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Molybdenum drawdown during Cretaceous Oceanic Anoxic Event 2

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1 **Abstract**

2 During the Cretaceous greenhouse, episodes of widespread ocean deoxygenation were
3 associated with globally occurring events of black shale deposition. Possibly the most
4 pronounced of these oceanic anoxic events (OAE's) was the Cenomanian-Turonian OAE2
5 (~94 Ma). However, although certain redox sensitive trace metals tend to be preferentially
6 sequestered in sediments deposited under anoxic conditions, with Mo drawdown being
7 specifically prone to euxinic settings, these elements are generally somewhat depleted in
8 sediments deposited during OAE2. To understand the driving factors responsible for this
9 depleted trace metal drawdown, we have studied a low latitude section from the proto-North
10 Atlantic Ocean (Tarfaya S57), where existing biomarker and iron-sulphur data point to a
11 dominantly euxinic water column, with periodic transitions to ferruginous (Fe-rich) water
12 column conditions. We utilise a variety of redox proxies (Fe-speciation, redox sensitive trace
13 metals and Mo isotopes), which, in combination, allows us to evaluate the detailed nature of
14 ocean redox conditions and hence controls on trace metal drawdown. The results suggest
15 that seawater $\delta^{98}\text{Mo}$ values may have ranged between ~ 0.6 and 1.1‰ during OAE2, likely
16 connected to changes in the local Mo reservoir as a consequence of low and probably
17 heterogeneous concentrations of Mo in the ocean. The very low Mo/TOC ratios at Tarfaya
18 and elsewhere in the proto-North Atlantic may support a model in which deep-water
19 circulation was partially restricted within and between the North Atlantic and other ocean
20 basins. We propose that the combination of a low and possibly heterogeneous $\delta^{98}\text{Mo}$ of
21 seawater Mo, together with low Mo/TOC ratios, points to a large decrease in the global
22 oceanic Mo reservoir during OAE2, reflecting a major global scale increase in Mo drawdown
23 under persistent euxinic conditions.

24 **1. Introduction**

25 The Cretaceous was a time of high global temperatures as a consequence of elevated
26 atmospheric CO₂¹. A series of major black shale deposition events during intervals of ocean
27 deoxygenation (termed oceanic anoxic events; OAEs) were associated with these extreme
28 greenhouse conditions². These fluctuations in Cretaceous seawater redox conditions
29 coincided with massive perturbations to the carbon and nutrient cycles within and between
30 the main global reservoirs¹. During the Cenomanian-Turonian (Bonarelli) event (OAE2) at
31 ~95 Ma, a worldwide positive carbon isotope excursion documents the globally enhanced
32 burial of marine organic carbon under anoxic conditions², likely driven by a global-scale
33 increase in primary productivity³⁻⁵.

34 Anoxic conditions favoured the widespread deposition of organic-rich black shales
35 during and intermittently prior to OAE2, in the proto-North Atlantic and western Tethys
36 Ocean⁶⁻⁹ and in other regions¹⁰. Several studies have argued that sluggish circulation within
37 the proto-North Atlantic and restricted deep-water exchange with other ocean basins^{1,7} was
38 responsible for black shale deposition^{11,12}. However, other studies have postulated that
39 sufficient ocean circulation existed to allow rigorous water exchange with the surrounding
40 ocean basins¹³.

41 Under anoxic conditions, many redox sensitive trace metals are preferentially
42 deposited^{14,15}, with Mo drawdown being specifically prone to euxinic (free H₂S) settings¹⁶.
43 However, during the onset of OAE2 a severe depletion of sedimentary Mo, V, Zn, Cr, Ni and U
44 (relative to total organic carbon; TOC) has been reported for the North Atlantic^{8,9}. This
45 observation has been explained by a reduction in the marine trace element inventory due to
46 the enhanced drawdown of redox sensitive elements through expansion of euxinic waters⁹.
47 However, low Mo/TOC ratios in euxinic sediments have also been suggested to be typical of
48 silled marine basins, where resupply of Mo via deep water renewal was limited, resulting in
49 lower oceanic Mo concentrations and hence less uptake of Mo per unit of organic matter
50 compared to fully connected ocean basins^{17,18}. This raises the question as to whether

51 drawdown of Mo during OAE2 occurred on a local, regional or global scale, with
52 consequences for identifying the global extent and severity of ocean anoxia during a period of
53 massive, global carbon-climate perturbation.

54 Mo isotopes have emerged as a powerful tool for evaluating the global extent of ocean
55 euxinia and the size of the oceanic Mo repository¹⁹⁻²². The relative extent of oxic and anoxic
56 sinks defines the amount and isotopic composition of Mo remaining in seawater (see
57 supplementary information). The ability of Mo isotopes to capture the seawater signal is,
58 however, limited to highly sulfidic environments, whereas under both oxic conditions and
59 anoxic conditions where H₂S is absent or concentrations are low, a wide range of Mo isotope
60 signatures may be encountered (Fig. 1).

61 This study focuses on a low latitude W-African shelf setting of the proto-North Atlantic
62 Ocean (Tarfaya Basin). We present high resolution (~0.3 ka scale) Mo isotope data that cover
63 the initial onset and first part of the maximum perturbation of OAE2, as defined by the
64 positive carbon isotope excursion^{8,23}. To determine the fidelity of sedimentary Mo isotopes to
65 reflect seawater values, we critically appraise the Mo isotope composition of marine
66 sediments with new and existing data that document local redox conditions (Fe-speciation,
67 organic carbon contents, biomarkers and trace elements). Indeed, while the sediments were
68 predominantly deposited under sulfidic conditions^{8,24}, regular cyclic (orbital timescale)
69 transitions to anoxic, Fe-rich (ferruginous) water column conditions were also a prominent
70 feature²⁵. By combining hydrographic and geochemical aspects, our Mo isotope data provide
71 a new view on euxinic water mass expansion and extensive Mo drawdown during OAE2.

72

73 ***1.1 The Late-Cretaceous Tarfaya shelf basin***

74 The Tarfaya Basin is located on the northwestern margin of the Sahara Craton. During
75 the Late-Cretaceous, the basin was situated at a latitude of ~15° N in a marine shelf setting
76 open to the proto-North Atlantic Ocean (Fig. 2)^{7,8,12,24,26}. The N-African palaeo-coast is
77 proposed to have been in the centre of an upwelling zone that covered large parts of the

78 subtropical African margin and was responsible for providing nutrient-rich water and
79 fostering the establishment of anoxia/euxinia^{7,8,12,24}.

