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5 **The impact of changing surface ocean conditions on the dissolution of**  
6 **aerosol iron**  
7

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35 Key points  
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- 37
- 38 • Aerosol source and composition have the greatest effect on iron dissolution
  - 39 • Ocean warming and acidification may not impact aerosol iron dissolution
  - 40 • Strong ligands draw most of the labile aerosol iron into the soluble fraction

41 Index terms and key words  
42

43 Index terms: ‘Trace elements; aerosols; chemical speciation and complexation;  
44 biogeochemical cycles, processes, and modeling’ (in ‘oceanography: biological and  
45 chemical).

46  
47 Key words: iron; biogeochemistry; marine aerosols; climate change; ligands; colloids.  
48

49

50 Abstract

51

52 The proportion of aerosol iron (Fe) that dissolves in seawater varies greatly and is dependent  
53 on aerosol composition and the physicochemical conditions of seawater, which may change  
54 depending on location or be altered by global environmental change. Aerosol and surface  
55 seawater samples were collected in the Sargasso Sea and used to investigate the impact of  
56 these changing conditions on aerosol Fe dissolution in seawater. Our data show that seawater  
57 temperature, pH and oxygen concentration, within the range of current and projected future  
58 values, had no significant effect on the dissolution of aerosol Fe. However, the source and  
59 composition of aerosols had the most significant effect on the aerosol Fe solubility, with the  
60 most anthropogenically influenced samples having the highest fractional solubility (up to  
61 3.2%). The impact of ocean warming and acidification on aerosol Fe dissolution is therefore  
62 unlikely to be as important as changes in land usage and fossil fuel combustion. Our  
63 experimental results also reveal important changes in the size distribution of soluble aerosol  
64 Fe in solution, depending on the chemical conditions of seawater. Under typical conditions,  
65 the majority (77 – 100%) of Fe released from aerosols into ambient seawater existed in the  
66 colloidal (0.02 – 0.4  $\mu\text{m}$ ) size fraction. However, in the presence of a sufficient concentration  
67 of strong Fe-binding organic ligands (10 nM) most of the aerosol-derived colloidal Fe was  
68 converted to soluble Fe (< 0.02  $\mu\text{m}$ ). This finding highlights the potential importance of  
69 organic ligands in retaining aerosol Fe in a biologically available form in the surface ocean.

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76 1. Introduction

77

78           During the past twenty years, extensive investigations of the marine  
79 biogeochemistry of iron (Fe) have demonstrated that this micronutrient limits primary  
80 production in vast areas of the world ocean [e.g., *Martin et al.*, 1994; *Coale et al.*, 1996; *Boyd*  
81 *et al.*, 2000; *Takeda and Tsuda*, 2005]. In particular, the supply of Fe controls phytoplankton  
82 growth in high nutrient, low chlorophyll (HNLC) waters, where the macronutrients nitrate  
83 and phosphate are replete. In these regions, there is the potential for increased primary  
84 production, carbon export to the deep ocean and associated atmospheric carbon dioxide  
85 (CO<sub>2</sub>) drawdown to be realized by increased inputs of Fe [*Martin*, 1990; *Kohfeld and*  
86 *Ridgwell*, 2009].

87           Atmospheric deposition of aerosols is an important pathway by which Fe is  
88 introduced into surface waters of the open ocean [*Duce*, 1986; *Martin and Gordon*, 1988;  
89 *Jickells et al.*, 2005]. The percentage of total Fe contained within aerosols that dissolves in  
90 seawater, known as the fractional solubility of aerosol Fe (%Fe<sub>s</sub>), is known to vary  
91 substantially, depending on a number of factors. A review by *Sholkovitz et al.* [2012] notes  
92 that empirical estimates of the %Fe<sub>s</sub> range from < 0.1% to > 95% (for ~1100 published  
93 values). Factors affecting the dissolution of aerosol Fe have been discussed by *Baker and*  
94 *Croot* [2010] and include the source and composition of the aerosols [*Bonnet and Guieu*,  
95 2004], the particle size [*Baker and Jickells*, 2006], the concentration of particles deposited at  
96 the ocean surface [*Zhuang et al.*, 1990] and atmospheric conditioning [*Zhu et al.*, 1997]. It is  
97 therefore important to consider differences in aerosol dissolution when constructing global  
98 biogeochemical models that include Fe input to the ocean. However, most global models

99 have thus far assumed a constant value for the %Fe<sub>s</sub> [e.g., *Aumont et al.*, 2003; *Moore et al.*,  
100 2004; *Parekh et al.*, 2005; *Tagliabue et al.*, 2009].

101 A number of studies have considered the effect of aerosol source on aerosol Fe  
102 dissolution in the marine environment, and concluded that anthropogenic or combustion  
103 aerosols (e.g., unrefined fuel combustion products, biomass burning) contain Fe with a  
104 significantly higher %Fe<sub>s</sub> compared to mineral aerosols [e.g., *Sedwick et al.*, 2007; *Aguilar-*  
105 *Islas et al.*, 2010]. Therefore, the potential increase in anthropogenic aerosol emissions due to  
106 rising global population and the industrialization of developing nations [*International Energy*  
107 *Agency*, 2009] may be expected to increase the aeolian input of dissolved Fe (dFe) to the  
108 world ocean.

109 Following deposition, the physicochemical conditions of seawater, including  
110 temperature, pH and dissolved oxygen (O<sub>2</sub>) concentration, will impact on the dissolution of  
111 aerosol Fe and the subsequent solution speciation of aeolian Fe [*Millero et al.*, 2009].  
112 Inorganic Fe(III) species have an extremely low solubility limit in seawater (< 80 pM) above  
113 which they can precipitate as ferric oxyhydroxides [*Liu and Millero*, 2002]. The solubility of  
114 Fe(III) species is known to increase with decreasing pH, although this trend is not strong for  
115 seawater over the pH range of 7.5 – 9 [*Kuma et al.*, 1996; *Liu and Millero*, 2002]. The effect  
116 of seawater temperature and dissolved O<sub>2</sub> concentration on Fe solubility in seawater is less  
117 clear. *Liu and Millero* [2002] report a higher solubility value for Fe(III) in 5 °C seawater (0.5  
118 nM) than in 25 °C seawater (0.35 nM) and 50 °C seawater (0.34 nM). However, *Kuma et al.*  
119 [1996] observed no change in the solubility of Fe(III) from 10 °C to 20 °C. In addition, the  
120 oxidation rate of the more soluble redox species Fe(II) is known to decrease with decreasing  
121 temperature, pH and O<sub>2</sub> concentration [*Millero et al.*, 1987; *Croot et al.*, 2001; *Hopkinson*  
122 *and Barbeau*, 2007; *Breitbarth et al.*, 2010].

123 Iron-binding ligands in seawater play a major role in Fe biogeochemistry. By  
124 keeping Fe in solution, ligands reduce the precipitation of ferric oxyhydroxides and thus the  
125 ultimate loss of dFe from surface waters via particle scavenging and export [*Boyd and*  
126 *Ellwood*, 2010]. Two classes of Fe-binding ligands have been characterized: strong ligands  
127 ('L<sub>1</sub>'), which occur mainly near the surface, and weak ligands ('L<sub>2</sub>'), which are more  
128 abundant and occur throughout the water column [*Rue and Bruland*, 1995; *Hunter and Boyd*,  
129 2007], with conditional stability constants ( $\log K_{FeL_i,Fe}^{cond}$ , where *i* denotes ligand class) of 11.1  
130 – 13.9 and 9.7 – 11.95, respectively [*Gledhill and Buck*, 2012]. Numerous studies have shown  
131 that complexation by dissolved organic matter (DOM) such as saccharides [*Hassler et al.*,  
132 2011], humic substances [*Laglera and van den Berg*, 2009] and other species that make up  
133 the L<sub>1</sub> ligands [*Rue and Bruland*, 1995] allow Fe to exist at concentrations well in excess of  
134 the solubility of inorganic Fe(III).

135 Anthropogenic greenhouse gas emissions are thought to be responsible for  
136 observed increases in surface seawater temperature (SST) [*IPCC*, 2013] and reductions in  
137 surface seawater pH [*Orr et al.*, 2005]. As a consequence of increased SST, the upper ocean  
138 is expected to become more stratified and less oxygenated [*Whitney et al.*, 2007; *Stramma et*  
139 *al.*, 2008]. Furthermore, the likely increase in anthropogenic aerosol emissions may result in  
140 an increase in the delivery of organic matter to surface waters, which may potentially contain  
141 Fe-binding ligands [*Wozniak et al.*, 2013]. These changing environmental parameters clearly  
142 have potential consequences for aerosol Fe dissolution, but the nature and magnitude of these  
143 effects are uncertain.

