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Stable isotope analysis of the Cenomanian–Turonian (Late Cretaceous) oceanic anoxic event in the Crimea

Jodie K. Fisher [a,*], Gregory D. Price [a], Malcolm B. Hart [a], Melanie J. Leng [b]

[a] *School of Earth, Ocean and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, Devon PL4 8AA, UK*
[b] *NERC Isotope Geosciences Laboratory, British Geological Survey, Nottingham NG12 5GG, and School of Geography, University of Nottingham, Nottingham, NG7 2RD, UK*

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Abstract

Carbon and oxygen isotope data from Cenomanian–Turonian sediments from the southwest of the Crimea are presented. The sediments consist of limestones, marls and organic-rich claystones, the latter with total organic carbon values up to 2.6 wt. %, representing Oceanic Anoxic Event 2. A shift to more negative $\delta^{18}O$ values through the uppermost Cenomanian into the lowermost Turonian may be the result of warming; however, petrographic analysis shows that the samples have undergone a degree of diagenetic alteration. The carbon isotope data reveal a positive excursion from ~2.7‰ to a peak of 4.3‰ at the Cenomanian/Turonian boundary; values then decrease in the early Turonian. This excursion is comparable to those of other Cenomanian–Turonian sections, such as those seen in the Anglo-Paris Basin, and is thought to be due to global changes in the oceanic carbon reservoir. On this curve are a number of negative $\delta^{13}C$ excursions, just below the Cenomanian/Turonian boundary. It is suggested that these negative excursions are associated with the uptake of light carbon derived from the oxidation and deterioration of organic material during localised exposure of the sediments to oxic or meteoric diagenetic conditions, possibly during sea-level fluctuations.

Keywords: Cenomanian/Turonian boundary; Crimea; Carbon isotopes; Oxygen isotopes; Foraminifera

1. Introduction

There are a number of oceanic anoxic events (OAEs) throughout the Cretaceous Period, from the early Aptian (OAE 1) to the Campanian (OAE 3). Particularly well researched is OAE 2 and the organic-rich black shales deposited during this interval at the Cenomanian/Turonian boundary (CTB) (Schlanger and Jenkyns, 1976; Jenkyns, 1980; Hart and Bigg, 1981; Arthur et al., 1987; Schlanger et al., 1987; Jarvis et al., 1988; Paul et al., 1999; Keller et al., 2001).

Two main models exist for black shale deposition: (1) increased productivity, the increased flux of organic matter to the sea floor exceeding the rate of oxidation (e.g., Parrish, 1995); and (2) enhanced preservation of organic matter on the sea floor (e.g., Tyson, 1995), formed due to the expansion of the oxygen minimum zone (OMZ). Precise mechanisms are, however, still controversial. The dominant mechanism may be related to the palaeoceanographic setting in which deposition occurred (Kuhnt and Wiedmann, 1995).

Associated with these organic-rich sediments is a global positive carbon isotope anomaly (Scholle and Arthur, 1980; Pratt and Threlkeld, 1984; Arthur et al., 1988; Hart et al., 1993; Gale et al., 1993; Jenkyns et al., 1994; Voigt and Hilbrecht, 1997). This excursion has a distinctive profile and has been used for global correlation. In addition to marine carbonates, a carbon excursion has also been described from marine organic carbon and terrestrial organic carbon (e.g., Hasegawa, 1997), indicating the linkage between the ocean-atmosphere CO_2 reservoirs.

At the time of the CTB, widespread faunal diversification and extinction occurred (e.g., Hart, 1996), sea levels increased rapidly (Haq et al., 1987; Hallam, 1992) and global temperatures were significantly warmer than today (Barron, 1983;

* Corresponding author.
E-mail address: jkfisher@plymouth.ac.uk (J.K. Fisher).

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Kaiho, 1994), representing an acme for the Late Cretaceous (e.g., Huber, 1998; Clarke and Jenkyns, 1999). It has been suggested that atmospheric levels of CO_2 were 3–12 times higher than at present (Berner and Kothavala, 2001) and both the increase in temperature and rise in sea level have been linked to the anomalous amount of oceanic volcanism during the mid-Cretaceous (Larson, 1991; Kerr, 1998).

Using high-resolution carbon and oxygen isotope analyses of marine carbonates, together with measurements of total organic carbon (TOC), Rock-Eval pyrolysis and petrographic analysis, fluctuations in the global carbon reservoir can be studied, and the environment of deposition assessed. This study is aimed at providing a better understanding of environmental conditions at the CTB in the eastern Tethyan region, much previous work having focused on the west. This enables us to assess changes in the partitioning between carbonate and organic carbon sinks associated with environmental changes that occurred over the CTB.

2. Geological location and depositional setting

The Crimean Peninsula is located in the south of the Ukraine, on the northern coast of the Black Sea (Fig. 1). The peninsula comprises a range of mountains in the south that make up one-fifth of the region, whilst the greater, northern part consists of a large plain. The mountains were formed during the Cimmerian (Triassic–Jurassic) and Alpine (Tertiary) orogenies, and extend for 200 km from the northeast to the southwest, with a maximum altitude of 1500 m. The Cretaceous sediments are found within the Crimean Mountains and further north on the Crimean Plain. These sediments range from shallow marine deposits in the north to deeper deposits in the south (Kopaevich and Kuzmicheva, 2002). This paper concentrates on the outcrops in the mountains of the south. Recent research has focused on a number of Cretaceous sections in this area, and work on the stratigraphy of this region has been presented by Naidin (1981), Naidin and Alekseev (1981), Alekseev (1989), Alekseev et al. (1997), Gabdullin et al. (1999), Gale et al. (1999), Kuzmicheva (2000) and Kopaevich and Kuzmicheva (2002), with data on the isotope stratigraphy and geochemistry published by Naidin and Kiyashko (1994a,b). Our study focuses on the sediments found at Aksudere. The section lies about 30 km south of Simferopol and just north of the Kacha River. It is one of the most southerly and complete of the Cenomanian–Turonian sections in the region.

