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Bioactive trace metals and their isotopes as paleoproductivity proxies: An assessment using GEOTRACES-era data

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Key Points

- This review assesses the potential of a number of bioactive trace elements and their isotopes to inform on past ocean productivity
- Distributions, drivers, and depositional archives are described for iron, zinc, copper, cadmium, molybdenum, barium, nickel, and silver
- Future priorities include quantification of ‘missing’ flux terms, constraining circulation influences, and identifying sedimentary archives

Keywords: marine chemistry; iron; zinc; copper; cadmium; molybdenum; barium; nickel; silver.

Abstract

1
2 The ocean's biological carbon pump redistributes climatically-significant quantities of carbon from the
3 atmosphere to the ocean interior and seafloor. How the biological pump operated in the past is therefore
4 important for understanding past atmospheric carbon dioxide concentrations and Earth's climate history.
5 Due to their intimate association with biological processes, several bioactive trace metals and their isotopes
6 are thought to be promising proxies for productivity, including: iron, zinc, copper, cadmium, molybdenum,
7 barium, nickel, and silver. Here we review the oceanic distributions, driving processes, and depositional
8 archives for these eight elements and their isotopes based on GEOTRACES-era datasets. We offer an
9 assessment of the overall maturity of each isotope system to serve as a proxy for diagnosing aspects of past
10 ocean export productivity, and identify priorities for future research. Despite many of the elements reviewed
11 here sharing a common biological driving processes, we show that key aspects of the biogeochemical cycle
12 of each element are often unique. Rather than being a source of confusion, it is our hope that combining the
13 unique perspectives afforded by each bioactive trace element will enable painting a more complete picture
14 of marine paleoproductivity, biogeochemical cycles, and Earth's climate history.

15 1. Introduction

16 The ocean plays host to three carbon ‘pumps’ that redistribute climatically-significant quantities of carbon
 17 dioxide (CO₂) from the atmosphere to the ocean interior and seafloor (Volk & Hoffert, 1985). These ocean
 18 carbon pumps—biological, carbonate, and solubility— influence Earth’s climate over timescales ranging
 19 from decades to millions of years (e.g., Volk & Hoffert, 1985; Sigman et al., 2010; Khatiwala et al., 2019).
 20 The biological pump is of particular interest as it connects the cycles of C to those of O₂, (micro)nutrients,
 21 and marine biology, and today accounts for as much as 70 % of the ‘contribution ’ of all three carbon pumps
 22 (Sarmiento & Gruber, 2006). The biological pump redistributes atmospheric carbon in two steps. First,
 23 phytoplankton, photoautotrophic microbes, use sunlight to transform ambient DIC (dissolved inorganic
 24 carbon) into POC (particulate organic carbon), represented here by CO₂ and glucose, respectively, by the
 25 simplified reaction:



27 The second step requires that some fraction of the newly-formed POC sinks into the ocean interior through
 28 a combination of biological and physical aggregation processes (e.g., Alldredge & Silver 1988). The
 29 resulting surface ocean DIC deficit promotes the invasion of atmospheric CO₂ into seawater to maintain
 30 air–sea CO₂ equilibrium, driving an overall reduction in atmospheric *p*CO₂. (This definition of the
 31 biological pump neglects dissolved organic carbon export, which is comparatively understudied, though
 32 may account for as much as one-third of C export; e.g., Carlson et al., 2010; Giering et al., 2014.)
 33 Importantly, Reaction [1] requires sunlight and can only occur in the euphotic layer of the ocean. In contrast,
 34 aerobic heterotrophic respiration can occur wherever POC and O₂ are present:



36 (There are a number of O₂-independent respiration pathways that are reviewed in detail elsewhere; e.g.,
 37 Froelich et al., 1979.)

38

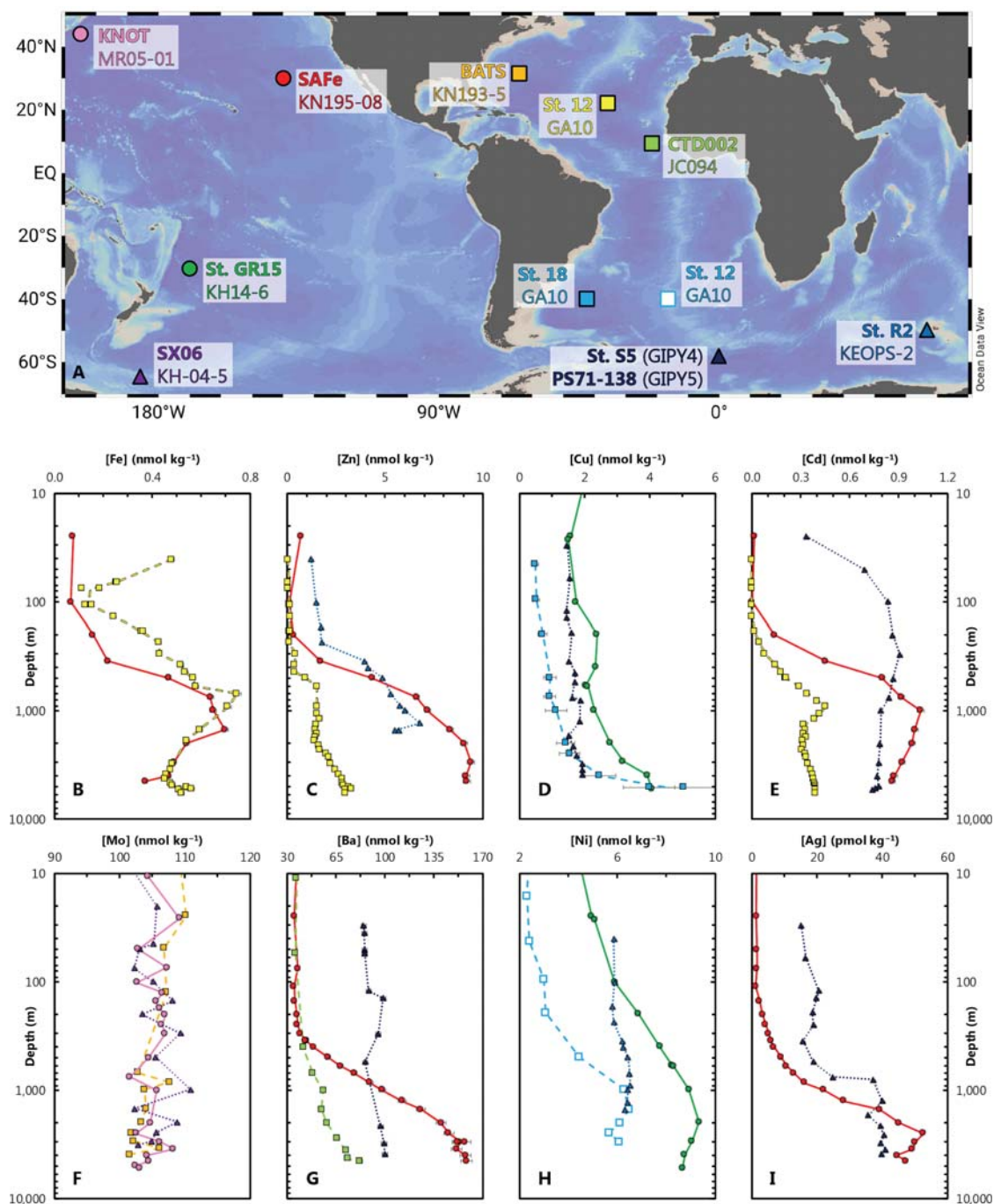
39 While the representation of all POC as glucose (CH₂O) is instructive for illustrating an important biotic
 40 transformation in the ocean, it is also simplistic; microbial biomass consists of dozens of bioactive elements
 41 that serve many essential functions (e.g., da Silva & Williams, 1991). The elemental stoichiometry of POC
 42 can thus be expanded to include a number of major and micronutrient elements, as illustrated by the
 43 extended Redfield ratio reported by Ho et al. (2003):



45 With this extended stoichiometry in mind, it is clear that Reactions [1] and [2]—the production and
46 regeneration of organic matter, respectively—will not only generate gradients in the dissolved
47 concentration of DIC and O₂, but also for many other bioactive elements associated with POC cycling.
48 These gradients will be steepest for those elements possessing shorter residence times and where biological
49 uptake and regeneration are the most important processes driving their vertical distributions. Likewise, such
50 gradients may be almost absent for elements that possess long residence times or are primarily cycled by
51 processes disconnected from productivity.

52

53 For those bioactive metals where biological processes are important, the implication of Reactions [1] and
54 [2] is that many of the metals listed in [3] may, in turn, be used as proxies of POC cycling and hence
55 paleoproductivity. A key motivation for using these elements as tracers of (past) POC cycling is that
56 bioactive metal distributions are often set over significant spatiotemporal scales. For example, temporal
57 changes in POC fluxes from a single sediment core would, at most, reflect local changes in export
58 productivity, though such reconstructions are oftentimes unreliable indicators of productivity owing to
59 significant preservation biases (e.g., Rühlemann et al., 1999). Biases aside, building a regional picture of
60 paleoproductivity in this manner would require sampling many regions of the seafloor (e.g., Cartapanis et
61 al., 2016) and conducting many more analyses. In contrast, the flux and residence time of nutrients in the
62 euphotic ocean can be diagnostic of the productivity of entire ecosystems (e.g., Dugdale & Goering, 1967).
63 Indeed, large-scale features of past ocean productivity are routinely reconstructed using the abundance and
64 stable isotopic compositions of macronutrient elements (C, N, and Si; see Farmer et al., *this issue*). It thus
65 follows that the abundance and isotopic compositions of several bioactive trace elements and their isotopes
66 (TEI's) cycled along with POC could also serve as valuable proxies for past export productivity. However,
67 in order to use systems of trace elements and their isotopes as proxies for productivity, it is necessary to
68 develop a comprehensive understanding of the marine behavior of these elements, including: mapping their
69 distribution in the ocean; elucidating the drivers of the distribution; characterizing sources, sinks, and
70 transformations associated with biological, physical and chemical (notably redox) reactions; and,
71 recognizing if (and how) a given element is incorporated and preserved in marine sediments.



72
 73 **Figure 1 | Overview of bioactive trace metal distributions discussed in this review. A** Map showing locations of
 74 the representative depth profiles shown in both the lower panels and discussed throughout this review (Sections. 3–
 75 10). The specific station (**bold**) and cruise identifier are given for each location; circles, squares, and triangles denote
 76 stations in the Pacific, Atlantic, and Southern Oceans, respectively. The lack of exemplar stations from the Indian Ocean
 77 reflects the current paucity of GEOTRACES-compliant campaigns in this basin. Two stations sampled from the Atlantic
 78 Sector of the Southern Ocean are designated by a single symbol: St. S5 (GIPY4), situated at 57.55 S, 0.04 W, and
 79 PS71-138 (GIPY5) at 61.00 S on the Zero Meridian. **B–I** Depth profiles of bioactive trace metal concentrations for Fe
 80 (B), Zn (C), Cu (D), Cd (E), Mo (F), Ba (G), Ni (H), and Ag (I). Profiles are shown in semi-log space to illustrate variations
 81 in the epi- and mesopelagic realm. Originators are cited in the Data Sources section. Map created using Ocean Data
 82 View (Schlitzer, R., <https://odv.awi.de>, 2018).

84 The wealth of new TEI data from the GEOTRACES program (Fig. 1) now permits an assessment of whether
85 certain bioactive metals are promising proxies for past ocean productivity. This contribution represents such
86 an assessment. Our study synthesizes what is known about the processes governing the cycling of several
87 bioactive TEIs in seawater, explores the level of development and readiness of each TEI system to inform
88 on aspects of past ocean productivity, and identifies areas where further research is most needed to improve
89 our understanding of the geochemistry of TEIs in the past and present ocean. We base our assessment on
90 publicly-available results from the international GEOTRACES programme (e.g., Mawji et al. 2015;
91 Schlitzer et al., 2018). Our study is not intended to be a thorough review of all available techniques used to
92 reconstruct paleoproductivity. Instead, we focus on bioactive TEI systems that are either recognized as
93 micronutrients (such as those in Eq. 3) or exhibit nutrient-like dissolved profiles in seawater, regardless of
94 their nutritional status to phytoplankton (e.g., Ba, Ag). This will not be the last word on the topic; our
95 understanding of many of these TEIs has rapidly evolved in recent years, and will continue to evolve as
96 new data are generated.

97

98 This contribution is structured such that each bioactive TEI system is reviewed similarly and systematically.
99 The order in which TEI's are assessed follows the extended Redfield ratio—iron (Fe; Sec. 3.), zinc (Zn;
100 Sec. 4), copper (Cu; Sec. 5), cadmium (Cd; Sec. 6), and molybdenum (Mo; Sec. 7)—before describing the
101 nonessential elements barium (Ba; Sec. 8), nickel (Ni; Sec. 9.), and silver (Ag, Sec. 10) in order of
102 decreasing dissolved concentration in seawater. The assessment of each TEI system is organized around
103 four questions:

- 104 1. What is the modern marine distribution of this TEI system?
- 105 2. Which biological, chemical, and physical processes are most important for maintaining this
106 distribution?
- 107 3. In what form is this TEI system incorporated into sediments?
- 108 4. Are there clear priorities for improving the utility of this system to track paleoproductivity?

109 This structure results in some repetition of the main distributions, drivers, and sedimentary archives
110 between individual TEI systems. This redundancy is deliberate: each section can be read independently
111 without reference to other TEIs. We close our review by assessing the 'maturity' of each system based on
112 a comparison to more established productivity proxies, offer suggestions for future studies, and discuss
113 prospects for paleoproductivity reconstructions using bioactive TEI isotope systems.

114 2. Definitions

115 2.1. Paleoproductivity

116 What is (paleo)productivity? This definition is significant since the biological productivity of an ecosystem
117 can be described by a number of nested C cycles, whereby only some sub-cycles contribute to the
118 sequestration of atmospheric CO₂ as POC in the ocean interior and the geological record. Moreover,
119 productivity estimates can diverge depending on the tracer (e.g., Bender et al., 1987) or reference depths
120 (e.g., Buesseler et al., 2020) used as the basis of any calculation. Individual proxies for POC cycling may
121 be sensitive to only certain components of the C cycle and could thus yield conflicting insights into
122 paleoproductivity. For consistency with the macronutrient literature, we use the definitions described by
123 Sigman & Hain (2012): GPP, NPP, and NEP, which correspond to gross primary production, net primary
124 production, and net ecosystem (or ‘export’) production, respectively. Gross PP refers to total autotrophic
125 production of POC (or O₂; i.e., Eq. [1]). Net PP is defined as GPP minus autotrophic respiration—the
126 metabolic O₂ requirements of primary producers—and is effectively the rate at which phytoplankton
127 produce new biomass. Lastly, NEP refers to GPP minus all autotrophic *and* heterotrophic respiration in an
128 ecosystem (i.e., NPP minus heterotrophic respiration). If considering only the sunlit surface ocean, NEP is
129 equivalent to export production; the flux of POC from the surface ocean must, over sufficiently long
130 timescales, balance the vertical supply of dissolved nutrients. Likewise, integrated over the entire euphotic
131 ocean, NEP represents the upper limit of the CO₂ sequestering capacity of the biological pump: the amount
132 of POC buried in marine sediments must be less than, or equivalent to, annual NEP (minus any contributions
133 from terrestrial OC). Accordingly, NEP is perhaps the most relevant term to understanding how the
134 biological pump draws down and stores atmospheric CO₂. Indeed, variations in NEP are implicated as a
135 key driver of glacial–interglacial variations in *p*CO₂ and hence climate (e.g., Broecker, 1982; Boyle, 1988a;
136 Berger et al., 1989; Paytan, 2009). Thus, when describing and assessing the utility of each TEI system to
137 inform on past productivity, we are specifically concerned with whether and how that system is related to
138 NEP.

139

140 2.2. Key processes

141 In addition to only being sensitive to certain POC sub-cycles, the TEI systems reviewed here exhibit a
142 number of instances where their cycling may be decoupled from those of POC. Broadly, these processes
143 can be categorized as affecting the sources, internal cycling, or sinks of TEIs, but not always the
144 macronutrients or C. These additional processes may lead to differences between, or even a complete

145 decoupling of (paleo)productivity estimates using TEI- and macronutrient-based productivity measures.
146 These three areas are introduced here and described in detail in the sections that follow.

147

148 First, many elements, including bioactive TEIs, can be decoupled from DIC cycling through ‘external’
149 sources that mask any POC-related drawdown. Though rarely significant for DIC, these sources—rivers,
150 dust, desorption from particles, sediments, and hydrothermalism—may be significant terms in local and
151 regional TEI budgets if the magnitude is comparable to the dissolved supply from ocean circulation.
152 Examples include dust-derived Cu to surface planktonic communities (e.g., Paytan et al., 2009) and
153 hydrothermal-derived Fe to the deep ocean (e.g., Resing et al., 2015). Consideration of these external
154 sources is particularly important when close to such point sources and for elements with residence times
155 that are less than or similar to the mixing time of the ocean (~1 kyr).

156

157 Second, the internal cycle of TEIs can be complex; TEI distributions can be decoupled from those of the
158 macronutrients through myriad interactions with particles, be they biological (uptake and remineralization),
159 physical (adsorption, desorption), or chemical (e.g., redox transformation leading to precipitation or
160 dissolution; e.g., Boyd et al., 2017).

161 Biological uptake itself may decouple TEIs from macronutrients since organisms appear to have wider
162 tolerances for the intracellular proportions of certain trace elements compared to those of C, N, and P. The
163 physiological mechanisms enabling this plasticity, and the feedback interactions that drive it, are beyond
164 the scope of this review, and are discussed in detail elsewhere (e.g., Sunda, 2012; Morel et al., 2020). From
165 a proxy perspective, this flexibility may cause uncertainty in paleoproductivity estimates; the more variable
166 the C:TEI stoichiometry of organisms within an ecosystem, the more uncertain the paleoproductivity
167 estimate derived from that trace element. (The corollary being that the more rigid the stoichiometry, the
168 more robust the paleoproductivity estimate.) An extreme example concerns nonessential elements (e.g.,
169 Ba), or metals that are only essential for certain groups of organisms within an ecosystem (e.g., Ni for
170 methanotrophs). Productivity estimates derived from the export of these nonessential elements are
171 potentially susceptible to decoupling from productivity cycles as their export is not intrinsically tied to the
172 overall functioning of an ecosystem.

173 Remineralization—the regeneration of POC to inorganic dissolved nutrients—can similarly decouple the
174 internal cycles of TEIs and macronutrients. In the case of a scarce nutrient, such as Fe, individual organisms
175 (e.g., Saito et al., 2011) and even entire ecosystems (e.g., Rafter et al., 2017) may have evolved mechanisms
176 to retain scarce resources. Likewise, macro- and micronutrient TEIs may be regenerated by heterotrophic

177 organisms at different rates (e.g., Twining et al., 2014; Ohnemus et al., 2019). Thus, the number of
178 productivity cycles that must occur before a trace element is exported out of the euphotic zone may differ
179 from that of C or other macronutrients.

180 The processes of adsorption and desorption can also fractionate TEI:macronutrient relationships. Originally
181 developed in the context of dissolved and particulate thorium isotopes (Bacon & Anderson, 1982),
182 reversible scavenging is now suggested to play a role in the vertical cycling of other metals, including Cu
183 (e.g., Little et al., 2013) and Fe (e.g., Abadie et al., 2017). Reversible scavenging is a continuous process
184 that occurs between particle surfaces and dissolved species. While this process can occur at any depth,
185 scavenging intensity is positively correlated with the quantity of particles, and so is most important in the
186 upper water column. Likewise, while dissolved TEIs may be scavenged by any class of particle (e.g., opal,
187 lithogenics), recent modeling efforts indicate that certain particle types may preferentially scavenge certain
188 elements (e.g., Lerner et al., 2018). Scavenging may also affect TEIs primarily cycled by organic matter;
189 secondary phases may scavenge metals during remineralization, which could affect TEI distributions in the
190 upper water column (e.g., Zn, John & Conway, 2014; Co, Hawco et al., 2018; Fe, Tagliabue et al., 2019).

191 Changes in the ambient redox environment, such as in an oxygen minimum zone (OMZ), may also enhance
192 dissolved–particulate transformations for certain TEIs. Whether OMZs act as a source or a sink depends on
193 the TEI; whereas some elements may be released during reductive dissolution of particulate Fe–Mn oxides,
194 others may exhibit enhanced scavenging onto particles in strongly reducing environments.

195

196 Third, many TEIs have significant output fluxes that are not associated with organic matter. The processes
197 mediating these burial fluxes are diverse, ranging from scavenging (e.g., Cu, Mo) to precipitation into
198 (organo)minerals (e.g., Ba; Défarge, 2011). Consequently, changes in the non POC-associated burial flux
199 term(s) may drive the ocean to a new TEI:C stoichiometry that could be difficult to recognize or interpret
200 in the sedimentary record.

201

202 While these three categories of processes may appear insurmountable obstacles to the reliable application
203 of TEIs to reconstruct paleoproductivity, there are reasons to be optimistic. Indeed, the fact that so many
204 confounding processes are now recognized highlights just how far our understanding of TEI geochemistry
205 has evolved in recent years. Moreover, many of these processes primarily concern the use of trace element
206 abundances to reconstruct past productivity. As we show in the following sections, the processes controlling
207 the abundance of an element may be distinct from that controlling its isotopic composition. These distinct
208 controls may enable isotopic analyses to reduce, or even eliminate, certain ambiguities in

209 paleoceanographic data, highlighting a potentially valuable role for TEI systems in the reconstruction of
 210 paleoproductivity.

211

212 **2.3. Isotope notation**

213 The bioactive TEI literature abounds with isotope notations (e.g., ϵ , δ), reference materials (e.g., JMC,
 214 NIST), and isotope ratio pairs (e.g., $^{57}\text{Fe}/^{54}\text{Fe}$ versus $^{56}\text{Fe}/^{54}\text{Fe}$; $^{137}\text{Ba}/^{134}\text{Ba}$ versus $^{138}\text{Ba}/^{134}\text{Ba}$). There are
 215 merits to each choice and it is not our intention to review these here. However, we believe that the sheer
 216 number of ways in which TEI data have been reported can be confusing to scientists in other disciplines
 217 and this confusion ultimately diminishes the reach and utility of TEI-based research. To avoid furthering
 218 this confusion, we have adopted a number of conventions that apply throughout this review, regardless of
 219 how literature data were originally reported. First, we use a single isotope notation throughout (' δ '; i.e., the
 220 delta notation). Second, we express all data relative to the most widely accepted standard for each isotope
 221 system. For many isotope systems, the most widely-accepted standard may have since been exhausted (e.g.,
 222 JMC Lyon for Zn). In those cases, there are usually cross-calibrated secondary materials that can be used
 223 to report new isotope data in terms of 'legacy' materials (e.g. AA-ETH for Zn, Archer et al., 2017). Third,
 224 we report TEI data using the same isotope ratio pairs as used in the GEOTRACES data products (e.g.,
 225 Mawji et al., 2015; Schlitzer et al., 2018). We note that isotope data are a unitless ratio quantity (Coplen,
 226 2011), though are commonly reported with 'units' of ‰ (i.e., parts per one-thousand):

$$227 \quad \delta^x\text{TE} = R_{\text{sample}} / R_{\text{standard}} - 1 \quad [4]$$

228 where $\delta^x\text{TE}$ represents $\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$, $\delta^{65}\text{Cu}$, $\delta^{114}\text{Cd}$, $\delta^{98}\text{Mo}$, $\delta^{138}\text{Ba}$, $\delta^{60}\text{Ni}$, or $\delta^{109}\text{Ag}$ and R represents
 229 $^{56}\text{Fe}/^{54}\text{Fe}$, $^{66}\text{Zn}/^{64}\text{Zn}$, $^{65}\text{Cu}/^{63}\text{Cu}$, $^{114}\text{Cd}/^{110}\text{Cd}$, $^{98}\text{Mo}/^{95}\text{Mo}$, $^{138}\text{Ba}/^{134}\text{Ba}$, $^{60}\text{Ni}/^{58}\text{Ni}$, or $^{109}\text{Ag}/^{107}\text{Ag}$ in either a
 230 sample or standard. For clarity, all isotopic data reviewed here have been calculated using notation in Eq.
 231 4, and renormalized to the following standards, regardless of how the data originators reported their results:
 232 IRMM-014 for Fe (e.g., Dauphas et al., 2017), JMC-Lyon for Zn (e.g., Moynier et al., 2017), NIST SRM
 233 976 for Cu (*ibid.*), NIST SRM 3108 for Cd (e.g., Abouchami et al., 2013), NIST SRM 3134 +0.25 ‰ for
 234 Mo (Nägler et al., 2014), NIST SRM 3104a for Ba (e.g., Horner et al., 2015a), NIST SRM 986 for Ni (e.g.,
 235 Elliott & Steele, 2017), and NIST SRM 978a for Ag (e.g., Woodland et al., 2005).

236

237 We summarize salient features of each TEI in Table 1. The review of each TEI system follows.

238

239

240
241

Table 1 | Summary of oceanic concentrations, isotopic compositions, and mean ocean residence times for bioactive TEIs discussed in this review. Superscripts denote references listed in the Data Sources section.

Element	Dissolved concentration range (nmol kg⁻¹)	Mean Upper Continental Crust composition (‰)	Mean deep ocean isotopic composition (‰)	Range of deep ocean isotope compositions (‰)	Residence time estimates (kyr)
Fe	0.01–100 ^a	+0.1 ^d	Variable ^k	-2.4 to +1.5 ^k	0.004–0.6 ^r
Zn	0.01–10 ^a	+0.3 ^e	≈+0.5 ^l	-0.2 to +0.6 ^l	1–11 ^r
Cu	0.5–4 ^a	+0.1 ^e	≈+0.7 ^m	+0.6 to +0.8 ^m	2–5 ^r
Cd	0.00003–1.2 ^a	0.0 ^f	≈+0.3 ⁿ	+0.2 to +0.4 ⁿ	22–105 ^r
Mo	100 ^b	+0.4 ^g	≈+2.3 ^o	Homogeneous ^o	440 ^s
Ba	35–160 ^a	0.0 ^h	≈+0.3 ^p	+0.2 to +0.4 ^p	8 ^t
Ni	1.5–11 ^a	+0.1 ⁱ	≈+1.3 ^q	Homogeneous ^q	10–30 ^u
Ag	0.0002–0.1 ^c	0.0 ^j	Unknown	Unknown	0.4 ^v

242 3. Iron

243 Iron (Fe) plays a key role within phytoplankton as an electron carrier for photosynthesis and respiration
244 processes, as well as within enzymes necessary for photosynthesis and nitrogen fixation (Morel & Price,
245 2003). However, in oxygenated seawater, Fe(II) is rapidly oxidized to Fe(III), which is highly insoluble
246 (Liu & Millero, 2002). Intense biological demand coupled to low solubility results in generally sub-
247 nanomolar concentrations for dissolved Fe throughout the oceans, and Fe concentrations approach the low
248 picomolar range in some surface regions far from Fe sources, such as the vast Southern Ocean (Chever et
249 al., 2010; Klunder et al., 2011; Schlitzer et al., 2018). Consequently, biological production in about 30 %
250 of the modern surface ocean is thought to be limited primarily by Fe (Moore et al., 2013), principally in
251 upwelling regions where deep water is depleted in Fe relative to the macronutrients nitrate and phosphate
252 (e.g., Moore, 2016; Boyd et al., 2017). In these regions, termed ‘High Nutrient Low Chlorophyll’ (HNLC),
253 Fe supply can limit primary productivity (e.g., Martin & Fitzwater, 1988) and potentially the exchange of
254 carbon between the ocean and atmosphere. Furthermore, a changing supply of Fe from sources such as
255 atmospheric dust, hydrothermal venting, or sedimentary release to the surface oceans through geological
256 time can exert a significant control on both the distribution of primary productivity in the oceans and,
257 through this, the global carbon cycle. Changes in supply of dust to the Fe-limited Southern Oceans has been
258 shown to correlate with climate variability on millennial time scales and has also been invoked to explain
259 the dramatic sawtooth glacial–interglacial shifts in atmospheric carbon dioxide (Martin, 1990; Sigman &
260 Boyle, 2000; Martínez-García et al., 2011; 2014). The strong link between Fe supply and primary
261 productivity means that ratios of Fe to other elements and/or Fe isotope ratios ($\delta^{56}\text{Fe}$) might be useful
262 proxies for investigating changes in paleoproductivity, provided the processes that fractionate them are
263 dominantly linked to primary production, can be constrained, and suitable archives identified.

264

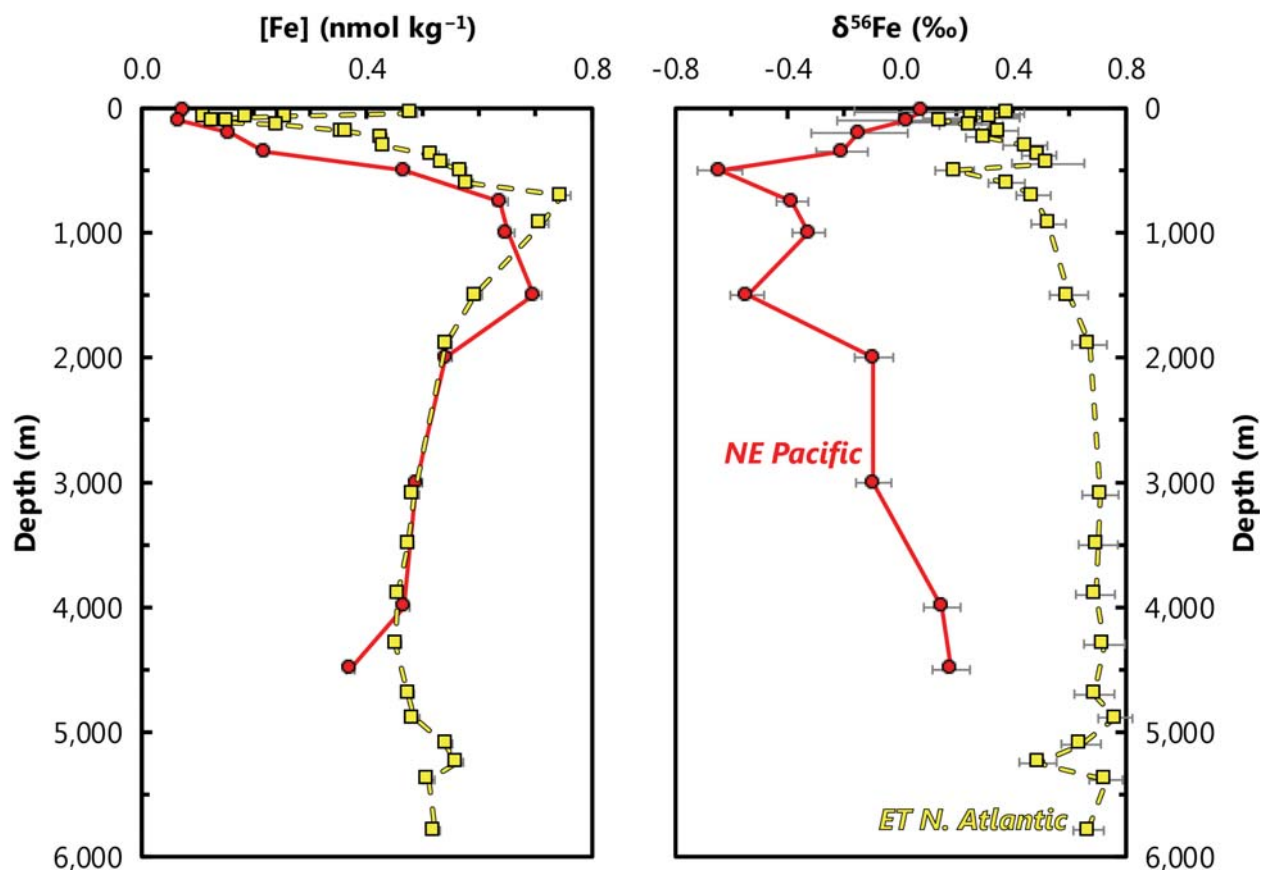
265 3.1. Marine distribution

266 The distribution of dissolved Fe in seawater is driven by a mixture of competing processes, including
267 biological uptake and (deeper) regeneration; distinct sources of Fe at shallow, intermediate, and deep
268 depths; adsorption/desorption processes onto organic and lithogenic particles; dissolution and precipitation
269 processes; and complexation to organic ligands (Fig. 2; e.g., Boyd & Ellwood, 2010; Labatut et al. 2014;
270 Tagliabue et al., 2017). As a result, dissolved Fe displays what has historically been termed as hybrid-type
271 depth profile in the open ocean, which exhibits a number of similarities between different ocean basins
272 (Fig. 3). Surface Fe is drawn down in surface waters by biological uptake, and can even be as low as 0.01
273 nmol kg⁻¹ in Fe limited regions. However, some areas of the oceans, such as the ‘dusty’ North Atlantic,

274 surface Fe concentrations can be driven as high as 2 nmol kg^{-1} as a result of dust events (Sedwick et al.,
275 2005). Below the surface mixed layers, regeneration of biogenic material, reversible particle scavenging,
276 and complexation by organic ligands act to keep the background deep ocean Fe concentrations at around
277 $0.4\text{--}0.6 \text{ nmol kg}^{-1}$ (e.g., Lauderdale et al., 2020). Against this background, it has been known for decades
278 that Fe concentrations in deeper waters are elevated near point sources such as sedimentary margins
279 (Johnson et al., 1999). Recently, a range of studies including those conducted as part of the GEOTRACES
280 program, have illuminated this picture, showing that deep sources of Fe—such as sedimentary and
281 hydrothermal release—are widespread, may have distinct traceable $\delta^{56}\text{Fe}$ source signatures, and that this
282 Fe can be transported over large distances through the ocean interior (e.g., Radic et al. 2011; Saito et al.,
283 2013; Conway and John, 2014; Resing et al., 2015; Nishioka et al., 2020). Despite exhibiting well-defined
284 deep maxima close to point sources, Fe distributions at shallow and intermediate depths are much more
285 variable and models have struggled to reproduce these variations (e.g., Tagliabue et al., 2016). The extent
286 to which deeply sourced Fe is supplied to surface seawater is thus equivocal (c.f., Tagliabue et al., 2010;
287 Roshan et al., 2020).

288
289 The origin of Fe variability in the shallow and intermediate ocean is thought to reflect local differences in
290 the competition between uptake, regeneration, sources, and scavenging. The same processes influence
291 $\delta^{56}\text{Fe}$; however, unlike variations in Fe concentrations, $\delta^{56}\text{Fe}$ exhibits dramatic variability between—and
292 even within—ocean basins (Fig. 2; Schlitzer et al., 2017). Such water column variability in $\delta^{56}\text{Fe}$, from
293 isotope compositions as light as -3 ‰ (John et al., 2012), to as heavy as $\sim +1.5 \text{ ‰}$ (Ellwood et al., 2020),
294 is thought to be driven by Fe source signatures and therefore also oceanic circulation, and a combination of
295 biological uptake, Fe complexation to organic ligands in surface waters, and non-reductive release of
296 dissolved Fe from particles (notably lithogenic particles) during desorption and/or ligand-promoted
297 dissolution (e.g. Conway and John, 2014; Abadie et al. 2017; Ellwood et al., 2020; Fig. 3). As such, $\delta^{56}\text{Fe}$
298 may provide insight to the contribution of Fe sources at the basin scale (e.g. Conway & John, 2014), as well
299 as for Fe cycling processes such as uptake and regeneration.