144 The experimental study described here aims to elucidate the main controls on  
145 aerosol Fe dissolution, by manipulating key parameters that are likely to be affected by future  
146 environmental change; namely, surface seawater temperature, pH, dissolved O<sub>2</sub> concentration  
147 and Fe-binding ligand concentration. Filtration using different pore size filters (0.4 μm and

148 0.02  $\mu\text{m}$ ) provided insight into the size-distribution of aerosol-derived dFe in seawater  
149 leachate, as well as possible dissolution mechanisms under the range of different  
150 physicochemical conditions. In addition, experiments using bulk aerosol samples collected  
151 over a full annual cycle allowed us to assess the impact of differing aerosol sources on  
152 aerosol Fe dissolution, in relation to differing physicochemical conditions in surface  
153 seawater.

154

## 155 2. Methods

156

### 157 2.1. *Seawater and aerosol sampling*

158 All handling of samples and reagents was carried out under a Class-5 laminar flow  
159 hood (ISO 14644-1:1999, Bassaire or AirClean units). Ultra high purity (UHP,  $\geq 18.2 \text{ M}\Omega$   
160 cm) deionized water from Milli-Q (Millipore) or Nanopure (Barnstead) systems was used  
161 throughout this work. All plastic labware was cleaned following GEOTRACES cleaning  
162 protocols detailed in *Cutter et al.* [2010].

163 Seawater was collected at the Bermuda Atlantic Time-series Study (BATS) site in  
164 the Sargasso Sea ( $31^{\circ}40'N$ ,  $64^{\circ}10'W$ ) on three cruises during the spring and summer period  
165 (April 2010 – July 2011) on board the *R/V Atlantic Explorer*. Polyvinylchloride (PVC) 10 L  
166 Teflon-lined, external-closure Niskin-type bottles (Ocean Test Equipment) were used to  
167 collect seawater samples at the deep chlorophyll maximum ( $\sim 60 - 120 \text{ m}$  depth), where Fe  
168 concentrations are typically lowest [*Sedwick et al.*, 2005]. Upon recovery, samples were  
169 immediately transferred from the Niskin bottles into acid-washed 50 L low density  
170 polyethylene (LDPE) carboys (Nalgene) inside a polyethylene-walled ‘clean bubble’ under  
171 positive pressure. The seawater was subsequently filtered through  $0.45 \mu\text{m}$   
172 polytetrafluoroethylene (PTFE) Osmonics membrane capsules (GE Water Systems) via  
173 gravity filtration into 25 L LDPE carboys (Nalgene) and stored in the dark under ambient

174 clean room laboratory conditions for no longer than three months before being used in  
175 leaching experiments. L<sub>1</sub>-type Fe-binding ligands in ambient seawater samples, as  
176 determined by competitive ligand exchange-adsorptive cathodic stripping voltammetry  
177 (CLE-CSV) prior to leaching experiments were found to be subnanomolar (~0.8 nM; *n* = 5)  
178 with a log  $K_{FeL_1,Fe'}^{cond}$  of ~12 (data not shown).

179 Four aerosol samples were collected from the Tudor Hill atmospheric observatory  
180 on the southwest coast of Bermuda (32°15.95'N, 64°52.65'W) from 13 July to 20 August 2009  
181 (AER 1, 38 days sampling), 27 September to 11 October 2010 (AER 2, 14 days sampling),  
182 22 February to 8 March 2010 (AER 3, 14 days sampling) and 11 October to 13 December  
183 2010 (AER 4, 63 days sampling). A high volume aerosol sampler drew air through 8 x 10  
184 inch sheets of 2.2 µm pore size quartz microfiber Whatman QMA filters (GE Healthcare).  
185 The total volume of air sampled for AER 1, AER 2, AER 3 and AER 4 over these sampling  
186 periods was 8,620 m<sup>3</sup>, 10,519 m<sup>3</sup>, 11,719 m<sup>3</sup> and 24,243 m<sup>3</sup>, respectively. The aerosol filters  
187 were previously acid-washed following a method described by *Morton et al.* [2013]. The  
188 aerosol sampler was located approximately 50 m above sea level on top of a 23 m high  
189 aluminum scaffolding tower. To avoid local aerosol sources and ensure only marine air was  
190 sampled, pumps were switched off when the wind direction was not in the onshore sector  
191 (210 – 315°), or if the wind speed was less than 1 m s<sup>-1</sup>. A procedural field blank was taken  
192 by loading an aerosol filter into the aerosol sampler, leaving it in the sampler (with pumps  
193 off) for 5 min and removing. Aerosol samples were removed and placed in zip-lock bags and  
194 stored frozen at -20 °C for between 6 – 24 months.

195

## 196 2.2. Seawater preconditioning

197 Separate 1 L aliquots of the 0.45 µm-filtered BATS seawater were preconditioned  
198 before use in the leaching experiments. Filtered seawater aliquots used in the variable



199 temperature experiments were equilibrated to 4 °C and 25 °C, using a fridge and temperature  
200 controlled laboratory, respectively. Filtered seawater aliquots used in the variable seawater  
201 pH experiments were preconditioned by sparging with filtered air/CO<sub>2</sub> mixtures using mass  
202 flow controllers until a stable pH was reached (between 48 – 72 h) [de Putron *et al.*, 2011].  
203 The sparging gas mixtures simulated equilibrium with atmospheric CO<sub>2</sub> concentrations of  
204 400 ppm CO<sub>2</sub> (present-day conditions) and 1250 ppm CO<sub>2</sub> (possible future conditions),  
205 resulting in seawater pH values of 8.0 (‘ambient seawater’) and 7.6 (‘acidified seawater’),  
206 respectively (‘total scale’ pH calculated using measured values of total dissolved inorganic  
207 carbon and alkalinity using ‘CO<sub>2</sub>sys’). Similarly, anoxic conditions (< 0.1% O<sub>2</sub>) were created  
208 by purging dissolved O<sub>2</sub> from filtered seawater by sparging with filtered nitrogen (N<sub>2</sub>) gas  
209 (for leaches 3 and 4 only). Filtered seawater aliquots used in organic ligand amendment  
210 experiments were preconditioned through the addition of a strong siderophore L<sub>1</sub>-type ligand  
211 (either 10 nM of aerobactin [EMC Microcollections] or desferrioxamine-B [Sigma-Aldrich])  
212 or weaker L<sub>2</sub>-type ligands (either 10 nM of protoporphyrin-IX [Sigma-Aldrich] or 1 μM of  
213 glucuronic acid [Sigma-Aldrich]). These ligands were intended to simulate the range of iron-  
214 binding ligands that exist in open ocean waters and were added in concentrations in excess  
215 (~1 order of magnitude) of typical open ocean surface water concentrations in the eastern  
216 North Atlantic [Cullen *et al.*, 2006] in order to observe a clear response in aerosol Fe  
217 complexation.

218

### 219 2.3. *Aerosol leaching experiments*

220 Aerosol leaching experiments were designed to replicate the process of dry  
221 deposition in the open ocean as closely as possible within the laboratory. Leaches were  
222 performed using an acid-washed filtration tower (Savillex) comprising a 47 mm  
223 perfluoroalkoxy (PFA) filter assembly clamp, 250 mL evacuated Teflon collection vessel and

224 0.25 inch diameter PTFE tubing. The PTFE tubing connected the collection vessel to a  
225 vacuum pump (GAST) via a 0.2  $\mu\text{m}$  Acrovent air filter (Pall Corporation) and water trap.  
226 Acid-washed 0.4  $\mu\text{m}$  pore size, 47 mm polycarbonate track-etched membrane filters  
227 (Nucleopore, GE Healthcare) were used to separate ‘dissolved Fe’ in the aerosol leachate  
228 solutions. Triplicate subsamples from each aerosol filter sample were taken using a 20 mm  
229 diameter polished steel arch punch (Osborne) and allowed to thaw at room temperature  
230 before being used for each different treatment in the aerosol leaching experiments.

