1   **Title page**

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3   # Iron colloids dominate sedimentary supply to the
4   ocean interior

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8   William B Homoky[ab1], Tim M Conway[c], Seth G John[d], Daniela Koenig[e], FeiFei

9   Deng[b], Alessandro Tagliabue[e], Rachel A. Mills[f]

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11   [a]University of Leeds, School of Earth and Environment, UK
12   [b]University of Oxford, Department of Earth Sciences, UK
13   [c]University of South Florida, College of Marine Science, USA
14   [d]University of Southern California, Department of Earth Sciences, USA
15   [e]University of Liverpool, School of Environmental Sciences, UK
16   [f]University of Southampton, School of Ocean and Earth Science, UK

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19   [1] To whom correspondence should be addressed. Email: W.Homoky@leeds.ac.uk

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Abstract

Dissolution of marine sediment is a key source of dissolved iron (Fe) that regulates the ocean carbon cycle. Currently, our prevailing understanding, encapsulated in ocean models, focuses on low oxygen reductive supply mechanisms and neglects the emerging evidence from iron isotopes in seawater and sediment porewaters for additional non-reductive dissolution processes. Here we combine new measurements of Fe colloids and dissolved $\delta^{56}Fe$ in shallow porewaters spanning the full depth of the South Atlantic Ocean to demonstrate that it is lithogenic colloid production that fuels sedimentary iron supply away from low oxygen systems. Iron colloids are ubiquitous in these oxic ocean sediment porewaters and account for the lithogenic isotope signature of dissolved Fe ($\delta^{56}Fe$ = +0.07±0.07‰) within and between ocean basins. Isotope model experiments demonstrate that only lithogenic weathering in both oxic and nitrogenous zones, rather than precipitation or ligand-complexation of reduced Fe species, can account for the production of these pore water Fe colloids. The broader covariance between colloidal Fe and organic carbon (OC) abundance suggests that sorption of OC may control the nano-scale stability of Fe minerals by inhibiting loss of Fe(oxyhydr)oxides to more crystalline minerals in the sediment. Oxic ocean sediments can therefore generate a large exchangeable reservoir of organo-mineral Fe colloids at the sediment water interface (a "rusty source") that dominates benthic supply of dissolved Fe to the ocean interior, alongside reductive supply pathways from shallower continental margins.

Keywords: ocean sediment; porewater; iron isotope; iron colloid; iron organo-mineral

52
53 **Significance statement**
54 Phytoplankton assimilate carbon dioxide, produce oxygen and nourish food
55 webs on a scale that impacts planetary processes but are limited by iron
56 deficiency over much of the global surface ocean. Therefore, we must
57 understand processes that regulate the ocean's iron inventory to accurately
58 simulate and predict the ocean's response to change. This study reveals that
59 the widespread production of nano-sized iron colloids from the weathering of
60 lithogenic material drives sedimentary iron supply throughout the deep ocean.
61 The discovery accounts for the unexplained occurrence of colloids and
62 patterns of iron isotope variation previously observed in other parts of the
63 deep ocean, and suggests how long standing assumptions we have used to
64 simulate iron supply in ocean models must be revised.
65
66 **Introduction**
67
68   Sediments undergo early diagenetic transformations that are understood to provide an
69 important source of dissolved iron (dFe) to the ocean that is used to fuel primary production
70 and secondary food webs, fix nitrogen and support the air-sea transfer of carbon dioxide (1, 2).
71 Nevertheless, fundamental questions remain concerning the magnitude of dFe released from
72 ocean sediments, and the mechanisms through which this supply may be moderated. Such
73 uncertainty is most acute in oxic and deep-water regions, which bear the fewest observations,
74 but represent the largest area of the ocean sediment-water interface (3). Here, comparatively
75 small sedimentary releases of dFe have the cumulative-potential to enhance the dFe inventory
76 of the deep ocean and – in so far as it connects with surface water – relieve iron-deficiency for
77 phytoplankton. Porewaters in these deep water regions maintain a persistently oxic and/or
78 nitrogenous state adjacent to bottom waters that is largely unexamined for its role in the marine
79 iron cycle. These gaps in knowledge hinder our ability to make more accurate simulations of
80 the carbon cycle in ocean biogeochemical models (4).
81   Two principle processes are thought to be driving Fe dissolution from sediments that
82 underpin the magnitude and variability of dFe inputs to the ocean. The first is a reductive-
83 dissolution (RD) process which demonstrably occurs during early diagenetic oxidation of
84 organic carbon (OC) and produces high abundances of reduced, soluble and isotopically light
85 Fe in ferruginous porewaters generally beneath the Fe-oxidising fronts of nitrous oxides and
86 oxygen (5-7). The second is a non-reductive dissolution (NRD) process to account for the
87 comparatively unfractionated or heavy isotope compositions of dFe attributed to sedimentary
88 inputs in some oxygenated regions of the open ocean (8) and in the oxic zones of marine
89 sediment porewaters (9), but the mechanisms governing so-called NRD in oxic sediments are
90 unclear.
91   Reductive dissolution of Fe is coupled to organic carbon oxidation and is widely
92 observed in shallow porewater in sediments with high oxygen consumption rates, under
93 productive shelf seas, near zones of upwelling and overlain by oxygen-depleted seawater (10).
94 Low seawater oxygen content serves to enhance the efflux of reduced and soluble Fe (sFe;
95 filtered $<0.02\,\mu$m) from ferruginous pore waters and enables sFe(II) to propagate further in the
96 water column (11-14). Subsequently, without sufficient chelation by organic ligands sFe(II)

97   will be lost to oxidative precipitation (7, 15, 16) scavenging (12) and sedimentation in deeper
98   water (16, 17). Sedimentary RD provides a key component of the ocean's dFe inventory that is
99   most pronounced in the upper ocean (1, 10, 11, 13). It is also the only mechanism by which
100 most ocean biogeochemical models simulate the sedimentary release of dFe (4), since model
101 parameterisations rely on empirical relationships between dFe fluxes, OC oxidation rates,
102 bottom water oxygen contents, and/or water depth (1, 11, 18, 19).
103   Non-reductive dissolution (NRD) is a term previously used to describe a sedimentary
104 source of isotopically heavy dFe to the water column (8), and has since been used to describe
105 the presence of lithogenic isotope compositions observed in oxidizing zones from some deep
106 ocean sediment porewaters (9). Similar observations have become commonplace in the ocean
107 interior (20-23), such that non-reductive sedimentary processes appear to be important for the
108 ocean's dFe inventory. However, the detection of lithogenic dFe isotope signatures in
109 porewaters (6, 9), within western North Atlantic benthic nepheloid layers, and in the water-
110 column far from sediment sources have been difficult to explain (24). The role played by this
111 additional source of dFe is not yet included in global ocean models.
112   Based on the very low solubility of silicate minerals and Fe(III) oxides in circumneutral
113 pH and oxygenated seawater, NRD ought to be incapable of sustaining a benthic flux of dFe
114 to the ocean without significant chelation by organic ligands (25). Due to a strong isotope
115 fractionation effect, however, ligand complexation of Fe would produce a much heavier Fe
116 isotope signal in the ocean (26), which is at odds with the isotopic evidence for NRD (20-23).
117 To reconcile these differences between NRD theories and dissolved Fe isotope observations we
118 ought to consider any physico-chemical partitioning within the dFe pool. The dissolved
119 measurement of Fe (dFe; <0.2 μm) and dFe isotopes, may reflect variable contributions of
120 ligand-bound and soluble Fe(II/III) (sFe; <0.02 μm) and larger mineral or organo-mineral forms
121 of colloidal Fe (cFe; 0.02 to 0.2 μm) in the ocean (23, 27). Such components of the dFe pool
122 are often unaccounted for and have been neglected in previous studies reporting the occurrence
123 of sedimentary NRD in the water column. However, sizable concentrations of colloidal Fe (10^1
124 μmoles L^{-1}) have been observed in oxic-nitrogenous porewaters from deep ocean turbidites of
125 the Southern Ocean, where dFe isotope compositions also matched the solid phase inputs from
126 ocean island basalt. Whether these colloids formed *in situ* through organic complexation, and/or
127 as secondary minerals from either reductive or non-reductive processes was unresolved. A
128 comparison to fresh tephra layers in the Caribbean Sea showed that ocean island basalt
129 weathering and production of nanoscale ferrihydrite or Fe-bearing smectite clays were
130 thermodynamically plausible explanations for cFe in the Southern Ocean porewaters (28).
131 Recently, Klar *et al*., (7) looked for Fe colloids in porewaters from a shallow shelf sediment,
132 but found few if any, and that the porewaters were dominated by light dFe isotope signatures
133 and sFe(II) attributable to RD by bacteria. Previous studies have not resolved where or why cFe
134 occurs in sediment porewaters of the continental shelf-slope-basin transition, or the extent to
135 which they may influence the inventory and isotope composition of dFe input to the ocean (20,
136 22). These lessons need to be learned by examining the soluble and colloidal partitioning of
137 dissolved Fe in porewaters and comparing them to dissolved Fe isotope signatures from a wider
138 range sedimentary carbon and oxygen regimes in the ocean environment.
139   Without appropriate simulation of this dFe source, ocean biogeochemical models will
140 fail to represent spatial patterns in dFe flux from the seafloor, the response of these fluxes to
141 changing ocean environments, and their consequences for ocean biogeochemistry.
142 Confounding this issue is the omitted role of advective transport mechanisms, internal waves
143 and benthic boundary layers that will facilitate exchanges between oxic sediments and the