80 Core samples were obtained from drill site S57 of the Tarfaya Basin, covering the core
81 interval between 50.04 to 54.35 m. Palaeowater depths at site S57 have been estimated as
82 ~250 to 300 m⁸. The section consists of pelagic organic-rich carbonates and marls, with 2 to
83 20 wt.% TOC and very little terrigenous input⁸. Turbidites are absent from the studied part of
84 the section. The last occurrence of *Rotalipora cushmani* (~93.9 Ma) was found at ~51.2 m²³.
85 The studied section covers the upper $\delta^{13}\text{C}$ phase A to lower phase B with a positive $\delta^{13}\text{C}$
86 excursion from -27 to -23‰ (Fig 3)⁸. Spectral analyses, based largely on cyclicity in organic
87 matter content, point to a dominance of obliquity forcing with a calculated average
88 sedimentation rate for the covered interval of ~6 cm/ka²⁷.

89

90 **2. Methods**

91 For trace element and Mo isotope analyses, 50 to 100 mg of sample powder was
92 digested in a mixture of HF (Optima, Fisher Scientific), HNO₃ (purified by sub-boiling
93 distillation in quartz stills) and HClO₄ (Omnipure, Fisher Scientific). The total Mo blank for
94 this procedure was ~0.12 ng. Once dissolved, an aliquot of the sample solution was analysed
95 for trace elements with a Varian ICP-MS instrument (Natural History Museum London). The
96 remaining solution was spiked with a Mo double-spike (to a 1:1 sample/spike ratio) for
97 subsequent stable isotope analyses. The chromatographic purification of Mo is described in
98 Goldberg et al. (2013)²⁸. All isotopic measurements were performed with a Nu Instruments
99 MC-ICP-MS (Department of Earth Science and Engineering, Imperial College London). For
100 further method specifications see Goldberg et al. (2013)²⁸. The samples were initially
101 measured relative to the in-house ICL-Mo isotope standard and these results were
102 subsequently re-normalised to NIST SRM 3134²⁸. Replicate analyses of several samples show
103 a typical reproducibility of better than $\pm 0.1\%$ (2sd). The uncertainties (2sd) for the element
104 concentration measurements are better than $\pm 5\%$ for Mo, Cr, U, Cd, Zn, and Re (at >0.1 ppb)

105 and better than $\pm 10\%$ for Re contents of <0.05 ppb. The Fe-speciation and total organic
106 carbon contents (TOC) are from Poulton et al. (2015)²⁵, organic carbon $\delta^{13}\text{C}$ values are from
107 Tsikos et al. (2004)²³, and additional trace metal data are from Kolonic et al. (2005)⁸.

108

109 **3. Results and Discussion**

110 ***3.1 Evaluation of local redox conditions***

111 The sediments contain high but variable concentrations of TOC (Fig. 3), from 2 to
112 20%^{8,25,29}. Most of the TOC-rich sediment is laminated with no visible bioturbation, implying
113 anoxic deposition. Between 51.74 and 53.06 m, however, intermittent bioturbation is
114 evident, with greatest intensity between 51.89 and 52.00 m, spanning roughly 2 ka. This
115 provides evidence for short-lived intervals of dysoxic-oxic conditions, which allowed larger
116 benthic fauna to infiltrate the sediment. Notably, these oxic intervals are not recorded by
117 fluctuations in the relative proportions of carbonate and organic carbon, and are thus not
118 easily detected by bulk geochemical data (which integrates longer time periods). It is difficult
119 to estimate the actual duration of these oxygenated periods because even short-lived water
120 column oxygenation can result in bioturbation to several centimetres depth.

121 The Fe speciation proxy is based on the presence or absence of enrichments in
122 (bio)geochemically available Fe minerals, termed highly reactive Fe (FeHR). Ratios of highly
123 reactive Fe to total Fe (FeHR/FeT) that exceed 0.38 provide evidence for anoxic depositional
124 conditions³⁰. Providing FeHR/FeT exceeds 0.38, the extent of pyritization of the highly
125 reactive Fe pool (FeP/FeHR >0.7 to 0.8) defines whether the bottom water was anoxic and
126 ferruginous (Fe-rich) or euxinic (containing H_2S). Throughout our analysed section, Fe-
127 speciation points to persistent anoxic bottom water conditions, with FeHR/FeT > 0.38 (Fig.
128 3)²⁵. Short-lived oxic intervals are not resolved at our sampling resolution. According to the
129 most recent dating constraints^{8,27}, our analyses of Fe-speciation for 2 cm intervals of
130 sediment have an average resolution of ~ 0.3 ka. Nevertheless, the absence of bioturbated
131 intervals throughout most of the section suggests that such episodes were not common or, if

132 so, of very short duration. More detailed consideration of the extent of sulfidation of the
133 FeHR pool (FeP/FeHR) suggests that bottom waters at S57 in the Tarfaya Basin fluctuated
134 between ferruginous (FeP/FeHR <0.7) and euxinic (Fig. 3)²⁵, while the presence of
135 isorenieratane in euxinic intervals suggests that sulfide extended from bottom waters into
136 the lower photic zone^{8,25}.

137 The preferential deposition of redox sensitive trace elements (e.g. Mo, U, V, Re, Cr) to
138 the sediment under anoxic to euxinic conditions has led to their exploitation as local redox
139 indicators (see supplement). Throughout the studied section, enrichment factors (EF) for Mo
140 (EF = 11 to 415, average 89), V (EF = 3 to 59, average 12) and U (EF = 11 to 201, average 36)
141 suggest significant drawdown of these elements relative to “Post-Archean Average Shale”
142 (Fig. 4; Table S1), consistent with deposition within an anoxic water column^{31,32}. However,
143 the enrichment factors do not vary systematically between periods of ferruginous and
144 sulfidic conditions, which in particular might be expected for sulfide-sensitive Mo (Figs. 3 and
145 4). Rather, the EF variation is primarily connected to the abundance of organic matter¹⁷, as
146 demonstrated by a correlation between Mo, U, V and TOC (Fig. 5). However, Poulton et al.
147 (2015)²⁵ suggest that very short-lived episodes of water column euxinia occurred during the
148 ferruginous intervals (as suggested by periodically high Fe_{py}/Fe_{HR} ratios and the low-level
149 presence of biomarkers indicative of photic zone euxinia), with dissolved sulfide being
150 persistently present in the sediment pore waters. Euxinic episodes within the dominantly
151 ferruginous intervals would provide an explanation for persistent Mo drawdown during
152 these intervals, although such enrichments could also have been a consequence of sulfidic
153 porewaters near-the sediment-water interface, allowing Mo diffusion and sequestration from
154 the overlying water column.

