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

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How to cite:

Dickson, Alexander J. and Cohen, Anthony S. (2012). A molybdenum isotope record of Eocene Thermal Maximum 2: implications for global ocean redox during the early Eocene. *Paleoceanography*, 27(3), article no. PA3230.

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Version: Accepted Manuscript

Link(s) to article on publisher's website:

<http://dx.doi.org/doi:10.1029/2012PA002346>

<http://www.agu.org/pubs/crossref/2012/2012PA002346.shtml>

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

3

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10

11 **Abstract**

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

27

28

29

30 **Keywords**

31 Hyperthermals, early Eocene, Eocene Thermal Maximum 2, Molybdenum isotopes,
32 deoxygenation, Arctic Ocean.

33

34 **Introduction**

35 Oxygen concentrations in seawater reflect the competing influences of temperature-dependent
36 oxygen diffusion over the air-sea boundary, ventilation by circulating water masses, and
37 consumption during the remineralisation of organic matter. Recent studies have highlighted a
38 seawater deoxygenation trend in several regions of the present day ocean [*Keeling et al., 2010*],
39 which has been linked to CO₂-driven global warming. Deoxygenation has the potential to have a
40 severe impact on marine biodiversity [*Stramma et al., 2008, 2010*] and biogeochemical processes
41 [e.g. *Deutsch et al., 2011*] in the future. At present, however, we do not have a complete
42 understanding of how different oxygen-controlling mechanisms have interacted to drive these
43 trends, or of how these competing influences are likely to evolve under future scenarios of
44 enhanced greenhouse warming [*Keeling et al., 2010*].

45 One way to understand how oxygen concentrations in seawater may evolve in the future as
46 a consequence of global environmental change is to reconstruct redox conditions in the oceans
47 during past global warming events. One such event is Eocene Thermal Maximum 2 (ETM-2, or
48 event H1 of *Cramer et al., [2003]*), a period of rapid CO₂ driven global warming that took place in
49 the early Eocene approximately 54.1 million years ago [*Zachos et al., 2010*]. ETM-2 is
50 characterised by deep-sea carbonate dissolution [*Lourens et al., 2005; Stap et al., 2009*], a
51 negative carbon isotope excursion (CIE) in marine carbonates, marine organic matter and
52 terrestrial pedogenic carbonates of 1-1.7‰, 3-4.5‰ and 3.8‰ respectively [*Cramer et al., 2003;*
53 *Lourens et al., 2005; Sluijs et al., 2009; Stap et al., 2009, 2010a, 2010b; Schoon et al., 2011; Abels*
54 *et al., 2012*] and ocean warming of 2-5°C above pre-event temperatures [*Sluijs et al., 2009; Stap et*
55 *al., 2010a, 2010b*]. ETM-2 was one of a series of abrupt global warming episodes that occurred
56 throughout the Eocene [*Cramer et al., 2003; Lourens et al., 2005; Nicolo et al., 2008; Zachos et al.,*
57 *2010; Sexton et al., 2011*], which were superimposed on a background climate state several
58 degrees warmer than the present day [*Sexton et al., 2006; Pearson et al., 2007; Sluijs et al., 2008;*

59 *Zachos et al., 2008; Bijl et al., 2009*]. Several reconstructions have suggested a trend towards
60 greater seawater deoxygenation during large hyperthermal events such as the Paleocene-Eocene
61 Thermal Maximum (PETM) in response to global warming and changes in ocean circulation [e.g.
62 *Bralower et al., 1997; Thomas et al., 1998; Chun et al., 2010; Winguth et al., 2012; Dickson et al.,*
63 *2012*].

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

75

76 *Molybdenum isotope systematics*

77 The utility of the Mo-isotope system as a global oxygenation proxy arises from the distinctive
78 chemical behaviour and associated isotope fractionations of Mo in different redox environments.
79 Molybdenum exists in oxygenated seawater primarily as the conservative molybdate anion (MoO_4^{2-})
80), which is slowly removed into sediments by adsorption to ferromanganese oxides. In contrast, in
81 sulphidic (euxinic) conditions, Mo forms particle-reactive thiomolybdates ($\text{MoO}_x\text{S}_{4-x}^{2-}$) that are
82 rapidly scavenged from seawater [*Crusius et al., 1996; Eriksson and Helz, 2000*].