144 ocean interior(3, 29, 30). To make progress on this important issue requires new understanding
145 on the mechanisms by which Fe dissolves and is supplied to the ocean by oxic sediments.
146   Herein, we present findings from surface sediment cores from sites that span the depth
147 and breadth of the Southwest Atlantic Ocean. The UK-led GEOTRACES expedition, GA10W,
148 recovered porewaters in 2011 from the Uruguayan continental shelf, slope, Argentine abyssal
149 floor and Mid-Atlantic Ridge (SI Appendix, Table S1). We report porewater dFe isotope
150 compositions and further evidence of the physico-chemical partitioning of dFe between soluble
151 and colloidal size fractions (where cFe = dFe-sFe) at selected locations and depths where
152 porewater inventories of Fe were sufficient to permit these determinations. We apply principles
153 of isotope fractionation and mass-balance across the dissolved and soluble size classes to test
154 hypothetical controls on the dFe pool in these porewaters. Our study reveals that oxidizing
155 zones of marine sediments are important regions of non-reductive cFe production derived from
156 lithogenic material, which ultimately determine the dFe inventory and isotope composition
157 supplied to the deep ocean.

158

159 **Results**

160

161 **South Atlantic sediment compositions.** Between the deepest abyssal station of GA10W (18)
162 to the shallowest shelf-top station (24) core top sediments were composed almost entirely of
163 lithogenic material (84 to >99%; Figure 1; averages from 0-5cmbsf, SI Appendix, Table S2) –
164 consistent with continental weathering input and dispersion to the shelf, slopes and abyssal
165 floor of the Argentine Basin (*Cf.* Weijer et al., (31)). Lithogenic material was the second most
166 significant component of core-top material (17%) at the most distal station located on the Mid-
167 Atlantic Ridge, Station 8, more than 3500km from the continental margin along the path of the
168 South Atlantic Current, and above the likely calcite saturation horizon (32). Station 8 was
169 predominantly biogenic carbonate (82%), with trace amounts (<1%) of biogenic opal, whereas
170 stations 18 to 24 contained at most only modest amounts of opal (up to 14%) and carbonate (up
171 to 8%). There was a gradient in total organic carbon (TOC) content from a mid-slope maximum
172 (3.9%, station 22) - coincident with a mid-slope peak in pelagic components - down to
173 minimum values on the permeable sandy shelf (0.2%, station 24) and across the basin on the
174 Mid-Atlantic Ridge (0.2%, station 8).

175

176 **Dissolved porewater contents.** Porewater O_2 was depleted from bottom water values and was
177 observed to penetrate between 0.4 and >9 cm below the seafloor (cmbsf) across all sites. There
178 was a strong exponential relationship between calculated rates of C oxidation (determined from
179 O_2 flux), and water depth (SI Appendix, Fig. S1 and Table S3). Other such indicators of early
180 diagenetic cycling in porewaters had equivalent water depth dependence between stations.
181   Porewater nitrite+nitrate (herein after termed nitrous oxides) were depleted down core
182 from bottom water values (SI Appendix, Fig. S2) and coincided with increased ammonia
183 concentrations (SI Appendix, Table S4). Taken together, these data indicate the reductive
184 cycling of nitrous oxides to ammonia in a nitrogenous zone underlying the oxic surface layer.
185 All stations contained sub-surface maxima in dissolved manganese (dMn) and dFe, up to 10
186 and 52 μM, respectively, consistent with the reductive-dissolution of these metals that has been
187 observed beneath oxic-nitrogenous zones elsewhere in deep-sea sediments (e.g. (9, 33)). A
188 single exception was station 8, where nitrous oxides were not obviously depleted, and where
189 neither dMn nor dFe maxima were observed (SI Appendix Fig. S2 and Table S5).

