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New tools, new discoveries in Marine Geochemistry

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Key Words: Ocean, Trace elements and isotopes, sampling and detecting challenges, oceanic (un)constrained budgets

94 words

Abstract: Progress in the development of seawater sampling systems, analytical procedures and mass spectrometry have allowed measurements of trace elements and their isotopes in the ocean at spatial resolutions and at concentrations never achieved before. Marine geochemists are now exploiting these new opportunities to measure, for the first time, the stable isotopes of trace metals that are essential for marine life (e.g: Fe, Cu, Ni, Mo, Zn). The new data have already produced new insights into the interaction of the ocean's life with dissolved trace constituents, and the sources and sinks of these trace elements.

3349 words

INTRODUCTION

The Earth's ocean is large ($371 \times 10^6 \text{ km}^2$, corresponding to 70.8% of the Earth's surface), deep (3800 m on average), and represents the largest reservoir of water on Earth ($1.4 \times 10^9 \text{ km}^3$). It is a remote and often hostile environment. Exploring the chemistry of this ocean is a challenge, the first constraint being the requirement for specialized oceanographic research vessels to collect samples. Beyond this primary and obvious challenge, there are three main obstacles that make sampling and analysis for trace elements and their isotopes ("TEI" hereafter) difficult: pressure, which increases by 1 bar every 10m, the fact that the water is very salty and the fact that most of the reactive species of interest to the marine geochemist occur at very low concentrations, often ranging from nanomolar (10^{-9} mol/L) to atomolar (10^{-18} mol/L). In other words, marine geochemists measure very rare substances: They are trying to isolate something like 1 gram of Fe from 1250 tons of salt.

The immediate consequence is that research in marine geochemistry is strongly dependent on very clean sampling and analytical tools, as well as their continuous technical development. With this article we wish to underline how progress in understanding ocean chemistry is closely tied to the development of such methodologies. In the last decade the GEOTRACES programme that has been instrumental in driving such progress, on the sea and back home in the laboratory. We cite, as an example, a recent compilation describing the collection and chemical analysis of suspended and sinking particles (McDonnell et al 2015; Lam et al 2015). In addition, because the GEOTRACES program is generating an open source data base, it has developed rigorous quality control of the data (Bowie and Tagliabue, toolkit section, this issue). Finally the availability of superb sample sets has driven the isotope community to perfect the complicated and rigorous laboratory approaches required for isotope analysis, and new disciplines have opened up as a consequence.

As a result, we have today a large spectrum of tracers that allow the description, understanding and quantification of many processes in the ocean. An example is the pioneering measurements of abyssal ^{14}C , requested in the early 1960s by Henry Stommel from geochemists able to perform these difficult analyses, like Wally Broecker at Columbia University, USA. The result was the first estimate of the average mixing time of the ocean, a major step forward. As detailed in this and the other papers in this issue, TEIs are the sources of information on an array of processes, from biological productivity to past ocean circulation.

49 **TRACING RARE METALS IN THE SEA: THE CHALLENGES**

50

51 *Sampling: Filling a bottle deep in the sea*

52 Collecting seawater under pressures that vary from 1 to 600 bars (up to 1000 bars in deep ocean trenches), and
53 preserving the integrity of the sample from the collection depth to the surface – i.e., avoiding leaks - remains a
54 challenge. The reliability of sampling bottles has improved with time: today, multiple bottles are mounted on a
55 “rosette” (cover figure) and operated using an electro-mechanical Kevlar cable. The low concentrations of the
56 TEIs impose the further requirement that these sampling systems be “clean”, in other words that there is no
57 contamination of the samples from the local environment. On a metal-rich and rusty ship, this is a major issue.

58

59 In addition to the dissolved pool, particle concentrations and composition are crucial parameters for
60 understanding ocean chemistry, including interaction with life in the ocean and transfer to sediment. Sinking
61 particles transfer solid material and associated chemical species from surface to deep, contributing to the
62 sequestration of these elements and species to sediment. In order to sample this vertical flux, sediment traps
63 have been developed and moored since the late 1970s, despite the pressure difficulty on the one hand, the
64 requirement for cleanliness on the other, and the risk of tilting by currents. However, this sinking material
65 represents less than 20% of the particle stock, the remainder being composed of small suspended particles,
66 which exchange chemical elements with the dissolved pool. Suspended particles are rare and precious sources
67 of information in the open ocean: their concentrations vary from 10 to 50 µg/L. It rapidly became clear that
68 filtering large volumes of seawater was necessary in order to obtain large enough suspended particulate
69 samples for the analysis of TEIs. This requires the deployment of *in situ* pumping systems that are also able to
70 work at high pressure, and to filter ~ 1000 L in a few hours. With the exception of a first pump developed by
71 our Indian colleagues in the 1970s (Krishnaswami et al, 1976), these *in situ* pumping systems have been fully
72 commercialized only since the late 1980s.

73

74 The other main constraint is imposed by the requirement for dense geographical coverage of a huge reservoir
75 in a limited time. An oceanographic cruise typically lasts 50 days, presenting the challenge of documenting TEI
76 distributions with the highest possible resolution in the time available. The classical tools described above are
77 still time limited: cables ascend and descend at 1m/s, bottles are classically 12 L in volume – so that several
78 casts at the same location are often required to satisfy all the TEI measurement requirements. *In situ* pumping
79 system casts often require 5 to 6 hours to filter large volumes of water at 8 depths only. Today, this
80 requirement of high resolution/high frequency sampling is driving the development of new tools: for example,
81 chemical sensors that can be mounted on gliders or floats. However, while these newest tools can deliver
82 nutrient and oxygen concentrations, they are still a long way from being able to detect the low concentrations
83 that characterize TEI distributions (Fassbender et al, 2017).

