

1 **Zinc- and cadmium-isotope evidence for redox-driven perturbations to global**
2 **micronutrient cycles during Oceanic Anoxic Event 2 (Late Cretaceous)**

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13

14 **Abstract**

15

16 This study uses organic-rich sediments from the Tarfaya Basin, Morocco, to assess the
17 Cd- and Zn-isotope response to dramatic global palaeoenvironmental change during the
18 Cenomanian–Turonian interval (Late Cretaceous). These organic-rich continental-
19 margin deposits include an expression of Oceanic Anoxic Event 2 (OAE 2, ~94 Ma), an
20 interval associated with the spread of low-oxygen marine environments and widespread
21 burial of organic-rich sediments. Due to placement of the Tarfaya Basin in a region of
22 upwelling and relatively constant local environmental conditions, the stratigraphic
23 variations in $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ values largely reflect changes in the seawater isotopic
24 composition of the sub-surface proto-North Atlantic Ocean. Positive shifts of ~0.2–0.3 ‰
25 away from background values in $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ are observed during the main phase

26 of the positive carbon-isotope excursion associated with OAE 2. These isotopic shifts
27 are coeval with decreases in Cd/TOC and Zn/TOC ratios and thus imply that drawdown
28 of isotopically light Cd and Zn from seawater inventories was a result of extensive burial
29 of these metals in organic-rich marine sediments globally. Low $\delta^{66}\text{Zn}$ values during the
30 Plenus Cold Event, a cooler episode during OAE 2, are similar in timing and magnitude
31 to variations found in the English Chalk (Eastbourne, UK) and support the inference of a
32 global control on these isotopic excursions. The $\delta^{66}\text{Zn}$ values during the Plenus Cold
33 Event are taken to record global oxygenation, possibly including the remobilization of
34 isotopically light Zn from continental-margin sediments. A considerably smaller change
35 in $\delta^{114}\text{Cd}$ values for this interval implies that the Cd- and Zn-isotope systems can provide
36 information about slightly different environmental processes, with global seawater
37 composition with respect to Zn also being influenced by the magnitude of oxic removal
38 sinks and isotopically light Zn input fluxes from sediments and hydrothermal fluids.
39

40 **1. Introduction**

41

42 Continental margins are important repositories for organic carbon in the modern ocean
43 and are hotspots of ocean deoxygenation (e.g. Muller-Karger et al., 2005). These
44 features are particularly pronounced in low-latitude sites of upwelling where Oxygen
45 Minimum Zones (OMZs) develop with high rates of organic-carbon burial occurring in
46 response to enhanced primary productivity. The immobilization of many redox-
47 dependent, bio-active trace metals such as Cd, Zn and Mo at these depositional settings
48 can have significant impact on the global cycles of these metals (e.g. Brumsack, 2006;
49 Scholz, 2018). Organic-rich continental-margin sediments also represent a possibly
50 important archive for the reconstruction of global metal budgets associated with past
51 global environmental change. Here, Cd- and Zn-isotope analyses of organic-rich
52 continental-margin sediments are used to evaluate the impact of global environmental
53 change on the mass balance of these elements in Late Cretaceous time.

54

55 *1.1. Oceanic Anoxic Event 2*

56 The widespread deposition of organic-rich sediments during a number of intervals in the
57 Mesozoic Era has been associated with global warming, the spread of low-oxygen
58 marine environments, and other perturbations to ocean chemistry (e.g. Jenkyns, 2010;
59 Dickson, 2017, O'Brien et al., 2017). One of the most severe and best-studied examples
60 of these events is the Cenomanian–Turonian (Late Cretaceous, ~94 Ma) Oceanic
61 Anoxic Event 2 (OAE 2) (Schlanger and Jenkyns, 1976; Arthur et al., 1990). To drive
62 and sustain the high export productivity rates needed to reproduce the oceanic redox
63 change associated with this event, geochemical models require a high availability of
64 nutrients in the surface ocean for timescales on the order of 10^5 years (Monteiro et al.,

65 2012). The availability of the major nutrients phosphorus and nitrogen can be explained
66 by their behaviour under anoxic conditions. Phosphorus can be regenerated from anoxic
67 sediments, while the increased fixation of atmospherically derived N₂ by cyanobacteria
68 acts to increase bio-available nitrogen (e.g. Kuypers et al., 2004; Mort et al., 2007; Kraal
69 et al., 2010; Monteiro et al., 2012). The overarching positive carbon-isotope excursion
70 that reflects globally enhanced marine organic-matter burial is conventionally taken to
71 define OAE 2 and can be used as a correlative tool (e.g. Schlanger & Jenkyns, 1976;
72 Arthur et al., 1990; Tsikos et al., 2004). Subdivisions of the carbon-isotope excursion
73 include the Plenus Cold Event interval (section 1.1.1) and the so-called plateau phase
74 that features high and relatively stable $\delta^{13}\text{C}$ values reflecting peak-organic carbon burial
75 conditions globally (Figure 2).

76 Cd and Zn are bio-active trace elements, with at least the latter involved in a
77 number of critical enzymes required for marine life, and both show strong nutrient-like
78 behaviour in the modern ocean (e.g. Bruland, 1980; Morel et al., 1994). Both these
79 elements have a strong affinity for sulfides and are therefore removed from the ocean
80 when reducing conditions increase the formation of such compounds (e.g. Little et al.,
81 2015). Previous studies have suggested that there were decreases in redox-sensitive or
82 chalcophilic trace-element concentrations in seawater during OAE 2 in response to the
83 spread of reducing environments (van Bentum et al., 2009; Hetzel et al., 2009; Owens et
84 al., 2016; Dickson et al., 2016, 2017). However, the magnitude and geographical extent
85 of trace-metal drawdown is difficult to assess from sediment concentration data, due to
86 strong redox controls on their burial in the local environment. Cd- and Zn-isotope ratios
87 offer a complementary way to quantify the behaviour of these important bioactive
88 elements during major environmental perturbations such as OAE 2, because changes in

89 the global mass balance will affect the seawater isotopic composition (e.g. John et al.,
90 2017; Isson et al., 2018).

91

92 1.1.1 The Plenus Cold Event

93 Environmental conditions were not uniform during OAE 2. The Plenus Cold Event
94 represents a period of intra-OAE cooling and was associated with major changes to
95 ocean chemistry (Gale & Christensen, 1996; Forster et al., 2007; Sinninghe Damsté et
96 al., 2010; van Helmond et al., 2014, 2016; Jenkyns et al., 2017; Gale et al., 2019;
97 O'Connor et al., 2020). This interval of cooling was associated with more oxygenated
98 conditions, illustrated by colonization of formerly anoxic sea floors by benthonic
99 organisms, and coincides with a slight negative excursion in the global C-isotope curve,
100 which likely indicates a temporary drop in global organic-carbon burial rates (Tsikos et
101 al., 2004; Jarvis et al., 2011; Jenkyns et al., 2017). Trace-element anomalies found in
102 carbonates recording the Plenus Cold Event have been linked to reoxygenation of
103 previously deposited organic matter and temporary loss of anoxic sinks for redox-
104 sensitive and chalcophilic elements (Jenkyns et al., 2017). Similar anomalies in trace-
105 element concentrations and Cr isotopes from time-equivalent sections from the Western
106 Interior Seaway have, however, stressed mafic volcanic influence without specific
107 attribution to the changing redox conditions (Eldrett et al., 2014; Holmden et al., 2016).
108 Perturbations to the global Zn and U cycles during the Plenus Cold Event interval have
109 also been inferred from seawater isotopic compositions of these elements preserved in
110 carbonate successions: data that are consistent with generally more oxygenated
111 conditions globally (Clarkson et al., 2018; Sweere et al., 2018).

112

113 1.2. Cd- and Zn-isotope systematics

114 Biological uptake of isotopically light Cd results in high $\delta^{114}\text{Cd}$ values in the modern
115 surface ocean, whereas $\delta^{66}\text{Zn}$ values of surface waters are generally lower than in deep
116 waters (e.g. Conway and John, 2014, 2015). For Zn, this observation is remarkable, as
117 culture studies have generally shown the preferential uptake of isotopically light Zn by
118 primary producers in most conditions (John et al., 2007, John and Conway, 2014,
119 Köbberich and Vance, 2019). One explanation for this apparent discrepancy is the
120 reversible scavenging of isotopically heavy Zn by sinking particles (John and Conway,
121 2014; Weber et al., 2018). Other studies have also stressed the importance of Southern
122 Ocean Zn cycling on global patterns (Vance et al., 2017; De Souza et al., 2018; Sieber
123 et al., 2020), whereas more recent studies show evidence for an (anthropogenic) source
124 of isotopically light Zn to the surface ocean (Lemaitre et al., 2020). Despite these
125 complexities, both elements are highly depleted in surface waters relative to deep waters
126 so that, to a first approximation, phytoplankton quantitatively remove the elements and
127 therefore have a similar isotope composition to that added to the surface by upwelling
128 and vertical diffusion. However, recent data on particulates suggests that partial
129 remineralization in sub-surface waters may leave sinking particles isotopically lighter
130 than dissolved Cd (Janssen et al., 2019). The isotopic composition of the deep ocean is
131 nearly homogeneous for both elements and is set by the relative proportions of different
132 oceanic input and output fluxes.

133 For Zn, the weighted mean of riverine $\delta^{66}\text{Zn}$ input to the modern ocean has a
134 value of $\sim 0.33\text{‰}$, which is within the uncertainties of estimates for the bulk silicate earth
135 composition ($0.28 \pm 0.05\text{‰}$, 2 SD) and aeolian input (Chen et al., 2013; Little et al.,
136 2014). Recent estimates for the isotopic composition of Zn inputs from continental
137 margins (-0.51 to $+0.01\text{‰}$) and hydrothermal sources ($\sim -0.42\text{‰}$) have considerably
138 lower $\delta^{66}\text{Zn}$ values than riverine inputs (Lemaitre et al., 2020), but the size and global

139 relevance of these fluxes are still debated (John et al., 2008; Conway and John, 2014;
140 Little et al., 2014; Roshan et al., 2016). Organic-rich continental-margin sediments
141 represent the only known sink for isotopically light Zn (Little et al., 2016). Sediments
142 underlying the restricted, euxinic deep waters of the Black Sea and Cariaco Basin have
143 average $\delta^{66}\text{Zn}$ values of ~ 0.5 ‰, identical to the average deep-ocean composition as a
144 result of near-quantitative removal of Zn under such conditions (Vance et al., 2016;
145 Isson et al., 2018). $\delta^{66}\text{Zn}$ values for other sinks in oxic environments (Fe-Mn
146 oxyhydroxides, carbonates) are 0.4–0.5 ‰ higher than those of average deep ocean
147 seawater (Pichat et al., 2003; Little et al., 2014).

148 The Cd cycle shows similarities to Zn as the average lithosphere (~ 0.04 ‰),
149 riverine (~ 0.24 ‰), aeolian (~ 0.02 ‰) and hydrothermal (~ 0.06 ‰) inputs of Cd to the
150 ocean all have lower $\delta^{114}\text{Cd}$ values than the dissolved deep-ocean composition (~ 0.3 ‰)
151 (John et al., 2017 and references therein). The isotopic compositions of ocean outputs
152 have not been characterized in great detail, apart from those of Fe-Mn oxyhydroxide
153 crusts, which are not associated with significant isotopic fractionation and record
154 seawater values (Schmitt et al., 2009; Horner et al., 2010). In contrast to Zn, Cd sinks
155 that are isotopically heavier than seawater have not been recognized.

156 Cd and Zn outputs to organic-rich marine sediments are likely to relate to two
157 main fluxes: organically bound metals and metal sulfides. Uptake in cellular organic
158 carbon generally represents the main export mechanism of Cd and Zn to the sediment,
159 where it may be buried as part of organic material or fixed as metal sulfides (Little et al.,
160 2015; Weber et al., 2018). The formation of Cd and Zn sulfides in sulfidic pore waters or
161 seawater is associated with the preferential incorporation of the lighter isotopes for both
162 Cd and Zn, which may lead to isotopic fractionation between water and sediment if
163 removal is non-quantitative (Conway and John, 2015; Little et al., 2016; Vance et al.,

164 2016; Guinoiseau et al., 2018). However, due to the high stability of CdS and ZnS
165 complexes (Al-Farawati and Van den Berg, 1999), sulfide precipitation for these
166 elements may generally be expected to be quantitative in most environments. Non-
167 quantitative sulfide formation may occur in conditions where dissolved Cd and Zn are
168 available in excess of sulfide, for example, in redox transition zones in pore waters
169 (Scholz and Neumann, 2007). It is unclear how relevant such conditions are for the
170 global isotopic mass balances. Nonetheless, sulfide formation can impact the isotopic
171 composition of the bulk sediment in various settings as it affects the relative proportion of
172 sedimentary Cd and Zn in other sedimentary phases (John et al., 2017; Isson et al.,
173 2018; Weber et al., 2018; Sweere et al., 2020). Of particular relevance to this study is
174 organic material for which the metal-isotope ratios may be isotopically lighter than
175 seawater due to non-quantitative biological uptake in the surface ocean or partial
176 remobilization of sinking particles (John et al., 2007; John and Conway, 2014; Janssen
177 et al., 2019).

