A molybdenum isotope record of Eocene Thermal Maximum 2: implications for global ocean redox during the early Eocene

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Abstract

During the early Eocene, a series of short-term global warming events (‘hyperthermals’) occurred in response to the rapid release of carbon into the oceans and atmosphere. In order to investigate the response of ocean redox to global warming, we have determined the molybdenum isotope compositions ($\delta^{\text{98/95}}_{\text{Mo}}$) of samples spanning one such hyperthermal (Eocene Thermal Maximum 2 (ETM-2, 54.1Ma)), from Integrated Ocean Drilling Program Expedition 302 Site M0004A in the Arctic Ocean. The highest $\delta^{\text{98/95}}_{\text{Mo}}$ in our sample set (2.00±0.11‰) corresponds to the development of local euxinia at Site M0004A during the peak of ETM-2, which we interpret as recording the global seawater $\delta^{\text{98/95}}_{\text{Mo}}$ at that time. The ETM-2 seawater $\delta^{\text{98/95}}_{\text{Mo}}$ is indistinguishable from a recent estimate of seawater $\delta^{\text{98/95}}_{\text{Mo}}$ from an earlier hyperthermal (Paleocene Eocene Thermal Maximum (PETM, 55.9Ma), $\delta^{\text{98/95}}_{\text{Mo}}$ = 2.08±0.11‰). It is argued that the similarity in seawater $\delta^{\text{98/95}}_{\text{Mo}}$ during ETM-2 and the PETM was caused by the development of transient euxinia in the Arctic Ocean during each hyperthermal that allowed sediments accumulating in this basin to capture the long term $\delta^{\text{98/95}}_{\text{Mo}}$ of early Eocene seawater. Our new data therefore place a minimum constraint on the magnitude of transient global seafloor deoxygenation during early Eocene hyperthermals.
Keywords
Hyperthermals, early Eocene, Eocene Thermal Maximum 2, Molybdenum isotopes, deoxygenation, Arctic Ocean.

Introduction
Oxygen concentrations in seawater reflect the competing influences of temperature-dependent oxygen diffusion over the air-sea boundary, ventilation by circulating water masses, and consumption during the remineralisation of organic matter. Recent studies have highlighted a seawater deoxygenation trend in several regions of the present day ocean [Keeling et al., 2010], which has been linked to CO$_2$-driven global warming. Deoxygenation has the potential to have a severe impact on marine biodiversity [Stramma et al., 2008, 2010] and biogeochemical processes [e.g. Deutsch et al., 2011] in the future. At present, however, we do not have a complete understanding of how different oxygen-controlling mechanisms have interacted to drive these trends, or of how these competing influences are likely to evolve under future scenarios of enhanced greenhouse warming [Keeling et al., 2010].

One way to understand how oxygen concentrations in seawater may evolve in the future as a consequence of global environmental change is to reconstruct redox conditions in the oceans during past global warming events. One such event is Eocene Thermal Maximum 2 (ETM-2, or event H1 of Cramer et al., [2003]), a period of rapid CO$_2$ driven global warming that took place in the early Eocene approximately 54.1 million years ago [Zachos et al., 2010]. ETM-2 is characterised by deep-sea carbonate dissolution [Lourens et al., 2005; Stap et al., 2009], a negative carbon isotope excursion (CIE) in marine carbonates, marine organic matter and terrestrial pedogenic carbonates of 1-1.7‰, 3-4.5‰ and 3.8‰ respectively [Cramer et al., 2003; Lourens et al., 2005; Sluijs et al., 2009; Stap et al., 2009, 2010a, 2010b; Schoon et al., 2011; Abels et al., 2012] and ocean warming of 2-5°C above pre-event temperatures [Sluijs et al., 2009; Stap et al., 2010a, 2010b]. ETM-2 was one of a series of abrupt global warming episodes that occurred throughout the Eocene [Cramer et al., 2003; Lourens et al., 2005; Nicolo et al., 2008; Zachos et al., 2010; Sexton et al., 2011], which were superimposed on a background climate state several degrees warmer than the present day [Sexton et al., 2006; Pearson et al., 2007; Sluijs et al., 2008;
Several reconstructions have suggested a trend towards greater seawater deoxygenation during large hyperthermal events such as the Paleocene-Eocene Thermal Maximum (PETM) in response to global warming and changes in ocean circulation [e.g. Bralower et al., 1997; Thomas et al., 1998; Chun et al., 2010; Winguth et al., 2012; Dickson et al., 2012].