155 Rhenium and Cr are also enriched above the crustal background (Fig. 4, Table S1)
156 throughout the section, as a result of anoxic sequestration. In comparison to Mo, however, Re
157 is more efficiently deposited under dysoxic to anoxic, non-sulfidic conditions^{14,33}. This has led
158 to the use of Re/Mo ratios to constrain changes in the local redox environment³⁴, specifically

159 to differentiate between sulfidic and low-oxygen, non-sulfidic conditions^{14,19,20}. Similar
160 observations have been made with regard to Cr, which may undergo dissolution under
161 sulfidic conditions, possibly due to breakdown of organically bound Cr species¹⁵. Thus,
162 variability in Re/Mo and Cr/Mo ratios throughout the anoxic water column at S57 likely
163 documents variations in dissolved sulfide availability, which is important for evaluating the
164 Mo isotope signal. The Re/Mo and Cr/Mo ratios (Fig. 4) are high (mostly ≥ 0.02 and ≥ 0.10 ,
165 respectively) across the middle ferruginous intervals (F2 and F3) and during the second and
166 third euxinic intervals (E2 and E3), indicating weakly euxinic conditions with limited Mo
167 sequestration. For the remaining part of the section, Re/Mo and Cr/Mo are low (< 0.1 and
168 < 10 , respectively), consistent with enhanced Mo drawdown under elevated concentrations of
169 dissolved sulfide.

170

171 ***3.2 Hydrography and Mo reservoir***

172 A conspicuous feature of the investigated section is the low sedimentary Mo/TOC
173 values, ranging from 0.2 to 2.4×10^{-4} , with an average of 1×10^{-4} (Figs. 5A, 6), despite euxinic
174 bottom water conditions throughout much of the succession. Today, low bottom water Mo
175 concentrations tend to be recorded in semi-isolated sulfidic basins, such as the Black Sea,
176 where higher rates of Mo burial than Mo resupply and long deep water residence times
177 (> 500 years) result in low Mo/TOC ratios of $4.5 \pm 1 \times 10^{-4}$ ¹⁷. In contrast, weakly restricted
178 anoxic basins, such as the Saanich Inlet (SE of Vancouver Island, Canada) have shorter deep
179 water residence times (< 2 years) and Mo/TOC ratios of $\sim 45 \pm 5 \times 10^{-4}$ ¹⁷. Low sedimentary
180 Mo/TOC ratios also occur in oxic and suboxic bottom waters, where the redoxcline is below
181 the sediment-water interface. For example, in open marine upwelling systems, such as the
182 modern Namibian shelf, rapid water mass exchange prevents sufficient build-up of H₂S and
183 lower Mo/TOC ratios of $\sim 6 \pm 3 \times 10^{-4}$ are recorded¹⁷. The low Mo/TOC values at Tarfaya S57,
184 however, cannot be a result of insufficient H₂S build-up as in the example of the modern

185 Namibian shelf, because predominantly sulfidic and periodically anoxic ferruginous bottom
186 water conditions are supported by Fe-speciation, high TOC, S-isotopes and the abundance of
187 isorenieratane²⁵.

188 Alternatively, the low Mo/TOC ratios recorded at Tarfaya may have been a
189 consequence of severe restriction of basin-wide ocean circulation. Algeo and Tribovillard
190 (2009)³¹ proposed that specific trends in sedimentary Mo and U EFs can be compared to the
191 Mo/U ratio of modern seawater to estimate the degree of basinal restriction (see Fig. 7). For
192 the Tarfaya section, the Mo and U EFs are predominantly high and they coincide with the
193 open marine trend, with relatively few values falling towards the basinal restriction line (Fig.
194 7), thus negating severe restriction as a likely explanation for low Mo/TOC.

195 With the onset of OAE2, a distinct decline in Mo/TOC ratios is evident in the Tarfaya
196 section, from ~ 4 to $\sim 1 \times 10^{-4}$ (Fig. 6). Despite evidence for anoxia on the Tarfaya shelf prior to
197 the global expression of OAE2²⁵, it is unlikely that anoxic bottom water conditions were more
198 globally prevalent prior to, rather than during, OAE2^{4,6,8,9}. Therefore, this Mo/TOC trend is
199 unlikely to be linked to more oxygenated bottom water conditions during OAE2.

200 At Demerara Rise off tropical South America, Hetzel et al. (2009)⁹ observed a similar
201 decline in Mo/TOC from $\sim 9 \times 10^{-4}$ before OAE2 with values dropping to an average of $\sim 2 \times 10^{-4}$
202 during OAE2 (Table 1; Fig. 2). At Demerara Rise, Mo (EF = 143 to 163) and U (EF = 17 to 30)
203 enrichments point towards an unrestricted, euxinic water body. Westermann et al. (2014)²²
204 report a decrease in average Mo/TOC from 11×10^{-4} prior to OAE2 to 5×10^{-4} during OAE2 in
205 anoxic sediments at site 367 (Cape Verde Basin), and low average Mo/TOC of $\sim 2 \times 10^{-4}$ at
206 ODP site 1276 during OAE2 (Fig. 2). The overall low Mo and U EFs at these sites point to an
207 unrestricted water body²². Alternating, hemipelagic euxinic OAE2 black claystones from
208 DSPD Site 603 (Fig. 2) in the northern part of the proto-North Atlantic also have Mo/TOC
209 ratios of 2 to 5×10^{-4} (average 2.8)⁶. Circulation patterns and palaeogeographic conditions do
210 not imply isolation of Demerara Rise or the proto-North Atlantic³⁵, nor do bulk geochemical
211 and molecular patterns^{6,12}, suggesting that deep water Mo concentrations were low

212 throughout the Cenomanian/Turonian proto-North Atlantic. In the central proto-North
213 Atlantic (DSDP Site 368; Fig. 2), Mo/TOC values of 5×10^{-4} from anoxic/sulfidic sediments are
214 consistent with low Mo concentrations³⁶. A contrasting picture is drawn by Mo/TOC values of
215 ~ 300 in the run-up, during and after OAE2 at ODP site 641 (Table 1). The origin of such
216 extreme enrichments was attributed to either proximity to hydrothermal vents or to very
217 low sedimentation rates³⁶, although similar sedimentation rates are associated with much
218 lower Mo/TOC values at other sites⁹. A further process that may lead to high Mo
219 concentrations is the operation of a metal-oxyhydroxide particulate shuttle (Figure 7)³². This
220 process has also been inferred for sites 367 and 1276²². Fluctuating redox conditions cause
221 Mo to be captured by Mn- (and Fe) oxides, released, and re-captured within the sulphide
222 layer repeatedly, thus accelerating the transfer of Mo to the seafloor³².