83 Molybdenum isotope fractionation (expressed hereafter as $\delta^{98/95}\text{Mo}$, where $\delta^{98/95}\text{Mo} =$
84 $((^{98}\text{Mo}/^{95}\text{Mo}_{\text{sample}}/^{98}\text{Mo}/^{95}\text{Mo}_{\text{sample}}) - 1) / 1000$) associated with adsorption to manganese (Mn) oxides is
85 approximately -3% relative to the present day seawater $\delta^{98/95}\text{Mo}$ of 2.3% [*Siebert et al., 2003;*
86 *Barling and Anbar, 2004; Neubert et al., 2008*]. In sub-oxic to anoxic environments, Mo is thought
87 to be sequestered into sediments by the reductive dissolution of Mn and iron (Fe) oxyhydroxides,

88 followed by reprecipitation as sulphide species with pyrite and/or organic matter. Although $\delta^{98/95}\text{Mo}$
89 reported for reducing sediments ranges from -0.5‰ to 1.8‰ [McManus et al., 2002; Siebert et al.,
90 2006; Poulson et al., 2006], observations of recent anoxic continental margin sediments show that
91 $\delta^{98/95}\text{Mo}$ cluster close to ~1.6‰, a value that is ~0.7‰ lower than seawater $\delta^{98/95}\text{Mo}$ [Poulson-
92 Brucker et al., 2009]. In sulphidic environments (>11 $\mu\text{mol/l}$ hydrogen sulphide, H_2S [Eriksson and
93 Helz, 2000]), the rapid removal of Mo from the water column following conversion to
94 thiomolybdates can lead to the drawdown of the seawater Mo reservoir and the quantitative
95 transfer of the seawater $\delta^{98/95}\text{Mo}$ into underlying sediments, as observed in the Black Sea [Neubert
96 et al., 2008; Nägler et al., 2011].

97 The seawater $\delta^{98/95}\text{Mo}$, recorded as the $\delta^{98/95}\text{Mo}$ in euxinic sediments, reflects the global
98 balance of Mo delivered to the oceans by rivers and hydrothermal inputs, and the relative
99 importance of its subsequent removal into the various seafloor redox environments (oxic, sub-oxic
100 to anoxic, euxinic). Generally, if the size of the oxic Mo sink were to decrease, the seawater
101 $\delta^{98/95}\text{Mo}$ would become lower, and vice-versa. In the present day ocean, the high concentration
102 (105 $\mu\text{mol/l}$) and conservative behaviour of MoO_4^{2-} in seawater contributes to its long residence
103 time of approximately 450,000-800,000 yrs [Emerson and Husted, 1991; Miller et al., 2011]. In
104 order for a secular change in $\delta^{98/95}\text{Mo}$ to be recorded in the sedimentary record when residence
105 times are similar to the present day value, any change in the relative importance of different
106 seafloor redox environments would have to either be large, or be sustained for at least $\sim 10^5$ yrs.
107 Transient variations in seawater $\delta^{98/95}\text{Mo}$ may be recorded in the sedimentary record if the
108 concentration of Mo in seawater was substantially less than present, since a lower Mo
109 concentration would correspondingly reduce its seawater residence time [e.g. Pearce et al., 2008;
110 Miller et al., 2011].

111

112 **Study Site**

113 IODP Expedition 302 Site M0004A is located on the Lomonosov Ridge in the Arctic Ocean
114 (87°51.995'N, 136°47 10.641'E, 1288m water depth). During the early Eocene Site M0004A was
115 located on a subsiding continental margin at a palaeodepth of <200m [Moran et al., 2006]. During
116 ETM-2, the local environment became highly productive in response to the enhanced delivery of

117 nutrients from weathering of the adjacent continental margin associated with warm, wet conditions
118 in the Arctic region [Sluijs et al., 2008, 2009]. Reductions in local seawater oxygen concentrations
119 appear to have occurred during ETM-2, as high organic carbon fluxes consumed available
120 dissolved oxygen and caused the redoxcline to shoal from within seafloor sediments into the water
121 column [Stein et al., 2006; Sluijs et al., 2009; März et al., 2010; Schoon et al., 2011]. Local
122 deoxygenation was likely to have been enhanced by a reduction in deepwater ventilation due the
123 formation of a low-salinity surface layer that served to inhibit local overturning [Waddell and Moore,
124 2008].