178 Consequently, local redox conditions may impact the proportion of Cd and Zn
179 removal in the form of CdS and ZnS and may thus explain differences in $\delta^{114}\text{Cd}$ and
180 $\delta^{66}\text{Zn}$ for various modern marine sediments. Modern organic-rich continental-margin
181 sediments accumulating underneath relatively shallow waters (~264 m) with anoxic to
182 mildly sulfidic conditions, such as in the Peruvian Margin, feature higher sedimentary
183 $\delta^{66}\text{Zn}$ values ($\delta^{66}\text{Zn} = -0.3\text{‰}$) than those from less reducing and deeper sites ($\delta^{66}\text{Zn} =$
184 -0.0‰) (Little et al., 2016). A mostly sulfidic water column results in quantitative Zn
185 removal in the restricted Black Sea and Cariaco Basin ($\delta^{66}\text{Zn} = -0.5\text{‰}$, Vance et al.,
186 2016; Isson et al., 2018). Modern sediment data are not available for Cd in such detail,
187 but the first results suggest generally similar patterns (Bryan, 2019).

188

189 **2. Material and methods**

190

191 *2.1 The Tarfaya Basin*

192 Sediments from the Tarfaya Basin (Morocco) comprise a well-studied Cenomanian–
193 Turonian boundary interval (e.g. Tsikos et al., 2004). The focus of this study is on core
194 S57, which contains ~37 m of cyclically bedded organic-rich calcareous sediments of
195 Cenomanian–Turonian age, well dated with nannofossils and planktonic foraminifera,
196 with a very low abundance of detrital minerals (Kolonic et al., 2005; Kuhnt et al., 2005).
197 During deposition, the basin was located in an open shelf setting at ~15°N and is
198 thought to have been fed by the upwelling of nutrient-rich waters (Lüning et al., 2004;
199 Kolonic et al., 2005; Figure 1). Organic biomarker, Fe-speciation, and trace-metal data
200 from high-resolution studies on part of this core, including the Plenus Cold Event
201 interval, have revealed dominantly euxinic conditions with short intervals of anoxic non-
202 sulfidic conditions (Kolonic et al., 2005; Poulton et al., 2015; Goldberg et al., 2016).
203 Conditions in the Tarfaya Basin during deposition of the rest of the core were likely at
204 least as reducing as implied by the generally higher Mo enrichments for these other
205 intervals (Kolonic et al., 2005; Goldberg et al., 2016; Dickson et al., 2016).

206

207 *2.2. Analytical methods*

208 Aliquots of powdered sample material taken from archived samples of drill core S57
209 were weighed into Teflon digestion vessels together with a ^{113}Cd - ^{111}Cd or ^{67}Zn - ^{64}Zn
210 double spike. The sample powders were digested on a hotplate for 48 hours in inverse
211 aqua regia (iAR, 3 parts HNO_3 , 1 part HCl) to preferentially dissolve authigenic shale
212 components. Cd and Zn were separated from major-element cations and interferences
213 in a two-stage anion column chromatography procedure modified from previous studies

214 (Dickson et al., 2016; Sweere et al., 2018; Sweere et al., 2020).

215 Stable-isotope analyses were performed on a Nu Instruments Plasma I multi-
216 collector ICP-MS at the University of Oxford. Data were processed offline using an
217 exponential mass-bias correction, measured relative to NIST-3108 Cd and IRMM-3702
218 Zn solutions, and reported as $\delta^{114}\text{Cd} = [^{114/110}\text{Cd}_{\text{sample}}/^{114/110}\text{Cd}_{\text{NIST}}]-1) \times 1000$ and $\delta^{66}\text{Zn} =$
219 $[^{66/64}\text{Zn}_{\text{sample}}/^{66/64}\text{Zn}_{\text{IRMM-3702}}]-1) \times 1000 + 0.28$. External reproducibility was estimated
220 based on repeated analyses of the USGS SDO-1 shale reference material: $\delta^{114}\text{Cd}_{\text{SDO-1}} =$
221 $0.13 \pm 0.06 \text{ ‰}$ (2 SD, n = 5), and $\delta^{66}\text{Zn}_{\text{SDO-1}} = 0.43 \pm 0.07 \text{ ‰}$ (2 SD, n=9). Reported
222 errors in Figure 2 are the 2 standard error propagated uncertainties based on the
223 reproducibility of the bracketing standards and the internal error of sample analysis.
224 Enrichment factors (EF) are calculated relative to average upper continental crust
225 concentrations as $\text{TM}_{\text{EF}} = (\text{TM}/\text{Al})_{\text{sample}} / (\text{TM}/\text{Al})_{\text{crust}}$ (Rudnick and Gao, 2003, $\text{Cd}/\text{Al}_{\text{crust}} =$
226 0.011×10^4 ; $\text{Zn}/\text{Al}_{\text{crust}} = 8.22 \times 10^4 \text{ g/g}$).

227

228 *2.3 English Chalk, Eastbourne*

229 For comparison of the Tarfaya data to other sedimentary archives, Cd/Ca data for time-
230 equivalent sediments from an outcrop near Eastbourne, UK are also presented. This
231 section consists of organic-lean epicontinental pelagic nannofossil-rich deposits of the
232 English Chalk, which have previously been studied for their $\delta^{66}\text{Zn}$ and Zn/Ca
233 compositions (Jenkyns et al., 2017; Sweere et al., 2018). The previously unpublished
234 Cd/Ca data presented here are from the same set of carbonate phase measurements
235 presented by Jenkyns et al. (2017). Briefly, carbonates were selectively dissolved from
236 bulk rock using 0.5M acetic acid. After centrifugation to remove undissolved sedimentary
237 components, the supernatant was diluted to 10 ppm Ca, and measured on a Thermo
238 Scientific Element 2 magnetic-sector ICP-MS.

239

240 *2.4. Chemostratigraphic Divisions*

241 To assess the environmental controls on stratigraphic $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ variations,
242 samples for the Tarfaya core were grouped into different chemostratigraphic divisions,
243 based mainly on the carbon-isotope stratigraphy. The shading of these different
244 divisions, as indicated in Figure 2, are used later to compare metal concentrations and
245 isotope compositions for these different intervals.

246

247 **3. Results**

248

249 Both Cd and Zn are strongly enriched in the Tarfaya sediments relative to upper
250 continental crust. Values for Cd_{EF} range from ~20–850, with an average of 238 ($n = 36$);
251 whilst those for Zn_{EF} range from ~3.2–207 and average 40 ($n = 35$). Enrichments of Zn
252 and Cd follow similar stratigraphic patterns (Figure 2).

253 The Cd- and Zn-isotope compositions for the S57 core show stratigraphic
254 patterns coincident with changes in other geochemical parameters. $\delta^{114}\text{Cd}$ values range
255 from ~-0.61 to 0.26‰ with an average of -0.07‰ ($n = 36$). The maximum $\delta^{114}\text{Cd}$ values
256 found for Tarfaya sediments approach the modern deep-ocean value of ~0.3‰ (e.g.
257 Conway and John, 2015). The lowest $\delta^{114}\text{Cd}$ observed are considerably lower than
258 dissolved $\delta^{114}\text{Cd}$ values generally found for the modern ocean and closer to values
259 found in CdS precipitation experiments (Guinoiseau et al., 2018). $\delta^{66}\text{Zn}$ values range
260 from ~-0.09 to 0.85‰ with an average of 0.32‰ ($n = 38$). The lowest $\delta^{66}\text{Zn}$ values
261 observed are lower than those of the bulk silicate Earth (~0.3‰, Chen et al., 2013) and
262 of riverine inputs (~0.3‰) but not lower than some estimates for Zn inputs from
263 continental margins (~-0.8 to -0.5‰) or hydrothermal vents (~-0.5 to 0.3‰) (Conway and

264 John, 2014; compilation in Vance et al., 2016). The maximum $\delta^{66}\text{Zn}$ values observed are
265 higher than dissolved $\delta^{66}\text{Zn}$ values measured for the modern deep ocean of $\delta^{66}\text{Zn}$
266 $=0.5\text{‰}$, but lower than some ocean outputs, including carbonates, which have average
267 $\delta^{66}\text{Zn}$ values of $\sim 0.9 \text{‰}$ and Fe-Mn oxyhydroxide crusts with values of $\sim 1.0\text{‰}$ (e.g.
268 Pichat et al., 2003; Little et al., 2014).

269 The average $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ values for background conditions are -0.10 ± 0.09
270 ($n = 17$) and 0.31 ± 0.12 and (1 SD, $n = 18$), respectively (Figure 2). The Plenus Cold
271 Event interval contains the lowest enrichments of Cd and Zn. This chemostratigraphic
272 division also hosts the lowest isotope values for both Cd and Zn with average $\delta^{114}\text{Cd}$ and
273 $\delta^{66}\text{Zn}$ values of -0.24 ± 0.23 and $0.14 \pm 0.18 \text{‰}$, respectively (1 SD, $n = 9$). However, low
274 $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ values during the Plenus Cold Event show different stratigraphic
275 patterns. The highest $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ values are found in the stratigraphic interval just
276 post-dating the Plenus Cold Event. Average $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ values observed for the
277 plateau-phase of the OAE 2 interval are 0.11 ± 0.09 ($n = 10$) and 0.45 ± 0.23 (1 SD, $n =$
278 11), respectively. Cd/Ca values for the Eastbourne chalk vary between 0.019 and 0.19
279 $\mu\text{mol/mol}$ with the highest values found in the interval of the Plenus Cold Event.

280

281 **4. Discussion**

282

283 The two most prominent features of the Tarfaya record are (i) higher Cd- and Zn-isotope
284 values during the plateau phase of OAE 2 and (ii) a decrease in Cd- and Zn-isotope
285 values during the PCE. The following discussion focuses on several key mechanisms
286 that might account for the observed variations.

287

288 *4.1. Hydrographic setting of the Tarfaya Basin*

289 The degree and nature of water exchange between the Tarfaya Basin and the open
290 ocean (proto-North Atlantic) are of critical importance in understanding stratigraphic
291 $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ patterns because these phenomena control the amount and isotopic
292 composition of dissolved Cd and Zn coming into the basin. The hydrographic conditions
293 of the Tarfaya Basin can be evaluated using a Cd/Mo vs Co \times Mn cross-plot, because
294 modern organic-rich sediments have distinct Cd/Mo and Co \times Mn values for different
295 hydrographic regimes (Sweere et al., 2016).

296 Cd/Mo ratios of organic-rich marine sediments are thought to reflect the relative
297 importance of export production *versus* preservation of organic material, due to the high
298 Cd uptake in organic cellular material (Little et al., 2015; Sweere et al., 2016). Co and
299 Mn concentrations are generally very low in sediments from oxygen minimum zones
300 below upwelling regions, in contrast to restricted basins like the Black Sea (Brumsack,
301 2006; Sweere et al., 2016). These different geochemical signatures are thought to reflect
302 the hydrographic conditions that impact both the supply and removal efficiencies of Co
303 and Mn to the sediment.

304 Low removal efficiencies of Mn are expected in both restricted basins and
305 upwelling settings, considering the high solubility of this element in reducing conditions
306 (e.g. Tribovillard et al., 2006 and references therein). However, the supply of Mn and Co
307 is likely to be higher in restricted basins as Co and Mn concentrations in rivers (and
308 surface waters) are much higher than in open-ocean sub-surface waters that feed
309 upwelling regions. With limited water exchange due to hydrographic restriction, these
310 elements are effectively trapped in restricted basins, allowing higher dissolved and
311 sedimentary concentrations to develop. Low supply in upwelling systems coupled to low
312 removal efficiencies from seawater to sediment in OMZs allows these elements to be

313 transported away from the OMZ and hence result in low sedimentary concentrations
314 compared with those in restricted basins (Sweere et al., 2016).

315 An empirical comparison between elemental data from Tarfaya with modern
316 marine sediment data suggests an open-ocean depositional regime for the Tarfaya
317 Basin (Figure 3). This regime probably had relatively high primary productivity that was
318 fed by upwelling of sub-surface waters from the proto-North Atlantic Ocean. Importantly,
319 no significant difference in Cd/Mo *versus* Mn × Co relationships is observed between the
320 three chemostratigraphic divisions, suggesting that the hydrographic conditions of the
321 Tarfaya Basin remained relatively constant during the studied interval. This
322 reconstruction agrees with previous suggestions that the Tarfaya Basin was situated in a
323 region of active upwelling of nutrient-rich sub-surface waters from the proto-North
324 Atlantic Ocean, promoting high primary productivity and high mass accumulation rates of
325 organic carbon (Lüning et al., 2004; Kolonic et al., 2005; Trabucho-Alexandre et al.,
326 2010; Dickson et al., 2016; Scholz et al., 2019).

327

328 *4.2. Redox variations in the Tarfaya Basin*

329 Despite the strong and relatively constant connection to the open ocean, there may have
330 been variations in local redox conditions of the Tarfaya Basin that impacted Cd and Zn
331 burial pathways and the isotopic offset between sediments and seawater. Temporarily
332 more oxygenated conditions could have resulted in a larger isotopic offset between
333 sediments and seawater, as found in modern continental-margin sediments (Little et al.,
334 2016; Bryan, 2019). Such conditions would be comparable to sediments deposited in
335 suboxic to anoxic environments in the modern ocean that show lower $\delta^{66}\text{Zn}$ values than
336 sediments from the anoxic to mildly sulfidic Peru Margin (Little et al., 2016).