This study presents molybdenum (Mo) isotope ratio and trace metal concentration data for sediments spanning ETM-2 obtained from IODP Expedition 302, Site M0004A in the Arctic Ocean. Our objective was to evaluate the effect on global ocean redox of environmental perturbations caused by carbon-led warming of differing magnitude and duration to the more widely studied PETM. The new isotope data allow us to constrain the molybdenum isotope composition of global seawater during ETM-2 to 2.00±0.11‰, which is indistinguishable from the Mo-isotope composition of seawater recorded during the PETM [Dickson et al., 2012]. We argue that the similarity of the Mo-isotope compositions of seawater during ETM-2 and the PETM reflects the long-term early Eocene seawater Mo-isotope composition. Our findings set a minimum constraint on the magnitude of short-term transient global deoxygenation during ETM-2 and other early Eocene hyperthermal events.

Molybdenum isotope systematics

The utility of the Mo-isotope system as a global oxygenation proxy arises from the distinctive chemical behaviour and associated isotope fractionations of Mo in different redox environments. Molybdenum exists in oxygenated seawater primarily as the conservative molybdate anion (MoO$_4^{2-}$), which is slowly removed into sediments by adsorption to ferromanganese oxides. In contrast, in sulphidic (euxinic) conditions, Mo forms particle-reactive thiomolybdates (MoO$_{S_{x}S_{4-x}}^{2-}$) that are rapidly scavenged from seawater [Crusius et al., 1996; Eriksson and Helz, 2000].

Molybdenum isotope fractionation (expressed hereafter as $\delta^{98/95}$Mo, where $\delta^{98/95}$Mo= $((^{98}Mo/^{95}Mo_{sample}/^{98}Mo/^{95}Mo_{sample})-1)/1000$) associated with adsorption to manganese (Mn) oxides is approximately -3‰ relative to the present day seawater $\delta^{98/95}$Mo of 2.3‰ [Siebert et al., 2003; Barling and Anbar, 2004; Neubert et al., 2008]. In sub-oxic to anoxic environments, Mo is thought to be sequestered into sediments by the reductive dissolution of Mn and iron (Fe) oxyhydroxides,
followed by reprecipitation as sulphide species with pyrite and/or organic matter. Although $\delta^{98/95}$Mo reported for reducing sediments ranges from -0.5‰ to 1.8‰ [McManus et al., 2002; Siebert et al., 2006; Poulson et al., 2006], observations of recent anoxic continental margin sediments show that $\delta^{98/95}$Mo cluster close to ~1.6‰, a value that is ~0.7‰ lower than seawater $\delta^{98/95}$Mo [Poulson-Brucker et al., 2009]. In sulphidic environments (>11µmol/l hydrogen sulphide, H$_2$S [Eriksson and Helz, 2000]), the rapid removal of Mo from the water column following conversion to thiomolybdates can lead to the drawdown of the seawater Mo reservoir and the quantitative transfer of the seawater $\delta^{98/95}$Mo into underlying sediments, as observed in the Black Sea [Neubert et al., 2008; Nägler et al., 2011].

The seawater $\delta^{98/95}$Mo, recorded as the $\delta^{98/95}$Mo in euxinic sediments, reflects the global balance of Mo delivered to the oceans by rivers and hydrothermal inputs, and the relative importance of its subsequent removal into the various seafloor redox environments (oxic, sub-oxic to anoxic, euxinic). Generally, if the size of the oxic Mo sink were to decrease, the seawater $\delta^{98/95}$Mo would become lower, and vice-versa. In the present day ocean, the high concentration (105µmol/l) and conservative behaviour of MoO$_4^{2-}$ in seawater contributes to its long residence time of approximately 450,000-800,000 yrs [Emerson and Huested, 1991; Miller et al., 2011]. In order for a secular change in $\delta^{98/95}$Mo to be recorded in the sedimentary record when residence times are similar to the present day value, any change in the relative importance of different seafloor redox environments would have to either be large, or be sustained for at least ~10$^5$ yrs. Transient variations in seawater $\delta^{98/95}$Mo may be recorded in the sedimentary record if the concentration of Mo in seawater was substantially less than present, since a lower Mo concentration would correspondingly reduce its seawater residence time [e.g. Pearce et al., 2008; Miller et al., 2011].