231           The leaching process (Figure 1) involved four sequential leaches to test different  
232 equilibration times (leach 1 = 0 – 5 min, leach 2 = 5 – 10 min, leach 3 = 10 min – 48 h, and  
233 leach 4 = 48 h – 30 days). These leaching times were chosen to represent the typical temporal  
234 range of aerosol particles in the upper surface ocean. For leach 1, a 20 mm diameter aerosol-  
235 filter subsample was placed on a polycarbonate filter mounted within the filtration tower  
236 (under vacuum). Then 250 mL of preconditioned filtered seawater was poured over the  
237 aerosol filter in a continuous leaching process, lasting 5 min, with the resulting leachate  
238 collected. This process was repeated for leach 2 using the same aerosol subsample used in  
239 leach 1. Leaches 3 and 4 were batch leaches where the same aerosol subsample and  
240 polycarbonate filters used in leaches 1 and 2 were placed in fluorinated polyethylene (FPE,  
241 Nalgene) bottles with 500 mL of preconditioned filtered seawater for 48 h and 30 days for  
242 leaches 3 and 4, respectively (Figure 1). Previous studies employing an aerosol batch leach  
243 methodology have observed only negligible adsorption of dFe to bottle walls when  
244 fluorinated polymer bottles are used [Séguret *et al.*, 2011]. To further minimize the effect of  
245 wall adsorption of dFe the FPE bottles were first preconditioned for 24 - 72 h with BATS  
246 seawater before batch leaches took place. To minimize the influence of ultraviolet light on Fe  
247 dissolution, leaches 1 and 2 were carried out under artificial light only, whereas leaches 3 and  
248 4 were stored in darkness. The seawater leachate solutions that passed through the 0.4  $\mu\text{m}$

249 filter membrane in each sequential leach were subsequently decanted into acid-washed 125  
250 mL LDPE bottles (Nalgene). The entire leaching process was conducted in triplicate for  
251 every experimental treatment.

252 To determine 'colloidal Fe' (cFe) and 'soluble Fe' (sFe), 125 mL of seawater  
253 leachate samples were filtered through 0.02  $\mu\text{m}$  pore size, 25 mm diameter aluminum oxide  
254 Whatman Anotop syringe filters (GE Healthcare) and collected in acid-washed 60 mL LDPE  
255 bottles (Nalgene) (Figure 1). In this study, following the definitions of *Wu et al.* [2001], dFe  
256 is defined as the  $< 0.4 \mu\text{m}$  fraction and sFe is defined as the  $< 0.02 \mu\text{m}$  fraction. Colloidal Fe  
257 is thus inferred from the difference between dFe and sFe, representing the  $0.02 - 0.4 \mu\text{m}$  size  
258 fraction (i.e.,  $\text{cFe} = \text{dFe} - \text{sFe}$ ). The Anotop filters used for ultrafiltration of aerosol leachate  
259 were set-up and conditioned following the inline filtration method detailed by *Ussher et al.*  
260 [2010]. Following aerosol leaches, all seawater leachate samples (including blanks) were  
261 acidified to pH  $\sim 1.7$  using HCl (Romil, UpA) and stored for  $> 1$  year before analysis. In  
262 addition to leachate samples, process blanks were prepared by passing ambient filtered  
263 seawater over a procedural field blank subsample (Section 2.1) and a 47 mm polycarbonate  
264 filter. Following analysis, the Fe concentrations of the relevant process blanks were  
265 subtracted from Fe concentrations of all leachate samples. The dFe concentrations of the  
266 process blanks were typically  $< 0.1 \text{ nM}$ .

267

#### 268 2.4. *Determination of iron in seawater leachates using flow injection with* 269 *chemiluminescence*

270 The concentrations of dFe and sFe in seawater leachate solutions were determined  
271 using flow injection with chemiluminescence detection (FI-CL) inside a Class-100 clean  
272 room (ISO 9001:2008), based on the method described by *Obata et al.* [1993]. Briefly,  
273 seawater leachate samples were buffered in-line to pH 3.5 with 0.35 M ammonium acetate  
274 (Romil, SpA) then loaded on a chelating column containing Toyopearl AF-Chelate-650M

275 iminodiacetate resin (IDA, Tosoh Bioscience). The seawater matrix major cations were  
276 removed using a 0.012 M HCl (Romil, SpA) rinse, then Fe was eluted from the column using  
277 0.23 M HCl (Romil, SpA). The acid/analyte eluent was then mixed with 0.25 mM luminol,  
278 0.5 M ammonium hydroxide and 0.3 M hydrogen peroxide to initiate the oxidation of  
279 luminol [Rose and Waite, 2001], which produced a chemiluminescence signal detected by a  
280 photomultiplier tube (PMT, Hamamatsu).

281           Iron concentrations were quantified using the method of standard additions to low-  
282 Fe seawater ( $< 0.35$  nM dFe), subsampled from the original filtered seawater used for leaches  
283 (four sets of concentration ranges were used: 0.6 – 12 nM, 0.6 – 5 nM, 0.6 – 2.4 nM, 0.2 –  
284 1.4 nM,  $n = 6$ ). All standards and samples were analyzed in triplicate. Accuracy of the  
285 method was checked daily by analyzing samples of SAFe and GEOTRACES reference  
286 seawater and comparing determined concentrations with consensus values: SAFe S =  $0.091 \pm$   
287  $0.008$  nM ( $n = 29$ ), SAFe D2 =  $0.910 \pm 0.022$  nM ( $n = 29$ ) and GEOTRACES GD =  $0.98 \pm$   
288  $0.10$  nM ( $n = 22$ ), (K. Bruland, unpublished data, 2008, available from the Bruland Research  
289 Laboratory at <http://es.ucsc.edu/~kbruland/GeotracessaFe/kwbGeotracessaFe.html>).  
290 Concentrations of Fe in reference seawater determined using this FI-CL system were  
291 consistently within the range of the consensus values (SAFe S =  $0.10 - 0.10$  nM [ $n = 3$ ],  
292 SAFe D2 =  $0.85 - 0.91$  nM [ $n = 4$ ] and GEOTRACES GD =  $0.83 - 0.99$  nM [ $n = 8$ ]).  
293 Analytical precision was typically better than  $\pm 5\%$  relative standard deviation for all  
294 standards, reference seawater and samples.

295

## 296 2.5. *Total trace metal determination by inductively coupled plasma mass spectrometry*

297           Triplicate subsamples of AER 1 – 4 and blanks were completely digested using  
298 concentrated hydrofluoric acid (28.9 M HF, Seastar, Baseline), concentrated nitric acid (15.8  
299 M HNO<sub>3</sub>, Seastar, Baseline) and heat [Morton et al., 2013] at the University of Delaware. As

300 acid digestion is a destructive process, it was necessary to use different subsamples of each  
301 aerosol sample in the aerosol leaching experiments and use the mean total Fe amount in  
302 fractional solubility calculations. Total element determinations were subsequently performed  
303 on the digests at Old Dominion University using an Element2 (Thermo Fisher) inductively  
304 coupled plasma-mass spectrometer (ICP-MS) in medium resolution mode. Samples were  
305 spiked with indium ( $^{115}\text{In}$ ) as an internal standard. Calibration standards were made up using  
306 a multi-elemental standard (QC Standard 4, PlasmaCal containing aluminum [Al], titanium  
307 [Ti], manganese [Mn], vanadium [V], chromium [Cr], Fe, cobalt [Co], nickel [Ni], copper  
308 [Cu], zinc [Zn], cadmium [Cd], antimony [Sb] and lead [Pb]) in the same 2% (v/v)  $\text{HNO}_3$   
309 matrix as the aerosol digest solutions.

310

### 311 2.6. *Air mass back trajectory analysis*

312 Air mass back trajectories were simulated using the Hybrid Single-Particle  
313 Lagrangian Integrated Trajectory (HYSPLIT) model developed by the U.S. National Oceanic  
314 and Atmospheric Administration (NOAA, available for download at  
315 [http://ready.arl.noaa.gov/hyreg/HYSPLIT\\_pchysplit.php](http://ready.arl.noaa.gov/hyreg/HYSPLIT_pchysplit.php)). Ten-day back trajectories at  
316 altitudes of 50 m, 500 m and 2000 m were performed for each day within the period over  
317 which aerosol samples were collected. Daily back trajectories were used in the cluster  
318 analysis function of HYSPLIT to generate ten mean back trajectories for each aerosol  
319 sampling period.

320

## 321 3. Results and Discussion

322

### 323 3.1. *Aerosol sample characterization*

324 The aerosol samples collected at Tudor Hill represent a seasonal-scale time series  
325 comprising a summer sample (AER 1), an autumn sample (AER 2), a spring sample (AER 3),

326 and a winter sample (AER 4). Daily 500 m elevation 10-day air mass back trajectories for  
327 each day of the collection period of each aerosol sample are provided in Figure 2. Air mass  
328 back trajectories modeled at 50 m and 2000 m elevation (not shown) were similar to those  
329 modeled at 500 m. The back trajectories for AER 1 (Figure 2A), collected between July and  
330 August 2009, suggest that the air had predominately travelled from the east, likely entraining  
331 soil dust from North Africa, as is typical for aerosols in the Bermuda region during summer  
332 [*Sedwick et al.*, 2007]. The back trajectories for AER 2 (Figure 2B), collected between  
333 September to October 2010 and AER 3 (Figure 2C), collected February to March 2010  
334 suggest a mixture of air masses that may have delivered aerosols from both North Africa and  
335 North America. The back trajectories for AER 4 (Figure 2D), collected between October and  
336 December 2010, suggest that the air had predominately travelled from the northwest,  
337 entraining aerosols from North America. These results are consistent with time-series aerosol  
338 observations from Bermuda over a number of decades [*Duce and Hoffman*, 1976; *Chen and*  
339 *Duce*, 1983; *Anderson et al.*, 1996; *Sholkovitz et al.*, 2009].