125

126 **Methods**

127 Site M0004A was sampled between 368 and 372 metres composite depth (mcd) to bracket the
128 ETM-2 interval as defined by a negative CIE in bulk organic matter and in algal biomarkers [Stein
129 et al., 2006; Sluijs et al., 2009, Schoon et al., 2011] and by dinocyst stratigraphy [Sluijs et al.,
130 2008]. For $\delta^{13}\text{C}_{\text{org}}$ analyses, 250mg aliquots of dried ground sample powders were de-calcified and
131 weighed into tin capsules. Isotope analyses were performed using a Thermo-Finnegan Mat 253
132 mass spectrometer. Long-term reproducibility was monitored using IAEA-CH6 sucrose standards,
133 and was better than $\pm 0.1\%$. The abundances of major element oxides were determined by fusing
134 ground sample powders to glass discs with Johnson Matthey Spectroflux[®] 100A. Analyses were
135 conducted using an ARL 8420+ dual goniometer wavelength dispersive XRF spectrometer.
136 Accuracy and precision were monitored with standard reference materials and were better than
137 $\pm 1\%$ and $\pm 2\%$ respectively. The abundances of minor elements were determined by ICP-MS
138 following acid digestion of 10-50mg aliquots of sample powders. Sample accuracy and precision
139 were monitored with certified and in-house reference materials and were better than $\pm 10\%$. Major
140 and minor element data are normalised to titanium and quoted as enrichment factors over average
141 upper continental crust values: $X_{\text{EF}} = (X_{\text{S}}/\text{Ti}_{\text{S}}) / (X_{\text{UC}}/\text{Ti}_{\text{UC}})$, where Ti is titanium, X is the normalised
142 element, _S is the analysed sample, and _{UC} is the average upper continental crust value [Rudnick
143 and Gao, 2003].

144 For Mo and Re analyses, 10-100mg sample aliquots were accurately weighed into Teflon
145 digestion vessels along with a ¹⁰⁰Mo and ⁹⁷Mo double spike and a ¹⁸⁵Re spike. An appropriate

146 amount of spike was added to obtain a spike:sample ratio of 3:1 [Pearce et al., 2009]. Spike
147 masses were calculated from Mo abundances determined for each sample by ICP-MS prior to a
148 separate digestion for Mo-isotope analysis. Samples were digested in inverse aqua-regia and were
149 subsequently purified for Mo-isotope determinations using a single anion-exchange column
150 procedure [Pearce et al., 2009]; Re purification employed a liquid-liquid separation technique [Birck
151 et al., 1997]. Mo isotope compositions were determined using a Thermo-Finnegan Neptune MC-
152 ICP-MS coupled to an Aridus desolvating nebuliser. Mo-isotope ratios were normalised to the daily
153 mean of Mo solution standards (Fischer Chemicals, ICP Mo standard solution, lot 9920914-150).
154 Reproducibility was monitored with repeat digestions of USGS Devonian Shale SD0-1 ($\delta^{98/95}\text{Mo} =$
155 $1.14 \pm 0.04\%$, 2 S.D., n=6) and an in-house mudrock standard (Monterey Formation mudrock
156 00N118, $\delta^{98/95}\text{Mo} = 2.06 \pm 0.07\%$, 2 S.D., n=9). All ETM-2 samples were processed in a single
157 batch with a Mo procedural blank of 6ng, typically contributing much less than 1% to all samples.
158 Re concentrations were determined by isotope dilution using a Thermo-Finnegan Neptune MC-
159 ICP-MS. Instrumental mass fractionation was corrected by normalising to a $^{193}\text{Ir}/^{191}\text{Ir}$ ratio of
160 1.68299.

161

162 **Results**

163 Results are shown in Fig. 1 and Table 1. The new $\delta^{13}\text{C}_{\text{org}}$ data refine and are consistent with
164 published $\delta^{13}\text{C}_{\text{org}}$ data for Site M0004A [Stein et al., 2006; Sluijs et al., 2009] (Fig.1). The compiled
165 data exhibit a negative CIE between 368.94 and 368.16 metres composite depth (mcd) that
166 corresponds to ETM-2 [Sluijs et al., 2009; Schoon et al., 2011]. The new data document a CIE
167 amplitude at Site M0004A of 4.9‰, which is 0.4‰ larger than previously reported.