223 Outside the proto-North Atlantic, stratigraphically equivalent anoxic/euxinic OAE2
224 sections, the Calabiancia, Bottacione, Contessa and Furlo sections in the western Tethys (Fig.
225 2), show Mo/TOC averages of 2×10^{-4} , 4×10^{-4} , 3×10^{-4} and 9×10^{-4} , respectively (Table 1)^{22,32}.
226 The latter two were however, deposited in anoxic, non-euxinic conditions with possible
227 contribution of Mo from metal-oxyhydroxide particulate shuttling²². In the Angola Basin (Site
228 530, Fig. 2) average Mo/TOC ratios of anoxic shales are somewhat, but not significantly,
229 higher (Table 1)³⁷. The oceanographic setting and U-Mo systematics imply that these South
230 Atlantic basins were also open to water exchange with the deep oceans and adjacent basins
231 (Fig. 7)^{22,32,37}. In combination, available data suggest that deep water Mo concentrations may
232 have been somewhat higher outside of the proto-North Atlantic, but possibly lower than in
233 weakly restricted euxinic environments of the present (e.g., Saanich Inlet Mo/TOC average =
234 $45 \times 10^{-4} \pm 5 \times 10^{-4}$)¹⁷. During the Cenomanian-Turonian period, deep water exchange with the
235 proto-North Atlantic occurred largely (if not solely) through the Western Tethys and the
236 Central American-Pacific Seaways^{7,13,35}, although the degree of exchange is still highly
237 debated. The hydrographic restriction of the proto-North Atlantic could thus have led to
238 basin wide Mo depletion during extended euxinic periods. However, unless the Tethys and

239 South Atlantic were equally restricted, the low Mo/TOC values of the North Atlantic sections
240 point to a more global mechanism of Mo depletion.

241

242 ***3.3 Constraints on $\delta^{98}\text{Mo}$ to reflect seawater***

243 To assess possible global mechanisms we draw upon Mo isotopes, which can give
244 insight into the spatial extent of euxinic conditions during OAE2. Mo isotopes can only be
245 exploited as a global redox proxy if sedimentary $\delta^{98}\text{Mo}$ records the global Mo seawater value.
246 The $\delta^{98}\text{Mo}$ of seawater is thought to be captured in sediments deposited under highly sulfidic
247 ($>11 \mu\text{M H}_2\text{S}_{\text{aq}}$) bottom waters, when all Mo exists in the form of MoS_4^{2-} and is quantitatively
248 scavenged to sinking particles^{16,38}. Transformation of MoO_4^{2-} to MoOS_3^{2-} via thiomolybdate
249 intermediates is relatively rapid (on a timescale of days), whereas the reaction kinetics for
250 full conversion of MoOS_3^{2-} to MoS_4^{2-} are slow (on a timescale of years) and can only be
251 completed in a water body with prolonged sulfidic conditions^{39,40}. Consequently, a semi-
252 restricted basin with a euxinic water column is the ideal setting for tracing seawater Mo^{40,41}.
253 The semi-isolated proto-North Atlantic offers such a setting. The palaeo-redox indicators
254 utilised in this study provide evidence for prolonged cyclic intervals of euxinia in the Tarfaya
255 Basin during OAE2, allowing us to specifically target samples that likely best record the
256 seawater $\delta^{98}\text{Mo}$ signal.

257 Higher $\delta^{98}\text{Mo}$ values close to seawater would be expected in highly sulfidic
258 environments, and lower (farther removed from seawater) $\delta^{98}\text{Mo}$ values are anticipated
259 under ferruginous bottom water conditions^{41,42}. The results shown in this study are,
260 however, not in accord with this expectation (Fig. 4). In fact, $\delta^{98}\text{Mo}$ values do not reveal a
261 specific trend associated with the ferruginous-euxinic redox fluctuations. At the top and
262 bottom of the studied section, $\delta^{98}\text{Mo}$ remains relatively stable throughout the euxinic and
263 ferruginous intervals, whereas positive and negative $\delta^{98}\text{Mo}$ shifts occur within euxinic
264 intervals E2 and E3, and ferruginous interval F3 (Fig. 4).

265 We observe three distinct $\delta^{98}\text{Mo}$ clusters/trends throughout the studied section:
266 I. Low $\delta^{98}\text{Mo}$ values of -0.3 to 0.1‰ between 53.12 and 52.10 m, during period E2.
267 II. Relatively constant $\delta^{98}\text{Mo}$ in the lower (F1, E1 and F2) and upper (upper E3, F4 and
268 E4) sections, with an average value of 0.6 ± 0.1 ‰ (NIST).
269 III. Intermittent shift to higher $\delta^{98}\text{Mo}$ of ~ 1.1 ‰ between 52.1 and 51.5 m,
270 corresponding to F3 and lower E3.

271
272 3.3.1 I. Low $\delta^{98}\text{Mo}$ values of -0.3 to 0.1‰
273 We propose that the low $\delta^{98}\text{Mo}$ values do not reflect either global or local seawater,
274 despite having been recorded in a sulfidic interval (according to Fe-speciation). The main
275 reason to negate a seawater origin is that values of -0.3 to 0.1‰ are lower than the modern
276 input value of ~ 0.4 ‰⁴³. As there is no documented process that exerts positive Mo isotope
277 fractionations, seawater $\delta^{98}\text{Mo}$ cannot be less than the $\delta^{98}\text{Mo}$ value of the Mo input to the
278 ocean (Fig. 1). Although the Mo isotope compositions of riverine and hydrothermal inputs to
279 the ocean may have varied in the past⁴⁴, the $\delta^{98}\text{Mo}$ value of the total input should not have
280 been lower than ~ 0.1 ‰^{21,43,44}. There are, however, several possible reasons for low $\delta^{98}\text{Mo}$
281 values.

282 1. Influence of freshwater input, lowering the local seawater signal
283 McArthur et al. (2008)¹⁸ suggested that low Mo/TOC ($< \sim 0.5$) is indicative of total
284 water mass isolation, where $\delta^{98}\text{Mo}$ is largely influenced by freshwater input. The cyclic
285 enhancement of reactive iron inputs, driven by increased silicate weathering during humid
286 periods, may explain the cycling between euxinic and ferruginous water column conditions in
287 the Tarfaya Basin²⁵. If correct, seawater $\delta^{98}\text{Mo}$ would have been driven towards lower values
288 during periods of enhanced riverine inputs (Fig. 1) or would have at least fluctuated during
289 ferruginous intervals. In this respect, the lack of covariation between FeP/FeHR and $\delta^{98}\text{Mo}$,
290 and the relatively stable $\delta^{98}\text{Mo}$ signal throughout the upper and lower parts of the section,

291 argues that $\delta^{98}\text{Mo}$ of the Tarfaya waters was not strongly affected by variations in fluxes from
292 the continent.

