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A Southern Hemisphere record of global trace-metal drawdown and orbital modulation of organic-matter burial across the Cenomanian–Turonian boundary (Ocean Drilling Program Site 1138, Kerguelen Plateau)

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ABSTRACT

Despite its assumed global nature, there are very few detailed stratigraphic records of the late Cenomanian to the early Turonian Oceanic Anoxic Event 2 from the Southern Hemisphere. A highly resolved record of environmental changes across the Cenomanian–Turonian boundary interval is presented from Ocean Drilling Program Site 1138 on the central Kerguelen Plateau (southern Indian Ocean). The new data lead to three key observations. Firstly, detailed biostratigraphy and chemostratigraphy indicate that the record of Oceanic Anoxic Event 2 is not complete, with a hiatus spanning the onset of the event. A decrease in glauconite and highly weathered clays after the onset of Oceanic Anoxic Event 2 marks the end of the hiatus interval, which can be explained by a relative sea-level rise that increased sediment accommodation space on the Kerguelen Plateau margin. This change in depositional environment controlled the timing of the delayed peak in organic-matter burial during Oceanic Anoxic Event 2 at Site 1138 compared with other Oceanic Anoxic Event 2 locations worldwide. A second key observation is the presence of cyclic fluctuations in the quantity and composition of organic matter being buried on the central Kerguelen Plateau throughout the latter stages of Oceanic Anoxic Event 2 and the early Turonian. A close correspondence between organic matter, sedimentary elemental compositions and sediments recording sea-floor oxygenation suggests that the cycles were mainly productivity-driven phenomena. Available age-control points constrain the periodicity of the coupled changes in sedimentary parameters to ca 20 to 70 ka, suggesting a link between carbon burial and astronomically forced climatic variations (precession or obliquity) in the Southern Hemisphere mid-latitudes both during, and after, Oceanic Anoxic Event 2: fluctuations that were superimposed on the impact of global-scale processes. Finally, trace-metal data from the black-shale unit at Site 1138 provide the first evidence from outside of the proto-North Atlantic region for a global drawdown of...
INTRODUCTION

The environmental systems on Earth are related in a complex and often non-linear fashion. Globally significant perturbations in climate, such as those that occurred throughout the Mesozoic (Jenkyns, 2003), produce a diverse array of sedimentary responses, because they are filtered through a host of local-scale to regional-scale sedimentary controls such as basin geometry, temperature, hydrological cycling, weathering rates, rock-types, biotic community composition, relative sea-level and nutrient dynamics, among others. During Oceanic Anoxic Event 2 (OAE-2), a large increase in organic-carbon burial at a global scale led to a positive carbon-isotope excursion (CIE) that can be used as a chemostratigraphic marker for the event in lithologically diverse sedimentary successions (Scholle & Arthur, 1980; Tsikos et al., 2004). However, even in well-studied regions, such as the proto-North Atlantic region and Western Interior Seaway of North America, the timing of organic-carbon accumulation and environmental change at a local scale does not always mirror the accompanying global carbon-isotope shift (e.g. Meyers et al., 2001; Jenkyns, 2010; Eldrett et al., 2014). Thus, the presence of a C-isotope excursion at any given location does not allow the direct extrapolation of global-scale climatic phenomena to that region.

Many hypotheses have been presented to account for increases in the global rate of organic-carbon burial during OAE-2. Possible mechanisms include eustatic sea-level rise that moved oxygen minimum zones onto the continental shelf (Schlanger & Jenkyns, 1976; Arthur et al., 1987; Gavrilov et al., 2013), an increase in the delivery of weathering-derived nutrients to the oceans (Friija & Parente, 2008; Pogge van Strandmann et al., 2013; Monteiro et al., 2012; Blättler et al., 2011), the input of volcanically derived nutrients to the oceans (Kerr, 1998; Larson & Erba, 1999; Turgeon & Creaser, 2008; Du Vivier et al., 2014), changes in the cycling of major nutrients (Mort et al., 2007; Adams et al., 2010; Higgins et al., 2012) and an expansion of sea-floor anoxia that inhibited carbon remineralization (Owens et al., 2013; Westermann et al., 2014). A global expansion of sea-floor anoxia has been most readily identified from the trace-metal abundances and isotopic signatures of proto-North Atlantic sedimentary deposits (e.g. Hetzel et al., 2009; Westermann et al., 2014). However, the proto-North Atlantic Ocean had a palaeoceanographic configuration that was unique in Late Cretaceous time for being affected by a high degree of hydrographic restriction, which might have induced basin-scale artifacts into trace-metal data.

The vast majority of the evidence underpinning hypotheses of carbon burial and environmental change during OAE-2 has been generated from the North Atlantic–Tethyan region (e.g. Kolonic et al., 2005; Turgeon & Brumsack, 2006; Parente et al., 2008; Turgeon & Creaser, 2008; Voigt et al., 2008; Owens et al., 2013; van Bentum et al., 2012; Du Vivier et al., 2014; Eldrett et al., 2014; Lenniger et al., 2014; van Helmond et al., 2014; Westermann et al., 2014). Consequently, it is unclear whether many of these hypotheses are relevant for locations outside of this region. The lack of data from the Southern Hemisphere also limits the potential to validate model simulations of environmental processes, such as the presence of sea-floor anoxia (total oxygen depletion) and euxinia (anoxia and the presence of H$_2$S in seawater), which has been argued to have occupied large areas of the sea floor during OAE-2 (e.g. Monteiro et al., 2012). This study addresses the Southern Hemisphere data ‘gap’ by generating new, multi-proxy records of the environmental changes spanning the late Cenomanian–early Turonian interval recorded from Ocean Drilling Program (ODP) Site 1138 on the central Kerguelen Plateau (Indian Ocean). Firstly, new nannofossil and carbon-isotope chemostratigraphic data are used to establish a high-precision (centimetre-scale) stratigraphic interpretation of the sedimentary succession at Site 1138 that was not possible with the existing lower resolution data from the core (Holbourn & Kuhnt, 2002; Meyers et al., 2009). Secondly, the work of Meyers et al. (2009) is built upon by using new geochemical and petrographic data to interpret the changes...
in depositional environment recorded at Site 1138, to characterize the type of organic matter being buried on the Kerguelen Plateau, and to evaluate the timing of organic-matter burial relative to other OAE-2 successions worldwide. Lastly, trace-metal data are used to test the hypothesis of a global drawdown in seawater inventories (specifically Mo) for the first time from a location outside of the hydrographically restricted proto-North Atlantic Ocean.

