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1 Pervasive sources of isotopically light zinc in the North Atlantic
2 Ocean

3

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15 Keywords: zinc isotopes, North Atlantic, zinc sources, GEOTRACES, GEOVIDE

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18 Highlights:

- 19 • Hydrothermal and sedimentary sources of light $\delta^{66}\text{Zn}$
20 • $\delta^{66}\text{Zn}$ and abundance ratios to the major nutrients deconvolve key processes
21 • Light $\delta^{66}\text{Zn}$ in the surface North Atlantic due to Zn addition, not scavenging

22

23 **Abstract**

24 In this study, we report seawater dissolved zinc (Zn) concentration and isotope
25 composition ($\delta^{66}\text{Zn}$) from the GEOTRACES GA01 (GEOVIDE) section in the North
26 Atlantic. Across the transect, three subsets of samples stand out due to their
27 isotopically light signature: those close to the Reykjanes Ridge, those close to the
28 sediments, and those, pervasively, in the upper ocean. Similar to observations at other
29 locations, the hydrothermal vent of the Reykjanes Ridge is responsible for the
30 isotopically light Zn composition of the surrounding waters, with an estimated source
31 $\delta^{66}\text{Zn}$ of -0.42‰ . This isotopically light Zn is then transported over a distance greater
32 than 1000km from the vent. Sedimentary inputs are also evident all across the trans-
33 Atlantic section, highlighting a much more pervasive process than previously thought.
34 These inputs of isotopically light Zn, ranging from -0.51 to $+0.01 \text{‰}$, may be caused
35 by diffusion out of Zn-rich pore waters, or by dissolution of sedimentary particles.

36 The upper North Atlantic is dominated by low $\delta^{66}\text{Zn}$, a feature that has been observed
37 in all Zn isotope datasets north of the Southern Ocean. Using macronutrient to Zn
38 ratios to better understand modifications of preformed signatures exported from the
39 Southern Ocean, we suggest that low upper-ocean $\delta^{66}\text{Zn}$ results from addition of
40 isotopically light Zn to the upper ocean, and not necessarily from removal of heavy Zn
41 through scavenging. Though the precise source of this isotopically light upper-ocean
42 Zn is not fully resolved, it seems possible that it is anthropogenic in origin. This view
43 of the controls on upper-ocean Zn is fundamentally different from those put forward
44 previously.

45

46 **1. Introduction**

47 Zinc (Zn) is an essential micronutrient for marine primary producers (Morel and Price,
48 2003). It is required for key metalloenzymes such as carbonic anhydrase, which is
49 involved in carbon fixation, or alkaline phosphatase, which gives phytoplankton access
50 to organic forms of phosphorus when phosphate concentrations are low (Sunda,
51 1989). As a result, the marine cycles of zinc and carbon are intrinsically linked.

52 Analytical advances over the last decade have enabled study of the stable isotope
53 composition of Zn ($\delta^{66}\text{Zn}$ = variations in $^{66}\text{Zn}/^{64}\text{Zn}$ expressed in parts per thousand
54 deviation from the JMC Lyon standard), to investigate the processes controlling the
55 marine Zn distribution (Bermin et al., 2006; Conway et al., 2013; Takano et al., 2013).
56 In addition, the recent international programme GEOTRACES has provided a large
57 quantity of high-quality data, from full-depth profiles and sections, allowing new
58 insights into the large-scale distribution of trace elements, including Zn (Conway and
59 John, 2014, 2015; Zhao et al., 2014; Vance et al., 2016; John et al., 2018; Weber et
60 al., 2018; Wang et al., 2019). However, gaps remain in our understanding of the
61 modern Zn cycle. Firstly, the $\delta^{66}\text{Zn}$ of seawater (averaging +0.46 ‰) is higher than the
62 known inputs and lower than most known outputs, pointing to a missing budget term
63 if the oceanic Zn cycle is in steady state (Little et al., 2014; Moynier et al., 2017).
64 Secondly, north of the Southern Ocean, a shift toward light Zn isotope signatures in
65 the dissolved pool is observed within the upper ocean (<1000m). This is surprising,
66 given that isotopic fractionation between phytoplankton cells and the dissolved pool is
67 thought to be close to zero, or slightly in favour of light isotope uptake, which should
68 leave the residual dissolved pool slightly heavy (John et al., 2007; Peel et al., 2009;
69 Samanta et al., 2017; Köbberich and Vance, 2019; Wang et al., 2019). Laboratory
70 experiments have suggested that Zn released from degrading phytoplankton cells can

71 be rapidly scavenged back onto organic matter, and that this adsorbed Zn is
72 isotopically heavier than the dissolved pool (John and Conway, 2014). Scavenging of
73 isotopically heavy Zn onto sinking biogenic particles has thus been suggested to
74 explain the low $\delta^{66}\text{Zn}$ values in the upper ocean (Conway and John, 2014, 2015; John
75 et al., 2018; Weber et al., 2018), although it should be noted that a dominant proportion
76 of marine dissolved Zn is complexed to natural organic ligands (e.g. Ellwood and Van
77 den Berg, 2000) and thus presumably not available for adsorption to particles.

78 Here we examine Zn isotopes and concentrations along a GEOTRACES section that
79 crosses the North Atlantic from the Iberian Peninsula to Newfoundland (Fig. 1). The
80 North Atlantic is a promising area to study biological, physical and geochemical
81 processes affecting micronutrient distributions, as it is characterised by a strong spring
82 bloom (Longhurst, 2010), the formation of globally-important deep water masses (e.g.
83 Danialt et al., 2016), and a variety of trace metal sources (Ohnemus and Lam, 2014).
84 In this study, we focus our discussion on the processes responsible for the light isotope
85 composition of Zn observed at the Reykjanes Ridge, at the sediment-water interface,
86 and in the upper 500m of the ocean. In doing so, we expand our analysis to data from
87 the entire North Atlantic. We combine macronutrient/Zn ratios with Zn stable isotope
88 data for the dissolved pool in order to better identify the processes that modify
89 preformed Southern Ocean signatures in the low-latitude oceans. In contrast to
90 previous studies that invoke scavenging removal of heavy Zn isotopes for the origin of
91 light upper-ocean Zn (e.g. John and Conway, 2014), we conclude that the Zn isotope
92 signature of the upper ocean is dominated by the addition of isotopically light Zn to
93 upper-ocean water masses, whose preformed Zn concentrations are extremely low
94 (Vance et al., 2017; de Souza et al., 2018; Middag et al., 2019), and which are thus
95 very sensitive to the addition of small amounts of Zn.

96

97 **2. Methods**

98 2.1. Study area and sample collection

99 Samples were collected during the GEOVIDE cruise (GEOTRACES GA01) from 15
100 May to 30 June 2014 (R/V Pourquoi Pas?). At six stations, 17 depths between the
101 surface and the seafloor were sampled for dissolved Zn concentrations and stable
102 isotope composition (expressed as $\delta^{66}\text{Zn}$; see Eq. 1 below). These 6 stations (Fig. 1)
103 are located within the Iberian basin (Station 13), the west European basin (Station
104 21), the Icelandic basin (Stations 32 and 38) with Station 38 just above the Reykjanes
105 Ridge, the Irminger basin (Station 44) and the Labrador basin (Station 69).

106 Samples were collected using a clean rosette equipped with cleaned 12 litre GO-FLO
107 bottles, following the recommendations of the GEOTRACES cookbook (Cutter et al.,
108 2017). After recovery, the bottles were transferred into a clean container and seawater
109 samples were filtered through 0.45 μm polyethersulfone filters (Pall, SuporTM) mounted
110 in Swinnex polypropylene filter holders (Millipore). Between 1 and 4 litres of filtrate
111 were collected into acid-cleaned polyethylene bottles. More details of the sampling
112 procedure can be found in Gourain et al. (2019).

113 2.2. Sample processing and analysis

114 At ETH Zürich, samples were acidified to pH ~2 by addition of concentrated
115 hydrochloric acid (HCl; Merck AnalaR grade, further purified by double sub-boiling
116 distillation) and left for at least 1 month before processing. All samples were processed
117 under clean laboratory conditions in clean hoods, using only trace metal clean Savillex
118 PFA labware. All water used was ultrapure ($\geq 18.2 \text{ M}\Omega\cdot\text{cm}$) and all acids and reagents
119 were Merck AnalaR grade, further purified by single or double sub-boiling distillation.