293 2. Operation of a Mn-Fe-oxyhydroxide shuttle

294 During short intervals of ferruginous conditions Mo would have been sequestered into
295 Mn-oxyhydroxides, which is connected with an isotope fractionation towards low $\delta^{98}\text{Mo}$
296 values (Barling & Anbar, 2004). Upon change to a euxinic water column, Mo would have been
297 released via Mn-oxyhydroxide dissolution and sequestered (quantitatively) as MoS_4 , thus
298 retaining the low Mo isotope composition^{22,46}. The same process also operated with Fe-
299 (oxyhydr)oxides, although these exert a smaller isotopic fractionation between seawater Mo
300 and adsorbed Mo than Mn-oxides⁴⁷. The operation of the Mn-Fe-oxyhydroxide shuttle is an
301 unlikely reason for the low values at Tarfaya site 57. Although FeP/FeHR fluctuates around
302 the ferruginous/anoxic threshold during E2, there is no distinct covariation between
303 FeP/FeHR < 0.7 and low $\delta^{98}\text{Mo}$. Furthermore, the operation of Mn-Fe-oxyhydroxide shuttle
304 should result in high Mo EFs coinciding with low U EFs³¹, which is not the case during E2 (Fig.
305 7).

306 3. Locally weakly euxinic bottom water

307 In this interval (53.12 and 52.10 m), both Re/Mo and Cr/Mo show a consistent inverse
308 relationship with $\delta^{98}\text{Mo}$ (Fig 4). The combined evidence of high Re/Mo and Cr/Mo ratios and
309 relatively low Mo enrichment factors (Fig. 4), argue for low sulfide availability in the water
310 column, implying that Mo isotope compositions do not record a seawater signal. During the
311 weakly euxinic conditions, formation of intermediate thiomolybdates ($\text{MoO}_3\text{S}^{2-}$ to MoOS_3^{2-}) is
312 favoured^{38,39}. The transformation of molybdate to various thiomolybdates is possibly
313 connected with a substantial negative fractionation during each sulfidation step^{40,48}.
314 Furthermore, the uptake of intermediate thiomolybdates is non-quantitative and thus results
315 in isotopic fractionations from global seawater of up to -2.9‰ (Fig. 1)⁴¹.

316 4. Non-ideal conditions for sufficient Mo-Fe-S formation

317 The Helz et al. (2011)⁴⁹ revised Mo model suggests that an only an interplay of ideal
318 pH, H₂S and reactive Fe availability can result in a quantitative scavenging of Mo, enabling the
319 preservation of the seawater $\delta^{98}\text{Mo}$. A more alkaline pH of > 8 would inhibit removal of Mo,
320 due to higher solubility of the Mo-Fe-S phases at higher pH. Sulphate reducing conditions
321 typically drive the pH to ~ 7, which is favourable for Mo removal to the sediment. Sufficient
322 reactive Fe is important in order to maintain Mo-Fe-S saturation. Finally, a non-intuitive but
323 evident outcome of the Helz et al. (2011)⁴⁹ model is that although H₂S needs to be sufficiently
324 high (>11 μm), a large excess of sulfide would reverse the efficient Mo removal.

325 We assume that the first two points are sustained for sufficient removal of Mo. It is
326 unlikely that the pH would have been higher during more sulfidic conditions through E2 than
327 during the ferruginous intervals. Reactive Fe would have been sufficient during both sulfidic
328 and ferruginous intervals²⁵. However, it should be noted that lower concentrations of highly
329 reactive Fe coincide with low $\delta^{98}\text{Mo}$ during this period. Weakly euxinic conditions are
330 feasible, as explained in the previous point. However, if the high Re/Mo and Cr/Mo are not
331 indicative of weakly sulfidic conditions and rather reflect the overall global preferential
332 removal of Mo to the sediment over Re and Cr, then H₂S may have been extremely high at
333 Tarfaya during E2 and according to the revised Helz et al. (2011)⁴⁹ model Mo would not have
334 been quantitatively scavenged to reflect the seawater $\delta^{98}\text{Mo}$.

335

336 3.3.2. II and III: constant value of ~ 0.6 and shift to ~ 1.1‰

337 The higher and relatively constant $\delta^{98}\text{Mo}$ in the upper and lower sections, with an
338 average value of $0.6 \pm 0.1\text{‰}$ and an intermittent increase to 1.1‰, coincide with low Re/Mo
339 and Cr/Mo ratios and the highest Mo enrichment factors, suggesting that dissolved sulfide
340 concentrations were at a maximum during these intervals (Fig. 4). The low variability in
341 $\delta^{98}\text{Mo}$ across ferruginous intervals is likely due to significant drawdown of Mo during short-
342 lived episodes of euxinia, and/or due to highly euxinic porewaters, which were open to Mo

343 exchange with the water column ^{22,25}. Thus, the upper and lower sections of Tarfaya site S57
344 may represent times of near-quantitative scavenging of Mo from the water column.
345 Nevertheless “non-ideal” conditions for Mo scavenging, as presented by Helz et al. (2011)⁴⁹
346 could be also operating during these intervals and thus the highest $\delta^{98}\text{Mo}$ may represent the
347 closest estimate to the global seawater value. It is also yet to be proven whether a “global”
348 $\delta^{98}\text{Mo}$ signal existed during OAE2.

349

350 ***3.4 Implications for the global Mo reservoir***

351 The low $\delta^{98}\text{Mo}$ of $\sim 0.6\text{‰}$ to 1.1‰ recorded at Tarfaya has the potential to represent
352 the global palaeo-seawater value. This implies a large decrease in the Mo reservoir during
353 OAE2 via an increase in euxinic Mo drawdown. The low Mo/TOC values recorded in euxinic
354 sections could therefore have been the result of a decrease in global Mo concentrations
355 during the event⁵⁰. Regarding the evidence for expanded sulfidic conditions prior to OAE2
356 together with the possible drawdown of redox sensitive elements^{4,8,9}, seawater $\delta^{98}\text{Mo}$ would
357 have been lower than today well before the onset of OAE2 and would have reached a
358 minimum during the peak of the event.

359 To provide further insight into whether $\delta^{98}\text{Mo}$ values of 0.6‰ and 1.1‰ may reflect
360 seawater signatures at different times, we employed a 1-box model that links the relative
361 burial of Mo into three sinks (oxic, anoxic and euxinic) to the areal extent of each redox
362 environment at different seawater $\delta^{98}\text{Mo}$ values. In the direct feedback model, the residence
363 time of Mo in seawater is calculated by a burial forcing function, in which the modern areal
364 extent of each sink and the removal fluxes to each sink are scaled to the ancient seafloor
365 coverage.