337 Mo_{EF} values provide an independent proxy for local redox conditions (Figures 2,
338 4, and 5; e.g. Scott and Lyons, 2012). Mo_{EF} values are generally high and reasonably
339 constant for the S57 core, implying that anoxic to euxinic environments dominated
340 conditions in the Tarfaya Basin during most of the studied interval (Kolonis et al., 2005;
341 Dickson et al., 2016; Figures 2 and 4). While global drawdown of Mo may have occurred
342 during the OAE 2 interval, there are no signs for severe local drawdown in the Tarfaya
343 Basin; thus, stratigraphic patterns in Mo_{EF} are thought to mostly reflect local redox
344 conditions (Dickson et al., 2016). Low Mo_{EF} values (<50) are almost exclusively limited to
345 the Plenus Cold Event interval (Division 2), suggesting temporarily more oxygenated
346 conditions. This interpretation of redox conditions in the Tarfaya Basin is generally
347 consistent with a study on a different core (SN4), which concluded that conditions for the
348 time-equivalent interval studied here were anoxic to mildly euxinic and relatively
349 constant, apart from more oxygenated conditions during the Plenus Cold Event interval
350 (Scholz et al., 2019).

351 The Plenus Cold Event interval also features the lowest $\delta^{114}Cd$ and $\delta^{66}Zn$ values
352 for the S57 core, which could thus be the result of temporarily more oxidizing conditions.
353 Stratigraphic patterns for both elements in sediments recording the Plenus Cold Event
354 interval, however, are considerably different. $\delta^{114}Cd$ shows two abrupt perturbations to
355 very low $\delta^{114}Cd$ (< -0.4‰), whereas $\delta^{66}Zn$ values display a gradual decrease throughout
356 the interval. High-resolution TOC, Fe-speciation, and Mo data from previous studies on
357 the same core offer a more detailed look at the possible impact of changing redox
358 environments on $\delta^{114}Cd$ and $\delta^{66}Zn$ patterns during the Plenus Cold Event (Figure 5;
359 Poulton et al., 2015; Dickson et al., 2016; Goldberg et al., 2016). The Fe-speciation data
360 indicate euxinic conditions with brief, cyclically occurring shifts to anoxic non-sulfidic
361 conditions. Patterns in Mo_{EF} do not vary systematically with the cyclic alternation in

362 Fe_{py}/Fe_{HR} and more closely resemble TOC patterns over this interval that show lower
363 values for two intervals around 51 and 53 m depth (Figure 5).

364 Cross-plots of $\delta^{114}Cd$ and $\delta^{66}Zn$ with Mo_{EF} for all samples (Figure 4) can be
365 considered alongside detailed stratigraphic information for the Plenus Cold Event
366 interval (Figure 5) to assess the impact of local redox conditions on $\delta^{114}Cd$ and $\delta^{66}Zn$.

367

368 4.2.1 Local redox controls on $\delta^{114}Cd$

369 High $\delta^{114}Cd$ values for the carbon-isotope plateau phase (Figure 2) of the OAE interval
370 can mostly be attributed to a change in $\delta^{114}Cd_{seawater}$ towards higher values, but some
371 effect of changing local redox conditions cannot be excluded. There is a generally
372 positive relationship observed between $\delta^{114}Cd$ and Mo_{EF} , based on all samples (Figure
373 4), which implies there was a local redox control on the Cd-isotope composition of
374 sediments in the Tarfaya Basin (Sweere et al., 2020). However, this positive relationship
375 is absent within the different chemostratigraphic divisions separately, despite
376 considerable variation in $\delta^{114}Cd$ and Mo_{EF} within them. Additionally, samples from the
377 carbon-isotope plateau phase of the OAE 2 interval show consistently higher $\delta^{114}Cd$
378 values than background conditions, even for low Mo_{EF} samples, implying that there was
379 likely a difference in $\delta^{114}Cd_{seawater}$ during deposition of sediments belonging to these two
380 divisions.

381 Outliers with very low $\delta^{114}Cd$ values (< -0.4 ‰), deposited during the Plenus Cold
382 Event interval (Division 2 in Figure 2), do suggest a larger isotopic offset between
383 sediments and seawater as they all feature relatively low Mo_{EF} values. In a more detailed
384 view of this interval (Figure 5), the lowest Cd-isotope values are not systematically
385 registered in non-sulfidic intervals, only one of the two perturbations to low $\delta^{114}Cd$ being
386 coincident with an interval of lower Fe_{py}/Fe_{HR} (Poulton et al., 2015; Figure 5). $\delta^{114}Cd$

387 patterns more closely follow trends in TOC and Mo_{EF} , with the lowest $\delta^{114}Cd$ consistently
388 occurring in low- Mo_{EF} and -TOC intervals. The anomalously low $\delta^{114}Cd$ values ($< -0.4\%$)
389 observed during the Plenus Cold Event are therefore attributed to a temporarily larger
390 isotopic offset between seawater and sediments preserved under more oxygenated
391 conditions.

392 When these samples (marked in red) are ignored, $\delta^{114}Cd$ values for the Plenus
393 Cold Event interval ($-0.09 \pm 0.16 \%$, 2 S.D., $n = 5$) are comparable to those of the
394 Cenomanian–Turonian background conditions ($-0.10 \pm 0.18 \%$) and lower than $\delta^{114}Cd$
395 values for the plateau phase of the carbon-isotope excursion (by up to $\sim 0.3 \%$). $\delta^{114}Cd$
396 values for the remaining samples gradually drop to a minimum of $\sim -0.2\%$ near the end of
397 the Plenus Cold Event interval. This geochemical change cannot directly be explained
398 by varying local redox conditions, as it changes independently of Mo_{EF} and Fe_{py}/Fe_{HR}
399 patterns (Figure 5). More likely, this gradual stratigraphic change in $\delta^{114}Cd$ during the
400 Plenus Cold Event reflects the evolution of $\delta^{114}Cd_{seawater}$ to lower values. This inferred
401 perturbation to the global Cd-isotope cycle is consistent with elevated Cd/Ca ratios for
402 the time-equivalent interval in the Eastbourne chalk, which indicates a substantial
403 increase in dissolved Cd in seawater during the Plenus Cold Event (Figure 7).

404

405 4.2.2 Local redox controls on $\delta^{66}Zn$

406 A cross-plot of $\delta^{66}Zn$ with Mo_{EF} values does not show a clear positive relationship, which
407 implies local redox conditions were not the dominant control on $\delta^{66}Zn$ values of the
408 Tarfaya Basin sediments. Samples with the lowest $\delta^{66}Zn$ values ($0.0\text{--}0.1\%$), found
409 exclusively for the Plenus Cold Event interval, generally do show low Mo_{EF} values.
410 However, there is no systematic relationship of stratigraphic $\delta^{66}Zn$ patterns with
411 Fe_{py}/Fe_{HR} , Mo_{EF} , or TOC, for this interval (Figure 5) and therefore no apparent local

412 redox or export productivity control on the decrease in $\delta^{66}\text{Zn}$. The stratigraphic change in
413 $\delta^{66}\text{Zn}$ values over the Plenus Cold Event interval is gradual, in contrast to patterns in
414 Mo_{EF} and $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ values that vary over shorter intervals. These observations imply
415 that the transition to lower $\delta^{66}\text{Zn}$ values can largely be attributed to a change in the
416 global seawater isotopic composition. Temporarily changing $\Delta^{66}\text{Zn}_{\text{sediment-seawater}}$, as a
417 function of local redox conditions, would have likely led to more abrupt changes in
418 sedimentary $\delta^{66}\text{Zn}$ values. This interpretation is consistent with a time-equivalent $\delta^{66}\text{Zn}$
419 shift of similar magnitude that has been found for organic-lean carbonate sediments from
420 the Plenus Cold Event interval in southern England (Eastbourne) and southern Italy
421 (Raia del Pedale) and was associated with higher Zn/Ca values (Figure 7, Sweere et al.,
422 2018). Together, these studies provide strong evidence for a global perturbation to the
423 Zn cycle during the Plenus Cold Event.

424

425 *4.3 Concentrations of dissolved Cd and Zn*

426 Sedimentary Cd and Zn concentrations relative to total organic carbon (TOC) can
427 provide information on the availability of the dissolved elements. Low dissolved Mo
428 concentrations in modern restricted euxinic basins have been shown to lead to
429 proportionally lower Mo/TOC ratios in accumulating sediments (Algeo and Lyons, 2006)
430 and a similar effect can be caused by the widespread removal of Mo from seawater
431 during global anoxic episodes such as OAE 2 (van Bentum et al., 2009; Hetzel et al.,
432 2009; Dickson et al., 2016, 2017; Owens et al., 2016). Considering the strong open-
433 ocean connection (section 4.1), local drawdown of the dissolved Cd and Zn pool is
434 unlikely to have impacted sedimentary enrichments for sediments of the Tarfaya Basin.
435 Notably, Mo isotopes also do not display any evidence of periodic trace-metal drawdown
436 at the study site (Dickson et al., 2016). More broadly, however, trace-metal drawdown in

437 the wider proto-North Atlantic/Tethys region, or globally, could have impacted supply to
438 the Tarfaya Basin and therefore the sedimentary Cd/TOC and Zn/TOC values.

439 Low Cd/TOC and, to a lesser extent, Zn/TOC values are observed for sediments
440 from the intervals of the Plenus Cold Event (Division 2) and plateau-phase of the OAE 2
441 (Division 3), in comparison to background values (Division 1) (Figures 2, 6). For the
442 Plenus Cold Event interval, these geochemical signatures can partly be explained by
443 more oxygenated conditions, as indicated by low Mo_{EF} values, that would have limited
444 the formation of sulfides. By contrast, samples from the plateau phase of the OAE 2
445 interval generally show high Mo_{EF} values, indicative of locally euxinic conditions, which
446 would have enhanced export and burial of Cd and Zn relative to TOC as sulfides. Low
447 Cd/TOC and Zn/TOC values for some of these samples therefore likely reflect the
448 drawdown of the dissolved elements in the wider proto-North Atlantic/Tethys region or
449 globally. This interpretation is consistent with anomalously low Zn concentrations that
450 have been reported previously for the OAE 2 interval on the Demerara Rise (Hetzl et
451 al., 2009; Owens et al., 2016).

452

453 *4.4 The Cd- and Zn-isotope composition of Cenomanian–Turonian seawater*

454 With relatively constant hydrographic (section 4.1) and redox (section 4.2) conditions in
455 the Tarfaya Basin for the studied interval, the main influence on stratigraphic $\delta^{114}Cd$ and
456 $\delta^{66}Zn$ patterns would have been the isotopic composition of the sub-surface proto-North
457 Atlantic waters that fed the basin. The Cd- and Zn-isotope composition of the modern
458 deep ocean is homogenous and set by the proportion of different inputs and outputs
459 (e.g. Conway and John 2014; 2015, Vance et al., 2016; Weber et al., 2018).
460 Reconstructions of sub-surface proto-North Atlantic $\delta^{114}Cd$ and $\delta^{66}Zn$ compositions may
461 thus be used to infer changes in the global mass balance associated with

462 paleoenvironmental change during the Cenomanian–Turonian interval. However, this
463 interpretation requires some assumptions on $\Delta^{66}\text{Zn}_{\text{sediment-seawater}}$ and $\Delta^{114}\text{Cd}_{\text{sediment-seawater}}$
464 to be made.

465

466 4.4.1 Constraining $\delta^{114}\text{Cd}_{\text{seawater}}$ values

467 The limited amount of available modern data suggest a $\Delta^{114}\text{Cd}_{\text{sediment-seawater}}$ value of ~-
468 0.3‰, for most organic-rich continental-margin sediments (Bryan, 2019). Application of
469 this offset to the data presented here, excluding outliers in the Plenus Cold Event
470 Interval (section 4.2), would imply a total range of Late Cretaceous $\delta^{114}\text{Cd}_{\text{seawater}}$ of 0.09
471 to 0.56 ‰. On average, $\delta^{114}\text{Cd}_{\text{seawater}}$ values for Division 1 (background conditions, 0.20
472 ± 0.09 , 1 SD) and Division 2 (Plenus Cold Event, 0.21 ± 0.08 ‰, 1SD) are
473 indistinguishable, and lower than values for Division 3 of Figure 2 (plateau phase, $0.41 \pm$
474 0.09 ‰, 1 SD). These values for Late Cretaceous $\delta^{114}\text{Cd}_{\text{seawater}}$ are plausible and roughly
475 vary around the modern deep-ocean composition (~ 0.3 ‰). However, the uncertainties
476 associated with these first reconstructions of Cenomanian–Turonian $\delta^{114}\text{Cd}_{\text{seawater}}$ values,
477 further complicated by poor constraints on some aspects of the modern global isotopic
478 mass balance, currently do not allow a meaningful quantitative assessment of variations
479 in the global mass Cd mass balance during Late Cretaceous time.

480

481 4.4.2 Constraining $\delta^{66}\text{Zn}_{\text{seawater}}$ values

482 Of the three modern continental-margin sites for which $\delta^{66}\text{Zn}$ data are available (Peru
483 Margin, Mexican Margin, California Borderland basins, Little et al., 2016), the highly
484 reducing, highly productive conditions in the Tarfaya Basin were probably most
485 comparable to the modern Peru Margin. This margin is characterized by high export
486 productivity and organic-carbon burial rates, anoxic to mildly sulfidic (euxinic) conditions,

487 and sediments with high TOC and total sulfur contents (Reimers and Suess, 1983; Suits
488 and Arthur, 2000; Little et al., 2016). The studied Peru Margin sediments also feature a
489 similar water depth (264 m) to that suggested for the Tarfaya Basin during Cenomanian–
490 Turonian times (~200–300 m). $\delta^{66}\text{Zn}$ values of the Tarfaya Basin sediments may
491 therefore be assumed to have been ~0.2‰ lower than the deep-ocean composition
492 during the Late Cretaceous, similar to the difference for the present-day Peruvian
493 Margin.