340 To gain an appreciation of the relative contributions of anthropogenic versus  
341 crustal materials to the aerosols, total masses of Fe, V, Ni, Cu, Pb and Sb in the aerosol  
342 samples (Table 1) were normalized to the mass of Al, and the resulting ratios compared to  
343 those of average continental crust [*Taylor and McLennan*, 1995] to calculate enrichment  
344 factors (Table 2). Samples collected in the winter (i.e., AER 4) were more enriched  
345 (enrichment factors > 10) in V, Ni, Cu, Pb and Sb relative to aerosols collected in the summer  
346 (i.e., AER 1 and AER 2). These results are consistent with the back trajectory models (Figure  
347 2), and agree with the suggestion by *Sedwick et al.* [2007] that marine air over the Sargasso  
348 Sea contains a greater proportion of anthropogenic combustion products (relative to  
349 continental soil dust) in the winter. Summer Fe and Al atmospheric loadings were higher than  
350 those determined in the winter (Table 1), consistent with previous work that has shown high

351 Fe and Al loadings in air masses dominated by lithogenic aerosols, relative to anthropogenic  
352 materials [Baker *et al.*, 2006; Buck *et al.*, 2010a; Séguret *et al.*, 2011].

353

### 354 3.2. *Effect of seawater temperature, pH and de-oxygenation on aerosol iron dissolution*

355 Total dFe leached from aerosols into preconditioned seawater samples of different  
356 temperature, pH and O<sub>2</sub> concentration were calculated from the process-blank-corrected dFe  
357 concentrations and volumes of seawater leachate (Figure 3). An alternative representation of  
358 these results, as fractional solubilities of aerosol Fe (total dFe released into solution divided  
359 by total aerosol Fe), are shown in Figure 4.

360 The mean total dFe leached from each aerosol sample (AER 1 – AER 4) into 4 °C  
361 and 25 °C seawater is shown in Figure 3A. The mean total dFe is the sum of all dFe released  
362 into seawater during all four sequential leaches and ranged from  $0.7 \pm 0.2$  nmol to  $4 \pm 2$  nmol  
363 for AER 1 – AER 4. The uncertainty was dominated by differences between replicate leaches  
364 of subsamples of the same aerosol sample, with a relative standard deviation (RSD) of 13 –  
365 45%, rather than replicate Fe analyses of the same leachate solution, with an RSD of 5 – 6%,  
366 in accord with results of other studies [e.g. Morton *et al.*, 2013]. Most of the aerosol Fe was  
367 released into solution during the first leach, with progressively less Fe released in the  
368 subsequent sequential leach steps. It is clear that the dissolution of Fe from aerosols occurred  
369 rapidly; the majority (84 – 94%) of the aerosol-derived dFe was released within the first 10  
370 minutes of contact with seawater. Similar kinetics were observed for all leaches assessed in  
371 this study and in other studies of aerosol Fe solubility [e.g., Buck *et al.*, 2006; Wu *et al.*,  
372 2007]. Importantly, the differences in the mean total dFe released into 4 °C versus 25 °C  
373 seawater were not statistically significant (two-tailed *t* test,  $p > 0.05$ ) for any of the aerosol  
374 samples, suggesting seawater temperature does not exert a major control on the dissolution of  
375 aerosol Fe.

376           The mean total sFe ( $< 0.02 \mu\text{m}$ ) leached from each aerosol sample (AER 1 – AER  
377 4) into  $4^\circ\text{C}$  and  $25^\circ\text{C}$  seawater is shown in Table 3. The mean total sFe is the sum of all sFe  
378 released during all four sequential leaches and ranged from 0.04 nmol to 0.41 nmol for AER  
379 1 – AER. The colloidal Fe size fraction (cFe,  $0.02 - 0.4 \mu\text{m}$ ) can be inferred by comparing  
380 the dFe and sFe in the seawater leachate. For all leaches, the majority (77 – 97%) of dFe  
381 released from the aerosols into the seawater leachate resided in the cFe size fraction (Table  
382 3). It should be noted that these data represent the size distribution of dFe in solution  
383 following leaching from aerosols, not the amount of sFe and cFe that has been directly  
384 leached from the aerosols. The differences in mean total sFe in the leachate using  $4^\circ\text{C}$   
385 seawater versus  $25^\circ\text{C}$  seawater were not statistically significant (two-tailed  $t$  test,  $p > 0.05$ )  
386 when the differences in dFe for replicate leaches is taken into account, suggesting that  
387 seawater temperature does not exert a major control on the size distribution (sFe versus cFe)  
388 of dFe in the aerosol leachate solutions.

389           The mean total quantities of dFe leached from each aerosol sample (AER 1 – AER  
390 4) into ‘ambient seawater’ ( $25^\circ\text{C}$ , pH 8.0, oxygenated), ‘acidified seawater’ (pH 7.6, sparged  
391 with air/ $\text{CO}_2$  mixture, 1250 ppm  $\text{CO}_2$ ) and ‘anoxic seawater’ (sparged with  $\text{N}_2$  for leaches 3  
392 and 4) are shown in Figure 3B. The mean total dFe is the sum of all dFe released during all  
393 leaches and ranged from  $0.6 \pm 0.2$  nmol to  $5 \pm 2$  nmol for AER 1 – AER 4. Our results show  
394 that the total dFe released into acidified and anoxic seawater was not statistically different  
395 (two-tailed  $t$  test,  $p > 0.05$ ) from the total dFe released into ambient seawater for all aerosol  
396 samples.

397           The mean total sFe in the seawater leached from each aerosol sample (AER 1 –  
398 AER 4) into ambient, acidified and anoxic seawater is shown in Table 3. The mean total sFe  
399 is the sum of all sFe released during all four sequential leaches and ranged from 0.02 nmol to  
400 0.16 nmol for AER 1 – AER4. In all cases, the majority (92 – 98%) of dFe in the seawater



401 leachate solutions resided in the cFe size fraction (Table 3). There were some differences  
402 observed between samples, however, similar to the dFe results, the differences in the mean  
403 total sFe in the various seawater leachate samples were not statistically significant (two-tailed  
404  $t$  test,  $p > 0.05$ ) when the differences in dFe for replicate leaching experiments is taken into  
405 account.

406 Thus our experimental results suggest that seawater temperature, pH (as controlled  
407 by  $p\text{CO}_2$ ) and  $\text{O}_2$  concentration did not exert a major control on the dissolution of aerosol Fe,  
408 nor on the size distribution of aerosol-derived dFe in seawater, within the experimental  
409 uncertainties and ranges of the parameters examined. These observations are in accord with  
410 those of *Kuma et al.* [1996], who reported no difference in the solubility of inorganic Fe(III)  
411 in seawater at  $10^\circ\text{C}$  versus  $20^\circ\text{C}$ . In contrast, however, *Liu and Millero* [2002] reported  
412 higher solubility of Fe(III) seawater at  $5^\circ\text{C}$  versus  $25^\circ\text{C}$  ( $0.5 \pm 0.07$  nM for  $5^\circ\text{C}$  seawater and  
413  $0.35 \pm 0.06$  nM for  $25^\circ\text{C}$  seawater). Other studies have demonstrated an increase in the  
414 solubility of inorganic Fe with decreasing pH [*Byrne and Kester*, 1976; *Kuma et al.*, 1996;  
415 *Liu and Millero*, 2002]. However, *Liu and Millero* [2002] report that Fe solubility does not  
416 change in the pH range of 7.5 – 9, due to the dominance of the neutrally charged species  
417  $\text{Fe}(\text{OH})_3^\circ$  [*Liu and Millero*, 1999]. It should be noted that in the case of *Liu and Millero*  
418 [2002] and *Byrne and Kester* [1976] equilibrium conditions were represented, whereas our  
419 leach experiments are not likely to represent equilibrium conditions. Data from our study also  
420 agree with empirical data that suggest little difference in the dissolution of aerosol Fe in  
421 seawater (pH ~8) versus UHP ( $\geq 18.2$  M $\Omega$  cm, pH 5.6) deionized water [*Aguilar-Islas et al.*,  
422 2010; *Buck et al.*, 2013].