**Study Site**

IODP Expedition 302 Site M0004A is located on the Lomonosov Ridge in the Arctic Ocean (87°51.995’N, 136°47 10.641’E, 1288m water depth). During the early Eocene Site M0004A was located on a subsiding continental margin at a palaeodepth of <200m [Moran et al., 2006]. During ETM-2, the local environment became highly productive in response to the enhanced delivery of
nutrients from weathering of the adjacent continental margin associated with warm, wet conditions in the Arctic region [Sluijs et al., 2008, 2009]. Reductions in local seawater oxygen concentrations appear to have occurred during ETM-2, as high organic carbon fluxes consumed available dissolved oxygen and caused the redoxcline to shoal from within seafloor sediments into the water column [Stein et al., 2006; Sluijs et al., 2009; Mä rz et al., 2010; Schoon et al., 2011]. Local deoxygenation was likely to have been enhanced by a reduction in deepwater ventilation due the formation of a low-salinity surface layer that served to inhibit local overturning [Waddell and Moore, 2008].

**Methods**

Site M0004A was sampled between 368 and 372 metres composite depth (mcd) to bracket the ETM-2 interval as defined by a negative CIE in bulk organic matter and in algal biomarkers [Stein et al., 2006; Sluijs et al., 2009, Schoon et al., 2011] and by dinocyst stratigraphy [Sluijs et al., 2008]. For δ$^{13}$C$_{org}$ analyses, 250mg aliquots of dried ground sample powders were de-calcified and weighed into tin capsules. Isotope analyses were performed using a Thermo-Finnegan Mat 253 mass spectrometer. Long-term reproducibility was monitored using IAEA-CH6 sucrose standards, and was better than ±0.1‰. The abundances of major element oxides were determined by fusing ground sample powders to glass discs with Johnson Matthey Spectroflux® 100A. Analyses were conducted using an ARL 8420+ dual goniometer wavelength dispersive XRF spectrometer. Accuracy and precision were monitored with standard reference materials and were better than ±1% and ±2% respectively. The abundances of minor elements were determined by ICP-MS following acid digestion of 10-50mg aliquots of sample powders. Sample accuracy and precision were monitored with certified and in-house reference materials and were better than ±10%. Major and minor element data are normalised to titanium and quoted as enrichment factors over average upper continental crust values: $X_{EF} = (X_S/Ti_S) / (X_{UC}/Ti_{UC})$, where Ti is titanium, X is the normalised element, _S_ is the analysed sample, and _UC_ is the average upper continental crust value [Rudnick and Gao, 2003].

For Mo and Re analyses, 10-100mg sample aliquots were accurately weighed into Teflon digestion vessels along with a $^{100}$Mo and $^{97}$Mo double spike and a $^{185}$Re spike. An appropriate
amount of spike was added to obtain a spike:sample ratio of 3:1 [Pearce et al., 2009]. Spike
masses were calculated from Mo abundances determined for each sample by ICP-MS prior to a
separate digestion for Mo-isotope analysis. Samples were digested in inverse aqua-regia and were
subsequently purified for Mo-isotope determinations using a single anion-exchange column
procedure [Pearce et al., 2009]; Re purification employed a liquid-liquid separation technique [Birck
et al., 1997]. Mo isotope compositions were determined using a Thermo-Finnegan Neptune MC-
ICP-MS coupled to an Aridus desolvating nebuliser. Mo-isotope ratios were normalised to the daily
mean of Mo solution standards (Fischer Chemicals, ICP Mo standard solution, lot 9920914-150).
Reproducibility was monitored with repeat digestions of USGS Devonian Shale SD0-1 (δ⁹⁸/⁹⁵Mo =
1.14±0.04‰, 2 S.D., n=6) and an in-house mudrock standard (Monterey Formation mudrock
00N118, δ⁹⁸/⁹⁵Mo = 2.06±0.07‰, 2 S.D., n=9). All ETM-2 samples were processed in a single
batch with a Mo procedural blank of 6ng, typically contributing much less than 1% to all samples.
Re concentrations were determined by isotope dilution using a Thermo-Finnegan Neptune MC-
ICP-MS. Instrumental mass fractionation was corrected by normalising to a ^{193}Ir/^{191}Ir ratio of
1.68299.