3. Stratigraphy of the Aksudere section

Within southwest Crimea, the Cenomanian comprises ~50–60 m of rhythmically-bedded (decimetre-scale) marly chalks, which show an overall decrease in the clay component up through the Cenomanian, and contain a number of erosion surfaces, seen across the region (Gale et al., 1999). The section studied at Aksudere includes Upper Cenomanian and Lower Turonian sediments, spanning the *Rotalipora cushmani* Total Range Zone (TRZ), *Whiteinella archaeocretacea* Partial Range Zone (PRZ) and *Helvetoglobotruncana helvetica*

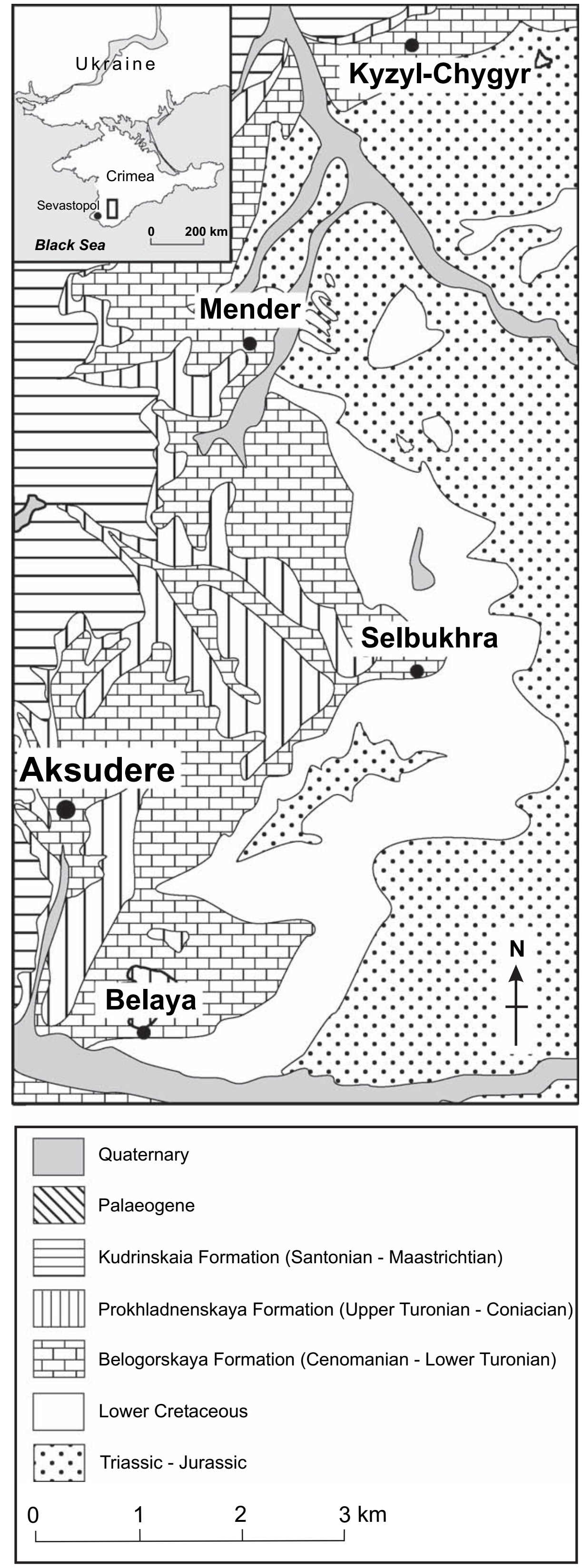

Fig. 1. Study area, showing outcrop of Upper Cretaceous sediments and location of Aksudere and other sites with Cenomanian–Turonian sections referred to in text (modified from Kopaevich and Kuzmicheva, 2002).

TRZ. For age determination of the sediments, the planktonic foraminiferal biozonation of Robaszynski and Caron (1995) was used.

The Upper Cenomanian makes up the lowermost 5 m of the section and is predominantly composed of carbonate-rich white limestones (Fig. 2). These limestones are terminated after 3.5 m by an erosion surface, at the top of the *Rotalipora cushmani* Foraminiferal Biozone. This surface is well documented by many researchers (Alekseev et al., 1997; Gale et al., 1999; Kopaevich and Kuzmicheva, 2002) and occurs in several sections across the Crimea. Gale et al. (1999) suggested that it is equivalent to the "sub-plenus erosion surface" of Jeffries (1963), seen in the Anglo-Paris Basin and the "Fazieswechsel" of Meyer (1990) in northern Germany.

Above this surface, the sediments vary greatly across the region. During the mid–late Cenomanian, the region was affected by the opening of the Black Sea and the southern margin of the Crimea developed as a continental slope of the passive margin. This had a significant effect on the water-depth of the area, the southern areas becoming significantly deeper than their northern counterparts. In the more northerly sections, such as Mender and Kyzyl-Chygyr (Fig. 1), the sediments are more condensed and incomplete, with deposits representing the *W. archaeocretacea* PRZ completely missing (Kopaevich and Kuzmicheva, 2002). Further south, at Selbukhra, the *W. archaeocretacea* PRZ is present, although only 1 m thick. The most southerly sections, at Aksudere and Belaya, however, contain a much thicker sequence (~2.5 m) of *W. archaeocretacea* PRZ sediments. Consisting of sandy marls, marls and organic-rich claystones, these sediments grade upwards into marls and limestones of early Turonian age. Aksudere is, therefore, one of the most complete sections in southwest Crimea, although foraminiferal data indicate that a small stratigraphic gap exists at the late Cenomanian erosion surface discussed above (Kopaevich and Kuzmicheva, 2002).