366 At steady state, the sum of the Mo fluxes to the ocean (F_{SOURCES}) is equal to the sum of
367 the Mo outputs (F_{SINKS}) to various sinks^{51,52}. The residence time (τ) of Mo in seawater is then

368 described by the global marine Mo inventory (M) in proportion to all source or sink fluxes
369 (F):

$$370 \quad \frac{M}{\tau} = F_{\text{SOURCES}} = F_{\text{SINKS}}$$

371 The total Mo flux to, or removal from, the ocean is the product of the areal extent (A) of each
372 sink (i) and the burial rate (R) into each sink:

$$373 \quad F(i) = A(i) \cdot R(i)$$

374 The Mo outflux from seawater is subdivided into three sinks: an oxic sink (f_{ox}), an
375 intermediate sink, comprising reducing conditions with H_2S build-up in sediment porewaters
376 and weakly euxinic environments (less than $11 \mu\text{M H}_2\text{S}$), termed f_{red} , and a euxinic sink (f_{eux})
377 with bottom water $\text{H}_2\text{S}_{\text{aq}} > 11 \mu\text{M}$. The sum of all fractional fluxes makes up the total Mo sink:

$$378 \quad F_{\text{SINKS}} = f_{\text{ox}} + f_{\text{red}} + f_{\text{eux}}$$

379 The respective Mo isotope signatures (δ_{ox} , δ_{red} and δ_{eux}) are tied into a Mo isotope mass
380 balance equation, where $\delta^{98}\text{Mo}$ of the sum of the sources (δ_{INPUT}) are equal to the sinks:

$$381 \quad \delta_{\text{INPUT}} = f_{\text{ox}} \cdot \delta_{\text{ox}} + f_{\text{red}} \cdot \delta_{\text{red}} + f_{\text{eux}} \cdot \delta_{\text{eux}}$$

382 Thus, oceanic $\delta^{98}\text{Mo}$ is defined as :

$$383 \quad \delta_{\text{SW}} = \delta_{\text{INPUT}} - f_{\text{ox}} \cdot \delta_{\text{ox}} + f_{\text{red}} \cdot \delta_{\text{red}} + f_{\text{eux}} \cdot \delta_{\text{eux}}$$

384 To calculate the Cretaceous (K) Mo budget, a self-regulated direct feedback function is
385 applied, where the Mo burial rates vary in proportion to the Mo inventory (first-order
386 process):

$$387 \quad R(i)_K = \frac{R(i) \cdot M}{M_K}$$

388 We can describe the rate of change of the Mo inventory as:

$$389 \quad \frac{dM}{dt} = F_{\text{SINKS}} - \frac{M}{\tau}$$

390 In the burial forcing function the modern areal extent of each sink is scaled back to the
391 Cretaceous areal extent to receive the Cretaceous Mo response time:

$$392 \quad \frac{\tau}{\tau_{(K)}} = \frac{f_{\text{ox}} \cdot A_{\text{ox}(K)}}{A_{\text{ox}}} + \frac{f_{\text{red}} \cdot A_{\text{red}(K)}}{A_{\text{red}}} + \frac{f_{\text{eux}} \cdot A_{\text{eux}(K)}}{A_{\text{eux}}}$$

393 Rivers are by far the biggest source of dissolved Mo to the ocean and account for at
394 least 90% of the influx⁵³, with low-temperature hydrothermal inputs accounting for the
395 remainder^{54,55}. As the latter input is poorly constrained in magnitude and Mo isotope
396 composition, we disregard this source of Mo to the ocean. Recently, the riverine Mo flux to
397 the ocean has been reassessed as $2.96 \times 10^7 \text{ kg a}^{-1}$ ³⁴, which is ~ 1.6 fold higher than
398 previously assumed. With a total seawater mass of $1.37 \times 10^{21} \text{ kg}$ (considering a seawater
399 density of 1.028 kg L^{-1}) and a Mo concentration of 104 nM kg^{-1} , we calculate a total marine
400 Mo inventory of $1.37 \times 10^{13} \text{ kg}$ and an oceanic Mo residence time of $\sim 460 \text{ ka}$ (similar to
401 previous calculation of 440 ka ³⁴), which is almost half of the residence time quoted in earlier
402 studies (700 to 800 ka)^{56,57}.

403 At present, oxic sediments are assessed to cover 96 to 97% of the ocean floor³³ whilst
404 A_{red} and A_{eux} are estimated at 1% and 0.05%, respectively^{50,58}. We hence subdivide the total
405 seafloor of $3.6 \times 10^8 \text{ km}^2$ into three redox regimes, with $A_{\text{ox}} = 97 \%$, $A_{\text{red}} = 1 \%$ and $A_{\text{eux}} = 0.05$
406 % of the ocean floor. For the model, the sum of the total seafloor coverage is kept constant.

407 At steady state, a higher input of Mo to the ocean requires a higher Mo output flux and
408 thus a higher burial rate. Previously, modern Mo burial rates were estimated at $r_{\text{ox}} = 0.002 \mu\text{g}$
409 $\text{cm}^{-2} \text{ a}^{-1}$, $r_{\text{red}} = 0.250 \mu\text{g cm}^{-2} \text{ a}^{-1}$ and $r_{\text{eux}} = 1.27 \mu\text{g cm}^{-2} \text{ a}^{-1}$ ^{50,58}. To balance the budget we scale
410 the rates up by a factor of ~ 1.6 (equivalent to the increase in the new riverine Mo flux),
411 resulting in $r_{\text{ox}} = 0.003 \mu\text{g cm}^{-2} \text{ a}^{-1}$, $r_{\text{red}} = 0.4 \mu\text{g cm}^{-2} \text{ a}^{-1}$ and $r_{\text{eux}} = 1.8 \mu\text{g cm}^{-2} \text{ a}^{-1}$. These rates
412 are consistent with the current knowledge of Mo accumulation rates in modern
413 environments (Table S2). However, these burial rates may be exaggerated for the deep ocean,
414 as the estimates are mainly based on data for shelf deposits. Nevertheless, we take these to
415 be the average burial rates for each of the redox environments.

416 For the modern Mo isotope budget, we apply measured offsets (the difference in
417 $\delta^{98}\text{Mo}$ between measured modern sediment and seawater values) to the modern seawater
418 $\delta^{98}\text{Mo}$ value of 2.09% ^{28,43}. In oxic environments, $\delta^{98}\text{Mo}$ is mainly attributed to
419 ferromanganese crusts and nodules, with a well-established offset (δ_{ox}) of -3% (Fig. 1). In

420 highly sulfidic environments, sedimentary $\delta^{98}\text{Mo}$ is slightly offset from global seawater (Fig.
421 1) and we therefore apply a small offset of -0.05‰ for δ_{EUX}^{59} . A relatively constant isotopic
422 fractionation relative to seawater of about -0.8‰ (renormalized to NIST SRM 3134) was
423 proposed to be driven by diagenesis beneath low oxygen to anoxic, non-sulfidic bottom
424 waters⁴², where the sediment porewaters become sulfidic (Fig. 1). To include the weakly
425 euxinic sinks, we apply a higher offset of -0.9‰ for the intermediate sink (δ_{RED}). The average
426 modern $\delta^{98}\text{Mo}$ value of dissolved riverine Mo is about 0.4‰ (renormalized to NIST SRM
427 3134), based on rivers that represent $\sim 22\%$ of the global river discharge⁴³. We assume a
428 constant riverine Mo flux and its isotopic composition, although these may have been offset
429 in the past^{44,60}.