190   Porewater $\delta^{56}Fe$ of dFe maxima averaged -0.93±0.2‰ (1 SD, $n = 5$) between stations
191   18 and 24 (SI Appendix, Fig. S2), and were isotopically lighter than average igneous crustal
192   material at $\delta^{56}Fe$ = +0.09‰ (34). Light dFe isotopic compositions shifted to heavier values
193   down core and exceeded the average isotopic composition of the crust beneath the ferruginous
194   zones of stations 23 and 22 (up to a maximum of +0.63‰). Nearly all stations contained
195   porewater concentrations of dFe in the surface oxic-nitrogenous zones 10 to 500 times higher
196   than background seawater concentrations with $\delta^{56}Fe$ (+0.07±0.07‰, $n = 11$) indistinguishable
197   from average crustal rocks. A single exception was station 23, where ferruginous conditions
198   extended into the upper centimetre of the sediment and a light dFe isotope composition was
199   observed (-1.37‰).
200
201   **Soluble and colloidal partitioning of dissolved Fe in porewaters.** A comparison of soluble
202   ($<0.02\mu$m) and dissolved ($<0.2\mu$m) porewater filtrates at stations 8, 18, 21 and 22 indicates that
203   sub-surface maxima in dMn and dFe concentration were almost exclusively due to the presence
204   of soluble and most likely reduced species of the metals (Fig. 2; SI Appendix, Table S5; *Cf.*
205   (7)). However, porewater also contained significant detectible quantities of dFe (between 0.01
206   and 0.5 μM) that was far in excess of sFe throughout the overlying nitrogenous and oxic zones.
207   Therefore, between 17±6 and 99±3% of dFe in oxic-nitrogenous porewater was in a colloidal
208   size-class (0.02 to 0.2 μm; Fig. 2). To a lesser but significant extent, dMn also occurred as
209   colloids in the oxic porewater (between 0 and 61±5 %; SI Appendix, Table S5).
210
211
212   **Discussion**
213
214   **Early diagenesis of Fe and Mn.** High proportions of lithogenics relative to pelagic material
215   on the Uruguayan margin and deep Argentine Basin compared to the Mid-Atlantic Ridge, (Fig.
216   1) broadly match regional sediment classifications in a recent census of the seafloor, which
217   indicates these sites are also typical of many other margin, basin and ridge environments of the
218   global ocean (35). Calculated fluxes of O_2 in cohesive sediments from the upper shelf slope (St
219   23) to Mid Atlantic Ridge (St 8), and the relationship of these fluxes to water depth (SI
220   Appendix, Fig. S1), follow an expected gradient in the amount of OC that survives
221   remineralisation in the water column and enters the sediment to fuel early diagenetic reactions
222   (36). Porewater properties reported here may therefore provide a suitable analogue for other
223   oxygenated shelf-slope-basin transitions of the global ocean.
224   Porewater concentration profiles provide evidence for a common down core sequence
225   of electron acceptor cycling in the order $O_2 > NO_x > Mn^{4+} > Fe^{3+} > SO_4^{2-}$, which follows the Gibbs
226   free energy available to the bacteria which catalyse these reduction-oxidation pathways (37).
227   The soluble nature of dFe and dMn maxima (SI Appendix, Fig. S2) is evidence for the reduced
228   species of these metals accumulating in porewaters (*c.f.* (7)). The light isotopic composition of
229   dFe in these ferruginous zones matches previous findings too, where reductive-dissolution of
230   Fe(III)oxyhydroxides to soluble $Fe(II)_{(aq)}$ was also reasoned to account for similar light $\delta^{56}Fe$
231   values (5-7, 9, 11, 38, 39), and is supported by experiments (40, 41). However, our novel
232   investigation of the oxic-nitrogenous zones provides evidence for a previously undocumented
233   reservoir of colloidal Fe (cFe) in continental slope and basin sediment porewater of the South
234   Atlantic Ocean (Fig. 2). These colloids will play a crucial role in regional Fe supply, particularly
235   in deep waters, and their occurrence signifies that they are likely to be prevalent in other
236   oxygenated slope and basin environments.

237

238 **The occurrence of Fe colloids in sediment porewater.** Iron colloids occur commonly in the
239 ocean (23, 27, 42). Most often they are attributed to organic complexation of Fe(III) (43, 44) or
240 nano-particulate Fe(oxyhdr)oxide, clay (45-47) or occasionally Fe sulphide (48) minerals.
241 Recent findings indicate deep Atlantic Ocean waters contain cFe that originates from the
242 seafloor (27), but there are comparatively few assessments of cFe in marine sediment
243 porewaters beyond those presented and discussed in this article (6, 7, 28).

244 Our study shows that the occurrence of cFe in surface sediment porewater is extensive
245 and, thus far, ubiquitous in oxic deep-ocean lithogenic sediments. What is more, these colloids
246 share a nearly identical Fe isotope composition throughout the ocean: in porewaters where dFe
247 has been shown to comprise between 70 and 100% cFe, the dFe isotope composition
248 ($+0.12\pm0.07$‰, $n = 24$) remains indistinguishable from the δ^{56}Fe of the average igneous
249 weathering product (+0.09‰ (34); Fig. 3). It stands to reason that a common mechanism must
250 be responsible for the formation of cFe from lithogenic material in oxidising environments,
251 which can operate independently of RD driven by bacteria to account for this isotopic
252 uniformity between cFe and lithogenics.

253 The Fe isotope composition of igneous rocks is reflected in its detrital weathering and
254 oxidation product (49, 50). We expect sediments derived from different igneous rocks with
255 different histories of siliciclastic cycling to exhibit variable rates of seafloor weathering,
256 dissolution and authigenesis (3, 9, 51, 52). Accordingly, the porewater content of cFe reported
257 from young deep-ocean Crozet Island Basalt is greater than we report here for the South
258 Atlantic, even for basaltic sites with comparatively low TOC (Fig. 2b). In the present study
259 however, between sites that share a similar lithogenic provenance, we see a strong positive
260 correlation between mean cFe concentration in oxidising porewater and the mean core-top
261 abundance of TOC ($r = 0.962$ $p = 0.04$, $n = 4$; Fig. 2b). Taken together, these igneous and
262 organic relationships reinforce the view that cFe is controlled by the weathering of lithogenic
263 detritus and that OC may be required for the stabilisation of cFe we observe in the porewaters.
264 For example, OC sorption to oxyhydroxide mineral surfaces can inhibit Fe transformation into
265 more crystalline and refractory minerals. This interaction is evidenced experimentally (53), and
266 by observations that show that one fifth of marine sedimentary OC is bound to reactive Fe
267 phases (54), which are predominantly nano-scale oxyhydroxides in marine sediment oxic layers
268 (47). Therefore, Lalonde *et al.*'s (54) proposition of a "rusty sink", in which formation of meta-
269 stable Fe(III) organo-minerals promotes OC burial, may here prove to be a "rusty source"
270 mechanism for the occurrence of cFe in oxic porewater. In other words, our assessment of core-
271 top TOC and cFe content could reflect the availability of OC compounds formed during organic
272 matter degradation and that are suited to stabilisation of nano-scale Fe oxyhydroxide.

273

274 **Mechanisms governing the production of porewater Fe solutes and mineral colloids.** It
275 is important to determine whether cFe in oxidising porewater is an authigenic precipitate of Fe
276 produced by RD or if it has formed by a distinctly non-reductive pathway, because these
277 processes of colloid production (or within our operational definitions here, sediment-
278 dissolution) will have different drivers and impacts in the ocean and may respond and feed back
279 differently to changes in the overlying ocean environment. Addressing this issue is essential if
280 we are to build confidence in the paradigms we depend upon to estimate the size and variability
281 of iron inputs in ocean biogeochemical models (3, 4, 18).

282 We can simulate the steady-state porewater production/consumption profiles needed to
283 reproduce measured soluble, dissolved, and colloidal Fe concentration profiles across an oxic-