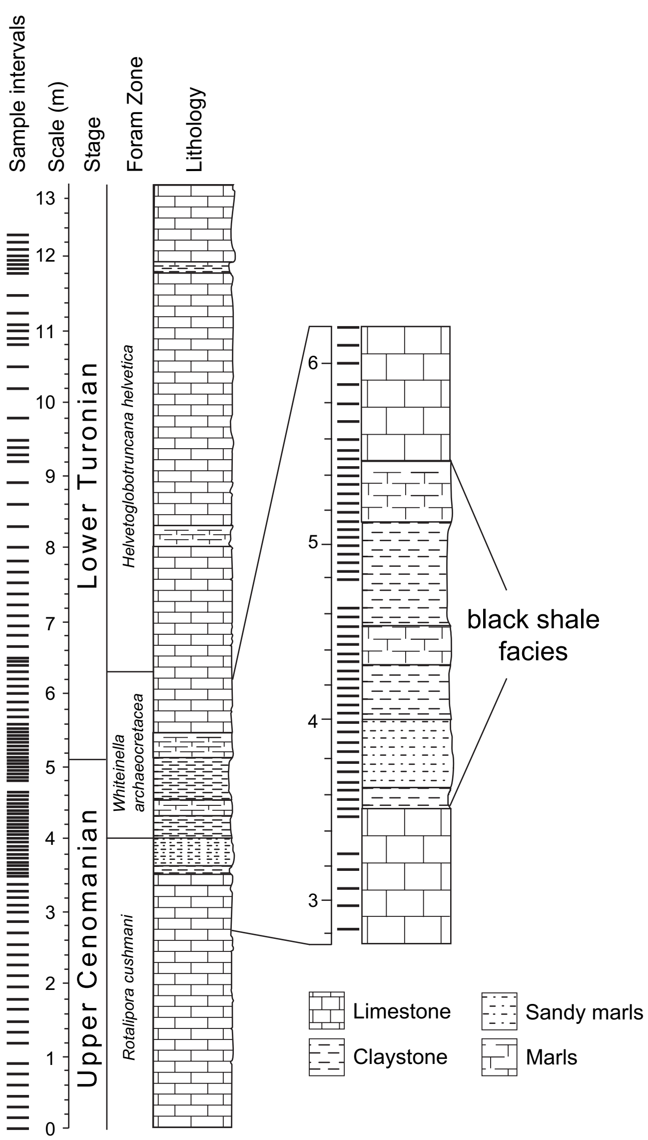

Fig. 2. Stratigraphical log of Cenomanian–Turonian sediments seen at Aksudere, based upon Alekseev et al. (1997) and this study. Foraminiferal biozonations after Robaszynski and Caron (1995).

At Aksudere, the late Cenomanian erosion surface is directly overlain by a 10-cm-thick dark claystone that grades upwards into a 40-cm-thick yellow, quartz-rich sandy marl. Gale et al. (1999) suggested that this was equivalent to Bed 3 of the Plenus Marls, the top of this bed marking the base of the *W. archaeocretacea* PRZ. This is overlain by a second claystone 30 cm thick, and grading up into 20 cm of pale grey marl. Above this lies a third claystone, 60 cm thick and laminated; it contains some thin quartz-sand layers. These dark claystones were described by Gale et al. (1999) and Naidin and Kiyashko (1994a,b) as organic-rich with TOC values up to 9 wt.%. Carbonate values were seen to be no lower than 45%, and as much as 65% in these beds (Naidin and Kiyashko, 1994a). The top of this bed marks the Cenomanian/Turonian boundary, defined by previous workers at Aksudere (e.g., Kopaevich and Kuzmicheva, 2002) by the first appearance of *Dicarinella hagni*. This claystone then grades into paler marls and limestones of Turonian age, as the sediments become less clay-rich. These sediments adjacent to the CTB can be defined as a "black shale facies", and are known locally as the Aksudere Beds (Alekseev et al., 1997). They are thought to be the local expression of OAE 2 (Naidin and Kiyashko, 1994a,b; Kopaevich and Kuzmicheva, 2002) (Fig. 2).

4. Material and methods

The Aksudere section was sampled at 5 to 15 cm intervals throughout the 12.5 m section to obtain 109, samples spanning the Upper Cenomanian–Lower Turonian *Rotalipora cushmani–Helvetoglobotruncana helvetica* foraminiferal biozones. The samples were disaggregated using standard techniques: the softer marls by soaking in a 10% solution of sodium hexametaphosphate (Calgon), and the harder samples using the solvent method of Brasier (1980). All samples were washed over a 63 μm sieve and dried at 40 °C. A portion of the fine (<63 μm) fraction was kept for whole-rock (fine-fraction) isotope analysis, whilst the >63 μm fraction was used for foraminiferal analysis. After drying, the fine-fraction samples were ground and homogenised in an agate pestle and mortar. Samples were processed a second time in order to obtain fine-fraction samples for treatment with 5% sodium hypochlorite, in order to remove any organic matter from the samples.

Oxygen and carbon isotope analyses on the fine-fraction carbonate were undertaken using standard offline vacuum methods (McCrea, 1950) on samples both treated and untreated with 5% sodium hypochlorite, using a dual-inlet stable isotope mass spectrometer.

The ratios are presented in relation to the heavier isotope using the δ notation and the VPDB scale. Analytical precision, based on duplicate samples, was typically $<0.1‰$ for both oxygen and carbon isotope ratios. Consistency of results was achieved by comparison of laboratory standards against NBS-19.

Analysis to determine the TOC was carried out using a TOC 5000 carbon analyser. A small amount of sample was crushed and homogenised in an agate pestle and mortar, and analysed in a solid sample module 55M-5000A. Samples were duplicated where possible and reproducibility was generally better than 0.1%. All results are given as wt. % TOC. Samples were also analysed with a Rock-Eval 6, at the University of Neuchâtel, to determine the source of organic matter within samples with TOC values >0.5 wt. %.

Thin sections were obtained from a selection of samples throughout the succession, in order to undertake petrographic analysis of the sediments and to observe any diagenetic alteration of the samples.

5. Results

5.1. Petrographic analysis

Thin sections of wackestones and mudstones from the Cenomanian limestones (Fig. 3A) reveal a diverse and abundant microfauna. This is characterised by single-keeled, large planktonic foraminifera such as *Rotalipora cushmani*, *Rotalipora greenhornensis* and *Praeglobotruncana gibba*, and smaller, shallower-dwelling foraminifera, such as *Heterohelix moremani*, *Hedbergella delrioensis*, *Hedbergella planispira*, *Whiteinella* spp. and *Guembelitria cenomana*. These are indicative of the Upper Cenomanian *R. cushmani* TRZ. This microfauna can