84

85 *Detection: finding a trace of Fe in tons of salt.*

86 Another route to increasing the number of samples is to reduce analytical detection limits, to reduce the
87 volume required for a given element – in effect reducing the “cable time” and improving the sampling density.
88 This field has undergone the greatest progress over the past 20 years, mostly with the laboratory-based
89 development of high performance resins and the availability of extremely sensitive mass spectrometers.

90

91 The main analytical challenge is to concentrate the desired chemical element(s) from the very dilute seawater
92 solution. Seawater is a complex matrix characterized by high concentrations of major ions composing the “salt”
93 (e.g; Na⁺, Cl⁻, K⁺, Ca⁺⁺, Mg⁺⁺, SO₄⁻, etc...). These ions can interfere with trace metal analysis. Moreover, salt is a
94 real poison for the analytical devices because it rapidly clogs their inlet systems, resulting in a critical drop in
95 their sensitivity. Given that one liter of seawater contains 35 g of salt and only a few nanograms, picograms or
96 femtograms of the target element, a concentration step that does not introduce contamination prior to
97 detection is challenging. Many pre-concentration methods have been developed: organic solvent extraction
98 (Bruland et al., 1979), co-precipitation with magnesium hydroxide (Wu and Boyle, 1997), solid phase extraction

99 using various chelating resins either in columns (Sohrin et al, 2010) or as batch extraction onto resin beads (Lee
100 et al., 2011). In this domain, again, considerable improvement of the chelating resin capacities by commercial
101 chemical companies has yielded progressively better recoveries and more efficient elimination of salt. The end
102 result has been a significant decrease in the required sample volume and analyst effort to perform any TEI
103 extraction. Chemical protocol improvement, together with the development of mass spectrometers coupled to
104 a plasma source (ICP-MS), operating at high mass resolution (HR-ICPMS) or with multiple collectors (MC-
105 ICPMS), has helped to propel marine geochemistry, technologically, into the 21st century.

106 107 *High resolution sampling: less means more*

108 In the late 70s, measuring marine Co, Cd, Zn and Ni concentrations required passing 4 l of seawater through a
109 Chelex-100 column (a tube filled with tiny resin beads designed to separate trace elements from a
110 concentrated matrix), followed by a flameless atomic absorption analysis (Bruland et al, 1979). Today, the same
111 set of tracers and others like Fe, Mn, Pb and Co can be simultaneously extracted and analyzed using only 12ml
112 of seawater (Milne et al., 2010). Such extremely powerful multi-element analysis results from the coupling of a
113 state of the art chelating resin to analysis by ICP-MS. This allows the documentation of oceanic sections for
114 trace metals at geographical resolutions that have never reached before, revealing: for example, uncovering
115 contrasting structures in the distributions of two similar lithogenic elements such as Al and Fe (Fig. 1).

116
117 Significant progress has also been made in the analysis of the concentrations of the rare radioactive isotopes of
118 thorium and protactinium in seawater, both quantitative tracers of particle dynamics (Geibert, this issue; Chase
119 et al., this issue). Early and seminal papers on the distributions of ²³⁰Th and ²³¹Pa in the open ocean required
120 samples of 1000 liters because of the very low abundance of these tracers (femtomoles per liter or less) and
121 the sensitivity constraint imposed by the detection method used at that time, alpha-counting (Nozaki et al,
122 1981, Bacon and Anderson, 1982). In the early 2000s, the advent of high resolution ICP-MS, revolutionized the
123 laborious data acquisition involved. The required volume dropped to 1-20 l (GEOTRACES cookbook, 2017),
124 resulting in the ability to produce oceanic sections at unprecedented vertical and horizontal resolution (e.g.
125 Hayes et al, 2015). In the North Atlantic, for example, these sections revealed the locations of intensified
126 scavenging (benthic layers, in the vicinity of continental margins, or in the hydrothermal plume emanating from
127 the Mid Atlantic Ridge, Fig. 2). Because the residence time of ²³¹Pa is longer than that of ²³⁰Th, it is transported
128 horizontally in deep waters until it encounters stronger particle fluxes. The relative roles of these twin
129 processes of horizontal advection versus element scavenging have also been better deciphered by these data
130 (Hayes et al, 2015).

131
132 Detailed ocean cross sections such as these, being published now, reveal more precisely than ever the particle
133 dynamics that transport not only TEIs but also carbon and nutrients, allowing us to better quantify how
134 elements are transferred to depth through processing by organisms, the so-called “biological pump” (Lohan
135 and Tagliabue, this issue, Hatje et al, this issue).

136 137 **NEW TRACERS, NEW IDEAS**

138 In this section we highlight some of the new tracers and new ideas that have recently emerged in marine
139 geochemistry, exploiting the technical advances summarized above. This brief survey cannot be exhaustive but
140 by focusing on selected examples offered by the new metal stable isotope tool set we convey an impression of
141 the excitement in this field.