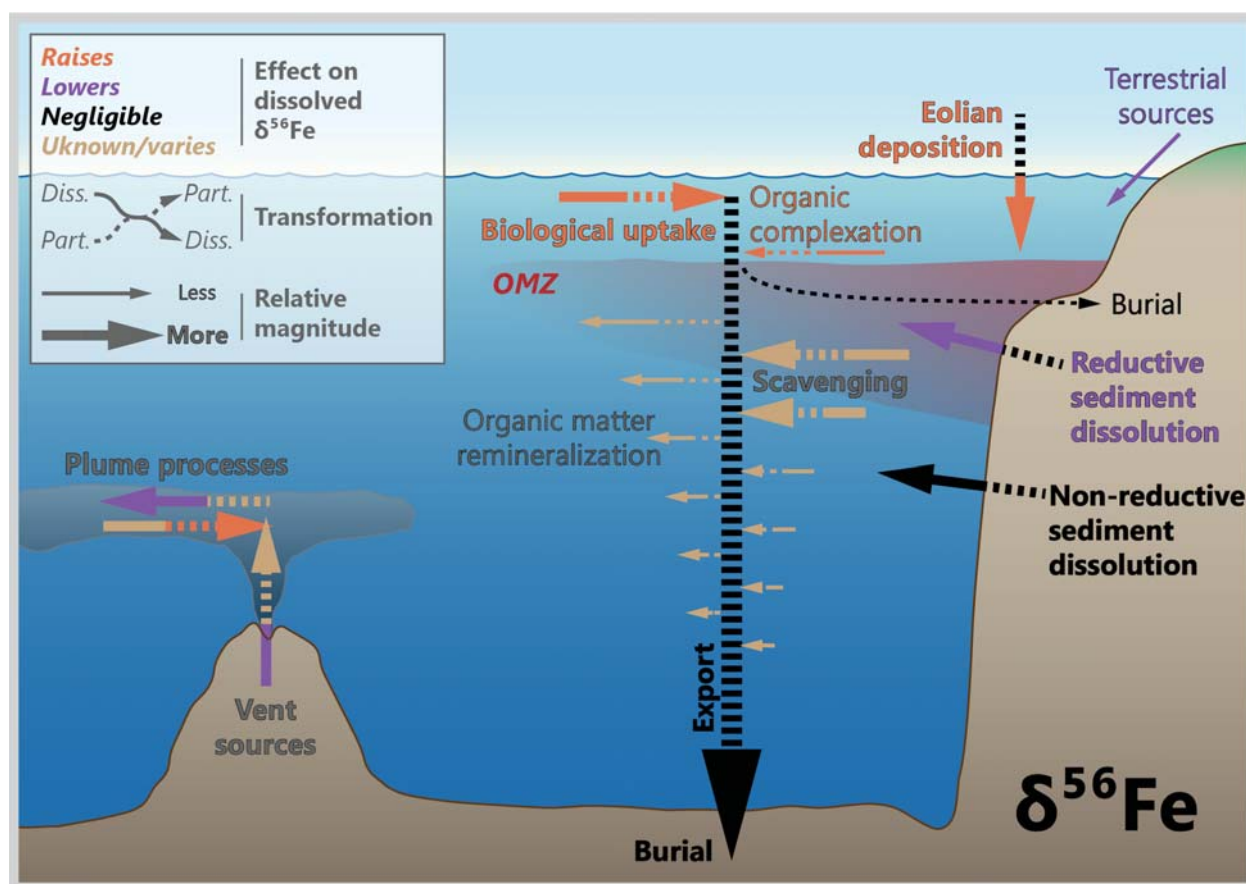
300



301
 302 **Figure 2 | Representative profiles of dissolved Fe concentrations ($[Fe]$) and Fe-isotopic compositions ($\delta^{56}Fe$)**
 303 **in the Eastern Tropical North Atlantic (squares, dashed line) and Northeast Pacific (circles, solid line) Oceans.**
 304 This comparison illustrates that despite possessing similar dissolved concentration profiles, the isotopic behavior of Fe
 305 is markedly different between basins.
 306

307 Despite numerous studies of both small- (e.g., Martin et al., 1990; Coale, 1991; Coale et al., 2003) and
 308 large-scale iron fertilization (e.g., de Baar et al., 2005; Boyd et al., 2007; Boyd & Ellwood, 2010), there are
 309 still uncertainties in how changing Fe supply to the surface ocean may affect phytoplankton growth in Fe-
 310 limited regions, and/or nitrogen fixers under nitrate limitation, leading to gaps in our understanding of
 311 linking Fe cycling directly to climate change (Misumi et al., 2014). One major challenge is assessing what
 312 portion of the dissolved Fe pool is available for uptake by different microbes, termed ‘bioavailable’ Fe.
 313 Such uncertainties on Fe supply, speciation, and bioavailability in the surface ocean are compounded by
 314 limitations in our ability to constrain the supply of dissolved Fe in upwelled deep waters. For example,
 315 while the ratio of C to macronutrients such N and P in the deep ocean is well known and the residence time
 316 and distribution can be accurately reproduced using apparent oxygen utilization (AOU), this is not the case
 317 for Fe. Only around 10–15 % of cellular Fe ($Fe:C = 18\text{--}33 \mu\text{mol}:\text{mol}$) appears to be regenerated in the deep
 318 ocean ($Fe:C = 4\text{--}6$; Twining & Baines, 2013), leading to a weaker correlation between Fe and AOU, even in
 319 regions away from Fe sources (Rijkenberg et al., 2014) and upwelling deep waters that are depleted in

320 dissolved Fe relative to macronutrients. Since incubation experiments show that Fe associated with sinking
 321 organic matter from the subsurface is effectively regenerated (Velasquez et al., 2016), much of the released
 322 Fe must be rapidly scavenged (Tagliabue et al., 2019). Despite this scavenging, vertical transport is still
 323 thought to be the major source of dissolved Fe for phytoplankton in most Fe-limited regions, indicating that
 324 additional research into the interplay between Fe supply (sources, stabilization, and transport) and demand
 325 (biological uptake, scavenging) are required.
 326
 327



328
 329 **Figure 3 | Processes driving iron isotope variations in modern seawater.** The oceans' internal cycle of Fe is
 330 perhaps the most complex of the TEIs discussed here, exhibiting several significant sources, sinks, and transformations
 331 not directly associated with biological productivity.

332
 333 **3.2. Driving processes**

334 **3.2.1. Biological**

335 Initial studies of processes that fractionate Fe isotopes were optimistic that $\delta^{56}\text{Fe}$ would make for a powerful
 336 proxy of physiological 'biosignatures' (Beard et al., 1999), especially once measurement of $\delta^{56}\text{Fe}$ was

337 extended to seawater by Lacan et al. (2008). However, much of this early optimism faded once it was found
338 that other factors were also important in setting dissolved $\delta^{56}\text{Fe}$, such as external Fe sources (e.g., Radic et
339 al., 2011; John et al., 2012; Sec. 3.2.3.). Moreover, organisms exhibit significant variability in Fe:C ratios
340 (e.g., Twining & Baines, 2013), suggesting that Fe cycling may be partially decoupled from ecosystem
341 productivity. Despite the more nuanced picture, there is a growing body of evidence suggesting that
342 phytoplankton probably preferentially incorporate light Fe isotopes from seawater and, in some
343 circumstances, can render detectable changes in dissolved $\delta^{56}\text{Fe}$. For example, studies from isolated eddies,
344 the Mertz Polynya, and the open Southern Ocean showed that surface $\delta^{56}\text{Fe}$ at picomolar dissolved Fe
345 concentrations are isotopically heavy ($>+1\text{‰}$), which has been attributed to the combination of surface
346 uptake, regeneration, and organic complexation (Lacan et al. 2008; Ellwood et al., 2015; 2020). Estimates
347 for the magnitude of fractionation due to biological uptake range between -0.1 (Radic et al., 2011) and -1.0
348 ‰ (Ellwood et al., 2020). The magnitude and direction of any Fe isotope fractionation during uptake may
349 depend on the phytoplankton species, uptake mechanism, and Fe species consumed. Additional research is
350 required on all three fronts. Below the surface mixed layer, $\delta^{56}\text{Fe}$ of dissolved Fe appears to be primarily a
351 reflection of the isotope signature of Fe sources, rather than reflecting a dominant influence from the
352 biological processes of remineralization (e.g. Abadie et al., 2017; Conway & John, 2014a; John et al.,
353 2018a; Labatut et al., 2014). Accordingly, there remains the possibility for $\delta^{56}\text{Fe}$ of surface seawater to be
354 linked to productivity in some oceanographic settings, though the relative role of other Fe-cycling processes
355 and the degree to which they erase any diagnostic productivity signatures requires further investigation.

356

357 3.2.2. *Chemical*

358 The chemical behavior of Fe in seawater is complex and has the potential to decouple Fe cycling from
359 macronutrients and thus productivity. Unlike the macronutrients, which are present as aqueous ions in
360 solution, Fe is scarcely soluble in seawater, and much of what constitutes ‘dissolved’ Fe—operationally
361 defined as that which can pass through a 0.2 or 0.4 μm filter—is in actuality a soup containing organic
362 complexes, nanoparticles, colloids, and a small fraction of truly ionic Fe. The controls governing, and the
363 extent to which exchange occurs between these forms of dissolved Fe, are areas of focused interest (e.g.,
364 Fitzsimmons & Boyle, 2014; Fitzsimmons et al., 2015). Additionally, dissolved Fe is subject to strong
365 removal via scavenging, which lowers the Fe:macronutrient ratio of waters returned to the surface via
366 upwelling (Moore, 2016). Chemical processes can also exert a significant influence over the isotopic

367 composition of Fe in seawater, such as through redox transformations, exchange reactions (e.g.,
368 complexation, particle interactions), and by authigenic precipitation, discussed below.

369 Redox transformations drive large Fe isotope effects (e.g., Johnson et al., 2002; Skulan et al., 2002; Welch
370 et al., 2003; Anbar et al., 2005). Indeed, much of the Fe isotope variation in Earth's ancient, more reducing
371 past likely derives from fractionations associated with redox transformations (e.g., Johnson et al., 2008).
372 While the role of redox relative to other processes is diminished in today's largely-oxygenated ocean, it is
373 nonetheless an important mediator of Fe isotope source compositions, particularly within the ocean interior.
374 This is neatly illustrated using the example of sediment dissolution, which can occur with or without a
375 change in the redox state of Fe. Bulk marine sediments typically possess a composition similar to the crustal
376 composition of +0.1 ‰ (Beard et al., 2003; Poitrasson, 2006). However, dissolved Fe(II) derived from
377 bacterially-mediated reductive dissolution in sediments has been characterized by $\delta^{56}\text{Fe}$ between -1 and -4
378 ‰ (Berquist & Boyle, 2006; Severmann et al., 2006; 2010; Homoky et al., 2009; 2013; Klar et al., 2017a;
379 Henkel et al., 2018), whereas Fe derived from non-reductive dissolution processes is thought to be
380 considerably heavier, between +0.1 to +0.3‰ (Homoky et al., 2009; 2013; Radic et al., 2011). Further
381 modification of reductive end-member compositions is possible upon contact with oxidizing seawater,
382 potentially masking true source signatures. Oceanic water column dissolved $\delta^{56}\text{Fe}$ compositions attributed
383 to either non-reductive (+0.1 to +0.4 ‰) or reductive (-0.3 to -3.3 ‰) release of Fe from sediments have
384 now been observed globally (Radic et al., 2011; John et al., 2012; Staubwasser et al., 2013; Conway &
385 John, 2014a; Labutut et al., 2014; Conway & John 2015a; Chever et al., 2015; Fitzsimmons et al., 2016;
386 Klar et al., 2017a; Abadie et al., 2017; Klar et al., 2018; Rolison et al., 2018; John et al., 2018a; Charette et
387 al., 2020).

388 Exchange reactions can also fractionate primary Fe isotope compositions. For example, natural lithogenic
389 dust is thought to possess a relatively narrow range of Fe isotope compositions (i.e., $\delta^{56}\text{Fe} \approx +0.1 \pm 0.2\text{‰}$;
390 Waeles et al., 2007; Mead et al., 2013; Conway et al., 2019; Chen et al., 2020), reflecting the overall
391 homogeneity of the upper continental crust. However, dissolved Fe in seawater attributed to dissolving dust
392 particles is isotopically heavy, around +0.7 ‰ (Conway & John, 2014a). This fractionation is thought to
393 reflect dissolution in concert with, and complexation by, strong (organic) ligands (Fishwick et al., 2014),
394 which have been experimentally shown to preferentially bind heavy Fe isotopes (Dideriksen et al., 2008;
395 Morgan et al., 2010). Fractionation effects may also arise during exchange of Fe between dissolved and
396 particulate forms, though the magnitude of the effect depends on whether the exchange is primarily physical

397 (negligible fractionation; e.g. Fitzsimmons et al., 2017) or chemical (from $\approx+0.3$ up to $+1$ ‰; Labutut et
398 al., 2014; Fitzsimmons et al., 2015).

399 Lastly, authigenic precipitation can control the isotopic composition of Fe released by large point sources,
400 such as hydrothermal vents and margin sediments. Iron in hydrothermal vent fluids possesses end-member
401 compositions ranging from -0.7 to $+0.1$ ‰ (Sharma et al., 2001; Beard et al., 2003; Severmann et al., 2004;
402 Rouxel et al., 2008; Bennett et al., 2009; Rouxel et al., 2016; Nasemann et al., 2018; Rouxel et al., 2018).
403 However, precipitation of Fe into authigenic minerals can render significant changes in dissolved $\delta^{56}\text{Fe}$
404 (e.g., Severmann et al., 2004; Bennett et al., 2009). The direction of fractionation depends on (e.g., Lough
405 et al., 2017)—and may thus be diagnostic of (e.g., Horner et al., 2015b)—the specific transformations
406 occurring: Fe sulfides and oxides preferentially incorporate isotopically light and heavy Fe, respectively
407 (e.g., Skulan et al. 2002; Rouxel et al., 2008). Mineral precipitation can drive $\delta^{56}\text{Fe}$ of residual Fe stabilized
408 in seawater to values ranging between -2.4 to $+1.5$ ‰, depending on the authigenic mineral produced
409 (Conway & John, 2014a; Ellwood et al., 2015; Fitzsimmons et al., 2016; 2017; Klar et al., 2017b; Lough
410 et al., 2017; Rouxel et al., 2018). Analogous processes appear to operate along continental margins,
411 whereby ‘light’ Fe, mobilized by reductive dissolution, encounters oxidizing seawater and forms
412 precipitates that are heavier than the source Fe (though overall still considerably lighter than background
413 seawater; e.g., Marsay et al., 2018).

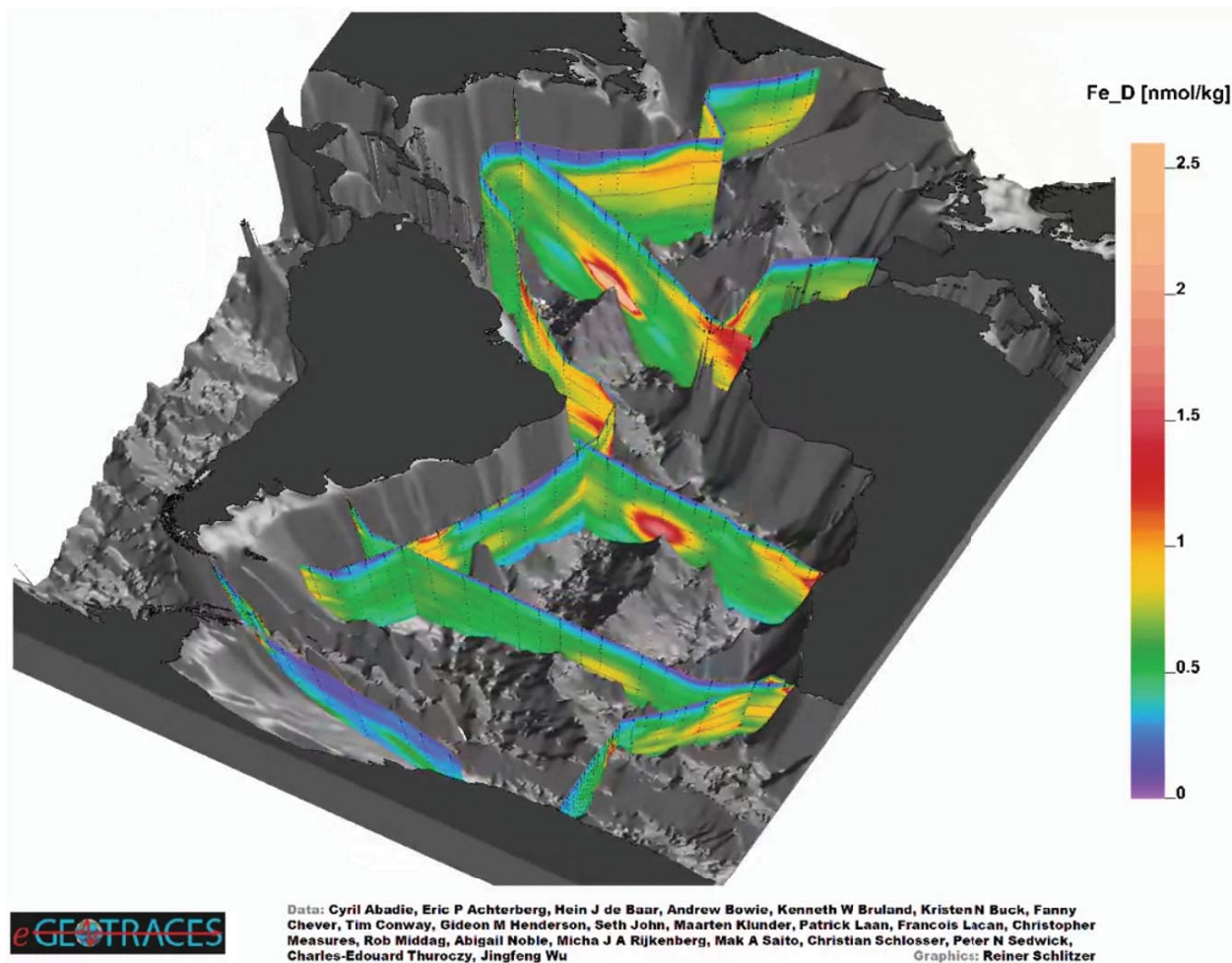
414 Additional nuances relating to $\delta^{56}\text{Fe}$ signatures of local point sources such as Fe released from
415 anthropogenic aerosol dust, glaciers, icebergs, and rivers are also emerging, with such sources varying
416 dramatically over short spatial and temporal scales and with *in situ* chemical reactions (e.g. Fantle &
417 DePaolo, 2004; Berquist & Boyle, 2006; Ingri et al., 2006; Escoube et al., 2009; Poitrasson et al., 2014;
418 Mead et al., 2013; Ilina et al., 2013; Akerman 2014; Chen et al., 2014; Escoube et al., 2015; Mullholland
419 2015; Zhang et al., 2015; Kurisu et al., 2016a;b; Stevenson et al., 2017; Conway et al., 2019). The net effect
420 of the dominance of Fe source on dissolved $\delta^{56}\text{Fe}$ in seawater means that any signal from biological uptake
421 in the Fe-depleted mixed layer, even if could be recorded in an archive, may be easily overprinted by even
422 a small addition of new Fe from either above or below.

423

424 3.2.3. Physical

425 The residence time of Fe in seawater is substantially less than the mixing time of the global ocean (Table
426 1). Local and regional Fe sources can thus drive large differences in dissolved [Fe] and $\delta^{56}\text{Fe}$ between ocean
427 basins (Fig. 3). Local source signatures—[Fe], $\delta^{56}\text{Fe}$, and perhaps Fe speciation—can be transported and

428 retained over the scale of individual ocean basins (Fig. 4; Conway & John, 2014a; Abadie et al., 2017).
 429 This is arguably one of the marquee findings of the GEOTRACES program, and underpins the utility of
 430 sedimentary $\delta^{56}\text{Fe}$ to reconstruct past marine Fe sources, discussed next.



431
 432 **Figure 4 | Three-dimensional scene depicting dissolved iron concentrations in the Atlantic Ocean** (Schlitzer,
 433 2017). This perspective illustrates the density of GEOTRACES data in the region as well as the influence of multiple
 434 Fe 'hot spots', such as mid-ocean ridges and continental margins. Data are available in the GEOTRACES Intermediate
 435 Data Product 2017 (Schlitzer et al., 2018); names of data originators appear in the figure.

436

437

438 3.3. Marine archives

439 3.3.1. Surface ocean

440 A requirement of the application of any paleoproxy is the availability of suitable sedimentary archives.

441 These archives must have both a high fidelity for the signal of interest and be robust to post-depositional

442 alteration. Archives most relevant to reconstructing paleoproductivity should capture surface ocean $\delta^{56}\text{Fe}$;
443 however, there are few—if any—reliable archives. The lack of surface-water archives reflects two related
444 challenges. First, most archives for surface seawater are derived from biominerals, such as foraminifera,
445 diatoms, sponges, and corals. These archives possess vanishingly low Fe concentrations, such that Fe
446 isotopic analysis of these substrates has proven difficult. Second, following burial, many biominerals will
447 act as substrates for authigenic mineral formation. These authigenic minerals, such as clays (e.g., Badaut &
448 Risacher, 1983) and Fe–Mn oxides (e.g., Boyle, 1981), possess Fe concentrations far in excess of those in
449 the underlying biomineral, necessitating significant physical and chemical cleaning (e.g., Cheng et al.,
450 2000).

451 Despite these obstacles, there are three positive signs that reconstructing past surface seawater $\delta^{56}\text{Fe}$ is
452 possible. First, biogenic opal may contain Fe at concentrations in the $\mu\text{g g}^{-1}$ range (Ellwood & Hunter, 2000;
453 Lal et al., 2006; Shemesh et al., 1988; Sun et al., 2016), which is tractable for $\delta^{56}\text{Fe}$ analysis. Second, the
454 Fe content of diatoms is correlated with ambient dissolved [Fe] (Twining & Baines, 2013). Lastly, the
455 positive relationship between the Fe content of diatoms and corresponding seawater appears to hold through
456 sinking and sedimentation (Pichevin et al., 2014), indicating that diatoms are a potential window into past
457 surface ocean Fe chemistry. Whether these relationships also extend to $\delta^{56}\text{Fe}$ remains to be seen, and will
458 require additional core-top calibrations, incubation experiments, and detailed assessment of the efficacy of
459 chemical cleaning.

460

461 3.3.2. *Deep ocean*

462 In contrast to surface seawater, there are a number of studies examining Fe sources and fluxes in the meso-
463 and bathypelagic ocean. To constrain Fe sources, researchers have examined the Fe isotope composition of
464 Fe-rich sediments, including red clays (Tegler et al., 2018), polymetallic nodules (Marcus et al., 2015), and
465 Fe–Mn crusts (Zhu et al., 2000; Levasseur et al., 2004; Chu et al., 2006; Horner et al., 2015b; Liu et al.,
466 2020). Ferromanganese crusts are currently the best-studied for Fe isotopes (Fig. 5); Fe–Mn crusts are
467 slowly-accumulating deposits ($\sim\text{mm Myr}^{-1}$) that record ambient seawater $\delta^{56}\text{Fe}$ with a spatially-invariant
468 offset of $-0.77\pm 0.06\text{‰}$ (Horner et al., 2015b). The constancy of the offset implies that the Fe isotope
469 composition of individual Fe–Mn crust layers can be interpreted in terms of past dissolved $\delta^{56}\text{Fe}$, and thus
470 past Fe sources. Curiously, however, the Fe-isotopic variability of Fe–Mn deposits recovered from the
471 central Pacific—particularly layers formed before $\sim 20\text{ Ma}$ —exceed the range of modern deep-ocean $\delta^{56}\text{Fe}$
472 (though only in the positive direction; Fig. 5). The reasons for elevated $\delta^{56}\text{Fe}$ in the past are debated. Horner
473 et al. (2015b) report that heavy $\delta^{56}\text{Fe}$ could arise through widespread secondary modification of large Fe

474 sources through authigenic reactions, such as sulfide precipitation. In contrast, Johnson et al. (2020) contend
475 that the elevated $\delta^{56}\text{Fe}$ reflects extensive biological modification of dissolved Fe, driven by large-scale Fe
476 fertilization. Regardless, the variation in these records points to a dynamic and enigmatic Fe cycle in Earth's
477 past, and indicates that Fe–Mn crusts have a largely untapped potential to reconstruct spatiotemporal
478 variations in this cycle.

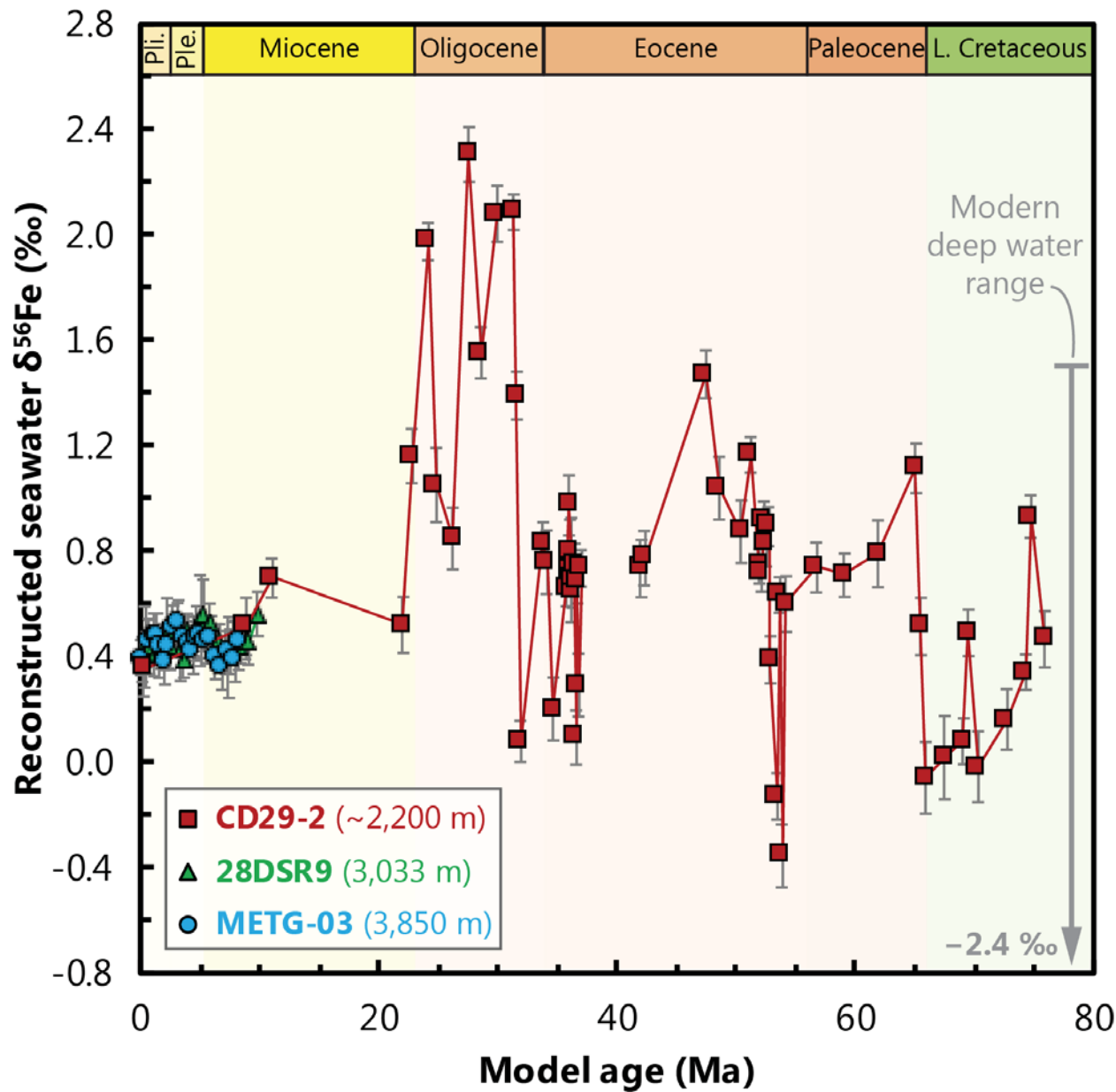
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480 Other approaches are also showing promise to study Fe fluxes to the deep ocean through time. For example,
481 researchers have constrained the rate of sedimentary accumulation of hydrothermally-derived Fe and Cu
482 using constant flux proxies such as extraterrestrial helium-3 (e.g., Middleton et al., 2016) or thorium-230
483 (Costa et al., 2017). These studies report that hydrothermal activity may be coherent with sea-level changes
484 on Quaternary glacial–interglacial cycles, suggesting a potentially remarkable set of connections between
485 the solid Earth, ocean chemistry, and global climate (e.g., Cullen & Coogan, 2017). Reconstruction of
486 hydrothermal metal fluxes over million-year timescales may also be possible using the geochemistry of
487 pelagic clays (e.g., Dunlea et al., 2015), though such approaches are still in their infancy.

488

489 Although existing Fe-isotopic and Fe flux records cannot be directly interpreted in terms of past
490 productivity, the supply and cycling of Fe in seawater is an important control over the biological
491 productivity of the ocean. Thus, records of past oceanic Fe sources may prove most valuable as context for

492 interpreting other proxy records, or for generating novel hypotheses regarding the connections between the
 493 Fe cycle and global climate.
 494



495
 496 **Figure 5 | Ferromanganese crust records of central Pacific $\delta^{56}\text{Fe}$ since the Late Cretaceous.** Records from CD29-
 497 2, 28DSR9, and METG-03 from Horner et al. (2015b), Chu et al. (2006) and Liu et al. (2020), respectively. The record
 498 from CD29-2 was interpreted by Horner et al. (2015b) as evidencing the importance of deep (non-eolian) Fe sources
 499 to central Pacific Fe budgets throughout much of the Cenozoic and Late Cretaceous. In contrast, the $\delta^{56}\text{Fe}$ recorded
 500 by three central Pacific Fe–Mn crusts have been similar since the late Miocene, consistent with a regional Fe source
 501 derived largely from non-reductive sediment dissolution and/or eolian deposition.

502 3.4. Prospects

503 While the marine Fe cycle is complex, Fe isotopes are proving to be a valuable tool for studying the modern
504 Fe cycle. Detailed study of this cycle reveals that it is driven by a multitude of biological, physical and
505 chemical processes, amongst which productivity is but one small part. In our view, this means that there
506 are considerable obstacles to using $\delta^{56}\text{Fe}$ as a paleoproductivity tracer. However, this does not preclude
507 $\delta^{56}\text{Fe}$ from emerging as a powerful tracer for studying the dynamics of the Fe cycle in the (paleo)oceans.
508 Such a tracer would be especially powerful given the proximal connection between Fe supply and the
509 biological productivity of the ocean.

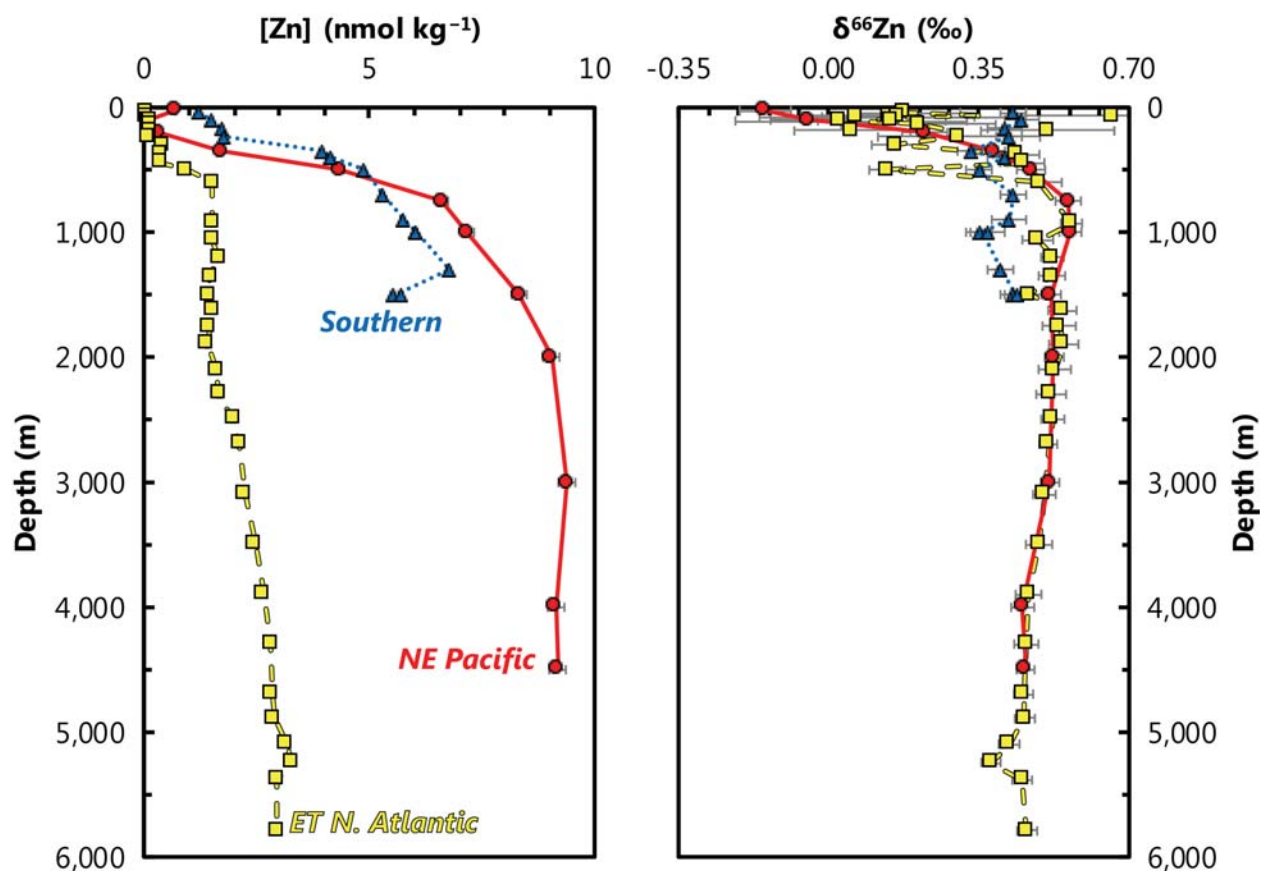
510 Exploiting $\delta^{56}\text{Fe}$ will require resolving and refining several ambiguities. First, there is a clear need to better
511 constrain the Fe-isotopic fractionation factor associated with biological uptake (in variable conditions and
512 from different species) and to diagnose locations where dissolved $\delta^{56}\text{Fe}$ is most affected by productivity.
513 Second, the fractionation factors for remineralization and scavenging are essentially unknown, though field
514 data suggests that the net result of these effects is relatively small (e.g. Radic et al., 2011; Labutut et al.,
515 2104). Constraining these fractionation factors will be particularly important for developing novel archives
516 of the paleo Fe cycle, such as pelagic clays (e.g., Tegler et al., 2018). Third, any sedimentary reconstruction
517 of past Fe-isotopic chemistry will need to consider the high degree of spatial variability in modern $\delta^{56}\text{Fe}$.
518 This will necessitate spatially-distributed core sampling, similar to the approach used to constrain basin-
519 scale patterns of dust deposition over glacial–interglacial timescales (e.g., Costa et al., 2016; Winckler et
520 al., 2016). Addressing these priorities will provide valuable constraints on the extent to which the Fe cycle
521 has influenced primary productivity over recent geological history, and provide key insights into the
522 potential sensitivity of Earth’s climate to perturbations in marine trace element cycles.