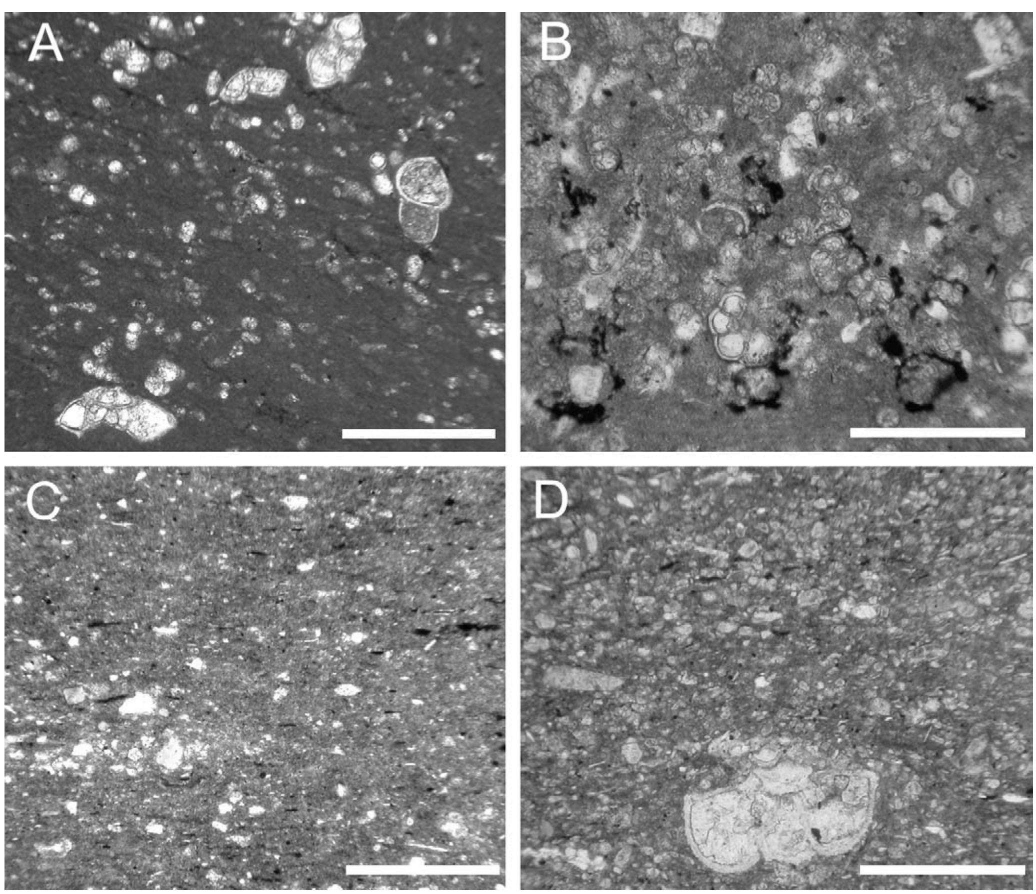

Fig. 3. Examples of lithologies and microfauna throughout the Aksudere section. A, wackestone from Cenomanian limestone, 1.8 m below the CTB. Diverse, high-abundance foraminiferal assemblage including *Rotalipora cushmani* indicating the *R. cushmani* Biozone. Infilling and recrystallisation of foraminiferal tests with sparry calcite is prevalent. B, wackestone from marls 75 cm below the CTB, showing a reduction in diversity of foraminifera and loss of keeled genus, *Rotalipora*. Dominated by *Hedbergella* spp. and *Whiteinella* spp., indicating the *Whiteinella archaeocretacea* Biozone. Again, specimens show poor preservation, with infilling and recrystallisation of tests. C, laminated claystone from the CTB, almost devoid of foraminifera. Quartz and glauconite present. D, packstone from Turonian limestones, 6.7 m above the CTB, showing a return to higher diversity and abundance. Large foraminifera return and new keeled species, such as *Helvetoglobotruncana helvetica*, are seen, indicating the *H. helvetica* Biozone. Infilling and recrystallisation of foraminiferal tests is prevalent. Scale bars represent 500, 200, 400 and 500 μm respectively.

be seen in Fig. 3A, where abundant recrystallisation of the test walls, and infilling of the tests with sparry calcite, can be seen.

Within the marls below the CTB (Fig. 3B), a very different assemblage from that of the underlying Cenomanian limestones is seen. These wackestones are dominated by small planktonics, predominantly *H. moremani* and *H. delrioensis*. There are no larger planktonics and the genus *Rotalipora* has disappeared completely, marking the *Whiteinella archaeocretacea* PRZ. The preservation of species is generally poor, showing high levels of recrystallisation and infilling. Small grains of glauconite and quartz are also seen.

The thick claystone layer, lying directly below the CTB, appears to be nearly devoid of any foraminifera (Fig. 3C); however, fine laminations within the claystone are apparent. Quartz and glauconite are present, concentrated in thin lenses within the claystone.

Another foraminiferal assemblage is seen in the Turonian limestones (Fig. 3D). A large increase in the number of specimens and species appear preserved in these packstones. They are dominated by small *H. delrioensis*, *Whiteinella* spp. and *H. moremani*, with less abundant large planktonic foraminifera present, such as species of *Praeglobotruncana*. These sediments also contain the first occurrences of the keeled species, *Dicarinella hagni* and *Helvetoglobotruncana helvetica*, characteristic of the *H. helvetica* TRZ. The preservation of the foraminifera is again poor, sparry calcite commonly infilling the recrystallised tests. Fragments of inoceramid bivalves are also seen throughout the *H. helvetica* Zone.

5.2. TOC

TOC values (Fig. 4) are low in the Upper Cenomanian limestones, reaching no more than 0.1%. A small increase, to 1.0%, is seen in the lowermost thin claystone; however values remain low ($<0.5\%$) through the overlying sandy marl, and into the *W. archaeocretacea* PRZ. They increase rapidly at the base of the upper claystone unit, peaking at 2.3%, 0.5 m below the CTB. The values then decrease back down to 0.2% over 0.1 m, prior to two subsequent peaks in this unit. TOC increases again to 2.0%, 0.3 m below the CTB, decreases to 0.8% and finally increases to the largest value of 2.6%, at the CTB. They then return to near zero, 0.15 m above the CTB, and remain low through the *H. helvetica* TRZ of the Lower Turonian.

These TOC values show that organic-rich samples lie in the *W. archaeocretacea* PRZ, in the upper claystone (from 0.7 m below the CTB to just below the CTB) and, in one sample, in the lowermost claystone at the top of the *R. cushmani* TRZ. All samples with TOC >0.5 wt. % were analysed with Rock-Eval pyrolysis. The data obtained are shown in Fig. 5. They indicate that the samples contain mixtures of Types II and III kerogen (organic matter derived from algae, bacteria and marine zooplankton, with some higher plant contribution), as indicated by hydrogen indices ranging from 142 to 321 mg HC/g TOC. The hydrogen indices appear to increase with organic richness, indicating a higher proportion of marine-derived organic matter in the organic-rich layers of the claystones, seen 0.5 m and 0.3 m below the CTB and at the CTB.