142 143 *Trace metal isotope budgeting of sinks: the example of molybdenum*

144
145 Amongst the new tools that have driven significant recent progress in ocean chemistry is our ability to
146 determine the relative abundancies of metal stable isotopes – which we could not measure to the required
147 precision before the turn of the century. These include the isotopes of trace metals essential for marine life
148 (e.g., Fe, Zn, Mo, Ni). The fluxes of these metals in and out of the dissolved pool are important to quantify for a

149 number of reasons. First, the input fluxes and residence time determine the inventory that is available to
150 phytoplankton and other organisms today. Second, the controls on the input and output fluxes reflect
151 important planetary processes, e.g., chemical weathering, biological uptake, burial of organic carbon, planetary
152 oxidation, whose rate and pattern on the modern and past Earth have much to tell us about the operation of
153 the Earth System. Quantifying these budgets using elemental inventories alone is, however, difficult. For
154 example, though trace metal concentrations have been measured in the dissolved load of many rivers, the
155 impact of the massive change in chemistry, from fresh to salt water, at the continent-ocean interface is still
156 poorly constrained. There is debate over whether the dissolved load is the dominant input of trace metals to
157 the oceans, or whether dissolution of metals from the particulate load can impact seawater chemistry (e.g.,
158 Jeandel and Oelkers, 2015). Such a mechanism is well illustrated and quantified by the distribution and fate of
159 $^{10}\text{Be}/^9\text{Be}$ ratio between rivers, estuaries and Open Ocean (von Blanckenburg and Bouchez, 2014).

160
161 Characterisation of sinks from the dissolved load of the oceans is also difficult, requiring a large number of
162 measurements of sediments in different oceanographic settings, a good knowledge of the geographic
163 distribution of those settings and, importantly, an understanding of the diagenetic processes that may re-
164 mobilise trace metals back into the aqueous phase. Isotope-based characterisation of the oceanic dissolved
165 pool, as well as these inputs and outputs, can provide a better route to understanding the ocean, and this tool
166 has received renewed impetus through GEOTRACES.

167
168 We first illustrate such an approach with a relatively well-understood element and isotope system,
169 molybdenum (Mo), and two of its stable isotopes: ^{98}Mo and ^{95}Mo . Fig. 3 shows a summary of the modern
170 oceanic budget of Mo from Kendall et al. (2017), and the narrative below is based on that synthesis. Mo, at a
171 concentration of about 105 nM, is the most abundant transition metal in the oceans and is well mixed and
172 homogenised due to its long residence time of about 450kyr. The continental crust is a principal source, via
173 rivers, with hydrothermal fluids contributing a more minor input. Molybdenum exhibits two distinct behaviours
174 in seawater, and key to this system is that the resulting pathways are associated with distinct stable isotope
175 signatures. Under the oxidised conditions that predominate in the modern ocean, Mo occurs as a highly inert
176 and soluble molybdate ion (MoO_4^{2-}), and in these conditions the main sink is via slow adsorption to particulate
177 Fe-Mn oxides. There is isotope fractionation associated with this slow sink: $^{98}\text{Mo}/^{95}\text{Mo}$ on the Fe-Mn oxide
178 surface is 3 permil lower than that of the MoO_4^{2-} dissolved in seawater. In contrast, under sulphidic conditions
179 such as in the modern Black Sea, dissolved Mo is progressively sulphidised, ultimately to MoS_4^{2-} . These species
180 are much more reactive and removed to sediment. Because this process is often almost quantitative, there is
181 little isotope fractionation associated with it. If we now know the isotope composition of the oceans' Mo
182 inputs, the Mo composition of the seawater, and the Mo composition of the sinks, we can quantify the
183 partitioning into oxic sinks (associated with isotope fractionation) and anoxic sinks (no isotope fractionation).

184
185 The Mo isotope composition of the dissolved pool of the oceans is homogeneous (as expected from its long
186 residence time) and distinctly heavier in Mo isotopes than either the upper continental crust at $\delta^{98}\text{Mo} \sim$
187 $+0.3\text{‰}$, or the dissolved load of rivers at about $+0.7\text{‰}$ (see Fig. 3 for details of notation). This difference is due
188 to the preferential removal of light isotopes from seawater onto Fe-Mn oxide particulates. The other principal
189 sink, that mediated by the conversion to much more reactive sulphide species in euxinic basins, results in
190 sediment with the $\delta^{98}\text{Mo}$ of seawater (Fig. 3), as there is no isotope fractionation associated with its complete
191 precipitation. Using an isotope mass-balance, we find that the oxic pool obtains 1×10^8 moles yr^{-1} , and the
192 euxinic pool 0.2×10^8 moles yr^{-1} (Fig. 3). However, a complication arose with the realisation that there are
193 isotope fractionations associated with other important sinks, namely those deposited at productive, upwelling,
194 ocean margins. Revised Mo isotope budgeting, in fact, puts upwelling margins at about 50% of the total output
195 (Fig. 3). This example illustrates how the isotopic fingerprinting of the main inputs and outputs serves to place
196 constraints on oceanic budgets.

197

198 There are bonuses in this story: because global ocean $\delta^{98}\text{Mo}$ is homogenous, and because ancient euxinic
199 sediments record the $\delta^{98}\text{Mo}$ of seawater from which they precipitated, records from such sediments have
200 allowed the reconstruction of $\delta^{98}\text{Mo}$ of ancient seawater. Consequently, many studies have sought to exploit
201 Mo isotopes to reconstruct secular trends in ocean redox state throughout Earth history.

202

203 *Trace metal isotope budgeting of sources and diagenesis: nickel*

204

205 Micronutrients such as Zn, Cd, Fe and Ni, have strong links with ocean biology (Lohan and Tagliabue, this issue).
206 Unlike Mo, they have short ocean residence times, partly a result of removal into cells but also in part because
207 of their insoluble nature in the oxidised form (e.g. Fe). The resulting spatial heterogeneity has made
208 establishing their elemental and isotope distributions more difficult, but has also offered exciting new research
209 avenues in that their isotope distribution patterns disclose the intensity of, for example, internal biological
210 cycling. Their isotope distributions have also uncovered imbalances in the oceanic budgets of some of these
211 metals.