168 Measured Mo and Re abundances across ETM-2 at Site M0004A range from 6-189ppm
169 and 16-359ppb respectively, and are all elevated above their average crustal values of ~1ppm and
170 ~0.2ppb [Rudnick and Gao, 2003]. Fe is also enriched by over a factor of four times the average
171 crustal abundance, consistent with the presence of abundant pyrite throughout the study section
172 [Stein et al., 2006] (Fig. 1). Increases in Mo, Re and Fe abundances correspond stratigraphically to
173 the onset of fine mm-scale sedimentary laminations at the base of the CIE [Expedition 302

174 *Scientists*, 2006]. However, maximum Mo and Fe abundances lag the onset of the laminations and
175 the negative peak of the CIE by ~25cm (Fig.1).

176 All measured Mo spike:sample ratios are in the optimum range of 1.5-4 [Pearce et al.,
177 2009], and are therefore of high quality. Below the CIE, $\delta^{98/95}\text{Mo}$ ranges from -0.34‰ to 0.49‰.
178 Between 369.15 and 368.8 mcd, an interval spanning the onset of the ETM-2 CIE and the
179 appearance of mm-scale laminations in the core, $\delta^{98/95}\text{Mo}$ increases progressively to a maximum of
180 2.00‰ at 368.6 mcd. $\delta^{98/95}\text{Mo}$ then declines abruptly to 0.55‰ above 368.5 mcd, at the same point
181 at which mm-scale laminations in the core temporarily disappear. The highest $\delta^{98/95}\text{Mo}$ during
182 ETM-2 of 1.58‰ to 2.00‰ occur in samples characterised by the highest Mo abundances (~119-
183 189ppm), the lowest Re/Mo ratios (~0.7), and by the presence of sulphur-bound isorenieratane
184 (0.3-0.5 $\mu\text{g/g}$, [Slujs et al., 2009]).

185

186 **Discussion**

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

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

200 We argue that under fully euxinic conditions during ETM-2, the highest observed $\delta^{98/95}\text{Mo}$ of
201 2.00‰ in deposits from ETM-2 in Site M0004A reflects the near-quantitative removal of Mo as
202 thiomolybdate from overlying seawater, and thus records the ambient seawater $\delta^{98/95}\text{Mo}$. The

203 presence of local euxinia is indicated by a range of observations. Firstly, extremely high (120-
204 190ppm) Mo abundances occur between 368.5 and 368.69 mcd. These significant Mo enrichments
205 are best explained by the presence of locally sulphidic conditions that facilitated the rapid
206 production of particle reactive MoS_4^{2-} from dissolved MoO_4^{2-} [Crusius et al., 1996]. Secondly, the
207 very high Mo enrichments also occur within the same stratigraphic horizon as mm-scale
208 sedimentary laminations, indicating the absence of bioturbation by benthic organisms [Expedition
209 302 Scientists, 2006] and supporting the presence of anoxic conditions at the seafloor. Thirdly,
210 Re/Mo ratios decrease to minimum values of ~ 0.7 ppb/ppm between 368.5 and 368.69 mcd. The
211 present day ratio of these elements in seawater is 0.4mmol/mol, which under sulphidic conditions
212 would be transferred into sediments with an abundance ratio of 0.75ppb/ppm [Crusius et al., 1996].
213 Thus the low Re/Mo ratios observed at Site M0004A are strong evidence that these elements were
214 scavenged quantitatively from seawater into Arctic Ocean seafloor sediments during ETM-2 was
215 near-complete. Fourthly, Fe reaches its highest enrichment of >4 times the average crustal
216 abundance between 368.5 and 368.69 mcd, suggesting that reactive iron was rapidly converted to
217 pyrite under sulphidic conditions [Poulton and Canfield, 2011]. Lastly, the ready availability of free
218 H_2S for pyrite formation is also consistent with low carbon/sulphur ratios during the ETM-2 interval
219 of Site M0004A [Stein et al., 2006] and a peak in sulphur-bound isorenieratane abundances
220 between 368.5 and 368.69 mcd, suggesting that sulphidic conditions extended into the photic zone
221 of the overlying water column at that time [Sluijs et al., 2009] (Fig.1). At present, it cannot be
222 quantitatively demonstrated that H_2S concentrations in Arctic Ocean seawater were above the ~ 11
223 $\mu\text{mol/l}$ required to fully convert dissolved MoO_4^{2-} to MoS_4^{2-} [Erickson and Helz, 2000; Neubert et al.,
224 2008]. The many lines of evidence for highly sulphidic conditions presented above, however,
225 qualitatively suggest that the highest $\delta^{98/95}\text{Mo}$ of $2.00 \pm 0.11\%$ measured during ETM-2 at Site
226 M0004A can be considered a close minimum estimate for the $\delta^{98/95}\text{Mo}$ of Arctic Ocean seawater.