SITE DESCRIPTION

The Kerguelen Plateau is a submarine large igneous province (LIP) that was formed mostly during the early part of the Cretaceous Period (Frey et al., 2000). Argon–Argon dating of basalts underlying marine sediments of Cretaceous age has shown that most of the central and southern portions of the Plateau were emplaced during eruptive phases older than ca 100 Ma (Frey et al., 2000; Duncan, 2002). However, in Cretaceous times, portions of the Plateau were subaerially exposed, as illustrated by the presence of pahoehoe lavas and pyroclastic flows interbedded with shallow-marine sediments in drill cores from ODP Leg 183 (Frey et al., 2000). At some sites, sediments containing terrestrially derived organic matter (for example, wood fragments and seeds) directly overlie the youngest lavas, indicating the presence of exposed land immediately after the major phase of Early Cretaceous volcanism (Mohr et al., 2002; Meyers et al., 2009). Site 1138 is located at 53°5′S, at a latitude that has remained the same since the Early Cretaceous (Shipboard Scientific Party, 2000) (Fig. 1). The sedimentary succession at Site 1138 records a transition from shallow-marine to deeper marine deposits throughout the Late Cretaceous, and its present-day water depth is ca 1400 m. (Shipboard Scientific Party, 2000; Meyers et al., 2009).

METHODS

Samples spanning the upper Cenomanian–lower Turonian were taken from the archive half of ODP Site 1138, core 69, at 5 cm intervals. Aliquots of each sample were used for nannofossil biostratigraphy, organic geochemistry and inorganic geochemistry.

Nannofossil biostratigraphy

Semi-quantitative analyses of calcareous nannofossils were performed on a total of 50 smear-slides using standard light microscope techniques under cross-polarized and transmitted light, at 1250× magnification. At least two traverses of each smear-slide were investigated. Smear-slides were prepared following the methodology described by Monechi & Thierstein (1985). A small amount of rock material was powdered into a mortar with few drops of bidistilled water and placed onto a glass coverslip. Using a toothpick, the suspension was repeatedly smeared along the coverslip to achieve the required thickness of smear, this being subsequently dried on a hotplate. The coverslip was

Fig. 1. MERLIN+ palaeogeography of the southern Tethys Ocean during the Cenomanian–Turonian boundary interval (ca 92 Ma). The location of ODP Site 1138 on the central Kerguelen Plateau is marked with a circle symbol. Additional Cenomanian–Turonian boundary locations in the region are marked with open square symbols. Projection is reproduced courtesy of Jim Harris, CGG Robertson, Merlin+ Project, 2015.
mounted onto the glass slide with Norland Optical Adhesive, and glued by exposure to UV light for a few minutes. The taxonomic concepts for calcareous nannofossil species identification follow the original descriptions and the discussions by Perch-Nielsen (1985), Burnett (1998) and Lees (2007). The nannofossil zonations used here for the Cenomanian–Turonian interval were adopted from Gambacorta et al. (2015).

**Organic geochemistry**

Total carbon (TC) and total inorganic-carbon (TIC) abundances were measured from ca 200 mg powder aliquots using a Ströhlein Coulomat device. Total inorganic-carbon (TIC) samples were analysed after removing organic carbon by furnacing overnight at 450°C. Total organic carbon (TOC) abundances were calculated by subtracting TIC from TC. The %CaCO₃ abundances were calculated by passing the total lipid extract through a column containing anhydrous Na₂SO₄. The apolar fraction was obtained by 8-fold dilutions for trace-element analysis and ca 500 000-fold dilutions for major-element analysis. Measurements were made using a Perkin-Elmer quadrupole ICP-MS (Perkin Elmer, Waltham, MA, USA). Precision (2 SD) and accuracy were assessed by repeat digestions of USGS (United States Geological Survey) Devonian Shale SDO-1, and were both better than 0.5% and 2%, respectively.

For biomarker analyses, ca 6 g powdered sample was ultrasonically extracted using methanol, then dichloromethane (DCM)/methanol (1 : 1, v/v) and, finally, 100% DCM. All extracts were combined and dried under N₂ at 40°C. Water was removed from the samples by passing the extracts [dissolved in DCM/methanol (3 : 1, v/v)] over a column containing anhydrous Na₂SO₄. The apolar fraction was obtained by passing the total lipid extract through a column containing activated Al₂O₃ using hexane/DCM (9 : 1, v/v). The apolar fraction was measured for compound-specific δ¹³C using an IsoPrime Limited, Stockport, UK) system at the Organic Geochemistry Unit, University of Bristol. To obtain enough organic matter for compound-specific δ¹³C from organic-lean intervals [for example, >656.9 mbsf (metres below sea floor)], up to five samples were combined. Samples were measured in duplicate and δ¹³C values were converted to VPDB by bracketing with CO₂ of known δ¹³C. The reported values are the average of the duplicate measurements. Instrument stability was monitored by regular analysis of an in-house fatty acid methyl ester standard mixture; long-term precision is ±0.3‰. After injection of 1 or 2 µl onto a Zebron-I non-polar column (50 m length × 0.32 mm diameter × 0.10 µm film thickness), the GC oven program was: 70°C (hold for 1 min) to 130°C at 20°C/min⁻¹, then to 300°C at 4°C/min⁻¹ and hold for 25 min. Samples were automatically integrated using the IonVantage software package.