212

213 We illustrate this with the example of nickel and its stable isotopes ^{60}Ni and ^{58}Ni . Nickel is a biologically-active
214 element that shows a concentration profile with depth similar to the major nutrients, depleted in the photic
215 zone due to biological uptake and enriched at depth where organic matter is re-oxidised by bacterial
216 respiration (e.g. Bruland et al., 1979). In the modern ocean, Ni is an essential element in at least seven enzymes
217 involved in the biological cycling of carbon, nitrogen and sulphur, and is also an essential element for one of the
218 most ancient organisms on Earth, methanogens (Ragsdale, 2009). New data show that uptake of Ni in the
219 photic zone preferentially removes the light isotopes, leaving the photic zone dissolved pool heavy at $\delta^{60}\text{Ni}$ up
220 to +1.8‰. Beneath the photic zone the deep ocean is homogeneous at $\delta^{60}\text{Ni}$ around +1.3 (see caption to Fig.
221 4).

222

223 In contrast to Mo the oceanic budget of Ni and its isotopes is not well balanced (Fig. 4). The average $\delta^{60}\text{Ni}$ of
224 oceanic dissolved Ni is much higher than external inputs – which are at 0.8‰ maximum. But, the sinks are even
225 heavier than the ocean (e.g. Gall et al., 2013; Ciscato et al, 2018, Fig.4). Low $\delta^{60}\text{Ni}$ sources and high $\delta^{60}\text{Ni}$ sinks
226 constitute an isotope imbalance that would drive the ocean to lighter isotope compositions through time. Since
227 there is no evidence for such secular change (e.g. Gall et al., 2013), geochemists are seeking an as yet
228 unidentified heavier source or a light and efficient sink. The biological output of light Ni does not solve the
229 problem, being too small and too close in $\delta^{60}\text{Ni}$ to the ocean. The same is true for euxinic settings like the Black
230 Sea (Fig. 4). Mn oxides are known as efficient scavengers of the trace metals, and the nature of this sink is often
231 characterized using Fe-Mn encrustations on the sea floor (e.g. Gall et al., 2013). It is the huge size and the high
232 $\delta^{60}\text{Ni}$ of this heavy sink on Fig. 4 that creates the budgetary problem. An intriguing possibility has been
233 suggested very recently. Recent experiments suggest that up to 50% of adsorbed Ni is released during
234 diagenetic transformation of Mn oxide in sediment during diagenesis (Atkins et al., 2016). The isotope effect of
235 this process has not yet been fully evaluated, but low $\delta^{60}\text{Ni}$ values that have been measured in Mn-rich hemi-
236 pelagic settings provide a promising explanation (Little et al., 2018).

237

238 Whatever the solution to this conundrum, the clear isotope fractionation of Ni isotopes by biology, as well as
239 the drivers of an isotopically heavy ocean, hold much potential for discoveries in marine biochemistry and
240 paleoceanography.

241

242 **SUMMARY OF PROGRESS AND WHAT REMAINS TO BE DONE**

243

244 Recent progresses based on isotopes have opened up new questions – as illustrated here with the apparent
245 imbalances in oceanic budgets of some trace elements. Identifying the missing sources and poorly understood
246 sinks is of prime importance. Constraining ocean budgets with high accuracy will rely on quantifying the impact

247 of diagenetic processing and remobilisation of sedimentary trace metals from seafloor sediment, and the
248 metals contained on the particulate load deposited by rivers, including the isotope fractionation involved with
249 particle-seawater exchange and during redox shifts. In other words, the particle-solution interactions at the
250 land-sea and air-sea interfaces may be key. A further example concerns the interactions between the biological
251 realm and oceanic TEIs, which remains an open field and is also associated with substantial isotope
252 fractionation: how do living species assimilate TEIs; what is the role of the bacteria in TE speciation? We
253 suggest that progress in understanding these processes is essential to support increasing applications of these
254 systems in Earth history. One of the next frontiers for ocean exploration lies in the development of *in situ*
255 sensors able to detect trace elements and automated clean sample collection systems.

256

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263 **REFERENCES (27, 695 words)**