430 For the modern burial rates and seafloor coverages for each sink, we calculate the
431 fraction of Mo deposited in each sink of $f_{\text{OX}} = 0.41$, $f_{\text{RED}} = 0.48$ and $f_{\text{EUX}} = 0.11$, which results in
432 a consistent value of 2.07‰ for modern seawater. The fluxes fall into the range of the
433 previously calculated Mo budget of 25 to 55% for oxic deposition, 45 to 70% for
434 suboxic/anoxic/sulfidic at depth deposition, and 5 to 15% for the euxinic sink^{20,42,50,58}. For
435 the modelling of past fluxes, we disregarded unlikely cases where the oxic and euxinic end-
436 member sinks are dominant in comparison to the intermediate sink^{21,40}.

437 Figure 8A displays the solution space for the possible combinations of A_{EUX} and A_{OX}
438 (A_{RED} is not displayed), resulting in different seawater $\delta^{98}\text{Mo}$ values and response times (τ).
439 The modelled residence times should be regarded as minimum values, because we mainly
440 employ average burial rates reported for shelf environments, thus overestimating the burial
441 rates of the deep ocean. Seawater $\delta^{98}\text{Mo}$ values of $1.1 \pm 0.1\text{‰}$ and $0.6 \pm 0.1\text{‰}$ are obtained
442 for various combinations that feature different areal extents for each sink (Fig. 8). Model
443 results hence provide a range of possible Mo residence times from 7 to 191 ka for $\delta^{98}\text{Mo} = 1.1$
444 $\pm 0.1\text{‰}$, and from 3 to 62 ka for $\delta^{98}\text{Mo} = 0.6 \pm 0.1\text{‰}$. According to the model, a change from
445 $\sim 0.6\text{‰}$ to $\sim 1.1\text{‰}$ within ~ 20 to 25 ka (corresponding to 53.1 to 51.7 m depth in the S57

446 core) is therefore possible. Constraints on the exact timing and rate of change of the seawater
447 $\delta^{98}\text{Mo}$ value from 0.6 to 1.1‰ (from F2 to F3) are not available, as it is unlikely that seawater
448 $\delta^{98}\text{Mo}$ was recorded across this interval (see 3.3.1). The increase of the global seawater value
449 during peak OAE2 is, however, counterintuitive, as it requires a decrease in the area of anoxic
450 and mainly euxinic seafloor.

451 Available chronological constraints for the Tarfaya section provide a time span of ~ 3
452 to 4 ka for the decrease in $\delta^{98}\text{Mo}$ from 1.1 to 0.6‰ at ~ 51.6 to 51.4 m, close to the modern
453 average ocean mixing time of ~ 1.5 ka (Sarmiento and Gruber, 2006). The model predicts that
454 to drive the $\delta^{98}\text{Mo}$ response time to less than ~ 10 ka at a $\delta^{98}\text{Mo}$ value of 1.1 ± 0.1 ‰, less than
455 30% of the global seafloor would need to have oxygenated bottom water (Fig 8). Whether
456 such a scenario is feasible is debated. A near-global spread of anoxia has been suggested for
457 OAE2^{3,11}. Further support comes from a recent modelling study, which suggests that $>90\%$ of
458 the deep ocean, excluding the Arctic and Southern oceans, would have been anoxic during
459 times of peak CO_2 (OAE2) and excess phosphate supply⁶¹. However, a less extreme spread of
460 anoxia during OAE2 is evidenced by some intermittent occurrences of oxic bottom water
461 during the event^{6,22,37} and possibly even widespread oxic depositional conditions in the
462 Pacific Ocean⁶³. In summary, we conclude that such a rapid decrease in the global $\delta^{98}\text{Mo}$
463 during OAE2 is highly unlikely.

464 A rapid change from a seawater value of 1.1‰ to 0.6‰ would only have been
465 possible if Mo was heterogeneously distributed across the different Cretaceous ocean basins
466 and possibly between deep, intermediate and shallow water bodies as a consequence of a
467 small Mo reservoir. If correct, the $\delta^{98}\text{Mo}$ values of 0.6 and 1.1‰ at Tarfaya would reflect the
468 Mo isotope signature of a local water mass. Westermann et al. (2014)²² recently reported
469 $\delta^{98}\text{Mo}$ of ~ 0.8 ‰ (recalculated to NIST SRM 3134) during OAE2 at site DSDP 367 (Fig 2) and
470 suggested that these reflect global seawater. This value would therefore represent the $\delta^{98}\text{Mo}$
471 of the deep Cape Verde water.

472 There is evidence of less reducing conditions during OAE2^{6,22} where the light Mo
473 isotopes were drawn down from seawater (e.g. site ODP 1276)²², thus increasing the ambient
474 seawater $\delta^{98}\text{Mo}$ value. Water circulation and water mass mixing would still have been
475 operational during OAE2⁶⁴. Consequently, the ambient seawater Mo composition could have
476 varied throughout the Cretaceous ocean during OAE2, in response to variable rates of
477 seawater renewal that were driven by more localised changes in runoff and water circulation,
478 which drove the changes in the Tarfayan seawater $\delta^{98}\text{Mo}$.

479 Alternatively, it is possible that “non-ideal” conditions were prevalent with regard to
480 Mo-Fe-S scavenging at Tarfaya S57. Most of the $\delta^{98}\text{Mo}$ record could either be driven by
481 concentrations of H_2S that were either too low or too high, as proposed by Helz et al. (2011)⁴⁹
482 (see section 3.1.1). In this case, the highest $\delta^{98}\text{Mo}$ of 1.1 ‰ (equivalent to 1.4 ‰ on the Roch-
483 Mo2 scale²⁸) would be closest to a global seawater signal. A clear indication can only be
484 supported by further Mo isotope evidence from other Tarfaya sections in combination with
485 water circulation indicators (e.g. Nd isotopes).

486

487 **4. Conclusions**

488 The new high-resolution $\delta^{98}\text{Mo}$ record from the Late-Cretaceous shelf off NW-Africa at
489 Tarfaya emphasises the need for a combination of redox proxies to differentiate between the
490 potential for quantitative and non-quantitative scavenging of Mo in seawater. This
491 information is essential to resolve whether sedimentary $\delta^{98}\text{Mo}$ records the overlying $\delta^{98}\text{Mo}$
492 seawater signal. Redox proxy records from Tarfaya site S57 and Mo-burial modelling suggest
493 that seawater $\delta^{98}\text{Mo}$ may have varied during OAE2 from about 0.6 to 1.1‰. The rapid
494 changes in seawater $\delta^{98}\text{Mo}$ can only be reconciled by heterogeneous oceanic $\delta^{98}\text{Mo}$ and Mo
495 concentrations during OAE2. Alternatively, a true $\delta^{98}\text{Mo}$ signal was not established at Tarfaya
496 site 57, and 1.1‰ represents the closest value to seawater $\delta^{98}\text{Mo}$.