120 Samples were first doped with a ^{67}Zn - ^{64}Zn double spike to achieve a sample:spike
121 ratio of ~ 1 . After 48 hours of equilibration, an ammonium acetate buffer solution was
122 added and pH was increased to 5.0 ± 0.3 . Zinc was extracted from seawater with
123 Nobias PA1 resin and purified using AGMP-1 anion exchange resin (Bermin et al.,
124 2006; Takano et al., 2013; Vance et al., 2016). Total procedural blanks were assessed
125 by processing ultrapure water as a sample, and were 1.8 ± 0.6 ng, with a $\delta^{66}\text{Zn}$ of
126 $+0.46 \pm 0.28$ ‰ (average and 2SD, $n=8$). Blank contributions were barely significant
127 (mostly involving a correction of 0.01-0.02 ‰) for all except three samples: Station 13-
128 15m (0.10 ‰ shift), Station 21-50m (0.08 ‰ shift) and Station 44-159m, (0.12 ‰ shift).
129 Nonetheless, Table S1 gives blank-corrected data with propagated uncertainty in the
130 blank amount and isotope composition.

131 Isotopic analyses were performed at ETH Zürich using a Thermo-Finnigan Neptune
132 Plus multi-collector inductively-coupled-plasma mass spectrometer (MC-ICPMS) in
133 'low-resolution' mode. Samples were introduced in 1 mL 0.3M nitric acid (HNO_3) via a
134 CPI PFA nebulizer ($50 \mu\text{L}\cdot\text{min}^{-1}$) attached to an Aridus II desolvating system. Dissolved
135 Zn concentrations were obtained by isotope dilution. Analytical mass bias correction
136 was performed using the double spike technique (Bermin et al., 2006). Dissolved Zn
137 isotope compositions ($\delta^{66}\text{Zn}$) were calculated following the iterative approach of
138 Siebert et al. (2001) and are given in the standard delta per mil notation relative to the
139 JMC-Lyon standard:

$$140 \quad \delta^{66}\text{Zn} (\text{‰}) = \left[\frac{\left(\frac{^{66}\text{Zn}}{^{64}\text{Zn}} \right)_{\text{sample}}}{\left(\frac{^{66}\text{Zn}}{^{64}\text{Zn}} \right)_{\text{JMC Lyon}}} - 1 \right] \times 1000 \quad (1)$$

141
142 During the course of this study, and owing to the exhaustion of the existing JMC-Lyon
143 stock, Zn data were normalised to a new primary standard, AA-ETH Zn. Where this

144 was the case, data were converted to the JMC-Lyon delta scale by applying a
145 conversion factor of -0.28 ‰ (Archer et al., 2017). Long-term reproducibility of Zn
146 isotope analysis on the instrument is monitored by repeat analysis of a secondary
147 standard, IRMM-3702, which yields $\delta^{66}\text{Zn} = +0.30 \pm 0.06$ ‰, relative to JMC-Lyon,
148 over 5 years ($n = 543$, 2SD). Internal errors obtained from the mass spectrometry
149 analysis, propagated through the double spike calculations and including the
150 uncertainty arising from the blank correction, were generally lower than the long-term
151 reproducibility. These internal uncertainties are given in the data table. Uncertainties
152 plotted on the figures are the internal uncertainties or the long-term reproducibility,
153 whichever is the larger. Zinc isotope reproducibility for samples, as assessed by full
154 analytical replicates of 14 samples, was consistent with long-term standard
155 reproducibility. Differences between these replicates ranged between 0.00 and 0.14
156 ‰ and averaged 0.05 ± 0.04 ‰. This laboratory has demonstrated agreement for Zn
157 concentrations and isotopes with the GEOTRACES standards SAFe D1 and D2 using
158 similar methods in a number of past papers (Zhao et al., 2014; Sieber et al., 2020) and
159 with the GEOTRACES intermediate data product (IDP 2017; Schlitzer et al., 2018).
160 Furthermore, analyses of deep ocean samples yield the same results as obtained in
161 other studies (e.g. Conway and John, 2014; Sieber et al., 2020; Vance et al., 2016;
162 Wang et al., 2019).

163 2.3. Other oceanographic parameters

164 Concentrations of the macronutrients silicate (Si) and nitrate (NO_3^-) were obtained by
165 the nutrient group at the LEMAR laboratory, using the method described in Aminot
166 and K erouel (2007). Because of technical problems, phosphate data are not available.
167 Hydrographic parameters (oxygen, salinity, temperature) were used to define the

168 water mass distribution and the general circulation along the GEOVIDE transect, as
169 described by García-Ibáñez et al. (2018).

170 2.4. Dissolved Zn*

171 Since the first reliable Zn data (Bruland, 1980), and further confirmed by the efforts of
172 the GEOTRACES programme to produce high-resolution Zn data (Schlitzer et al.,
173 2018), a strong correlation is observed between Zn and Si concentrations throughout
174 the global ocean (Vance et al., 2017; de Souza et al., 2018). Any variability in this
175 relationship highlights either sources or sinks of Zn relative to Si, such as biological
176 uptake or regeneration of Zn and Si at different rates, or an addition to or loss from the
177 water column (Wyatt et al., 2014; Roshan and Wu, 2015; Kim et al., 2017). To illustrate
178 deviations from the global marine Zn-Si correlation, we use the Zn* parameter, which
179 is defined as:

$$180 \quad Zn^* = [Zn]_{measured} - \left(Zn/Si_{deep} \times [Si]_{measured} \right) \quad (2)$$

181 with Zn/Si_{deep} set at 0.06 mmol.mol⁻¹, representing the average Zn/Si ratios in the
182 global deep ocean. Note that the average Zn/Si ratios across the GEOVIDE transect
183 for depths ≥3000m (excluding the deepest samples, closest to the sediment-water
184 interface, in each depth profile; see section 4.2) is 0.08 mmol.mol⁻¹.

185

186 3. Results

187 Dissolved Zn concentrations vary from 0.07 to 5.95 nmol.L⁻¹, δ⁶⁶Zn values from -0.22
188 to +0.53 ‰, and Zn* from -0.25 to +5.29 nmol.L⁻¹ across the entire GEOVIDE section
189 (Fig. 2 and 3; Table S1). Dissolved Zn concentrations exhibit a typical nutrient-type
190 profile, with low concentrations throughout the surface ocean (<0.50 nmol.L⁻¹ in the

191 upper 20m, except at Station 32 where it reaches 1.00 nmol.L^{-1} at 30m) and an
192 increase with depth, reaching up to 5.95 nmol.L^{-1} close to the Reykjanes Ridge.

193 Zn^* values in the upper ocean are close to zero, even if slightly positive ($+0.08 \pm 0.30$
194 nmol.L^{-1} , $n=9$, median $\pm 1\text{SD}$), and increase with depth, reaching maximum values
195 close to the sea floor. The picture in the deep eastern part of the section (Iberian and
196 west European basins) is slightly more complex, with a mid-depth maximum in Zn^*
197 values overlying lower values between 2000 and 5000m. Overall, Zn^* values are
198 positive, indicating an enrichment of Zn relative to Si. This general Zn enrichment is
199 also indicated by the greater $\text{Zn/Si}_{\text{deep}}$ ratio of the North Atlantic along GEOVIDE
200 ($0.08 \pm 0.03 \text{ mmol.mol}^{-1}$) compared to the world ocean ($0.06 \pm 0.02 \text{ mmol.mol}^{-1}$; Schlitzer
201 et al., 2018).

202 The deep ocean ($>1500\text{m}$) across the GEOVIDE transect averages $+0.38 \pm 0.07 \text{ ‰}$
203 (average $\pm 1\text{SD}$, $n=27$) in $\delta^{66}\text{Zn}$, which is nominally lighter than, but within error of, the
204 global average deep ocean $\delta^{66}\text{Zn}$ value ($+0.46 \pm 0.13 \text{ ‰}$; 2SD , $n = 312$, $2\text{SE} = 0.01$
205 ‰ ; Schlitzer et al., 2018). Apart from this, three zones stand out from the rest of the
206 section: the upper ocean (between the surface and $\sim 1000\text{m}$), the area close to the
207 Reykjanes Ridge, and the sediment-water interface (Fig. 2). All are characterised by
208 light Zn signatures, with median $\delta^{66}\text{Zn}$ values of $-0.13 \pm 0.07 \text{ ‰}$ for the upper ocean
209 ($n=8$), $-0.01 \pm 0.07 \text{ ‰}$ around the Reykjanes Ridge ($n=4$), and $+0.12 \pm 0.16 \text{ ‰}$ for the
210 sediment-water interface ($n=5$), but they are associated with either high Zn
211 concentrations (close to the Reykjanes Ridge and the bottom) or low Zn
212 concentrations (upper ocean).