- 264 Atkins AL, Shaw S, Peacock CL (2016) Release of Ni from birnessite during transformation of birnessite to
265 todorokite: implications for Ni cycling in marine sediments. *Geochimica et Cosmochimica Acta* 189, 158-183.
- 266 Bacon MP, Anderson RF (1982) Distribution of thorium isotopes between dissolved and particulate forms in the
267 deep sea. *Journal of Geophysical Research* 87: 2045-2056
- 268 Bowie A, Tagliabue A (this issue) ELEMENTS Toolkit: Building the GEOTRACES Intermediate Data Product 2017
- 269 Bruland KW, Franks RP, Knauer GA, Martin JH (1979) Sampling and analytical methods for the determination of
270 copper, cadmium, zinc, and nickel. *Analytica Chimica Acta* 105: 233-245
- 271 Chase Z, Ellwood MJ, van de Flierdt T (this issue) Discovering the ocean's past through geochemistry
- 272 Ciscato ER, Bontognali TR, Vance D (2018) Nickel and its isotopes in organic-rich sediments: implications for
273 oceanic budgets and a potential record of ancient seawater. *Earth and Planetary Science Letters* 494: 239-250.
- 274 Fassbender AJ and many coauthors (2017) Perspectives on Chemical Oceanography in the 21st century:
275 Participants of the COME ABOARD Meeting examine aspects of the field in the context of 40 years of DISCO.
276 *Marine Chemistry* 196:181-190
- 277 Gall L and 5 coauthors (2013) Nickel isotopic compositions of ferromanganese crusts and the constancy of deep
278 ocean inputs and continental weathering effects over the Cenozoic. *Earth and Planetary Science Letters* 375:
279 148-155
- 280 Geibert W (this issue) Processes that regulate trace element distribution in the ocean
- 281 GEOTRACES cookbook (2017)
- 282 <http://www.geotraces.org/images/stories/documents/intercalibration/Cookbook.pdf>
- 283 Hatje V, Lamborg CH, Boyle EA (this issue) Trace metal contaminants: human footprint on the ocean
- 284 Hayes CT and 8 coauthors (2015) ²³⁰Th and ²³¹Pa on GEOTRACES GA03, the U.S. GEOTRACES North Atlantic
285 transect, and implications for modern and paleoceanographic chemical fluxes. *Deep-Sea Research II* 116: 29–41
- 286 Jeandel C, Oelkers E (2015) The influence of terrigenous particulate material dissolution on ocean chemistry
287 and global element cycles. *Chemical Geology*, 395: 50-66
- 288 Kendall B, Dahl TW, Anbar AD (2017) The stable isotope geochemistry of molybdenum. *Reviews in Mineralogy*
289 *and Geochemistry* 82: 683-732
- 290 Krishnaswami S, Lal D, Somayajulu BLK (1976) Large-volume in-situ filtration of deep Pacific waters:
291 Mineralogical and radioisotope studies. *Earth Planetary Science Letters* 32: 420-429
- 292 Lam PJ and 7 coauthors (2015) Methods for analyzing the concentration and speciation of major and trace
293 elements in marine particles. *Progress in Oceanography* 133: 32-42
- 294 Lee and 5 coauthors (2011) Analysis of trace metals (Cu, Cd, Pb, and Fe) in seawater using single batch
295 Nitrioltriacetate resin extraction and isotope dilution inductively coupled plasma mass spectrometry. *Analytica*
296 *Chimica Acta* 686: 93–101
- 297 Little SH, Vance D, Walker-Brown C, Landing WM (2014) The oceanic mass balance of copper and zinc isotopes,
298 investigated by analysis of their inputs and outputs to ferromanganese oxide sediments. *Geochimica et*
299 *Cosmochimica Acta* 125: 673-693
- 300 Little SH and 4 coauthors (2018) Metal isotope signatures in Mn-rich pelagic sediments: Implications for
301 oceanic budgets. *Goldschmidt Abstracts*, Invited talk, Boston.
- 302 Lohan MC and Tagliabue A (this issue) Oceanic micronutrients: Trace metals that are essential for marine life
- 303 McDonnell AMP and 10 coauthors (2015) The oceanographic toolbox for the collection of sinking and
304 suspended marine particles. *Progress in Oceanography* 133:17-31
- 305 Milne A, Landing W, Bizimis M, Morton P (2010) Determination of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in
306 seawater using high resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS). *Analytica*
307 *Chimica Acta* 665:200-207

- 308 Nozaki Y, Horibe Y, Tsubota H (1981) The water column distributions of thorium isotopes in the western North
309 Pacific Earth and Planetary Science Letters 54: 203-216
- 310 Ragsdale SW (2009) Nickel-based enzyme systems. Journal of Biological Chemistry 284: 18571-18575.
- 311 Sohrin Y and 7 coauthors (2008) Multielemental determination of GEOTRACES key trace metals in seawater by
312 ICPMS after preconcentration using an ethylenediaminetriacetic acid chelating resin. Analytical Chemistry 80:
313 6267–6273
- 314 Twining BS and Baines, SB (2013) The trace metal composition of marine phytoplankton. Annual Review of
315 Marine Science 5: 191-215.
- 316 Vance D and 5 coauthors (2017) Silicon and zinc biogeochemical cycles coupled through the Southern Ocean.
317 Nature Geoscience 10: 202-206.
- 318 Von Blanckenburg F, Bouchez J (2014) River fluxes to the sea from the ocean's $^{10}\text{Be}/^9\text{Be}$ ratio. Earth and
319 Planetary Science Letters 387: 34-43
- 320 Weber T, John SG, Tagliabuie A, DeVries T (2018) Biological uptake and reversible scavenging of zinc in the
321 global ocean. Science 361: 72-76.
- 322 Wu JF, Boyle EA (1997) Low blank preconcentration technique for the determination of lead, copper, and
323 cadmium in small-volume seawater samples by isotope dilution ICPMS. Analytical Chemistry 69: 2464–2470.
- 324

325 Figure Captions

326 385 words

327 **Figure 1:** Contrasting distributions of dissolved Al (dAl, top) and Fe (dFe, bottom) along the meridional
328 GEOTRACES section GA02 in the Atlantic Ocean. Note the contrasting patterns despite the fact that both
329 elements are of lithogenic origin: Dissolved Al distribution maps the main water masses encountered in the
330 Atlantic Ocean: with North Atlantic Deep Waters (NADW) enriched by inputs from the continents versus
331 depleted water masses originating from the remote Southern Ocean (Antarctic Intermediate Water AAIW, and
332 Antarctic Bottom Water AABW). High surface values in the tropics reflect Saharan dust inputs. Dissolved Fe
333 distributions are patchier, mostly reflecting the micro-nutrient properties of this tracer: depleted at the surface
334 due to biological uptake and enriched at depth due to redissolution.