**Organic petrography**

For maceral analysis, chipped rock pieces were embedded in epoxy resin and prepared as polished sections. These sections were investigated using a Leica DMRX MPVSP microscope photometer (Leica Microsystems, Wetzlar, Germany) in both reflected white light and fluorescent mode under oil immersion at a magnification of 500×. The relative abundances of macerals, mineral groundmass and minerals were determined using a semi-automatic point counter. The maceral analysis is based on 1000 counts distributed regularly on the whole polished section. The nomenclature of the macerals of vitrinite and inerinite groups is based on Taylor et al. (1998), and the nomenclature of liptinite groups is based on Hutton (1987).

**Inorganic geochemistry**

Element abundances were measured by digesting 50 mg sample aliquots in a mixture of concentrated HNO₃/HCl/HF acids. Sample solutions were evaporated to dryness and re-dissolved in 2% HNO₃ at ca 5000-fold dilutions for trace-element analysis and ca 50 000-fold dilutions for major-element analysis. Measurements were made using a Perkin-Elmer quadrupole ICP-MS (Perkin Elmer, Waltham, MA, USA). Precision (2 SD) and accuracy were assessed by repeat digestions of USGS (United States Geological Survey) Devonian Shale SDO-1, and were both better than

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±10% for Al, Mg, Na, Fe, Li, Mn, Mo and U. Results are expressed as enrichment factors [EF = (element/Al)_{sample}/(element/Al)_{UCC}], where upper continental-crust (UCC) abundances were taken from Rudnick & Gao (2003). Molybdenum isotopes were measured by adding a precise mass of a 100Mo-enriched and 97Mo-enriched double-isotope spike to sample aliquots containing ca 400 ng of natural Mo. The samples were digested in inverse aqua regia at 150°C for 48 h to ensure spike-sample equilibration, before purification of Mo using anion-exchange chromatography (Dickson et al., 2016). Isotope ratios were measured using a Nu Plasma MC-ICP-MS (Nu Instruments Limited, Wrexham, UK) and are expressed as δ^{98/95}Mo = ([^{98/95}Mo_{sample} - ^{98/95}Mo_{standard}]/^{98/95}Mo_{standard})*1000) relative to NIST 3134 (Nägler et al., 2014). External reproducibility was calculated by repeatedly processing aliquots of USGS SDO-1 shale through the full chemical and analytical procedure and was ±0.08‰ (2 SD, n = 26).

RESULTS

Nannofossil biostratigraphy

Moderately to well-preserved nannofossils are present in all samples apart from two barren intervals between 656-64 to 656-04 mbsf and 655-89 to 655-81 mbsf. Key marker events corresponding to the upper Cenomanian–lower Turonian interval were recognized as follows. Highest occurrences (HO) of Corollithion kenneedyi and Axopodorhabdus albianus were observed at 656-89 mbsf and Microstaurus chiaastius at 656-69 mbsf. Lowest occurrences (LO) of Eprolithus octopetalus, Quadrum gartneri and Eprolithus eptapetalus were identified at 655-99 mbsf, 655-75 mbsf and 655-47 mbsf, respectively (Figs 2 and 3; Table 1). Based on bio-events, zones and subzones were determined following the calcareous nannofossil biozones of Sissingh (1977) implemented by Perch-Nielsen (1985), Bralower et al. (1995), Burnett (1998), Tsikos et al. (2004) and Gambacorta et al. (2015). The studied interval covers zones CC10 to CC11 of Sissingh (1977), zones NC11* to NC13* of Bralower et al. (1995), zones UC3a-c to UC7 of Burnett (1998), and zones NC11* to NC13** of Tsikos et al. (2004). The interval between 656-89 mbsf and the top of the studied section is characterized by nannofossil events that provide a continuous zonation without evidence of hiatuses.

Organic geochemistry

The δ^{13}CTOC fluctuates between ca -25.5‰ and -27‰ for the majority of the record (Figs 2 and 3), with transient positive and negative excursions superimposed on these background values. The main feature of the record is a >3‰ increase at 657 mbsf to -23.6‰, which is accompanied by increases in δ^{13}C of n-C27 and n-C25 n-alkanes (reflecting terrestrial leaf waxes), n-C19 n-alkanes (algal organic matter) and n-C31 ββ-hopanes (bacterial biomass) of a similar magnitude, albeit offset to slightly lighter values. The positive δ^{13}C excursion can be broken into two parts, with a lower interval (656-79 to 656-49 mbsf) of higher δ^{13}CTOC, and a second interval (656-49 to 655-68 mbsf) of slightly lower δ^{13}CTOC. The abundance of total organic carbon (%TOC) fluctuates around minimum values of ca 0.1 to 0.5% throughout the section, with common increases to ca 3 to 15% (Fig. 3). The first significant increase in %TOC (to ca 15%) occurs during the major positive C-isotope excursion that correlates with and can be used to define the duration of OAE-2 (Tsikos et al., 2004; Jarvis et al., 2011). However, at Site 1138, the timing of this increase stratigraphically lags the onset of the positive C-isotope excursion, thereby demonstrating a difference in the timing of carbon burial on the Kerguelen Plateau with respect to average global carbon burial in the latest Cenomanian.