Results

Results are shown in Fig. 1 and Table 1. The new δ¹³C_org data refine and are consistent with
published δ¹⁵C_org data for Site M0004A [Stein et al., 2006; Sluijs et al., 2009] (Fig.1). The compiled
data exhibit a negative CIE between 368.94 and 368.16 metres composite depth (mcd) that
corresponds to ETM-2 [Sluijs et al., 2009; Schoon et al., 2011]. The new data document a CIE
amplitude at Site M0004A of 4.9‰, which is 0.4‰ larger than previously reported.

Measured Mo and Re abundances across ETM-2 at Site M0004A range from 6-189ppm
and 16-359ppb respectively, and are all elevated above their average crustal values of ~1ppm and
~0.2ppb [Rudnick and Gao, 2003]. Fe is also enriched by over a factor of four times the average
crustal abundance, consistent with the presence of abundant pyrite throughout the study section
[Stein et al., 2006] (Fig. 1). Increases in Mo, Re and Fe abundances correspond stratigraphically to
the onset of fine mm-scale sedimentary laminations at the base of the CIE [Expedition 302
Scientists, 2006]. However, maximum Mo and Fe abundances lag the onset of the laminations and
the negative peak of the CIE by ~25cm (Fig.1).

All measured Mo spike:sample ratios are in the optimum range of 1.5-4 [Pearce et al.,
2009], and are therefore of high quality. Below the CIE, $\delta^{98/95}$Mo ranges from -0.34‰ to 0.49‰.
Between 369.15 and 368.8 mcd, an interval spanning the onset of the ETM-2 CIE and the
appearance of mm-scale laminations in the core, $\delta^{98/95}$Mo increases progressively to a maximum of
2.00‰ at 368.6 mcd. $\delta^{98/95}$Mo then declines abruptly to 0.55‰ above 368.5 mcd, at the same point
at which mm-scale laminations in the core temporarily disappear. The highest $\delta^{98/95}$Mo during
ETM-2 of 1.58‰ to 2.00‰ occur in samples characterised by the highest Mo abundances (~119-
189ppm), the lowest Re/Mo ratios (~0.7), and by the presence of sulphur-bound isorenieratane
(0.3-0.5µg/g, [Sluijs et al., 2009]).

Discussion

Origin of $\delta^{98/95}$Mo variations across ETM-2

The stratigraphic variations in $\delta^{98/95}$Mo that we observe across ETM-2 at Site M0004A are likely to
have been caused by mixing between (i) adsorbed Mo released during the dissolution of Fe and
Mn oxide phases within sediment pore waters, followed by re-precipitation as Mo-sulphides [e.g.
Poulson et al., 2006; Goldberg et al., 2009], and (ii) Mo delivered to the seafloor as thiomolybdate.
This model is supported by the progressive shift from low to high $\delta^{98/95}$Mo across the redox
boundary at the base of the ETM-2 CIE in Site M0004A (Fig. 1), which is defined by the onset of
sedimentary laminations and by increases in the abundance of redox sensitive elements such as
Mo, Re and Fe (Fig.1). The steady decline in porewater oxygen concentrations across the onset of
ETM-2 would have decreased the ratio of isotopically light Mo liberated from oxide phases to
isotopically heavy thiomolybdate [Poulson et al., 2006; Goldberg et al., 2009] thus altering the
average sediment $\delta^{98/95}$Mo. A local redox control on stratigraphic variations in $\delta^{98/95}$Mo is clearly
demonstrated by correlations between $\delta^{98/95}$Mo, Mo abundances and Fe enrichments (Fig. 2).