284 nitrogenous zone. Of the GA10W transect, Station 21 offers uniquely detailed data resolution
285 to perform this assessment with the 1-dimensional steady-state "Rate Estimates from
286 Concentration profiles" or REC model previously described by Lettman *et al*. (55). If we
287 impose a lower boundary condition for sFe and dFe concentrations equal to porewater values
288 at 9.5 cmbsf, and a surface boundary condition of 1 nmol L^{-1} to approximate bottom water (24),
289 model fits to sFe and dFe data (and cFe by difference) may be calculated (Fig. 4).
290   The sFe profile is reproduced with a single region of production in the ferruginous zone
291 (>7.5 cmbsf) and a single region of consumption above it (5-7.5 cmbsf) in accordance with the
292 oxidising potential of nitrous oxides. A more complex production profile is required to simulate
293 dFe, which is predominantly determined by the production of cFe rather than sFe. Production
294 of cFe coincides with a region of sFe consumption (between 5 and 7.5 cmbsf), indicating sFe-
295 oxidation could partially contribute an authigenic source to cFe in porewater. However, the dFe
296 profile requires similar magnitudes of cFe production in oxic, nitrogenous, and ferruginous
297 zones. Therefore, sFe oxidation alone does not fully account for the production of cFe.
298
299 **Porewater isotopic constraints on the genesis of colloidal Fe.** We can further test
300 hypothetical controls on the genesis of cFe using an isotopic mass-balance model. We consider
301 two scenarios in which the isotopic composition of dFe is determined by theoretical controls
302 on soluble and colloidal Fe species: In the first scenario, sFe (assumed here to be Fe(II)$_{aq}$) is
303 oxidised and isotopically fractionated, and cFe is assumed to form entirely from the authigenic
304 products of sFe oxidation. In the second scenario, sFe is oxidised and isotopically fractionated,
305 but removed to the sediment, and cFe is formed entirely from the oxidative weathering of
306 lithogenic material without any Fe isotope fractionation. Initial isotope ratios for sFe and cFe
307 can be adjusted so that the resultant dFe isotope ratio matches the observed value at the dFe
308 maxima 9.5 cmbsf. The isotope compositions of sFe and authigenic cFe can then be determined
309 by an isotope fractionation factor (α) during Fe(II)$_{aq}$ oxidation. Herein we choose to evaluate
310 values of α <1 and >1, such that $\Delta_{sFe\text{-}cFe}$ was ±0.5‰ (SI Appendix, SI Text 2).
311   By modelling these idealised controls on the isotopic composition of porewater dFe,
312 we make two interesting observations. Firstly, porewater dFe isotopes cannot be reproduced
313 when oxidation of sFe determines the isotope composition of cFe (Figure 5ab), whereas dFe
314 isotopes are reproduced quite well when cFe reflects a homogenous crustal weathering product
315 (Figure 5cd). Secondly, dFe isotopes are most accurately reproduced at the transition between
316 ferruginous and oxic-nitrogenous conditions (i.e. region of maximum sFe consumption; *c.f.* Fig.
317 4) when α is <1. We achieve our best simulation of porewater dFe isotopes when cFe is
318 lithogenic and sFe is consumed by oxidation with α of 0.9995 (Figure 5d).
319   We note that the nature of authigenic mineral sinks linked to sFe oxidation will be more
320 complex than has been represented in our simplified approach to isotopic mass-balance above.
321 For example, sFe oxidation may be catalysed by NO$_3$-reducing Fe(II)-oxidizing bacteria - most
322 prevalent in marine sediments with low to moderate TOC content (56). Siderite (Fe(II)CO$_3$) is
323 also a common authigenic precipitate of Fe(II)$_{aq}$ that produces kinetic and equilibrium isotope
324 effects (Fe(II)$_{aq}$-FeCO$_3$ = Δ +1.2 and 0.0 ‰, respectively) (57).
325   Crucially, however, authigenic Fe minerals must either preserve or fractionate isotope
326 ratios from their source of aqueous Fe(II). If Fe(II) is produced from ferruginous depths in
327 porewater following conventional RD theory then any such authigenic minerals must either
328 preserve (e.g. *via* siderite) or fractionate (e.g. *via* oxidation to ferrihydrite) the light isotope
329 composition of the Fe(II) supplied from the ferruginous zone. Because we have chosen to
330 consider a range of α values (from 0.9995 to 1.0005), our simulations may represent a wide

331 range of potential isotope fractionations that might reasonably be achieved by formation of
332 common authigenic Fe minerals (40, 41, 57, 58) or by complexation of soluble Fe with organic
333 ligands (26, 50). Yet we still determine colloidal Fe isotopes to be almost uniformly identical
334 to the continental crust, within and between ocean basins. This occurs in the presence of
335 contrasting sediment composition (e.g. opaline, carbonate, basaltic, siliciclastic and TOC
336 content) between sites. Such compositional variability would theoretically encourage variations
337 in the solubility of different authigenic phases, and therefore impart different isotope
338 fractionation effects upon $Fe(II)_{aq}$ between sites, but this variability in the cFe pool is simply
339 not observed (Fig. 3). For these reasons we consider that cFe is principally formed by oxidative
340 weathering of lithogenic material without dissimilatory reduction and isotope fractionation by
341 bacteria. While bacterial siderophores may promote Fe oxide and Fe-bearing silicate mineral
342 dissolution, they can do so indirectly via proton-promoted dissolution (59), which does not
343 fractionate Fe isotopes (60). We posit that nano-scale ferrihydrite produced by oxidative
344 weathering is further stabilised by the sorption of OC, but sorption to the Fe mineral surface
345 imparts no fractionation effect and therefore preserves its Fe isotope composition.

346

347 **Implications for the ocean Fe inventory.** A lithological source of Fe colloids in surface
348 oxidising porewater has important implications for our assessment of benthic Fe supply to the
349 ocean. The oxidising conditions reported here reflect those that occur commonly below the
350 sediment-water interface of major open ocean margins and basins (36). Thus we provide key
351 new evidence to further disqualify the assumption that only RD controls benthic input of
352 dissolved iron to the ocean (8, 9). Organo-mineral Fe weathering products with a longer oceanic
353 residence time than reduced Fe species may explain how dFe bearing non-reductive crustal
354 isotopic signatures can escape the seafloor and be transported to the ocean interior.

355 The resultant flux of lithogenic Fe colloids to the ocean will reflect the balance of *in*
356 *situ* production rates and benthic exchange mechanisms (Fig. 6). We find that the absolute
357 abundance of cFe in porewater remains greatest in sediments composed of fresh basaltic
358 weathering products, likely indicative of the higher Fe and Mn contents of mafic source rocks
359 and the susceptibility of mafic minerals (e.g. basalt glass, olivine, amphibole) to weather rapidly
360 and produce Fe(oxy)hydroxides and clays during marine early diagenesis (*c.f.* Fig. 2b). We also
361 find that OC is an important additional factor in the production of cFe, but we can only speculate
362 as to the nature of OC moieties in porewater that might elicit the strong cFe relationship with
363 TOC observed in South Atlantic sediments. We suggest that degradation of organic matter may
364 yield bacterial communities and compounds with functional groups suited to (a) enhance the
365 oxidative weathering Fe oxide and Fe-bearing silicate minerals (59), and (b) the sorption of
366 Fe(oxyhy)oxides present in oxic zones (61), which inhibits the loss of Fe to more crystalline
367 phases and encourages preservation as nano-minerals (54). If so, then seafloor organic carbon
368 supply may still exert an important overarching influence on sedimentary dFe fluxes to the
369 ocean, only here it is due to enhanced non-reductive dissolution and mineral-protection effects,
370 rather than reductive dissolution or ionic complexation processes that fractionate Fe isotopes
371 (5, 26).

372 Benthic exchange mechanisms will promote the flux of cFe produced by seafloor
373 weathering and OC complexation to the ocean interior (Fig. 6). Established gradients in cFe
374 concentration between porewater and bottom water may promote a diffusive flux of colloids
375 towards the deep ocean. Without knowledge of cFe diffusion coefficients, diffusive flux
376 calculations may inaccurately need to assume their behaviours match those of the aqueous ion.
377 On the other hand, the stability of organo-mineral colloids in the presence of oxygen means

