norris (2001). Hence the upwelling of ^{12}C-enriched waters to the surface, exceeding any preferential extraction of ^{12}C initiated by enhanced surface water productivity, is considered as a plausible mechanism to account for the observed trend.

6. Conclusions

Data from DSDP site 463 reveal a double positive carbon isotope excursion within the Aptian. Despite differences in palaeoceanographic setting, the profile is remarkably similar to isotope records from Tethyan successions. The earliest Aptian positive event is preceded by an abrupt large negative isotope excursion confined to the *G. blowi* zone. Synchronous with this negative excursion are increased TOC values, in addition to large increases in Mn and Fe. Integration with biostratigraphic and magnetostratigraphic data supports the view that these organic-rich units are correlatable with the OAE1a. It is suggested that the input of isotopically light volcanic CO_2, in concert with the intensification and upwelling of intermediate water enriched in ^{12}C induced by volcanism, could account for the observed trends. A potential trigger may have been the destabilization of the water column and the prodigious CO_2 emissions associated with hydrothermal activity and the emplacement of the Ontong Java Plateau. A link between the formation of large igneous provinces and the release of methane hydrates enriched in ^{12}C is possible but yet to be established (Beerling, Lomas & Gröcke, 2002; Jahren, 2002). The ensuing positive carbon isotope excursion coupled with faunal evidence (e.g. Leckie, 1989; Erbacher & Thurow, 1997) suggests that the Aptian interval was characterized by initially high productivity and weak but increasing ocean stratification resulting in strong carbon isotopic gradients and ^{13}C-enriched surface waters. The decrease in $\delta^{13}C$ within the *G. algerianus* zone is interpreted as an interval of cooling and possibly a waning of C_{org} cycling. Following the late Aptian positive excursion, the observed $\delta^{13}C$ decrease is considered to be related to the increasing influence of upwelling introducing isotopically light carbon to the surface, arresting the stratified oceanic conditions of the Aptian and early Albian. The upwelling of ^{12}C-enriched waters would have to have exceeded any extraction of ^{12}C initiated by enhanced surface water productivity.

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