We argue that under fully euxinic conditions during ETM-2, the highest observed $\delta^{98/95}$Mo of
2.00‰ in deposits from ETM-2 in Site M0004A reflects the near-quantitative removal of Mo as
thiomolybdate from overlying seawater, and thus records the ambient seawater $\delta^{98/95}$Mo. The
presence of local euxinia is indicated by a range of observations. Firstly, extremely high (120-190 ppm) Mo abundances occur between 368.5 and 368.69 mcd. These significant Mo enrichments are best explained by the presence of locally sulphidic conditions that facilitated the rapid production of particle reactive \(\text{MoS}_4^{2-}\) from dissolved \(\text{MoO}_4^{2-}\) \cite{Crusius et al., 1996}. Secondly, the very high Mo enrichments also occur within the same stratigraphic horizon as mm-scale sedimentary laminations, indicating the absence of bioturbation by benthic organisms \cite{Expedition 302 Scientists, 2006} and supporting the presence of anoxic conditions at the seafloor. Thirdly, Re/Mo ratios decrease to minimum values of \(~0.7\text{ppb/ppm}\) between 368.5 and 368.69 mcd. The present day ratio of these elements in seawater is 0.4 mmol/mol, which under sulphidic conditions would be transferred into sediments with an abundance ratio of 0.75 ppb/ppm \cite{Crusius et al., 1996}. Thus the low Re/Mo ratios observed at Site M0004A are strong evidence that these elements were scavenged quantitatively from seawater into Arctic Ocean seafloor sediments during ETM-2 was near-complete. Fourthly, Fe reaches its highest enrichment of \(>4\) times the average crustal abundance between 368.5 and 368.69 mcd, suggesting that reactive iron was rapidly converted to pyrite under sulphidic conditions \cite{Poulton and Canfield, 2011}. Lastly, the ready availability of free \(\text{H}_2\text{S}\) for pyrite formation is also consistent with low carbon/sulphur ratios during the ETM-2 interval of Site M0004A \cite{Stein et al., 2006} and a peak in sulphur-bound isorenieratane abundances between 368.5 and 368.69 mcd, suggesting that sulphidic conditions extended into the photic zone of the overlying water column at that time \cite{Sluijs et al., 2009} (Fig.1). At present, it cannot be quantitatively demonstrated that \(\text{H}_2\text{S}\) concentrations in Arctic Ocean seawater were above the \(~11 \mu\text{mol/l}\) required to fully convert dissolved \(\text{MoO}_4^{2-}\) to \(\text{MoS}_4^{2-}\) \cite{Erickson and Helz, 2000; Neubert et al., 2008}. The many lines of evidence for highly sulphidic conditions presented above, however, qualitatively suggest that the highest \(\delta^{98/95}\text{Mo}\) of \(2.00\pm0.11\%\) measured during ETM-2 at Site M0004A can be considered a close minimum estimate for the \(\delta^{98/95}\text{Mo}\) of Arctic Ocean seawater.

It is likely that \(\delta^{98/95}\text{Mo}\) of \(2.00\pm0.11\%\) also reflects the global seawater \(\delta^{98/95}\text{Mo}\) during ETM-2 because despite rapid Mo drawdown from the Arctic Ocean water column, Mo supply to the Arctic basin was not limited during the peak of the CIE. This is demonstrated by the co-variation of Mo and U abundances in sediments spanning ETM-2 (Fig.3) that parallels the ratio of Mo and U in present day seawater. If the Arctic basin had been totally restricted and the supply of Mo...
consequently limited, Mo and U abundances would define a shallower gradient as Mo abundances evolved to lower values through time with respect to U [Algeo and Tribovillard, 2009; Tribovillard et al., in press]. Lastly, dinocyst assemblage variations during ETM-2 at Site M0004A are similar to assemblage changes in the North Sea [Sluijs et al., 2008], which again suggests that seawater was able to exchange between the Arctic and surrounding oceans.