213

214 **4. Discussion**

215 Apart from the marked maximum extending eastwards from the Reykjanes Ridge, the
216 distribution of Zn (Fig. 2) along the GEOVIDE transect bears a strong resemblance to
217 those of the major nutrients (cf. García-Ibáñez et al., 2018), and especially that of Si,
218 reflected by the close correlation between their concentrations that is typical for the
219 open ocean (Fig. 4; Bruland, 1980; Vance et al., 2017; de Souza et al., 2018; Weber
220 et al., 2018). To first order, the cross-basin distributions of Zn, Si and other
221 macronutrients are largely governed by the properties of the water masses found
222 along the transect: water masses formed in the North Atlantic and Nordic Seas are
223 macronutrient- and Zn-poor, and fill the basins west of the Reykjanes Ridge as well as
224 the mid-depths across the entire transect, whereas macronutrient- and Zn-rich waters
225 of southern origin fill the abyss east of the ridge, below about 3000 m (e.g. García-
226 Ibañez et al., 2018). However, despite this first-order water mass control on the
227 elemental distributions of Zn and Si, and in marked contrast to the silicon stable
228 isotope distribution along GEOVIDE (Sutton et al., 2018), the $\delta^{66}\text{Zn}$ distribution (Fig.
229 2) displays little systematic cross-basin variation. What stands out instead are the low
230 $\delta^{66}\text{Zn}$ values at mid-depths, near the bottom, and in the upper ocean. In the following,
231 we discuss each of these in turn.

232

233 **4.1. Light Zn isotope signatures in the vicinity of the** 234 **Reykjanes Ridge**

235 Elevated Zn concentrations (5.95 nmol.L^{-1}), high Zn^* (up to $+5 \text{ nmol.L}^{-1}$) and light $\delta^{66}\text{Zn}$
236 values (-0.22 ‰) were determined at Station 38, just above the Reykjanes Ridge (Figs.
237 2 and 3), suggesting the input of hydrothermally-sourced Zn here. Interestingly, high

238 Zn concentrations ($>2.40 \text{ nmol.L}^{-1}$), again associated with high Zn^* ($>+1.7 \text{ nmol.L}^{-1}$)
239 and light $\delta^{66}\text{Zn}$ values ($<+0.02 \text{ ‰}$), were also observed between 1500 and 2000m
240 within the Icelandic and west European basins to the east of the ridge (Stations 32
241 and 21, respectively). Data across this mid-depth Zn maximum from all three stations
242 exhibit a strong positive correlation between $\delta^{66}\text{Zn}$ and $1/[\text{Zn}]$ (Fig. 5a), suggesting
243 that the “plume” of elevated Zn above and to the east of the Reykjanes Ridge can be
244 explained by mixing between two components: ambient deep seawater and a
245 hydrothermal source. Indeed, hydrothermal vents along the Reykjanes Ridge have
246 been shown to act as a source of other dissolved trace elements, such as iron and
247 manganese (Achterberg et al., 2018). Although their origin could not be definitively
248 determined, it has also been suggested that the enrichments in particulate and
249 dissolved iron and aluminium concentrations observed above Reykjanes Ridge during
250 GEOVIDE (Gourain et al., 2019; Tonnard et al., 2020), as well as the elevated radium-
251 226 activity seen there (Le Roy et al., 2018), may also reflect the influence of
252 hydrothermal activity.

253 To assess the $\delta^{66}\text{Zn}$ value of the hydrothermal end-member, we compare Zn
254 concentrations and isotopes observed within the hydrothermal plume at Station 38
255 with those of background deep seawater from surrounding stations (Station 32: 990-
256 1235m and 2463-3177m; Station 44: 1087-2851m; $[\text{Zn}]_{\text{background}} = 1.46 \pm 0.22 \text{ nmol.L}^{-1}$
257 ¹ and $\delta^{66}\text{Zn}_{\text{background}} = +0.42 \pm 0.06 \text{ ‰}$; median values; $n=12$). The quantity of
258 hydrothermally-sourced Zn at any depth is estimated by subtracting this background
259 concentration from the measured concentration at this depth. The strong linear
260 correlation between $\delta^{66}\text{Zn}$ and the fraction of hydrothermally-derived Zn (calculated
261 by dividing the estimated quantity of hydrothermal Zn by the total Zn concentration)
262 suggests that the hydrothermal end-member bears a $\delta^{66}\text{Zn}$ value of $-0.42 \pm 0.11 \text{ ‰}$

263 (Fig. 5b). This value is very similar to the hydrothermal $\delta^{66}\text{Zn}$ signature of -0.5‰
264 estimated for the TAG hydrothermal field at 26°N in the North Atlantic (Conway and
265 John, 2014). The total range of $\delta^{66}\text{Zn}$ in pure hydrothermal fluids, from 0.00 to $+1.33$
266 ‰ (John et al., 2008), with recent inferred values of $+0.24\text{‰}$ at the East Pacific Rise
267 (John et al., 2018), suggest that the hydrothermal $\delta^{66}\text{Zn}$ signature likely depends on
268 the ridge characteristics.

269 The low $\delta^{66}\text{Zn}$ observed at Stations 32 and 21 is likely the result of transport by
270 Labrador Sea Water (LSW; Fig. 1), which crosses the Mid-Atlantic Ridge (MAR) at
271 latitudes around 50°N and spreads eastward into the Icelandic and west European
272 basins (e.g. Paillet et al., 1998; Sutton et al., 2018). The hydrothermal signal, acquired
273 when crossing the MAR, thus seems to propagate over a distance of 1000km (from
274 the MAR to Station 21). This is in contrast to the observations of Conway and John
275 (2014) who did not find any extension of the Zn hydrothermal signal away from the
276 MAR along their east-west section, likely because of the north-south deep water mass
277 circulation there (Jenkins et al., 2015). Our results are, however, similar to other
278 studies that have reported long-distance transport of hydrothermally-derived Zn along
279 with the deep water mass flow direction (Wheat et al., 2002; Roshan et al., 2016; John
280 et al., 2018). The light hydrothermal $\delta^{66}\text{Zn}$ signature may be transported as
281 nanoparticulate sulphide species (Conway and John, 2014; John et al., 2018), since
282 sulphide is known to preferentially sequester light Zn (Archer et al., 2004; Fujii et al.,
283 2011; Vance et al., 2016).

284

285 **4.2. Light Zn isotope signatures at the sediment-water** 286 **interface**

287 A striking feature all across the transect is the sharp increase in Zn concentrations and
288 Zn* at the very bottom of each profile (up to 4.02 nmol.L⁻¹ and +2.5 nmol.L⁻¹,
289 respectively; Fig. 3), associated with a shift to lighter $\delta^{66}\text{Zn}$ signatures (as low as -0.16
290 ‰). Importantly, this shift consistently occurs between the deepest sample and the
291 one immediately above it, i.e. over a depth interval of 25 to 425m. The mirror image
292 between $\delta^{66}\text{Zn}$ and Zn* profiles suggests the addition of isotopically light Zn to
293 seawater close to the seafloor.

294 The fact that we observe isotopically-light sedimentary Zn input all across the transect
295 is surprising compared to the findings of previous studies, in which such isotopic
296 signals were observed only near margin sediments in the subtropical North Atlantic
297 (from -0.7 to -0.5 ‰; Conway and John, 2014) and the California basin (-0.3 ‰;
298 Conway and John, 2015). Since all our near-bottom samples were taken from the
299 same GO-FLO bottle (in rosette position 1), we must consider the possibility of
300 contamination. Zurbrick et al. (2018) observed a decrease of the excess lead (Pb)
301 concentration in this bottle (i.e. the difference in Pb concentrations between the near-
302 bottom sample and its nearest neighbour) as the GEOVIDE cruise proceeded, pointing
303 to a wash-out of Pb contamination from the GO-FLO bottle with time. However, we
304 observe no decrease of excess Zn over time (Fig. S1). Furthermore, unlike Zn, Pb
305 concentrations are very low in the deep North Atlantic due to its different geochemical
306 behaviour (~ 0.02 nmol Pb.L⁻¹ compared to ~ 2.0 nmol Zn.L⁻¹), such that Pb is much
307 more prone to contamination in deep-water samples than Zn. Therefore, we suggest
308 that these near-bottom samples reflect true ocean Zn signals that document a
309 sedimentary source of Zn.

310 On the GEOVIDE cruise, the deepest sample was taken at 4-32m (15m on average)
311 above the seafloor. This is in contrast to the subtropical North Atlantic section, along
312 which the light signal at the bottom was only found at the continental margins, where
313 the deepest samples came from between 33 and 299m above the seafloor (76m on
314 average; Conway and John, 2014). This greater difference from the seafloor could
315 explain why the sedimentary input was not observed across the entire transect by
316 Conway and John (2014), and would suggest that the light sediment-derived $\delta^{66}\text{Zn}$
317 signal does not persist far from the seafloor.

318 By comparing the deepest Zn concentration and $\delta^{66}\text{Zn}$ value with those of the deep
319 seawater background at each station, the $\delta^{66}\text{Zn}$ value of the local sedimentary source
320 (Table S2) can be deduced from mass balance. This calculation results in different
321 sedimentary Zn isotope signatures for the eastern (Iberian and west European basins)
322 and western (Icelandic, Irminger and Labrador basins) sections of the transect, with
323 $\delta^{66}\text{Zn}$ values of $0.01 \pm 0.02 \text{ ‰}$ and $-0.51 \pm 0.04 \text{ ‰}$ respectively (Table S2). This
324 variation might be explained by different types of sediment, or different processes
325 releasing Zn to seawater, on either side of the sub-arctic front (SAF; Fig. 1).