523

524 **4. Zinc**

525 **4.1. Marine distribution**

526 Consistent with its importance as a micronutrient, dissolved Zn has a nutrient-type distribution in the ocean
 527 (e.g., Bruland, 1980). Typical surface ocean Zn concentrations are 0.01 to 0.5 nmol kg⁻¹, compared to deep
 528 water concentrations of ~2.5 nmol kg⁻¹ in the north Atlantic and ~10 nmol kg⁻¹ in the north Pacific (Schlitzer
 529 et al., 2018; Fig. 6). The dissolved Zn distribution in the ocean closely follows that of the macronutrient Si
 530 (Bruland, 1980), at least partially due to the similar behaviour of both elements in the Southern Ocean
 531 (Vance et al., 2017; de Souza et al., 2018; Weber et al., 2018; Roshan et al., 2018; Middag et al., 2019).
 532 Decoupling of Zn from Si is observed in regions remote from Southern Ocean influence (Janssen & Cullen,
 533 2015; Vance et al., 2019).



534
 535 **Figure 6 | Representative profiles of dissolved Zn concentrations ([Zn]) and Zn-isotopic compositions ($\delta^{66}\text{Zn}$)**
 536 **in the Eastern Tropical North Atlantic (squares, dashed line), Northeast Pacific (circles, solid line) and Southern**
 537 **(triangles, dotted line) Oceans.** This comparison illustrates that despite possessing distinct dissolved concentration
 538 profiles, the isotopic behavior of Zn is similar between basins.

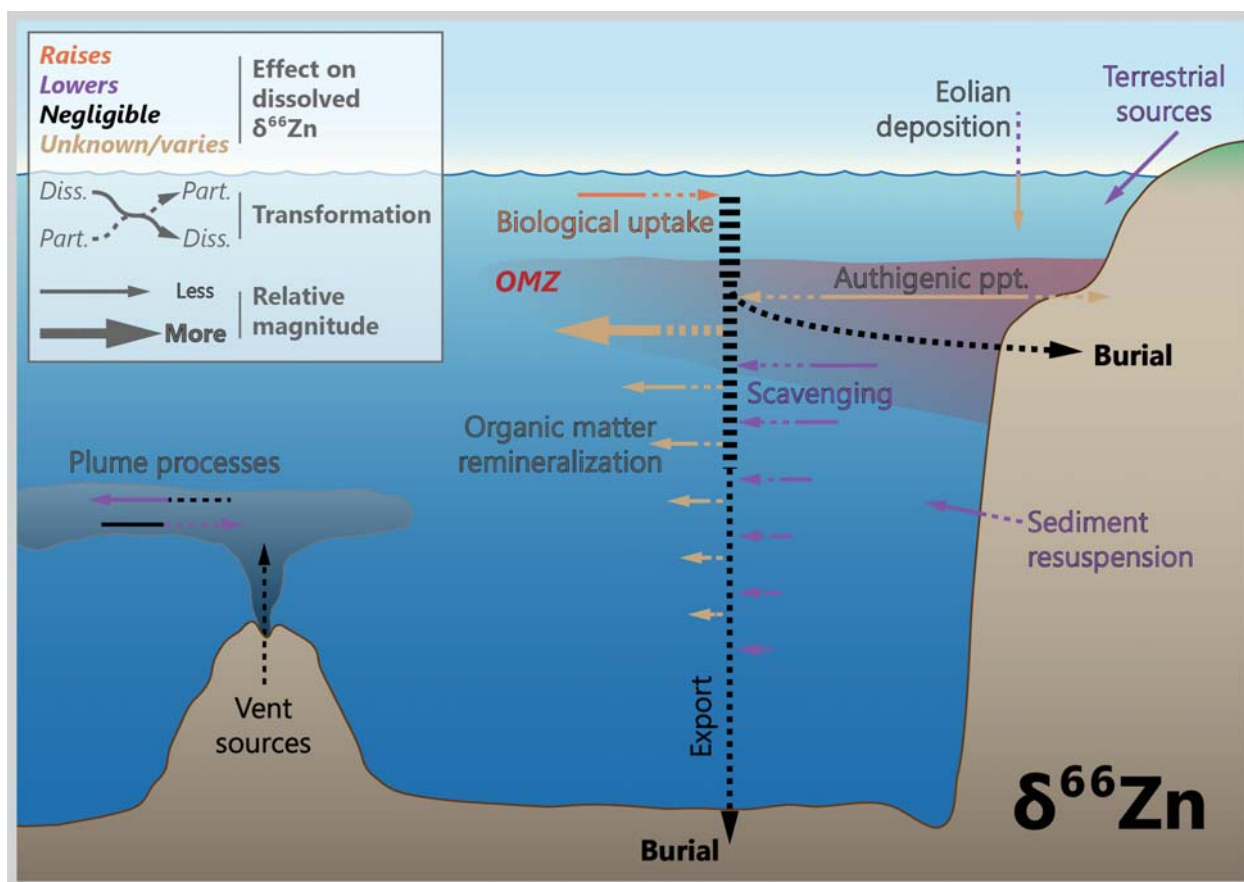
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540 It was hoped that Zn isotope ratios would provide a means of tracing biological carbon cycling in the past
541 and present ocean (e.g., Maréchal et al., 2000; Pichat et al., 2003; Bermin et al., 2006). Zinc isotope data
542 are reported relative to JMC-Lyon, which has now expired. New $\delta^{66}\text{Zn}$ data are typically measured relative
543 to AA-ETH or IRMM-3702 Zn standards and corrected by the offset between these and JMC-Lyon ($\approx 0.3\%$;
544 Moeller et al., 2006; Archer et al., 2017). The apparent preferential uptake of light Zn isotopes by
545 phytoplankton observed in some culture experiments (John et al., 2007; Köbberich and Vance, 2017;
546 Samanta et al., 2018) predicted an isotopically heavy residual pool in surface seawater, analogous to that
547 observed for $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{30}\text{Si}$ and $\delta^{114}\text{Cd}$ (Cd reviewed in Sec. 6., C, N and Si in Farmer et al., *this issue*).
548 However, the test of this hypothesis, through analyses of $\delta^{66}\text{Zn}$ in seawater, awaited a GEOTRACES-driven
549 revolution in large volume trace metal clean sampling (Cutter et al., 2017), alongside analytical advances
550 including new chemical separation procedures and MC-ICP-MS (multiple-collector inductively-coupled
551 plasma mass spectrometry; Bermin et al., 2006; Conway et al., 2013; Takano et al., 2017).

552

553 A consistent picture of the distribution of $\delta^{66}\text{Zn}$ in the ocean has since emerged. The deep ocean is
554 isotopically homogeneous, with a $\delta^{66}\text{Zn}$ signature of about $+0.45\%$ (Fig. 6.; Conway & John, 2014b; Zhao
555 et al., 2014; Conway & John, 2015a; Samanta et al., 2017; Takano et al., 2017; John et al., 2018b; Wang et
556 al., 2019a; Vance et al., 2019; Sieber et al., 2020; Liao et al., 2020; Lemaitre et al., 2020), and isotopically
557 heavier than the upper continental crust (UCC; $\delta^{66}\text{Zn} +0.3\%$; Moynier et al., 2017). Deviations to deep
558 ocean $\delta^{66}\text{Zn}$ compositions as light as -0.2% have been observed near sediments or hydrothermal Zn sources
559 (Conway and John, 2014b; Lemaitre et al., 2020). In the surface, while heavy $\delta^{66}\text{Zn}$ isotope compositions
560 have been observed, the upper water column for Zn is often isotopically light or, in the Southern Ocean and
561 North Pacific, only very slightly fractionated towards heavier values (Conway & John, 2014b; 2015a; Zhao
562 et al., 2014; Samanta et al., 2017; Takano et al., 2017; Wang et al., 2019a; Sieber et al., 2020; Vance et al.,
563 2019; Liao et al., 2020; Lemaitre et al., 2020). Possible reasons for the discrepancy between expected and
564 observed upper water column $\delta^{66}\text{Zn}$ are discussed in detail below. They include preferential scavenging of
565 isotopically heavy Zn on particle surfaces (e.g., John & Conway, 2014; Weber et al., 2018), an isotopically
566 light source of Zn, possibly from shallow remineralization of organic material (Samanta et al., 2017; Vance
567 et al., 2019) or from anthropogenic aerosols (Liao et al., 2020; Lemaitre et al., 2020). We note here that
568 these complexities will likely make it challenging to use Zn isotopes as a paleoproductivity proxy.

569



570
 571 **Figure 7 | Processes driving zinc isotope variations in modern seawater.** Though biological processes are capable
 572 of influencing dissolved $\delta^{66}\text{Zn}$, they do not appear to be the dominant driver of Zn isotope variations in the marine realm.

573

574 4.2. Driving processes

575 4.2.1 Biological

576 Zinc is a metal center in two key enzymes: carbonic anhydrase, necessary for carbon fixation, and alkaline
 577 phosphatase, necessary for dissolved organic phosphorus uptake by marine organisms (Morel et al., 1994;
 578 Shaked et al., 2006; reviewed by Sinoir et al., 2012). Zinc also has an array of other physiological roles in
 579 marine organisms, as exemplified by the observation that Zn contents of phytoplankton cells are of similar
 580 magnitude to the micronutrient Fe (Twining & Baines, 2013).

581 Zinc can be growth-limiting for phytoplankton grown in culture (Anderson et al., 1978; Brand et al., 1983;
 582 Morel et al., 1994), but Zn (co)-limitation (with Fe, Co) has only rarely been observed in the open ocean
 583 (e.g., Coale, 1991; Coale et al., 2003; Franck et al., 2003; Ellwood, 2004; Lohan et al., 2005). This
 584 difference between culture and field may reflect the ability of some phytoplankton to substitute Cd or Co

585 for Zn in some enzyme systems when ambient Zn concentrations are low (e.g., Morel et al., 1994; Lee &
586 Morel, 1995; Yee & Morel, 1996; Kellogg et al., 2020). Nevertheless, Zn availability has been shown to
587 influence species composition and phytoplankton growth, including rates of calcification and alkaline
588 phosphatase activity (Sunda & Huntsman, 1995; Crawford et al., 2003; Schulz et al., 2004; Shaked et al.,
589 2006; Mahaffey et al., 2014). In culture, phytoplankton biomass is typically enriched in the light isotopes
590 of Zn (John et al., 2007; Köbberich and Vance, 2017; 2019; Samanta et al., 2018). Rather than reflecting a
591 kinetic isotope effect on uptake, it has been suggested that Zn speciation in the media controls cellular $\delta^{66}\text{Zn}$
592 values; specifically, strong organic ligands (e.g., EDTA) present in the media preferentially complex heavy
593 Zn isotopes, rendering the bioavailable Zn pool isotopically light (John et al., 2007; Köbberich and Vance,
594 2017; 2019; Fig. 7).

595

596 4.2.2. Chemical

597 Like most bioessential metals, Zn bioavailability is dictated by its chemical speciation (e.g., Anderson et
598 al., 1978), which is dominated in the ocean by complexation to strong ($K' \sim 10^9 - 10^{11}$) organic ligands
599 (Bruland, 1989; Donat & Bruland, 1990; Ellwood & Van Den Berg, 2000; Jakuba et al., 2012; Kim et al.,
600 2015). Inorganic Zn is considered to make up <5% of the total Zn pool in most ocean regions, with the
601 exception of the Southern Ocean, where strong upwelling of nutrient-rich deep waters leads to Zn
602 concentrations in excess of complexing ligands (Baars & Croot, 2011). Note that while strongly-complexed
603 Zn is unlikely to be bioavailable, the presence of 'weak' ligands (or more labile ligands) can enhance Zn
604 uptake (Aristilde & Xu, 2012). As noted above, the role of the diversity of organic (and inorganic) Zn-
605 binding ligands in determining dissolved and particulate $\delta^{66}\text{Zn}$ values remains to be fully evaluated.

606 A role for scavenging in the marine cycling of Zn and Zn isotopes has been widely cited (e.g., John &
607 Conway, 2014; Weber et al., 2018; Roshan et al., 2018; Liao et al., 2020; Fig. 7). It is argued that scavenging
608 can a) explain the widespread observation of isotopically light Zn in the upper ocean, via preferential
609 removal of heavy Zn isotopes on particles, and b) explain elevated concentration of Zn in the deep Pacific
610 compared to that supplied in southern-sourced deep waters (Weber et al., 2018; Roshan et al., 2018).
611 Elevated Zn in the deep Pacific has also been attributed to additional Zn input via, e.g., hydrothermalism
612 (Roshan et al., 2018), with a lighter than deep ocean $\delta^{66}\text{Zn}$ signature (John et al., 2018b). Local and basin
613 scale deviations towards lighter deep ocean $\delta^{66}\text{Zn}$ compositions in both the Atlantic and Pacific have been
614 attributed to sedimentary input (Conway & John, 2014b; John et al., 2017; Liao et al., 2020; Lemaitre et
615 al., 2020), and could also reflect hydrothermalism (Conway & John, 2014b; John et al., 2018b; Lemaitre et
616 al., 2020). Anthropogenic aerosol deposition is thought to supply significant Zn to regions of the surface

617 ocean (e.g., Liao & Ho, 2018), with possible direct and indirect (via scavenging) regional impacts on upper
618 ocean $\delta^{66}\text{Zn}$ values (Liao et al., 2020; Lemaitre et al., 2020).

619 Lastly, Janssen & Cullen (2015) suggest that decoupling of Zn and Si in the northeast Pacific reflects the
620 formation of Zn sulfides in the oxygen deficient zone (ODZ), directly equivalent to proposed Cd sulfide
621 precipitation; this hypothesis is discussed in more detail in Sec. 6.2.3. To date, however, there remains scant
622 evidence for water column Zn-sulfide precipitation in ODZs (e.g., Conway & John, 2014b; John et al.,
623 2018b; Vance et al., 2019). That said, Zn-sulfide precipitation is undoubtedly important in euxinic basins
624 such as the Black Sea and Cariaco Basin (Vance et al., 2016; Isson et al., 2018), and has been postulated to
625 occur within the porewaters of oxygen deficient, organic-rich sediments (Sec. 4.3.3.; Little et al., 2016).

626

627 *4.2.3. Physical*

628 In common with many of the TEIs discussed here, the physical ocean circulation exerts a first order control
629 on the distribution of dissolved Zn and $\delta^{66}\text{Zn}$ compositions (Vance et al., 2017; de Souza et al., 2018; Weber
630 et al., 2018; Sieber et al., 2020). Subantarctic water masses have distinct low Zn:PO₄ and Si:PO₄ ratios, due
631 to the elevated uptake of Zn and Si by diatoms in the surface Southern Ocean (Sarmiento et al., 2004; Vance
632 et al., 2017). Remineralization of these Zn- and Si-rich diatoms at depth imprints a correspondingly high
633 Zn:PO₄ and high Si:PO₄ fingerprint on Antarctic bottom waters. This coupling of Zn and Si in the Southern
634 Ocean forms the basis of the global Zn:Si correlation via the advection of southern sourced water masses
635 towards the low latitudes, where they fill much of the ocean interior (de Souza et al., 2012; Holzer et al.,
636 2014). The homogeneity of deep ocean Zn isotope compositions reflects the limited degree of Zn isotope
637 fractionation on uptake by Southern Ocean diatoms (Zhao et al., 2014; Wang et al., 2019a), which results
638 in intermediate and deep southern-sourced water masses with limited or no isotopic contrast (Sieber et al.,
639 2020). The oceanic Zn:Si correlation persists despite shallower remineralization of Zn relative to Si
640 (Twining et al., 2014), and is especially clear in the Atlantic, underlining that the mixing of water masses
641 is the dominant control on dissolved Zn in this basin (Vance et al., 2017; Weber et al., 2018; Middag et al.,
642 2019). Decoupling of Zn and Si is observed in the upper water column of the northeast Pacific, far from the
643 Southern Ocean influence (Janssen & Cullen, 2015; Vance et al., 2019), likely resulting from the shallower
644 remineralisation of Zn (from organic ‘soft parts’) relative to Si (from opal; Vance et al., 2019).

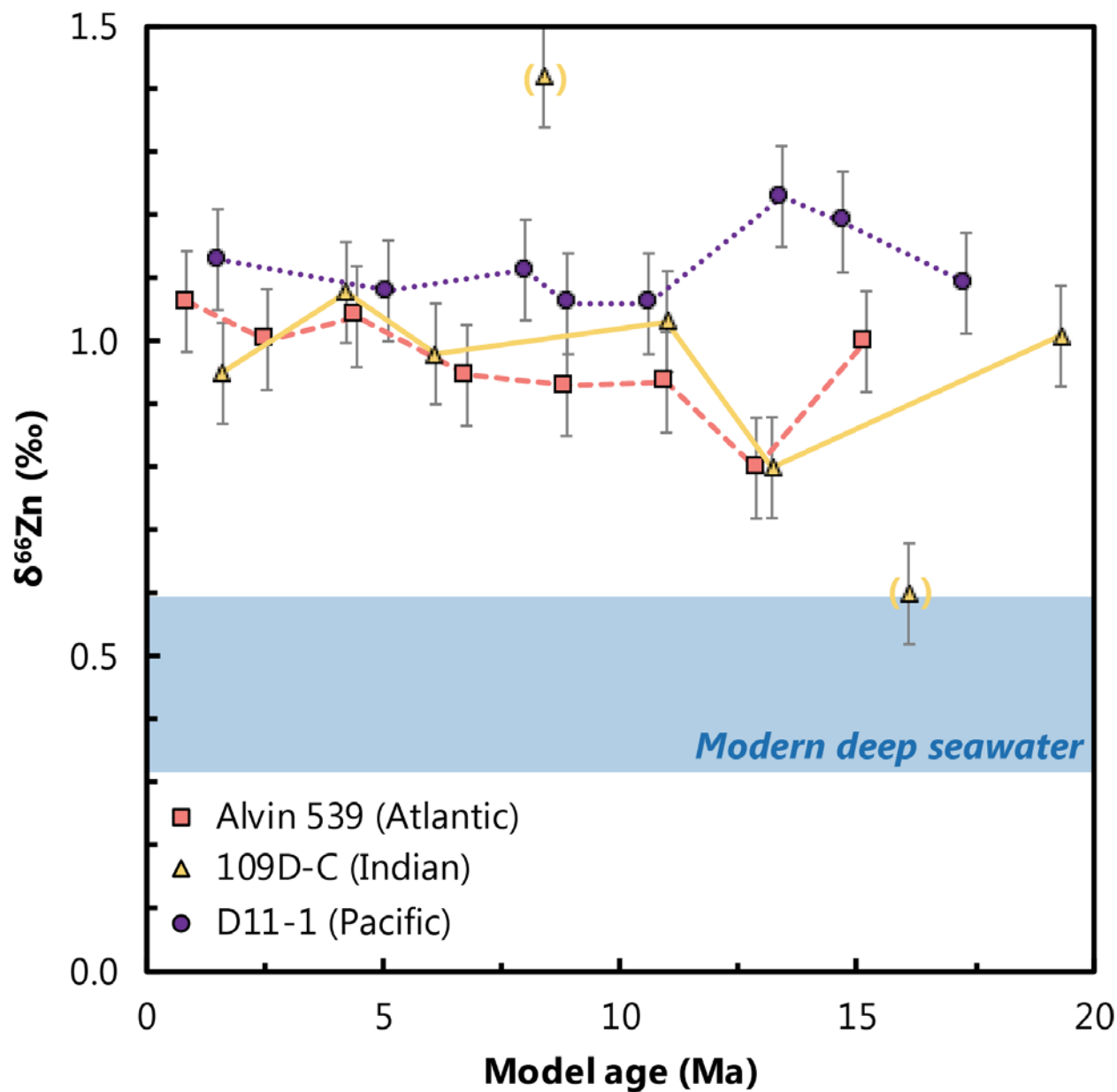
645 **4.3. Sedimentary archives**

646 *4.3.1. Ferromanganese sediments*

647 Manganese oxides are strong sorbents of positively charged, divalent trace metals, due to their negative
648 layer charge at the pH of natural waters (e.g., Koschinsky & Halbach, 1995). The phylломanganate
649 birnessite is the main Mn- and TE-bearing phase in oxic marine sediments (e.g., Koschinsky and Hein,
650 2003), as well as for several elements described here, including Zn, Cu, Ni, Cd, and Mo (though Mo exists
651 in seawater as the molybdate anion). Ferromanganese crusts and nodules incorporate TEs during growth,
652 leading to 10^6 -fold enrichments compared to seawater concentrations (e.g., Arrhenius, 1963; Aplin and
653 Cronan, 1985). As a result, Fe–Mn sediments are often one of the first marine sediment types to be targeted
654 in the development of a new isotopic tracer.

655 In the case of Zn, Fe–Mn crusts and nodules are isotopically heavy compared to seawater ($\approx +0.45\text{‰}$),
656 exhibiting compositions between $+0.9$ to $+1 \text{‰}$ (Maréchal et al., 2000; Little et al., 2014a; Fig. 8). The
657 heavy signature is broadly consistent with inorganic sorption experiments of Zn on birnessite, with
658 experiments at high ionic strength yielding $\Delta^{66}\text{Zn}_{\text{sorbed-aqueous}}$ (where $\Delta^{66}\text{Zn}_{\text{sorbed-aqueous}} = \delta^{66}\text{Zn}_{\text{sorbed}} -$
659 $\delta^{66}\text{Zn}_{\text{aqueous}}$) of $+0.16$ to $+2.7\text{‰}$ (Bryan et al., 2015). The magnitude of fractionation observed in experiments
660 is typically considerably larger than in natural Fe–Mn crusts and nodules, which Bryan et al. (2015) suggest
661 may reflect sorption of Zn on birnessite via two different molecular mechanisms, each associated with
662 different isotopic fractionation factors, as is the case for thallium (e.g., Nielsen et al., 2013). In addition,
663 the influence of organic and inorganic speciation of Zn in seawater may play a role, though this remains to
664 be fully evaluated (e.g., Little et al., 2014b).

665 Little et al. (2014a) observed no marked temporal changes in $\delta^{66}\text{Zn}$ values for three Fe–Mn crusts from
666 each of the major ocean basins over the last ~ 20 Ma. Assuming no significant diffusion or resetting of crust
667 Zn isotope compositions on this timescale, this observation suggests that, on a global basis, the marine Zn
668 cycle has been in isotopic steady state for at least 20 Myr (Fig. 8)



669

670 **Figure 8 | Deep ocean Zn isotope constancy over the past 20 Myr.** These records are derived from Fe–Mn crusts
 671 recovered from the Atlantic (square, dashed line), Indian (triangle, solid line), and Pacific (circle, dotted line) Oceans.
 672 Assuming the isotopic offset between dissolved Zn in seawater and Fe–Mn crusts has remained unchanged at ≈0.55
 673 ‰ over this time, these records imply only minimal Zn-isotopic variations in the deep ocean over the past ~20 Myr. Two
 674 anomalous measurements from 109D-C (in parentheses) possess low levels of authigenic Zn enrichment, indicative of
 675 detrital contamination (Little et al., 2014a).

676

677 4.3.2. Biogenic silica

678 The correlation of Zn with Si in the modern ocean led to the suggestion that Zn/Si measured in diatom opal
679 may be a proxy for Zn/Si (and thus [Zn]) of past seawater. However, culturing and μ -XRF analyses revealed
680 that only a small fraction (1–3%) of the diatom Zn quota is incorporated into the opal frustules, with the
681 remainder present in the organic ‘soft parts’ of the diatom cells (Ellwood & Hunter, 2000; Twining et al.,
682 2004). The Zn concentration in opal (Zn_{opal}) also more closely reflects the bioavailable Zn in seawater than
683 ambient Zn:Si (Ellwood & Hunter, 2000). Nevertheless, if the mechanisms of Zn incorporation into
684 biogenic opal can be understood, and calibrated, a Zn:Si proxy of Zn bioavailability could help shed light
685 on micronutrient limitation of the biological pump.

686 Andersen et al. (2011) analyzed Zn isotopes ($\delta^{66}Zn_{\text{opal}}$) and Zn/Si_{opal} in diatom opal isolated from core top
687 sediments from the Southern Ocean. They observed isotopically heavy Zn in opal (at +0.7 to +1.5‰), and
688 an inverse relationship of $\delta^{66}Zn_{\text{opal}}$ with Zn/Si_{opal} . Consistent with culturing studies, core top Zn/Si_{opal}
689 appears to be linked to bioavailable Zn concentrations in ambient surface seawater. The authors suggested
690 that $\delta^{66}Zn_{\text{opal}}$ should also reflect the isotope composition of bioavailable Zn in surface seawater, which, they
691 predicted, should be isotopically heavy due to the predicted preferential incorporation of light isotopes into
692 phytoplankton organic material. In this view, the extent of uptake—nutrient utilization—would be recorded
693 by the systematics of Zn/Si_{opal} and $\delta^{66}Zn_{\text{opal}}$. However, this study predated the recent surge in seawater $\delta^{66}Zn$
694 measurements. As discussed above, surface water $\delta^{66}Zn$ analyses in the Southern Ocean have not borne out
695 the prediction of isotopically-heavy residual surface waters, with little to no fractionation observed (Zhao
696 et al., 2014; Wang et al., 2019a; Sieber et al., 2020).

697 More recently, Hendry and Andersen (2013) have shown that some sponge spicules faithfully record
698 seawater $\delta^{66}Zn$. Sponges are primarily deep-sea organisms. Hence, if we can deconvolve the controls on
699 diatom Zn/Si and $\delta^{66}Zn_{\text{opal}}$, a combination of Zn/Si and $\delta^{66}Zn$ measurements in diatoms and sponges (as
700 used for Si isotopes, Farmer et al., *this issue*) could provide a strong basis for unravelling the past ocean
701 global Zn cycle, including the role of Southern Ocean processes in the biological carbon pump.

702

703 4.3.3. Carbonates

704 Carbonates may provide an alternative archive for Zn (as Zn/Ca) and $\delta^{66}Zn$. For example, Marchitto et al.
705 (2000) showed that Zn/Ca ratios in benthic foraminifera reflect bottom water dissolved Zn concentrations.
706 However, Zn concentrations in individual microfossil shells are extremely low (of the order ~ 0.1 ng); at

707 this level, with current analytical capabilities and blank contributions, more than one hundred benthic
708 foraminifera would be required for a single Zn isotope measurement.

709 To circumvent the issue of low Zn contents of individual shells, Pichat et al. (2003) utilized a selective
710 carbonate dissolution procedure on bulk sediment from the equatorial Pacific, mostly consisting of
711 coccoliths. These authors argued that isotopically heavy $\delta^{66}\text{Zn}_{\text{carb}}$ reflected ambient surface seawater, with
712 values modulated by changes in biological productivity due to varying seasonal insolation. Similarly
713 isotopically heavy Zn in ancient carbonates has also been argued to reflect strong biological utilization in
714 surface waters (Kunzmann et al., 2013; cf. John et al., 2017; Liu et al., 2017). However, as discussed, the
715 interpretation of these data should be revisited in the light of recent seawater $\delta^{66}\text{Zn}$ data, where isotopically
716 heavy surface ocean Zn isotope compositions are rarely observed.

717 Selective carbonate dissolution procedures present two problems. First, Zn is present at high concentrations
718 in potential contaminating material, e.g., lithogenic or authigenic (e.g. Fe-Mn oxide) phases, and second,
719 non-quantitative leaching introduces the potential for stable isotope fractionation (Revels et al., 2015).
720 Nevertheless, several lab groups are now investing considerable effort to systematically assess these
721 procedures, with promising results (e.g., Clarkson et al., 2018).

722 Finally, deep-sea coral skeletons also provide promise as a potential intermediate-deep water archive of
723 $\delta^{66}\text{Zn}$ (e.g., Little et al., 2017a). Their size and global distribution, combined with the ability to assign
724 precise ages to individual specimens, gives corals some distinct advantages over traditional sedimentary
725 paleoclimate archives (Robinson et al., 2014).

726

727 *4.3.4. Organic-rich sediments*

728 Quantitative removal of Zn into Zn sulfides in the euxinic Black Sea water column leads to sedimentary
729 $\delta^{66}\text{Zn}$ values that preserve the global seawater signature (Vance et al., 2016). This behaviour is analogous
730 to the Mo isotope system (Sec. 7; e.g., Neubert et al., 2008; Nägler et al., 2011), and suggests that euxinic
731 black shales represent an archive for seawater $\delta^{66}\text{Zn}$ values. By extension, Isson et al. (2018) propose that
732 a chemically isolated sulfide-bound Zn fraction also preserves seawater $\delta^{66}\text{Zn}$ values, demonstrating the
733 effectiveness of their approach for core top sediments from the euxinic Cariaco Basin. However, it is not
734 yet clear if the sulfide fraction of organic shales from non-euxinic sites will necessarily record seawater
735 $\delta^{66}\text{Zn}$, as (non-quantitative) precipitation of Zn sulfides is associated with light isotope fractionation (Fujii
736 et al., 2011a; Vance et al., 2016).

737 Authigenic Zn in organic rich sediments deposited in productive continental margin settings is isotopically
738 light (on average, about +0.1‰) compared to seawater (at about +0.45 ‰; Little et al., 2016). One possible
739 explanation for this signature is the preferential biological uptake of light isotopes into organic matter (Little
740 et al., 2016; John et al., 2017). The second possible explanation, touched upon above, is light Zn isotope
741 fractionation during Zn sulfide precipitation, either in sediments or, possibly, in reducing
742 microenvironments in the water column (Janssen & Cullen, 2015; Little et al., 2016; Vance et al., 2016;
743 Bianchi et al., 2018). While a biologically-driven signature would suggest utility for $\delta^{66}\text{Zn}$ in organic-rich
744 sediments as a paleoproductivity proxy, a role for sulfidation highlights the importance of redox conditions
745 during diagenesis, particularly sulphate reduction, in driving the $\delta^{66}\text{Zn}$ values preserved in organic-rich
746 sediments. We note that sedimentary redox is linked to overlying productivity (e.g., Hartnett et al., 1998),
747 but in a complex manner that would make a purely productivity based interpretation of preserved $\delta^{66}\text{Zn}$
748 values in black shales challenging.

749

750 **4.4. Prospects**

751 To summarize, recent seawater, experimental, and sedimentary Zn isotope research implies that the
752 relationship between Zn isotopes and (paleo)productivity is not straightforward. This adds uncertainty to
753 the application of using Zn isotopes as a tracer of paleoproductivity. Fundamental to the application of Zn
754 isotopes as a paleoproductivity proxy (or other type of paleoenvironmental tracer) is a better understanding
755 of the mechanisms driving the modern upper water column distribution of $\delta^{66}\text{Zn}$. Future work should target
756 coupled dissolved and particulate phase $\delta^{66}\text{Zn}$ data, in concert with detailed biological and chemical
757 speciation data. To date, particulate phase $\delta^{66}\text{Zn}$ data has proved particularly challenging due to Zn being
758 extremely contamination prone.

759 We recommend revisiting existing archive data in the context of modern seawater $\delta^{66}\text{Zn}$ data. In general,
760 we encourage that the future interpretation of Zn/Si, Zn/Ca, Zn-TOC and $\delta^{66}\text{Zn}$ data be made within a
761 mechanistic framework, via careful sequential extraction procedures, application of appropriate micro-
762 analytical techniques (e.g., LA-ICP-MS, nano-SIMS, μ -XAFS), and further experimental and theoretical
763 work.

764 We note that there are systematic variations in sedimentary Zn isotope compositions on Gyr timescales. For
765 example, Isson et al. (2018) reported $\delta^{66}\text{Zn}$ of black-shale associated Zn spanning ~ 3.5 Gyr, as well as
766 bitumen and kerogen spanning the last 1.5 Gyr. The black shale record shows a shift from UCC-like values
767 (centered on $\approx +0.4$ ‰) to more marine-like $\delta^{66}\text{Zn}$ (centered on $\approx +0.6$ ‰) around 800 Ma, which the authors

768 interpret as evidencing a transition to a more eukaryote-dominated marine ecosystem. While this feature is
769 consistent with the higher affinity of eukaryotes for Zn compared to prokaryotes (Dupont et al., 2006; 2010),
770 there remains considerable uncertainty regarding the influence of Earth's overall redox state on marine Zn
771 isotope systematics.