423 Given the year 2100 projections for average sea surface temperatures to increase  
424 by  $1^\circ\text{C}$  [*Meehl et al.*, 2007], seawater pH to decrease by 0.25 [*Caldeira and Wickett*, 2003],  
425 and oceanic oxygen minimum zones (OMZs) to expand [*Shaffer et al.*, 2009], our data

426 suggest that such changes will not significantly impact on aerosol Fe dissolution in surface  
427 ocean waters. However, it should be stressed that the combined effect of such changes, or the  
428 impact of such changes on other factors that impact aerosol Fe dissolution, cannot be ruled  
429 out. Our findings have important implications for modeling the impact of future changes in  
430 aerosol input to the global cycling of Fe and carbon, as well as phytoplankton growth and  
431 community structure. Specifically, our experimental results suggest that, to a first  
432 approximation, models do not need to consider that aerosol Fe dissolution will vary as a  
433 function of projected variations in seawater temperature, pH or oxygen saturation. Whilst  
434 seawater temperature, pH and O<sub>2</sub> concentration had no significant effect on aerosol Fe  
435 dissolution, we observed pronounced differences in aerosol Fe solubilities for aerosols from  
436 different source regions with different bulk compositions.

437

### 438 3.3. *Effect of aerosol source and composition on aerosol iron dissolution*

439 Seawater leaching of aerosol samples of different source and composition resulted  
440 in different fractional solubilities of aerosol Fe under all conditions (Figure 4). Indeed, there  
441 is nearly an order of magnitude difference in the %Fe<sub>s</sub> for the more ‘anthropogenic’ type  
442 aerosol (AER 4) relative to the ‘mineral dust’ type aerosol (AER 1). The operationally-  
443 defined %Fe<sub>s</sub> for aerosol AER 1 was consistently lower ( $0.3 \pm 0.1\%$  to  $0.5 \pm 0.2\%$ ) than that  
444 for aerosol AER 4 ( $2.5 \pm 0.8\%$  to  $3.2 \pm 0.8\%$ ), under all physicochemical conditions of the  
445 seawater leaching experiments. The dependence of aerosol Fe solubility on aerosol type and  
446 source has been noted in previous studies [*Sedwick et al.*, 2007; *Sholkovitz et al.*, 2009; *Buck*  
447 *et al.*, 2010b; *Séguret et al.*, 2011; *Shelley et al.*, 2012; *Baker et al.*, 2013; *Wozniak et al.*,  
448 2013]. It has been suggested that the elevated %Fe<sub>s</sub> in anthropogenically influenced aerosols  
449 reflects acidic processing at the particle surface [*Meskhidze et al.*, 2005; *Hsu et al.*, 2010], the  
450 presence of labile Fe sulfates and other soluble Fe phases [*Oakes et al.*, 2012], and the

451 tendency for anthropogenic aerosols to be smaller than mineral dust particles [*Chen and*  
452 *Siefert, 2004; Jang et al., 2007*]. Conversely, mineral aerosol particles tend to be larger, with  
453 much of the Fe contained in refractory minerals [*Desboeufs et al., 2005*].

454 *Sholkovitz et al.* [2009] show a linear relationship between the %Fe<sub>s</sub> and the V/Al  
455 mass ratio of bulk aerosol samples collected over the Sargasso Sea. That linear relationship  
456 and the V/Al mass ratios of bulk aerosol samples collected in this study were used to predict  
457 fractional solubilities in ambient seawater; these predictions were then compared to  
458 empirically determined fractional solubilities. Whilst absolute values of the predicted and  
459 determined fractional solubilities differed (predicted values of 1.4%, 2.0%, 2.7% and 3.8%,  
460 for AER 1, AER 2 and AER 3 and AER 4, respectively, versus observed values of 0.5%,  
461 1.2%, 1.3% and 2.8%, for AER 1, AER 2 and AER 3 and AER 4, respectively), the predicted  
462 trend of increasing solubility with increasing V/Al mass ratio matched the empirical values.  
463 Thus, our results indicate greater %Fe<sub>s</sub> in aerosols containing a larger proportion of  
464 anthropogenic material.

465 Whilst this study is unable to provide insight into the mechanism of enhanced Fe  
466 solubility in non-soil dust aerosols, the results add to the existing evidence that Fe in  
467 anthropogenic aerosols is more soluble than Fe in soil-derived mineral dust and that this  
468 variability dominates over potential changes in the fundamental parameters of temperature,  
469 pH and O<sub>2</sub> concentration of the seawater in which aerosols are deposited. These results  
470 suggest that the potential for an increase in anthropogenic aerosol emissions accompanying  
471 rising global population and the industrialization of developing nations [*International Energy*  
472 *Agency, 2009*] could conceivably increase the atmospheric flux of dFe to the global ocean,  
473 although soil dust is likely to continue to dominate the total aerosol Fe deposition and  
474 therefore the global importance of anthropogenic aerosol Fe input is likely to remain  
475 marginal. These results reinforce the idea that modeling efforts must consider the source of

476 aerosols deposited in different ocean regions, as well as the potential for future changes in the  
477 composition of aerosols entering the ocean.

478

#### 479 3.4. *Effect of organic ligands on aerosol iron dissolution*

480 Figure 5A shows the mean total dFe leached from aerosol sample AER 1 into  
481 ambient seawater and into seawater samples amended with various organic ligands. Despite  
482 the added ligands having very different conditional stability constants with respect to Fe  
483 complexation, the mean total dFe leached from aerosols following all leaches (including a  
484 control using seawater with no added ligands) fell in the narrow range of  $0.8 \pm 0.1$  nmol to  
485  $1.2 \pm 0.5$  nmol. Interestingly, there was no statistical difference between the mean total dFe  
486 leached into each ligand-amended seawater sample and that leached into unamended ambient  
487 seawater (two-tailed *t* test,  $p > 0.05$ ), which contrasts with the results of previous work by  
488 *Aguilar-Islas et al.* [2010]. However, this earlier study did not include replicate leaches using  
489 subsamples of a single aerosol sample. Our study has shown that the RSD associated with  
490 replicate leaches can exceed 50%, and whilst the mean total amounts of dFe leached into  
491 ligand-amended seawater appeared to differ from that leached into ambient seawater, these  
492 differences were not statistically significant. The majority of the variation in dFe leached  
493 from sub-samples of a single aerosol filter reflects either the inherent variability of the  
494 leaching process (i.e. the leaching mechanism or variability in the Fe species or particle  
495 character) or heterogeneity of Fe species with different fractional solubilities across the  
496 aerosol filter. Bulk analysis of an extended suite of aerosol digest solutions (data not shown)  
497 suggests that heterogeneity in total Fe contained on the aerosol filter is unlikely to be  
498 responsible for the observed variability in dFe between replicate leaches (RSD on mean of  
499 total Fe in subsamples of a single aerosol sample is  $< 3\%$ ).

500 In stark contrast, there were pronounced differences in the mean total sFe in  
501 leachate solutions after leaching with unamended ambient seawater versus seawater amended  
502 with the L<sub>1</sub>-type ligands aerobactin and desferrioxamine-B (Figure 5B). The mean total sFe  
503 leached into ambient seawater leachate was 0.02 nmol, whereas leachate from seawater  
504 amended with aerobactin and desferrioxamine-B contained 1.3 nmol and 1.1 nmol sFe,  
505 respectively. This large impact observed with L<sub>1</sub>-type ligand amended seawater was not seen  
506 with the weaker organic ligands glucuronic acid and protoporphyrin-IX, for which leachate  
507 solutions contained 0.10 nmol and 0.16 nmol sFe, respectively.

508 In comparing the dFe and sFe in the seawater leachate solutions, it is apparent that  
509 the majority (100%) of the dFe in ambient seawater leachate existed as cFe. The same was  
510 true for all of the seawater leachate solutions from the temperature, pH and dissolved O<sub>2</sub>  
511 experiments. This observation is consistent with the results of previous laboratory studies and  
512 field observations [*Wu et al.*, 2001; *Bergquist et al.*, 2007; *Aguilar-Islas et al.*, 2010; *Ussher*  
513 *et al.*, 2013; *Fitzsimmons and Boyle*, 2014; *S. J. Ussher*, manuscript in preparation, 2014].  
514 Conversely, for aerosols leached with seawater amended with the L<sub>1</sub>-type ligands aerobactin  
515 and desferrioxamine-B, the majority of dFe in the leachate (77 – 98%) resided in the sFe  
516 fraction. However, for leaches with seawater amended with the weaker ligands; glucuronic  
517 acid and protoporphyrin-IX, there was only a small increase in the proportion of sFe in the  
518 leachate compared with the control experiment using ambient conditions (sFe accounted for  
519 11 – 21% of dFe). This observation suggests that the stronger L<sub>1</sub>-type ligands may play an  
520 important role in the dissolution of aerosol Fe in the surface ocean.