326 The processes that might provide light Zn to the bottom waters are not constrained by
327 our data. However, upward diffusion from Zn-rich pore waters is consistent with ^{226}Ra
328 enrichments close to the seafloor (Le Roy et al., 2018) in the eastern basin. In the
329 western basin, dissolution of sedimentary particles might be the important process
330 controlling the Zn source, as Gourain et al. (2019) observed high particulate iron,
331 manganese and aluminium concentrations associated with low beam transmissometry
332 values, suggesting sediment resuspension. Release of biogenic Zn from the
333 sediments or dissolution of Zn sulphides could also explain the near-bottom
334 isotopically light Zn signatures (Conway and John, 2014, 2015). Regardless of the

335 precise process of addition, the extension of this near-bottom feature all the way
336 across the GEOVIDE transect suggests that the addition of isotopically-light zinc from
337 sediments is a much more pervasive process in the ocean than previously thought.

338

339 **4.3. Light Zn isotope signatures in the upper ocean**

340 Within the upper 500m, low Zn concentrations are observed in our North Atlantic
341 transect (as low as 0.07 nmol.L⁻¹; Fig. 2 and 3) as well as other oceanic regions north
342 of the Southern Ocean (Conway and John, 2014, 2015; John et al., 2018). Zn* values
343 in the GEOVIDE data are close to zero as a result of low Zn and Si concentrations,
344 though 13 out of 14 data points are positive (between -0.21 and +0.87 nmol.L⁻¹; Fig.
345 3), and $\delta^{66}\text{Zn}$ values are low (as low as -0.18 ‰). Other studies, in the North Atlantic
346 as well as in the tropical and North Pacific, have noted similarly low $\delta^{66}\text{Zn}$ values in
347 the upper ocean (Conway and John, 2014, 2015; John et al., 2018; Vance et al., 2019;
348 Liao et al., 2020), which is at odds with the first-order expectation that biological Zn
349 uptake should slightly enrich upper-ocean Zn in its heavy isotopes, given the
350 fractionation observed in culture and deduced for natural freshwater systems (John et
351 al., 2007; Peel et al., 2009; Samanta et al., 2018; Köbberich and Vance, 2019). This
352 finding has led to the hypothesis that isotopically heavy Zn is removed by scavenging,
353 explaining the light $\delta^{66}\text{Zn}$ values in the upper ocean (Conway and John, 2014, 2015;
354 John et al., 2018; Weber et al., 2018). However, given the strong preformed upper-
355 ocean gradients in Zn concentrations resulting from interactions between biological
356 activity and physical circulation at the large scale, which primarily occur in the
357 Southern Ocean (e.g. Vance et al., 2017), assessing the presence of a small *in-situ*
358 upper-ocean source or sink in the lower latitudes is a significant challenge.

359 In order to disentangle the signal of local/regional upper-ocean processes from large-
360 scale nutrient cycling, we compare $\delta^{66}\text{Zn}$ values and macronutrient/Zn ratios observed
361 across the GEOVIDE section with data from the Southern Ocean (Fig. 6; we use
362 macronutrient/Zn ratios, and not Zn/macronutrient ratios, since binary mixing produces
363 linear relationships between $\delta^{66}\text{Zn}$ and $1/\text{Zn}$). The GEOVIDE isotope profiles, in
364 common with all others north of the Southern Ocean, contrast strongly with the
365 homogeneous isotope profiles observed south of the Antarctic Polar Front (Zhao et
366 al., 2014; Wang et al., 2019; Sieber et al., 2020). Water masses that fill the global
367 ocean transport this homogeneous Southern Ocean $\delta^{66}\text{Zn}$ signature northwards,
368 whilst also influencing global distributions of Zn and the macronutrients nitrate (NO_3^-)
369 and Si (Sarmiento et al., 2004; Vance et al., 2017). Southern Ocean waters supplying
370 the upper ocean are stripped of Zn relative to NO_3^- and phosphate, and thus bear high
371 NO_3^-/Zn ratios, whilst abyssal waters carry the equivalent regenerated Zn, and thus
372 bear NO_3^-/Zn ratios 1-2 orders of magnitude lower. Ratios of Si/Zn in the Southern
373 Ocean source waters vary much less than NO_3^-/Zn , by less than factor 2, due to
374 coupled uptake of Zn and Si at the surface by Southern Ocean diatoms (Vance et al.,
375 2017; de Souza et al., 2018). These Southern Ocean water masses are transported
376 northwards globally, including into the northern North Atlantic: abyssal water masses
377 of Southern Ocean origin can be traced as far north as 58°N (e.g. van Aken and
378 Becker, 1996), whilst the upper limb of the meridional overturning circulation transports
379 upper Southern Ocean water masses into the North Atlantic (e.g. Marshall and Speer,
380 2012) where they influence the biogeochemical characteristics of water masses
381 formed in the North Atlantic and Nordic seas (e.g. (Williams et al., 2006; de Souza et
382 al., 2012, 2015). The isotopic and elemental ratio signatures of Southern Ocean water
383 masses (black rectangles in Fig. 6; Sieber et al., 2020) thus provide the framework

384 within which we interpret the controls on Zn and its isotopes here: deviations from the
385 Southern Ocean elemental ratio signatures indicate a decoupling of Zn from the
386 macronutrients, which may reflect either differential biogeochemical cycling (e.g.
387 different depths of remineralisation) or the presence of sources or sinks of Zn that do
388 not affect macronutrient concentrations.

389 As can be seen in Fig. 6, NO_3^-/Zn and Si/Zn in the deepest ocean across GEOVIDE
390 (i.e., in southern-sourced deep waters, depths > 3000m east of the Reykjanes Ridge;
391 empty symbols in Fig. 6) are generally near-identical to the signatures observed in
392 deep Southern Ocean waters. In the intermediate and upper ocean, however, the
393 GEOVIDE data show lower NO_3^-/Zn and Si/Zn ratios than the relevant Southern
394 Ocean source, up to a factor of 260 and 11 respectively. This decoupling between Zn
395 and the macronutrients, with a decrease in macronutrient/Zn ratios, suggests that
396 there is an *addition*, not removal, of Zn relative to NO_3^- and Si, especially in the upper
397 ocean. In the next section, we consider the influence of this relative Zn source on the
398 $\delta^{66}\text{Zn}$ distribution over the entire North Atlantic.

399

400 **4.4. Addition of isotopically light Zn: a pervasive process in** 401 **the North Atlantic**

402 Isotopically light Zn signatures in the upper ocean have also been observed in the
403 subtropical North Atlantic ($\delta^{66}\text{Zn}$ as low as -0.69 ‰ at 80m, GA03 transect; Conway
404 and John, 2014), as well as in other ocean basins (John et al., 2018). Here, we aim to
405 demonstrate that the low upper-ocean $\delta^{66}\text{Zn}$ signature observed in the entire North
406 Atlantic (GA03 & GEOVIDE sections; Schlitzer et al., 2018) has a single cause: the
407 addition of isotopically light Zn.

408 Figure 7 shows the relationship between NO_3^-/Zn (Fig. 7a) or Si/Zn (Fig. 7b) and $\delta^{66}\text{Zn}$
409 for all North Atlantic data. These North Atlantic data are compared to the
410 corresponding Southern Ocean signatures (black rectangles), which vary in elemental
411 ratios but not in $\delta^{66}\text{Zn}$. Samples from oxygen-rich waters (oxygen saturation > 60%;
412 colour coding in Fig. 7) generally follow trends towards lower $\delta^{66}\text{Zn}$ values with
413 decreasing NO_3^-/Zn and Si/Zn (black arrows). These trends illustrate the fact that light
414 $\delta^{66}\text{Zn}$ values are mostly associated with an enrichment in Zn relative to Si or NO_3^- (i.e.,
415 lower macronutrient/Zn ratios). This relationship suggests that the North Atlantic $\delta^{66}\text{Zn}$
416 distribution is influenced by the addition of isotopically light Zn, similar to the recent
417 inference of an isotopically light external source influencing the $\delta^{66}\text{Zn}$ distribution of
418 the Northwest Pacific (Liao et al., 2020). In Figure 7, Zn-poor upper-ocean samples,
419 which plot towards the bottom left corner of each plot, tend to be more strongly
420 affected, appearing to have both a stronger *relative* source (at lower macronutrient
421 and Zn concentrations) and lower $\delta^{66}\text{Zn}$ values. Conversely, samples from oxygen-
422 poor regions (oxygen saturation < 50%) such as at the Mauritanian upwelling regime
423 show an opposite trend, towards higher NO_3^-/Zn and Si/Zn ratios than the Southern
424 Ocean. This depletion of Zn relative to the macronutrients was noted by Conway and
425 John (2014), who attributed it to Zn loss either through sulphide precipitation or
426 scavenging onto particles sinking through the oxygen-poor zone.