The composition of the bulk organic matter is represented geochemically by the hydrogen index [HI = (S2/%TOC)*100, where S2 (mg g⁻¹ TOC) is the hydrocarbon yield during Rock-Eval pyrolysis]. Values of HI reflect the presence of hydrogen-rich organic matter versus the presence of hydrogen-poor (higher plant) organic matter, although values can also be lowered by oxidative degradation and thermal maturity; HI fluctuates around a minimum of <50, with short-term excursions to maximum values of ca 100 to 300 upward from 657 mbsf. The transient increases in HI are tightly correlated with %TOC, demonstrating a close coupling between the amount and composition of buried organic matter (Fig. 3). Overall, Rock-Eval pyrolysis indicators (HI versus OI) tend to characterize the bulk of the organic matter as a mixture of type II algal and type IV hydrogen-poor (oxidized) algal matter (Fig. 4A). The weak positive
Fig. 2. Stratigraphic correlation of Site 1138 to chemostratigraphically and biostratigraphically constrained Cenomanian–Turonian boundary locations worldwide. (A) $^{13}$C$_{\text{TOC}}$ and compound-specific $^{13}$C for Site 1138, plotted against foraminiferal biozones (Shipboard Scientific Party, 2000; Holbourn & Kuhnt, 2002), and nannofossil lowest and highest occurrences (this study). Vertical uncertainties on the compound-specific data indicate the depth ranges where samples had to be combined due to the low abundances of individual compounds. Horizontal uncertainties for the compound-specific data are the 1 SD of replicate analyses. (B) $^{13}$C$_{\text{CARB}}$ data from the Eastbourne section, southern England (Tsikos et al., 2004), plotted against foraminiferal biozones and nannofossil highest and lowest occurrences (Gale et al., 1993; Paul et al. 1999). (C) $^{13}$C$_{\text{TOC}}$ data from the Portland-1 core, Pueblo, USA (Sageman et al., 2006), plotted against foraminiferal biozones and nannofossil highest and lowest occurrences (Pratt & Threlkeld, 1984; Bralower & Bergen, 1998; Keller & Pardo, 2004; Kennedy et al., 2005). Dashed lines are correlations based on the chemostratigraphic and biostratigraphic datum levels, discussed in the text. The Cenomanian–Turonian boundary has been located based on the last relatively elevated C-isotope data point following the OAE-2 plateau intervals (Tsikos et al., 2004). Nannofossil zones after: ‘1’ Sissingh (1977); ‘2’ Bralower et al. (1995); ‘3’ Burnett (1998); ‘4’ Tsikos et al. (2004). C. k. = Corollithion kennedyi; A. a. = Axopodorhabdus albianus; M. c. = Microstaurus chiastius; E. o. = Eprolithus octopetalus; Q. g. = Quadrum gartneri; E. e. = Eprolithus eptapetalus; R. a. = Rhagodiscus asper. The grey vertical line in panel (A) indicates an interval barren of nannofossils. PCE, Plenus Cold Event; BOE, Benthic Oxic Event.
Fig. 3. Geochemical data for Site 1138 plotted against core depth corrected for post-recovery core expansion. Samples examined for organic macerals are indicated by an asterisk. Zigzag lines indicate stratigraphic hiatuses or intervals of slow sedimentation. Horizontal shaded bands indicate intervals of elevated organic-carbon concentration. The black and blue arrows indicate the enrichments of Rb and Li over average continental-crust concentrations in basalts drilled at Site 1138 (Neal et al., 2002). The 2 SD external reproducibility for the δ^{98/95}Mo data (±0.09‰) is shown as a horizontal error bar (see text for details). See Fig. 2 for details of nannofossil zonations.
The correlation between %TOC and the \( n-C_{31} \) hopane \( \beta\beta/(\beta\beta+\alpha\beta+\alpha\alpha) \) ratio (Fig. 4B) is also suggestive of a contribution of older reworked organic matter (relatively fewer \( \beta\beta \) hopanes) to TOC in the organic-lean intervals.

**Organic petrography**

Petrographic examination of the organic and inorganic components and mineral groundmass in six samples (Table 2) supports the inferences from organic geochemistry by showing the presence of macerals of the liptinite group as varying proportions of primary macerals such as liptodetrinite, *Botryococcus* algae, acritarch and dinoflagellate remains, and secondary solid or migrabitumen, with higher proportions of these macerals occurring in the samples with higher %TOC and HI (Fig. 5; Table 2). There are very low amounts of vitrinite (terrestrial macerals) in all of the studied samples, with detectable amounts (ca 0.1 vol.%) occurring in only two samples stratigraphically above 657 mbsf. The low proportion of terrestrially derived organic matter throughout the section agrees well with the interpretation of low-HI samples from Rock-Eval pyrolysis as reflecting oxidized type IV algal matter. Furthermore, inertinite is present in low proportions in all studied samples above 656-49 mbsf, supporting the inference of oxidized type IV organic matter obtained from Rock-Eval pyrolysis.

**Inorganic geochemistry**

Enrichment factors for rubidium (RbEF), lithium (LiEF) and iron (FeEF) range between ca 0.5 and ca 6.5, and have very similar stratigraphic fluctuations (Fig. 3). Enrichment factors are moderately high stratigraphically below 657-14 mbsf (RbEF = 6.2; LiEF = 4.8; FeEF = 6.2). Above this level, enrichment factors of all three elements decrease to much lower values ([RbEF = 0.5 to 1.5; LiEF = 0.5 to 1.5; FeEF = 1.4 to 3.4]. Enrichment factors for sodium (NaEF) show the opposite trend to RbEF, LiEF and FeEF, with a

![Fig. 4. Organic geochemical data for Site 1138. Filled circles are samples from within the OAE-2 interval of Site 1138. Open squares are all other data. (A) Characterization of bulk organic matter using Hydrogen Index versus Oxygen Index. (B) Thermal maturity of organic matter at Site 1138 using TOC versus the \( n-C_{31} \) hopane \( \beta\beta/(\beta\beta+\alpha\beta+\alpha\alpha) \) index. The data indicate a trend of decreasing thermal maturity at higher %TOC.](image-url)