494 Applying a $\Delta^{66}\text{Zn}_{\text{sediment-seawater}}$ of -0.2‰ to all samples results in an average
495 $\delta^{66}\text{Zn}_{\text{seawater}}$ composition for the proto-North Atlantic deep ocean during background
496 conditions (Division 1 in Figure 2) of 0.51‰, which is indistinguishable from modern
497 deep-ocean compositions (e.g. Conway and John, 2014). Based on a 3-point moving
498 average, $\delta^{66}\text{Zn}_{\text{seawater}}$ values for the studied interval range from 0.14 to 0.76 ‰. The
499 magnitude and timing of major stratigraphic trends are generally consistent with data
500 from the Chalk of southern England at Eastbourne (Figure 7, Sweere et al., 2018).
501 These observations thus support the inference of a change to the global zinc cycle,
502 represented by its seawater composition, across an interval of widespread
503 environmental change.

504

505 *4.5 Drivers of $\delta^{66}\text{Zn}_{\text{seawater}}$ change*

506

507 4.5.1 Defining the isotopic mass balance

508 A simplified global isotopic mass-balance model is used to assess the drivers of the
509 reconstructed $\delta^{66}\text{Zn}_{\text{seawater}}$ change. In steady state, the total input flux (F_{input}) is equal to
510 the sum of the outputs (F_{output}) into oxic (F_{ox}), anoxic (F_{anox}) and euxinic (F_{eux}) sediments
511 so that $1 = f_{\text{ox}} + f_{\text{anox}} + f_{\text{eux}}$. Here, f_{oxic} reflects Zn burial in Fe-Mn phases in oxic conditions

512 (e.g. Little et al., 2014), f_{anoxic} refers to the Zn burial in organic-rich sediments on
 513 continental margins (Little et al., 2016), and f_{euxinic} reflects the burial of Zn in strongly
 514 euxinic (restricted) basins, like the modern Black Sea (Vance et al., 2016; Isson et al.,
 515 2018).

516 The isotopic mass balance is as follows:

517

$$518 \quad \delta^{66}\text{Zn}_{\text{input}} = \delta^{66}\text{Zn}_{\text{oxic}} * f_{\text{oxic}} + \delta^{66}\text{Zn}_{\text{anoxic}} * f_{\text{anoxic}} + \delta^{66}\text{Zn}_{\text{euxinic}} * f_{\text{euxinic}} \quad (1),$$

519

520 The isotopic composition of ocean outputs can all be expressed relative to the seawater
 521 isotope composition ($\Delta^{66}\text{Zn}_{\text{output-sw}} = \delta^{66}\text{Zn}_{\text{output}} - \delta^{66}\text{Zn}_{\text{seawater}}$). By combining the two
 522 equations above, the Zn-isotope composition of seawater can then be expressed as a
 523 function of f_{anox} and f_{eux} as:

524

$$525 \quad \delta^{66}\text{Zn}_{\text{sw}} = (\Delta^{66}\text{Zn}_{\text{oxic-sw}} - \Delta^{66}\text{Zn}_{\text{anox-sw}}) * f_{\text{anox}} + (\Delta^{66}\text{Zn}_{\text{oxic-sw}} - \Delta^{66}\text{Zn}_{\text{eux-sw}}) * f_{\text{eux}} +$$

$$526 \quad \delta^{66}\text{Zn}_{\text{input}} - \Delta^{66}\text{Zn}_{\text{oxic-sw}} \quad (2).$$

527

528 By assuming f_{eux} is a fixed proportion (b) of f_{anox} (i.e. $f_{\text{eux}} = b \times f_{\text{anox}}$), $\delta^{66}\text{Zn}_{\text{sw}}$ can then be
 529 plotted against f_{anox} (Figure 8). Here, the gradient is given by $(\Delta^{66}\text{Zn}_{\text{oxic-sw}} - \Delta^{66}\text{Zn}_{\text{anox-sw}}) +$
 530 $(\Delta^{66}\text{Zn}_{\text{oxic-sw}} - \Delta^{66}\text{Zn}_{\text{eux-sw}}) \times b$, and the y-axis intercept by $\delta^{66}\text{Zn}_{\text{input}} - \Delta^{66}\text{Zn}_{\text{oxic-sw}}$.

531

532 4.5.1 The Plenus Cold Event interval and pre-OAE $\delta^{66}\text{Zn}$ excursion.

533 This isotopic mass-balance model implies that the inferred drop in the $\delta^{66}\text{Zn}_{\text{seawater}}$ value
 534 for the Plenus Cold Event interval reflects a global decrease in the proportion of Zn
 535 removal into anoxic organic-rich sediments relative to oxic sediments (Figure 8). This
 536 interpretation is consistent with U-isotope evidence for a more oxygenated seafloor

537 during the Plenus Cold Event (Clarkson et al., 2018). These lower $\delta^{66}\text{Zn}_{\text{seawater}}$ values
538 also might reflect the remobilization of previously buried isotopically light Zn from
539 organic-rich continental-margin sediments following large-scale ocean oxygenation (cf.
540 Conway and John, 2014; Lemaitre et al., 2020), alongside other chalcophilic and redox-
541 sensitive trace metals as inferred for data from carbonate successions for this interval
542 (Jenkyns et al., 2017; Clarkson et al., 2018; Sweere et al., 2018). Spikes in
543 concentrations of the trace metals Co, Cu, Sc, and Cr, and the negative shift in Cr
544 isotopes, as found in sediments from the Western Interior Seaway, have also been
545 linked to mafic input from the Caribbean and High Arctic Large Igneous Provinces (LIPs)
546 during the Plenus Cold Event interval (e.g. Eldrett et al., 2014; Holmden et al., 2016).
547 This mafic event may have also impacted the Zn (and Cd) cycle and contributed to an
548 inferred lower $\delta^{66}\text{Zn}_{\text{seawater}}$ value for this interval.

549 Another negative shift in $\delta^{66}\text{Zn}$ values of similar magnitude has been observed in
550 European carbonate archives stratigraphically just below the onset of the carbon-isotope
551 excursion that defines the OAE 2 interval (Sweere et al., 2018). This drop in $\delta^{66}\text{Zn}$
552 values could represent a particularly strong pulse of isotopically light Zn to the ocean
553 from hydrothermal fluids or low-temperature reactions between seawater and mafic
554 rocks due to the onset of a LIP, for which there is independent evidence from the global
555 osmium-isotope record (Turgeon and Creaser, 2008; Du Vivier et al., 2014, 2015). The
556 corresponding interval in the Tarfaya succession also features anomalously low $\delta^{66}\text{Zn}$
557 values, as well as low $\delta^{114}\text{Cd}$ values (Figure 7). These observations provide support for
558 a direct link between the onset of a major magmatic episode and ocean nutrification as a
559 trigger for increased carbon burial.

560

561 4.5.2 Carbon-isotopic plateau-phase of the OAE 2 interval

562 Higher $\delta^{66}\text{Zn}_{\text{seawater}}$ values for the plateau phase of the OAE 2 interval require a higher
563 proportion of isotopically light Zn burial into anoxic organic-rich sediments relative to
564 background conditions (Figure 8). An increase of $\sim 0.25\text{‰}$ for the plateau phase of the
565 OAE interval, from 0.5 to 0.75‰, would have required most of the Zn output to have
566 been into anoxic organic-rich sediments. This interpretation is generally consistent with
567 evidence from other proxies. Mn-oxide burial is estimated to have decreased by 40 to
568 80% associated with a positive thallium-isotope shift during the OAE 2 interval
569 (Ostrander et al., 2017), so a decrease in Zn burial in oxic sediments of similar
570 magnitude is likely. Organic-carbon burial rates during OAE 2 are estimated to be ~ 1.7
571 to 3.1 times higher than modern ocean burial rates based on TOC and $\delta^{13}\text{C}$ patterns
572 (Owens et al., 2018).

573

574 The current uncertainties in the quantitative interpretation of the global Zn-isotope mass
575 balance changes may be improved by: (i) The analysis of OAE 2 sediments from other
576 sites, to constrain $\delta^{66}\text{Zn}_{\text{seawater}}$ more accurately; (ii) Improved understanding of the
577 processes leading to isotopic differences between seawater and various sediment types
578 in the modern ocean, particularly for organic-rich continental- margin sediments; and (iii)
579 Better constraints on possible past variations in $\delta^{66}\text{Zn}_{\text{input}}$, through assessment of the
580 flux and isotopic composition of Zn inputs from hydrothermal systems, LIPs, and
581 sedimentary sources.

582

583 *4.6 Comparing $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$*

584 Despite uncertainties on the absolute values of the Cd-isotope composition of the
585 Cenomanian–Turonian ocean, the relative changes are clear and generally show a
586 remarkably similar stratigraphic pattern to $\delta^{66}\text{Zn}$. A strong correlation in a cross-plot of

587 Cd and Zn concentrations implies that local controls on export and burial of these
588 elements were also generally similar. However, $\delta^{114}\text{Cd}$ versus $\delta^{66}\text{Zn}$ reveals
589 considerable scatter (Figure 9). Most notably, $\delta^{114}\text{Cd}$ values comprise a much smaller
590 range and values for the Plenus Cold Event interval are similar to background values for
591 the OAE 2 interval, while $\delta^{66}\text{Zn}$ values show considerably lower values. This contrast
592 may reflect the lack of a Cd output flux heavier than seawater compositions, in contrast
593 to Zn where oxic outputs provide a substantial sink of isotopically heavy Zn (e.g. Little et
594 al., 2014). Additionally, the disparity in $\delta^{114}\text{Cd}$ versus $\delta^{66}\text{Zn}$ values may reflect
595 differences in the isotopic composition of ocean inputs. Zn may be more easily
596 remobilized from continental-margin sediments or have a larger, more isotopically
597 distinct hydrothermal/volcanic source signatures (Lemaitre et al., 2020), as also implied
598 by comparison of dissolved $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ patterns from the North Atlantic Ocean
599 (Conway and John, 2014; 2015). A substantial input of isotopically light Zn from
600 enhanced basalt-seawater interaction or the release from continental-margin sediments
601 associated with large-scale oxygenation during the Plenus Cold Event may explain
602 differences in $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ patterns.

603

604 **5. Conclusions**

605

606 - Stratigraphic patterns of $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ in the Tarfaya Basin S57 core
607 (Morocco) can largely be interpreted as a result of changing seawater values.
608 The location of the Tarfaya Basin in an upwelling zone on the margins of the
609 proto North-Atlantic Ocean suggests that the $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ values of
610 seawater supplied to the basin represent sub-surface conditions and may thus be
611 extrapolated to infer changes in the global mass balance of these elements.

- 612 - A combination of Cd and Zn concentrations relative to TOC, Mo enrichments,
613 and $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ values of the sediments suggests ocean-wide drawdown of
614 Cd and Zn resulting from extensive organic-rich sediment burial during the main
615 phase of the OAE. This drawdown is expressed as isotopic shifts of $\sim +0.2\text{--}0.3$
616 ‰ in the $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ composition of sub-surface waters, relative to
617 background conditions.
- 618 - Pelagic carbonate (English Chalk, Eastbourne) and organic-rich sedimentary
619 archives (Tarfaya) from different oceanic regimes record similar stratigraphic
620 patterns in $\delta^{66}\text{Zn}$ during the Cenomanian–Turonian interval, particularly during
621 the Plenus Cold Event. The similarities imply that common changes in the $\delta^{66}\text{Zn}$
622 stratigraphy derive from the oceanic dissolved $\delta^{66}\text{Zn}$, and that these archives
623 record global palaeo-environmental information.
- 624 - Perturbations to the global Zn cycle during the Plenus Cold Event are suggested
625 to reflect widespread ocean re-oxygenation, thereby lowering the fraction of
626 isotopically light Zn buried in organic-rich sediments and possibly re-mobilizing
627 previously buried isotopically light material by the oxygenation of organic-rich
628 sediments. The increased input of isotopically light Zn from enhanced basalt-
629 seawater interaction during this interval may have also contributed to relatively
630 low $\delta^{66}\text{Zn}$ values.
- 631

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633

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638

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1007

1008 **Figure captions**

1009

1010 Figure 1. Palaeogeographical reconstruction at 90 Ma with approximate study locations,
1011 modified from Jarvis et al. (2011).

1012

1013 Figure 2. Cenomanian–Turonian $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ stratigraphy of the S57 core from the
1014 Tarfaya Basin compared with a) $\delta^{13}\text{C}$ data from Tsikos et al., 2004, (b) TOC data from
1015 Kolonic et al., 2005, and (c) $\delta^{98}\text{Mo}$ and Mo_{EF} data from Dickson et al., 2016. The
1016 chemostratigraphic divisions are as follows: (Division 1) In white are samples from
1017 stratigraphically below the onset level of the carbon-isotope excursion that demarcates
1018 OAE 2, as well as those from above the termination of the so-called plateau phase that
1019 is characterized by the highest carbon-isotope values (c.f. Tsikos et al., 2004). These
1020 samples represent background conditions for the Cenomanian–Turonian interval.
1021 (Division 2) In dark grey are samples from an interval approximately coeval with the
1022 Plenus Cold Event. The timing of this event, initially recognized by the occurrence of
1023 boreal fauna and relatively heavy bulk oxygen-isotope compositions in the English chalk,
1024 can be correlated to sections that lack characteristic fossils by carbon-isotope chemo-
1025 stratigraphy (Gale and Christensen, 1996; Jenkyns et al., 2017; Gale et al., 2019; Gangl

1026 et al., 2019). Here, this chemostratigraphic division is extended just beyond the slight dip
1027 in the carbon-isotope curve to cover the interval of relatively lower Cd, Mo, and Zn
1028 enrichment factors. (Division 3) In light grey are samples from the intervals that record
1029 maximum organic-carbon burial globally during the peak of OAE 2. This division covers
1030 a short interval stratigraphically just below sediments recording the Plenus Cold Event
1031 and sediments from the overlying plateau phase of the carbon-isotope excursion (c.f.
1032 Tsikos et al., 2004).