Comparison of ETM-2 to the PETM

The geochemistry of sediments deposited at Site M0004A during the early Eocene generally reflects a low-oxygen seafloor environment [Stein et al., 2006; März et al., 2010]. However, the presence of locally sulphidic conditions seems to have been restricted to shorter intervals of time when elevated biological productivity and a salinity-stratified water column helped to consume all available oxygen and caused the redox cline to shoal from porewaters into the overlying water column. The new data from euxinic sediments deposited during ETM-2 presented here can be directly compared to published data spanning the euxinic section of the PETM from the same core [Dickson et al., 2012] (Fig. 4). The seawater δ\(^{98/95}\)Mo for ETM-2 and the PETM were 2.00±0.11‰ and 2.08±0.11‰, respectively, which are indistinguishable within the respective uncertainties. This observation suggests two possibilities: (i) that transient changes in global ocean oxygenation during both ETM-2 and the PETM were identical; or (ii) that transient changes towards local euxinia in the Arctic Ocean during the PETM and ETM-2 allowed sediments from Site M0004A to temporarily capture the ambient long-term seawater δ\(^{98/95}\)Mo, thereby reflecting the mean oxygenation state of the early Eocene global ocean.

Option (ii) is more likely to be correct for several reasons. Firstly, identical transient responses of global ocean oxygenation would require a near perfect balance of the different controls on mean seawater redox during both ETM-2 and the PETM. Such a delicate balance is difficult to envisage given that the magnitude of the ETM-2 CIE and associated global warming was approximately half that of the PETM [Cramer et al., 2003; Lourens et al., 2005; Stap et al., 2009, 2010a]. Also, the influence of ocean productivity and circulation on oxygen distributions in seawater during ETM-2 and the PETM are likely to have differed, although these parameters are currently poorly constrained by proxy data.
Option (ii) is also favoured because the sedimentary abundances of Mo measured during the euxinic intervals of ETM-2 and the PETM at Site M0004A are consistent with a high seawater Mo inventory that would have been relatively insensitive to changes in ocean redox at timescales shorter than either the PETM or ETM-2 (<~200,000 yrs) \cite{Rohl2007, Stap2009, Murphy2010}. This argument arises from the rapidity of Mo enrichment into euxinic sediments, which acts to draw down the concentrations of Mo in overlying seawater \cite{Emerson1991}. Consequently, the concentration of Mo in seawater, which is linked to its seawater residence time, is directly reflected by Mo enrichments in euxinic sediments. Seawater Mo concentrations lower than present have been inferred using Mo enrichments in euxinic sediments across ocean anoxic events (OAEs) in the Cretaceous \cite{Hetzel2007} and early Jurassic \cite{Pearce2008} periods, and during the Cambrian \cite{Gill2011} and mid-Proterozoic \cite{Scott2008}. In the case of the early Jurassic Toarcian OAE \cite{Pearce2008}, Mo abundances in euxinic sediments of the Cleveland Basin, UK, were only 5-7ppm, consistent with a seawater residence time of ~27ka \cite{Miller2011}. In contrast, Mo abundances at Site M0004A reach 189ppm and 102ppm in the euxinic sedimentary intervals of ETM-2 and the PETM respectively. These observations are consistent with a high concentration of Mo in early Eocene seawater, and consequently with a long seawater residence time.

The present day concentration of dissolved \( \text{MoO}_4^{2-} \) in seawater is 105nmol/kg \cite{Collier1985}. This value corresponds to a global ocean Mo inventory of ~1.4x10^{14} mol and a steady state seawater residence time of ~440,000-800,000yrs \cite{Emerson1991, Miller2011}. Given that the PETM lasted for approximately ~200,000yrs \cite{Rohl2007, Murphy2010}, and ETM-2 lasted approximately 100,000yrs \cite{Stap2009}, the seawater Mo inventory would have to have declined by at least 75% from its modern value for transient changes in the amount of Mo sequestered into each redox-dependent seafloor Mo sink to be recorded by a change in the seawater \( \delta^{98/95}\text{Mo} \). The magnitude of this reduction in \( \delta^{98/95}\text{Mo} \) is inconsistent with the very high sedimentary Mo enrichments discussed above. Additionally, such a dramatic reduction in the dissolved Mo inventory would be likely to have occurred alongside a significant expansion of seafloor anoxia, which is inconsistent with global mass balance constraints imposed by the
seawater $\delta^{98/95}\text{Mo}$ of $>2\%$ inferred from Site M0004A inferred from both this study of ETM-2 and the earlier study of the PETM by Dickson et al. [2012].