427 Figure 8 shows the correlation between Si and Zn concentrations in the North Atlantic,
428 with data points colour-coded for $\delta^{66}\text{Zn}$ values. Vertical deviations from the well-known
429 near-linear global Zn-Si relationship (Vance et al., 2017; de Souza et al., 2018; Roshan
430 et al., 2018; Weber et al., 2018) indicate either addition (data above the dotted line) or
431 removal (data below the dotted line) of Zn relative to Si. Even in this simple
432 representation, numerous sources of relative Zn addition are visible in the North

433 Atlantic data. Hydrothermal and sedimentary addition of Zn relative to Si is seen for
434 the deep ocean (Si concentrations $\geq 10 \mu\text{mol.L}^{-1}$), with the associated $\delta^{66}\text{Zn}$ being
435 variable but relatively low (between -0.2 and +0.3 ‰). However, the cluster of data
436 points above the global relationship at low Si concentrations ($< 5 \mu\text{mol.L}^{-1}$) is a clear
437 sign of relative excess Zn in the Si-poor shallow ocean. Importantly, these samples
438 are characterised by the lowest $\delta^{66}\text{Zn}$ values observed in the North Atlantic (between
439 -0.6 and -0.1 ‰).

440 Taken together, our analysis of the North Atlantic $\delta^{66}\text{Zn}$ distribution in the large-scale
441 biogeochemical context suggests that addition of isotopically light Zn is the dominant
442 process controlling the upper-ocean Zn isotope signature, at least in the North Atlantic.
443 Macronutrient/Zn depth profiles (Fig. 6) and systematics (Fig. 7 and 8) suggest that
444 this addition may be pervasive over the upper 2000 – 3000m of the water column; this
445 suggests that the addition is most clearly reflected in *upper-ocean* $\delta^{66}\text{Zn}$ values mainly
446 because preformed Zn concentrations are extremely low there (Middag et al., 2019).
447 In these waters, Zn isotope compositions can be more easily modified by modest Zn
448 inputs compared to Zn-rich deep waters, such that a broadly-distributed source of
449 isotopically light Zn addition would be more easily observed in the Zn-poor upper
450 ocean.

451

452 **4.5. Potential sources of isotopically light Zn**

453 It is clear from the preceding discussion that different sources contribute to the
454 isotopically light Zn observed throughout the GEOVIDE section. Hydrothermal inputs
455 and sedimentary sources (see Sections 4.1 and 4.2 respectively) have $\delta^{66}\text{Zn}$ values
456 of around -0.5 ‰. The most important new conclusion here is that the open upper

457 ocean also sees the addition of light Zn. We see two broad mechanisms for the origin
458 of this light Zn.

459 It is possible that the source responsible for the isotopically light Zn in the upper ocean
460 (see Sections 4.3 and 4.4), which bears a similar isotope signature to the hydrothermal
461 and sedimentary sources (Fig. 7), is the same as one of these, transported laterally,
462 and with a much more obvious impact on the open upper ocean because of the low
463 Zn concentrations there. Thus, for example, sedimentary sources of isotopically light
464 Zn observed previously in bottom waters close to the Iberian, North and South
465 American margins (Conway and John, 2014, 2015; John et al., 2018), and here more
466 pervasively at the sediment-water interface, could be transported laterally into the
467 open upper ocean, where its influence may remain visible over greater spatial scales
468 than in the deep ocean due to lower background concentrations. Conway and John
469 (2014) have pointed to the potential role of the Gulf Stream in transporting light surface
470 Zn isotope signatures from the North American coast into the basin. Similarly, currents
471 or water masses may have played a role in transporting the isotopically light Zn across
472 the GEOVIDE transect. For example, an isotopically light Zn signal could be
473 transported from the Caribbean and the American coasts across the North Atlantic,
474 via the North Atlantic Current (NAC; Fig. 1).

475 It is also possible that the light zinc in the upper ocean and close to the sediment-water
476 interface both have their ultimate origin in the upper ocean. For example, particulate
477 material from the atmosphere or from rivers transits the surface ocean on its way to
478 the sediment, potentially releasing labile Zn in the upper ocean and continuing to act
479 as a source from the seafloor over longer timescales. Zinc isotope signatures for rivers
480 and aeolian dust have been reported by Little et al. (2014) and average +0.33 and
481 +0.37 ‰ respectively, values that are similar to the upper continental crust (UCC;

482 +0.31 ± 0.12 ‰; Moynier et al., 2017). These sources are thus too heavy to explain
483 the isotopically light Zn signature. However, across the GEOVIDE transect, Zn in dust
484 is a mixture of mineral and anthropogenic sources (Shelley et al., 2017), and the
485 anthropogenic component is more important close to the European and American
486 continents (Shelley et al. 2018). Volatile contaminants (smelter dust, fly ash,
487 emissions) tend to have light Zn isotope signatures (from -0.67 to +0.21 ‰; Mattielli et
488 al., 2009; Fekiacova et al., 2015), which are consistent with the light Zn values in the
489 upper 100m (between -0.17 and -0.01 ‰). It is also well known that these
490 anthropogenic components are much more labile than mineral dust (Conway et al.,
491 2019; Desboeufs et al., 2005; Hsu et al., 2005; Shelley et al., 2018). Alternatively, the
492 Tagus river, which drains into the Atlantic ocean near Lisbon, is affected by agriculture
493 and industrial activities; it is known to discharge large quantities of Zn (Le Gall et al.,
494 1999; Cotté-Krief et al., 2000) but, to our knowledge, there are no Zn isotope data
495 available. These riverine contaminants could be transmitted to estuarine sediments,
496 and transported off the coast to transmit their isotope signatures to the dissolved pool
497 after dissolution. In summary, there is at least the potential for both aeolian and riverine
498 sources of anthropogenically-sourced light Zn to the ocean.

499

500 **5. Conclusion**

501 We have analysed Zn concentrations and stable isotope compositions in the North
502 Atlantic across the GEOVIDE section. The greatest variations in $\delta^{66}\text{Zn}$, all associated
503 with isotopically light Zn, are observed close to the Reykjanes Ridge, close to the
504 seafloor and in the upper ocean. Close to the Reykjanes Ridge, the hydrothermal vent
505 releases isotopically light Zn to the ocean that is transported eastwards into the
506 northeast Atlantic. This hydrothermal Zn may not be truly dissolved, but rather

507 associated with sulphide nanoparticles. We also show that the addition of isotopically
508 light Zn from the sediments is a much more pervasive process in the ocean than
509 previously recognised. Possibly due to higher depth resolution near the sediment-
510 water interface than previous studies, we observed this feature all across the transect,
511 rather than just at the margins. Finally, our analysis of the relationships between
512 macronutrient/Zn ratios and Zn isotopes strongly suggests that the isotopically light Zn
513 signature of the upper ocean is also caused by an addition of Zn to the ocean.

514 Overall, we put forward a fundamentally different view of upper-ocean Zn and its
515 isotopes than that presented in previous studies, one whose framework for the
516 interpretation of oceanic Zn and its isotopes emphasises preformed Southern Ocean-
517 derived water mass signatures and how they are modified in the low-latitude oceans.
518 If correct, it is the addition of light Zn that explains the low $\delta^{66}\text{Zn}$ values of the low-
519 latitude upper ocean, and not the removal of heavy isotopes. Though the precise
520 source of the light Zn added to the upper ocean remains an open question, it seems
521 possible that it could be anthropogenic in origin.