227 It is likely that $\delta^{98/95}\text{Mo}$ of $2.00 \pm 0.11\%$ also reflects the global seawater $\delta^{98/95}\text{Mo}$ during
228 ETM-2 because despite rapid Mo drawdown from the Arctic Ocean water column, Mo supply to the
229 Arctic basin was not limited during the peak of the CIE. This is demonstrated by the co-variation of
230 Mo and U abundances in sediments spanning ETM-2 (Fig.3) that parallels the ratio of Mo and U in
231 present day seawater. If the Arctic basin had been totally restricted and the supply of Mo

232 consequently limited, Mo and U abundances would define a shallower gradient as Mo abundances
233 evolved to lower values through time with respect to U [*Algeo and Tribovillard, 2009; Tribovillard et*
234 *al., in press*]. Lastly, dinocyst assemblage variations during ETM-2 at Site M0004A are similar to
235 assemblage changes in the North Sea [*Sluijs et al., 2008*], which again suggests that seawater
236 was able to exchange between the Arctic and surrounding oceans.

237

238 *Comparison of ETM-2 to the PETM*

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

253 Option (ii) is more likely to be correct for several reasons. Firstly, identical transient
254 responses of global ocean oxygenation would require a near perfect balance of the different
255 controls on mean seawater redox during both ETM-2 and the PETM. Such a delicate balance is
256 difficult to envisage given that the magnitude of the ETM-2 CIE and associated global warming was
257 approximately half that of the PETM [*Cramer et al., 2003; Lourens et al., 2005; Stap et al., 2009,*
258 *2010a*]. Also, the influence of ocean productivity and circulation on oxygen distributions in
259 seawater during ETM-2 and the PETM are likely to have differed, although these parameters are
260 currently poorly constrained by proxy data.

261 Option (ii) is also favoured because the sedimentary abundances of Mo measured during
262 the euxinic intervals of ETM-2 and the PETM at Site M0004A are consistent with a high seawater
263 Mo inventory that would have been relatively insensitive to changes in ocean redox at timescales
264 shorter than either the PETM or ETM-2 (<~200,000 yrs) [Röhl et al., 2007, Stap et al., 2009;
265 Murphy et al., 2010]. This argument arises from the rapidity of Mo enrichment into euxinic
266 sediments, which acts to draw down the concentrations of Mo in overlying seawater [Emerson and
267 Huested, 1991]. Consequently, the concentration of Mo in seawater, which is linked to its seawater
268 residence time, is directly reflected by Mo enrichments in euxinic sediments. Seawater Mo
269 concentrations lower than present have been inferred using Mo enrichments in euxinic sediments
270 across ocean anoxic events (OAEs) in the Cretaceous [e.g. Hetzel et al., 2007] and early Jurassic
271 [Pearce et al., 2008] periods, and during the Cambrian [Gill et al., 2011] and mid-Proterozoic [Scott
272 et al., 2008]. In the case of the early Jurassic Toarcian OAE [Pearce et al., 2008], Mo abundances
273 in euxinic sediments of the Cleveland Basin, UK, were only 5-7ppm, consistent with a seawater
274 residence time of ~27ka [Miller et al., 2011]. In contrast, Mo abundances at Site M0004A reach
275 189ppm and 102ppm in the euxinic sedimentary intervals of ETM-2 and the PETM respectively.
276 These observations are consistent with a high concentration of Mo in early Eocene seawater, and
277 consequently with a long seawater residence time.