5.3. Carbon and oxygen isotope ratios

The analytical data are presented in Figs. 4 and 6. The Upper Cenomanian (*R. cushmani* TRZ) has $\delta^{13}C$ background values of $\sim 2.7‰$. These values decrease slightly to 1.9‰ in the lowermost claystone of the Aksudere Beds, then increase rapidly to a peak at the top of the sandy marl at the very top of the *R. cushmani* TRZ. Values then plateau through the *W. archaeocretacea* PRZ at around 3.3‰, peaking again at 4.4‰ at the top of the upper claystone unit, at the CTB. $\delta^{13}C$ values then decrease slowly through the rest of the *W. archaeocretacea* PRZ and into the *H. helvetica* TRZ of the Lower Turonian, to steady values of $\sim 2.9‰$ at a level 1 m above the CTB.

The $\delta^{18}O$ values show greater fluctuations than the carbon isotope data. $\delta^{18}O$ values of $\sim -3.4‰$ are observed in the Upper Cenomanian, up to the base of the sandy marl. After this point, values decrease rapidly to $-5.0‰$ at the top of the sandy marl, the top of the *R. cushmani* TRZ. Values then fluctuate between -4.0 and $-5.0‰$ through the whole *W. archaeocretacea* PRZ before decreasing slowly, as the limestones become less marly, to background values of $\sim -3.8‰$ at 3.5 m above the CTB. These oxygen and carbon isotope values are in the same range as those of Naidin and Kiyashko (1994a,b).

In addition to these main trends, however, four negative excursions not recorded previously are particularly prominent on the $\delta^{13}C$ curve. The lowest is in the sandy marl 1.4 m below the CTB, in the *R. cushmani* TRZ; the other three lie in the upper thick claystone unit of the *W. archaeocretacea* PRZ, at 0.6, 0.45 and 0.1 m below the CTB, respectively. In order to rule out contamination of the samples by organic matter, they were treated with sodium hypochlorite, as described above. The results for both treated and untreated samples are nearly identical, ruling out contamination.

6. Discussion

Both carbon and oxygen isotope profiles show excursions that are comparable to those seen elsewhere across the CTB. Fig. 7 shows the correlation of the carbon isotope curve with the profile of Gale et al. (1993) from Eastbourne, UK. The shape of the latter is identical to those of Paul et al. (1999), Keller et al. (2001) and Tsikos et al. (2004). As indicated above, Gale et al. (1999) suggested that the sandy marl unit lying directly above the erosion surface is probably equivalent to Bed 3 of the Plenus Marls, the erosion surface itself being the equivalent of the "sub-plenus erosion surface". At Eastbourne, the carbon excursion begins at the base of the Plenus Marls. In the Crimea, it begins above the erosion surface. This may be due to the longer duration of the erosion event in the Crimea (see below). Both profiles increase rapidly to an initial peak at the top of the *Rotalipora cushmani* TRZ. Plateauing within the lower part of the *Whiteinella archaeocretacea* PRZ, they both record a second peak around the CTB. Both

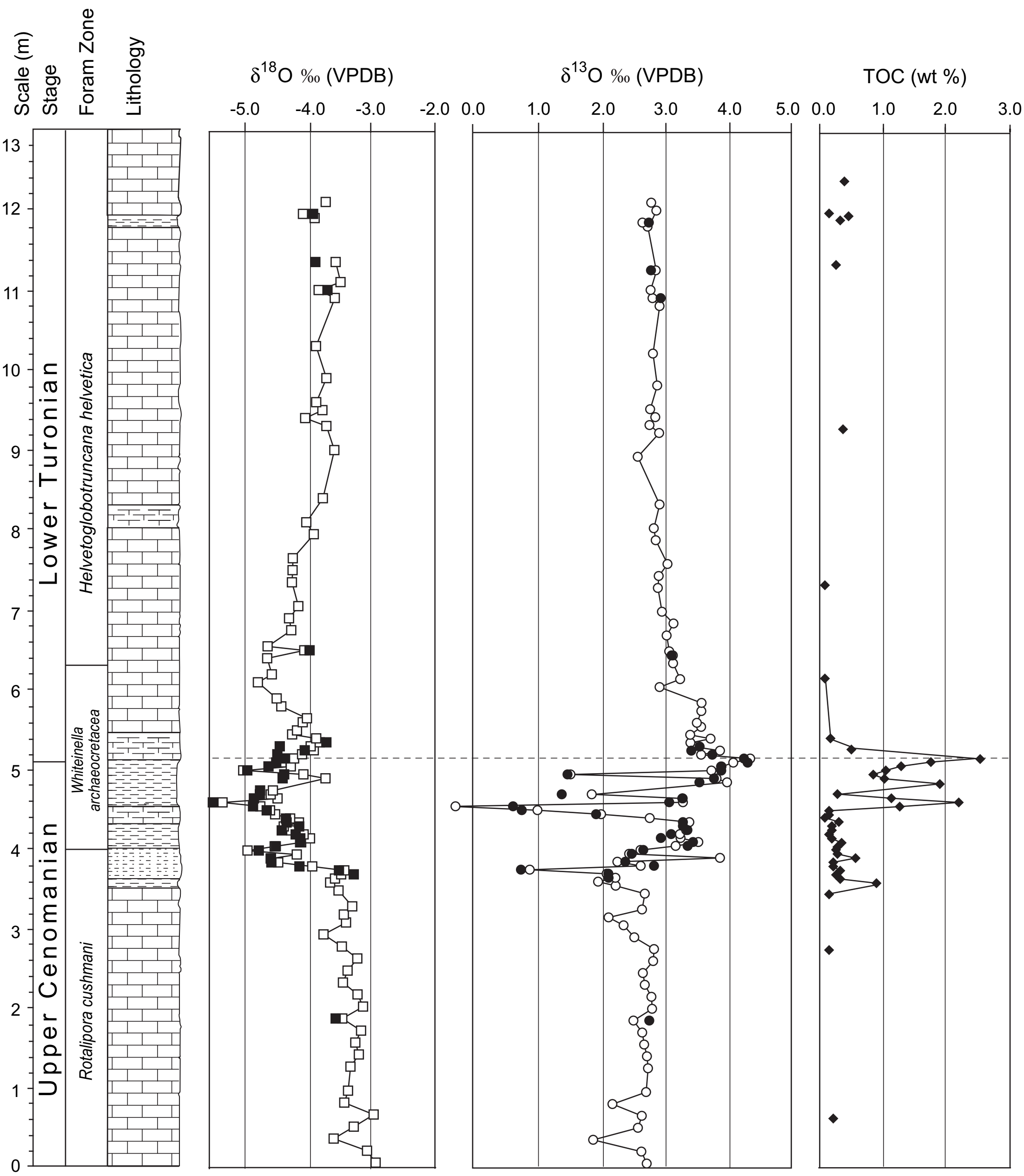

Fig. 4. Carbon and oxygen isotope results of fine-fraction (<63 μm) samples of both untreated (open squares and open circles) and treated (organic carbon removed) (filled squares and filled circles) samples, and TOC results from Aksudere. Foraminiferal biozonation after Robaszynski and Caron (1995).