378   that large reactive losses, such as those required to account for oxidation of aqueous Fe(II) (7,
379   12), may not be applicable to an assessment of cFe (28). Of further significance, biophysical
380   activity and bottom shear stress will promote the entrainment of surface sediment and
381   porewaters in the ocean (46, 62). These entrainments can encourage the scavenging-removal of
382   aqueous Fe(II) and Fe(III) species present in excess of ligand concentrations (e.g. (12)), and
383   simultaneously promote the exchange of mineral solids (including colloids) between the
384   sediments and the water column (27, 29). Energy for the generation and transport of a benthic
385   nepheloid inventory appears unevenly in the ocean. It is tied to upper ocean dynamics and the
386   internal tide and is compounded by bathymetric roughness, island mass effects and reflection
387   angles (29, 63, 64). Despite complexity to these interactions, their importance for boundary
388   exchange and transport in the ocean is well recognised (16, 30) and even evidenced to facilitate
389   the supply of cFe (23, 27) and lithogenic Fe isotopes to the water column (20) (Fig. 6).
390   Where sites of maximum cFe production and potential benthic entrainment overlap,
391   conditions suited to produce a flux of cFe and crustal isotope signatures to the ocean ought to
392   be optimised (Fig. 7). Improved knowledge of where cFe fluxes occur would assist their
393   inclusion in new generations of ocean iron cycle models, which would, in turn, provide an
394   opportunity to update our understanding of how sedimentary iron supply impacts the ocean
395   carbon cycle (2). Optimal conditions for sedimentary cFe input in the ocean may be predicted,
396   firstly, by considering the known surface exchangeable (0-1 cmbsf) inventory of porewater Fe
397   bearing crustal isotope compositions (Fig. 7a). Large differences exist in the dFe isotopic
398   signature of surface exchangeable porewater in the upper 1500m of the ocean with a tendency
399   towards light values that are attributable to the variable influence of reductive and non-
400   reductive sediment dissolution. By contrast the isotopic signatures from equivalent porewater
401   depths are far more uniform and crustal in ocean sediments beneath 1500m due to the lithogenic
402   production of cFe in oxic-nitrogenous zones. These sites also correspond to low benthic oxygen
403   consumption rates ($<$2 mmol m^{-2} d^{-1}) sufficient to supress the generation of sFe by RD in
404   ferruginous zones well below the sediment-water interface. Secondly, the entrainment potential
405   for cFe is illustrated by comparing compilations of benthic O$_2$ flux (sediment community O$_2$
406   consumption rates (65)) and the benthic nepheloid inventories observed in bottom water (29)
407   (Fig. 7b). Sediments below 1500m water depth exhibit the lowest rates of O$_2$ consumption,
408   almost exclusively $<$2 mmol m^{-2} d^{-1}, so that they are most likely to contain exchangeable
409   porewater inventories of lithogenic cFe (*c.f*. Fig. 7a). Bottom waters bearing the highest benthic
410   nepheloid inventories are also found in deep waters, notably in western margins and basins of
411   the North and South Atlantic Ocean, indicating that these regions could optimise the
412   entrainment of cFe and lithogenic isotopes in the ocean. Shelf and slope sediments above
413   1500m, show the highest benthic fluxes of O$_2$, consistent with these regions supporting
414   reservoirs of reduced, soluble and light Fe isotopes in porewaters that can be exchanged with
415   the upper ocean (7, 11). A high degree of variation to benthic nepheloid inventories and oxygen
416   flux ($<$1 to $>$10 mmol m^{-2} d^{-1}) is also shown in sediments above 1500m (Fig. 7b) and suggests
417   the relative contributions of RD and NRD might vary considerably between regions of the upper
418   ocean.
419   Further localised and seasonal variations in sediment dissolution and mechanisms of
420   entrainment are certain to exist, particularly close to margins, that are not represented by the
421   data or grid resolution presented here. The exchangeable inventories of cFe in oxidising
422   porewaters will also respond to the underlying influence of igneous provenance and OC (*c.f.*
423   Fig. 2b), which we have not explicitly accounted for. Therefore, the broader implications of our
424   findings are potentially significant but not yet known. The stability of organo-mineral Fe

425   colloids means they may not succumb to the same fate (rapid precipitation, aggregation, and
426   removal) that limits the extent to which reductive Fe inputs influence the ocean interior. By the
427   same token, the bioavailability of these organo-mineral Fe colloids is unknown, and begs the
428   question: Is there a trade-off between the endurance of Fe colloids in the ocean and their
429   accessibility for phytoplankton? An additional, more stable source of dFe deeper in the water
430   column governed by lithogenic colloid production, which has been ignored in our earlier
431   numerical and conceptual models of the iron cycle, will contribute to the buffering of the ocean
432   dFe inventory against variability from other sources and lower further the mean residence time
433   of dFe.

434

Conclusions

436   South Atlantic Sediments contain a non-linear down slope gradient in O_2 consumption rates,
437   with coupled porewater depth zonation of nitrous oxide, Mn oxide, and Fe oxide reduction
438   pathways, which are consistent with anticipated down-slope gradients in OC flux and
439   decomposition at the ocean floor. Porewater maxima in dissolved Fe contents have light Fe
440   isotopic composition in the form of mostly soluble Fe species, reflecting the reductive-
441   dissolution of Fe(III) to Fe(II) by bacteria in ferruginous zones. Beneath these maxima in
442   dissolved Fe contents, heavy dissolved Fe isotopes corresponded to the reactive loss of soluble
443   Fe(II) with free sulphide. Detectable amounts of dissolved Fe in the overlying oxic-nitrogenous
444   zones have dissolved Fe isotope compositions that are indistinguishable from average igneous
445   weathering products due to the production of Fe colloids from lithogenic weathering. Based on
446   a strong correlation between colloidal Fe abundance and TOC, we propose colloidal Fe stability
447   may be promoted by Fe(oxyhydr)oxide adsorption to OC and the formation of nano-scale
448   ferrihydrite organo-mineral composites.

449   Modelled porewater production and consumption profiles indicate that a soluble Fe
450   pool of Fe(II) accounts for the light isotopic composition of ferruginous zones, whereas
451   dissolved Fe and its isotope composition was mostly determined by the genesis of colloidal Fe
452   in overlying oxic-nitrogenous zones of marine sediments. Our isotopically-constrained model
453   experiments show that non-reductive weathering of lithogenic material is required to account
454   for the widespread occurrence of colloidal Fe in porewater – oxidative conversion of soluble
455   Fe(II) to colloidal Fe(III) alone, was an insufficient explanation for the presence of Fe colloids
456   and their isotope composition, as were alternative authigenic mineral or ligand-stabilised
457   "sinks" for soluble Fe(II) supplied by reductive dissolution.

458   We determine that oxic-nitrogenous ocean sediments are sites of lithogenic weathering
459   and organo-mineral formation that will be provide a "rusty source" of colloidal Fe throughout
460   the global ocean. Coupled to the generation of benthic nepheloid inventories, oxidising
461   sediments will be important sites for benthic Fe exchange that need to be reappraised for their
462   role in ocean biogeochemical cycles.

463

464

Materials and methods

466

467   A Bowers Connelly Mega Corer collected multiple intact surface sediment cores from 6 sites
468   in the South Atlantic during occupation by the RRS *James Cook* (JC068) in 2011. All cores
469   were transferred to a controlled temperature laboratory replicating bottom water conditions
470   (4-8°C) for microsensor profiling and porewater extraction, where all apparatus in contact
471   with the samples (syringes, Teflon, centrifuge tubes and Low-Density Polyethylene (LDPE)

472   bottles were cleaned prior to use (72 hours in 10% Decon; 72 hours in 6M HCl; 72 hours in

473   6M HNO_3; rinsed by 18.2MΩ deionised water).

474   Microsensor determinations of dissolved oxygen were performed by a Unisense micro-

475   profiling suite of apparatus following analytical procedures previously described and used in

476   coastal and deep-sea sediments elsewhere (7, 9, 28). Oxygen penetration depths were either

477   measured directly in the upper 6cm or estimated from model fits to steady state oxygen

478   consumption rates as previously described (7, 9).

479   Rhizon samplers (2.5 x 50 mm "CSS" type, Rhizosphere Research Products) were

480   inserted at 1cm depth intervals through pre-drilled holes into a second sediment core recovered

481   from the Mega Core deployment. Porewater was filtered (~0.15 μm) by suction through each

482   Rhizon into a BD Discardit syringe in an ambient atmosphere. Sample aliquots (2 ml) were

483   diluted 15-fold by 18.2 MΩ deionised water and stored in the dark prior to ship-board nutrient

484   analyses (NO_3^-, NO_2^-, NH_4^+) by a 5-channel Bran and Luebbe AAIII segmented flow

485   colorimetric auto analyser after Homoky et al. (9) and previously reported by Bridgestock *et*

486   *al*. (66).