278 The present day concentration of dissolved MoO_4^{2-} in seawater is 105nmol/kg [Collier et al.,
279 1985]. This value corresponds to a global ocean Mo inventory of $\sim 1.4 \times 10^{14}$ mol and a steady state
280 seawater residence time of ~440,000-800,000yrs [Emerson and Huested, 1991; Miller et al., 2011].
281 Given that the PETM lasted for approximately ~200,000yrs [Röhl et al., 2007; Murphy et al., 2010],
282 and ETM-2 lasted approximately 100,000yrs [Stap et al., 2009], the seawater Mo inventory would
283 have to have declined by at least 75% from its modern value for transient changes in the amount of
284 Mo sequestered into each redox-dependent seafloor Mo sink to be recorded by a change in the
285 seawater $\delta^{98/95}\text{Mo}$. The magnitude of this reduction in $\delta^{98/95}\text{Mo}$ is inconsistent with the very high
286 sedimentary Mo enrichments discussed above. Additionally, such a dramatic reduction in the
287 dissolved Mo inventory would be likely to have occurred alongside a significant expansion of
288 seafloor anoxia, which is inconsistent with global mass balance constraints imposed by the

289 seawater $\delta^{98/95}\text{Mo}$ of $>2\text{‰}$ inferred from Site M0004A inferred from both this study of ETM-2 and
290 the earlier study of the PETM by *Dickson et al.* [2012].

291 The most parsimonious explanation for the $\delta^{98/95}\text{Mo}$ data for the early Eocene is therefore
292 that the global ocean at that time was characterised by high concentrations of dissolved
293 molybdenum, and by a seawater $\delta^{98/95}\text{Mo}$ of $\sim 2.04 \pm 0.15\text{‰}$ (the average value recorded by euxinic
294 ETM-2 and PETM samples). This value for the early Eocene seawater $\delta^{98/95}\text{Mo}$ reflects the mean
295 oxygenation state of the global ocean under greenhouse climate conditions significantly warmer
296 than at present, with the $\delta^{98/95}\text{Mo}$ being captured periodically by the unique palaeoenvironmental
297 conditions that occurred in the Arctic Ocean during the PETM and ETM-2. Our interpretation is
298 supported by very low-resolution Fe-Mn crust data from the Atlantic Ocean that indicates an oxic
299 $\delta^{98/95}\text{Mo}$ of $-0.80\text{--}0.90\text{‰}$ between 52-56Ma, and by a single data point from a Pacific Ocean Fe-Mn
300 crust that indicates a $\delta^{98/95}\text{Mo}$ of -0.6‰ [*Siebert et al.*, 2003]. Experimental observations suggest
301 that adsorption of MoO_4^{2-} from seawater onto Mn-oxides has an equilibrium isotope fractionation of
302 -3‰ , and adsorption to hematite has a fractionation of -2.2‰ [*Goldberg*, 2009]. If these
303 fractionation factors between ferromanganese crusts and seawater are assumed to apply to the
304 early Eocene ocean, the Fe-Mn crust data would indicate an early Eocene seawater $\delta^{98/95}\text{Mo}$ of
305 $2.1\text{--}2.4\text{‰}$, which is consistent with our observations from the euxinic Arctic Ocean.

306

307 *Implications for the development of transient deoxygenation during early Eocene hyperthermals*

308 With the new data presented here for ETM-2, we suggest that reducing environments in the early
309 Eocene ocean were consistently expanded over multi-million year timescales by a small but
310 significant amount compared with the present day. Mass balance modelling using conservative
311 estimates for oxic (-0.9‰), anoxic (1.6‰) and terrestrial ($0\text{--}0.7\text{‰}$) $\delta^{98/95}\text{Mo}$ endmembers suggest
312 that the amount of Mo sequestered in anoxic seafloor environments may have been proportionally
313 $\sim 3\text{--}6\%$ higher than at the present day. Lower average oxygen concentrations in the early Eocene
314 ocean may have been directly related to higher global temperatures [*Sexton et al.*, 2006; *Pearson*
315 *et al.*, 2007; *Sluijs et al.*, 2008; *Zachos et al.*, 2008; *Bijl et al.*, 2009], which would have lowered the
316 solubility of oxygen in seawater. However, the quantitative effect of warming on seawater oxygen
317 concentrations in the early Eocene ocean would be complicated by differences in