excursions then decrease slowly to reach pre-excursion values in the *Helvetoglobotruncana helvetica* TRZ. Regionally, the data show that both Crimean and northwest European sections may have undergone similar palaeoceanographic change around the CTB, the correlative erosion surface possibly indicating a regional European regression. Foraminiferal data, however, indicate that the duration of this hiatus is longer in the Crimea than in the Anglo-Paris Basin (Kopaevich and Kuzmicheva, 2002). The increased duration in the Crimea was probably due to large-scale tectonics, leading to uplift and prolonged exposure of the sediments to erosion. Tectonic rebuilding of the region during the Albian–Cenomanian and the rifting and/or extension in the Crimean and Caucasus region (Nikishin et al., 1997) possibly contributing to this.

In the Aksudere section the oxygen isotope data show a sharp decrease in values coincident with a distinct increase in the carbon isotope values. This may indicate increased sea-surface temperatures around the time of the CTB. As noted above, evidence suggests that sea-surface temperatures were higher during the mid-Cretaceous, reaching an all time high for the Phanerozoic in the Turonian. The low values and rapid fluctuations seen in the $\delta^{18}O$ profile for the Crimea are, however, possibly consistent with diagenesis of the sediments. Petrographic observations support this, showing sparry calcite cement and an infilling of foraminiferal tests to be present throughout the succession (Fig. 3A–D), indicating that diagenesis affected sediments throughout the section.

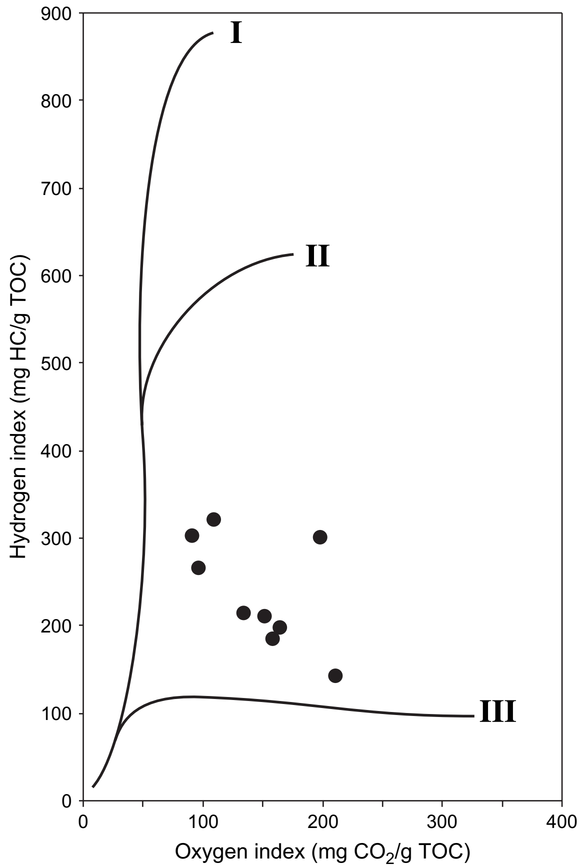

Fig. 5. Van Krevelen plot indicating nature and source of organic matter in organic-rich claystones at Aksudere.

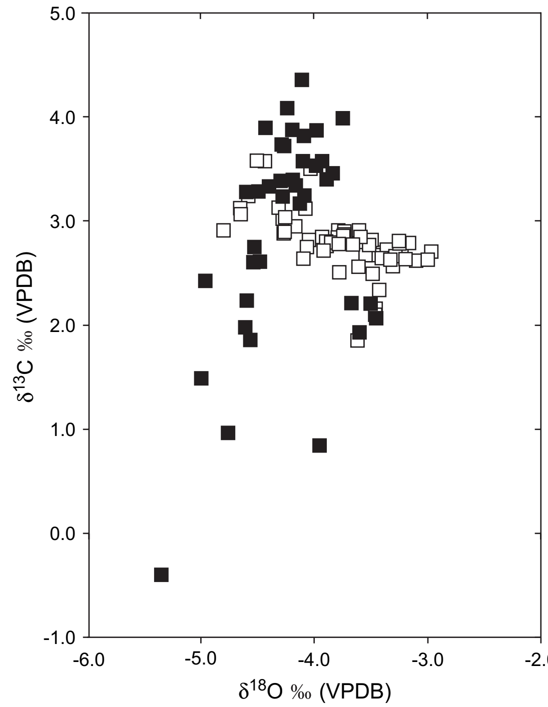

Fig. 6. Cross-plot of oxygen and carbon isotopes from fine-fraction samples of both treated (organic carbon removed) and untreated (organic carbon present) samples. Carbonate samples, open squares; "black shale facies" samples, closed squares.

During diagenesis, primary calcite can be replaced by calcite in equilibrium with the diagenetic environment, whether within the sediments during burial, or on the sea floor. Oxygen isotopes are more susceptible to diagenesis than the more robust carbon isotopes. This is partly due to the large temperature-related fractionation seen in oxygen isotopes. Scholle (1977) found untectonised European chalks to have average $\delta^{18}O$ values of −2.9‰, ranging generally between −2 and −4‰. Diagenesis of chalks, however, can lead to much lighter values, as low as −8‰ (Jørgensen, 1987). Using a standard temperature equation (e.g., Anderson and Arthur, 1983) would suggest an increase of ocean temperatures of ~6 °C as the values decrease from −3.5 to −5‰ at Aksudere. A similar trend is seen in other Cenomanian–Turonian sections (e.g., Jenkyns et al., 1994). However, these values equate to temperatures of ~30–35 °C, considerably warmer than temperatures postulated for the mid-Cretaceous (Barron, 1983) at a palaeolatitude for the Crimea of ~35 °N (Smith et al., 1994).