335 **Figure 2:** Distribution of the radioactive ^{230}Th isotope formed by decay of ^{238}U in the Atlantic Ocean,
336 represented in a 3D view. Concentrations of dissolved ^{230}Th are low where a high density of particles scavenges
337 Th, and vice versa. The distributions indicate striking features: (1) intensified scavenging due to the presence of
338 a hydrothermal plume; (2) boundary scavenging; (3) bottom scavenging.

339 **Figure 3:** A simplified oceanic budget for Mo and its isotopes showing the main inputs and outputs to and from
340 the dissolved pool (after Kendall et al., 2017). The numbers below each sink and source are elemental fluxes in
341 units of 10^8 moles yr^{-1} (top) and isotopic composition of that flux. $\delta^{98}\text{Mo}$ is the $^{98}\text{Mo}/^{95}\text{Mo}$ ratio expressed
342 relative to a value of +0.25‰ for NIST SRM 3134.

343
344 **Figure 4:** Simplified oceanic budget for Ni and its isotopes, showing the main inputs and outputs to and from
345 the dissolved pool (after Ciscato et al., 2018). $\delta^{60}\text{Ni}$ is the $^{60}\text{Ni}/^{58}\text{Ni}$ ratio expressed relative to a value of 0‰ for
346 NIST SRM 986. Unlike Mo, at our present level of understanding this budget appears not to be balanced. The
347 apparent imbalance is represented on the diagram as a missing input. But an alternative explanation of the
348 imbalance is that the output fluxes shown here do not represent real burial fluxes, quantitatively or
349 isotopically: i.e., that there is diagenetic remobilisation within sediment and a poorly quantified back flux to the
350 water column.

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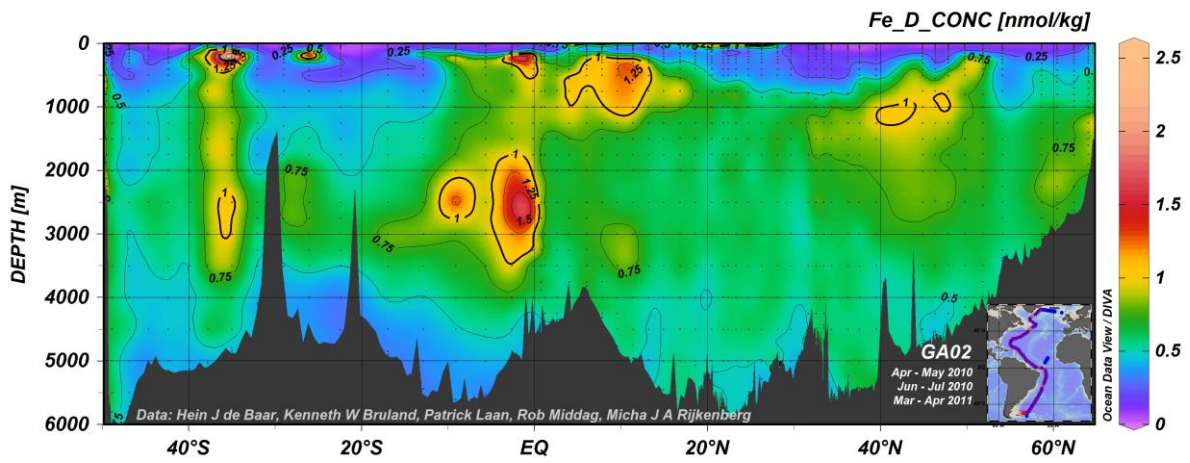
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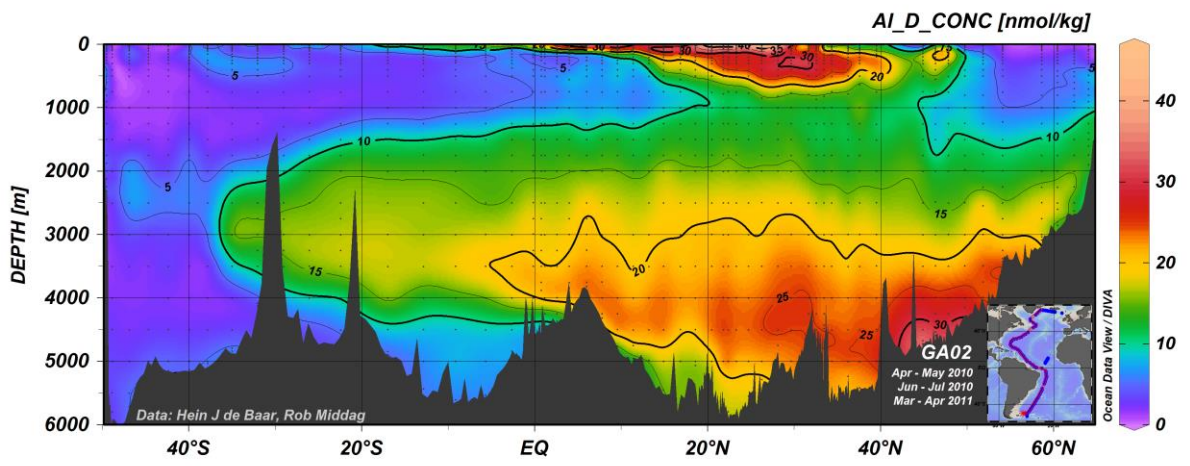
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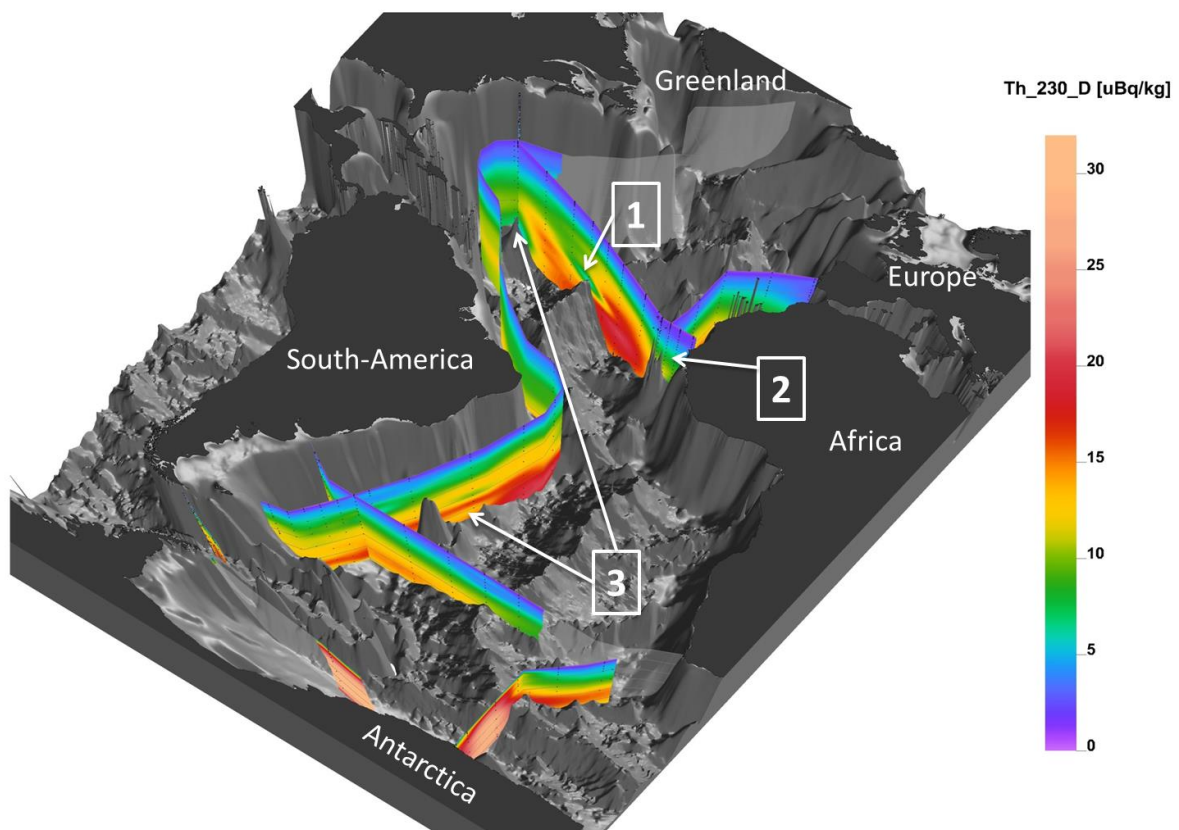
363 Figure 1