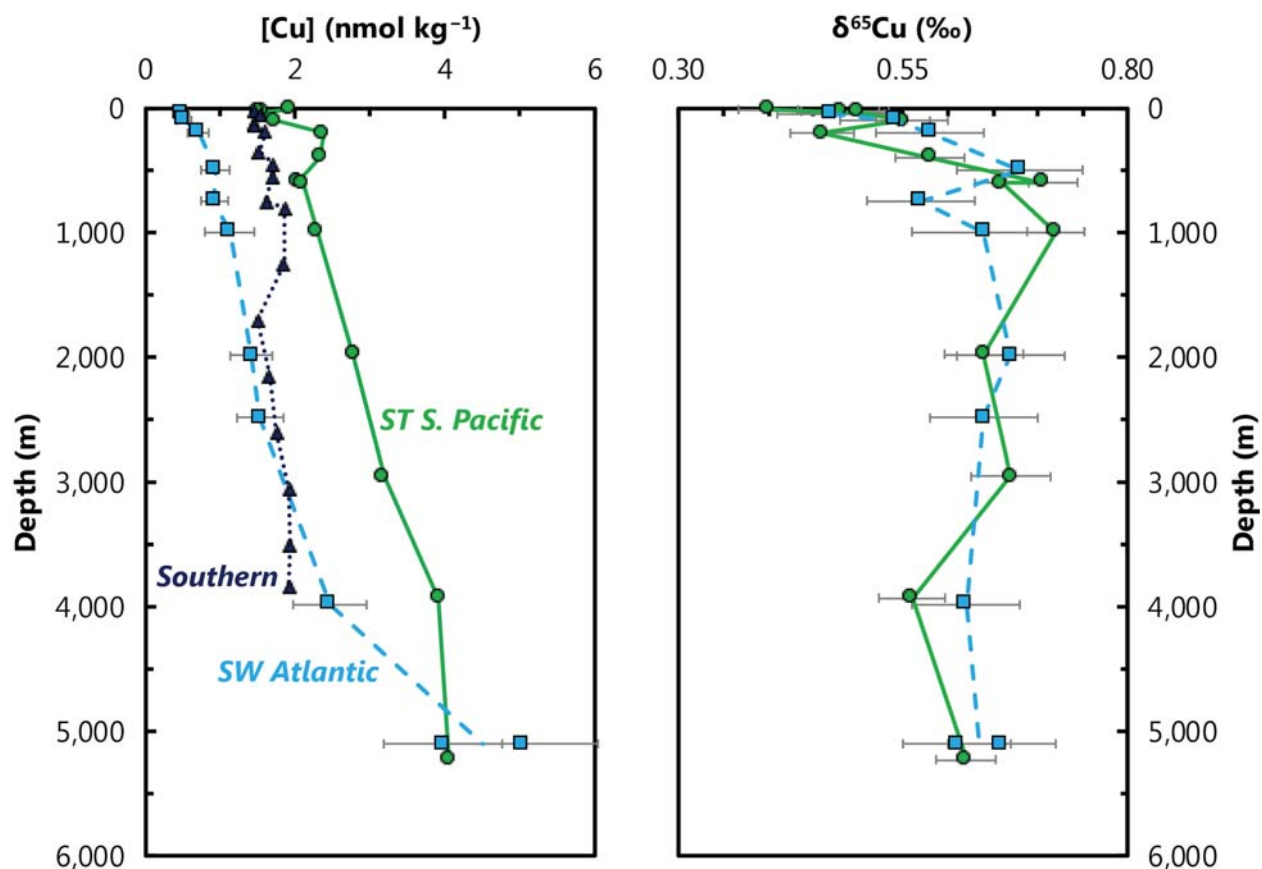
772 In carbonates, Yan et al. (2019) compile three $\delta^{66}\text{Zn}$ datasets from contemporaneous Ediacaran (635 Ma,
773 Marinoan) post-glacial cap carbonates (Kunzmann et al., 2013; John et al., 2017; Lv et al., 2018), which
774 show systematic changes in Zn isotope compositions over this period of marked global change. Similarly,
775 Sweere et al. (2018) present data showing marked shifts in carbonate-bound Zn isotope compositions in
776 several geological sections spanning a Cretaceous ocean anoxic event (OAE 2). As yet, there is no
777 consensus on the drivers of these intriguing isotopic shifts, but these and similar records serve to motivate
778 the future of Zn isotope research.

779

780 **5. Copper**

781 **5.1. Marine distribution**

782 The distribution of Cu in the ocean has been described as ‘hybrid-type’, because it is intermediate between
 783 nutrient- and scavenged-type elements (Bruland & Lohan, 2003). Depth profiles of dissolved Cu typically
 784 show approximately linear increases in concentration with depth (e.g., Boyle et al., 1977). Surface dissolved
 785 Cu concentrations are typically about 0.5 to 1 nmol kg⁻¹, compared to deep Atlantic concentrations of ~2.5
 786 nmol kg⁻¹ and deep Pacific concentrations of ~4 nmol kg⁻¹ (Fig. 9). The distribution of dissolved Cu has
 787 been attributed to a combination of biological uptake and remineralization, benthic flux from sediments
 788 (e.g., Boyle et al., 1977; Roshan & Wu, 2015a; Little et al., 2018), and/or reversible scavenging (Little et
 789 al., 2013; Richon et al., 2019). These processes are superimposed on the first-order distribution established
 790 via the physical ocean circulation (Roshan & Wu, 2015a).

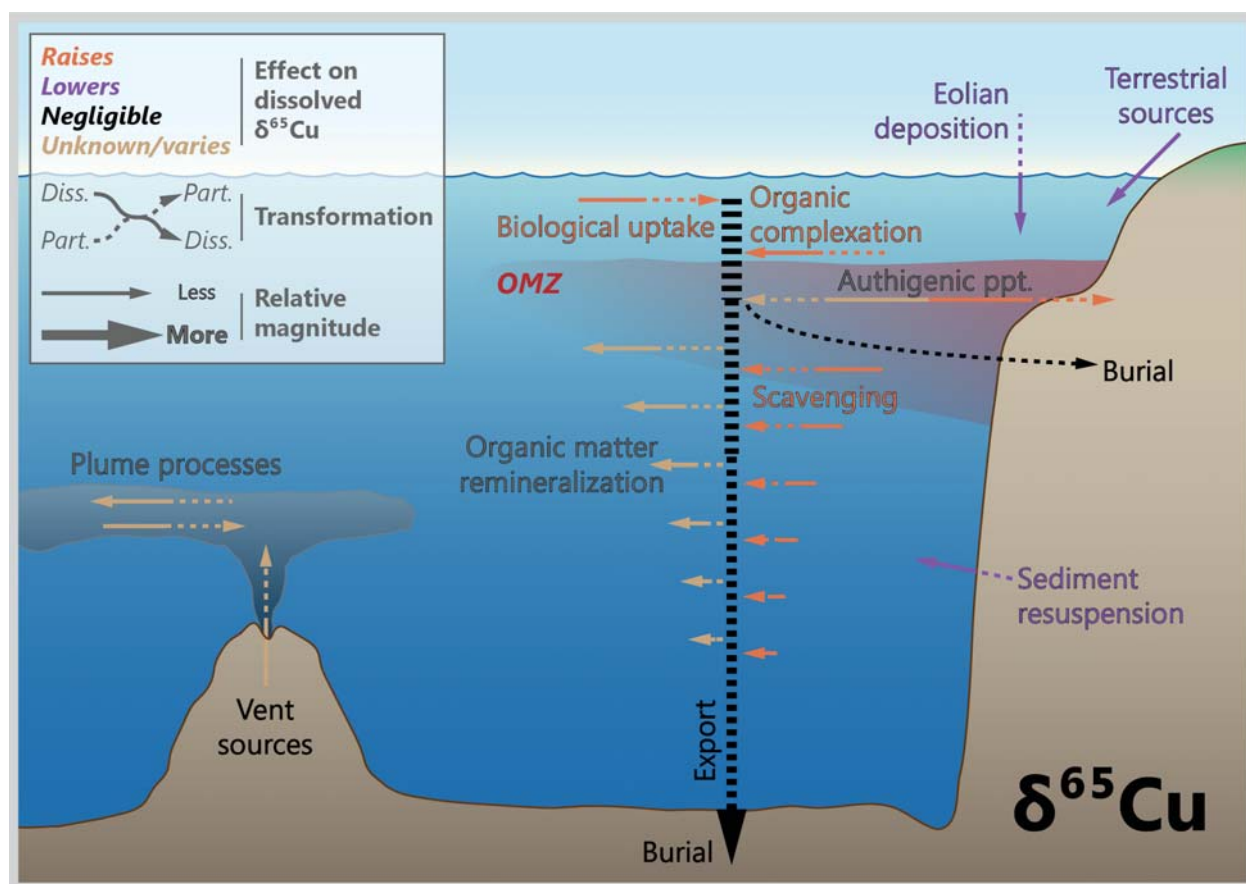


791 **Figure 9 | Representative profiles of dissolved Cu concentrations ([Cu]) and Cu-isotopic compositions (δ⁶⁵Cu)**
 792 **in the Southwest Atlantic (squares, dashed line), Subtropical South Pacific (circles, solid line) and Southern**
 793 **(triangles, dotted line) Oceans. This comparison illustrates that the isotopic behavior of Cu is similar between basins,**
 794 **reflecting the importance of complexation by strong organic ligands.**
 795

796

797 Copper isotopes are reported as relative to the NIST SRM 976 standard, though due to a shortage of this
 798 material, two other certified reference standards are now available: ERM-AE633 ($\delta^{65}\text{Cu}_{\text{SRM976}} = -0.01 \pm 0.05$
 799 ‰) and ERM-AE647 ($\delta^{65}\text{Cu}_{\text{SRM976}} = +0.21 \pm 0.05$ ‰; Moeller et al., 2012; Moynier et al., 2017). For
 800 consistency and ease of comparison, Moynier et al. (2017) recommend that future data be reported relative
 801 to NIST SRM 976. We adopt this convention. The analysis of Cu isotopes in seawater is challenging, due
 802 to both Cu's strong organic complexation, and only two isotopes precluding the use of a double spike
 803 technique (reviewed in Little et al., 2018). The data presented to date indicate that deep seawater $\delta^{65}\text{Cu}$
 804 values are isotopically heavy (at about +0.7 ‰) compared to the upper continental crust (UCC; at about
 805 +0.1 ‰; Table 1; Moynier et al., 2017). Lighter Cu isotope compositions in the upper water column and
 806 along margins are thought to reflect local sources of isotopically light Cu (e.g., aerosols, riverine
 807 particulates, sediments; Takano et al., 2014; Little et al., 2018).

808



809

810 **Figure 10 | Processes driving copper isotope variations in modern seawater.** Biological productivity exerts only a
 811 modest impact on the marine Cu isotope cycle and thus there is no obvious route to developing Cu isotopes (or Cu
 812 concentrations) as a paleoproductivity proxy.

813 **5.2. Driving processes**

814 *5.2.1. Biological*

815 Copper is bioessential, but cellular Cu contents are approximately 2–10 fold lower than the micronutrients
816 Fe and Zn (Twining & Baines, 2013). The redox-active behaviour of Cu (existing as Cu^{2+} or Cu^+ in
817 biological systems) enables its role in electron transport, for example in the Cu-containing proteins
818 plastocyanin and cytochrome c oxidase (Ridge et al., 2008). Copper uptake of some Fe-limited
819 phytoplankton may increase, either due to the replacement of Fe-containing with Cu-containing enzymes
820 (e.g., Peers and Price, 2006), or the involvement of Cu in the high-affinity Fe uptake systems (Annett et al.,
821 2008; Maldonado et al., 2006; Guo et al., 2012). Despite its biological function, Cu is also extremely toxic
822 due to the formation of reactive oxygen species, which pose a threat to DNA, lipids, and proteins (Ridge et
823 al., 2008). Copper toxicity thresholds vary by phytoplankton group, with smaller organisms generally more
824 sensitive than larger ones (e.g., cyanobacteria cf. diatoms; Brand et al., 1986), and coastal strains more
825 resistant than open ocean strains (e.g., Peers et al., 2005).

826 A small number of studies have investigated Cu isotope fractionation during cellular uptake or cell surface
827 adsorption by microorganisms (Pokrovsky et al., 2008; Navarrete et al., 2011; Cadiou et al., 2017; Coutaud
828 et al., 2018; 2019). The results of these experiments are somewhat variable, with enrichment of either light
829 or heavy Cu isotopes observed during assimilation and adsorption. However, assimilation in culture
830 generally favours light Cu isotopes (Navarrete et al., 2011; Cadiou et al., 2017; Fig. 10). The complexity in
831 Cu isotopic behaviour has been attributed to small changes in Cu speciation or redox during uptake and/or
832 release of Cu (Coutaud et al., 2018; 2019).

833

834 *5.2.2. Chemical*

835 In seawater, the vast majority of Cu is complexed to strong organic ligands (more than 99.8% complexed
836 in surface northeast Pacific), which lower free Cu^{2+} concentrations to below toxic levels (e.g., Coale &
837 Bruland, 1988; 1990; Moffett & Dupont, 2007). It is thought that ligands are primarily produced by biota
838 for the purpose of detoxification (e.g., Moffett et al., 1990; Moffett & Brand, 1996), albeit recent work
839 suggesting that strongly complexed Cu is bioavailable to some eukaryotes, which appear to have a higher
840 cellular Cu requirement (and higher thresholds of Cu toxicity) than prokaryotes (Semeniuk et al., 2009;
841 2015).

842 Both theory and experiments predict preferential complexation of heavy isotopes by strong organic ligands
843 (Sherman, 2013; Fujii et al., 2013; Ryan et al., 2014; Sherman et al., 2015), and organic complexation is
844 thought to play a key role in the modern oceanic budget and distribution of Cu isotopes (Vance et al., 2008;
845 Little et al., 2014a; Thompson & Ellwood, 2014; Takano et al., 2014; Little et al., 2018). The small pool of
846 non-complexed Cu^{2+} in seawater is thus expected to be isotopically light (e.g., Little et al., 2014b, 2018).

847 Based on a surface complexation model with the phylломanganate birnessite, the principal scavenging
848 phase of divalent trace metals in oxic sediments, Sherman & Peacock (2010) calculated that the
849 concentration of dissolved Cu in deep waters should be orders of magnitude lower than is actually observed.
850 They attribute this difference to the chelation of “*essentially all dissolved Cu*” by organic ligands (Sherman
851 & Peacock, 2010), consistent with observations (e.g., Moffett & Dupont, 2007; Heller & Croot, 2015;
852 Jacquot & Moffett, 2015). Nevertheless, some form or forms of scavenging are also thought to play a role
853 in the oceanic Cu distribution.

854 Reversible scavenging, a term used to describe the equilibrium between a scavenged and dissolved metal
855 pool, has been proposed as the driving process behind the generally monotonic, linear increases in dissolved
856 [Cu] depth (Little et al., 2013; Richon et al., 2019; Fig. 9). In some regions with high particulate loads (e.g.,
857 some hydrothermal plumes, benthic nepheloid layers), scavenging removal of Cu has been observed
858 (Jacquot and Moffett, 2015; Roshan & Wu, 2015a). Preferential scavenging of light Cu isotopes by
859 particulate (e.g., oxyhydroxide) phases has also been proposed as an explanation for isotopically heavy
860 seawater Cu isotope compositions (e.g., Takano et al., 2014), though the driving mechanisms leading to
861 isotopically light particulate Cu remain to be fully established (see section 5.3; Fig. 10).

862 The shorter residence time of Cu (2-3.3 kyr; Little et al., 2017b), compared to metals with longer residence
863 times (e.g., Cd, Zn, Ni), mean that, as for Fe, regional and local sources of Cu to the ocean play a relatively
864 larger role in determining dissolved Cu distributions than for some other TEIs. Sources of Cu include
865 aerosols (both natural and anthropogenic; e.g., Takano et al., 2014; Yang et al., 2019), benthic fluxes from
866 sediments (e.g., Boyle et al., 1977; Heller & Croot, 2015; Roshan & Wu, 2015a; Little et al., 2018), and
867 dissolved or particulate riverine sources (e.g., Vance et al., 2008; Little et al., 2018; Richon et al., 2019). A
868 possible small hydrothermal source has been identified in the South Pacific from the East Pacific Rise
869 (Roshan & Wu, 2018), which is in contrast to the scavenging removal of Cu observed around hydrothermal
870 vents elsewhere (e.g., Jacquot and Moffett, 2015).

871

872 *5.2.3. Physical*

873 Copper's shorter residence time relative to Cd, Zn and Ni also means that the Southern Ocean and wider
874 physical ocean circulation play a somewhat smaller role in oceanic Cu and $\delta^{65}\text{Cu}$ distributions compared to
875 many of the other TEIs discussed herein. Nonetheless, the imprint of circulation is evident in certain
876 circumstances, such as in the Atlantic and the upper 2 km of the South Pacific where dissolved Cu is
877 correlated with dissolved silicate (Roshan & Wu, 2015a; 2018; Little et al., 2018).

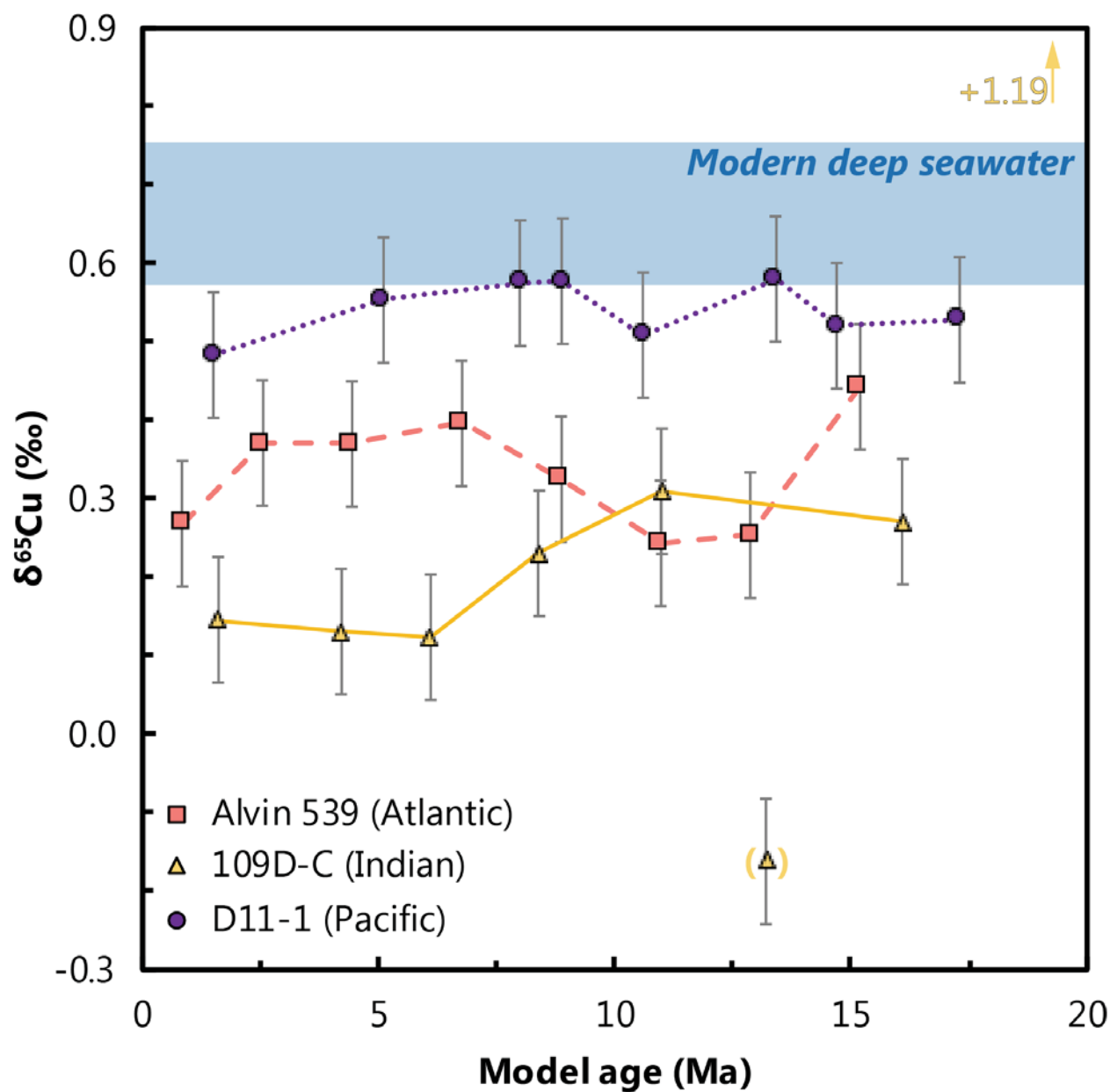
878

879 **5.3. Marine archives**880 *5.3.1. Ferromanganese sediments*

881 Ferromanganese sediments (crusts and nodules) exhibit Cu isotope compositions of +0.3 to +0.5 ‰
882 (Albarède, 2004; Little et al., 2014). This means that, on average, Fe–Mn sediments are approximately 0.35
883 ‰ lighter than deep seawater, which averages +0.7 ‰ (Fig. 11). The explanation for this offset is uncertain,
884 but may reflect either strong organic complexation of Cu in seawater (Little et al., 2014b), or the enrichment
885 of light Cu isotopes on the birnessite mineral surface, as recently observed in inorganic experiments
886 whereby sorbed Cu exhibited $\delta^{65}\text{Cu}$ that was 0.45 ± 0.18 ‰ lighter than Cu in solution (Ijichi et al., 2018).
887 At equilibrium in seawater, however, the strong complexation and mineral sorption effects should be
888 additive, leading to a much larger isotopic offset than the ~ 0.35 ‰ observed, suggesting that one of the two
889 effects is not expressed in nature for reasons as yet unclear.

890 Little et al. (2014a) observed no marked changes in deep-ocean $\delta^{65}\text{Cu}$ recovered from three Fe–Mn crusts
891 from each of the major ocean basins over the last ~ 20 Ma. Assuming Cu diffusion is slower than crust
892 growth rate, the lack of Cu isotope variation indicates that, on a global basis, the marine Cu cycle has been
893 in isotopic steady state for at least 20 Myr (Fig. 10).

894



895

896 **Figure 11 | Deep ocean Cu isotope constancy over the past 20 Myr.** These records are derived from Fe–Mn crusts
 897 recovered from the Atlantic (square, dashed line), Indian (triangle, solid line), and Pacific (circle, dotted line) Oceans.
 898 Assuming the isotopic offset between dissolved Cu in seawater and Fe–Mn crusts has remained unchanged at ≈ 0.35
 899 ‰ over this time, these records imply that the inter-basin Cu-isotopic variations observed in modern crusts and the Cu
 900 isotope cycle itself have remained relatively stable for at least 20 Myr. Two samples from 109D-C possess low levels
 901 of authigenic Cu enrichment indicating detrital contamination (parentheses, arrow; Little et al., 2014a).
 902

903 5.3.2. *Organic-rich sediments*

904 Qualitative arguments for high organic matter fluxes (i.e., higher paleoproductivity) have been made based
905 on elevated Cu and Ni concentrations in ancient organic-rich sediments (e.g., Tribovillard et al., 2006). This
906 approach is supported by positive correlations between Cu and Ni with TOC in modern continental margin
907 sediments (Sec. 9.3). Applying this [metal]–TOC approach to study past productivity has three
908 prerequisites:

- 909 1. Organic matter is the primary vector supplying the TE to sediments;
- 910 2. Sediments are reducing, and must remain reducing during diagenesis and burial (note that this
911 differs for Ba, since BaSO₄ preservation requires more oxidizing conditions; Sec. 8);
- 912 3. The system is open marine

913 A significant challenge to this approach for Cu (as well as Zn, Cd, Mo, and other chalcophile elements) is
914 its reactivity towards sulfide, as illustrated by the quantitative removal of Cu from the euxinic Black Sea
915 water column and resultant enrichment in underlying sediments (Tankéré et al., 2001; Little et al., 2015).
916 Thus, for Cu, prerequisite number (1), that the metal is primarily supplied to sediment associated with
917 organic matter, is not fulfilled. We return to this approach for Ni in Sec. 9.3.2.

918 Authigenic Cu in modern organic-rich sediments is generally similar in isotopic composition to Fe–Mn
919 sediments and suspended particulate material collected from the South Atlantic, all at about +0.3‰ (Little
920 et al., 2017b; 2018; Ciscato et al., 2019). This homogeneity in authigenic Cu isotope compositions has been
921 suggested to reflect an equilibrium isotope fractionation in the aqueous phase between organically
922 complexed Cu and inorganic Cu²⁺, with the latter approximately 0.4‰ lighter than ligand-bound Cu,
923 followed by near quantitative scavenging of inorganic Cu²⁺ by (any type of) particulate material (Little et
924 al., 2017b; 2018). If correct, this hypothesis suggests that authigenic Cu isotope compositions in marine
925 sediments may reflect the evolution of organic complexation on geological timescales.

926 Ciscato et al. (2018; 2019) developed a new approach to isolate TEIs associated with two different fractions
927 in organic-rich sediments, the ‘organic-pyrite fraction’ (OPF) and ‘HF-digestible fraction’ (HFD). They
928 find that the OPF of modern Peru margin sediments typically contains >50 % of total Cu and is variably
929 isotopically light compared to bulk authigenic Cu. They suggest this signature reflects incomplete
930 sulfidation under variable water column and sedimentary redox conditions (e.g., Bianchi et al., 2018).
931 Unlike in modern sediments, in ancient shales (ranging in age from 0.4 to 3.4 Ga) bulk Cu concentrations
932 do not correlate with TOC and >80% of Cu is hosted in the HFD fraction. In addition, the OPF fraction in
933 ancient shales is markedly isotopically heavier than it is in modern sediments (Ciscato et al., 2019). This

934 difference between modern and ancient Cu partitioning may reflect diagenetic or metamorphic processing,
935 or it may be a primary feature relating to differences in the Cu isotope composition of seawater, or
936 differences in the mechanism(s) of Cu sequestration into sediments.

937

938 **5.4. Prospects**

939 Despite the biological importance of Cu, the modern biogeochemical cycle of Cu suggests there is no clear
940 route to developing Cu isotopes (or Cu concentrations) as a paleoproductivity proxy. However, organic
941 ligands play a key role in the cycling of Cu and Cu isotopes, suggesting potential for the use of Cu isotopes
942 in tracing the evolution of organic complexation on geological timescales. Additionally, careful sequential
943 extraction procedures, such as those described by Ciscato et al. (2019), may allow for the direct probing of
944 past seawater properties, such as redox state.

945 At present, there are few applications of Cu isotopes to study ancient biogeochemical cycles. Interestingly
946 however, there are two black shale records that indicate a shift from UCC-like to heavy Cu isotope values
947 across the Great Oxidation Event (GOE, ~2.4 Ga; Chi Fru et al., 2016; Ciscato et al., 2019). Chi Fru et al.
948 (2016) interpreted this shift as reflecting the onset of oxidative weathering and waning of iron formation
949 deposition, with the latter process driving pre-GOE seawater isotopically light due to the preferential
950 scavenging of heavy Cu isotopes to Fe oxides. However, a recent analysis of two classic pre-GOE sequences
951 containing iron formations do not support this earlier hypothesis, with $\delta^{65}\text{Cu}$ remaining close to 0 ‰
952 (Thibon et al., 2019). Thus, while the limited available data preclude confident interpretations, there are
953 tantalizing tastes of future research directions in Cu isotope geochemistry.

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960 **6. Cadmium**

961 Dissolved cadmium (Cd) concentrations closely correlate with the macronutrient phosphate in the oceans
962 (PO_4^{3-} ; e.g., Boyle et al., 1976; Bruland, 1980). The nutrient-like properties of Cd—and attendant
963 correlations with PO_4^{3-} —have been documented in multiple ocean basins and in multiple dimensions (i.e.,
964 vertically, spatially, and temporally). This overall behavior implies that Cd somehow participates in marine
965 biological processes and that the resulting distribution captured by sediments can be connected to
966 underlying patterns of primary productivity. Recently, results from the GEOTRACES program have
967 highlighted new nuances to this cycle that act to decouple phosphate and Cd in certain situations, which
968 affect the interpretation of Cd distributions in the modern ocean as well as in the sedimentary record.
969 Accordingly, this section will review the first-order features of marine Cd (and Cd isotope) distributions,
970 discuss known driving mechanisms, highlight recent progress on identifying suitable sedimentary archives,
971 and offer recommendations for future studies.

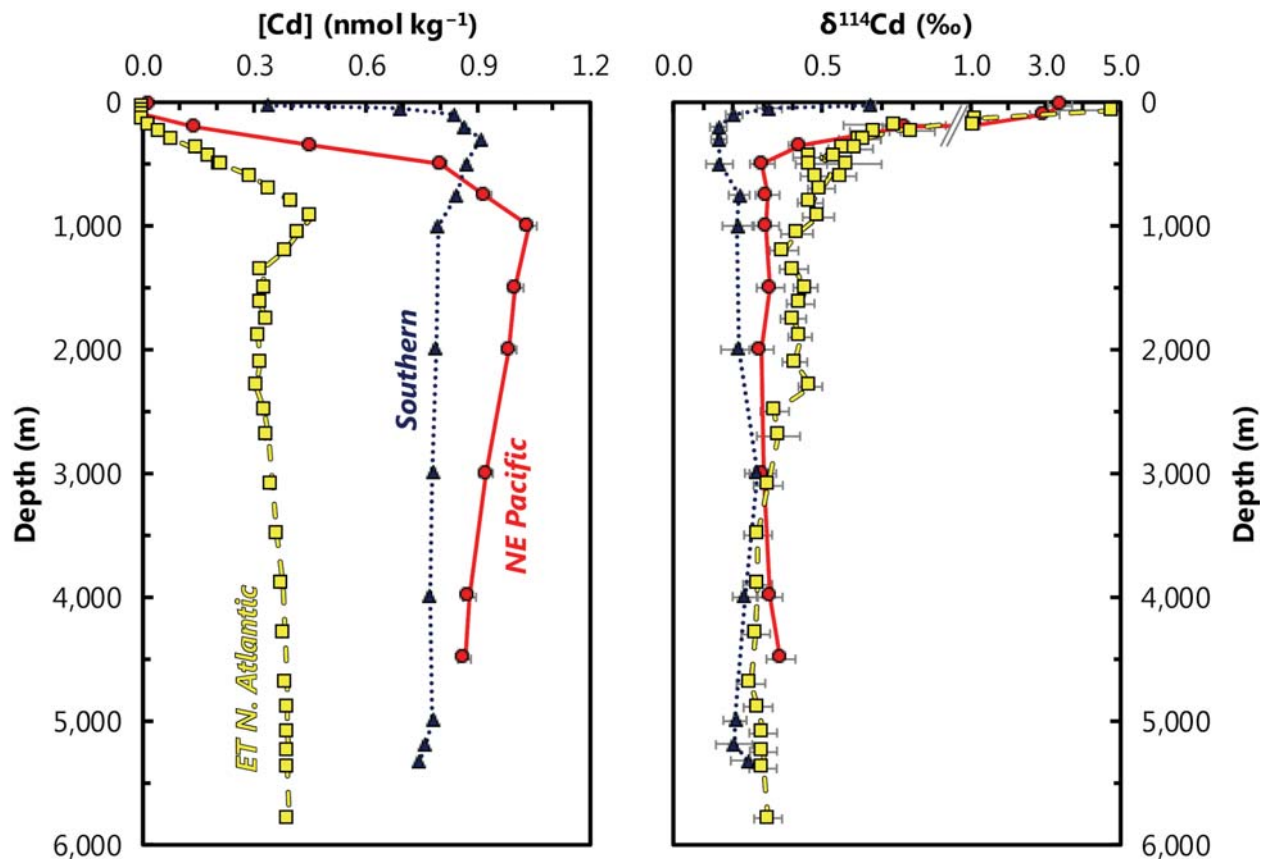
972

973 **6.1. Marine distribution**

974 Away from major upwelling regions, surface water dissolved Cd concentrations are typically between 1–
975 100 pmol kg^{-1} , but can reach as low as 30 fmol kg^{-1} (Schlitzer et al., 2017; Fig. 12). The majority of this
976 small surface inventory is thought to be complexed by strong organic ligands (e.g., Bruland, 1992; Ellwood,
977 2004). In intermediate and deep waters, dissolved Cd concentrations are significantly elevated relative to
978 surface waters, ranging from 0.5 nmol kg^{-1} in intermediate and deep waters in the north Atlantic to ≈ 1.2
979 nmol kg^{-1} in the oldest deep waters of the north Pacific (Schlitzer et al., 2018). As with Zn (Sec. 4.), the
980 overall distribution of dissolved Cd throughout the oceans is driven principally by biological and physical
981 processes in the Southern Ocean, and the lateral circulation of Southern Ocean water masses (e.g., Baars et
982 al., 2014; Middag et al., 2018; Sieber et al., 2019a). Thus, the shape of vertical Cd concentration profiles at
983 lower latitudes arises largely from horizontal transport and mixing of high-Cd Southern Ocean-sourced
984 water masses, with a modest contribution from regeneration of sinking particles (i.e., 5–40 %; Middag et
985 al., 2018). These processes result in Cd having ‘nutrient-type’ one dimensional water column profiles, with

986 a progressive increase in intermediate- and deep-water [Cd] along the pathways of meridional overturning
 987 circulation (e.g., de Baar et al., 1994; Middag et al., 2018).

988



989
 990 **Figure 12 | Representative profiles of dissolved Cd concentrations ([Cd]) and Cd-isotopic compositions**
 991 **($\delta^{114}\text{Cd}$) in the Eastern Tropical North Atlantic (squares, dashed line), Northeast Pacific (circles, solid line), and**
 992 **Southern (triangles, dotted) Oceans.** Note the break in scale in $\delta^{114}\text{Cd}$ above 1 ‰, illustrating the extreme isotopic
 993 compositions observed in the most Cd-depleted surface samples. Notably, such extreme compositions are not
 994 observed in the similarly Cd-depleted surface waters of the southern hemisphere gyres (e.g., Gault-Ringold et al., 2011;
 995 Xie et al., 2017; George et al., 2019), nor in the surface of the high-latitude Southern Ocean, where dissolved [Cd] is
 996 elevated (e.g., Abouchami et al., 2011; 2014). This comparison illustrates that the processes leading to distinct
 997 dissolved concentration profiles effect only modest changes in dissolved $\delta^{114}\text{Cd}$ between basins.

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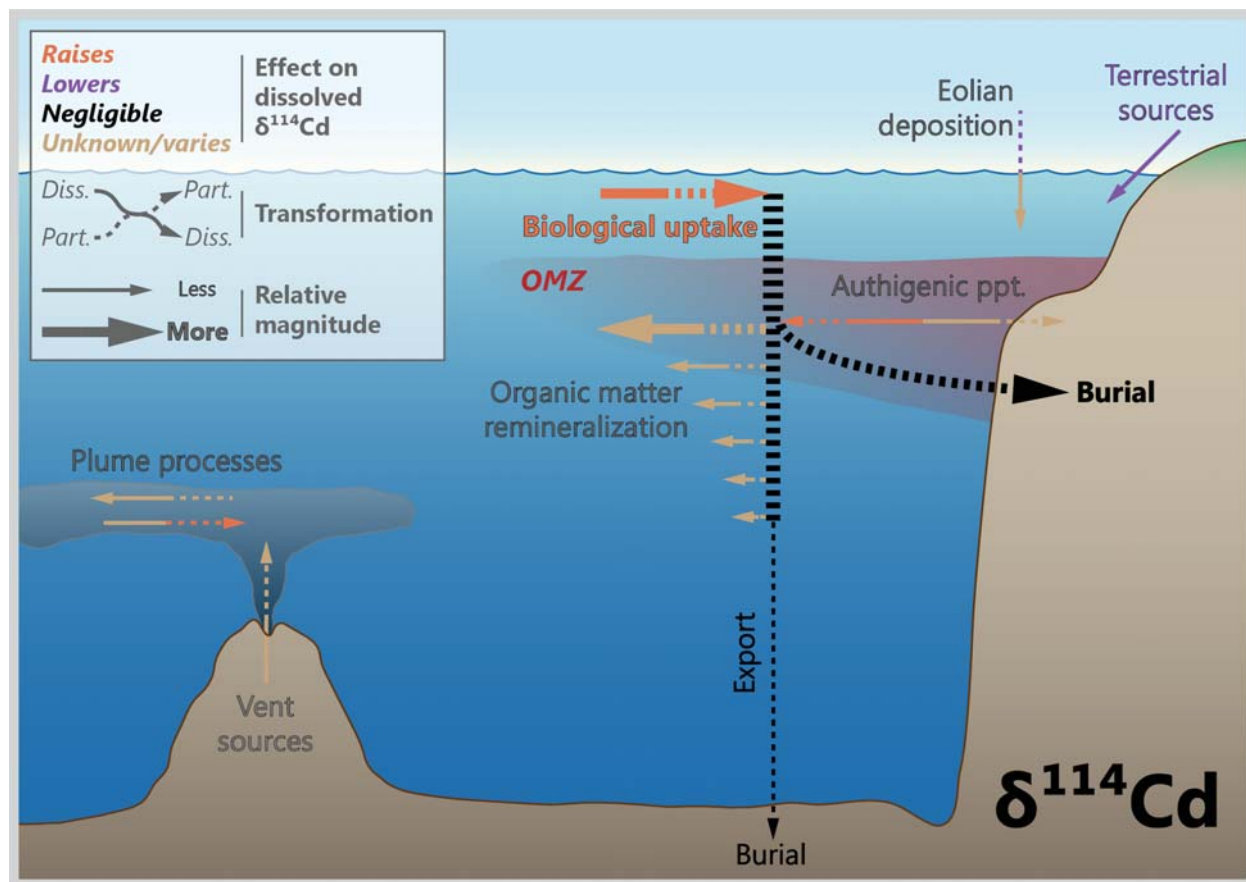
999 The past decade has seen an explosion in the number of studies employing Cd stable isotopes to investigate
 1000 marine Cd cycling. The majority of extant Cd isotope data are reported relative to the NIST SRM 3108
 1001 standard, though several earlier studies, reviewed by Rehkämper et al. (2012), were reported relative to
 1002 other in-house materials. Cross-calibration of these materials is described in detail by Abouchami et al.
 1003 (2013). While the earliest study of Cd isotope variations in seawater was unable to unambiguously identify
 1004 systematic patterns in the water column, the authors noted that cultures of phytoplankton preferentially

1005 incorporated isotopically-light Cd relative to the media (Lacan et al., 2006). Assuming biological processes
1006 were responsible for Cd uptake, this observation led to two key predictions for marine Cd isotope
1007 systematics: that Cd-depleted surface waters should exhibit isotopically ‘heavier’ compositions than Cd-
1008 replete deep waters; and, that the degree of isotopic fractionation should be proportional to the extent of Cd
1009 removal into particles. Indeed, this is precisely the pattern that was first reported by Ripperger et al. (2007).