It is likely, therefore, that the $\delta^{18}O$ results at Aksudere were affected by diagenesis shifting the primary signal to more negative values. A cross-plot of $\delta^{13}C$ and $\delta^{18}O$ data (Fig. 6) also shows a weak positive correlation typical of sediments thought to have been affected by meteoric diagenesis (e.g., Allan and Matthews, 1982; Marshall, 1992; Buonocunto et al., 2002).

The positive carbon isotope excursion, also seen in isotope data from organic carbon (Naidin and Kiyashko, 1994a,b), can be interpreted as a response to the abnormally high burial rates of organic carbon that characterise the Cenomanian–Turonian sediments seen globally and at Aksudere. Rock-Eval data indicate that the organic matter in the organic-rich claystones at the CTB of Aksudere is autochthonous, marine-derived carbon predominantly from phytoplankton, with some contribution from higher plant matter.

As described above, in addition to the long-term trends in the isotope profiles, a number of negative carbon isotope events are clearly seen in the carbon isotope data, and also to a smaller extent in the oxygen isotope data. It is possible that negative values arise from contamination of the carbonate from organic matter. However, the similarity between carbon and oxygen isotope values of both the untreated samples and the samples with organic material chemically removed rules out this possibility. It can be postulated, therefore, that the negative values are a result of environmental effects and/or diagenesis.

6.1. Environmental effects

Negative carbon excursions have been considered to be a result of changes in ocean circulation and chemistry. Recent work, however, has focused on the effect of the introduction of isotopically light carbon into the system from magmatically-derived CO_2 and methane (e.g., Bralower et al., 1994; Jahren et al., 2001; Price, 2003).

There is a great deal of evidence for volcanism during the Cretaceous and around the CTB (Kerr, 1998). Widespread ocean plateau volcanism (e.g., the Caribbean-Colombian and Ontong Java plateaus in the Pacific, and the Kerguelen Plateau

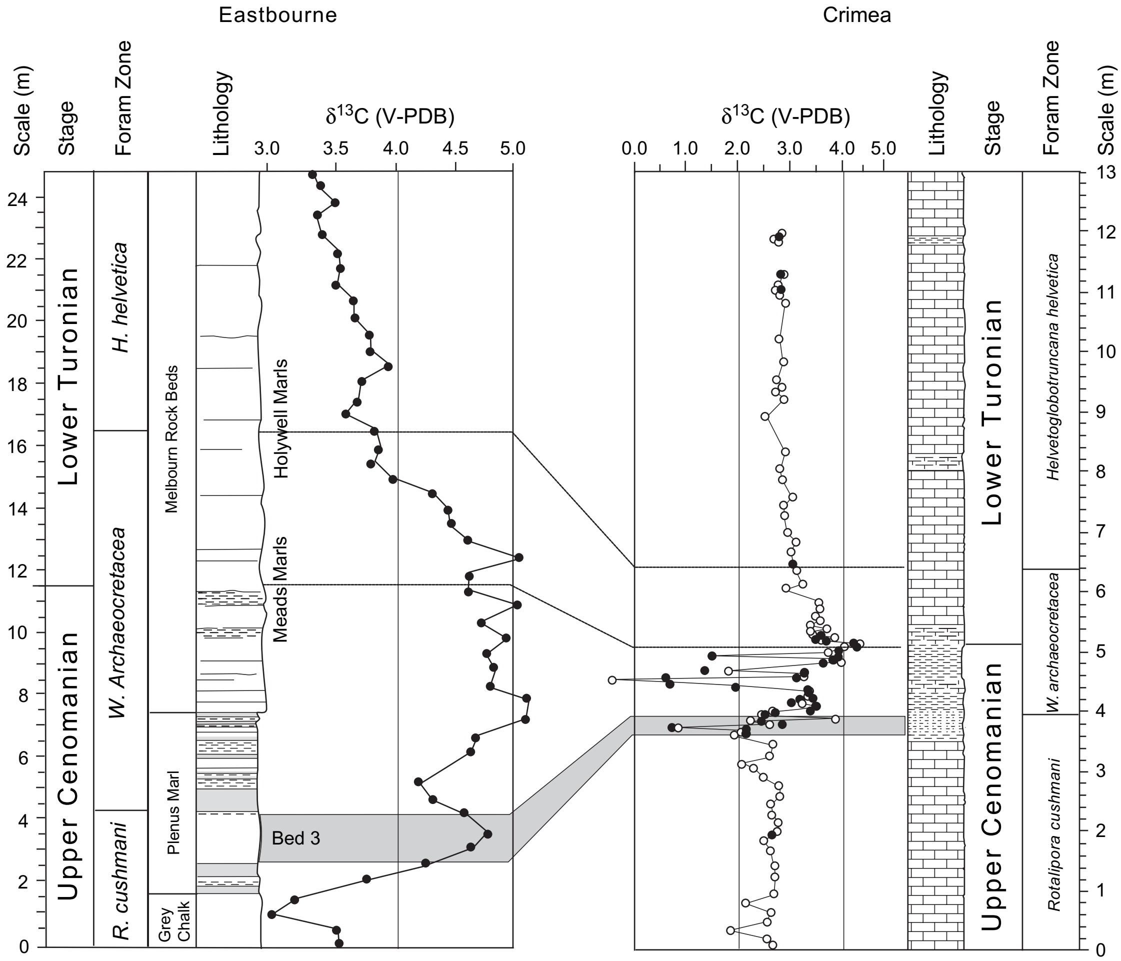

Fig. 7. Correlation of carbon isotope results from this study with carbon isotope profile from Eastbourne, UK from Gale et al. (1993). Eastbourne bed number assignment according to Gale et al. (1993). Eastbourne foraminiferal biostratigraphy from Keller et al. (2001), Crimean biozonation after Robaszynski and Caron (1995). Crimean profile: open circles, untreated values; filled circles, chemically treated (organic carbon removed) values.

in the Indian Ocean) caused the expulsion of isotopically light (typically 6–7‰) carbon into the atmosphere and carbon cycle. Volcanism has been suggested to account for negative isotope shifts in the early Aptian (OAE 1a) (e.g., Bralower et al., 1994; Larson and Erba, 1999; Price, 2003). However, no direct effect upon carbon isotope profiles has been suggested for the CTB.