521 Based on the results of this study, we hypothesize a two-stage mechanism for the  
522 dissolution of aerosol Fe in seawater (Figure 6). First, upon deposition of aerosols at the  
523 ocean surface, labile inorganic Fe(II) and Fe(III) is released into seawater, whereupon it is  
524 rapidly forms colloidal-sized ferric oxyhydroxides [following oxidation, if Fe(II)], or is

525 adsorbed or complexed by colloidal-sized organic matter (e.g., saccharides [Hassler *et al.*,  
526 2011], amino acids [Benner, 2011] and humic substances [Laglera and van den Berg, 2009]).  
527 After this first stage, the dissolved aerosol Fe exists predominantly in the cFe size fraction, as  
528 observed in the majority of our experimental leachate solutions. During the second stage of  
529 our hypothesized mechanism, strong L<sub>1</sub>-type ligands, such as siderophores, if present un-  
530 complexed in sufficient concentration, form strong Fe-ligand complexes, whereby there is a  
531 transfer of dissolved aerosol Fe from the colloidal to the soluble size fraction, as low  
532 molecular weight (~300 – 1000 Da) Fe-ligand complexes [Macrellis *et al.*, 2001]. The fact  
533 that not all Fe is ‘solubilized’ by L<sub>1</sub>-type ligands, despite seawater being amended with large  
534 excess concentrations (10 nM) in our experiments, may reflect the physical or chemical  
535 association of some L<sub>1</sub>-type ligands with colloidal material present in the seawater.

536           An alternative hypothesis is that upon deposition at the surface seawater, aerosols  
537 may release colloidal-sized organic matter or inorganic phases with which Fe is already  
538 associated [Raiswell and Canfield, 2012; Paris and Desboeufs, 2013]. In seawater, L<sub>1</sub>-type  
539 ligands can then draw the aeolian cFe into the soluble fraction, as described above. If this is  
540 the case, it suggests ligands associated with aerosols are weak and colloidal, contrary to  
541 findings of Wozniak *et al.* [2013]. However, we suggest it is more likely that dFe released  
542 from aerosols enters the colloidal size fraction in seawater. This conclusion is based on  
543 results for the leaching of aerosols using seawater preconditioned by filtration (< 0.4 µm) and  
544 ultrafiltration (< 0.02 µm), which show lower dFe concentrations in leachate derived using  
545 ultrafiltered seawater [Ussher, 2005]. In addition, Dammshäuser and Croot [2012] showed  
546 that aerosol Al and titanium (Ti) colloidal associations are very low following dissolution  
547 into seawater, potentially indicating low input of colloidal matter from aerosols. An  
548 important factor that determines whether colloidal Fe is delivered by aerosols or forms in  
549 seawater following deposition maybe the particle size of deposited aerosols, which is related

550 to aerosol composition (i.e., mineral dust versus combustion products). Certainly, a higher  
551 proportion of colloidal Fe has been observed in regions of fine mode aerosol deposition in  
552 comparison to coarse mode aerosol deposition, and this fine size fraction results in higher  
553 fractional solubilities of Fe [*Buck et al.*, 2010b; *Ussher et al.*, 2013].

554 In summary, from our experimental results, it seems clear that stronger organic Fe-  
555 binding ligands play an important role in the dissolution of aerosol Fe. This observation has  
556 important implications for our understanding of the biogeochemical role of organic ligands  
557 with regard to the cycling of Fe. In the absence of such organic ligands, aerosol-derived dFe  
558 will remain largely in the colloidal size fraction in seawater, in which case it is expected to be  
559 more rapidly lost from surface ocean waters over a period of weeks to months [*Moran and*  
560 *Buesseler*, 1992; *Boyd et al.*, 2010]. In the presence of sufficient concentrations of strong  
561 ligands, however, aerosol-derived dFe may be transferred from the colloidal to the soluble  
562 size fraction, where it may be expected to have a longer residence time in the euphotic zone  
563 [*Boyd and Ellwood*, 2010] and thus have greater biological availability to phytoplankton. It is  
564 important to note that the role that biological organisms play in aerosol Fe dissolution has not  
565 been considered in this study and should be included when attempting to understand the  
566 complete aerosol Fe dissolution mechanism.

567

#### 568 4. Conclusions

569

570 The results of this experimental study suggest that plausible future variations in the  
571 temperature, pH and O<sub>2</sub> concentration of seawater will have a minor impact on the  
572 dissolution of aerosol Fe. However, in accord with other studies, our data indicate that  
573 aerosol composition has the most significant effect on the dissolution of aerosol Fe, with  
574 North Atlantic aerosol samples with the greatest ‘anthropogenic’ components having the  
575 highest fractional solubility. Hence, we surmise that future increases in the proportion of

576 combustion aerosols, relative to mineral dust, are likely to be the most important driver of  
577 changes in the atmospheric flux of dFe to the surface ocean. Therefore, it is reasonable for  
578 modelers not to prioritize the inclusion of seawater temperature, pH and O<sub>2</sub> concentration  
579 effects on aerosol Fe dissolution, but instead focus attention on the regional differences in the  
580 original source of deposition aerosols.

581 Furthermore, our results highlight the likely importance of strong Fe-binding  
582 organic ligands in regulating the size distribution of aerosol-derived dFe in surface ocean  
583 waters; specifically, in increasing the residence time and biological availability of aerosol-  
584 derived Fe in the surface ocean. A conceptual model of aerosol Fe dissolution is proposed in  
585 which strong Fe-binding organic ligands play a key role. The proposed two-stage mechanism  
586 highlights the significance of the colloidal phase and the strong L<sub>1</sub>-type ligands in retaining  
587 biologically-available aerosol Fe in surface ocean waters following deposition of aerosols.

588

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590

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601



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603 6. References

604

605 Aguilar-Islas, A. M., J. Wu, R. Rember, A. M. Johansen, and L. M. Shank (2010),  
606 Dissolution of aerosol-derived iron in seawater: Leach solution chemistry, aerosol type, and  
607 colloidal iron fraction, *Marine Chemistry*, 120(1–4), 25–33.  
608 doi:10.1016/j.marchem.2009.01.011

609 Anderson, J. R., P. R. Buseck, T. L. Patterson, and R. Arimoto (1996), Characterization of  
610 the Bermuda tropospheric aerosol by combined individual-particle and bulk-aerosol analysis,  
611 *Atmospheric Environment*, 30(2), 319–338. doi:10.1016/1352-2310(95)00170-4

612 Aumont, O., E. Maier-Reimer, S. Blain, and P. Monfray (2003), An ecosystem model of the  
613 global ocean including Fe, Si, P colimitations, *Global Biogeochemical Cycles*, 17(2), 1060.  
614 doi:10.1029/2001gb001745

615 Baker, A. R., and T. D. Jickells (2006), Mineral particle size as a control on aerosol iron  
616 solubility, *Geophysical Research Letters*, 33(17), L17608. doi:10.1029/2006gl026557

617 Baker, A. R., T. D. Jickells, K. F. Biswas, K. Weston, and M. French (2006), Nutrients in  
618 atmospheric aerosol particles along the Atlantic Meridional Transect, *Deep Sea Research*  
619 *Part II: Topical Studies in Oceanography*, 53(14–16), 1706–1719. doi:  
620 10.1016/j.dsr2.2006.05.012

621 Baker, A. R., and P. L. Croot (2010), Atmospheric and marine controls on aerosol iron  
622 solubility in seawater, *Marine Chemistry*, 120(1–4), 4–13. doi:10.1016/j.marchem.2008.09.003

623 Baker, A. R., C. Adams, T. G. Bell, T. D. Jickells, and L. Ganzeveld (2013), Estimation of  
624 atmospheric nutrient inputs to the Atlantic Ocean from 50°N to 50°S based on large-scale  
625 field sampling: Iron and other dust-associated elements, *Global Biogeochemical Cycles*,  
626 27(3), 755–767. doi: 10.1002/gbc.20062

627 Benner, R. (2011), Loose ligands and available iron in the ocean, *Proceedings of the National*  
628 *Academy of Sciences*, 108(3), 893–894. doi:10.1073/pnas.1018163108

629 Bergquist, B. A., J. Wu, and E. A. Boyle (2007), Variability in oceanic dissolved iron is  
630 dominated by the colloidal fraction, *Geochimica et Cosmochimica Acta*, 71(12), 2960–2974.  
631 doi:10.1016/j.gca.2007.03.013

632 Bonnet, S., and C. Guieu (2004), Dissolution of atmospheric iron in seawater, *Geophysical*  
633 *Research Letters*, 31(3), L03303. doi:10.1029/2003gl018423

634 Boyd, P. W., A. J. Watson, C. S. Law, E. R. Abraham, T. Trull, R. Murdoch, D. C. E.  
635 Bakker, A. R. Bowie, K. O. Buesseler, H. Chang, M. Charette, P. Croot, K. Downing, R.  
636 Frew, M. Gall, M. Hadfield, J. Hall, M. Harvey, G. Jameson, J. LaRoche, M. Liddicoat, R.  
637 Ling, M. T. Maldonado, R. M. McKay, S. Nodder, S. Pickmere, R. Pridmore, S. Rintoul, K.  
638 Safi, P. Sutton, R. Strzepek, K. Tanneberger, S. Turner, A. Waite, and J. Zeldis (2000), A  
639 mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization,  
640 *Nature*, 407(6805), 695–702. doi:10.1038/35037500