1033

1034 Figure 3. Cd/Mo and Co × Mn values for the Tarfaya Basin sediments compared to
1035 values for modern organic-rich sediments from various environments following Sweere
1036 et al. (2016). The shading represents the different chemostratigraphic divisions as
1037 highlighted in Figure 2.

1038

1039 Figure 4. $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ versus Mo_{EF} . Mo_{EF} is used as a proxy for local redox
1040 conditions (e.g. Scott and Lyons, 2012). Some outliers of very low $\delta^{114}\text{Cd}$ and low Mo_{EF}
1041 are attributed to a larger isotopic offset between sediments and seawater in more
1042 oxygenated conditions. Patterns for the remaining data imply that local redox conditions
1043 were not the dominant control on $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$.

1044

1045 Figure 5. Close-up of an interval from the S57 core comparing $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ values
1046 with high-resolution $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ and Mo isotope and concentration data. Samples marked
1047 in red highlight intervals that are taken to reflect a larger isotopic offset between
1048 sediments and seawater in more oxygenated conditions. See text for discussion. a)
1049 Tsikos et al., 2004, (b) Poulton et al., 2015 (c) Goldberg et al., 2016. The grey-shaded
1050 bands reflect anoxic non-sulfidic intervals (Poulton et al., 2015).

1051

1052 Figure 6. Cd and Zn concentrations *versus* Total Organic Carbon (TOC). The shading in
1053 (A) reflects the chemostratigraphic divisions as defined in Figure 2. The colours in (B)
1054 indicate different ranges of Mo_{EF} values, a proxy for local redox conditions (e.g. Scott
1055 and Lyons, 2012).

1056

1057 Figure 7. Comparison of data from organic-rich sediments (this study) and the organic-
1058 lean English Chalk at Eastbourne (Sweere et al., 2018) during the Cenomanian–
1059 Turonian boundary interval. The two sites are correlated using key points in the C-
1060 isotope stratigraphy (Tsikos et al., 2004), as indicated by the dashed lines. The grey-
1061 shaded bands highlight time-equivalent intervals of lower $\delta^{66}Zn$.

1062

1063 Figure 8. Simplified global isotopic mass-balance model based on steady-state
1064 conditions for different $\delta^{66}Zn_{inputs}$ values. f_{oxic} reflects Zn burial in Fe-Mn phases in oxic
1065 conditions (e.g. Little et al., 2014), f_{anoxic} refers to the Zn burial in organic-rich sediments
1066 on continental margins (Little et al., 2016), and $f_{euxinic}$ reflects the burial of Zn in strongly
1067 euxinic (restricted) basins, like the modern Black Sea (Vance et al., 2016; Isson et al.,
1068 2018). The horizontal black line represents modern ocean conditions, the red and blue
1069 lines +0.25 and -0.4‰ changes in $\delta^{66}Zn_{seawater}$, as constrained in section 4.4, for the OAE
1070 2 carbon-isotope plateau phase and PCE conditions, respectively. The isotopic offsets
1071 between different sedimentary archives and seawater used here are based on
1072 observations in the modern ocean as summarized in Vance et al. (2016) and are as
1073 follows: $\Delta^{66}Zn_{oxic-sw} = +0.4 \text{ ‰}$, $\Delta^{66}Zn_{anox-sw} = -0.5 \text{ ‰}$, $\Delta^{66}Zn_{eux-sw} = 0.0 \text{ ‰}$. *The estimate
1074 for the proportion of f_{eux} relative to f_{anox} comes from output flux estimates by Isson et al.
1075 (2018).

1076

1077 Figure 9. Comparison of Cd and Zn data generated in this study. The concentrations
1078 show very similar patterns, whereas the $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ are considerably different.
1079 This observation implies that $\delta^{114}\text{Cd}$ and $\delta^{66}\text{Zn}$ values provide complementary
1080 information on the proportion of oxic sinks and sedimentary and hydrothermal inputs.

Figure 1

[Click here to download Figure: Tarfaya ms⁵⁷- Fig 1.pdf](#)

Eastbourne

proto-North
Atlantic

S57

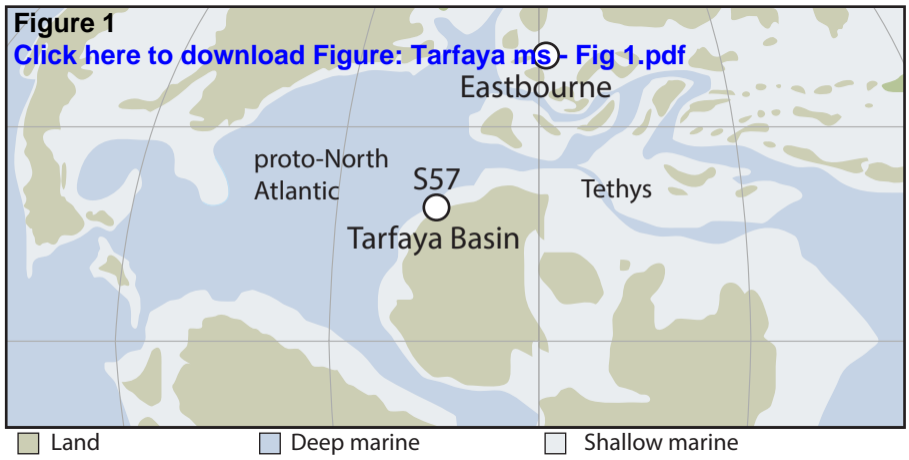
Tethys

Tarfaya Basin

Land

Deep marine

Shallow marine



Tarfaya S-57

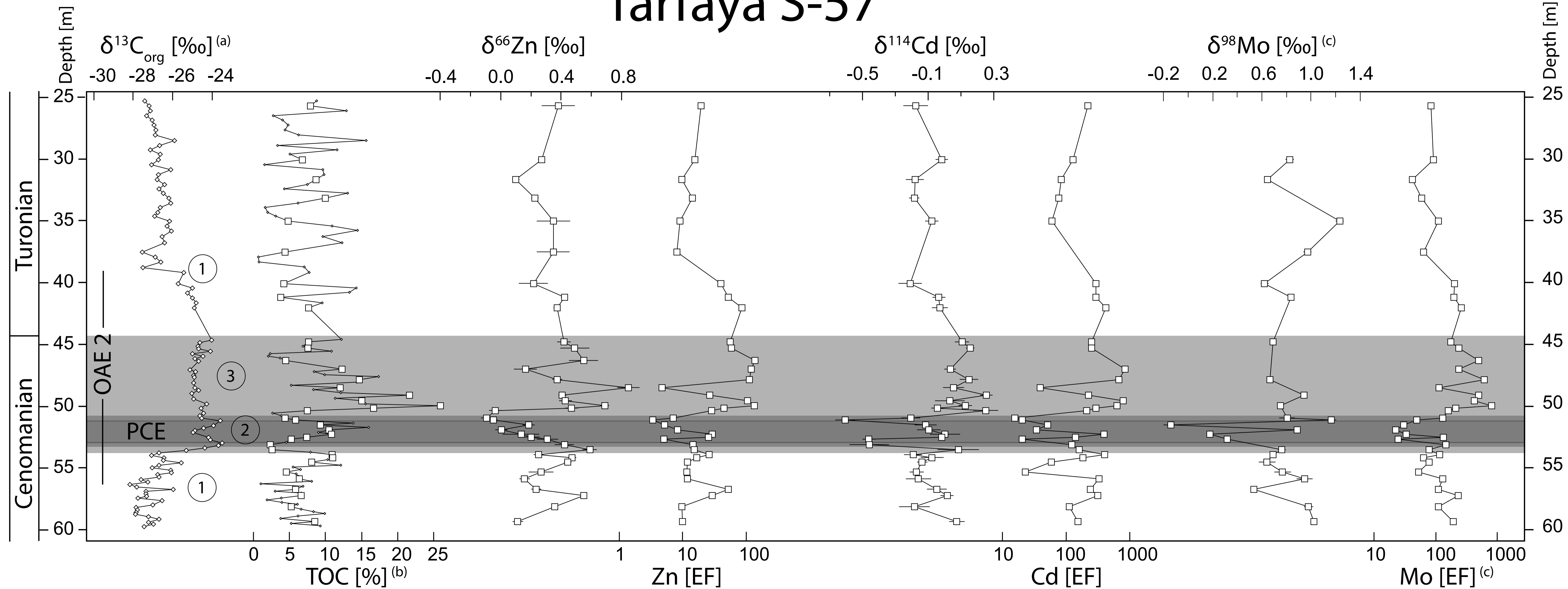


Figure 3

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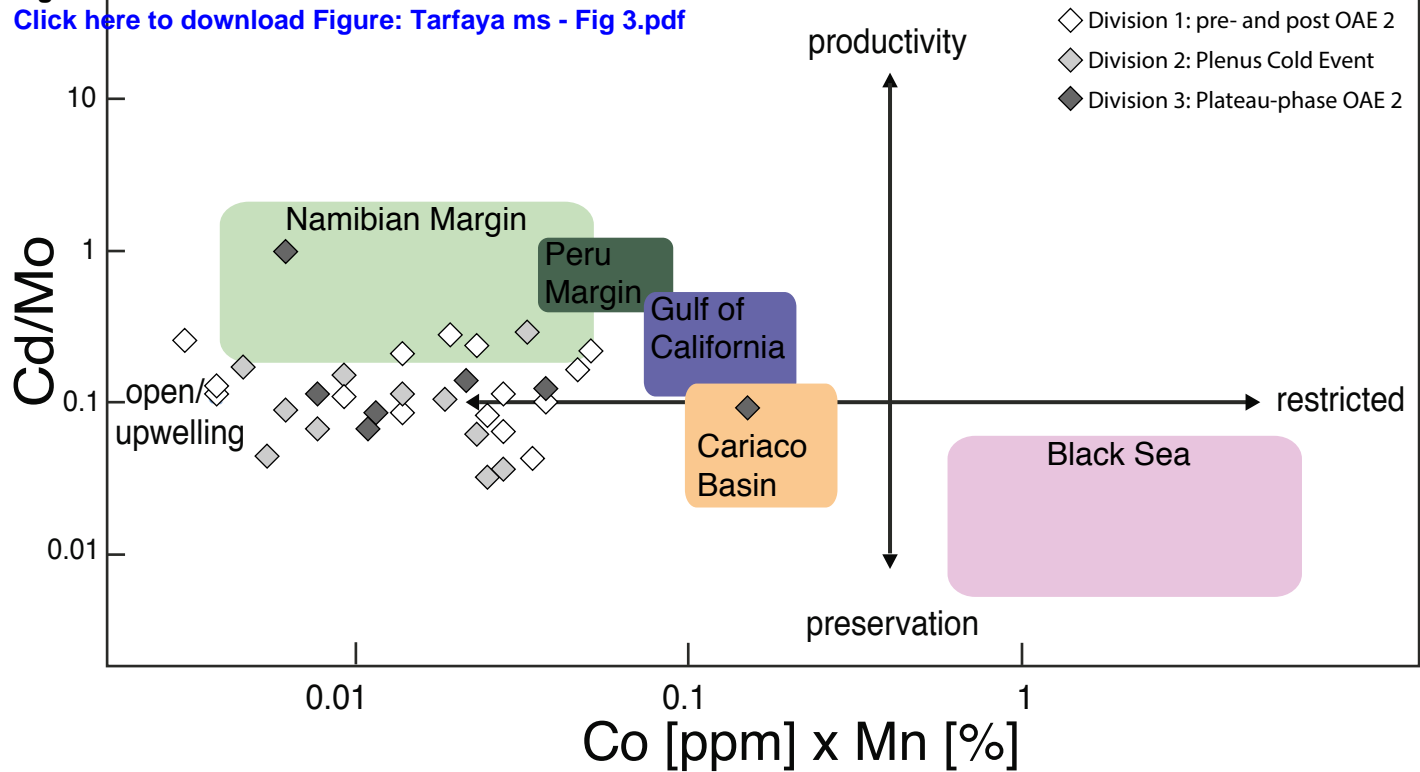