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Data: Robert F Anderson, Hai Cheng, Feifei Deng, R Lawrence Edwards, Martin Q Fleisher, Christopher T Hayes, Gideon M Henderson, Kuo-Fang Huang, Sven Kretschmer, Michiel M Rutgers van der Loeff, Yanbin Lu, Laura F Robinson, Alexander Thomas, Celia Venchiarutti
Graphics: Reiner Schlitzer

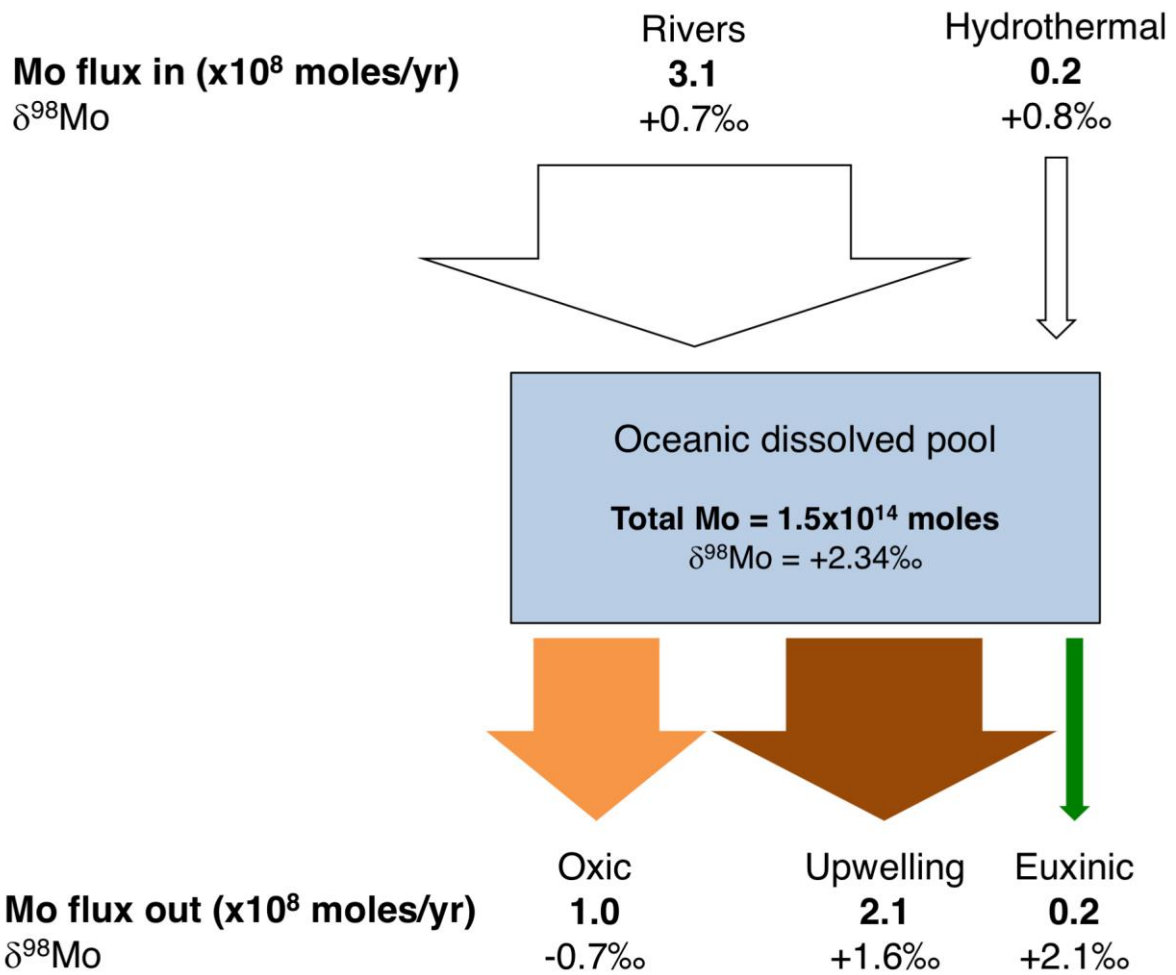
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369 Figure 3