522

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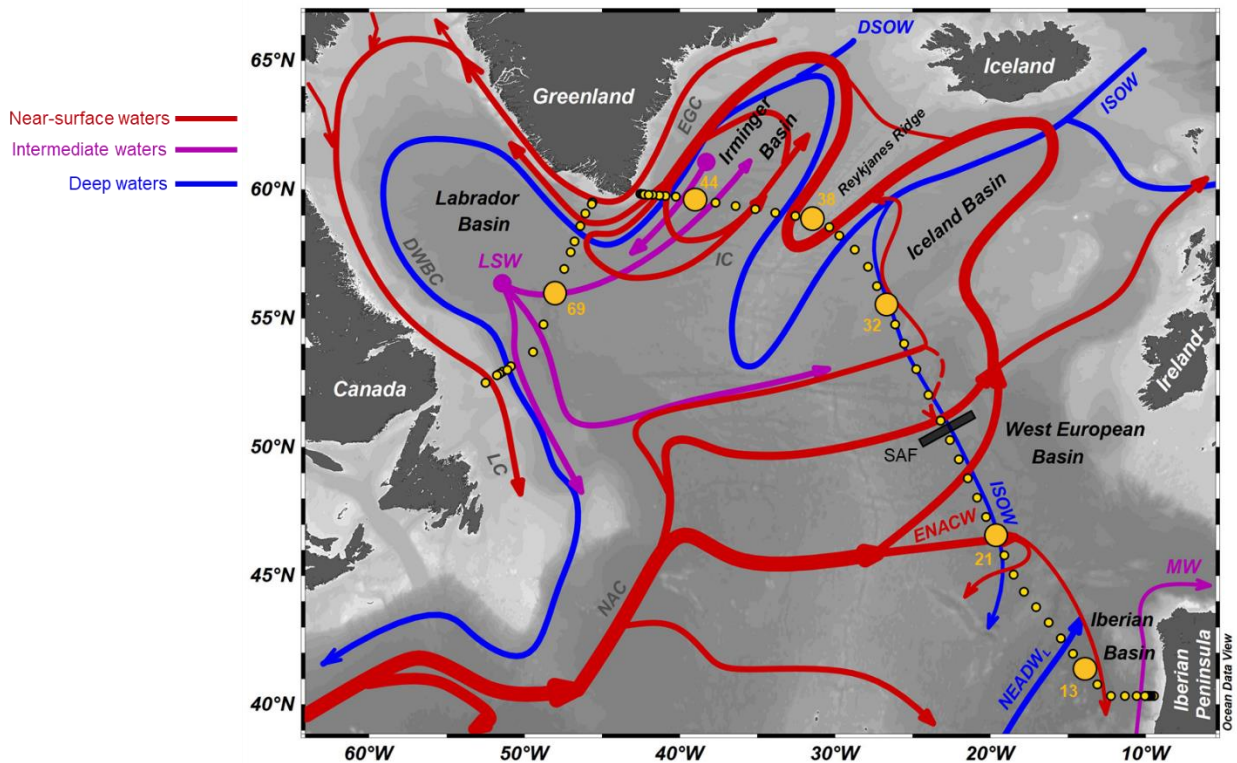
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Figure 1



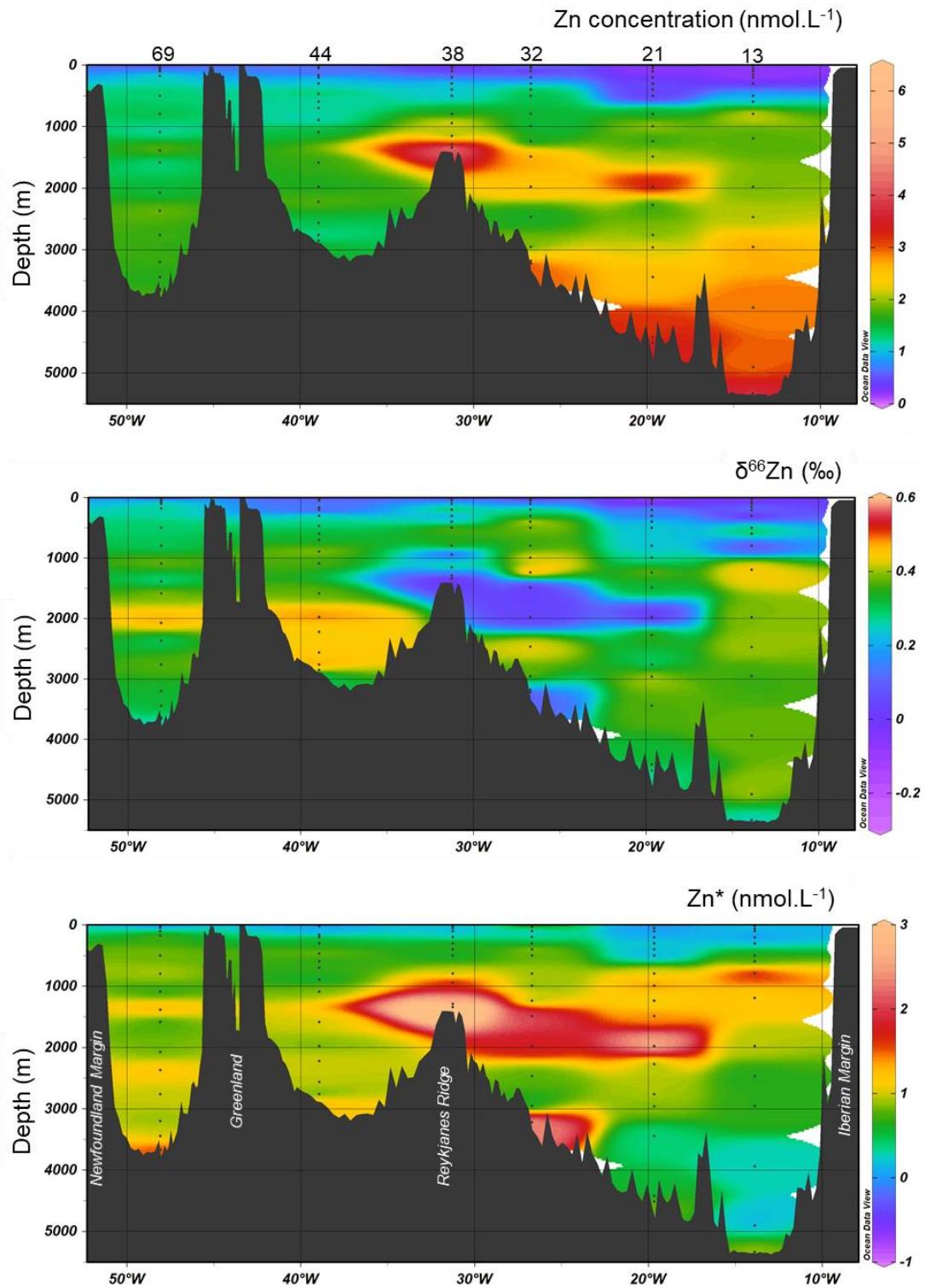
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837 **Figure 1:** Schematic diagram of the large scale circulation in the North Atlantic, adapted from García-Ibáñez et al.,
 838 (2018). Abbreviations for the main hydrographic features indicated are as follows: Denmark Strait Overflow Water
 839 (DSOW), Iceland-Scotland Overflow Water (ISOW), Labrador Sea Water (LSW), Mediterranean Water (MW), North
 840 East Atlantic Deep Water lower (NEADW.L), East North Atlantic Central Water (ENACW), Labrador Current (LC),
 841 East Greenland Current (EGC), Irminger Current (IC) and the North Atlantic Current (NAC), Subarctic front (SAF).
 842 Yellow circles mark all stations sampled during GEOVIDE, with the large symbols representing the stations
 843 discussed in this study.