1010 Subsequent studies have corroborated this general one-dimensional pattern in the Southern (e.g.,
1011 Abouchami et al., 2011; 2014; Xue et al., 2013; Sieber et al. 2019a), Atlantic (e.g., Xue et al., 2012; Conway
1012 & John, 2015a; Xie et al., 2017; Xie et al., 2019a), Arctic (Zhang et al., 2019), and Pacific Oceans (Yang
1013 et al., 2012; Yang et al., 2014; Conway & John, 2015b; Janssen et al., 2017; John et al., 2018; Yang et al.,
1014 2018; Xie et al., 2019b; Sieber et al., 2019b). These studies have shown that the deep ocean (>500–1,000
1015 m) is largely homogenous in Cd isotope composition ($\delta^{114}\text{Cd}$ of +0.2 to +0.3 ‰). This deep water $\delta^{114}\text{Cd}$
1016 value is heavier than the upper continental crust $\delta^{114}\text{Cd}$ signature of ~0‰ (Schmitt et al., 2009a), similar to
1017 that observed for other metals such as Zn, Ba, and Ni (Sections 4, 8, and 9.). Intermediate-depth waters
1018 relating to water masses such as Antarctic Intermediate Water (AAIW) exhibit slightly heavier $\delta^{114}\text{Cd}$
1019 values (+0.4 to +0.5 ‰), while surface waters generally exhibit heavier isotopic compositions (up to
1020 ~+1‰). As for Cd concentrations, these one dimensional $\delta^{114}\text{Cd}$ profile shapes arise largely from the
1021 combination of Southern Ocean biological processes and lateral circulation of water masses, as well as
1022 some contribution from local surface uptake and regeneration (Abouchami et al., 2014; Sieber et al., 2019b).
1023 Some studies have reported $\delta^{114}\text{Cd}$ values of up to +5 ‰ in surface waters of the northern hemisphere gyres
1024 (Ripperger et al., 2007; Xue et al., 2012; Conway & John, 2015a; 2015b), while others have reported more
1025 muted fractionation or even a switch to lighter than deep-ocean compositions in surface waters (Gault-
1026 Ringold et al., 2012; Xie et al., 2017; Janssen et al., 2017; Xie et al., 2019a; George et al., 2019; Sieber et
1027 al., 2019b; Xie et al., 2019). The origin of these extreme $\delta^{114}\text{Cd}$ values remains ambiguous.

1028 Overall, although the first-order distributions of dissolved Cd concentration and isotope composition in
1029 surface waters are consistent with intense cycling by biological processes, this range of observations
1030 suggests that the processes influencing surface Cd isotope compositions may be more complex. For
1031 example, interactions with ligands, effects arising from recycling of organic matter, differences in
1032 fractionation factor between different organisms, and supply of Cd from external Cd sources may all
1033 influence surface water dissolved $\delta^{114}\text{Cd}$. This raises three related questions to be addressed in the remainder
1034 of this section: What are the candidate biological processes that drive these patterns? How do other physical

1035 or chemical processes play a role in setting marine Cd distributions? Can Cd-based reconstructions of these
 1036 processes be used to inform on past productivity?
 1037



1038
 1039 **Figure 13 | Processes driving cadmium isotope variations in modern seawater.** Biological processes exert a
 1040 significant control on surface water Cd cycling, implying that $\delta^{114}\text{Cd}$ is broadly responsive to productivity. However,
 1041 important redox-dependent processes remain to be fully elucidated, particularly those occurring around OMZs.

1042
 1043 **6.2. Driving processes**

1044 **6.2.1. Biological**

1045 As noted above, the nutrient-like distribution of Cd implies intense biological cycling in seawater, even
 1046 though Cd is considered toxic (e.g., Waldron & Robinson, 2009). This dichotomy has inspired a significant
 1047 body of research investigating the role that Cd plays in microbial physiology. These studies showed that
 1048 Cd uptake by marine microbes exhibits three noteworthy dependencies. First, cellular Cd quotas are
 1049 strongly positively correlated with the Cd content of their environment, both in culture (see compilation by
 1050 Twining & Baines, 2013) and from oceanographic data (Middag et al., 2018). Second, microbial Cd uptake

1051 is diminished when the concentration of other divalent cations increases, particularly so for Fe, Mn, and
1052 Zn. Likewise, lower concentrations of these divalent cations cause increases in Cd uptake (e.g., Sunda &
1053 Huntsman, 2000; Cullen et al., 2003). Some diatoms have even shown capacity to substitute much of their
1054 metabolic Zn requirements with Cd (Price & Morel, 1990). Third, Cd uptake is also influenced by speciation
1055 of inorganic carbon, with low $p\text{CO}_2$ promoting higher cellular Cd quotas (e.g., Cullen et al., 1999; Cullen
1056 & Sherrell, 2005; de Baar et al., 2017). The connection between Cd and carbon speciation is particularly
1057 intriguing given the discovery of the ζ -class of carbonic anhydrase that can utilize Cd (or Zn) as the catalytic
1058 metal (e.g., Lane et al., 2005; Xu et al., 2008).

1059 Despite these dependencies, the extent to which active physiological utilization of Cd controls global
1060 patterns of Cd uptake is unclear. For example, genes encoding the ζ carbonic anhydrase metalloenzyme
1061 were not found in green algae nor coccolithophores, and were similarly absent from many species of diatom
1062 (Park et al., 2007). Thus, it is similarly plausible that some part of the biological Cd cycle is driven by
1063 organisms inadvertently removing Cd from seawater while attempting to source other metals (e.g., Boyle,
1064 1988b; Horner et al., 2013), or that microbes require Cd to populate other Cd-centered metalloenzymes that
1065 await discovery.

1066 The role of microbial physiology in mediating Cd isotope fractionation is comparatively understudied.
1067 Despite this, it appears that biological fractionation of Cd isotopes is ubiquitous; fresh- (Lacan et al., 2006)
1068 and saltwater (John & Conway, 2014) green algae, incubations of unfiltered seawater (Xue et al., 2012),
1069 heterotrophic bacteria (Horner et al., 2013), and shallow marine particles (e.g., Yang et al., 2015; Janssen
1070 et al., 2019) all indicate that biological particles accumulate isotopically-light Cd from their environment
1071 with a fractionation between -0.3 to -0.8 ‰ (Fig. 13). How—and perhaps even whether—this range of
1072 offsets is related to environmental context, experimental setup, species, or specific microbial functions is
1073 unknown.

1074

1075 *6.2.2. Chemical*

1076 The role of chemical processes in mediating global Cd distributions is the most under-constrained. Recent
1077 studies suggested that pelagic partitioning of Cd into sulfides in oxygen-minimum zones may be a
1078 significant loss term (Janssen et al., 2014; Bianchi et al., 2018; Plass et al., 2020). Moreover, the Cd isotope
1079 effect associated with sulfide precipitation identified by Guoinseau et al. (2018) is consistent with field
1080 data, and particulate Cd is known to accumulate more rapidly in sediments that are bathed by bottom waters
1081 containing low dissolved oxygen (e.g., van Geen et al., 1995; Sec. 6.3; Fig. 13). Collectively, these

1082 observations suggest a potential redox sensitivity in sedimentary Cd isotope distributions that deserves
1083 additional scrutiny. Indeed, the influence of sediments as the most important marine Cd sink can be seen in
1084 some water column profiles of $\delta^{114}\text{Cd}$ (Xie et al., 2019b). Similarly, data from the hydrothermal TAG site
1085 in the North Atlantic suggests that hydrothermal plumes may scavenge Cd from seawater, constituting a
1086 small sink of isotopically-light Cd, though this does not have an observable effect on deep ocean $\delta^{114}\text{Cd}$
1087 values outside of the plume itself (Conway & John, 2015b; Fig. 13).

1088 Other potential sources and sinks include rivers, atmospheric deposition, and sediments; however, none of
1089 these interfaces exhibit significant anomalies in Cd concentration or $\delta^{114}\text{Cd}$ in GEOTRACES-era datasets.
1090 This finding is in accord with earlier research by Martin & Thomas (1994), though there exist two possible
1091 exceptions. The first concerns the role of atmospheric aerosols, which have been invoked to explain the Cd
1092 isotope composition of surface waters in the Southwest Pacific (e.g., George et al., 2019) and South China
1093 Sea (e.g., Yang et al., 2012). Modern aerosol inputs may be largely anthropogenic in origin. Anthropogenic
1094 forms of Cd exhibit a relatively narrow range of isotopic compositions that are typically—though not
1095 always (e.g., Shiel et al., 2010)—lighter than dust-derived Cd (e.g., Bridgestock et al., 2017). Second,
1096 interactions with organic ligands have also been invoked to explain the relatively muted pattern of Cd
1097 isotope fractionation in the surface of the south Atlantic Ocean (e.g. Xie et al., 2017; Guinoiseau et al.,
1098 2018), but there are as yet no corroborating field or experimental data examining the role of organic ligands
1099 in mediating Cd isotope fractionation in seawater.

1100

1101 6.2.3. *Physical*

1102 Physical processes are similarly influential in mediating the global distribution and isotopic composition of
1103 Cd throughout the global ocean, particularly those processes occurring in the Southern Ocean. Antarctic
1104 Intermediate- and Bottom Waters masses possess higher dissolved $[\text{Cd}]:[\text{PO}_4^{3-}]$ than North Atlantic Deep
1105 Water (e.g., de Baar et al., 1994; Middag et al., 2018). Mixing between these southern- and northern-sourced
1106 water masses likely contributes to the well-known ‘kink’ in the Cd– PO_4^{3-} relationship (e.g., Frew & Hunter,
1107 1992; Elderfield & Rickaby, 2000; Quay & Wu, 2015). Why northern- and southern-sourced intermediate
1108 and deep waters possess different dissolved $[\text{Cd}]:[\text{PO}_4^{3-}]$ is debated, and likely reflects regionally-distinct
1109 fractionation of Cd and P during biological uptake (e.g., Sunda & Huntsman, 2000; Cullen et al., 2003) and
1110 during remineralization (e.g., Baars et al., 2014; Roshan & Wu, 2015). In the Atlantic, however, the
1111 importance of remineralization to deep water Cd budgets is of secondary significance: the ratio of
1112 regenerated-to-preformed $[\text{Cd}]$ is ~30 % in the mesopelagic, and generally <10 % in the deep ocean (Roshan
1113 & Wu, 2015b; Middag et al., 2018). Given the low proportion of regenerated Cd in the deep Atlantic, the

1114 ratio of dissolved $[Cd]:[PO_4^{3-}]$ and the overall distribution of $[Cd]$ are essentially governed by the
1115 $[Cd]:[PO_4^{3-}]$ of the source waters (Middag et al., 2018) and the prevailing geometry of ocean circulation,
1116 respectively (Boyle, 1988b).

1117 Recent Cd isotope data from the South Atlantic (Xie et al., 2017), South Pacific (George et al., 2019; Sieber
1118 et al., 2019a), and Arctic (Zhang et al., 2019) also support the importance of mixing in mediating deep-
1119 ocean Cd distributions, though it should be noted that the isotopic contrast between mixing end-members
1120 is small, relative to measurement precision (e.g., Janssen et al., 2017; Fig. 12). For example, biological
1121 uptake of light Cd in the source regions of intermediate waters in the surface Southern Ocean results in
1122 isotopically-heavy pre-formed $\delta^{114}Cd$ signatures being imparted to Cd-depleted intermediate water masses
1123 (e.g., +0.45 ‰ in AAIW; +0.65 ‰ in Subantarctic Mode Water, SAMW; Xue et al., 2013; Abouchami et
1124 al., 2014; Sieber et al., 2019b). Lateral circulation of these southern-sourced water masses then transfer this
1125 signature northward to intermediate depths in the Atlantic and Pacific Oceans (e.g. Xue et al., 2012;
1126 Abouchami et al., 2014; Conway & John, 2015a; Sieber et al., 2019b). This effect is more pronounced in
1127 the North Atlantic than in the Pacific, where southward flowing NADW also carries isotopically-heavy Cd
1128 southward at depths of 1,000–3,000m (Xue et al., 2012; Conway & John, 2015a).

1129

1130 **6.3. Marine archives**

1131 *6.3.1. Carbonates*

1132 There is a long history of Cd concentration measurements in marine carbonates, particularly corals and
1133 foraminifera, most commonly reported as Cd:Ca molar ratios. In principle, carbonates are an appealing
1134 archive of ambient Cd chemistry since inorganic partition coefficients are $\gg 1$ (e.g., Tesoriero & Pankow,
1135 1996) and the Cd:Ca of many types of carbonate exhibit a strong proportionality with ambient dissolved
1136 $[Cd]$. In practice, however, most biogenic carbonates exhibit partition coefficients closer to unity (Boyle,
1137 1988b), and resultant Cd:Ca is also sensitive to the species (Boyle, 1992) and temperature of calcification
1138 (e.g., Rickaby & Elderfield, 1999). As such, Cd:Ca in carbonates has found the most utility where ambient
1139 dissolved $[Cd]$ —and attendant carbonate Cd:Ca—exceeds several 100 pmol kg^{-1} , such as in tracing
1140 industrial fallout (e.g., Shen et al., 1987) or in studies of Quaternary deep ocean circulation (e.g., Boyle &
1141 Keigwin, 1985; van Geen et al., 1992; Adkins et al., 1998; Farmer et al., 2019).

1142 There are far fewer studies examining the Cd isotope composition of marine carbonates as tracers of
1143 historical Cd isotope chemistry. Inorganic partitioning experiments indicate that Cd isotopes are
1144 fractionated during incorporation into calcite by $\approx -0.5 \text{ ‰}$ (Horner et al., 2011). The isotopic effect is

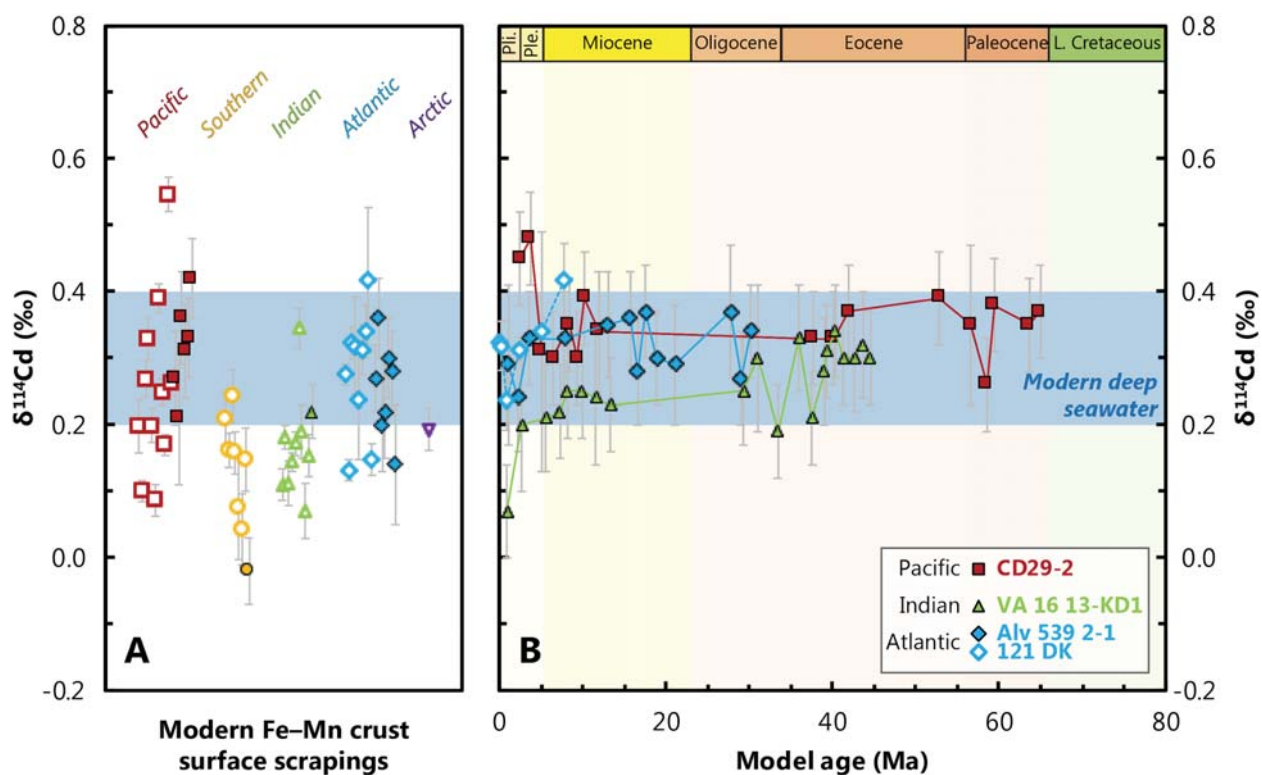
1145 temperature- and Mg-independent, but vanishes at low salinity. This inorganic calibration has been used to
1146 interpret patterns of Cd isotope fractionation preserved in bulk carbonates from the Neoproterozoic Eon
1147 (1,000–541 Ma). The variations in these sediments are interpreted as evidencing changes in biological
1148 productivity (e.g., Hohl et al., 2017) and Cd sinks (e.g., John et al., 2017) through time. Applications of Cd
1149 isotopes to foraminifera to study problems in Quaternary paleoceanography are precluded by the large
1150 sample requirements; obtaining 1 ng of Cd—the minimum quantity needed for a reasonable isotope
1151 measurement (Ripperger & Rehkämper, 2007; Schmitt et al., 2009b)—requires picking (and cleaning) of
1152 10's of mg of foraminiferal tests. Alleviation of such limitations awaits development of automated picking
1153 and screening systems, or vast improvements in ion transmission efficiency for isotope ratio mass
1154 spectrometry.

1155

1156 6.3.2. *Ferromanganese sediments*

1157 Ferromanganese sediments have shown the most promise for recording deep-ocean Cd isotope chemistry.
1158 Both ferromanganese nodules (Schmitt et al., 2009a) and crusts (Horner et al., 2010) reflect ambient
1159 seawater Cd isotope compositions with negligible fractionation (Fig. 14A), consistent with Cd–Mn-
1160 oxyhydroxide partitioning experiments conducted at high ionic strength that show only minor Cd isotope
1161 fractionation (Wasylenki et al., 2014). Cadmium is predicted to have a similar diffusivity in Fe–Mn crusts
1162 to Hf (Horner et al., 2010), implying that long-term records are likely to exhibit some diffusive smoothing
1163 while preserving larger variations (e.g., Henderson & Burton, 1999). As with Zn and Cu isotopes however,
1164 time-resolved records of $\delta^{114}\text{Cd}$ recovered from Fe–Mn crusts indicate minimal variation over the last 20
1165 Myr, and perhaps even the Cenozoic (Fig. 14B); modeling conducted by Murphy (2016) suggests that Cd
1166 diffusion may occur much faster than predicted by the diffusion model of Henderson & Burton (1999). If

1167 so, the lack of variation in $\delta^{114}\text{Cd}$ over the Cenozoic may simply reflect a ‘resetting’ of all crust layers
 1168 toward modern deep-ocean Cd isotope compositions.



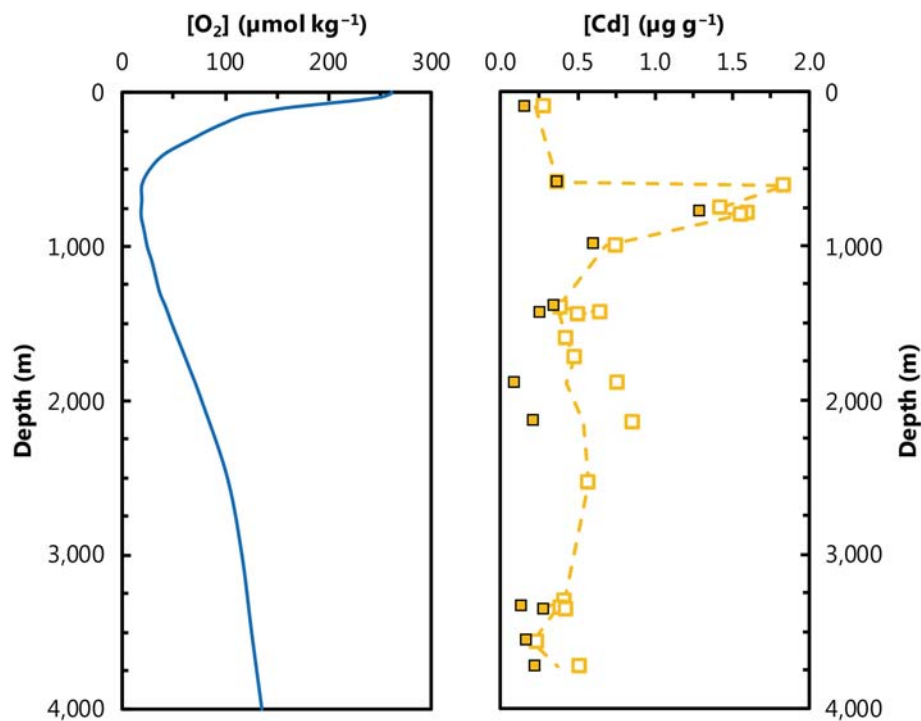
1169
 1170 **Figure 14 | Ferromanganese crusts records of deep-water Cd isotope compositions. (A)** Compilation of ‘core-
 1171 top’ Fe–Mn crust $\delta^{114}\text{Cd}$; data from Schmitt et al. (2009a; open symbols) and Horner et al. (2010; closed symbols). In
 1172 general, Southern Ocean samples exhibit lighter $\delta^{114}\text{Cd}$ than other basins, consistent with profiles of $\delta^{114}\text{Cd}$ (e.g., Fig.
 1173 12). **(B)** Cenozoic records of deep-water $\delta^{114}\text{Cd}$ recovered from four Fe–Mn crusts; data from Murphy, 2016 (closed
 1174 symbols) and Schmitt et al. (2009a; open symbols). These records have been plotted using the authors’ preferred age
 1175 models, meaning that there are some differences between the chronology of CD29-2 shown here compared to Fig. 5.
 1176 Such differences may be immaterial however, given that Cd isotopes in Fe–Mn crusts are potentially subject to diffusive
 1177 ‘resetting’ over time (Murphy, 2016).

1178
 1179 **6.3.3. Organic-rich sediments**

1180 Organic-rich sediments are the principal sink of dissolved Cd from the modern oceans (e.g., Rosenthal et
 1181 al., 1995; van Geen et al., 1995; Little et al., 2015). A significant fraction of the total Cd in organic-rich
 1182 sediments is derived from sinking organic matter. Accordingly, the Cd content of organic-rich sediments
 1183 has been applied as a proxy for past productivity (e.g., Brumsack, 2006). However, there is also a redox
 1184 sensitivity: Cd contents are generally elevated in organic-rich sediments that are bathed by low-oxygen
 1185 waters (Fig. 15). This enrichment likely derives from three processes. First, low-oxygen environments may
 1186 limit oxidation—and thus favor preservation—of settling Cd sulfide particles formed in the water column.
 1187 Second, the chalcophile nature of Cd means that even trace levels of hydrogen sulfide may cause Cd to (co-

1188)precipitate. Thus, as organic matter is remineralized within the sediment column, any Cd liberated to
 1189 porewaters is proportionally more likely to re-precipitate into sulfide minerals, relative to harder metals
 1190 (and carbon), effectively ‘trapping’ remineralized Cd in sediments (e.g., Rosenthal et al., 1995). Third,
 1191 recent evidence suggests that Cd may also directly (co-)precipitate from seawater and into sediments when
 1192 plumes of hydrogen sulfide interact with bottom waters (e.g., Xie et al., 2019b; Plass et al., 2020). The
 1193 relative importance of these three processes to the O₂-dependent pattern of Cd accumulation remains to be
 1194 fully elucidated.

1195 While the contribution of organic-rich sediments to the isotopic mass balance of Cd is presently unknown,
 1196 their significance to the marine Cd budget suggests that, globally, the Cd isotope composition of these
 1197 sediments should balance the riverine flux $\delta^{114}\text{Cd} \approx +0.1 \pm 0.1\%$ (Lambelet et al., 2013). Alternatively, the
 1198 other minor sinks of Cd—carbonates, ferromanganese oxides, clays—must possess large isotopic offsets
 1199 relative to seawater, which seems unlikely given existing field and experimental data. Obtaining modern
 1200 calibrations of Cd isotope partitioning into organic-rich sediments should be considered a priority.



1201
 1202 **Figure 15 | Cadmium concentrations in California Margin sediments.** Left: Regionally-representative dissolved
 1203 [O₂] profile from the northeast Pacific showing broad minimum between 600–800 m. Profile from 35.5°N, 122.5°W (from
 1204 World Ocean Atlas; Garcia et al., 2013). Right: Solid-phase Cd concentrations for northeast Pacific core-top (closed
 1205 symbols) and “slightly deeper” (8–10 cm; open symbols) sediment samples; dashed line indicates arithmetic mean.
 1206 These samples evidence a maximum in authigenic Cd deposition at the top of the OMZ, which may originate from
 1207 processes occurring in the water or sediment column.

1208

1209 **6.4 Prospects**

1210 The overview provided above indicates that Cd participates in marine biological processes and that its
 1211 distribution is sensitive to the biological productivity of the oceans. How this sensitivity is transcribed into
 1212 marine sediments remains uncertain, however. Additionally, there are several other processes that have the
 1213 potential to render isotope effects that require further exploration before Cd isotopes can be solely
 1214 interpreted as a productivity proxy, such as: biological fractionation effects, authigenic transformations,
 1215 and redox sensitivities. Relatedly, the fidelity of many types of marine sediment to record ambient Cd
 1216 isotope chemistry remain inadequately constrained. With these two themes in mind, we suggest several
 1217 areas for additional research that may help to address the overarching question as to whether Cd isotope-
 1218 based reconstructions can be used to inform on past ocean productivity.

1219

1220 **6.4.1. Modern**

1221 Several questions persist regarding the modern Cd isotope cycle. We list five of the most pressing below
 1222 and offer possible remedies to each.

- 1223 ● Are the ‘extreme’ (i.e., $\delta^{114}\text{Cd}$ of + 5 ‰; Fig. 12) values seen in surface waters of the northern-
 1224 hemisphere gyres real? That is, are these heavy compositions true oceanographic features that are
 1225 absent from the southern hemisphere, or do they represent analytical artifacts unique to MC-ICP-
 1226 MS? This issue will require intercalibration between the two main approaches—the other being
 1227 thermal ionization mass spectrometry (TIMS)—that various groups use to measure Cd isotopes in
 1228 seawater.
- 1229 ● To what extent do local Cd isotope compositions in surface waters reflect larger-scale processes?
 1230 Addressing this issue will require elucidating the role of organismal uptake, ligands, and mixing,
 1231 which would benefit from conducting additional experimentation with plankton, coupling of
 1232 isotope methods with electrochemistry, and numerical modeling, respectively.
- 1233 ● Is there a ‘Redfield’ stoichiometry for Cd in organic matter? If so, what controls it? Existing culture
 1234 (Ho et al., 2003) and field (Ohnemus et al., 2017) data suggest a wide range of cellular Cd:P, which

1235 have been suggested as reflecting species and local supply ratios, respectively (in addition to the
 1236 aforementioned feedback interactions). Further experimentation with model organisms is needed.

1237 ● Do all organisms contribute to Cd isotope fractionation in seawater? Uptake of Cd into cells is
 1238 widespread, whereas the genes encoding the ζ -class of carbonic anhydrases are not. Again, further
 1239 experimentation with marine-relevant organisms is necessary.

1240 ● How are the ‘light’ Cd isotope compositions seen in suspended particles above oxygen-minimum
 1241 zones related to those putatively accumulating in sediments? Do these values relate to sulfide
 1242 precipitation and what is their influence on the global mass balance? What controls the Cd isotope
 1243 composition of these particles? Addressing these questions will require examining the Cd isotope
 1244 composition of particles from oxygen-rich oceanographic regions, identifying whether processes
 1245 associated with particle regeneration affect Cd isotope compositions, and surveying core-top
 1246 sediments.

1247

1248 *6.4.2. Paleo*

1249 As with the modern cycle, several ambiguities persist, though the most pressing relates to archives. Indeed,
 1250 it appears that a major obstacle preventing the widespread application of Cd isotope-based proxies in
 1251 paleoceanography has been the lack of suitable archives.

1252 ● Concerning carbonates, the main question is still whether it is possible to isolate sufficient
 1253 quantities of foraminiferal-bound Cd to reconstruct past seawater $\delta^{114}\text{Cd}$. Does species matter, or
 1254 can mixed assemblages be used?

1255 ● For organic-rich sediments, the role of biology itself must be considered. That is, how important
 1256 might it be that different organisms exhibit different magnitudes of Cd isotope fractionation (and
 1257 Cd:C stoichiometry)? If important, how best to interpret Cd isotope records—species, evolutionary
 1258 innovations, productivity?

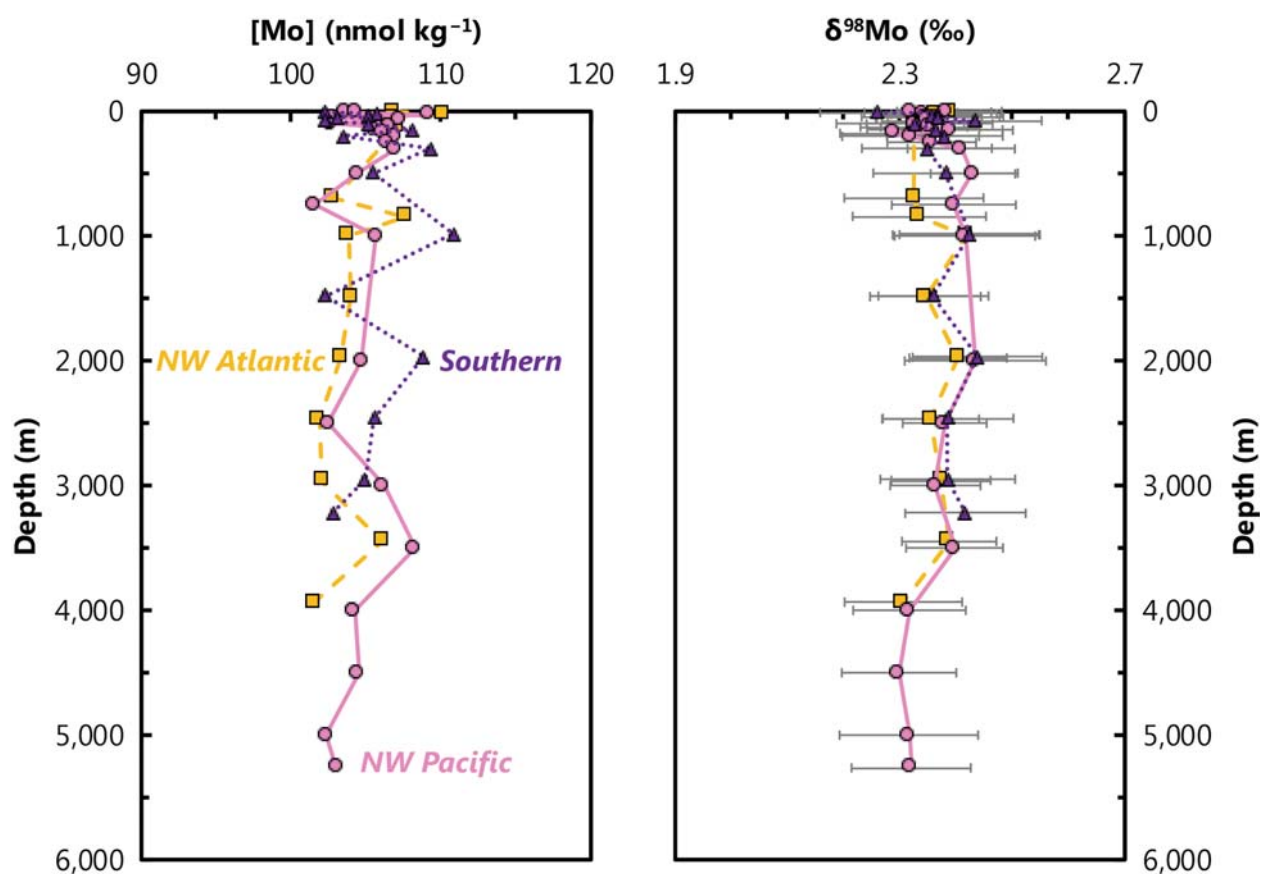
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1260

1261 **7. Molybdenum**

1262 **7.1. Marine distribution**

1263 Today, Mo is one of the most abundant trace metals in seawater (Morris, 1975; Bruland 1983; Collier 1985).
 1264 Molybdenum possesses a long residence time (~440,000 yr; Miller et al., 2011), is conservative with respect
 1265 to salinity, and exhibits a uniform isotopic composition in oxygenated seawater (e.g., Barling et al., 2001;
 1266 Siebert et al., 2003). Based on 168 seawater samples from the Atlantic, Pacific, and Southern Oceans
 1267 analyzed by Nakagawa et al. (2012), the average salinity-normalized dissolved [Mo] and $\delta^{98}\text{Mo}$ of the ocean
 1268 are $107 \pm 6 \text{ nmol kg}^{-1}$ and $+2.36 \pm 0.10 \text{ ‰}$, respectively (both values $\pm 2 \text{ SD}$; Fig. 16).