- 641 Boyd, P. W., and M. J. Ellwood (2010), The biogeochemical cycle of iron in the ocean,  
642 *Nature Geoscience*, 3(10), 675-682. doi:10.1038/ngeo964
- 643 Boyd, P. W., E. Ibanami, S. G. Sander, K. A. Hunter, and G. A. Jackson (2010),  
644 Remineralization of upper ocean particles: Implications for iron biogeochemistry, *Limnology*  
645 *and Oceanography*, 55(3), 1271-1288. doi: 10.4319/lo.2010.55.3.1271
- 646 Breitbarth, E., R. Bellerby, C. Neill, M. Ardelan, M. Meyerhöfer, E. Zöllner, P. Croot, and U.  
647 Riebesell (2010), Ocean acidification affects iron speciation during a coastal seawater  
648 mesocosm experiment, *Biogeosciences*, 7(3), 1065-1073. doi:10.5194/bg-7-1065-2010
- 649 Buck, C. S., W. M. Landing, J. A. Resing, and G. T. Lebon (2006), Aerosol iron and  
650 aluminum solubility in the northwest Pacific Ocean: Results from the 2002 IOC cruise,  
651 *Geochemistry, Geophysics, Geosystems*, 7(4), Q04M07. doi:10.1029/2005gc000977
- 652 Buck, C. S., W. M. Landing, and J. A. Resing (2010a), Particle size and aerosol iron  
653 solubility: A high-resolution analysis of Atlantic aerosols, *Marine Chemistry*, 120(1-4), 14-  
654 24. doi:10.1016/j.marchem.2008.11.002
- 655 Buck, C. S., W. M. Landing, J. A. Resing, and C. I. Measures (2010b), The solubility and  
656 deposition of aerosol Fe and other trace elements in the North Atlantic Ocean: Observations  
657 from the A16N CLIVAR/CO2 repeat hydrography section, *Marine Chemistry*, 120(1-4), 57-  
658 70. doi: 10.1016/j.marchem.2008.08.003
- 659 Buck, C. S., W. M. Landing, and J. Resing (2013), Pacific Ocean aerosols: Deposition and  
660 solubility of iron, aluminum, and other trace elements, *Marine Chemistry*, 157, 117-130.  
661 doi:10.1016/j.marchem.2013.09.005
- 662 Byrne, R. H., and D. R. Kester (1976), Solubility of hydrous ferric oxide and iron speciation  
663 in seawater, *Marine Chemistry*, 4(3), 255-274. doi:10.1016/0304-4203(76)90012-8
- 664 Caldeira, K., and M. E. Wickett (2003), Oceanography: anthropogenic carbon and ocean pH,  
665 *Nature*, 425(6956), 365-365. doi:10.1038/425365a
- 666 Chen, L., and R. A. Duce (1983), The sources of sulfate, vanadium and mineral matter in  
667 aerosol particles over Bermuda, *Atmospheric Environment*, 17(10), 2055-2064.  
668 doi:10.1016/0004-6981(83)90362-1
- 669 Chen, Y., and R. L. Siefert (2004), Seasonal and spatial distributions and dry deposition  
670 fluxes of atmospheric total and labile iron over the tropical and subtropical North Atlantic  
671 Ocean, *Journal of Geophysical Research: Atmospheres*, 109(D9), D09305.  
672 10.1029/2003jd003958
- 673 Coale, K. H., K. S. Johnson, S. E. Fitzwater, R. M. Gordon, S. Tanner, F. P. Chavez, L.  
674 Ferioli, C. Sakamoto, P. Rogers, F. Millero, P. Steinberg, P. Nightingale, D. Cooper, W. P.  
675 Cochlan, M. R. Landry, J. Constantinou, G. Rollwagen, A. Trasvina, and R. Kudela (1996),  
676 A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment  
677 in the equatorial Pacific Ocean, *Nature*, 383(6600), 495-501. doi:10.1038/383495a0
- 678 Croot, P. L., A. R. Bowie, R. D. Frew, M. T. Maldonado, J. A. Hall, K. A. Safi, J. La Roche,  
679 P. W. Boyd, and C. S. Law (2001), Retention of dissolved iron and Fe II in an iron induced

- 680 Southern Ocean phytoplankton bloom, *Geophysical Research Letters*, 28(18), 3425-3428.  
681 doi: 10.1029/2001gl013023
- 682 Cullen, J. T., B. A. Bergquist, and J. W. Moffett (2006), Thermodynamic characterization of  
683 the partitioning of iron between soluble and colloidal species in the Atlantic Ocean, *Marine*  
684 *Chemistry*, 98(2-4), 295-303. doi:10.1016/j.marchem.2005.10.007
- 685 Cutter, G., P. Andersson, L. Codispoti, P. Croot, R. Francois, M. Lohan, H. Obata, and M.  
686 Rutgers vd Loeff (2010), Sampling and sample-handling protocols for GEOTRACES Cruises  
687 *Rep.*, GEOTRACES, Toulouse.
- 688 Dammshäuser, A., and P. L. Croot (2012), Low colloidal associations of aluminium and  
689 titanium in surface waters of the tropical Atlantic, *Geochimica et Cosmochimica Acta*, 96(0),  
690 304-318. doi:10.1016/j.gca.2012.07.032
- 691 de Putron, S. J., D. C. McCorkle, A. L. Cohen, and A. Dillon (2011), The impact of seawater  
692 saturation state and bicarbonate ion concentration on calcification by new recruits of two  
693 Atlantic corals, *Coral Reefs*, 30(2), 321-328. doi:10.1007/s00338-010-0697-z
- 694 Desboeufs, K. V., A. Sofikitis, R. Losno, J. L. Colin, and P. Ausset (2005), Dissolution and  
695 solubility of trace metals from natural and anthropogenic aerosol particulate matter,  
696 *Chemosphere*, 58(2), 195-203. doi:10.1016/j.chemosphere.2004.02.025
- 697 Duce, R., A. (1986), The Impact of Atmospheric Nitrogen, Phosphorus, and Iron Species on  
698 Marine Biological Productivity, in *The Role of Air-Sea Exchange in Geochemical Cycling*,  
699 edited by P. Buat-Ménard, pp. 497-529, Springer Netherlands.
- 700 Duce, R. A., and G. L. Hoffman (1976), Atmospheric vanadium transport to the ocean,  
701 *Atmospheric Environment (1967)*, 10(11), 989-996. doi:10.1016/0004-6981(76)90207-9
- 702 Fitzsimmons, J. N., and E. A. Boyle (2014), Both soluble and colloidal iron phases control  
703 dissolved iron variability in the tropical North Atlantic Ocean, *Geochimica et Cosmochimica*  
704 *Acta*, 125(0), 539-550. doi: 10.1016/j.gca.2013.10.032
- 705 Gledhill, M., and K. N. Buck (2012), The organic complexation of iron in the marine  
706 environment: A review, *Frontiers in Microbiology*, 3. doi:10.3389/fmicb.2012.00069
- 707 Hassler, C. S., V. Schoemann, C. M. Nichols, E. C. Butler, and P. W. Boyd (2011),  
708 Saccharides enhance iron bioavailability to Southern Ocean phytoplankton, *Proceedings of*  
709 *the National Academy of Sciences*, 108(3), 1076-1081. doi:10.1073/pnas.1010963108
- 710 Hopkinson, B. M., and K. A. Barbeau (2007), Organic and redox speciation of iron in the  
711 eastern tropical North Pacific suboxic zone, *Marine Chemistry*, 106(1-2), 2-17.  
712 doi:10.1016/j.marchem.2006.02.008
- 713 Hsu, S.-C., G. T. F. Wong, G.-C. Gong, F.-K. Shiah, Y.-T. Huang, S.-J. Kao, F. Tsai, S.-C.  
714 Candice Lung, F.-J. Lin, I. I. Lin, C.-C. Hung, and C.-M. Tseng (2010), Sources, solubility,  
715 and dry deposition of aerosol trace elements over the East China Sea, *Marine Chemistry*,  
716 120(1-4), 116-127. doi:10.1016/j.marchem.2008.10.003
- 717 Hunter, K. A., and P. W. Boyd (2007), Iron-binding ligands and their role in the ocean  
718 biogeochemistry of iron, *Environmental Chemistry*, 4(4), 221-232. doi:10.1071/EN07012