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Figure 2

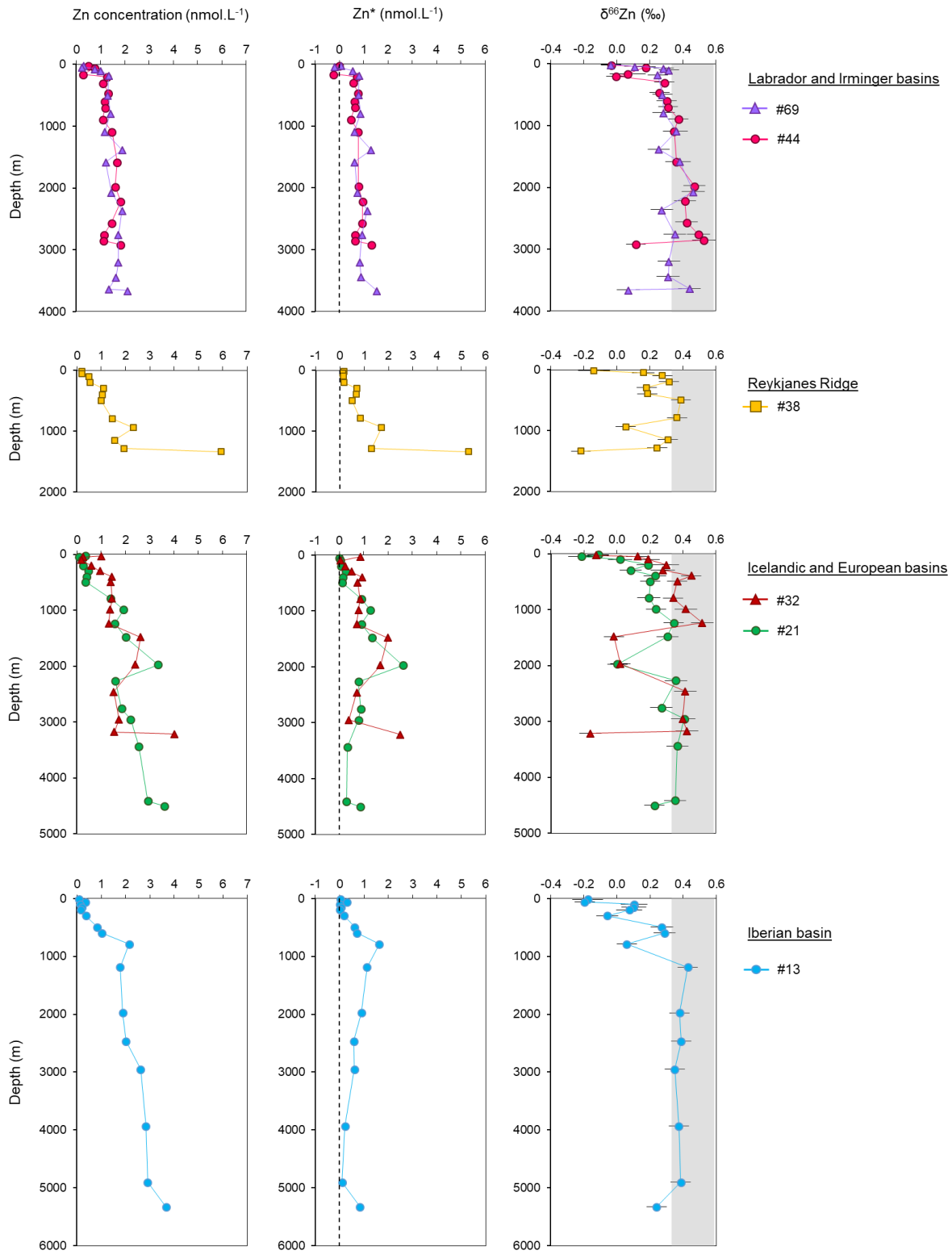


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847 **Figure 2:** Zn concentrations, Zn stable isotope composition ($\delta^{66}\text{Zn}$) and Zn^* along the GEOVIDE transect. Black
848 dots represent sample locations. Station numbers are indicated at the top of the Zn concentration section.

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Figure 3



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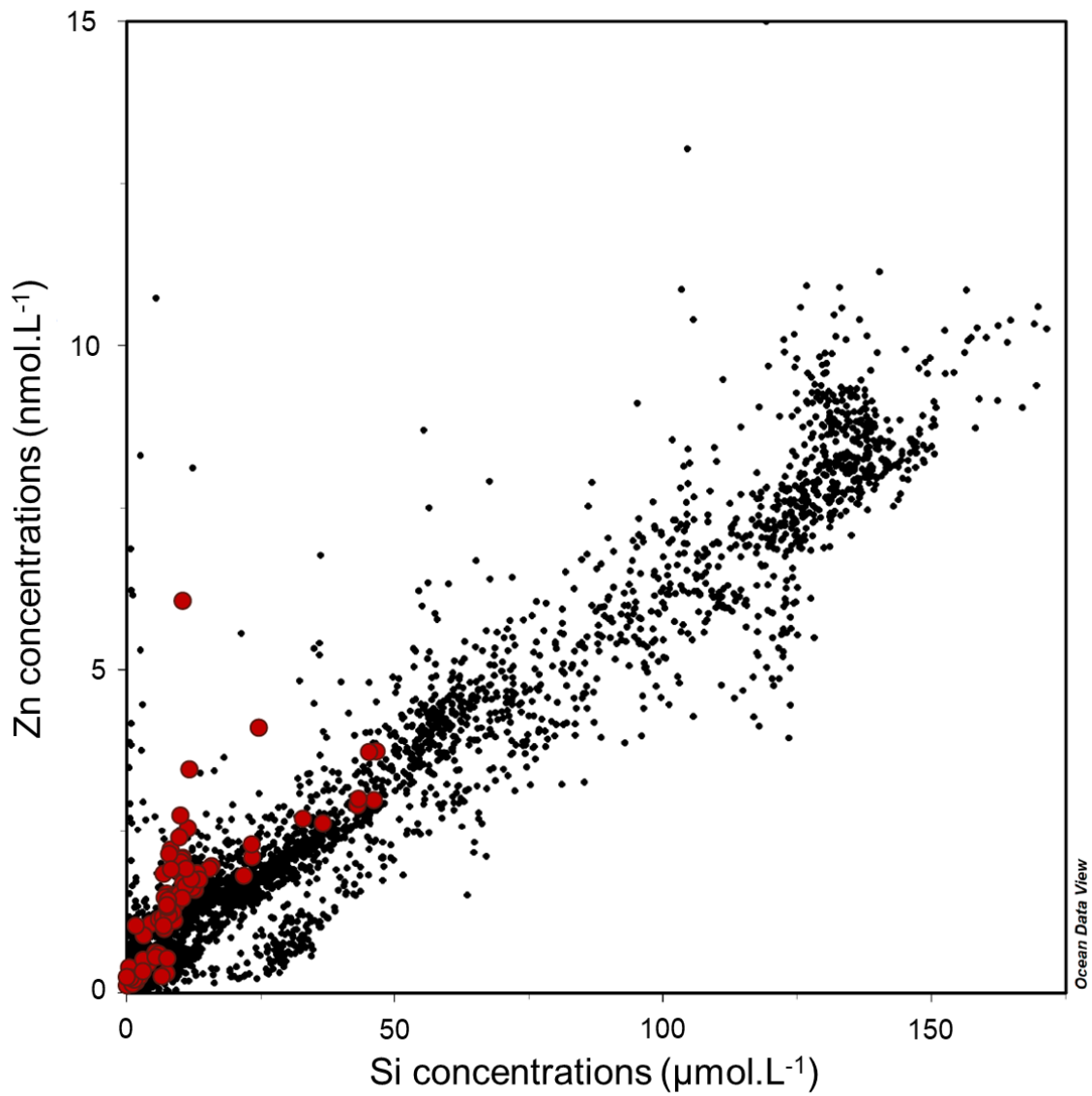
Figure 3: Zn concentrations, Zn* and $\delta^{66}\text{Zn}$ signatures for the stations of the GEOVIDE transect. The shaded grey band shows the average $\delta^{66}\text{Zn}$ in the deep ocean.

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Figure 4

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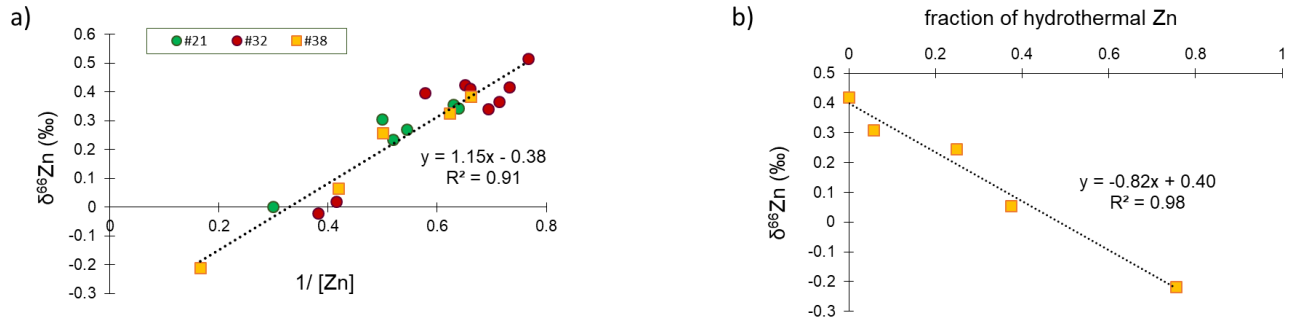
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858 **Figure 4:** Zinc concentrations plotted versus Si concentrations for all samples in the GEOTRACES IDP 2017
859 (Schlitzer et al., 2018; black dots), with our data from GEOVIDE in red.

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Figure 5



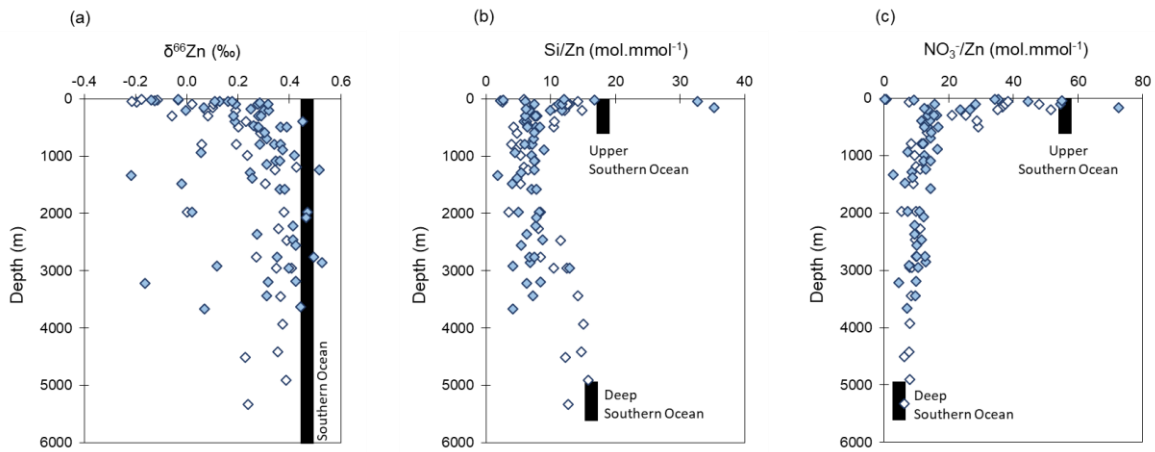
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863 **Figure 5:** a) Zinc isotope composition ($\delta^{66}\text{Zn}$) plotted against $1/[\text{Zn}]$ at depths between 1337m (deepest data
864 point) and 700m at Station 38, and between 3000m and 700m for Stations 21 and 32. b) Zinc isotope composition
865 as a function of the fraction of hydrothermal Zn (see explanations in the text) for all samples at Station 38 that are
866 influenced by the hydrothermal vent, and for background deep seawater ($x = 0$). The linear correlation provides an
867 estimate of the isotope composition of a hydrothermal end-member when $x = 1$ ($\delta^{66}\text{Zn} = -0.42$ ‰).