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Table 2. Results of organic petrographic analyses

| Inertinite (%) | Liptinite (%) | Pyrite | Lipt. | Solid bitumen | Isolated crystals | White peloids |
|----------------|---------------|--------|-------|--------------|------------------|--------------|
| 655.01         | 1.0           | 0.7    | 3.4   | 1.8          | 0.2              | 0.2          |
| 655.63         | 0.1           | 0.0    | 0.0   | 0.0          | 0.0              | 0.0          |
| 655.69         | 0.1           | 0.0    | 0.0   | 0.0          | 0.0              | 0.0          |
| 656.01         | 0.1           | 0.0    | 0.0   | 0.0          | 0.0              | 0.0          |
| 656.04         | 0.1           | 0.0    | 0.0   | 0.0          | 0.0              | 0.0          |
| 656.66         | 0.1           | 0.0    | 0.0   | 0.0          | 0.0              | 0.0          |
| 657.19         | 0.1           | 0.0    | 0.0   | 0.0          | 0.0              | 0.0          |
| 658.20         | 0.1           | 0.0    | 0.0   | 0.0          | 0.0              | 0.0          |

DISCUSSION

Stratigraphic succession and depositional environments of the Cenomanian–Turonian boundary interval at Site 1138

The stratigraphy of the deposits spanning the Cenomanian–Turonian boundary at Site 1138 can be described with new high-resolution $\delta^{13}C_{TOC}$, compound-specific $\delta^{13}C$ and nannofossil datasets, in combination with the published foraminiferal biostratigraphy for the core stepwise increase to ca 1.2 at 656-44 mbsf. Further up-section, Na$_{Eff}$ remains high and fluctuates between ca 0.7 and 1.2. The stepwise shifts in elemental abundances are accompanied by changes in the mineral composition of the deposits. The two lowermost samples examined contained 56-6 to 67-8 vol.% of glauconite. However, at 656-64 mbsf, glauconite is far less abundant (7-8 vol.%), and is only a negligible constituent of the samples examined from further up-section (<0.5 vol.%). These elemental and mineralogical associations indicate a decrease in the proportion of highly weathered clays versus less weathered primary minerals over the onset of the positive C-isotope excursion recorded at Site 1138.

Enrichment factors of the redox-sensitive elements molybdenum (Mo$_{Eff}$) and manganese (Mn$_{Eff}$) are both <0.5 below 656-49 mbsf, apart from a brief increase in Mn$_{Eff}$ to ca 2 between 657-15 and 656-94 mbsf. Above 656-44 mbsf, Mo$_{Eff}$ repeatedly increases over short intervals to ca 1.5 to 5.0 and Mn$_{Eff}$ repeatedly increases to higher values of ca 1 to 4 above 655-76 mbsf. Many of the elemental enrichment factors (Rb$$_{Eff}$$, Li$_{Eff}$, Fe$$_{Eff}$, Na$_{Eff}$, Mn$_{Eff}$ and Mo$_{Eff}$) fluctuate in tandem above 656-44 mbsf, suggesting a link between the processes governing sea-floor redox and sediment delivery.

Values of $\delta^{98/95}$Mo at the base of the studied section are −0.5 to −0.0, and increase above 657 mbsf to between −0.18 and 0.57. Above 655-70 mbsf, $\delta^{98/95}$Mo decreases towards lower values of −0.77 in the uppermost measured samples. This general positive excursion in $\delta^{98/95}$Mo is interrupted by two features: firstly, $\delta^{98/95}$Mo decreases to lower values of ca −1.10 in two short intervals at 656-49 mbsf and 655-55 mbsf; and, secondly, $\delta^{98/95}$Mo increases to 1.65 over a ca 5 cm interval beginning at 656-79 mbsf.
The similarity of the different C-isotope records, potentially recording marine and atmospheric carbon reservoirs, shows that the major positive C-isotope excursion at Site 1138 mainly records changes in global, rather than local, carbon cycling and, in conjunction with the nannofossil data, can be reliably correlated with the OAE-2 global C-isotope excursion (Tsikos et al., 2004). These data are compared to the Cenomanian–Turonian record from the USGS Portland-1 research core (Pratt & Threlkeld, 1984; Keller & Pardo, 2004; Kennedy et al., 2005; Sageman et al., 2006), which is similar to the C/T GSSP (Cenomanian/Turonian Global Stratotype Section and Point) at Pueblo, Colorado; and Eastbourne, UK (Gale et al., 1993; Tsikos et al., 2004; Paul et al., 1999; Jarvis et al., 2006) in order to identify the completeness of the Site 1138 succession (Fig. 2).

The correlation in Fig. 2 indicates that the onset of OAE-2 is not captured within the ODP Site 1138 sedimentary succession. Three considerations support this argument. Firstly, the new high-resolution nannofossil biostratigraphy constrains the HO of *A. albianus* and *C. kennedyi* to the same stratigraphic level at Site 1138, prior to the increase in $\delta^{13}C_{\text{TOC}}$. At Pueblo and Eastbourne, the HO of *C. kennedyi* occurs in the upper *Rotalipora cushmani* zone, with the HO of *A. albianus* occurring higher upsection, during the *Whiteinella archaeocretacea* zone and within the interval recording the Pleknus Cold Event/Benthic Oxic Event (Gale et al., 1993; Bralower & Bergen, 1998; Paul et al., 1999; Kennedy et al., 2005). Thus, part of Zone CC10a (Sissingh, 1977), the upper part of Zone NC11* (of Bralower et al., 1995 and Tsikos et al., 2004) and Zones UC3e to UC5a (of Burnett, 1998) are not present in the core.