Figure 4
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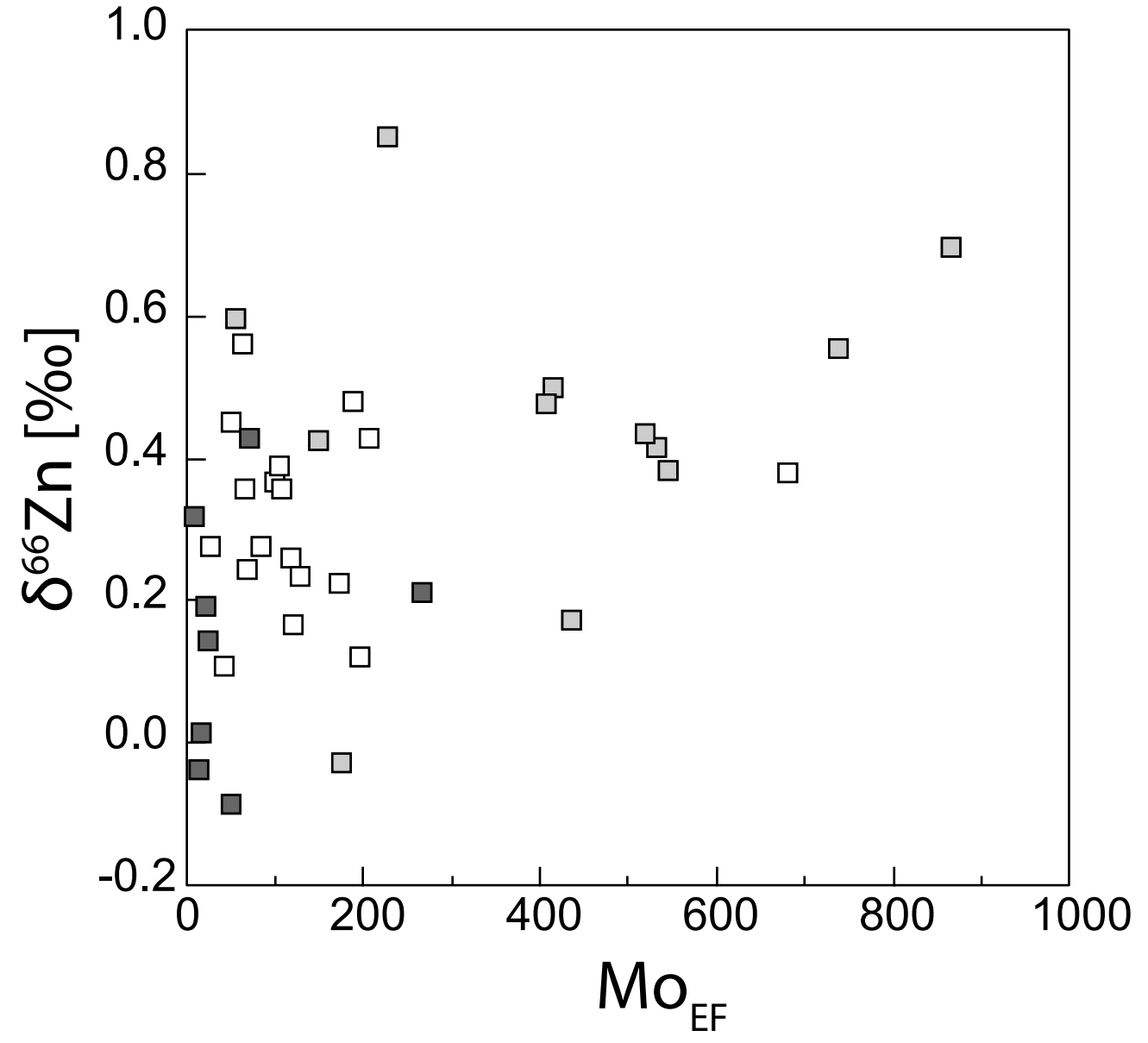
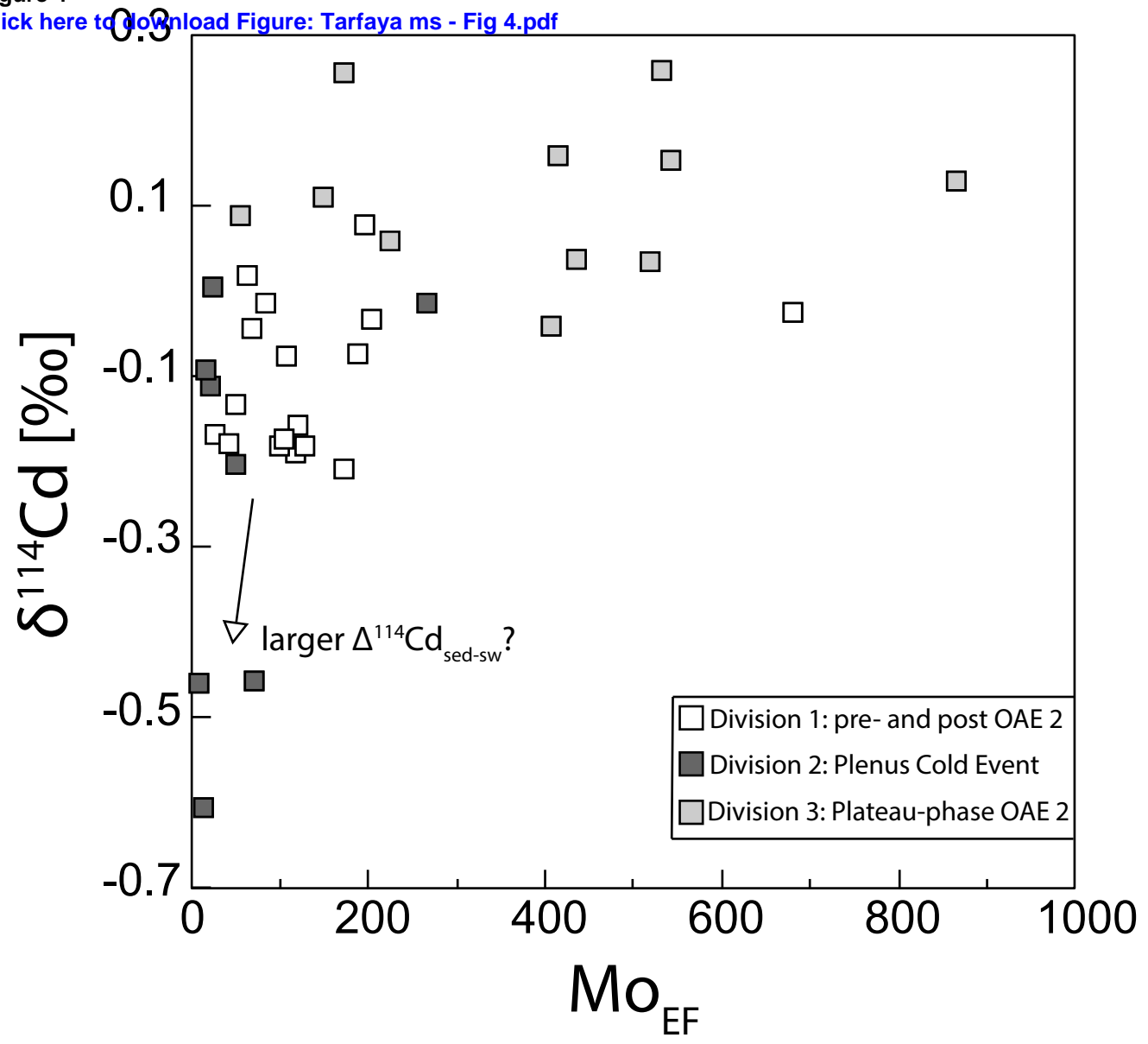
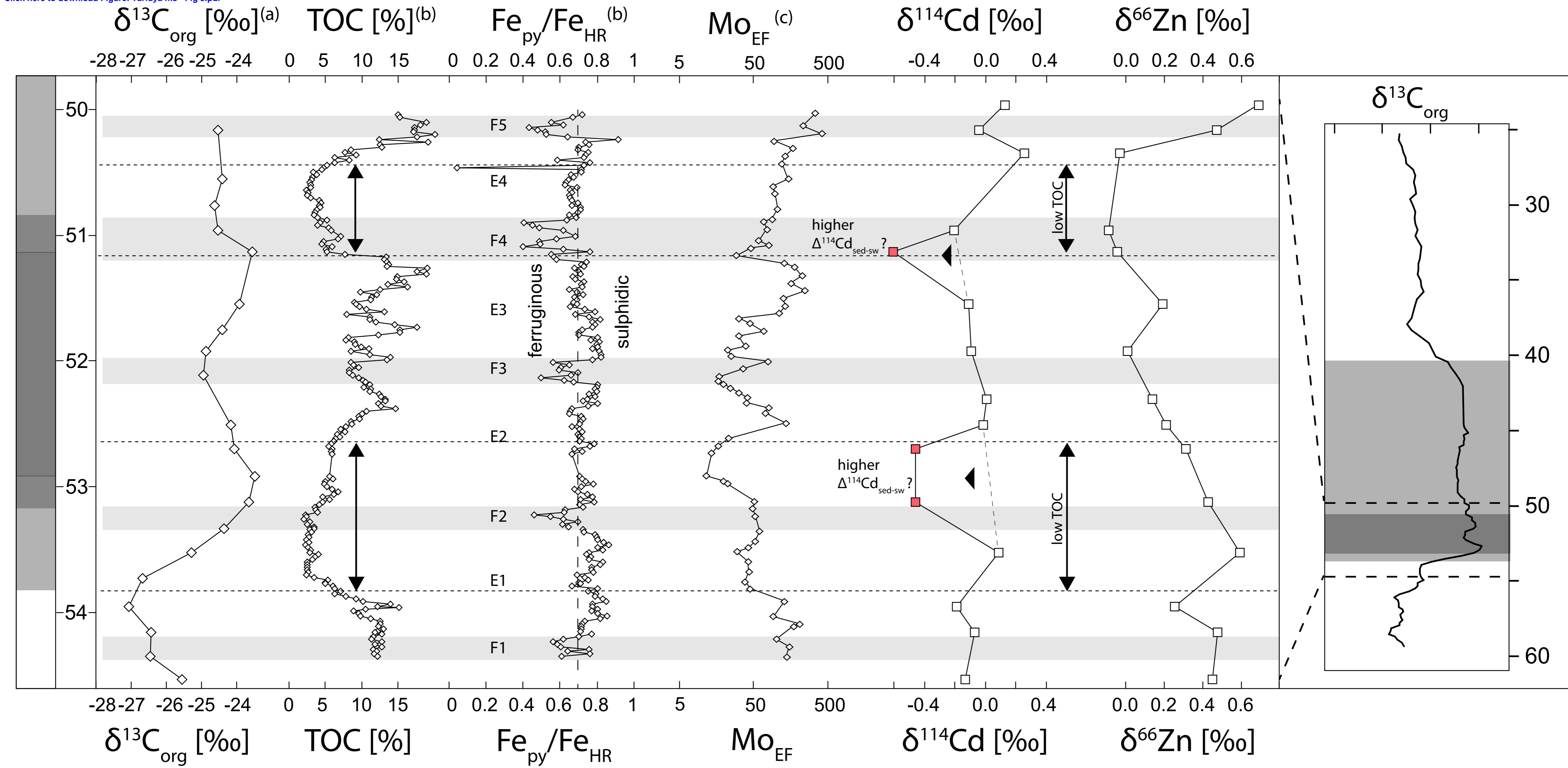
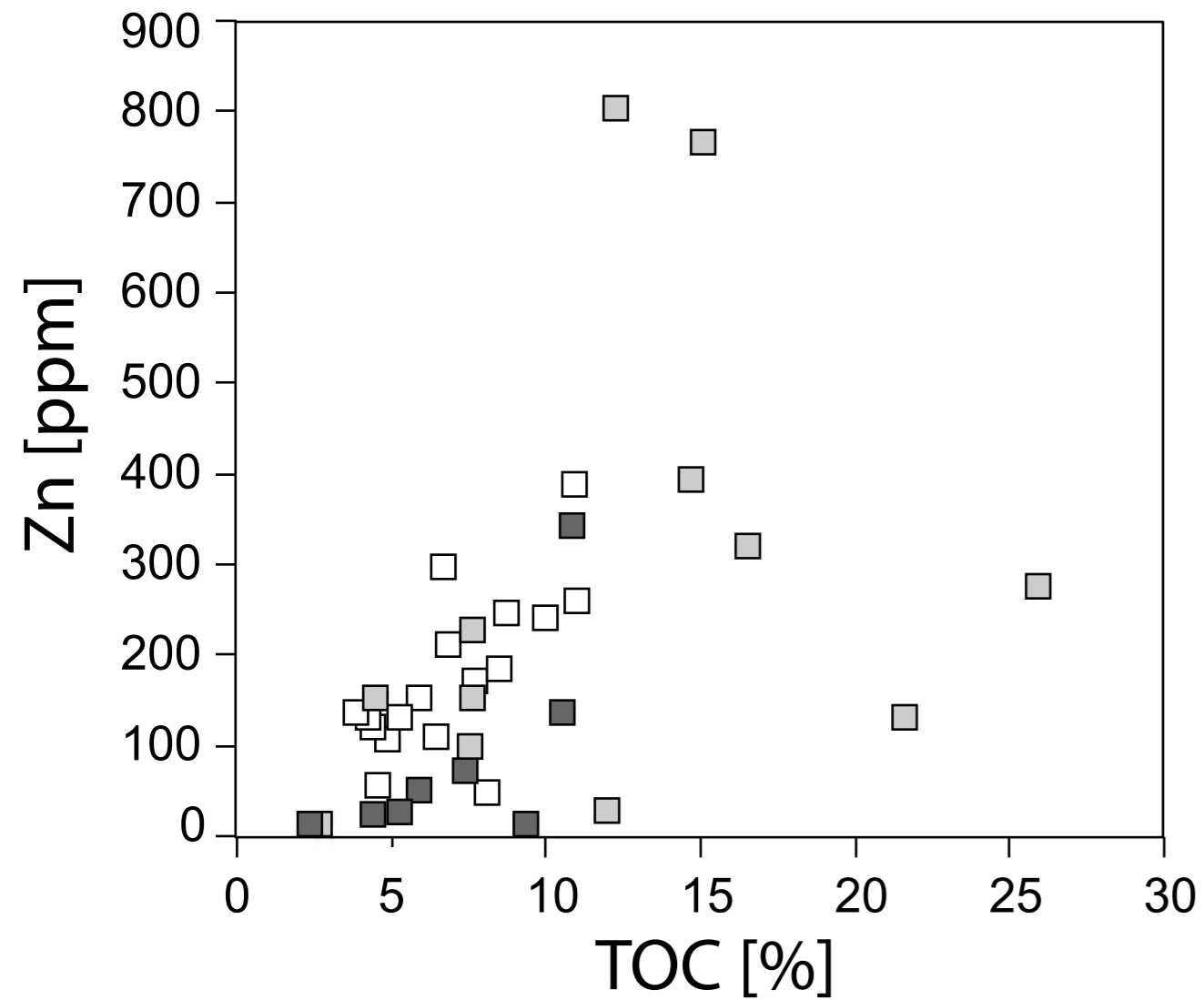