The most parsimonious explanation for the $\delta^{98/95}\text{Mo}$ data for the early Eocene is therefore that the global ocean at that time was characterised by high concentrations of dissolved molybdenum, and by a seawater $\delta^{98/95}\text{Mo}$ of $\sim 2.04 \pm 0.15\%$ (the average value recorded by euxinic ETM-2 and PETM samples). This value for the early Eocene seawater $\delta^{98/95}\text{Mo}$ reflects the mean oxygenation state of the global ocean under greenhouse climate conditions significantly warmer than at present, with the $\delta^{98/95}\text{Mo}$ being captured periodically by the unique palaeoenvironmental conditions that occurred in the Arctic Ocean during the PETM and ETM-2. Our interpretation is supported by very low-resolution Fe-Mn crust data from the Atlantic Ocean that indicates an oxic $\delta^{98/95}\text{Mo}$ of $-0.80-0.90\%$ between 52-56Ma, and by a single data point from a Pacific Ocean Fe-Mn crust that indicates a $\delta^{98/95}\text{Mo}$ of $-0.6\%$ [Siebert et al., 2003]. Experimental observations suggest that adsorption of MoO$_4^{2-}$ from seawater onto Mn-oxides has an equilibrium isotope fractionation of $-3\%$, and adsorption to hematite has a fractionation of $-2.2\%$ [Goldberg, 2009]. If these fractionation factors between ferromanganese crusts and seawater are assumed to apply to the early Eocene ocean, the Fe-Mn crust data would indicate an early Eocene seawater $\delta^{98/95}\text{Mo}$ of $2.1-2.4\%$, which is consistent with our observations from the euxinic Arctic Ocean.

Implications for the development of transient deoxygenation during early Eocene hyperthermals

With the new data presented here for ETM-2, we suggest that reducing environments in the early Eocene ocean were consistently expanded over multi-million year timescales by a small but significant amount compared with the present day. Mass balance modelling using conservative estimates for oxic ($-0.9\%$), anoxic ($1.6\%$) and terrestrial ($0-0.7\%$) $\delta^{98/95}\text{Mo}$ endmembers suggest that the amount of Mo sequestered in anoxic seafloor environments may have been proportionally $\sim 3-6\%$ higher than at the present day. Lower average oxygen concentrations in the early Eocene ocean may have been directly related to higher global temperatures [Sexton et al., 2006; Pearson et al., 2007; Sluijs et al., 2008; Zachos et al., 2008; Bijl et al., 2009], which would have lowered the solubility of oxygen in seawater. However, the quantitative effect of warming on seawater oxygen concentrations in the early Eocene ocean would be complicated by differences in
palaeogeography, ocean circulation [Thomas et al., 2003; Nunes and Norris, 2006] and marine productivity [e.g. Stoll and Bains, 2003; Gibbs et al., 2006; Paytan et al., 2007]. Consequently, a full understanding of oxygenation responses to global warming during the early Eocene is likely to require additional proxy data constraints on these different parameters, along with their incorporation into Earth system models.

It has been suggested that oxygen concentrations in seawater became temporarily lower during the PETM compared to the situation immediately before the PETM, suggesting a shift to greater oxygen deficiency in response to transient environmental change and global warming [e.g. Bralower et al., 1997; Thomas et al., 1998; Chun et al., 2010; Kaiho et al., 2006; Nicolo et al., 2010; Speijer et al., 1997; Speijer and Schmitz, 1998; Gavrilov et al., 1997; Stein et al., 2006; Lippert and Zachos, 2007; Schulte et al., 2011; Soliman et al., 2011; Stassen et al., 2012; Winguth et al., 2012; Dickson et al., 2012]. Our new Mo-isotope data indicate that a ~3-6% expansion of the anoxic seafloor Mo sink represents a minimum estimate for the effects of global seawater deoxygenation during the PETM and ETM-2.