497 Low Mo/TOC ratios in several regions of the proto-North Atlantic in comparison to
498 other oceanic basins argue for partial restriction of the proto-North Atlantic deep water in
499 the Late-Cretaceous. However, the inferred restriction cannot account for the 2 to 8 times
500 lower Mo/TOC ratios of the proto-North Atlantic, compared to the modern Black Sea, and the
501 overall low Mo accumulation rate, as observed in the Tethyan and South Atlantic regions. If
502 true, then the low $\delta^{98}\text{Mo}$ values are consistent with enhanced drawdown of Mo through
503 expansion of euxinic bottom waters across large parts of the global ocean during OAE2.
504 Taken together, the decline in Mo/TOC values in the Tarfaya and Demerara Rise sites during
505 the onset of the OAE2, and the Mo isotope evidence for a low and possibly heterogeneous
506 seawater $\delta^{98}\text{Mo}$, point towards a decrease in the global marine concentration of Mo during
507 OAE2, with enhanced euxinic Mo drawdown under expanded sulfidic conditions. As such,
508 care should be exercised when utilising Mo concentrations alone as an indicator of water
509 column euxinia during OAE2 and maybe other OAEs. It is also possible that other redox
510 sensitive trace elements were extensively buried during expanded and prolonged euxinia,
511 and hence were depleted in the water column.

512

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519 contents.

520

521 **Figure and Table Captions**

522 Figure 1 The main oceanic Mo sources and sinks, and their isotopic compositions. Note that
523 $\delta^{98}\text{Mo}$ has been renormalised to NIST SRM 3134, according to Goldberg et al. (2013)²⁸.

524 Narrow boxes represent the reported data range for each environment; wide boxes represent
525 areas of data concentration. $\delta^{98}\text{Mo}$ values compiled from Vögelin et al. (2012 and references
526 therein)⁶⁰ and Goldberg et al. (2012, 2013, and references therein)^{28,47}.

527
528 Figure 2 Continental reconstruction for 94 Ma (modified from Forster et al., 2008), with the
529 study site (Tarfaya S57) and other locations discussed in this study. Light grey areas
530 represent land and middle grey areas represent flooded continental plates. Thin black lines
531 outline present day coastlines.

532
533 Figure 3 Total organic carbon ($\delta^{13}\text{C}$) from Tsikos et al., (2004)²³ and division into $\delta^{13}\text{C}$ phases
534 A and B, with indication of first occurrence of *R. cushmani*, after Kolonic et al. (2005)⁸ for the
535 studied S57 Tarfaya section. Fe-speciation from Poulton et al. (2015)²⁵, with grey shaded
536 intervals representing ferruginous bottom water conditions, numbered F1 to F5, between
537 predominantly euxinic bottom water intervals, numbered E1 to E4.

538
539 Figure 4. Trace element enrichment factors (Mo, U, V, Cr and Re) and Mo/Re and Mo/Cr
540 ratios and $\delta^{98}\text{Mo}$ (relative to NIST SRM 3134) throughout the studied S57 Tarfaya section.
541 Mo, U and V concentrations are compared to oxic background values, as represented by Post-
542 Archean Average Shale (PAAS)⁶⁵, and are calculated as enrichment factors (EF =
543 $\text{element}/\text{Al})_{\text{sample}}/(\text{element}/\text{Al})_{\text{PAAS}}$). Rhenium and Cr EFs are normalised to their crustal
544 values, with Re = 0.06×10^{-7} ¹⁴ and Cr = 11×10^{-4} ⁶⁵, respectively. Ferruginous and euxinic
545 intervals are numbered F1 to F5 and E1 to E4, respectively.

546
547 Figure 5: TOC plotted against A: Mo, B: U and C: V. Dashed line represents Black Sea average
548 Mo/TOC. Correlation between TOC and Mo is not particularly strong. This may be connected

549 to the fact that Mo is associated both with pyrite and TOC and/or may depend on the type of
550 organic matter.

551
552 Figure 6: Data from the study site (Tarfaya S57). Mo/TOC x 10⁻⁴ data from Kolonic et al.
553 (2005)⁸ and this study. Grey boxes represent the span of OAE2 and white boxes represent
554 time period analysed in this study.

555
556 Figure 7. Mo and U systematics from Algeo & Tribovillard (2009)³¹ and Tribovillard et al.
557 (2012)³². At high Mo and U EFs (indicative of euxinic conditions) progressively greater
558 enrichment of Mo over U (Mo:U > seawater) is considered to reflect unrestricted anoxic
559 conditions (grey arrow), as Mo is constantly sourced from the open ocean. In semi-closed
560 sulfidic water bodies, Mo burial overwhelms Mo resupply faster than U, resulting in Mo:U
561 ratios that are smaller compared to seawater as EFs increase. A third process describes an
562 enhanced export of aqueous Mo to the sediment via a metal oxyhydroxide particulate shuttle
563 with little effect on U. This process is characterised by high Mo EFs and low U EFs, but Mo:U
564 ratios that exceed the seawater value by up to a factor of 3. Black and grey symbols represent
565 EFs from this study and white symbols represent EFs for black shales from the South Atlantic
566 site DSDP 603B (data from Forster et al., 2008³⁷). Grey symbols are data from period E2.
567 Diagonal lines represent multiples of the Mo:U present day seawater.

568
569 Figure 8. A. Solution space of the box model. To maintain visibility, a limited number of
570 possible combinations is displayed. White lines represent a specific areal extent of bottom
571 water euxinia (eux) and grey lines represent a specific areal extent for oxic (ox) bottom
572 water. Areal extent for reducing (red) conditions is not shown. Different combinations of
573 residence times (τ) and seawater $\delta^{98}\text{Mo}$ are possible within the solution space. B. Mo burial is
574 subdivided into three sinks: an oxic sink (ox), an intermediate sink (red), comprising
575 reducing conditions with H₂S and build-up in sediment porewaters and weakly euxinic

576 environments (less than $11\mu\text{M H}_2\text{S}_{\text{aq}}$), and a euxinic sink (eux) with bottom water $\text{H}_2\text{S}_{\text{aq}}$
577 $>11\mu\text{M}$. Possible combinations of seafloor area (in %) representing these sinks along with the
578 respective Mo residence time are displayed for $\delta^{98}\text{Mo}$ seawater values of $1.1 \pm 0.1\text{‰}$ and 0.6
579 $\pm 0.1\text{‰}$.

580

581 Table 1: Overview of Mo/TOC values during and prior to OAE2.

582

583 **Supplement**

584 Supplement 1.

585 Table S1: $\delta^{98}\text{Mo}$ and trace element data

586 Table S2: Mo accumulation rates in modern settings at different oxygen and H_2S content.

587

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