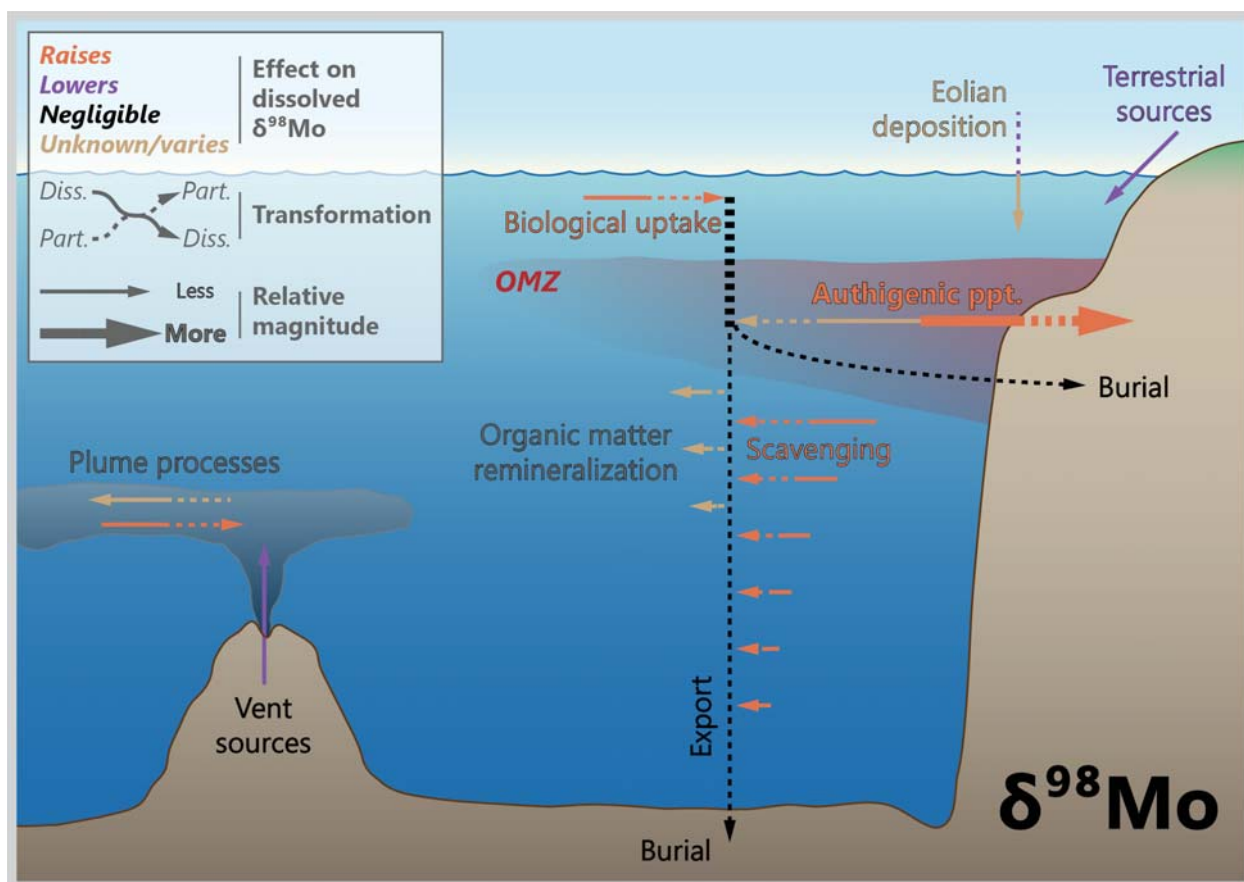


1269
 1270 **Figure 16 | Representative profiles of dissolved Mo concentrations ([Mo]) and Mo-isotopic compositions**
 1271 **($\delta^{98}\text{Mo}$) in the Northwest Atlantic (squares, dashed line), Southern (triangles, dotted line), and Northwest**
 1272 **Pacific (circles, solid line) Oceans. This comparison illustrates that the dissolved behavior of Mo is essentially**
 1273 **invariant throughout the global oceans.**

1274
 1275 Given that no significant gradients in dissolved [Mo] are expected, there are few new open-ocean $\delta^{98}\text{Mo}$
 1276 data measured as part of GEOTRACES. However, dissolved [Mo] has been measured on two
 1277 GEOTRACES transects (GP16 and GA02), demonstrating four intriguing instances where [Mo] deviated

1278 from an otherwise conservative distribution. These instances are briefly described below and covered in
1279 detail by Ho et al. (2018). First, the most significant dissolved [Mo] anomalies (~5 % drawdown) are
1280 associated with intense scavenging by particulate Fe (oxy)hydroxides close to the Peruvian OMZ. Second,
1281 dissolved [Mo] is slightly drawn down (<5 %) in some samples directly above the East Pacific Rise
1282 hydrothermal ridge crest, again mostly likely driven by scavenging onto hydrothermally-derived Fe–Mn
1283 oxides. Some Mo drawdown is also observed in some far-field hydrothermal samples, though the
1284 mechanism is unclear. Third, following normalization to a salinity of 35, surface seawater shows a minor
1285 dissolved [Mo] drawdown, implying either biological uptake or adsorption to biotic particles. Though not
1286 a true oceanographic feature, a fourth type of dissolved Mo anomaly is also noteworthy: bottle storage
1287 artefacts. Ho et al. (2018) found that many samples with initially low values showed an increase in dissolved
1288 [Mo] with increasing storage time, implying a change in Mo speciation to a form that is detectable by ICP-
1289 MS. In contrast to the relative constancy of dissolved [Mo] in open ocean settings, there are a number of
1290 studies of showing striking dissolved Mo variations in coastal and estuarine systems (e.g., Dalai et al., 2005;
1291 Dellwig et al., 2007; Joung and Shiller, 2016; Wang et al., 2016) as well as in modern restricted settings,
1292 such as the Black and Baltic Seas (Nägler et al., 2011).

1293



1294

1295 **Figure 17 | Processes driving molybdenum isotope variations in modern seawater.** While biological processes
 1296 may exert a slight influence on surface water Mo distributions, the main drivers of marine Mo cycling are related to the
 1297 balance between scavenging pathways, which are redox dependent.

1298

1299 7.2. Driving processes

1300 7.2.1. Biological

1301 Molybdenum is a bio-essential micronutrient required by enzymes that catalyze key reactions in the global
 1302 C, N, and S cycles (Mendel & Bittner, 2006). Importantly, Mo is a co-factor of the primary nitrogenase
 1303 enzyme complex, meaning that Mo is required for energy-efficient nitrogen fixation. Additionally, Mo is
 1304 required for over 30 other enzymes that control biologically essential redox processes (Kendall et al., 2017).
 1305 Despite its biological importance, biological activity does not appear to be a dominant process in setting
 1306 the distribution of Mo in seawater (Fig. 17), likely due to the high abundance of Mo in the modern ocean.
 1307 Results from the East Pacific Zonal Transect do, however, suggest some Mo removal by biological uptake
 1308 and/or adsorption onto biogenic particles within regions of elevated chlorophyll (Ho et al., 2018).
 1309 Experimental data indicate that biological uptake of Mo imparts a small negative isotope fractionation on
 1310 the order of 0.3 ‰ (Wasylenki et al., 2007).

1311 Enhanced removal of Mo from seawater in regions with high export of organic carbon likely explains some
1312 of the non-conservative behavior observed in modern coastal regions. A significant relationship between
1313 Mo and total organic carbon has also been observed in marine euxinic sediments (e.g. Helz et al., 1996;
1314 Algeo & Lyons, 2006; McManus et al., 2006; Lyons et al., 2009). Furthermore, it has been shown that Mo
1315 interactions with organic matter can control Mo cycling in both soils (Wichard et al., 2009; King et al.,
1316 2014, 2016; Marks et al., 2015; Siebert et al., 2015) and marine sediments (Wagner et al., 2017; Tessin et
1317 al., 2019). The formation of Mo complexes containing organic ligands has been proposed as an explanation
1318 for the correlation between sedimentary Mo and organic carbon, suggesting that organic matter may play
1319 an important role in both the delivery and burial of Mo in sediments (Wagner et al., 2017). Accordingly, it
1320 is possible that Mo accumulation in marine sediments is linked to export production and, more specifically,
1321 delivery and burial of organic carbon in sediments.

1322

1323 *7.2.2. Chemical*

1324 Due to the long residence time and abundance of Mo, non-conservative Mo behavior is typically localized
1325 to areas with high particle concentrations, such as close to the continental margin, in the euphotic ocean, or
1326 around hydrothermal vents (e.g., Goto et al., 2020). In the present oxic water column, Mo is present
1327 primarily as the oxyanion molybdate (MoO_4^{2-}) and Mo sorption onto Mn oxyhydroxides represents the
1328 most significant modern Mo sink (Fig. 17; Bertine & Turekian, 1973; Scott & Lyons, 2012). Since the Fe–
1329 Mn oxide sink preferentially incorporates isotopically light Mo from seawater with an isotopic effect of
1330 ≈ 3.0 ‰, the fraction of Mo that is buried in Fe–Mn oxides exerts a major control over the Mo isotope
1331 composition of seawater.

1332 In the presence of sulfide, the oxygen atoms in molybdate are progressively substituted for sulfur, producing
1333 particle reactive thiomolybdate species ($\text{MoO}_{4-x}\text{S}_x^{2-}$; Erickson & Helz, 2000; Vorlicek et al., 2015).
1334 Dissolved Mo can thus be strongly drawn down in sulfidic environments, such as the Black Sea.
1335 Importantly, this drawdown occurs with a small, but non-zero isotope effect of $\approx 0.5 \pm 0.3$ ‰, whereby
1336 isotopically light Mo is preferentially scavenged (e.g., Nägler et al., 2011). Thiomolybdate is also
1337 scavenged in from sulfidic sediment porewaters leading to significant Mo accumulations within sediments
1338 deposited in anoxic and euxinic environments (e.g., Emerson & Husted, 1991; Crusius et al., 1996; Scott
1339 & Lyons, 2012). Long-term Mo burial is associated with Fe–S minerals (Chappaz et al., 2014; Vorlicek et
1340 al., 2018) and/or organic matter (Dahl et al., 2017; Tessin et al., 2019), depending on the biogeochemical
1341 conditions prevailing at a given basin.

1342

1343 **7.2.3. Physical**

1344 The residence time of dissolved Mo is significantly longer than the mixing time of the ocean (Table 1).
 1345 Thus, variations in dissolved [Mo] and $\delta^{98}\text{Mo}$ are not influenced by the geometry of modern overturning
 1346 circulation. Whole-ocean changes in dissolved [Mo] and $\delta^{98}\text{Mo}$ are, however, possible, and much of what
 1347 we know about such changes is gleaned from studies of the geological past, particularly during periods of
 1348 ocean anoxia. Based on this research, it has been suggested that during intervals of lower ocean
 1349 oxygenation, the ocean Mo inventory may have been low enough to limit marine primary productivity
 1350 (Anbar & Knoll, 2002; Algeo, 2004; Glass et al., 2009; Reinhard et al., 2013). This limitation has been
 1351 demonstrated in certain lake ecosystems (Goldman, 1960; Glass et al., 2012). Under strongly euxinic
 1352 conditions ($[\text{H}_2\text{S}]_{\text{aq}} > 11 \mu\text{M}$), thermodynamic calculations predict that tetrathiomolybdate (MoS_4^{2-}) becomes
 1353 the most predominant species (Erickson and Helz, 2000), which can result in quantitative Mo drawdown
 1354 from seawater into seawater with negligible isotope fractionation. Evidence from Lake Cadagno, the Black
 1355 and Baltic Seas, and seasonally anoxic fjords supports the occurrence of near-quantitative drawdown of Mo
 1356 from seawater in these environments (Neubert et al., 2008; Dahl et al., 2010; Nägler et al., 2011;
 1357 Noordmann et al., 2015). Indeed, this hypothesis is the foundation of several paleoceanographic studies that
 1358 assume that the sedimentary Mo isotopic signatures, deposited in euxinic settings, faithfully capture the
 1359 $\delta^{98}\text{Mo}$ of oxygenated (surface) seawater and can be further interpreted in terms of the fraction of the seafloor
 1360 that is oxygenated (e.g., Kendall et al., 2015; Dickson, 2017).

1361

1362 **7.3. Sedimentary archives**

1363 The majority of Mo paleoceanographic studies focus on the measurement of Mo concentrations and
 1364 isotopes within bulk sediments. While many applications of Mo within the sedimentary record focus on
 1365 early Earth, Mo proxies have been used to constrain environmental conditions in the Holocene (e.g.
 1366 Hardisty et al., 2016; van Helmond et al., 2018) and Pleistocene (e.g. Dean et al., 2006; Scholz et al., 2017).
 1367 However, Mo and its isotopes are predominantly used as tracers of redox conditions and not productivity.

1368 Research on biological archives of Mo concentrations and isotopes has met with mixed results. Research
 1369 examining $\delta^{98}\text{Mo}$ in corals indicates that corals may accurately record seawater Mo isotope concentrations
 1370 (Voegelin et al., 2009). However, follow-up studies suggested a temperature-dependent fractionation
 1371 between seawater and corals that is related to the activity of symbiotic zooxanthellae (Wang et al., 2019b).
 1372 Moreover, bivalve shell Mo:Ca ratios have been determined to have no relationship to oceanographic

1373 conditions (Vihtakari et al., 2017), whereas Tabouret et al. (2012) suggest a mechanism related to trophic
1374 uptake, but not to ambient dissolved [Mo]. A third study proposed that Mo:Ca peaks in bivalve carbonate
1375 are controlled by ingestion of phytoplankton grown on nitrate due to high concentrations of Mo associated
1376 with nitrate reductase, indicating that bivalves may provide an archive for surface water nitrate uptake and
1377 a potential proxy for the balance between new and regenerated productivity (Thebault et al., 2009).

1378

1379 **7.4. Prospects**

1380 At present, it does not appear that bulk sediment $\delta^{98}\text{Mo}$ will be useful for reconstructing biological
1381 productivity, even though Mo is cycled by organic matter both actively (e.g., Liermann et al., 2005;
1382 Wasylenki et al., 2007) and passively (e.g., Kowalski et al., 2013; King et al., 2018). That we see no
1383 pathway to using Mo as a productivity tracer reflects, in part, the difficulty in disentangling biological
1384 processes that exert relatively modest Mo isotope fractionations from those associated with thiomolybdate
1385 transformations (Tossell, 2005), or scavenging processes that possess large fractionation effects (e.g., Mn-
1386 or Fe-oxide scavenging; Siebert et al., 2003; Barling & Anbar, 2004; Wasylenki et al., 2008; Brucker et al.,
1387 2009; Goldberg et al., 2009; 2012). Additionally, within the modern ocean and likely within the recent
1388 geologic past, the global ocean reservoir of Mo is too large and well mixed for biological associated
1389 fractionations to significantly impact the global Mo isotopic composition.

1390 The use of bulk sedimentary Mo concentrations as a proxy for export of organic carbon to the seafloor is
1391 more promising, but numerous caveats exist. Specifically, other mechanisms for enhanced delivery,
1392 sequestration, and burial complicate any efforts to quantitatively relate Mo enrichments to increased export
1393 productivity (e.g., Scholz et al., 2017). Redox conditions and, in particular, the presence of sulfide in the
1394 water column and sediment pore waters will be a primary control on Mo accumulation (e.g., Hardisty et al.,
1395 2018). Sedimentary Mo enrichments can also be produced through shuttling of Mo adsorbed to the surface
1396 of Fe and Mn oxides to the seafloor (Algeo & Lyons, 2006; Algeo & Tribovillard, 2009; Dellwig et al.,
1397 2010; Scholz et al., 2013). At a minimum, independent constraints on water column and pore water redox
1398 conditions using Fe speciation, other trace metals and/or fossil redox proxies are required before an
1399 argument can be made relating Mo concentrations to export productivity. Additionally, the quantitative
1400 relationship between Mo and organic carbon may be impacted by aqueous Mo concentrations, which may
1401 have varied over Earth's history, or if depositional environments become restricted (i.e., Mo drawdown
1402 leads to a lower Mo:TOC ratio; Algeo & Lyons, 2006). Conversely, the utility of bulk sediment Mo

1403 concentrations and isotopes may lie in constraining redox conditions to improve the interpretation of other
1404 trace metal proxies that are more strongly controlled by primary and/or export productivity.

1405 The most promising future avenue for Mo-based productivity proxies may emerge from fossil-specific
1406 measurements of Mo concentrations (and perhaps $\delta^{98}\text{Mo}$). Currently, research has focused on large fossils
1407 (corals and bivalves) and has led to mixed results on the utility of Mo in reconstructing productivity-related
1408 parameters. However, analytical progress may allow for measurement of smaller sample sizes, which may
1409 provide opportunities to explore new archives of past marine Mo geochemistry.

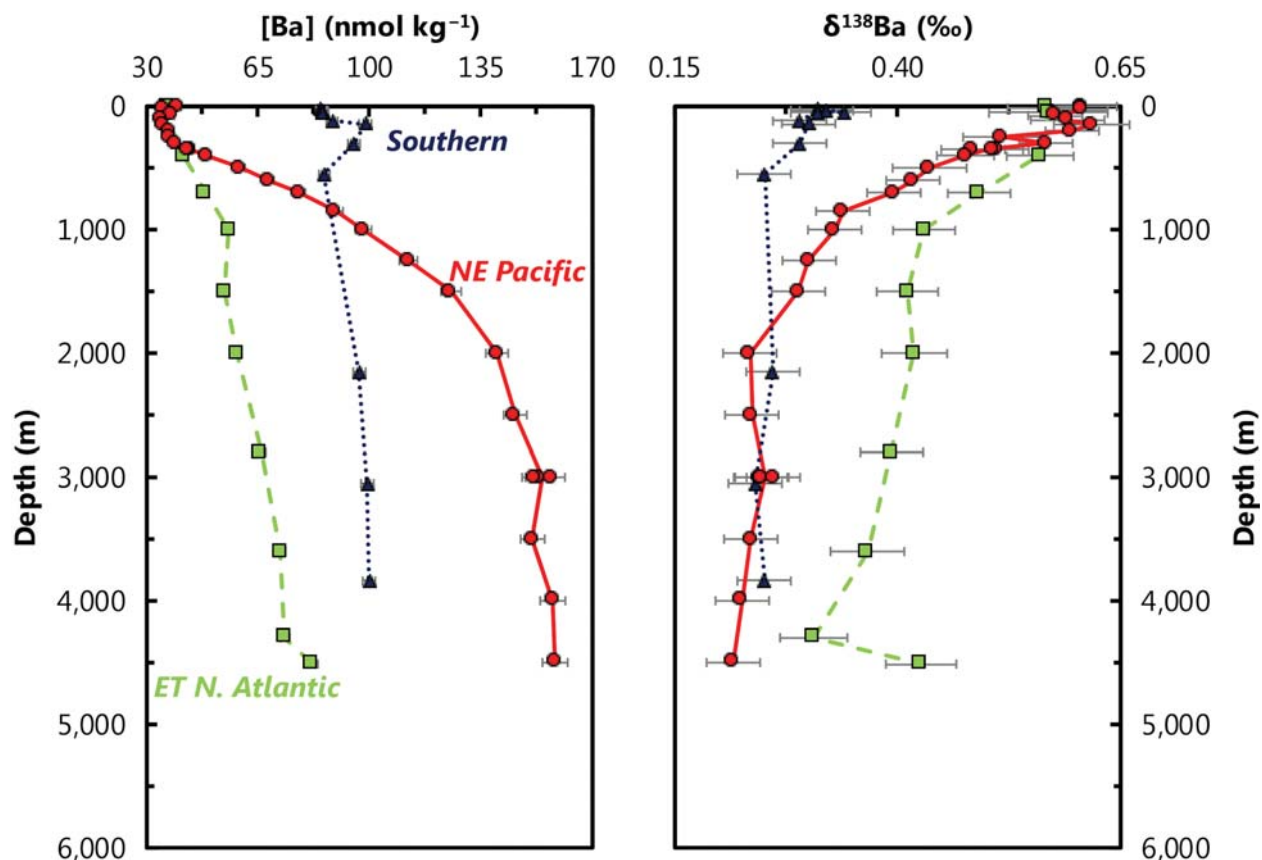
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1412

1413 **8. Barium**

1414 Barium is a widely-used tracer of marine export production, past and present. This section provides an
 1415 overview of marine Ba geochemistry, focusing on driving mechanisms, palaeoceanographic applications,
 1416 and emerging insights from Ba stable isotopes. We close by suggesting several areas for additional research.



1417
 1418 **Figure 18 | Representative profiles of dissolved Ba concentrations ($[Ba]$) and Ba-isotopic compositions ($\delta^{138}Ba$)**
 1419 **from the Eastern Tropical North Atlantic (squares, dashed line), northeast Pacific (circles, solid line), and**
 1420 **Southern (triangles, dotted lines) Oceans. This comparison illustrates that the oceanographic processes leading to**
 1421 **distinct dissolved concentration profiles render significant changes in dissolved $\delta^{138}Ba$ between basins.**

1422

1423 **8.1. Marine distribution**

1424 The nutrient-like distribution of dissolved Ba has been documented in the literature since the 1970's (e.g.,
 1425 Wolgemuth & Broecker, 1970). However, it was not until later in the decade that the GEOSECS Program
 1426 fully revealed the three-dimensional marine distribution of Ba (e.g., Chan et al., 1976; 1977). These
 1427 geochemical ocean sections highlighted vertical, zonal, and meridional variations in dissolved $[Ba]$ related
 1428 to the major biogeochemical and hydrographic features of the ocean. In nutrient-depleted surface waters,
 1429 dissolved $[Ba]$ exhibits low concentrations between 35–45 nM. Similarly, nutrient-replete deep waters are

1430 enriched in [Ba], though typically by no more than a factor of four above surface values. The spatial
1431 resolution of GEOSECS illustrated the importance of hydrography; [Ba] increases along the meridional
1432 overturning circulation from ≈ 50 nM in deep waters of the North Atlantic, to ≈ 90 nM in the Southern Ocean,
1433 up to ≈ 180 nM in the deep northeast Pacific (Fig. 18; Chan et al., 1976; 1977).

1434 Though it was long suspected that the major dissolved–particulate transformation of Ba was related to the
1435 mineral barite (BaSO_4 ; e.g., Chow & Goldberg, 1960; Turekian, 1968), this was not confirmed until the
1436 1980's (e.g., Dehairs et al., 1980; Bishop, 1988). Barite crystals are now recognized as an ubiquitous
1437 component of marine particulate matter, with up to 10^4 discrete, micron-sized crystals present per L of
1438 seawater (Dehairs et al., 1980). However, the distribution of particulate BaSO_4 is distinct from primary
1439 biogenic phases that exhibit Martin-like distributions with maxima in the euphotic zone. The minimum
1440 particulate Ba concentration is typically situated in the euphotic zone and the maximum slightly below,
1441 usually in the upper mesopelagic (e.g., Ohnemus & Lam, 2015; Ohnemus et al., 2019). This distribution
1442 likely reflects the fact that neither Ba nor BaSO_4 are utilized for physiological processes by any of the major
1443 marine primary producers. Particulate Ba fluxes are nevertheless strongly correlated with export
1444 productivity in well-oxygenated environments (e.g., Bishop, 1988; Dymond et al., 1992; Francois et al.,
1445 1995; Dymond & Collier, 1996; McManus et al., 2002) and therefore sedimentary Ba abundances have
1446 been widely used as a proxy to reconstruct past changes in ocean export production (e.g., Francois et al.,
1447 1995; Paytan et al., 1996; Paytan & Griffith, 2007 and references therein; Costa et al., 2016, Winckler et
1448 al., 2016).

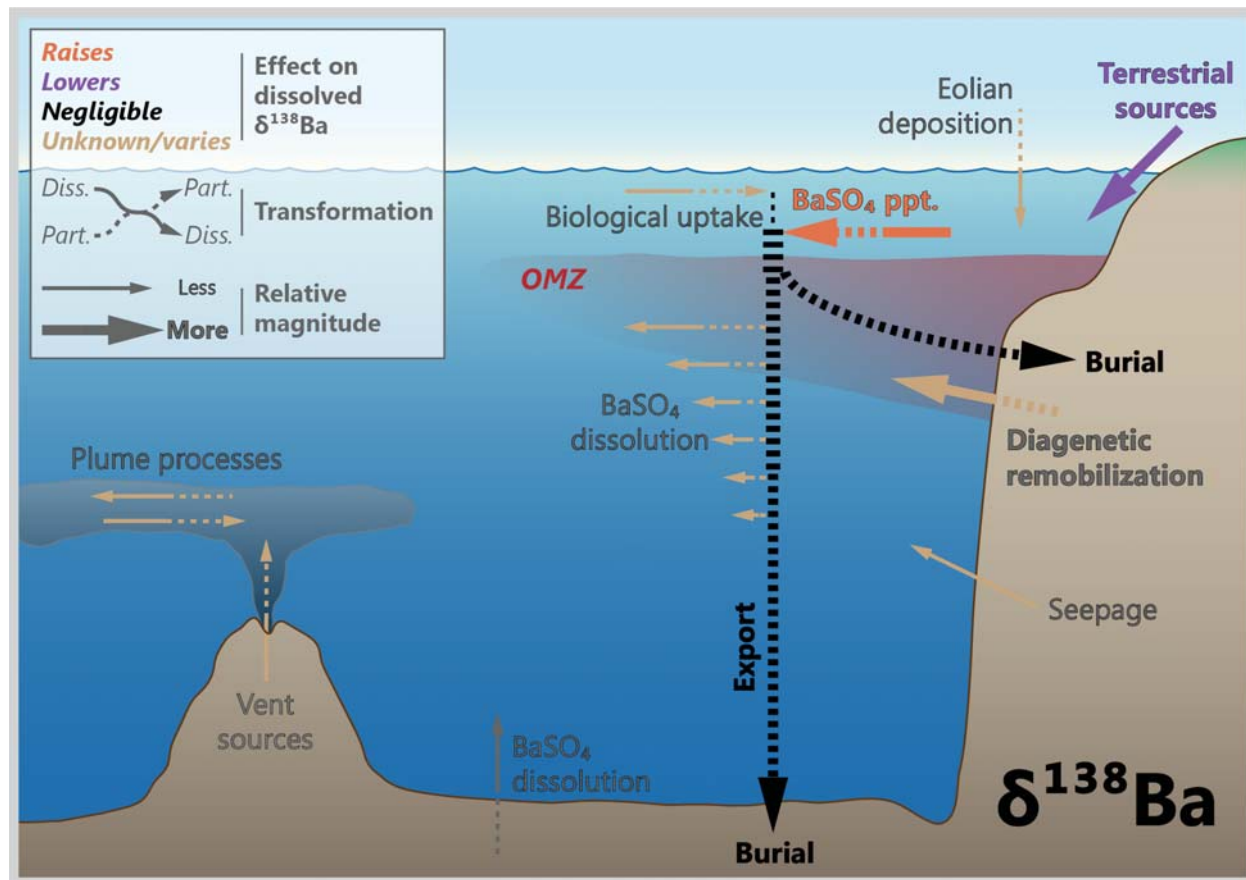
1449 Recent studies of Ba stable isotope geochemistry have added a new dimension with which to study marine
1450 Ba cycling. Von Allmen et al. (2010) first reported that isotopically light Ba is preferentially incorporated
1451 into BaSO_4 , with a particulate–dissolved Ba-isotopic offset of ≈ -0.3 ‰. The direction of this offset implies
1452 that residual solutions, such as seawater, should exhibit Ba-isotopic compositions heavier than those of
1453 sedimented BaSO_4 . This was corroborated for Atlantic seawater by Horner et al. (2015a), showing that
1454 dissolved $\delta^{138}\text{Ba}$ displays a mirror image of dissolved [Ba]: Ba-depleted surface water masses exhibited
1455 ‘heavy’ Ba-isotopic compositions ($\approx +0.6$ ‰), whereas Ba-replete deep waters possessed ‘lighter’ values
1456 $\approx +0.3$ ‰. (Notably, all values are considerably heavier than the upper continental crust, which possesses
1457 $\delta^{138}\text{Ba} \approx 0.0 \pm 0.1$ ‰; Nan et al., 2018.) Similar patterns have since been corroborated in other ocean basins
1458 (Bates et al., 2017; Hsieh & Henderson, 2017; Bridgestock et al., 2018; Geyman et al., 2019; Cao et al.,
1459 2020; Fig. 18).

1460 These isotopic studies have yielded a number of novel insights into the marine Ba cycle. First, these data
1461 underscore the importance of physical mixing (i.e., ocean circulation) in mediating patterns of dissolved

1462 $\delta^{138}\text{Ba}$ and, by extension, [Ba]. Second, both the regression of dissolved Ba-isotopic data (Bates et al., 2017;
1463 Hsieh & Henderson, 2017) and comparison of co-located seawater and particulates (Horner et al., 2017)
1464 imply an average particulate–dissolved Ba-isotopic offset ≈ -0.5 ‰, somewhat larger than the experimental
1465 results reported by Von Allmen et al. (2010). Third, marine sediments—both bulk (Bridgestock et al., 2018)
1466 and BaSO_4 isolates therefrom (Crockford et al., 2019)—faithfully reflect the ≈ -0.5 ‰ Ba-isotopic offset
1467 from surface seawater. Consequently, the mean $\delta^{138}\text{Ba}$ of globally-sedimented BaSO_4 is $\approx +0.1 \pm 0.1$ ‰
1468 (Crockford et al., 2019). Since BaSO_4 is the dominant oceanic output (e.g., Paytan & Kastner, 1996), these
1469 data imply that mean isotopic composition of Ba delivered to the ocean should possess an average
1470 composition $\approx +0.1 \pm 0.1$ ‰. At present however, the main Ba inputs are unable to close the marine Ba-
1471 isotopic budget: rivers, the principal Ba source to seawater, rivers, are too heavy, exhibiting compositions
1472 generally $\geq +0.2$ ‰ (e.g., Cao et al., 2020; Gou et al., 2020); and, groundwater discharge, while possessing
1473 the necessary ‘light’ composition of $\approx +0.1 \pm 0.1$ ‰, is too small a Ba flux to balance the budget (Mayfield

1474 et al., in press). Thus, either the marine Ba-isotopic budget is currently out of steady state, or an additional
 1475 Ba source possessing a light isotopic composition remains to be identified.

1476



1477
 1478 **Figure 19 | Processes driving barium isotope variations in modern seawater.** Though biological processes exert
 1479 only a minor direct influence on $\delta^{138}Ba$, the biologically-mediated cycling of $BaSO_4$ drives large variations in marine Ba
 1480 isotope cycling, thereby connecting $\delta^{138}Ba$ to (paleo)productivity.

1481

1482 8.2. Driving processes

1483 Seawater is undersaturated with respect to $BaSO_4$ almost everywhere (Monnin et al., 1999; Rushdi et al.,
 1484 2000; Monnin & Cividini, 2006). However, micro-crystalline $BaSO_4$ is ubiquitous in the ocean. This ‘barite

1485 paradox' remains an area of active research. Proposed driving mechanisms broadly fall into two categories:
1486 'active' biological and 'passive' chemical precipitation.

1487

1488 *8.2.1. Biological*

1489 Several organisms are known to precipitate BaSO₄ intracellularly, possibly for the purposes of gravitropism
1490 (e.g., Gooday & Nott, 1982; Finlay et al., 1983). However, the organisms known to actively precipitate
1491 BaSO₄ are not abundant in seawater, nor do they constitute a significant fraction of marine primary
1492 productivity. Likewise, acantharea—organisms that precipitate SrSO₄ (celestite) tests that can contain
1493 considerable quantities of Ba (e.g., Bernstein & Byrne, 2004)—are not necessary for driving significant
1494 dissolved [Ba] drawdown in the ocean (Esser & Volpe, 2002) or for barite precipitation (Ganeshram et al.,
1495 2003). Thus, existing evidence does not support a significant role for active biological processes in driving
1496 marine Ba cycling (Fig. 19).

1497

1498 *8.2.2. Chemical*

1499 Passive chemical precipitation is likely the major contributor to particulate BaSO₄ stocks and
1500 sedimentation. Given that seawater is largely undersaturated with respect to BaSO₄, passive precipitation
1501 is thought to occur within particle-associated microenvironments that are supersaturated with respect to
1502 BaSO₄ (e.g., Chow & Goldberg, 1960; Dehairs et al., 1987). The development of BaSO₄-supersaturated
1503 microenvironments is hypothesized to relate to the heterotrophic oxidation of organic matter (Chow &
1504 Goldberg, 1960), whereby Ba and sulfate ions are concentrated in chemically-isolated micro-zones during
1505 bacterially-mediated mineralization of organic matter. Once sufficient quantities of Ba and sulfate ions have
1506 accumulated and the microenvironment becomes supersaturated, BaSO₄ precipitation occurs. Thus, passive
1507 precipitation of BaSO₄ is possible even in strongly undersaturated environments with low ambient sulfate
1508 (e.g., Horner et al., 2017). Continued mineralization destroys the microenvironment, ceasing precipitation
1509 and exposing BaSO₄ precipitates to undersaturated seawater where they begin to dissolve.

1510 The widespread association between pelagic BaSO₄ and aggregates of decaying organic matter provides
1511 indirect support for this process (Dehairs et al., 1980; Bishop, 1988). Indeed, the peak in particulate Ba—
1512 and presumably BaSO₄—abundance is found in the upper mesopelagic zone where most organic matter
1513 mineralization occurs (e.g., Sternberg et al., 2008). Microscale mechanisms remain unresolved, however;
1514 recent studies indicate that biofilms may play an important role accumulating Ba (e.g., Martinez-Ruiz et

1515 al., 2018; 2019), which can promote precipitation of BaSO₄ nanoparticles from undersaturated solutions
1516 (Deng et al., 2019).

1517 Regardless of the precise microscale mechanism, precipitation of particulate BaSO₄ is ubiquitous in the
1518 marine realm. Given that BaSO₄ precipitation renders a substantial negative isotope fractionation of ≈ 0.5
1519 ‰, it is highly likely that BaSO₄ cycling drives much of the Ba isotope variability in the ocean (Fig. 19).
1520 From a paleoproxy perspective, this is ideal; BaSO₄ formation is related to the decay of organic matter and
1521 not by the presence of any specific organism (e.g., Jacquet et al., 2007; Dehairs et al., 2008). Downward
1522 transport of particulate BaSO₄ is driven by aggregation with larger particles (Lam & Marchal, 2014). The
1523 efficiency of this downward transport depends on the same biophysical processes that export organic matter,
1524 thus connecting the export flux of BaSO₄ to that of organic carbon (Fig. 19).

1525 Barites formed in the ocean through this passive chemical pathway are commonly termed marine, pelagic,
1526 authigenic, or biogenic. Though none of these terms are perfect descriptors of the chemical processes
1527 involved, ‘marine’ and ‘biogenic’ are the most ambiguous and their use is discouraged; the former
1528 encompasses all BaSO₄ formed in the marine realm—including diagenetic, cold seep, and hydrothermal—
1529 whereas the latter could be taken to imply only those precipitates brought about by active biological
1530 processes. While ‘authigenic’ is an informative descriptor, it has also been used to describe sedimentary
1531 BaSO₄ that formed via diagenetic redistribution on or below the seafloor (e.g., Torres et al., 1996). Thus,
1532 we recommend use of the term ‘pelagic’ when describing chemically-precipitated microcrystalline BaSO₄,
1533 and encourage authors to include this definition in their works.