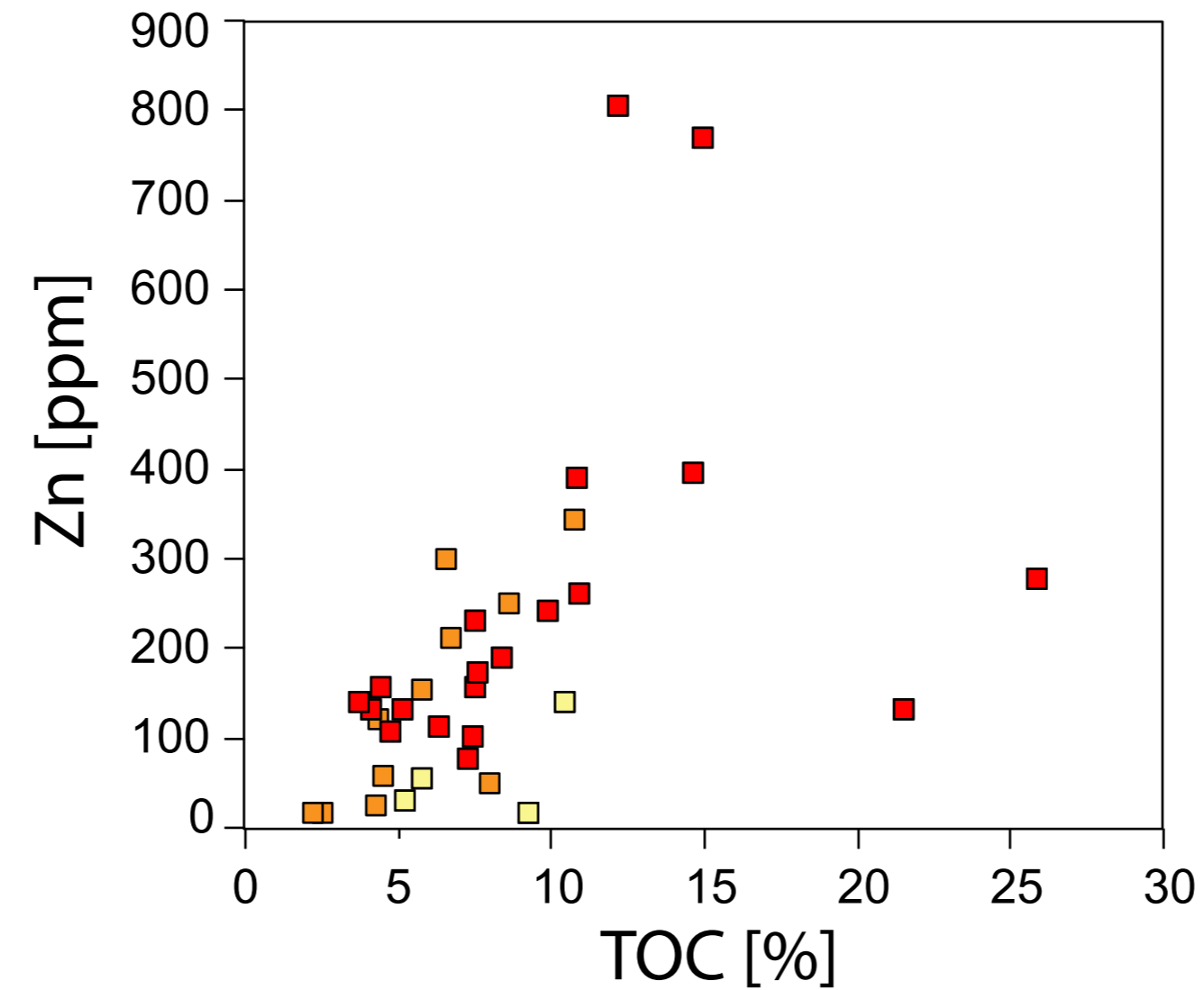
Figure 5
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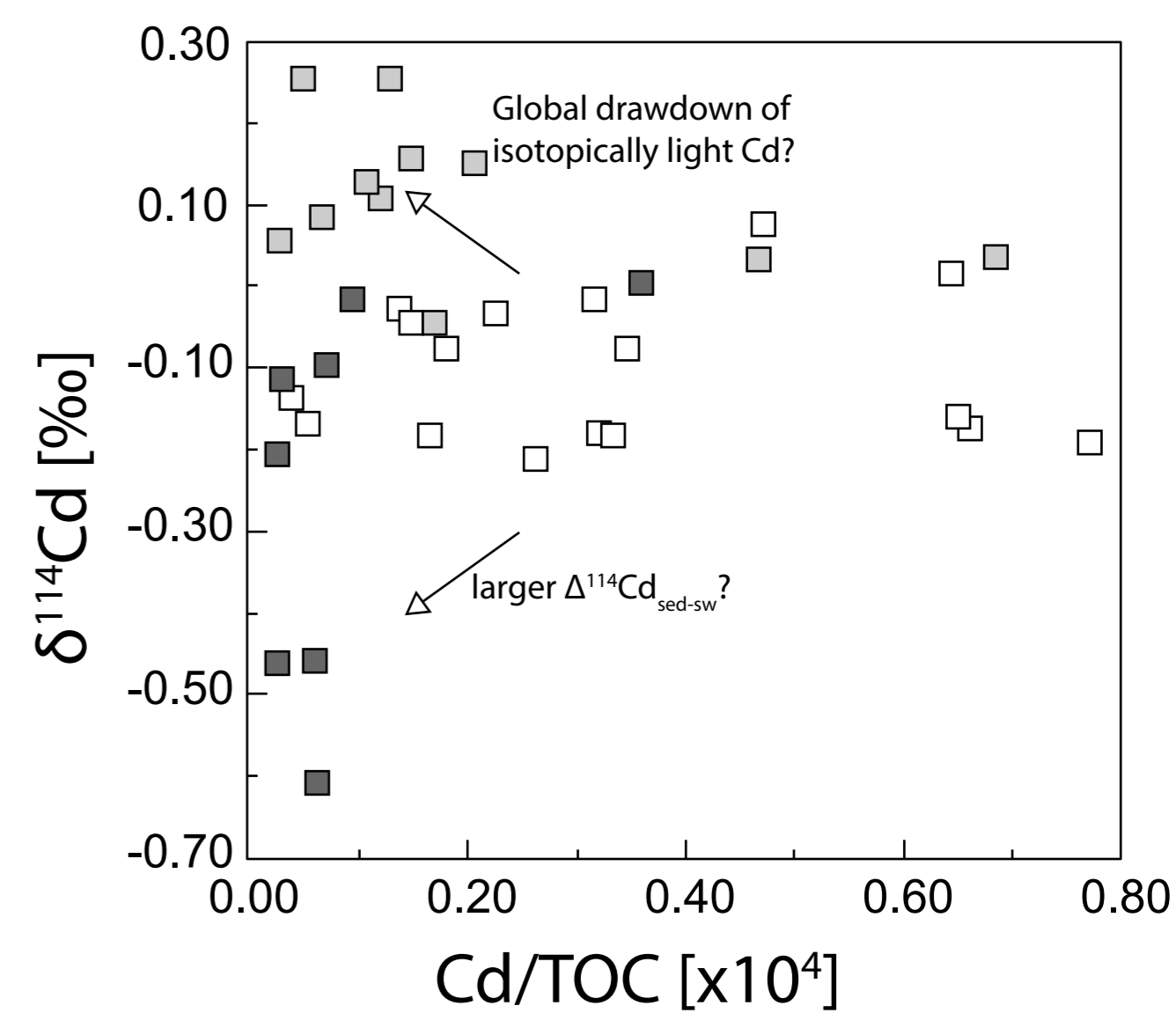
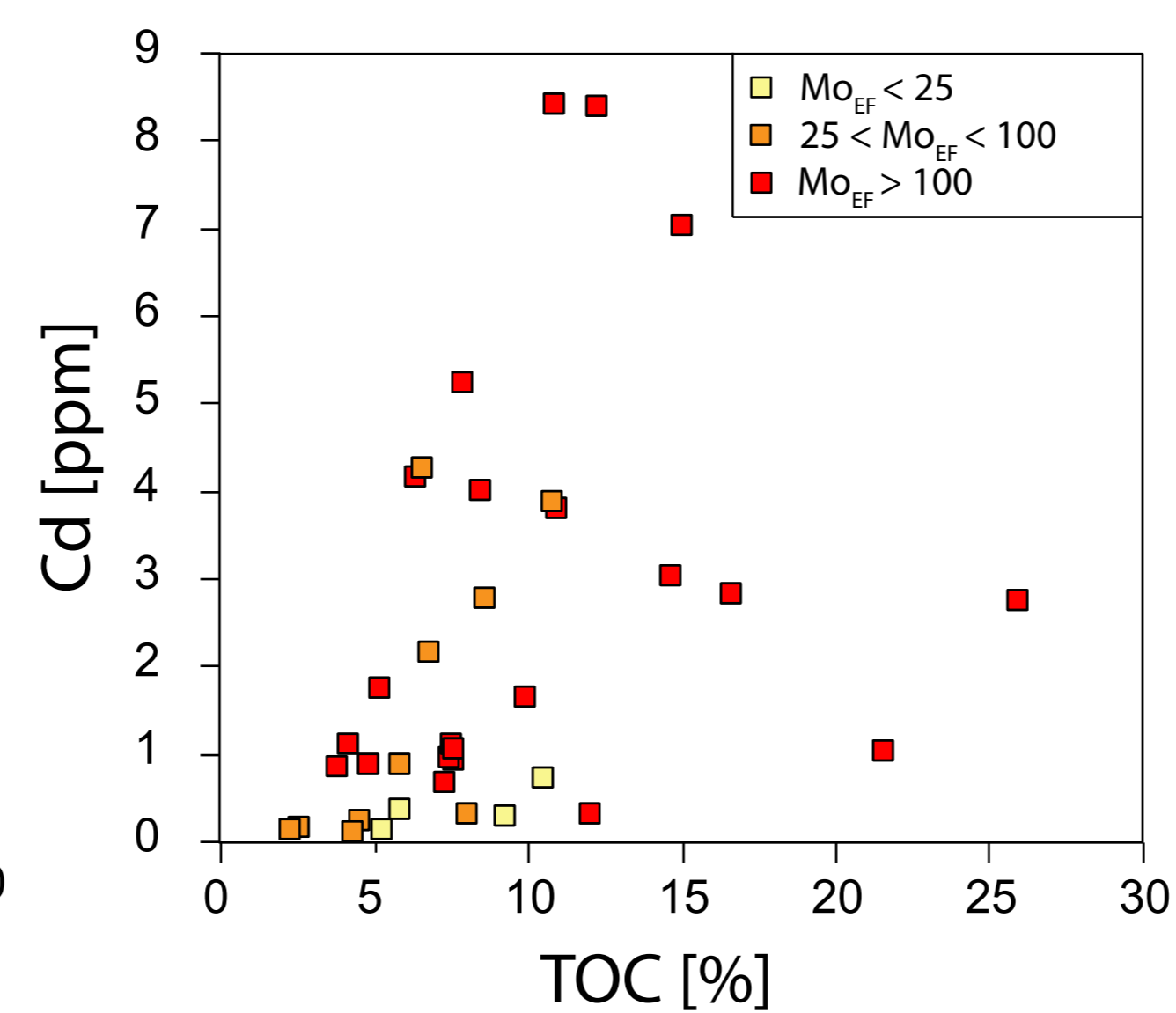
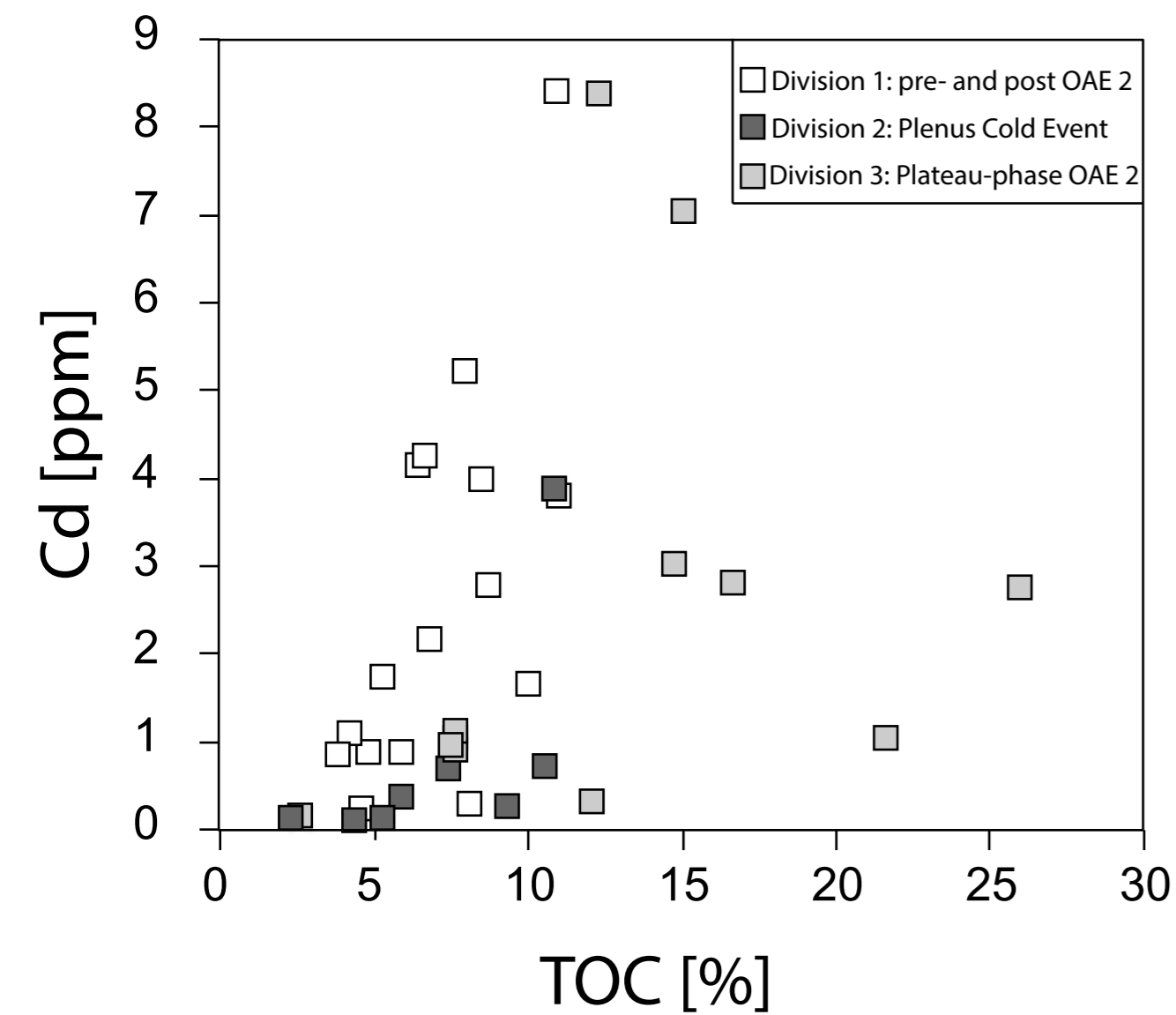
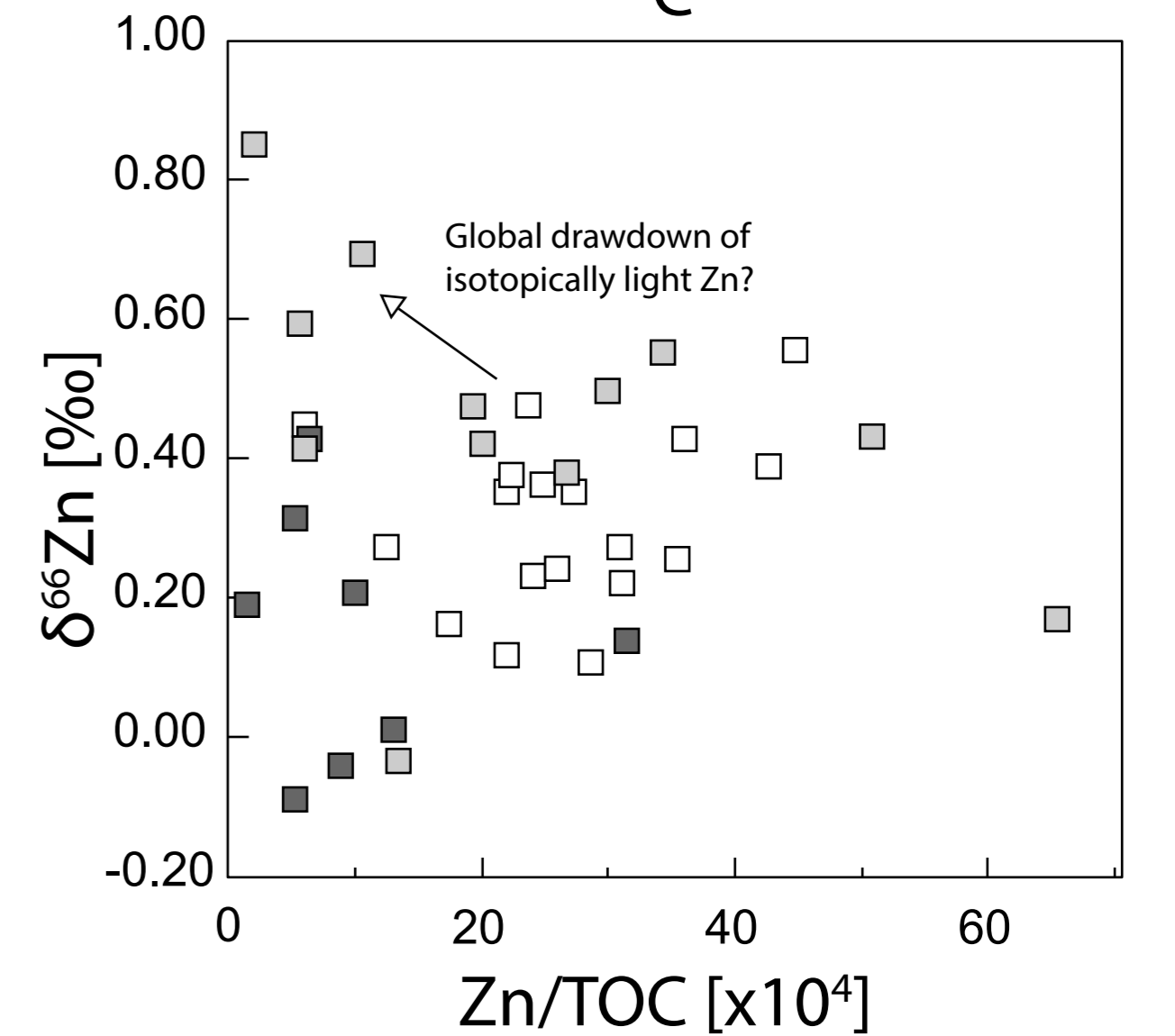
A