318 palaeogeography, ocean circulation [Thomas et al., 2003; Nunes and Norris, 2006] and marine
319 productivity [e.g. Stoll and Bains, 2003; Gibbs et al., 2006; Paytan et al., 2007]. Consequently, a
320 full understanding of oxygenation responses to global warming during the early Eocene is likely to
321 require additional proxy data constraints on these different parameters, along with their
322 incorporation into Earth system models.

323 It has been suggested that oxygen concentrations in seawater became temporarily lower
324 during the PETM compared to the situation immediately before the PETM, suggesting a shift to
325 greater oxygen deficiency in response to transient environmental change and global warming [e.g.
326 Bralower et al., 1997; Thomas et al., 1998; Chun et al., 2010; Kaiho et al., 2006; Nicolo et al.,
327 2010; Speijer et al., 1997; Speijer and Schmitz, 1998; Gavrillov et al., 1997; Stein et al., 2006;
328 Lippert and Zachos, 2007; Schulte et al., 2011; Soliman et al., 2011; Stassen et al., 2012; Winguth
329 et al., 2012; Dickson et al., 2012]. Our new Mo-isotope data indicate that a ~3-6% expansion of the
330 anoxic seafloor Mo sink represents a minimum estimate for the effects of global seawater
331 deoxygenation during the PETM and ETM-2.

332

333 **Conclusions**

334 The $\delta^{98/95}\text{Mo}$ of sediments spanning ETM-2 from Arctic Ocean IODP Expedition 302 Site M0004A
335 range between -0.34‰ and 2.00‰. Stratigraphic variations in $\delta^{98/95}\text{Mo}$ mainly correspond to local
336 redox fluctuations recorded by associated sedimentological, elemental and organic geochemical
337 data. The maximum $\delta^{98/95}\text{Mo}$ of $2.00 \pm 0.11\%$ at Site M0004A occurred together with the
338 development of locally euxinic conditions, and thus can be considered as a close minimum
339 estimate for the seawater $\delta^{98/95}\text{Mo}$ during ETM-2. This value is indistinguishable from the
340 previously identified seawater $\delta^{98/95}\text{Mo}$ from the PETM interval of the same core [Dickson et al.,
341 2012]. It is suggested that the average $\delta^{98/95}\text{Mo}$ for both events ($2.04 \pm 0.15\%$) represents the long-
342 term seawater composition for the early Eocene global ocean, given that seawater Mo
343 concentrations were likely to have been too high for seawater $\delta^{98/95}\text{Mo}$ to respond to transient
344 changes in ocean oxygenation across these relatively brief hyperthermal events. Our maximum
345 estimate of a of 3-6% expansion of the anoxic seafloor Mo reservoir in the early Eocene compared
346 to the present day is therefore consistent with more extensive low-oxygen marine environments

347 under conditions of elevated global temperatures. The low sensitivity of $\delta^{98/95}\text{Mo}$ to short-term
348 redox perturbations does not preclude the possibility of a more significant expansion of low-oxygen
349 marine environments in response to transient environmental changes during early Eocene
350 hyperthermal episodes [e.g. Bralower et al., 1997; Chun et al., 2010; Winguth et al., 2012].

351

352 **Acknowledgements**

353 We wish to thank Manuela Fehr, John Watson and Mabs Gilmour for laboratory assistance, and
354 Gareth Izon, Chris Pearce and Phil Sexton for useful discussions. The Integrated Ocean Drilling
355 Program provided sample material. This work was funded by the Natural Environment Research
356 Council (NE/F021313/1) and was supported by the Open University.