1534

1535 *8.2.3. Physical*

1536 Barium exhibits a nutrient-like profile in the oceans, similar to that of Si (silicic acid) and alkalinity (Fig.
1537 18). However, the extent to which this pattern arises from non-conservative biogeochemical processes
1538 versus physical mixing remains unresolved. Results from the GEOTRACES program are facilitating
1539 renewed interest into this topic, which is being investigated using two complementary approaches. In the
1540 first, biogeochemical contributions to basin-scale Ba distributions are isolated using statistical methods,
1541 such as OMPA (Optimum Multiparameter water mass Analysis). These statistical methods showed that
1542 mixing is dominant in the Mediterranean (Jullion et al., 2017) and North Atlantic (Le Roy et al., 2018), but
1543 that sea ice-related processes may be important in the Arctic (Hendry et al., 2018). Second, the influence
1544 of mixing is evidenced from emerging Ba stable isotope data. Indeed, the importance of mixing has been
1545 documented vertically (Horner et al., 2015a), zonally (Bates et al., 2017; Bridgestock et al., 2018), and

1546 meridionally (Bates et al., 2017; Hsieh & Henderson, 2017). Together, these new approaches imply that *in*
1547 *situ* biogeochemical processes exert a relatively minor influence on basin-scale Ba distributions.

1548

1549 **8.3. Marine archives**

1550 Given the connections between export production and BaSO₄ fluxes, the major archive of historical changes
1551 in Ba cycling is BaSO₄ itself. Indeed, the sedimentary accumulation of BaSO₄—most commonly
1552 determined as the fraction of Ba in excess of the detrital Ba background or the deposition rate of BaSO₄
1553 itself—has been extensively used to reconstruct past changes in export production (e.g., Schmitz, 1987;
1554 Francois et al., 1995; Paytan et al., 1996; Frank et al., 2000; Jaccard et al., 2005; Jaccard et al., 2013; Ma
1555 et al., 2014; 2015, Costa et al. 2016, Winckler et al., 2016). An estimated 30 % of the BaSO₄ microcrystals
1556 formed in seawater are buried in oxygenated sediments (e.g. Dymond et al., 1992), a considerably higher
1557 fraction than for organic carbon (Paytan & Kastner, 1996). However, in oligotrophic regimes where both
1558 BaSO₄ fluxes and sedimentation rates are low, prolonged exposure to undersaturated seawater results in
1559 poor preservation (Eagle et al., 2003; Serno et al., 2014). Similarly, in high-productivity coastal upwelling
1560 settings, sedimentary mineralization of organic matter consumes oxygen present in pore waters, driving
1561 conditions down the redox tower and toward sulfate reduction, hampering BaSO₄ preservation (McManus
1562 et al., 1998; Paytan & Griffith, 2007; Carter et al., 2020).

1563 Recently, the isotopic composition of Ba in bulk sediments has been investigated as a proxy for the Ba
1564 isotope composition of the Ba source (i.e., dissolved Ba in epipelagic and upper-mesopelagic seawater).
1565 Applications to date have explored the recovery of the biological carbon pump following the PETM (~56
1566 Ma; Bridgestock et al., 2019) and the origin of enigmatic sedimentary BaSO₄ deposited in the aftermath of
1567 the Marinoan glaciation (~635 Ma; Crockford et al., 2019) and Great Oxidation Event (~2,000 Ma;
1568 Hodgskiss et al., 2019). Proceedings from recent geochemistry conferences indicate that many more
1569 investigations are underway.

1570 Lastly, the amount—and, more recently the isotopic composition (e.g., Hemsing et al., 2018; Geyman et
1571 al., 2019; Liu et al., 2019)—of Ba in marine carbonates has been extensively used to reconstruct the Ba
1572 content of past environments. These studies are not discussed here as they only indirectly relate to
1573 productivity, and instead pertain primarily to reconstructing ocean circulation and/or terrestrial runoff.

1574

1575 **8.4. Prospects**

1576 Barium exhibits several nutrient-like properties. Dissolved Ba distributions resemble those of other
 1577 nutrients and particulate abundances are intimately associated with the processes of organic carbon
 1578 remineralization and export. Despite these connections, several aspects of Ba cycling—both in the modern
 1579 and past oceans—remain unresolved. We suggest several areas for additional research that will help widen
 1580 the applicability of Ba-based proxies in paleoceanography.

1581

1582 *8.4.1. Modern*

1583 Several questions persist regarding the modern Ba cycle. Below we list three and offer possible remedies
 1584 to each.

- 1585 • To what extent do the similar distributions in [Ba], [Si], alkalinity, and [²²⁶Ra] reflect true
 1586 biogeochemical coupling versus passive physical mixing? As noted above, statistical analysis of
 1587 Ba (and Si, Ra) distributions in regions will offer valuable insights, particularly if conducted in
 1588 regions with weaker overturning circulation. Likewise, additional profiles of dissolved Ba isotope
 1589 distributions will enable quantification of mixing relationships.
- 1590 • Closing the Ba-isotopic mass balance of the ocean. This will require detailed evaluation of other
 1591 putative Ba sources, such as hydrothermal vents, cold seeps and other benthic sources (e.g.,
 1592 Hoppema et al., 2010), atmospheric deposition, and the importance of estuarine enhancement of
 1593 riverine Ba fluxes (e.g., Hanor & Chan, 1977; Edmond et al., 1978) as well as Ba fractionation
 1594 associated with other phases like the adsorption on Fe-Mn oxyhydroxides.
- 1595 • What is the mechanism of BaSO₄ precipitation? While the microenvironment-mediated model
 1596 appears most likely, the (bio)chemical mechanisms of precipitation remain ambiguous: How and
 1597 from what are Ba and sulfate ions liberated during bacterial mineralization? How are they
 1598 accumulated? Do different substrate organisms and/or heterotrophic communities influence the
 1599 amount of BaSO₄ precipitated? Addressing these questions will require additional field and
 1600 laboratory studies, which can then be compared against distributions of particulate BaSO₄ in the
 1601 ocean interior. Depending on their importance, these nuances may require ecological
 1602 parameterizations in numerical models of Ba cycling.
- 1603 • Narrowing estimates of the fractionation factor between BaSO₄ and seawater. Existing laboratory
 1604 studies place this estimate ≈ -0.3 ‰, whereas a wide-range of field data suggest that it is
 1605 considerably larger at ≈ -0.5 ‰. Accounting for this ≈ 0.2 ‰ difference is both important and

1606 justifies additional experimentation, as it indicates incomplete understanding of the processes that
 1607 fractionate Ba isotopes in the marine realm.

1608

1609 *8.4.2. Paleo*

1610 As with the modern cycle, several ambiguities persist. Assuming that BaSO₄ remains the preferred archive
 1611 of past Ba cycle variations, the most pressing relates to diagenesis.

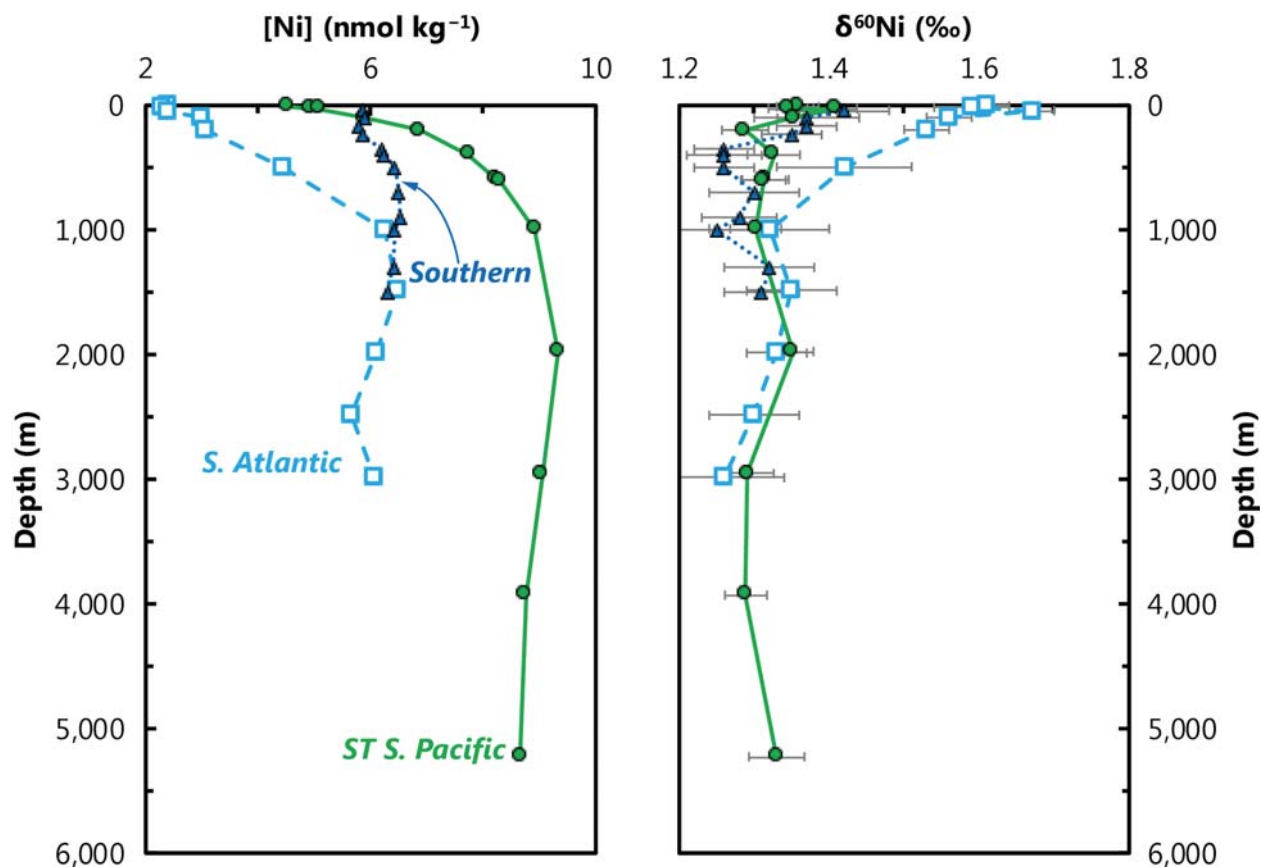
1612 • What is the effect of early diagenesis on the Ba isotope composition of sedimentary BaSO₄?
 1613 Likewise, do diagenetic BaSO₄ retain any primary Ba isotope information? Assessing these
 1614 questions will require studies of co-located BaSO₄ and porewaters from environments at various
 1615 stages of early diagenesis. Answering these questions is critical in establishing the validity of Ba
 1616 isotopes in barite as a paleoceanographic proxy.

1617 • Are BaSO₄ accumulation rates impacted by ambient [Ba]? Related to the question concerning
 1618 BaSO₄ precipitation mechanisms above, it is presently unknown if the quantity of BaSO₄ yielded
 1619 by remineralization is impacted by ambient [Ba]—does more BaSO₄ precipitation occur at higher
 1620 ambient [Ba]? Likewise, to what extent does BaSO₄ preservation depend on ambient [Ba]? These
 1621 considerations are significant when considering longer-term records, particularly when marine
 1622 sulfate levels were lower-than-modern (and [Ba] presumably higher; e.g., Hanor, 2000; Wei &
 1623 Algeo, in press). Finally, does the seawater temperature at the depth of POC mineralization impact
 1624 the relationship between POC and barite formation? These questions are best addressed through a
 1625 combination of experimentation (e.g., cultures, precipitation), field studies in basins with large
 1626 gradients in [Ba], and numerical experiments incorporating saturation state modeling.

1627 **9. Nickel**

1628 **9.1. Marine distribution**

1629 Nickel has a classic nutrient-type distribution in the oceans with one unusual feature; surface dissolved Ni
 1630 concentrations never drop below around 1.8–2 nmol kg⁻¹ (e.g., Sclater et al., 1976; Bruland, 1980; Fig. 20).
 1631 There is evidence, however, that this residual pool in surface waters is not bioavailable, as summarized
 1632 recently by Archer et al. (2020). Deep water dissolved Ni concentrations are 4–5 nmol kg⁻¹ in the Atlantic,
 1633 and ~9 nmol kg⁻¹ in the north Pacific (Fig. 20).

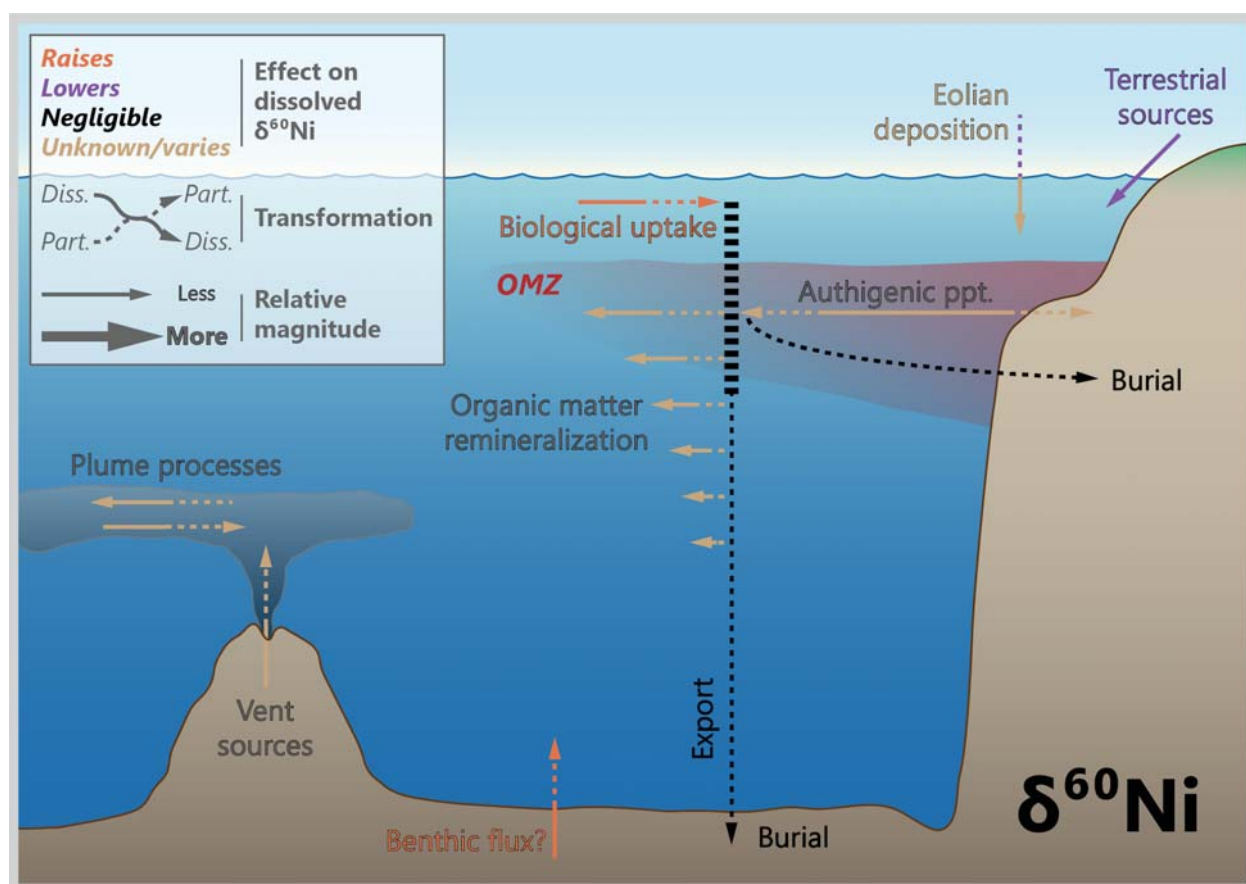


1634 **Figure 20 | Representative profiles of dissolved Ni concentrations ([Ni]) and Ni-isotopic compositions (δ⁶⁰Ni)**
 1635 **from the South Atlantic (squares, dashed line), Southern (triangles, dotted line), and Subtropical South Pacific**
 1636 **(circles, solid line) Oceans. This comparison illustrates that the oceanographic processes leading to distinct dissolved**
 1637 **concentration profiles render only small changes in dissolved δ⁶⁰Ni between basins.**
 1638

1639
 1640 Developing robust analytical protocols for analyzing Ni isotopes for a range of sample matrices has proven
 1641 somewhat more challenging than for some of the other TEIs discussed here due to the difficulty in
 1642 separating Ni from interfering elements (e.g., Fe, a major isobaric interference on ⁵⁸Ni). Chemical
 1643 purification protocols now use a sequence of resins including anion exchange (e.g., AG MP-1M or AG1-

1644 X8, Bio-Rad) and either a Ni-specific resin (containing dimethylglyoxime) or Nobias PA-1 (Hitachi High
 1645 Technologies; e.g., Cameron et al., 2009; Gueguen et al., 2013; Wang et al., 2019a; Yang et al., 2020). The
 1646 limited data subsequently reported for the oceanic dissolved pool of Ni is isotopically homogeneous at
 1647 depth ($\delta^{60}\text{Ni} \approx +1.3 \text{ ‰}$), with a small shift towards heavier values (up to +1.7 ‰) in the upper water column
 1648 (Takano et al., 2017; Wang et al., 2019a; Yang et al., 2020; Archer et al., 2020). The latter is proposed to
 1649 reflect a small kinetic isotope fractionation during biological uptake. Similar to Zn, Cu, Cd, Mo, and Ba,
 1650 the isotopic composition of Ni in seawater is isotopically heavy compared to the UCC (Table 1).

1651



1652 **Figure 21 | Processes driving nickel isotope variations in modern seawater.** Biological processes are recognized
 1653 to drive a small, but systematic increase in dissolved $\delta^{60}\text{Ni}$ and marine Ni isotope values are preserved in certain
 1654 sediments. Other abiotic Ni cycling processes may be important however, such as sorption to Mn-oxide minerals, and
 1655 the significance of these fractionations to global Ni cycling remains to be fully elucidated.
 1656

1657

1658

1659

1660

1661 **9.2. Driving processes**

1662 *9.2.1 Biological*

1663 To date, eight Ni-based enzyme systems have been identified (Ragsdale, 2009), including urease, which is
1664 key to the global nitrogen cycle, and methyl-CoM reductase, which catalyses the production of all
1665 biologically generated methane on Earth. The obligate requirement of methanogens for Ni has led to interest
1666 in developing Ni and Ni isotopes as a tracer of methane production on the early Earth (e.g. Cameron et al.,
1667 2009; Konhauser et al., 2009; Wang et al., 2019c). In the modern ocean the highest Ni quotas are found in
1668 diazotrophs (N-fixers), thought to reflect the presence of Ni-Fe hydrogenases (which catalyse H₂ produced
1669 during N fixation), Ni-superoxide dismutase (Ni-SOD) and urease (Tamagnini et al., 2002; Dupont et al.,
1670 2008a; 2008b; Nuester et al., 2012). Nickel limitation of phytoplankton grown on urea has been shown in
1671 culture and in natural assemblages, suggesting the Ni-N co-limitation of phytoplankton growth may be
1672 relevant in the ocean (Price & Morel, 1991; Dupont et al. 2008a; 2010). Significant Ni is also found in
1673 diatom frustules (about 50 % of diatom cellular quotas; Twining et al., 2012). The latter observation is
1674 thought to play a role in the similarity of Ni and Si oceanic distributions (Twining et al., 2012).

1675 No culture data are available to determine the degree of Ni isotope fractionation during biological uptake.
1676 Upper ocean data suggest no fractionation or a small preference for the light isotope (up to $\alpha \approx 0.9997$;
1677 Takano et al., 2017; Archer et al., 2020; Yang et al., 2020; Fig. 21), consistent with the Ni isotope
1678 systematics observed in organic-rich sediments (Ciscato et al., 2018) and water column particulates (Takano
1679 et al., 2020). Interestingly, new water column data from the South Atlantic suggest distinct ecological
1680 differences in Ni drawdown and Ni isotope fractionation compared to other TEIs (e.g., Zn, Cd). Limited
1681 drawdown and Ni isotope fractionation is observed in the diatom-dominated regime south of the Polar Front
1682 in the Southern Ocean. In contrast, more marked drawdown and significant Ni isotope fractionation is
1683 observed north of the Polar Front, which has been attributed to the predominance of nitrate-limited, Ni-
1684 requiring cyanobacteria (Archer et al., 2020).

1685

1686 *9.2.2 Chemical*

1687 Nickel is partially complexed by strong organic ligands in coastal and open ocean environments (5–70 %;
1688 e.g., Donat et al., 1994; Saito et al., 2004; Boiteau et al., 2016), though slow water exchange kinetics of Ni
1689 make these complexation measurements particularly challenging (Hudson & Morel, 1993). Slow exchange
1690 kinetics may also explain the residual pool of non-bioavailable Ni in the surface ocean (e.g., Mackay et al.,

1691 2002; Dupont et al., 2010). Speciation models suggest that the remainder of the Ni is present as free Ni^{2+}
1692 and NiCl^+ , with a small fraction present as NiCO_3^0 (Zirino and Yamamoto, 1972; Turner et al., 1981).

1693 Nickel cycling is tightly coupled to that of Mn, in sediments, pore waters, and across the redoxcline of the
1694 Black Sea (e.g., Klinkhammer, 1980; Koschinsky and Hein, 2003; Vance et al., 2016). In the Black Sea,
1695 for example, Mn redox cycling is associated with preferential sorption of light Ni isotopes, with a large
1696 negative fractionation of $\approx -4\text{‰}$ (Vance et al., 2016). This large fractionation is consistent with experimental
1697 sorption of Ni on birnessite (Wasylenki et al., 2014; Sorensen et al., 2020).

1698 Unlike more strongly chalcophile elements like Cd, Cu, and Zn, dissolved Ni is not strongly drawn down
1699 in the euxinic portion of the Black Sea water column (Tankéré et al., 2001; Vance et al., 2016). However,
1700 Ni is enriched in Black Sea sediments (Little et al., 2015), with $\delta^{60}\text{Ni}$ compositions notably lighter (at +0.3
1701 to +0.6‰) than Ni sources to the basin (at about +1.3‰; Vance et al., 2016; Fig. 21). Vance et al. (2016)
1702 attributed these light isotope compositions to the scavenging of sulfidized Ni species, which are predicted
1703 to be isotopically light (Fujii et al., 2011b).

1704

1705 *9.2.3 Physical*

1706 The most recent estimate for residence time of Ni in the ocean is approximately ~ 20 kyr (Little et al., 2020),
1707 considerably longer than the mixing time of the ocean. As a result, in parallel with the other TEIs discussed
1708 herein, Ni and Ni isotope distributions are modulated at first order by the geometry of physical ocean
1709 circulation. The importance of diatom uptake in the Southern Ocean in partially coupling oceanic Ni and
1710 Si (Twining et al., 2012) was introduced above, and the homogeneity of deep ocean Ni isotope compositions
1711 supports an important role for southern-sourced water masses in the Ni distribution (Takano et al., 2017;
1712 Wang et al., 2019a; Archer et al., 2020).

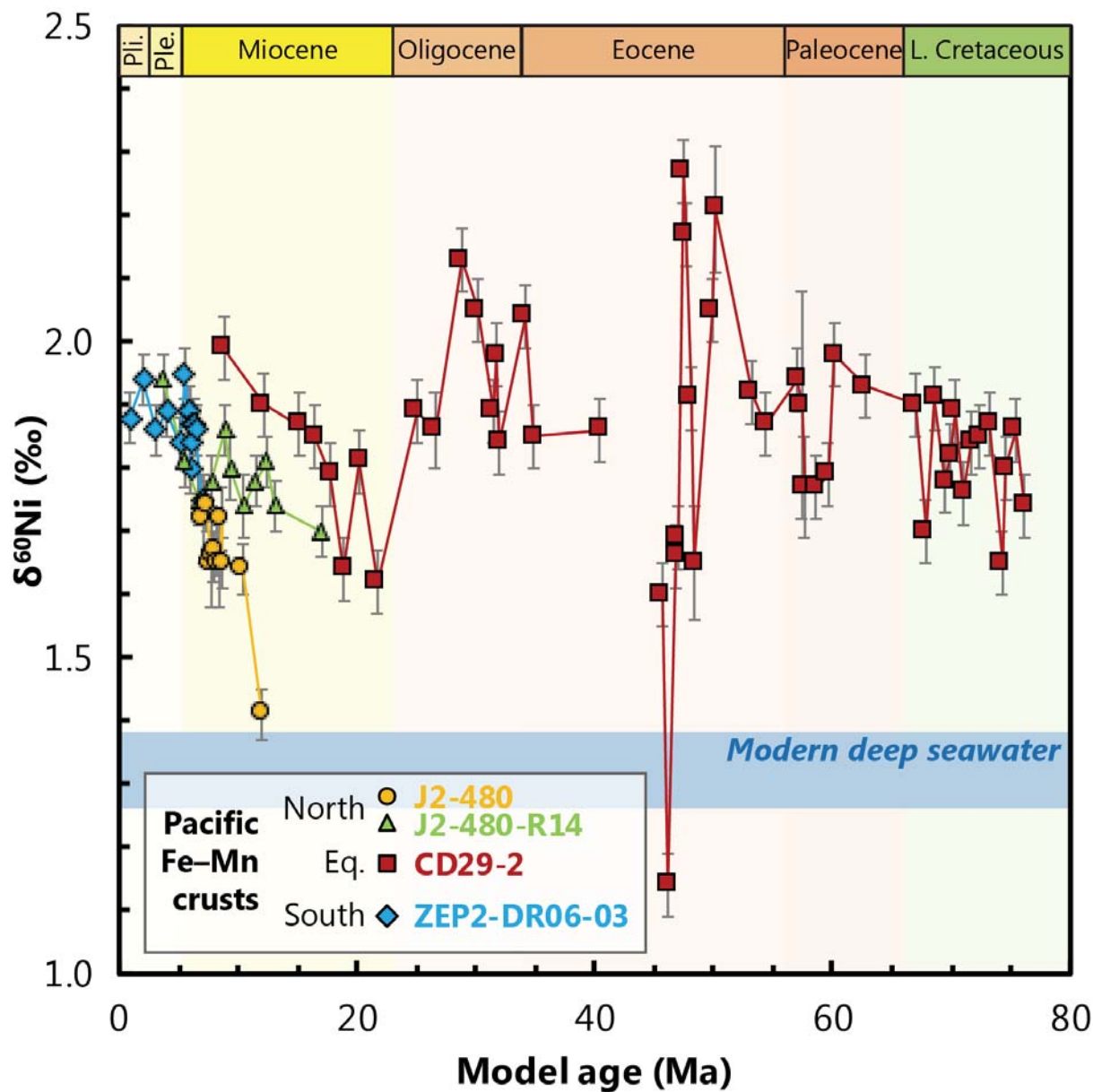
1713

1714 **9.3. Marine archives**

1715 *9.3.1. Ferromanganese sediments*

1716 Ferromanganese crusts exhibit variable Ni isotope compositions (Fig. 22; Gall et al., 2013; Gueguen et al.,
1717 2016), which are, on average, slightly isotopically heavier (at $\delta^{60}\text{Ni}$ of +1.6‰) than seawater ($\delta^{60}\text{Ni}$ at about
1718 +1.3‰). However, experiments suggest that sorption of Ni to birnessite (the primary Ni-hosting phase in
1719 Fe–Mn sediments) should be associated with a large negative isotope effect (of about 3 to 4 ‰; Wasylenki

1720 et al., 2014; Sorensen et al., 2020). It remains unclear why the full isotope effect is not expressed in Fe–Mn
 1721 crusts. Intense Mn cycling occurs across the redoxcline of the Black Sea; this cycling is associated with
 1722 large variations in Ni and Ni isotopes, consistent with the experimentally observed light isotope effect on
 1723 sorption to birnessite (Vance et al., 2016). Recent data from Mn-rich sediments that have undergone
 1724 diagenesis also point to the preservation of a large negative Ni isotope effect (Little et al., 2020).



1725
 1726 **Figure 22 | Four Fe–Mn records of Ni isotope compositions from the Pacific Ocean.** Assuming that Fe–Mn crusts
 1727 have always formed with an offset $\approx +0.5$ ‰ with respect to ambient dissolved Ni in seawater, these records illustrate
 1728 that the Ni isotope composition of seawater has varied by only ± 0.2 ‰ over the Cenozoic. Data for J2-480, J2-480-
 1729 R14, and ZEP2-DR06-03 are from Gueguen et al. (2016). Data from CD29-2 are from Gall et al. (2013). All four records
 1730 have been plotted using the authors' preferred age model, meaning that there are some differences between the
 1731 chronology of CD29-2 shown here compared to Figs. 5, 14.

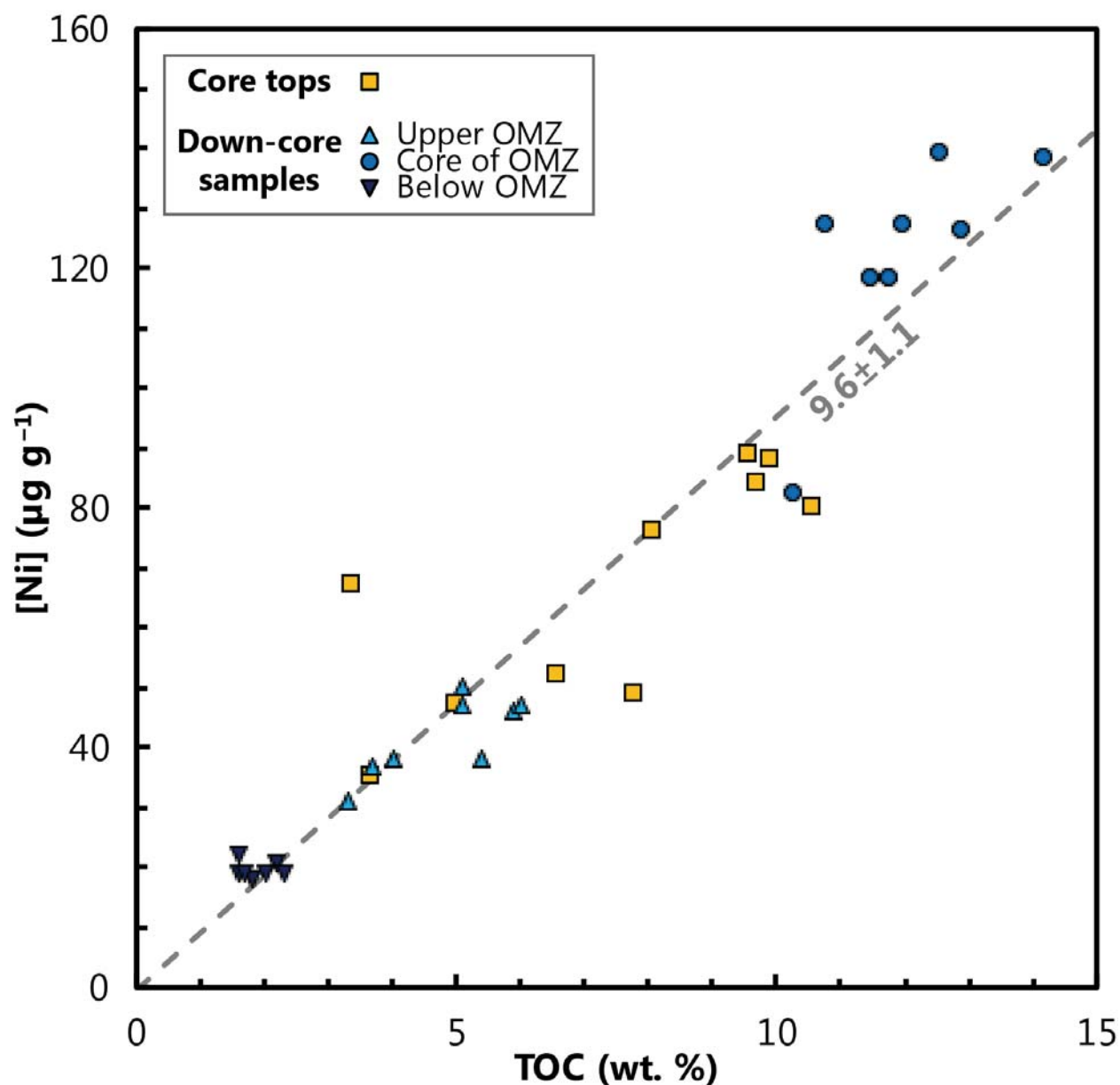
1732 Though promising, the development of Fe–Mn crusts as a tracer of past oceanic Ni cycling awaits a
1733 mechanistic understanding of the processes driving their variably isotopically heavy signature, as well as
1734 an awareness of the likely complicating role of diagenetic remobilisation of Ni (e.g., Atkins et al., 2016;
1735 Little et al., 2020).

1736

1737 9.3.2. *Organic-rich sediments*

1738 As introduced in section 5.3.2 (Cu), qualitative arguments for high organic matter fluxes (i.e., increased
1739 paleoproductivity) have been made based on elevated Cu and Ni concentrations in ancient organic-rich
1740 sediments (e.g., Tribovillard et al., 2006). For Ni, this approach is supported by positive correlations with
1741 TOC in modern continental margin sediments (Fig. 23).

1742 Nickel does not precipitate in the presence of water column dissolved sulfide and is therefore a better
1743 candidate for the Metal–TOC approach than the more strongly chalcophile elements, like Cu. Nevertheless,
1744 Ni cycling is strongly linked to the redox cycling of Mn, so prerequisite (2)—that depositional environments
1745 remain reducing—is critical. In addition, sedimentary and water column data from the Black Sea indicate
1746 that the Fe–Mn redox shuttle provides an alternative supply route for Ni to sediments in these settings (Little
1747 et al., 2015; Vance et al., 2016). Finally, an open marine setting (prerequisite 3) would be required to make
1748 estimates of the relative productivity of two different sites based on their absolute measured Ni:TOC ratios.
1749 Otherwise the degree of basin restriction will exert the primary control on nutrient supply, and therefore
1750 the degree of trace metal enrichment (Algeo & Maynard, 2008; Little et al., 2015).



1751
 1752 **Figure 23 | Correlation of Ni and TOC content in organic-rich sediments from the Peru Margin.** Data from Ciscato
 1753 et al. (2018). The best-fit regression of these data yields a Ni–TOC slope of 9.6 ± 1.1 (mean \pm 2 SD), similar to the “ ≈ 9 ”
 1754 reported by Böning et al. (2015).

1755
 1756 Ciscato et al. (2018) investigated the distribution of Ni and its isotopes in two fractions isolated from Peru
 1757 margin organic-rich sediments. The HF-HCl digestible fraction (usually containing >80% of total Ni)
 1758 exhibited $\delta^{60}\text{Ni}$ values similar to modern deep seawater (at about +1.2‰). Meanwhile, these authors found
 1759 variable Ni isotope compositions in the organic-pyrite fraction (OPF), which they suggested record the
 1760 fractionation imparted by biological uptake in the photic zone. Systematic relationships between Ni–TOC,

1761 $\delta^{60}\text{Ni}_{\text{OPF}}$, and $\delta^{13}\text{C}$ indicate that there is merit in continuing to investigate Ni and Ni isotopes as a
1762 paleoproductivity tracer (Ciscato et al., 2018).