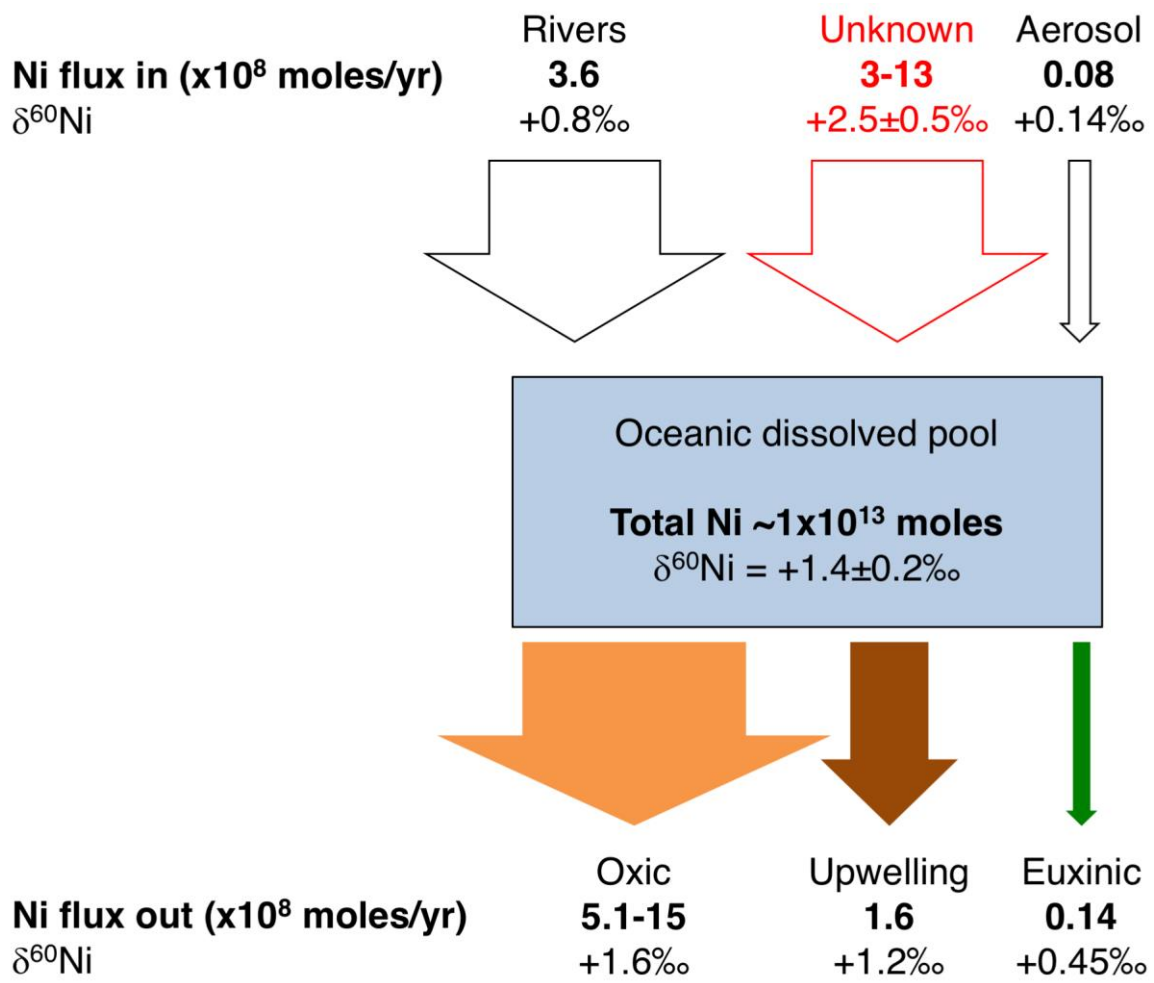
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