Conclusions

The $\delta^{98/95}$Mo of sediments spanning ETM-2 from Arctic Ocean IODP Expedition 302 Site M0004A range between -0.34‰ and 2.00‰. Stratigraphic variations in $\delta^{98/95}$Mo mainly correspond to local redox fluctuations recorded by associated sedimentological, elemental and organic geochemical data. The maximum $\delta^{98/95}$Mo of 2.00±0.11‰ at Site M0004A occurred together with the development of locally euxinic conditions, and thus can be considered as a close minimum estimate for the seawater $\delta^{98/95}$Mo during ETM-2. This value is indistinguishable from the previously identified seawater $\delta^{98/95}$Mo from the PETM interval of the same core [Dickson et al., 2012]. It is suggested that the average $\delta^{98/95}$Mo for both events (2.04±0.15‰) represents the long-term seawater composition for the early Eocene global ocean, given that seawater Mo concentrations were likely to have been too high for seawater $\delta^{98/95}$Mo to respond to transient changes in ocean oxygenation across these relatively brief hyperthermal events. Our maximum estimate of a of 3-6% expansion of the anoxic seafloor Mo reservoir in the early Eocene compared to the present day is therefore consistent with more extensive low-oxygen marine environments.
under conditions of elevated global temperatures. The low sensitivity of $\delta^{98/95}{\text{Mo}}$ to short-term redox perturbations does not preclude the possibility of a more significant expansion of low-oxygen marine environments in response to transient environmental changes during early Eocene hyperthermal episodes [e.g. Bralower et al., 1997; Chun et al., 2010; Winguth et al., 2012].

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**Figure captions**

**Figure 1:** Geochemical data from IODP Expedition 302 Site M0004A spanning ETM-2. A: Compilation of δ¹³C<sub>org</sub> data. White circles from Stein et al. [2006]; black diamonds from Sluijs et al. [2006]; white squares from this study. B: δ⁹⁸/⁹⁵Mo compositions. White square denote repeat digestions. Error bars denote analytical uncertainty (2 standard errors) apart from data points at 368.5, 368.6 and 368.77 mcd, which denote 2 S.D. errors on duplicate analyses (n=2-5). C: Molybdenum abundances. D: Ratios of sedimentary abundances of Re and Mo (ppb/ppm). E: Total Fe enrichments. F: Abundance of sulphur-bound isorenieratane [Sluijs et al., 2009]. Horizontal lines on the stratigraphic column indicate the position of mm-scale laminations [Expedition 302 Scientific Party, 2006].

**Figure 2:** Relationship of δ⁹⁸/⁹⁵Mo to local redox indicators. A: δ⁹⁸/⁹⁵Mo – 1/[Mo] scatter plot. B: δ⁹⁸/⁹⁵Mo – Fe<sub>EF</sub> scatter plot.

**Figure 3:** Covariation of Mo and U abundances across the PETM and ETM-2 intervals of Site M0004A. Dashed lines show proportions of the present day seawater Mo/U molar ratio (7.5 mol/mmol) expressed as a sedimentary mass ratio of 3.1:1.

**Figure 4:** Geochemical data from IODP Expedition 302 Site M0004A spanning ETM-2 [this study] and the PETM [Dickson et al., 2012]. A: Compilation of δ¹³C<sub>org</sub> data. White circles from Stein et al. [2006]; black diamonds from Sluijs et al. [2006, 2009]; white squares from this study and Dickson et al. [2012]. B: δ⁹⁸/⁹⁵Mo compositions. Euxinic intervals used to estimate global seawater δ⁹⁸/⁹⁵Mo are marked by shaded bands. The vertical dashed line indicates the average early Eocene seawater δ⁹⁸/⁹⁵Mo of 2.04±0.15‰ derived from both intervals.
Table 1: Geochemical data spanning ETM-2 from IODP Expedition 302, Site M0004A

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (mcd)</th>
<th>δ(^{13})C(_{org})</th>
<th>δ(^{98/95})Mo</th>
<th>2 S.E.</th>
<th>[Mo], ppm</th>
<th>[Re], ppb</th>
<th>%TiO(_2)</th>
<th>%Fe(_2)O(_3)</th>
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<tbody>
<tr>
<td>27-1 (76-77)</td>
<td>368.160</td>
<td>-27.481</td>
<td>0.779</td>
<td>0.032</td>
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<td>65.212</td>
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<td>27-1 (94-95)</td>
<td>368.34</td>
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<td>0.031</td>
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<td>119.093</td>
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<td>143.017</td>
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