487   Under a nitrogen atmosphere, a third sediment core was extruded, sliced at 1cm depth

488   intervals, and centrifuged at 9,000g for 6 minutes, before supernatant porewaters were siphoned

489   through Teflon tubes into BD Discardit syringes. Samples for dissolved metals were passed

490   through Whatmann Puradisc 25 syringe filters with polyethersulphone membranes (0.2 μm)

491   and selected sub-samples for soluble metals were passed through a second, in-line Whatman

492   Anatop 25 syringe filter with aluminium oxide membrane (0.02 μm). All porewater samples

493   were later acidified to pH<2 by adding 6 μl of 6M quartz distilled (Q) HCl per millilitre of

494   sample and stored refrigerated prior to analyses.

495   Sediment residues from centrifugation were freeze dried under vacuum and later

496   pulverised in an agate pestle and mortar for carbon, and opal determinations. The bulk

497   composition of sediment cores is described by dry-mass measurements of the total carbonate

498   ($CaCO_3$), total organic carbon (TOC), opal and - by difference from the total dry mass -

499   lithogenic material. The difference between coulometric determination (UIC 5012 Coulometer)

500   of total carbon (TC) and total inorganic carbon (TIC) content of powdered sediments were used

501   to calculate TOC. TC was calculated from CO_2 released during sample combustion, and TIC

502   was calculated from CO_2 released during heated sample reaction with 1.5 M H_3PO_4. Accuracy

503   of TC and TIC determinations was assessed with anhydrous $CaCO_3$ powder, with a mean

504   recovery of 100.4±0.8% (1SD, n=15). The limit of detection (LOD = 3SD of blanks) was 10

505   mg C, equivalent to 0.03 wt% TOC. Opal content was measured by molybdate blue

506   spectrometry on Si extracted solutions from dry homogenized sediments following the sodium

507   bicarbonate sequential leaching method according to Mortlock and Froelich (67). Accuracy of

508   opal determination was assessed by multiple analyses of a laboratory bulk sediment at the

509   School of Geosciences, University of Edinburgh with a reproducibility of 1.54%.

510   A Thermo Scientific Element X2 Inductively Coupled Plasma-Mass Spectrometer

511   (ICP-MS) was used to determine the concentration of aqueous metals in acidified porewater

512   samples and sediment digests following Homoky *et al*. (9) and previously reported by

513   Bridgestock *et al* (66). Briefly, porewaters were diluted 100-fold with 0.48 M Q-HNO_3, and

514   external calibration standards were matrix matched to samples with 1% of the seawater

515   standard NASS-5 (National Research Council Canada). The mass of ^{45}Sc spiked to all

516   samples was used as an internal standard to monitor and correct for a reduction in signal

517   intensity of over time. Accuracy of the method was verified by the intermittent analysis of

518   blank-bracketed SLRS-5 (National Research Council Canada) within certified values, with a

519 RSD of 1.1 and 1.3% for Fe and Mn respectively. The LOD (3SD of analytical blanks, n=9)
520 for reported Fe and Mn were 1 and 0.1 nmol l⁻¹, and procedural blanks were below these
521 limits of detection.
522   Dissolved Fe isotopic compositions from porewaters were measured following
523 previously published methods (9, 68). Aliquots of porewater containing Fe inventories from 20
524 to 104 ng were spiked with an ^{57}Fe-^{58}Fe double spike (in a 1:2 sample:spike ratio), evaporated
525 to dryness in 7 mL Savillex^{TM} PFA Teflon vials, and then re-dissolved in 5 M quartz-distilled
526 HCl + 0.001% v/v Optima H_2O_2 before being passed through 135 μL AGMP-1 column
527 purification. Fe was eluted from the columns in 0.8 mL of 1M quartz-distilled HCl and
528 evaporated to dryness before being re-dissolved in 0.5 mL of 0.1 M Teflon-distilled HNO_3 for
529 analysis by Multi Collector (MC)-ICPMS. Procedural blanks for this method have previously
530 been shown to be 3 ng of Fe per sample (9). Samples were then analysed for Fe isotopic
531 composition by Thermo Neptune MC-ICPMS with jet interface at the University of South
532 Carolina, using an ESI Apex-Q introduction system, Pt Jet and Al X cones, following methods
533 identical to those described previously (9). Fe isotopic compositions (δ^{56}Fe) are expressed in
534 typical delta notion relative to the IRMM-014 international Fe standard. The accuracy of this
535 procedure has been previously demonstrated on seawater samples (68, 69), and here we assign
536 0.05‰ as an estimate of external precision of analysis, based on duplicate measurements of 60
537 GA10 seawater samples (0.1-1.8 nmol kg⁻¹), measured over multiple analytical sessions during
538 the same time interval (69). In cases where the 2 standard internal error is larger than 0.05‰,
539 we consider the 2SE a more representative estimate of uncertainty.
540

Acknowledgments

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744   dissimilatory hydrous ferric oxide reduction. *Geochimica et Cosmochimica Acta* **69**,
745   963-993 (2005).

746

747

Figure legends.

749

750   **Figure 1. The location and core-top composition of sediment samples from GA10W.** A
751   blue colour index shows 500 m water depth intervals in a plan view (top) of the study region
752   and a section view (bottom) along the GA10W sample transect. Sediment classifications of
753   stations 8-23 include cohesive silts-clays, whereas station 24 is a non-cohesive permeable sand.
754   Station 18 lies well beneath the likely Carbonate Compensation Depth (CCD). Pie charts
755   indicate the mean surface (0-5 cmbs) proportions of lithogenic and pelagic components between
756   all sites (SI Appendix, Tables S1and S2).

757

758   **Figure 2. (a) Porewater concentrations of dFe verses cFe.** Error bars (±2sigma) are typically
759   within the size of individual data markers. Discrete observations from oxic-nitrogenous zones
760   fall along a 1:1 line due to the high relative abundance of cFe. dFe exceeds cFe concentrations
761   in underlying ferruginous zones due to the low relative abundance of cFe in these regions of
762   the sediment. Concentrations of cFe span 3 orders of magnitude in porewater oxic-nitrogenous
763   zones across all sites and exceed the concentrations of ocean bottom water (24), **(b) Mean**
764   **porewater cFe concentration verses mean total organic carbon (TOC) in core top**
765   **sediments (0-5cmbsf).** A dashed black line shows a significant linear fit through GA10W sites
766   ($r = 0.962$, $p = 0.038$). Values from mafic volcanic sediments in the Southern Ocean (28),
767   indicate that additional factors other than TOC also control the abundance of cFe in porewater,
768   such as lithogenic provenance.

769

770   **Figure 3. The relationship between δ^{56}dFe and relative abundance of cFe in ocean**
771   **sediment porewater.** Values compiled from the South Atlantic (this study sites 18, 21 and 22),
772   and previous studies by (a) Homoky *et al.* (6) and (b) Klar *et al.* (7). Error bars (±2sigma) are
773   within the size of individual data markers. The grey bar indicates the average Fe isotopic
774   composition of crustal rocks.