B



C



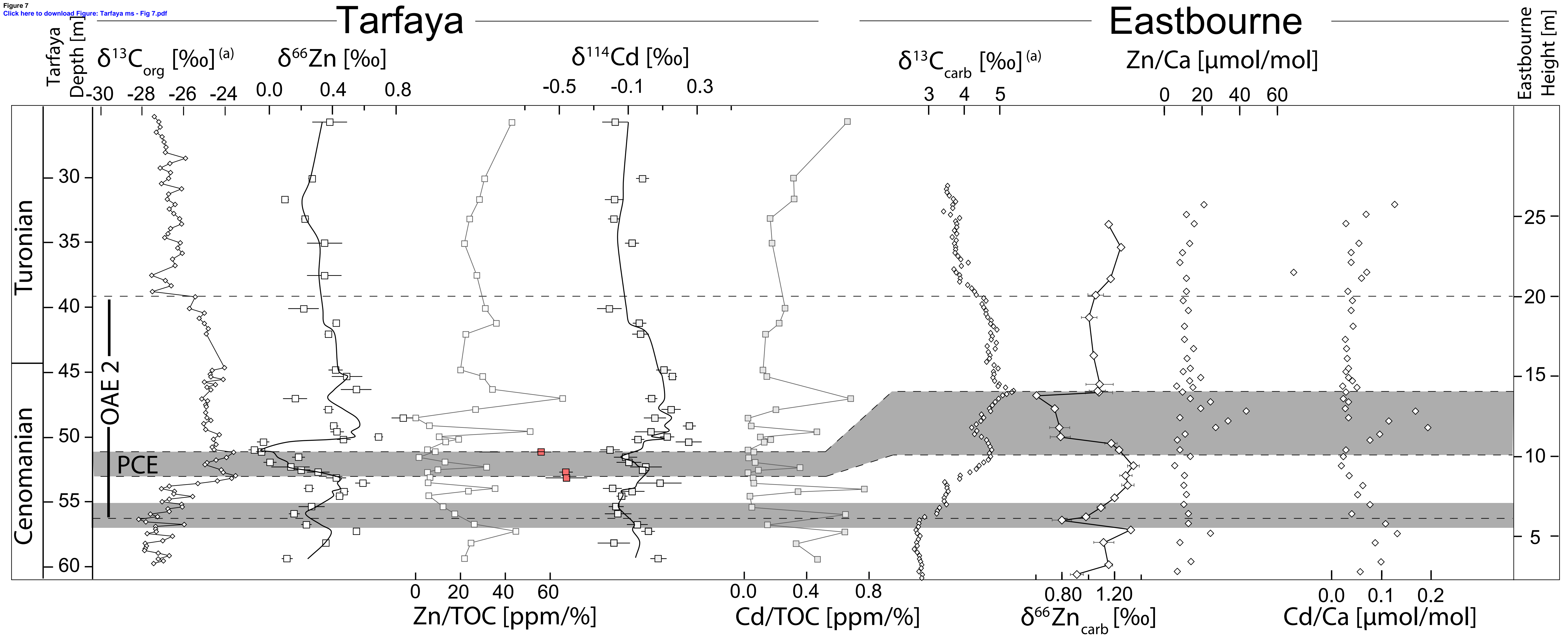


Figure 8
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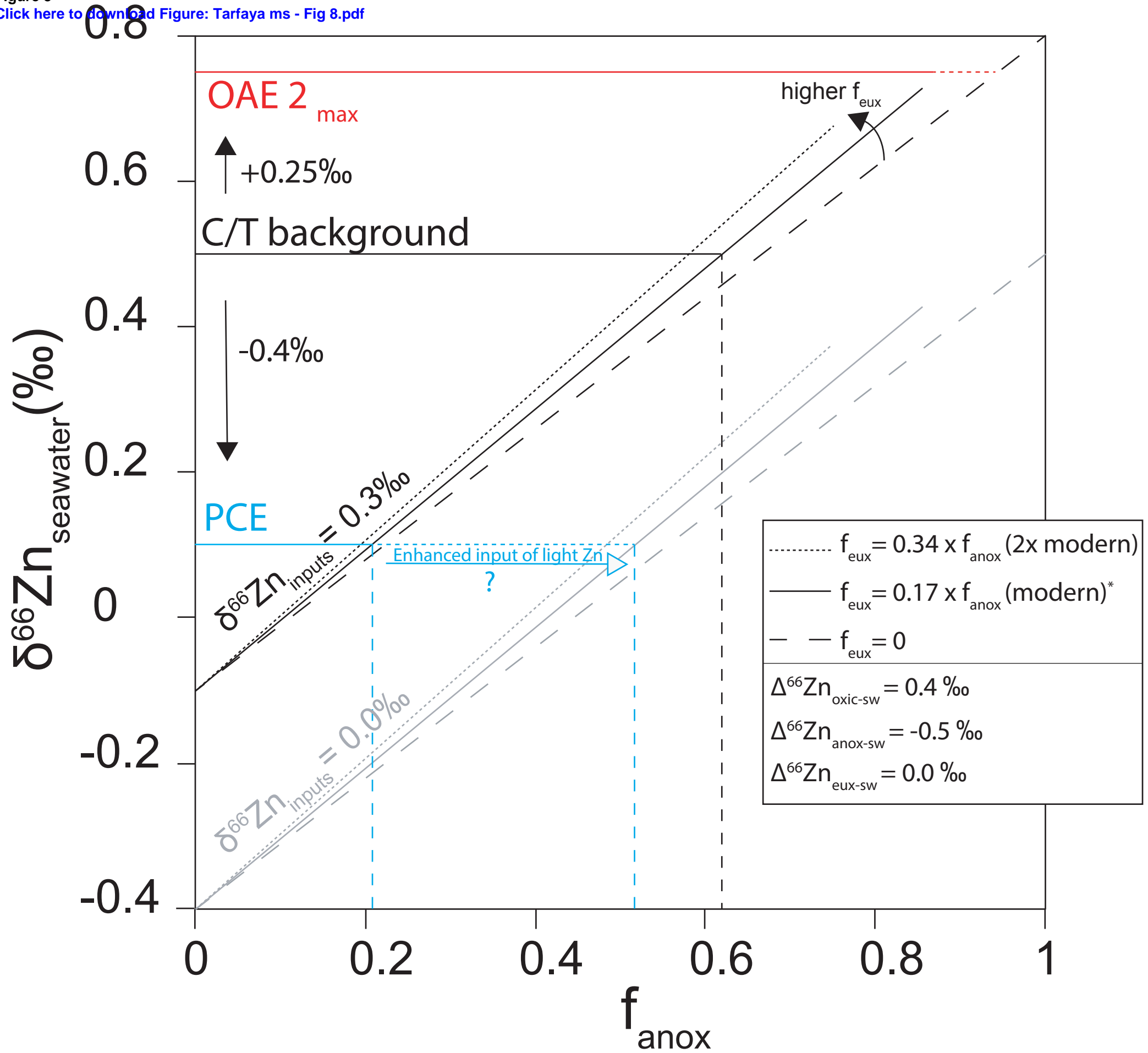


Figure 9

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