1763

1764 **9.4. Prospects**

1765 To date, Ni and its isotopes have been under-developed as a potential paleoproductivity proxy. Recent data,
1766 both from the dissolved phase in seawater and in two different fractions isolated from anoxic organic-rich
1767 sediments, suggest promise in the coupling of Ni and C and their isotopes. However, in oxic-to-suboxic
1768 settings, Ni and its isotopes in sediments are strongly influenced by the diagenetic redox cycling of Mn. In
1769 these settings, we recommend exploratory Ni and $\delta^{60}\text{Ni}$ work focusing on carbonate and siliceous
1770 biominerals, work that is increasingly tractable with new and improved chemical separation and analytical
1771 techniques.

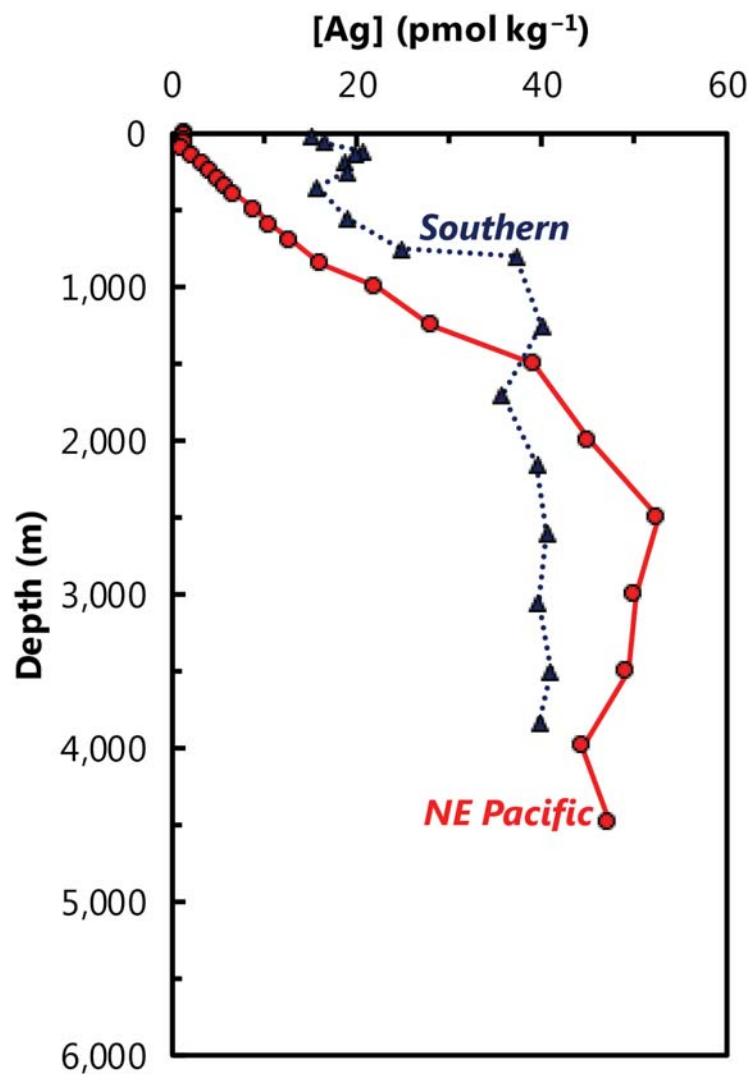
1772 Finally, in a completely different approach, Wang et al. (2019c) present $\delta^{60}\text{Ni}$ values of Precambrian glacial
1773 diamictites, which are suggested to represent the chemical weathering residues of the UCC. They find a
1774 small shift towards heavier Ni isotope compositions across the Great Oxidation Event, which they relate to
1775 the onset of oxidative weathering of crustal sulfides (Wang et al., 2019c). Combined with the proposed
1776 importance of Ni to the maintenance of methanogenesis during this time period (e.g. Konhauser et al.,
1777 2009), it is hoped that future Ni stable isotope analyses will shed further light on the paleoenvironmental
1778 conditions on the early Earth.

1779

1780 **10. Silver**

1781 **10.1. Marine distribution**

1782 Silver is the scarcest of the TEIs described here, both within Earth’s crust and in the modern ocean.
 1783 Moreover, Ag is an usual candidate for a paleoproductivity proxy given that it possesses no known
 1784 biological function and is most widely known for its antimicrobial properties. Despite this, Ag exhibits a
 1785 characteristic nutrient-like profile in seawater, most similar to that of Si (and Zn, Ba; Fig. 24).

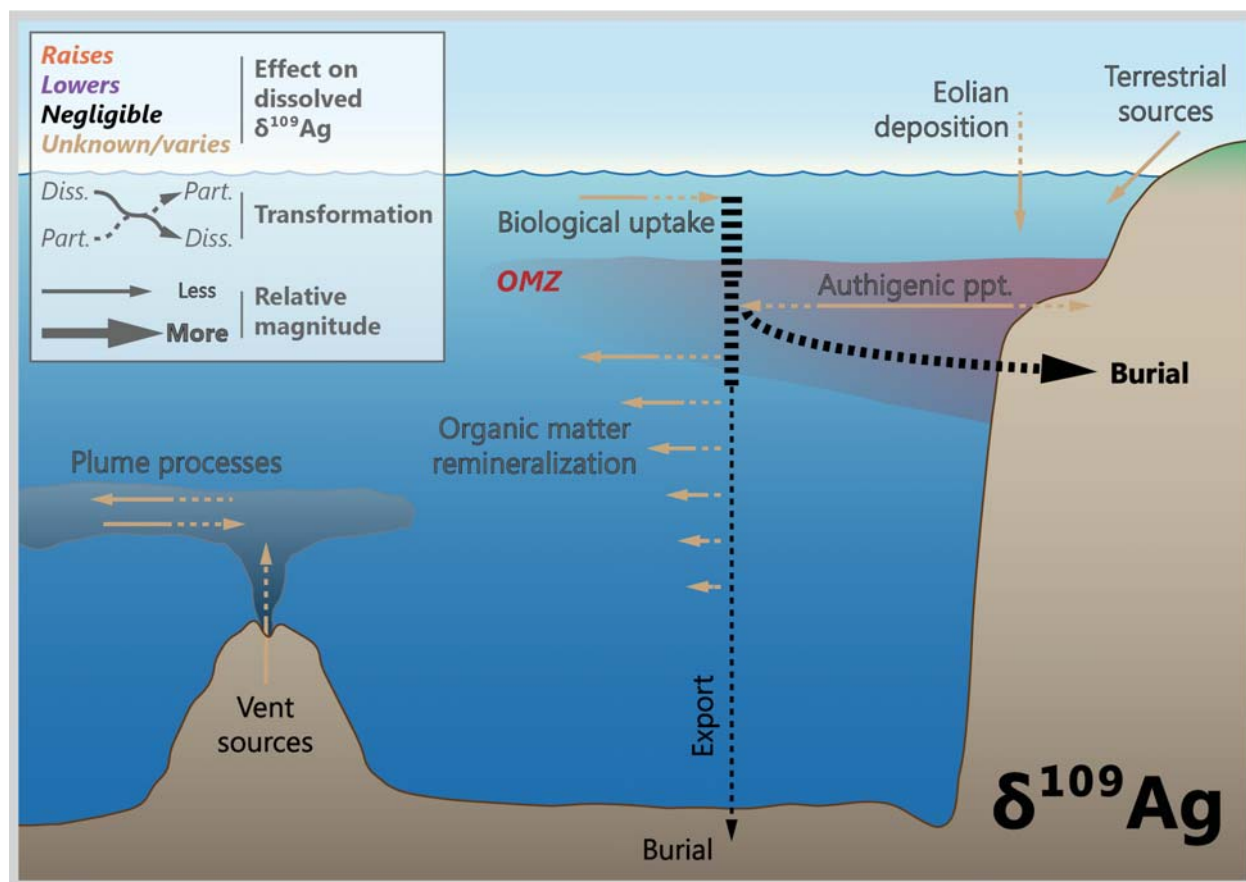


1786 **Figure 24 | Representative profiles of dissolved Ag concentrations ([Ag]) from the Northeast Pacific (circles,**
 1787 **solid line) and Southern (triangles, dotted line) Ocean. No Ag-isotopic data for seawater are available at this time.**
 1788

1789
 1790 Dissolved Ag occurs primarily as chloride complexes in seawater (Cowan et al., 1985, Miller & Bruland,
 1791 1995) and exhibits a nutrient-type depth profile. Dissolved [Ag] in surface waters is typically <5 pmol kg⁻¹,
 1792 and ranges from 5–30 pmol kg⁻¹ in deep waters of the Atlantic Ocean to 50–114 pmol kg⁻¹ in the Pacific

1793 Ocean (Fig. 24; Flegal et al., 1995; Rivera-Duarte et al., 1999; Ndung'u et al., 2001; Zhang et al., 2001;
 1794 2004; Ranville and Flegal, 2005; Boye et al., 2012). The total observed range in seawater is 0.2–115 pmol
 1795 kg⁻¹ (Gallon and Flegal, 2014). Despite its potential as a biogeochemical proxy, no Ag isotope data yet
 1796 exist for dissolved or particulate phases in the water column, nor in marine sedimentary archives.
 1797 Accordingly, we cannot directly assess the utility of Ag isotopes to infer paleoproductivity, though we can
 1798 deduce a number of processes that are likely to influence dissolved $\delta^{109}\text{Ag}$ based on the processes known
 1799 to cycle Ag (Fig. 25).

1800



1801
 1802 **Figure 25 | Processes likely to drive silver isotope variations in modern seawater.** Despite there being no Ag
 1803 isotope data for seawater at this time, we can infer a number of processes that are most likely to influence dissolved
 1804 $\delta^{109}\text{Ag}$ from measurements of [Ag] in seawater and sediments.

1805

1806

1807 **10.2. Driving processes**

1808 The 1D depth profile for dissolved Ag is similar to that of Si (and Zn, Ba), resulting in a strong positive
 1809 correlation between these elements (Fig. 1). This has led researchers to suggest that Ag is taken up by
 1810 diatoms, incorporated into their frustules, and then released as the frustules dissolve (e.g., Flegal et al.,

1811 1995). Silver might then be delivered to the seafloor with opal, potentially making it useful as a
1812 paleoproductivity proxy (Friedl & Pedersen, 2002). However, the correlation between dissolved Ag and Si
1813 is non-linear, indicating that other factors are at play (Zhang et al., 2001; 2004). Furthermore, while Ag is
1814 taken up by various types of phytoplankton, including diatoms (Fisher & Wentz, 1993), experiments
1815 conducted using the marine diatom *Thalassiosira pseudonana* show that most of the Ag is associated with
1816 the organic fraction rather than the opal (Wagner, 2013; Fig. 25). Martin et al. (1983) also hypothesized
1817 that high particulate Ag concentration within the euphotic zone (40–70 m) off the west coast of Mexico
1818 were due to the formation of Ag-organic complexes. Interestingly, particulate Ag concentrations are even
1819 higher well below the euphotic zone, at a depth corresponding to the upper portion of the oxygen minimum
1820 zone (Martin et al., 1983). It could also be that a global Ag:Si correlation arises at least in part from
1821 biological processes occurring in the surface of the Southern Ocean, whereby intermediate and mode water
1822 masses with low preformed [Ag] are advected to lower latitudes, analogous to the mechanism proposed for
1823 Zn–Si (Vance et al., 2017) and Ba–Si coupling (Horner et al., 2015a). If correct, Ag is unlikely to be coupled
1824 directly to opal with a simple relationship that can be used to reconstruct past diatom productivity.

1825

1826 Dissolved Ag cycling may become decoupled from productivity by possessing different source and sink
1827 terms relative to carbon and the macronutrients (Gallon and Flegal, 2014 and references therein). For
1828 example, Ranville & Flegal (2005) and Ranville et al. (2010) invoked an anthropogenic aerosol source of
1829 Ag to surface and intermediate waters to explain north Pacific water column data. Other complications may
1830 arise in low-oxygen environments—waters from the northeast Pacific (Kramer et al., 2011) and
1831 southeastern Atlantic (Boye et al., 2012) exhibit a deficit in dissolved Ag relative to Si within their
1832 respective OMZs. These deficits imply preferential removal of Ag over Si, which may occur locally or
1833 ‘upstream’. If occurring locally, a putative mechanism is (co-)precipitation with other chalcophile elements,
1834 analogous to the sulfide-mediated mechanism proposed for Cd in OMZs (Janssen et al., 2014; Sec. 6).
1835 Alternatively, the deficit may reflect low preformed Ag:Si in intermediate waters, which is inherited from
1836 preferential drawdown of Ag over Si in regions upstream where these intermediate waters were last
1837 ventilated. Both interpretations have implications for the use of Ag (isotopes) as a paleoproxy: the former
1838 implies a redox sensitivity that depends on the changing location, spatial extent, and intensity of low-oxygen
1839 regions in the oceans over time. The latter implies a sensitivity to ecology and the geometry of ocean
1840 circulation. Both warrant additional scrutiny.

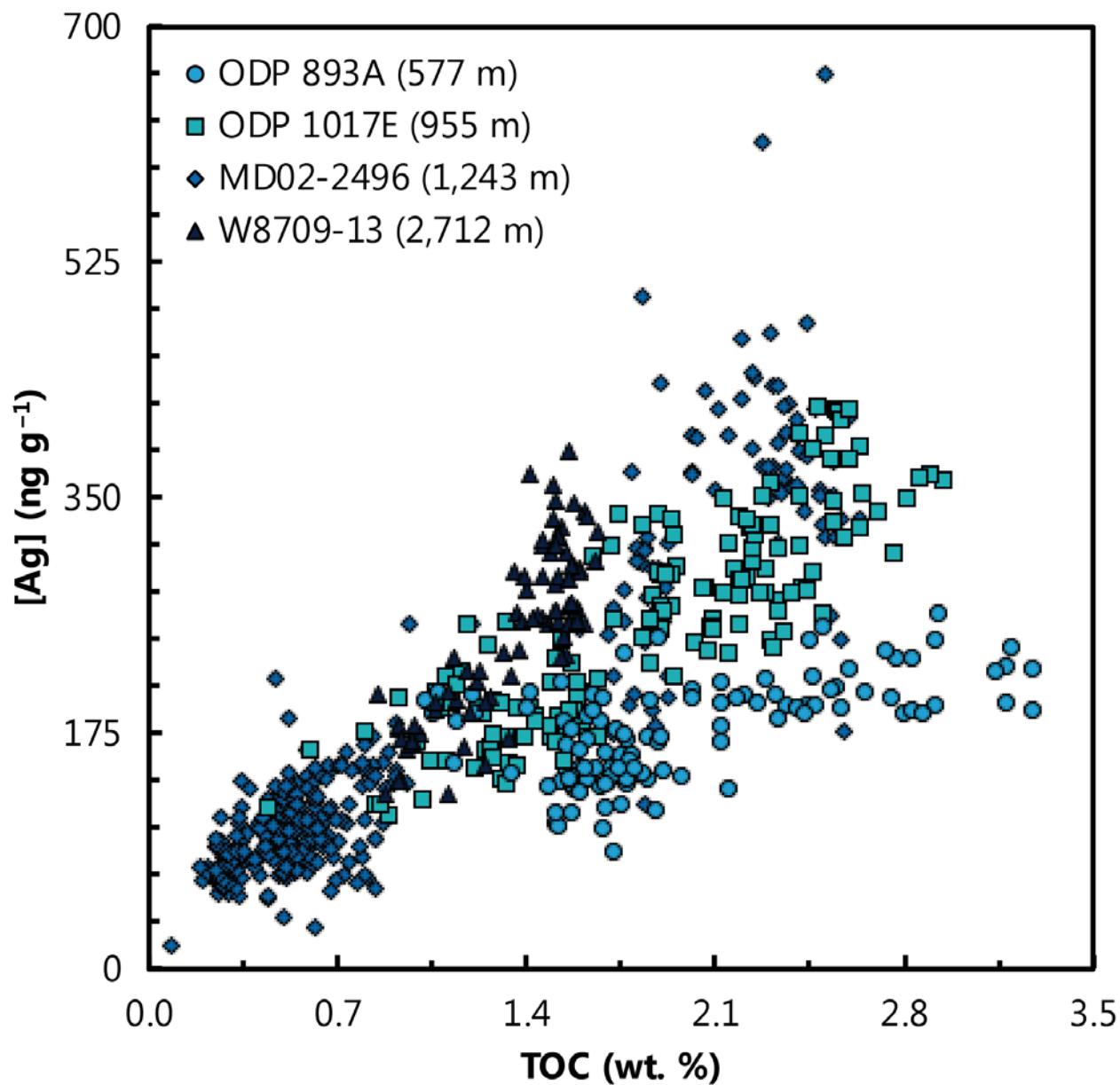
1841

1842 **10.3. Marine archives**

1843 Bulk sediments are the main archive that has been investigated for their potential to record information
1844 about the marine Ag cycle. Silver concentrations in bulk sediments from open-marine environments range
1845 from $\leq 100 \text{ ng g}^{-1}$ (i.e., typical lithogenic values) up to 100s of ng g^{-1} (Koide et al., 1986). In general, low
1846 concentrations are typical of well-oxygenated sediments, while higher concentrations are found in oxygen-
1847 poor and sulfidic environments. The general consensus has been that Ag enrichment in anoxic sediments is
1848 the result of post-depositional precipitation of Ag_2S (Koide et al., 1986) or possibly Ag selenide (Crusius
1849 & Thomson, 2003; Böning et al., 2005). However, high Ag concentrations are also documented in marine
1850 sediments that are only weakly reducing (Böning et al., 2004, 2005; McKay & Pedersen, 2008; Morford et
1851 al., 2008). Furthermore, even in anoxic sediments, the degree of Ag enrichment exceeds what would be
1852 expected from post-depositional Ag precipitation alone (Borchers et al., 2005; McKay and Pedersen, 2008;
1853 Böning et al., 2009). Thus, redox-controlled, post-depositional precipitation is not the primary control on
1854 Ag accumulation in marine sediments; there must also be a flux of non-lithogenic, particulate Ag to the
1855 seafloor (McKay & Pedersen, 2008).

1856 McKay & Pedersen (2008) hypothesized that Ag, like Ba, accumulates in organic-rich settling particles.
1857 However, in contrast to Ba, Ag precipitation requires a reduced microenvironment within the particle,
1858 which is only favored in oxygen-poor waters. The analysis of sediment trap samples from the northeast
1859 Pacific show that the fluxes of particulate Ag and particulate organic carbon flux positively correlate
1860 (Martin et al., 1983). This correlation is also seen in surface sediments (McKay & Pedersen, 2008) and
1861 sediment cores from the northeastern Pacific (Fig. 26). These data broadly support the use of Ag
1862 concentrations as a paleoproductivity proxy, with an important caveat: the post-depositional preservation
1863 of particulate Ag requires that sediments remain reducing (prerequisite 2.), as settling particulate Ag formed
1864 below the euphotic zone is not preserved if sediments are oxidizing (McKay and Pedersen, 2008; Morford
1865 et al., 2008). Thus, while the delivery of Ag to sediments appears related to productivity (Wagner et al.,
1866 2013), Ag preservation will likely depend on the depositional environment. Regardless, these observations
1867 are promising from the point of view of tracing past productivity.

1868



1869

1870 **Figure 26 | Concentrations of silver and total organic carbon in sediment cores from the northeast Pacific**
 1871 **Ocean.** These data illustrate that Ag is broadly correlated with organic matter in bulk sediments, which is highly
 1872 promising from the perspective of developing Ag as a paleoproductivity proxy.

1873

1874

1875 **10.4. Prospects**

1876 The apparent linkages between dissolved and particulate [Ag], macronutrients, and organic matter provides
 1877 tantalizing evidence that Ag may be coupled to surface productivity (Fig. 24). Moreover, core-top studies
 1878 indicate that the geochemical signature of this coupling is preserved under certain environmental conditions

1879 (Fig. 26). Despite this progress, the study of Ag in marine biogeochemical cycles remains in its infancy,
1880 particularly compared to many of the other elements described here. Additional constraints are needed in
1881 several areas, including: the role of biogeochemical processes in mediating Ag distributions in the water
1882 column, the dominant controls on the downward transport of Ag through the oceans, and on the controls on
1883 Ag preservation in sediments. Given what has been learned from the application of the other TEI systems
1884 described here, new analytical developments in Ag isotope geochemistry could help place valuable
1885 constraints in several of these areas.

1886

1887

1888 **11. Synthesis**

1889 We now assess the overall readiness of each TEI system to reconstruct productivity, summarized in Table
1890 2. This exercise is analogous to the assessment of analytical techniques used in chemical oceanography
1891 described by Fassbender et al. (2017). Our assessment is similarly conducted in two dimensions. First, we
1892 identify five objectives toward the development of a reliable productivity proxy, ranging from development
1893 of the analytical capabilities necessary to measure that species, to constraining diagenetic effects, and
1894 ending with the goal of using that species to reliably reconstruct paleoproductivity itself. Second, we assess
1895 the level of development within each objective. Our reasoning behind the assignments is described above
1896 in Sections 3–10.

1897

1898 Reliable application of a proxy requires that five objectives be serially met (e.g., Hillaire-Marcel & Vernal,
1899 2007; Table 2). In practical terms, however, the final stage (proxy application) is often realized before many
1900 of the supporting objectives; variations in TEI ratios in the sedimentary record commonly provide the
1901 motivation for developing a more holistic understanding of that TEI system in the modern environment. (A
1902 common critique of this approach being that subsequent studies often invalidate earlier interpretations.) The
1903 five objectives that follow are common to the development of almost any proxy. First, it is essential to
1904 develop the analytical capability to measure the species of interest commensurate with the quantities
1905 typically encountered in the environment. In the case of TEI abundance proxies, the development and
1906 widespread adoption of ICP-MS instrumentation coupled to automated sample preparation systems has
1907 enabled low-blank–high-throughput–high-sensitivity analyses of multiple TE's in both seawater (e.g.,
1908 Wuttig et al., 2019) and sediments alike (e.g., Wefing et al., 2017). In contrast, the techniques required to
1909 measure many TEI systems have only been developed within the past decade—or are still in development—
1910 and generally remain labor intensive and time consuming. Second, it is important to map the broad vertical
1911 and spatial patterns of a TEI system in the modern ocean. The GEOTRACES program has provided a
1912 coordinated opportunity to study the basin-scale distributions of multiple TEIs. Third, the utility of a proxy
1913 is significantly increased if the driving processes are understood. These processes may be isolated through
1914 a number of approaches, including: lab-based analogue experimentation, numerical modeling, and high-
1915 resolution spatiotemporal environmental studies. Fourth, paleoceanographic proxies require sedimentary
1916 archives—a substrate from which to reconstruct the variable of interest. The latter necessitates knowledge
1917 of how a TEI system partitions between seawater and sediment, such as through a core-top study, ideally
1918 conducted across large environmental gradients. Since many marine sedimentary archives are biogenic in
1919 origin, additional experimentation isolating ‘vital effects’ may be necessary. Fifth, proxies are only as

1920 reliable as their archives are hardy. Diagenetic processes may alter primary environmental signatures, and
 1921 recognizing these effects is imperative for reliably reconstructing past environmental conditions.

1922

1923 We assess the level of development within each objective on a four-point scale: unknown, developing,
 1924 applied, and unlikely. The levels define a continuum from least to most understood, and are a useful
 1925 shorthand for illustrating where additional work is most needed. Assignment of ‘unknown,’ implies that
 1926 too little is presently known to reliably assess progress towards that objective. These TEI systems may or
 1927 may not ultimately be useful in reconstructing ocean productivity. ‘Developing’ objectives are those where
 1928 there are pilot studies on that topic, but overall there are an insufficient number to define general rules for
 1929 that TEI system. If a TEI system is widely recognized to be useful towards some objective, it is given a
 1930 score of ‘applied’. Though these scores are subjective, they are roughly equivalent to the number of
 1931 spatiotemporal and lab studies of that TEI system, and the number of inter-calibrated laboratories. If the
 1932 evidence indicates that a TEI system is not suitable for reconstruction of past productivity, a score of
 1933 ‘unlikely’ is given. This does not rule out future developments, such as identification of environmental
 1934 control variables or new sedimentary archives, only that current data (and archives) do not support use of
 1935 the TEI system towards this goal. Lastly, we recognize that there are continual refinements to analytical
 1936 protocols, environmental distributions, etc. and thus, at some level, all five objectives could reasonably be
 1937 described as ‘developing’. Rather, our assignments are intended to give a relative sense of understanding
 1938 between different TEI systems toward the overarching goal of reconstructing past ocean productivity.

1939

1940

1941

1942 **Table 2 | Proxy development assessment.** The progress toward five objectives is assessed for each TE proxy system
 1943 and assigned a development level ranging unknown to unlikely, corresponding to the least and most certain
 1944 assignments, respectively. Some TEI systems possess split designations. Definitions of each development level are
 1945 described in Sec. 11. and discussed in detail for each TEI system in the corresponding TEI section.

Proxy	1. Analytical protocols?	2. Distribution in environment?	3. Driving process isolated?	4. Sedimentary archives?	5. Effect of diagenesis?	Goal: Productivity reconstruction?
[Fe] $\delta^{56}\text{Fe}$	Applied	Applied	Developing	Developing	Developing	Unknown
[Zn] $\delta^{66}\text{Zn}$	Applied	Applied	Developing	Developing	Developing	Unknown
[Cu] $\delta^{65}\text{Cu}$	Applied	Applied	Developing	Developing	Developing	Unknown
[Ni] $\delta^{60}\text{Ni}$	Applied	Applied	Developing	Developing	Developing	Unknown
[Cd] $\delta^{114}\text{Cd}$	Applied	Applied	Developing	Developing	Developing	Unknown
[Ba] $\delta^{138}\text{Ba}$	Applied	Applied	Developing	Developing	Unknown	Unknown
[Mo] $\delta^{98}\text{Mo}$	Applied	Applied	Applied	Developing	Unknown	Unknown
[Ag] $\delta^{109}\text{Ag}$	Developing	Unknown	Unknown	Unknown	Unknown	Unknown

Key

- Unknown
- Developing
- Applied
- Unlikely

1946
 1947
 1948

1949 **12. Conclusions and outlook**

1950

1951 This review and synthesis allows us to draw a number of inferences regarding the overall suitability,
1952 similarities, and research priorities for using Fe, Zn, Cu, Cd, Mo, Ba, Ni, and Ag and their isotopes as
1953 paleoproductivity proxies. Regarding suitability, our proxy development assessment highlights that our
1954 knowledge of bioactive trace metal isotope systematics lags far behind those of trace-element abundances.
1955 This field is nascent; excepting Mo, the very first isotope data for seawater for all of the elements reviewed
1956 here were published within the last 15 year, or are yet to be reported, as is the case for Ag. The field is thus
1957 decades behind the trace element concentration community. Despite the lack of detail however, we can
1958 classify the elements reviewed here into three broad categories: those where the preponderance of evidence
1959 indicates that a particular bioactive metal isotope system is unlikely to inform on paleoproductivity, such
1960 as $\delta^{56}\text{Fe}$, $\delta^{65}\text{Cu}$, and $\delta^{98}\text{Mo}$; those where there are promising signs, but significant calibration and validation
1961 remains to be completed, such as for $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$; and, those elements where simply too little is
1962 presently known to confidently assign utility in diagnosing paleoproductivity such as for $\delta^{138}\text{Ba}$, $\delta^{60}\text{Ni}$, and
1963 $\delta^{109}\text{Ag}$.

1964

1965 Our review highlights a number of instances where the bioactive metals and their isotopes share similarities
1966 or—perhaps more importantly—exhibit divergent behaviors, despite sharing a common biological driver.
1967 The most significant similarity is ocean circulation; trace element isotope distributions reflect a mixture of
1968 local (i.e., *in situ*) processes, and regional (or *ex situ*) conditions that are set ‘upstream’ of any given locality.
1969 Indeed, researchers are recognizing that, much like the macronutrients (see Farmer et al., *this issue*), the
1970 first-order features of marine $\delta^{66}\text{Zn}$, $\delta^{65}\text{Cu}$, $\delta^{114}\text{Cd}$, $\delta^{138}\text{Ba}$, and $\delta^{60}\text{Ni}$ distributions are not controlled locally
1971 by dissolved–particulate transformations, but reflect a regionally-integrated history of vertical cycling and
1972 mixing that is imparted over the scale of an ocean basin. Today, the Southern Ocean represents the common
1973 starting point in controlling nutrient and bioactive metal inventories for much of the low latitude
1974 thermocline; whether, when, and how this pattern might have changed in Earth’s past will be an important
1975 consideration for interpreting paleoproductivity records derived from these proxies. Where the bioactive
1976 metals diverge in their response is equally instructive from the point of view of proxy development. For
1977 example, if experiencing a common forcing, such as a temporary shift in the loci of most intense primary
1978 productivity, subtle differences in the response of the various bioactive metals reviewed here may hold the
1979 key to understanding whether the underlying change was truly productivity related. For example,
1980 sedimentary accumulation and preservation of Cd and Ba exhibit opposing redox sensitivities; Cd burial is
1981 enhanced at low $[\text{O}_2]$, whereas Ba is oftentimes diminished. Recognizing these opposing controls may

1982 enable reconciling inconsistent proxy records, thus building a more holistic picture of marine
1983 biogeochemistry at key points in Earth's history.

1984

1985 Lastly, we outline three priorities for further study. First, a number of modern ambiguities require
1986 addressing. Most notable is the apparent 'missing' source and/or sink terms for the whole-ocean isotopic
1987 budgets of several elements, including Cu, Cd, Ba, and Ni. Though it is possible that these missing source
1988 and sink terms represent actual short-term imbalances in the flux of these elements to and from the ocean,
1989 we view it more likely that there are major fluxes that remain uncharacterized. The origin of these
1990 imbalances is most pressing for elements where the output flux associated with organic matter constitutes
1991 a secondary sink (e.g., Zn, Ni), as the isotopic budget of these elements is most susceptible to decoupling
1992 from productivity. Second, the significance of ocean circulation in mediating basin-scale bioactive metal
1993 isotope distributions implies that paleoceanographic interpretations made from a single site cannot be
1994 uniquely interpreted in terms of either changes in productivity or ocean circulation without additional
1995 constraints. Such constraints could take the form of independent circulation estimates—from numerical
1996 models or canonical circulation proxies measured in the same samples—or by measuring bioactive metal
1997 isotope distributions in spatially-distributed sediment samples. Third, the lack of suitable archives with
1998 which to reconstruct surface water bioactive metal isotope compositions afflicts almost every element
1999 reviewed here. Overcoming this limitation will require the most creativity; we suggest more studies testing
2000 the fidelity of non-traditional substrates (e.g., mixed foraminiferal assemblages, coccolith calcite, diatom
2001 opal), periodic re-assessment of the feasibility of traditional substrates following analytical advancements
2002 (e.g., improvements in ion transmission efficiency, large-scale [automated and/or crowd-sourced] picking
2003 of monospecific foraminiferal assemblages), and development and validation of selective extraction
2004 protocols that can be used to isolate phases of interest from complex matrices. Though attempting to
2005 overcome these limitations may be considered high risk, we believe that this risk is more than justified by
2006 the reward of developing a more complete understanding of Earth's biogeochemical history.

2007

2008

2009

2010

2011 **Postscripts**

2012

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2023

2024 **Data sources**

2025 Dissolved TEI data are sourced from the GEOTRACES Intermediate Data Products in 2014 (Mawji et al.,
 2026 2015) and 2017 (Schlitzer et al., 2018). Citations to the primary data sources used in the figures and Table
 2027 1 are given below.

2028

2029 *Figures*

2030 Iron: Conway & John, 2014a (Atlantic); Conway & John, 2015a (Pacific); Horner et al., 2015b (CD29-2
 2031 record); Chu et al., 2006 (28DSR9 record); Liu et al., 2020 (METG-03 record). Zinc: Conway & John,
 2032 2014b (Atlantic); Conway & John, 2015a (Pacific); Wang et al., 2019a (Southern); Little et al., 2014 (Fe–
 2033 Mn crust records). Copper: Little et al., 2018 (Atlantic); Takano et al., 2017 (Pacific); Boye et al., 2012
 2034 (Southern); Little et al., 2014 (Fe–Mn crust records). Cadmium: Conway and John, 2015b (Atlantic);
 2035 Conway & John, 2015a (Pacific); Abouchami et al., 2014 (Southern); Schmitt et al., 2009a (Fe–Mn crust
 2036 data); Horner et al., 2010 (Fe–Mn crust ‘core-top’ data); Murphy, 2016 (‘down core’ Fe–Mn crust records);
 2037 Schmitt et al., 2009a (‘down core’ Fe–Mn crust record); van Geen et al., 1995 (California Margin core-top
 2038 data). Molybdenum: Nakagawa et al., 2012 (all basins). Barium: Bates et al., 2017 (Atlantic); Geyman et
 2039 al., 2019 (Pacific); Hsieh & Henderson, 2017 (Southern). Nickel: Archer et al., 2020 (Atlantic); Takano et
 2040 al., 2017 (Pacific); Wang et al., 2019a (Southern); Gall et al., 2013 (CD29-2 record); Gueguen et al., 2016
 2041 (Fe–Mn crust records). Silver: Fischer et al., 2018 (Pacific); Boye et al., 2012 (Southern). Core MD02-2496
 2042 (Vancouver Island Margin; 48.97°N, 127.04°W, 1,243 m water depth) from Chang et al., 2014; Core

2043 W8709-13PC (Oregon Margin; 42.116°N, 125.75°W; 2,712 m water depth) from Kienast, 2003; ODP
 2044 1017E (Southern California; 34.53°N, 121.1°W; 955 m water depth) from Hendy & Pedersen, 2005; ODP
 2045 893A (Santa Barbara Basin; 34.287°N, 120.036°W; 576.5 m water depth) from Ivanochko, 2001.

2046 *Table 1*

2047 ^aSchlitzer (2017); ^bMorris et al. (1975); ^cGallon and Flegal, 2014; ^dBeard et al. (2003); ^eMoynier et al.
 2048 (2017) and references therein; ^fSchmitt et al. (2009a); ^gWillbold & Elliott (2017); ^hNan et al., 2018;
 2049 ⁱCameron et al. (2009); ^jUSGS reference material SCO-1 (Cody Shale) is used given paucity of
 2050 representative data; Schönbacher et al. (2007); ^kSection 3 and references therein; ^lSection 4 and references
 2051 therein; ^mSection 5 and references therein; ⁿSection 6 and references therein; ^oData from Nakagawa et al.
 2052 (2012) renormalized to NIST SRM 3134 + 0.25 ‰ based on Goldberg et al. (2013); ^pSection 8 and
 2053 references therein; ^qSection 9 and references therein; ^rHayes et al. (2018) and references therein; ^sMiller et
 2054 al. (2011); ^tDickens et al. (2003); ^uCameron & Vance (2014) and references therein; Little et al. (2015;
 2055 2020); ^vBroecker & Peng (1982).

2056

2057 **Competing interests**

2058 The authors declare that they are not aware of any financial conflicts of interest, real or perceived.

2059

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