The second line of evidence for a hiatus near the base of the studied succession is that the bulk and compound-specific C-isotope data contain only one positive shift, while most OAE-2 C-isotope records contain two positive shifts near the onset of the event, separated by a brief return to slightly less positive values (e.g. Pratt &
The inferred chemostratigraphic hiatus agrees with the nannofossil zonation in showing that the early stages of OAE-2 are not recorded at Site 1138. Consequently, the Plenus Cold Event, which falls stratigraphically within this missing interval, cannot be traced into the Southern Hemisphere using the Site 1138 deposits.

Thirdly, the presence of a hiatus at the base of the positive C-isotope excursion is also supported by the high abundance of glauconite grains below ca 656-79 mbsf, reflected in enrichments of Fe and Mg (Figs 3 and 5A). Glauconite typically requires very slow sedimentation rates and mildly reducing conditions in sediment micro-pores to precipitate, a process that is typically accompanied by dissolution and alteration of the host substrate (Odin & Matter, 1981; Chafetz & Reid, 2000). Corresponding high enrichments of Rb and Li can be explained by the partitioning of these elements into secondary minerals during the chemical weathering of primary rocks (Pistiner & Henderson, 2003; Pogge van Strandmann et al., 2006). The presence of glauconite points to a shallow-marine environment with either in situ alteration of primary minerals to clays, or the delivery of highly weathered clays from nearby exposed portions of the central Kerguelen Plateau, and supports the inference of a break in sedimentation, or an extremely slow sedimentation rate.

The enrichments of Fe, Mg, Rb and Li decline abruptly above the onset level of the CIE, at ca 657 mbsf, and point to a reduction of in situ glauconite and clay-mineral formation (or the delivery of clays from subaerial landmasses). These changes can be explained by an increase in relative sea-level (RSL) that would have created accommodation space for more rapid sedimentation on the Kerguelen Plateau margin. A transgressive trend has been identified at many OAE-2 successions worldwide, an observation that has been used to propose a eustatic sea-level rise on the order of a few tens of metres in the latest Cenomanian (e.g. Arthur et al., 1987; Gale et al., 2008). It is not likely that plateau subsidence occurring during the hiatus in sedimentation at the base of OAE-2 alone could have caused the RSL rise, given that the duration of the hiatus is not likely to exceed ca 400 kyr, and is probably closer to ca 200 kyr (Sageman et al., 2006; Voigt et al., 2008; Meyers et al., 2012; Eldrett et al., 2015). Assuming a 22 mm kyr⁻¹ subsidence rate, these durations would allow only a modest ca 4 to 9 m of RSL rise. These subsidence estimates may be further reduced when it is considered that enrichments of Mn and Fe, and a decrease in δ⁹⁸/⁹⁵Mo at 656-54 mbsf, indicate the re-oxidation of sediment pore waters and perhaps the presence of a second sedimentary hiatus. A eustatic contribution to RSL rise is needed to accommodate the significant shift in sedimentary facies, along with the accompanying changes in sediment geochemistry. Such a rise is not inconceivable in light of the evidence for sea-level rise at numerous locations during the late Cretaceous (Hancock & Kauffman, 1979).

The delayed onset of maximum organic-matter burial during OAE-2 at Site 1138 compared with other locations worldwide, therefore, can be explained partly by the effect of local RSL rise. Relative sea-level rise would have created accommodation space for organic-carbon burial around the margins of the central Kerguelen Plateau during OAE-2, but not until several tens of thousands of years after the start of the CIE. Enrichments in %TOC similar to those observed at Site 1138 have also been identified at ODP Site 763 on Exmouth Plateau, off Western Australia (Thurow et al., 1992), and have been linked to the presence of an oxygen minimum zone impinging on the upper continental slope. It is interesting to speculate whether or not the enhanced organic-matter burial at the relatively shallow palaeodepths of Sites 1138 and 763 was influenced by a common oxygen-depleted water-mass extending over much of the proto-Indian Ocean.

**Controls on cyclic organic-matter burial on the central Kerguelen Plateau**

The Cenomanian–Turonian record of organic-carbon enrichment at Site 1138 is highly cyclic up-section from the level of initial increase in %TOC that characterizes the OAE-2 interval (Fig. 3). The low abundance of vitrinite in the studied samples indicates that the cyclicity in TOC is not likely to be explained by large changes in the flux of terrestrial organic matter. Likewise, low T_max values and n-C₃₁ hopane ββ⁺/(ββ⁺+βα⁺+αβ) ratios >ca 0.5 are not consistent with large changes in organic-matter maturity across each TOC cycle, although slightly lower n-C₃₁ hopane ββ⁺/(ββ⁺+βα⁺+αβ) ratios during
%TOC minima in the lower Turonian might point to localized re-working of older organic matter from the Kerguelen Plateau at these times (Fig. 4). These observations therefore require a greater burial efficiency of marine-derived organic matter during TOC-rich intervals, which may have been promoted either by a reduction in seawater oxygen concentrations that inhibited organic-matter remineralization (preservation), and/or by a higher flux of organic matter to the sea floor (higher productivity).

Peaks in the %TOC and HI cycles correlate with higher abundances of molybdenum and uranium, which become enriched in sediments under low-oxygen conditions, and with low abundances of manganese, which becomes mobile under lowered oxygen conditions (Crusiús et al., 1996; Tribovillard et al., 2006). These elemental associations support the notion of a redox influence on the TOC cyclicity at Site 1138, which might have been caused by expansions and contractions of an oxygen minimum zone impinging on the margin of the central Kerguelen Plateau. Such fluctuations in the depth of the oxygen minimum zone must have been driven either by changes in oxygen consumption related to local organic-carbon remineralization, or alternatively to changes in the production of oxygen-depleted deepwater masses further afield. In support of the latter mechanism, Earth-system model results have indicated that large areas of the deep proto-Indian Ocean sea floor in the vicinity of the central Kerguelen Plateau might have experienced anoxia during OAE-2, with surrounding shallow sea-floor regions remaining oxic (Monteiro et al., 2012). Repeated shoaling and deepening of an oxygen-depleted water mass might possibly have controlled the rate of carbon oxidation in shallow pore waters at Site 1138, and thus promoted the observed cyclicity in organic-carbon burial.