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629

630 **Figure captions**

631

632 **Figure 1:** Geochemical data from IODP Expedition 302 Site M0004A spanning ETM-2. A:
633 Compilation of $\delta^{13}\text{C}_{\text{org}}$ data. White circles from Stein et al. [2006]; black diamonds from *Sluijs* et al.
634 [2006]; white squares from this study. B: $\delta^{98/95}\text{Mo}$ compositions. White square denote repeat
635 digestions. Error bars denote analytical uncertainty (2 standard errors) apart from data points at
636 368.5, 368.6 and 368.77mcd, which denote 2 S.D. errors on duplicate analyses (n=2-5). C:
637 Molybdenum abundances. D: Ratios of sedimentary abundances of Re and Mo (ppb/ppm). E: Total
638 Fe enrichments. F: Abundance of sulphur-bound isorenieratane [*Sluijs* et al., 2009]. Horizontal
639 lines on the stratigraphic column indicate the position of mm-scale laminations [*Expedition 302*
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641

642 **Figure 2:** Relationship of $\delta^{98/95}\text{Mo}$ to local redox indicators. A: $\delta^{98/95}\text{Mo} - 1/[\text{Mo}]$ scatter plot. B:
643 $\delta^{98/95}\text{Mo} - \text{Fe}_{\text{EF}}$ scatter plot.

644

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

648

649 **Figure 4:** Geochemical data from IODP Expedition 302 Site M0004A spanning ETM-2 [this study]
650 and the PETM [*Dickson* et al., 2012]. A: Compilation of $\delta^{13}\text{C}_{\text{org}}$ data. White circles from *Stein* et al.
651 [2006]; black diamonds from *Sluijs* et al. [2006, 2009]; white squares from this study and *Dickson*
652 et al. [2012]. B: $\delta^{98/95}\text{Mo}$ compositions. Euxinic intervals used to estimate global seawater $\delta^{98/95}\text{Mo}$
653 are marked by shaded bands. The vertical dashed line indicates the average early Eocene
654 seawater $\delta^{98/95}\text{Mo}$ of $2.04 \pm 0.15\%$ derived from both intervals.

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658

659 Table 1: Geochemical data spanning ETM-2 from IODP Expedition 302, Site M0004A

| Sample | Depth (mcd) | $\delta^{13}\text{C}_{\text{org}}$ | $\delta^{98/95}\text{Mo}$ | 2 S.E. | [Mo], ppm | [Re], ppb | %TiO ₂ | %Fe ₂ O ₃ |
|----------------|-------------|------------------------------------|---------------------------|--------|-----------|-----------|-------------------|---------------------------------|
| 27-1 (76-77) | 368.160 | -27.481 | 0.779 | 0.032 | 6.489 | 65.212 | 0.728 | 4.295 |
| 27-1 (94-95) | 368.34 | -29.143 | 0.549 | 0.031 | 58.190 | 359.342 | 0.576 | 9.195 |
| 27-1 (110-111) | 368.5 | -29.957 | 1.891 | 0.049 | 188.984 | 161.193 | 0.445 | 15.579 |
| 27-1 (120-121) | 368.6 | -29.079 | 2.001 | 0.119 | 119.093 | 76.287 | | |
| 27-1 (129-130) | 368.69 | -30.871 | 1.579 | 0.040 | 143.017 | 99.661 | 0.481 | 12.591 |
| 27-1 (129-130) | 368.69 | | 1.658 | 0.050 | | | | |
| 27-1 (137-138) | 368.77 | -31.584 | 1.219 | 0.060 | 33.289 | 147.746 | 0.522 | 12.424 |
| 27-1 (149-150) | 368.89 | -28.032 | 0.591 | 0.061 | 22.376 | 116.293 | 0.633 | 8.178 |
| 27-2 (4-5) | 368.94 | -27.072 | 0.537 | 0.061 | 8.646 | 15.694 | 0.794 | 4.931 |
| 27-2 (15-16) | 369.05 | -28.066 | 0.256 | 0.068 | 14.698 | 214.954 | 0.646 | 5.887 |
| 27-2 (25-26) | 369.15 | -26.580 | -0.343 | 0.058 | 5.862 | 31.756 | 0.754 | 4.767 |
| 27-2 (60-61) | 369.5 | -27.927 | 0.238 | 0.059 | 12.468 | 87.639 | 0.643 | 9.732 |
| 27-2 (131-132) | 370.21 | -26.842 | -0.005 | 0.060 | 6.850 | 25.294 | 0.743 | 4.279 |
| 27-3 (22-23) | 370.62 | -27.416 | 0.489 | 0.058 | 6.890 | 67.587 | 0.762 | 5.500 |

660