Methane is also a viable source of light carbon (isotopic values ~−60‰), able to produce the rapid and large negative shifts observed at a number of OAEs (e.g., the Toarcian and Aptian OAEs) (Hesselbo et al., 2000; Jahren et al., 2001; Beerling et al., 2002). Negative excursions have been seen prior to the positive excursion at the CTB (e.g., Pratt, 1985; Arthur et al., 1988; Hasegawa, 1997), although none has been convincingly attributed to methane hydrate dissociation.

In the Crimean section, the negative carbon isotope events occur during the positive isotope excursion, as opposed to preceding it. Negative excursions, similar to those seen in the Crimea, are observed at the Devonian Frasnian/Famennian boundary (364 Ma), interrupting the positive $\delta^{13}C$ excursion seen in South China and Canada (e.g., Wang et al., 1996; Chen et al., 2002). Dissociation of methane hydrates has been suggested, the late Frasnian regression triggering their release, leading to increased levels of ^{12}C in the biosphere, rapid global warming, rapid sea-level rise and oceanic anoxia. Similarly, at the CTB, a section in New Jersey (USA) was found to have two negative peaks, both short (10 kyr) and large (>5‰); it has been postulated that methane release was a possible mechanism to explain such a signal (Wright et al., 2001). The presence of coincident negative oxygen and carbon isotope shifts, however, would suggest that such a signal was more likely to be diagenetic in origin (see below).

At Aksudere, it is also unlikely that the negative shifts are due to the introduction of light carbon from methane or volcanism. No global negative signal is seen at the CTB, unlike for the events discussed above, which would be expected with such a large influx of methane or volcanically-sourced ^{12}C into the biosphere.

6.2. Diagenetic signal

The presence of an erosion surface at the base of the Aksudere Beds, and the sandy nature of the sediments, indicates a possible regression in the region, just below the CTB. During the lowering of sea level, organic matter can become oxidised, leading to localised diagenetic environments with relatively high amounts of ^{12}C and potentially ^{16}O (e.g., Jarvis et al., 1988; Malone et al., 2001). During diagenesis, this light carbon and oxygen would be incorporated into reprecipitated calcite, leading to negative excursions on the $\delta^{13}C$ and $\delta^{18}O$ isotope profiles. Through lithological and palaeontological investigation, Alekseev et al. (1997) suggest that the black shale facies (Aksudere Beds) are a result of a short-term regression during the global eustatic transgressive interval of the CTB. Although Gale et al. (1999) proposed that the organic rich marls represent a transgressive system, it is possible that there were short-lived, localised regressions, possibly related to local tectonic activity, overprinting the overall transgressive trend. The presence of detrital quartz grains in layers throughout the section at Aksudere (Fig. 3A–D), and the presence of regional erosion surfaces, support this fluctuation in sea level.

Coinciding with the negative excursions on the $\delta^{13}C$ profile are lowered values of TOC (Fig. 4). Similar fluctuations in TOC levels in the upper claystone layer were identified by Naidin (1993) and Naidin and Kiyashko (1994a,b). Although Naidin (1993) suggested that they represented fluctuations of pelagic productivity controlled by climatic fluctuations and Milankovitch cycles, deterioration of organic matter has also been thought to affect other Cenomanian–Turonian localities. Jenkyns et al. (1994) attributed a dampening of the Cenomanian–Turonian positive excursion, in the stratigraphical vicinity of the Livello Bonarelli at Gubbio, to early diagenetic degradation of organic matter in the claystone.

In addition to the oxidation of organic matter, both $\delta^{13}C$ and $\delta^{18}O$ values could also have been lowered during exposure of the sediments to meteoric water during sea-level fall. Meteoric water has lower $\delta^{18}O$ than marine water and can be accompanied by low $\delta^{13}C$ where the waters contain isotopically light carbon from soil-derived CO_2 (e.g., Allan and Matthews, 1982; Marshall, 1992). During early diagenesis, it is possible that the carbonates partially equilibrate with these fluids, causing lower $\delta^{13}C$ and $\delta^{18}O$ (e.g., van Buchem et al., 1999). The isotope data therefore appear to show the influence of post-depositional oxidation and degradation of organic matter during early diagenesis, associated with a fall in sea level and the influx of meteoric waters to the sediments.

7. Conclusions

The Cenomanian–Turonian section at Aksudere clearly shows a carbon isotope profile reflecting enhanced drawdown of ^{12}C into organic-rich sediments, and the enrichment of marine waters in ^{13}C. This $\delta^{13}C$ excursion can be directly correlated with carbon isotope profiles seen elsewhere in northwest Europe (e.g., Eastbourne, UK), indicating the widespread nature of the changes to the ocean-atmosphere CO_2 reservoir, caused by global factors.

Synchronous with the positive excursion are increased TOC values, indicating the isotope excursion to have occurred synchronously with the deposition of organic-rich sediments, possibly in anoxic bottom conditions. It is likely that the degree of anoxia fluctuated through the *Whiteinella archaeocretacea* PRZ, in which the Aksudere Beds were deposited, with the presence of marls interbedded with organic-rich claystones indicating that dysoxic conditions prevailed intermittently, at times. Although the region was undergoing a global transgression, it is possible that the activation of geodynamic processes led to local, short, periodic regressions. These regressions are indicated by the number of small hiatuses in the region, and sandy layers within the deeper-water sediments. Additionally, a regional regression may have occurred at the base of the *W. archaeocretacea* PRZ, correlative with the sub-plenus erosion surface (e.g., Gale et al., 1999) of the Anglo-Paris Basin.

Coincident with the positive carbon excursion is an apparent negative excursion in the $\delta^{18}O$ profile, possibly indicating warming over the CTB into the early Turonian. The $\delta^{18}O$ values are, however, considered to have been diagenetically altered, shifting the primary signal to more negative values. Negative excursions seen on the $\delta^{13}C$ profile are interpreted as being, in part, an effect of diagenesis. Coinciding with the most negative $\delta^{18}O$ values, the $\delta^{13}C$ values indicate post-depositional oxidation of organic matter during localised exposure of the sediments to oxic or meteoric conditions during a lowering of sea level or tectonic uplift.

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