775

776   **Figure 4. Modelled porewater Fe production rate profiles.** Comparison of measured sFe and
777   dFe with REC model fits to observations across the oxic/nitrogenous-ferruginous transition of
778   GA10W station 21. The concentrations and production rates of cFe are calculated by model
779   difference (cFe = dFe-sFe).
780
781   **Figure 5. Porewater sFe and cFe isotope mass-balance experiments.** Summary of results in
782   which porewater dFe isotope compositions are simulated by two idealised controls on the sFe
783   and cFe isotope reservoirs: Firstly, the isotope fraction effect (α) attributed to sFe loss (e.g.
784   oxidation), and secondly, the origin of porewater cFe. The value of α is either >1 (a, c) as is
785   commonly predicted for Fe(oxyhydr)oxide formation or <1 (b, d), as has been attributed to Fe
786   (oxyhydr)oxide formation across some ocean chemoclines (15) and is predicted by some other
787   (e.g. carbonate) mineral formations (70) and Fe(III)-ligand complexes (26). cFe is either an
788   authigenic mineral supplied by sFe oxidation with a corresponding isotope composition (a, b),
789   or cFe is supplied by non-reductive weathering of lithogenic material with crustal isotope
790   compositions (c, d). In all scenarios, the resultant composition of dFe reflects the isotopic mass
791   balance of sFe and cFe pools. Model equations are provided in the SI Appendix (SI Appendix,
792   SI Text 1).
793
794   **Figure 6**. **A revised scheme of sedimentary iron supply depicting seven processes that may**
795   **promote the exchange of lithogenic iron colloids (cFe) and isotopes to ocean interior.** (1)
796   Production and diffusion of lithogenic cFe (depecited as cFeOOH(orgC)) in oxic-nitrogenous
797   ocean sediment porewater; (2) Enhanced cFe production from dissolution of mafic minerals;
798   (3) Enhanced cFe stablisation by organic C; (4) Porewater advection through permeable
799   sediments of the continental shelf; (5) Entrainment by internal waves and density horizons; (6)
800   Entrainments by a Benthic Boundary Layer (BBL) coupled to surface ocean EKE; (7)
801   Entrainment by the Surface Mixed Layer (SML) and Island Mass Effects. Sedimentary release