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Figure 6

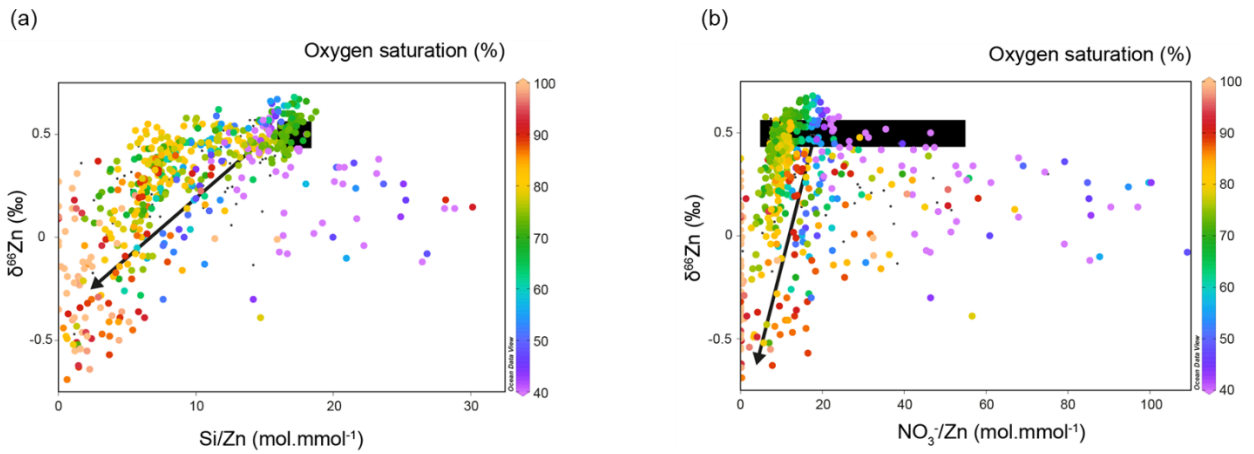


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871 **Figure 6:** Depth distribution of (a) $\delta^{66}\text{Zn}$, (b) Si/Zn and (c) NO₃⁻/Zn ratios for the GEOVIDE stations 13 and 21 east
 872 of the Reykjanes Ridge, where abyssal waters of Southern Ocean origin dominate the deep ocean below 3000m
 873 (empty symbols) and for the GEOVIDE stations 32, 38, 44 and 69 (blue symbols). The black rectangles show the
 874 average $\delta^{66}\text{Zn}$, Si/Zn and NO₃⁻/Zn ratios of the upper and deep Southern Ocean. While the deep North Atlantic has
 875 Zn isotope compositions and macronutrient/Zn ratios that are very close to the ultimate source of these water
 876 masses in the Southern Ocean, the upper ocean shows low Si/Zn, low NO₃⁻/Zn and light Zn isotopes that are most
 877 consistent with a source of isotopically light Zn.

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Figure 7



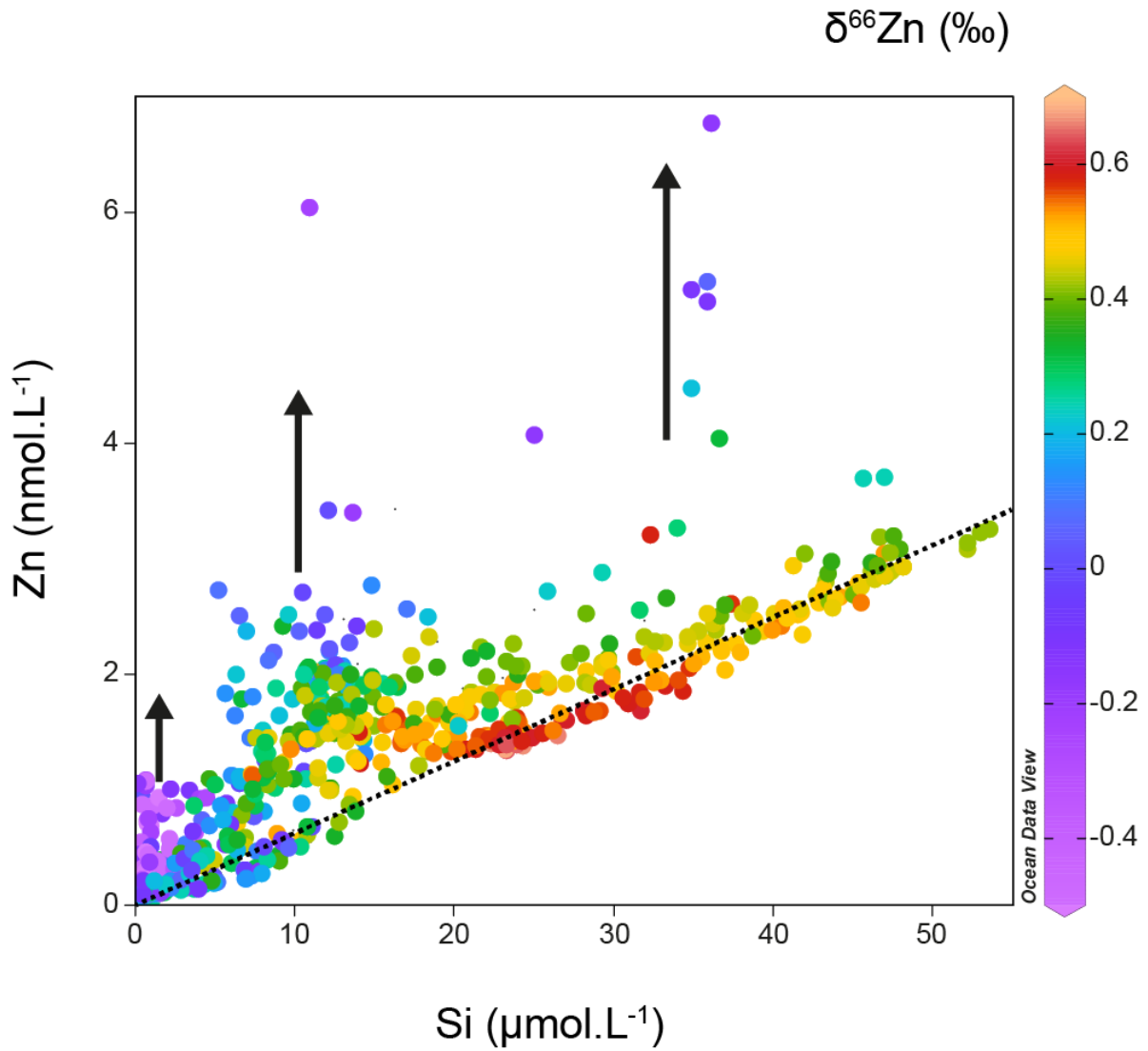
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881 **Figure 7:** $\delta^{66}\text{Zn}$ plotted against (a) Si/Zn and (b) NO_3^-/Zn ratios for the North Atlantic (GEOVIDE and GA03 cruises;
 882 this study and Conway and John, 2014). Data are colour-coded for oxygen saturation. The black rectangles show
 883 the average $\delta^{66}\text{Zn}$ and concentration ratios for the Southern Ocean. Black arrows indicate addition of isotopically
 884 light Zn relative to major nutrient. The intercepts of the black arrows, at NO_3^-/Zn and $\text{Si}/\text{Zn} = 0$ constrain the source
 885 of added Zn to have a $\delta^{66}\text{Zn}$ of around -0.5‰ .

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Figure 8

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888

889 **Figure 8:** Zinc concentrations against Si concentrations, with colours indicating Zn isotope composition, for the
890 entire North Atlantic (GEOVIDE and GA03 cruises; this study and Conway and John, 2014). Black arrows indicate
891 additions of Zn relative to Si. The dotted line represents the global Zn-Si relationship (GEOTRACES IDP 2017).

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