However, because variations in sea-floor redox conditions can also be controlled by changes in the flux of organic matter to the sea floor, productivity changes might also have played a major role in driving the %TOC cycles at Site 1138. Such a relationship has been documented for the proto-North Atlantic Ocean (Kuypers et al., 2004), where productivity, redox and %TOC might all ultimately be linked by periodic variations in the flux of weathered nutrients from surrounding landmasses, as well as changes in the basin redox (Poulton et al., 2015; Dickson et al., 2016). At Site 1138, indications of changes in primary productivity during each %TOC cycle derive from two lines of evidence. Firstly, low nitrogen-isotope compositions of the bulk organic matter during the OAE-2 interval (Meyers et al., 2009) suggest a greater abundance of nitrogen-fixing bacteria living in poorly ventilated surface waters, although the data may also be consistent with high rates of production by eukaryotes, coupled with recycling of NH₄ to surface waters (Higgins et al., 2012). Changes in the community structure of primary producers might also have been encouraged by inhibition of enzyme function in marine algae due to the low abundances of bio-essential trace metals (Zn and Mo) in seawater (Hetzel et al., 2009). Secondly, the association of peaks in the TOC and HI cycles with higher Na enrichment factors (Fig. 3) circumstantially points to higher primary productivity at these times. Sodium is highly depleted in weathered rocks, due to its removal during feldspar alteration (Nesbitt & Young, 1982), and intervals of relative enrichment in Site 1138 therefore record the delivery of less highly weathered detrital sediments, presumably due to incongruent weathering of exposed basalts on the central Kerguelen Plateau.

Taken together, these arguments suggest that the local seawater nutrient inventory, controlled by periodic variations in weathering rates on the central Kerguelen Plateau, acted as a primary control on cyclic organic-matter burial at Site 1138. The remineralization of the (periodically) enhanced organic-matter fluxes probably lowered seawater oxygen concentrations sufficiently for redox to further raise the efficiency of organic-matter burial.

The periodic nature of organic-carbon burial on the central Kerguelen Plateau during the early Turonian suggests a climatic control, potentially related to changes in temperature and/or precipitation regimes. The duration between the LO of Q. gartneri and LO of Helvetoglobotruncata helvetica has been estimated as ca 225 ka from cyclostratigraphic tuning of the USGS Portland Core-1 at Pueblo, Colorado (Sageman et al., 2006) and ca 690 ± 130 ka from the Shell Iona-1 research core at Del Rio, Texas (Eldrett et al., 2015). Transferring these durations to the 3·94 to 4·44 m equivalent section at Site 1138, estimated from the new nanofossil data presented here, and the existing foraminiferal biostratigraphy of Holbourn & Kuhnt (2002), generates sedimentation rate estimates of 0·57 to 1·97 cm ka⁻¹. Sedimentation...
rates in this range imply average durations of \( \text{ca} \) 20 to 70 ka for the 10/11 cycles in %TOC spanning the LO of \( Q. \) gartneri to the top of the studied section at Site 1138. These durations span the range of orbital precession (\( \text{ca} \) 23 kyr) and orbital obliquity (\( \text{ca} \) 41 kyr) and might implicate monsoonal dynamics and/or changes in ocean circulation as possible climatic drivers for the observed coupling between weathering and organic-matter burial on the central Kerguelen Plateau.

**Seawater trace-metal inventories**

Two geochemical indices (\( \text{Mo}_{\text{EF}}/\text{UEF} \) and \( \text{Mo}/\text{TOC} \)) have been used as palaeoenvironmental indicators for marginal ocean basins (Algeo & Tribovillard, 2009; Tribovillard et al., 2011; Algeo & Lyons, 2006; Algeo & Rowe, 2011). The \( \text{Mo}_{\text{EF}}/\text{UEF} \) proxy exploits the differing sensitivity of these two elements to euxinic and anoxic depositional conditions, respectively, in order to characterize local redox changes, and the degree of local watermass restriction. In open-marine settings, Mo-U co-variation in sediments proceeds along a trajectory that initially enriches U under sub-oxic conditions [at the \( \text{Fe(III)}-\text{Fe(II)} \) boundary] before the development of anoxic and euxinic conditions starts to enrich Mo. Deviations from this trajectory indicate preferential enrichment of Mo due to a strong hydrographic connection with the global ocean, coupled with a strong chemocline and the presence of Fe-Mn ‘shuttling’ across this boundary (Algeo & Tribovillard, 2009; Tribovillard et al., 2011). The sedimentary \( \text{Mo}/\text{TOC} \) proxy utilizes the common enrichment of both of these parameters in the oxygen-depleted environments commonly found within hydrographically restricted marginal marine basins (Algeo & Lyons, 2006). As the trace-metal inventory within the basin changes, due to drawdown under low-oxygen conditions coupled with limited re-supply by inter-basinal transfer of water masses, the sedimentary \( \text{Mo}/\text{TOC} \) ratio decreases. Different \( \text{Mo}/\text{TOC} \) gradients have been observed for modern marine basins characterized by different seawater residence times. The \( \text{Mo}/\text{TOC} \) proxy can consequently be used as an indicator of Mo concentrations in basinal seawater (Algeo & Lyons, 2006; Algeo & Rowe, 2011).