802   by reductive dissolution is restricted to shoaled porewater ferriclines beneath high organic
803   matter flux or Oxygen Minimum Zones (OMZs) in the upper 1500m of the ocean, and rely on
804   stabilisation by organic Ligands to resist secondary oxidation and precipitation from the water
805   column.
806
807   **Figure 7. (a) The isotopic signature of dissolved Fe in surface exchangeable sediment**
808   **porewaters.** Data markers correspond to measured surface values compiled from this study (SI
809   Appendix, Table S5), the South Atlantic, Cape margin (9), the North Pacific, Oregon and
810   California margins and Borderland Basins (6, 11), the North Atlantic, Celtic Sea (7), and the
811   Southern Ocean, Crozet Island abyss (6). The measured surface inventory of porewater dFe is
812   illustrated by the size of data markers, and the associated benthic flux (sediment consumption)
813   of O_2 by the colour scale. **(b) The entrainment potential for colloidal Fe and lithogenic**
814   **isotope signatures in the ocean.** Mean sediment community O_2 consumption rates complied
815   by Stratmann *et al*. (65) are gridded here at 2 degrees and plotted using the same colour scale
816   to data in (a). The suspended particle load in bottom waters reported by Gardner *et al*. (29) is
817   reproduced with interpolated lines of equal concentration using means values from a 2-degree
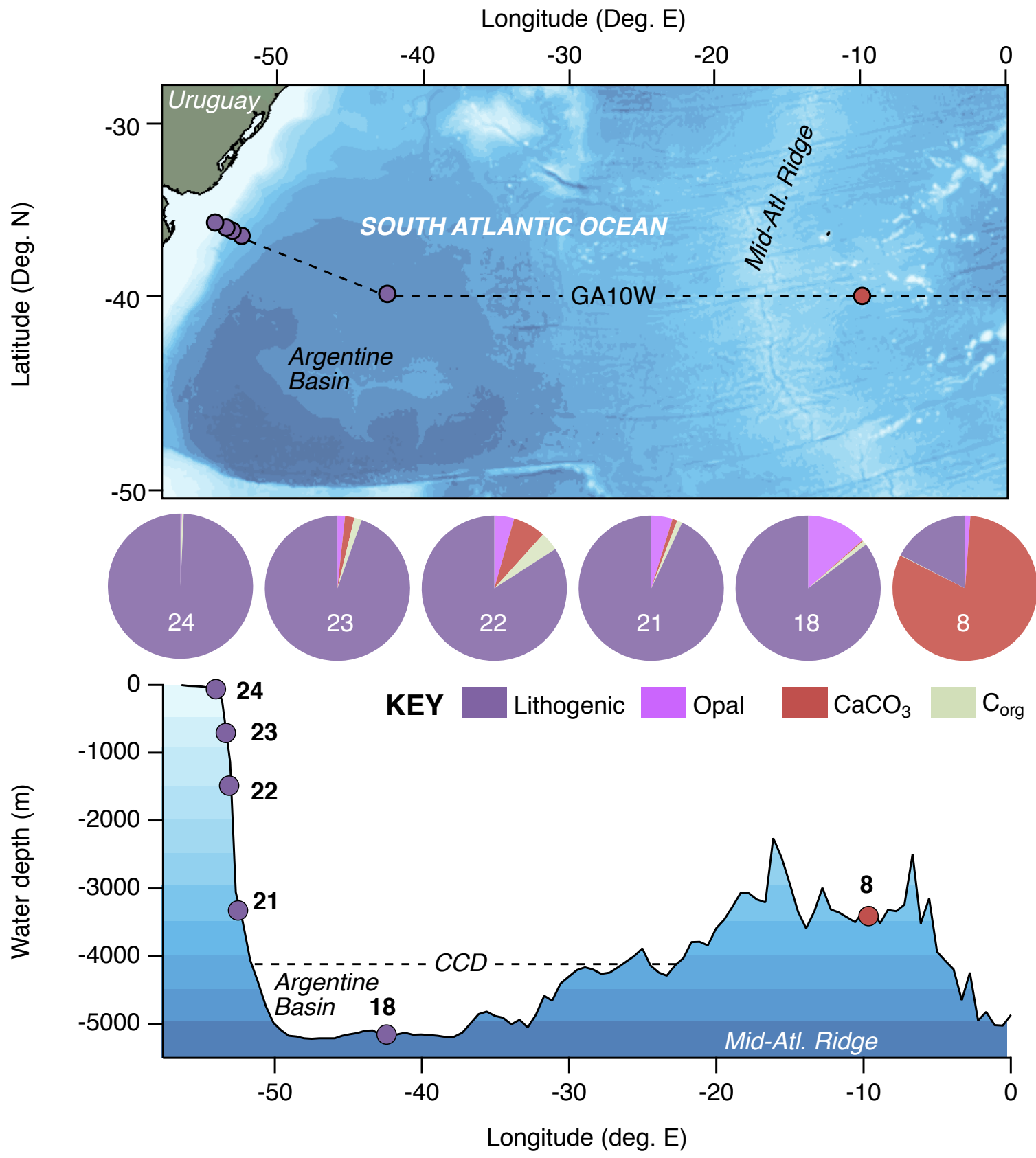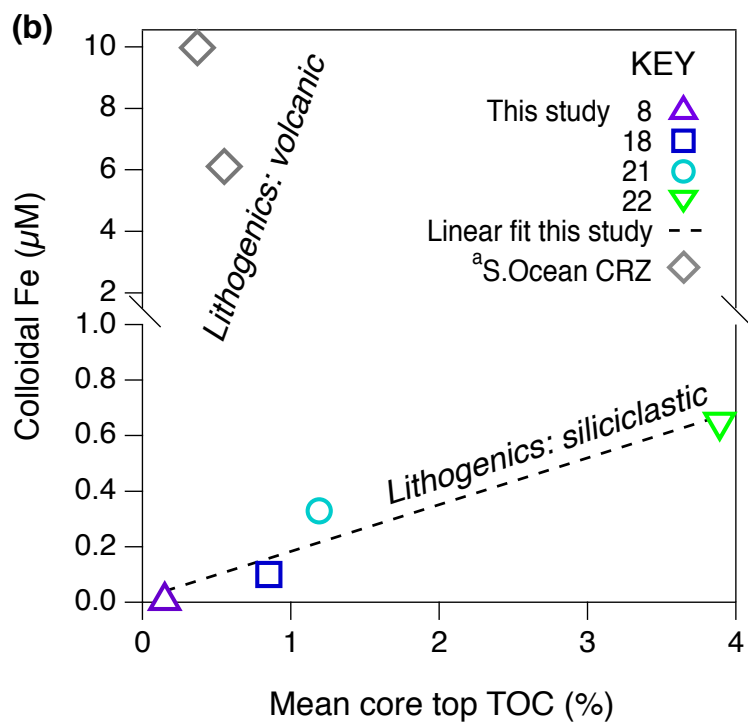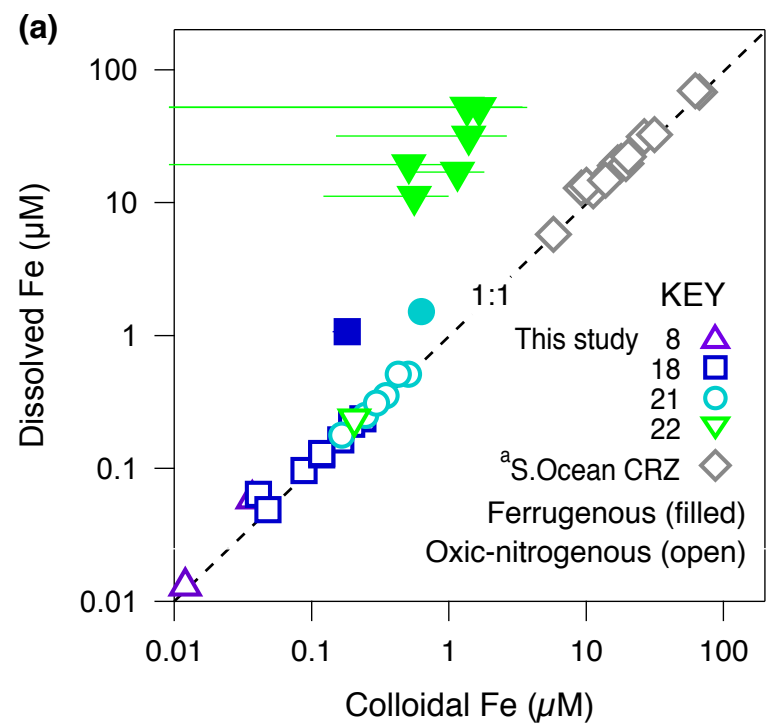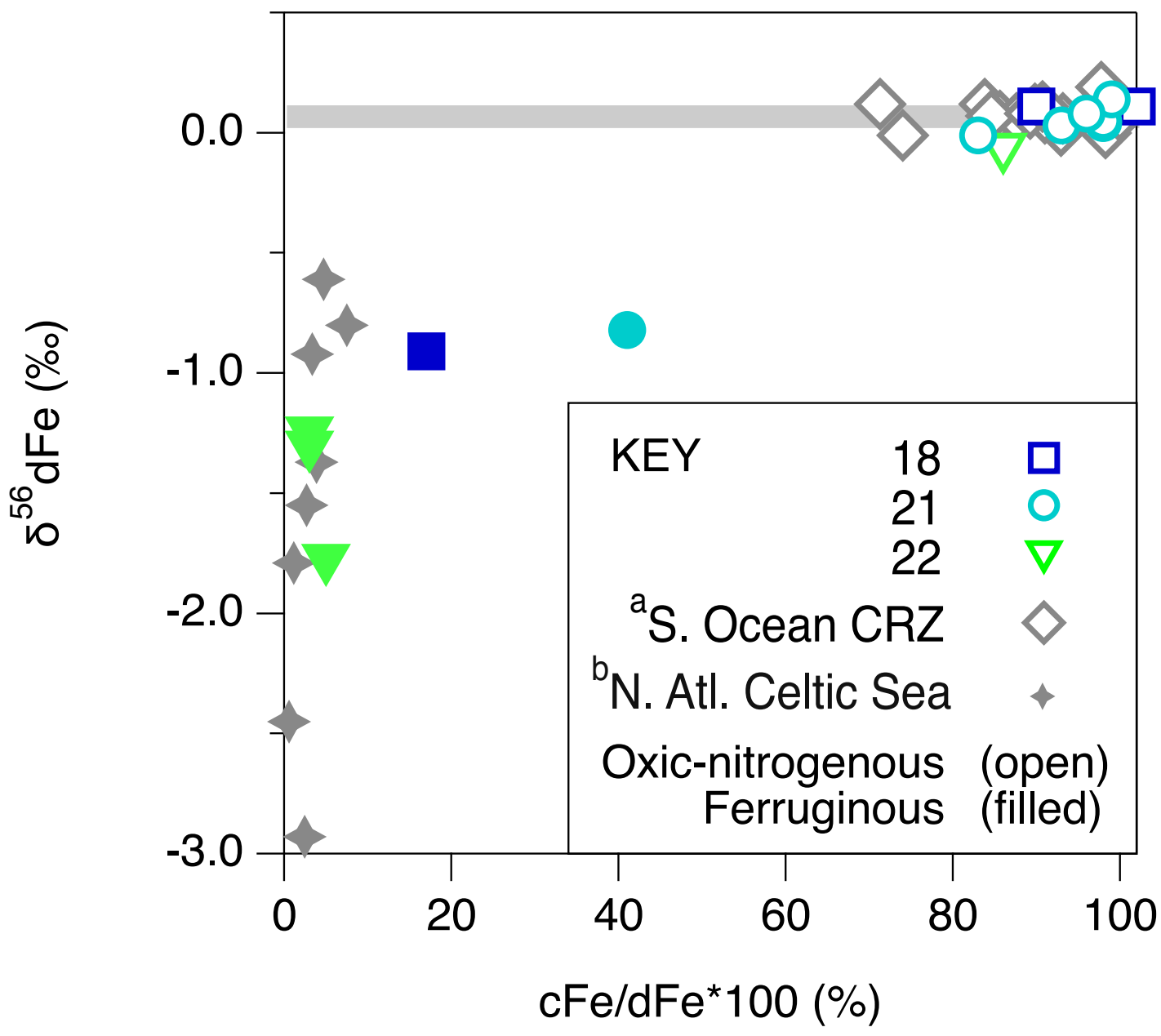818   grid.
819

Figure 1

(a)

Dissolved Fe (µM)

100

10

1

0.1

0.01

1:1

KEY

This study
8
18
21
22

ᵃS.Ocean CRZ

Ferrugenous (filled)
Oxic-nitrogenous (open)

0.01   0.1   1   10   100

Colloidal Fe (µM)

(b)

10
8
6
4
2

1.0
0.8
0.6
0.4
0.2
0.0

Colloidal Fe (µM)

Lithogenics: volcanic

Lithogenics: siliciclastic

KEY

This study
8
18
21
22

Linear fit this study

ᵃS.Ocean CRZ

0   1   2   3   4

Mean core top TOC (%)

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

A Exchangeable porewater δ�56Fe (‰)

B Suspended particle load and benthic O₂ flux

Figure 7