For Site 1138, the \( \text{Mo}_{\text{EF}}/\text{UEF} \) data follow the present-day open-marine trajectory, with an initial enrichment of U under sub-oxic conditions, followed by progressive enrichment of Mo as anoxic conditions developed (Fig. 6A). However, despite the relative enrichments of U and Mo

![Fig. 6. Elemental co-variations. (A) \( \text{Mo}_{\text{EF}} \) versus \( \text{U}_{\text{EF}} \) for Site 1138 (open blue squares) and Site 367 (open red circles). Dashed lines show the sedimentary enrichments corresponding to modern seawater Mo/U molar ratios of \( \text{ca} \) 7.5 to 7.9 (Algeo & Tribovillard, 2009). Arrow indicates an open-marine trajectory of U enrichment followed by Mo enrichment under increasingly sulphidic depositional conditions (Algeo & Tribovillard, 2009). (B) Mo versus %TOC for Site 1138 (open blue squares) and Site 367 (open red circles). Dashed lines show the Mo/TOC gradients for modern marine basins experiencing differing degrees of watermass restriction (Algeo & Lyons, 2006).](image-url)
during OAE-2, two lines of evidence show that euxinic conditions did not develop on the central Kerguelen Plateau: (i) Mo$_{EF}$/U$_{EF}$ values never increase above the seawater molar ratio of ca 7:7, the level that would suggest the presence of sulphidic depositional conditions; and (ii) $\delta^{98/95}$Mo values during the OAE-2 interval of Site 1138 are $<0.5^{\circ}$ (Fig. 3), which is significantly lower than temporally coeval data from the highly euxinic proto-North Atlantic Ocean (Westermann et al., 2014; Dickson et al., 2016) indicating the presence of sulphidic pore waters, but not a sulphidic water column. In contrast, the Mo/TOC data (Fig. 6B) follow a gradient that is significantly lower than the present-day Black Sea, which is characterized by highly restricted deep watermasses, with Mo concentrations >90% lower than in the present-day open ocean (Pilipchuk & Volkov, 1974; Emerson & Huested, 1991; Nägler et al., 2011). The very low abundance of terrestrial macerals (Table 2) rules out significant changes in organic-matter type as a primary control on the Mo/TOC ratios; likewise, the relative enrichments in trace metals and Mo-isotope compositions across the Site 1138 black-shale interval confirm that localized oxygenation [as seen in the Western Interior Seaway (Eldrett et al., 2013; Westermann et al., 2014)] is not responsible. Therefore, reconciling a low Mo/TOC gradient with a hydrographically unrestricted setting requires an extremely low concentration of Mo in global ocean seawater, rather than a locally restricted hydrographic regime.

These observations are the first of their kind from outside of the proto-North Atlantic Ocean to demonstrate the widespread and global nature of trace-metal depletion during OAE-2. However, widespread trace-metal drawdown does not necessarily point towards a ‘globally’ euxinic ocean, but rather a significant spread of deoxygenated zones occupying <10% of the global sea floor that acted as large ‘sinks’ for redox-sensitive metals (Montoyo-Pina et al., 2010; Owens et al., 2013; Westermann et al., 2014). The observation of an extremely low Mo inventory in global seawater during OAE-2 also highlights the pitfalls of using Mo/TOC gradients as quantitative indicators of basin palaeohydrology. Van Helmond et al. (2014) recently used a Mo/TOC gradient from DSDP Site 367 in the central proto-North Atlantic Ocean to infer a watermass residence time of 500 to 4000 years during OAE-2, by comparison to the present-day Black Sea Mo/TOC gradient. However, this estimate is probably inaccurate for two reasons. Firstly, the global Mo inventory was considerably depleted compared with the present day, thus lowering ‘apparent’ Mo/TOC ratios and inhibiting direct comparison with present-day analogues. Secondly, additional sedimentary Mo enrichment at Site 367 may have occurred due to Mo ‘shuttling’ across a sharply developed chemocline, by adsorption and desorption to Fe/Mn-oxhydroxides. Figure 6B demonstrates that the Mo/TOC gradient was actually lower at the hydrographically exposed central Kerguelen Plateau than in the restricted proto-North Atlantic Ocean. Although elemental proxies are clearly very valuable palaeoceanographic tools, caution is required when trying to draw quantitative inferences from these data.

**CONCLUSIONS**

New palaeontological and geochemical data from Ocean Drilling Program (ODP) Site 1138 on the central Kerguelen Plateau allow a detailed view of the environmental changes that affected the mid-latitude Southern Hemisphere across the Cenomanian–Turonian boundary interval. The initial onset and early stages of Oceanic Anoxic Event 2 (OAE-2) on the central Kerguelen Plateau had a very close temporal relationship with an episode of relative sea-level rise that brought to an end a period of glauconite formation in poorly oxygenated, slowly accumulating shallow-marine sediments, that prevented the early stages of OAE-2 from being recorded in the sedimentary succession of Site 1138 (Fig. 7A). An increase in water depth is credited with creating the accommodation space to allow the accumulation and burial of deeper marine chalks and marls during the OAE-2 interval and the early Turonian (Fig. 7B and C), and explaining the apparent lag in maximum organic-matter burial during OAE-2 at Site 1138 compared with other locations worldwide. Cyclical episodes of organic-matter burial during OAE-2 and during the early Turonian appear to have been productivity-driven phenomena, related to variations in the delivery of nutrients by the weathering of exposed portions of the central Kerguelen Plateau. In turn, trace-element concentration data show that enhanced carbon burial was aided by reductions in bottom-water oxygen concentrations, although Mo-isotope and elemental ratios indicate that this location was not affected by pervasive sulphidic depositional conditions. Sediments deposited under locally oxygen-depleted conditions at Site 1138, with minimal change in organic-matter type, provide the first
clear evidence from outside the proto-North Atlantic Ocean that there was a dramatic global drawdown in the oceanic trace-metal inventory during OAE-2.

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