- 719 International Energy Agency (2009), *World Energy Outlook 2009 Rep.*, International Energy  
720 Agency, Cedex.
- 721 IPCC (2013), Working Group I Contribution to the IPCC Fifth Assessment Report Climate  
722 Change 2013: The Physical Science Basis, Summary for Policymakers *Rep.*, IPCC, Geneva.
- 723 Jang, H.-N., Y.-C. Seo, J.-H. Lee, K.-W. Hwang, J.-I. Yoo, C.-H. Sok, and S.-H. Kim (2007),  
724 Formation of fine particles enriched by V and Ni from heavy oil combustion: Anthropogenic  
725 sources and drop-tube furnace experiments, *Atmospheric Environment*, 41(5), 1053-1063.  
726 doi:10.1016/j.atmosenv.2006.09.011
- 727 Jickells, T. D., Z. S. An, K. K. Andersen, A. R. Baker, G. Bergametti, N. Brooks, J. J. Cao, P.  
728 W. Boyd, R. A. Duce, K. A. Hunter, H. Kawahata, N. Kubilay, J. laRoche, P. S. Liss, N.  
729 Mahowald, J. M. Prospero, A. J. Ridgwell, I. Tegen, and R. Torres (2005), Global iron  
730 connections between desert dust, ocean biogeochemistry, and climate, *Science*, 308(5718),  
731 67-71. doi: 10.1126/science.1105959
- 732 Kohfeld, K. E., and A. Ridgwell (2009), Glacial-interglacial variability in atmospheric CO<sub>2</sub>,  
733 *Geophysical Monograph Series*, 187, 251-286. doi: 10.1029/2008GM000845
- 734 Kuma, K., J. Nishioka, and K. Matsunaga (1996), Controls on iron (III) hydroxide solubility  
735 in seawater: The influence of pH and natural organic chelators, *Limnology and*  
736 *Oceanography*, 41(3), 396-407. doi:10.4319/lo.1996.41.3.0396
- 737 Laglera, L. M., and C. M. G. van den Berg (2009), Evidence for geochemical control of iron  
738 by humic substances in seawater, *Limnology and Oceanography*, 54(2), 610-619.  
739 doi:10.4319/lo.2009.54.2.0610
- 740 Liu, X., and F. J. Millero (1999), The solubility of iron hydroxide in sodium chloride  
741 solutions, *Geochimica et Cosmochimica Acta*, 63(19-20), 3487-3497. doi:10.1016/S0016-  
742 7037(99)00270-7
- 743 Liu, X., and F. J. Millero (2002), The solubility of iron in seawater, *Marine Chemistry*, 77(1),  
744 43-54. doi:10.1016/S0304-4203(01)00074-3
- 745 Macrellis, H. M., C. G. Trick, E. L. Rue, G. Smith, and K. W. Bruland (2001), Collection and  
746 detection of natural iron-binding ligands from seawater, *Marine Chemistry*, 76(3), 175-187.  
747 doi:10.1016/S0304-4203(01)00061-5
- 748 Martin, J. H., and M. R. Gordon (1988), Northeast Pacific iron distributions in relation to  
749 phytoplankton productivity, *Deep Sea Research Part A. Oceanographic Research Papers*,  
750 35(2), 177-196. doi: 10.1016/0198-0149(88)90035-0
- 751 Martin, J. H. (1990), Glacial-Interglacial CO<sub>2</sub> Change: The Iron Hypothesis,  
752 *Paleoceanography*, 5(1), 1-13. doi:10.1029/PA005i001p00001
- 753 Martin, J. H., K. H. Coale, K. S. Johnson, S. E. Fitzwater, R. M. Gordon, S. J. Tanner, C. N.  
754 Hunter, V. A. Elrod, J. L. Nowicki, T. L. Coley, R. T. Barber, S. Lindley, A. J. Watson, K.  
755 Vanscoy, C. S. Law, M. I. Liddicoat, R. Ling, T. Stanton, J. Stockel, C. Collins, A. Anderson,  
756 R. Bidigare, M. Ondrusek, M. Latasa, F. J. Millero, K. Lee, W. Yao, J. Z. Zhang, G.  
757 Friederich, C. Sakamoto, F. Chavez, K. Buck, Z. Kolber, R. Greene, P. Falkowski, S. W.  
758 Chisholm, F. Hoge, R. Swift, J. Yungel, S. Turner, P. Nightingale, A. Hatton, P. Liss, and N.

- 759 W. Tindale (1994), Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean,  
760 *Nature*, 371(6493), 123-129. doi:10.1038/371123a0
- 761 Meehl, G. A., T. F. Stocker, W. D. Collins, P. Friedlingstein, A. T. Gaye, J. M. Gregory, A.  
762 Kitoh, R. Knutti, J. M. Murphy, A. Noda, S. C. B. Raper, I. G. Watterson, A. J. Weaver, and  
763 Z.-C. Zhao (Eds.) (2007), *Global climate projections*, Cambridge University Press,  
764 Cambridge.
- 765 Meskhidze, N., A. Nenes, W. C. Conant, and J. H. Seinfeld (2005), Evaluation of a new  
766 cloud droplet activation parameterization with in situ data from CRYSTAL-FACE and  
767 CSTRIFE, *Journal of Geophysical Research: Atmospheres*, 110(D16), D16202. doi:  
768 10.1029/2004jd005703
- 769 Millero, F. J., S. Sotolongo, and M. Izaguirre (1987), The oxidation kinetics of Fe(II) in  
770 seawater, *Geochimica et Cosmochimica Acta*, 51(4), 793-801. doi: 10.1016/0016-  
771 7037(87)90093-7
- 772 Millero, F. J., R. Woosley, B. DiTrolino, and J. Waters (2009), Effect of Ocean Acidification  
773 on the Speciation of Metals in Seawater, *Oceanography*, 22, 72-85. doi:  
774 10.5670/oceanog.2009.98
- 775 Moore, J. K., S. C. Doney, and K. Lindsay (2004), Upper ocean ecosystem dynamics and  
776 iron cycling in a global three-dimensional model, *Global Biogeochemical Cycles*, 18(4),  
777 GB4028. doi:10.1029/2004gb002220
- 778 Moran, S. B., and K. O. Buesseler (1992), Short residence time of colloids in the upper ocean  
779 estimated from <sup>238</sup>U–<sup>234</sup>Th disequilibria
- 780 Morton, P. L., W. M. Landing, S.-C. Hsu, A. Milne, A. M. Aguilar-Islas, A. R. Baker, A. R.  
781 Bowie, C. S. Buck, Y. Gao, and S. Gichuki (2013), Methods for the sampling and analysis of  
782 marine aerosols: results from the 2008 GEOTRACES aerosol intercalibration experiment,  
783 *Limnology and Oceanography: Methods*, 11, 62-78. doi:10.4319/lom.2013.11.62
- 784 Oakes, M., R. Weber, B. Lai, A. Russell, and E. Ingall (2012), Characterization of iron  
785 speciation in urban and rural single particles using XANES spectroscopy and micro X-ray  
786 fluorescence measurements: investigating the relationship between speciation and fractional  
787 iron solubility, *Atmospheric Chemistry and Physics*, 12(2), 745-756. doi: 10.5194/acp-12-  
788 745-2012
- 789 Obata, H., H. Karatani, and E. Nakayama (1993), Automated determination of iron in  
790 seawater by chelating resin concentration and chemiluminescence detection, *Analytical*  
791 *Chemistry*, 65(11), 1524-1528. 10.1021/ac00059a007
- 792 Orr, J. C., V. J. Fabry, O. Aumont, L. Bopp, S. C. Doney, R. A. Feely, A. Gnanadesikan, N.  
793 Gruber, A. Ishida, and F. Joos (2005), Anthropogenic ocean acidification over the twenty-  
794 first century and its impact on calcifying organisms, *Nature*, 437(7059), 681-686.  
795 doi:10.1038/nature04095
- 796 Parekh, P., M. J. Follows, and E. A. Boyle (2005), Decoupling of iron and phosphate in the  
797 global ocean, *Global Biogeochemical Cycles*, 19(2), GB2020. doi:10.1029/2004gb002280

798 Paris, R., and K. V. Desboeufs (2013), Effect of atmospheric organic complexation on iron-  
799 bearing dust solubility, *Atmospheric Chemistry and Physics*, 13(9), 4895-4905.  
800 doi:10.5194/acp-13-4895-2013

801 Raiswell, R., and D. E. Canfield (2012), The iron biogeochemical cycle past and present,  
802 *Geochemical Perspectives*, 1(1), 1-322. doi: 10.7185/geochempersp.1.1

803 Rose, A. L., and T. D. Waite (2001), Chemiluminescence of Luminol in the Presence of  
804 Iron(II) and Oxygen: Oxidation Mechanism and Implications for Its Analytical Use,  
805 *Analytical Chemistry*, 73(24), 5909-5920. doi:10.1021/ac015547q

806 Rue, E. L., and K. W. Bruland (1995), Complexation of iron(III) by natural organic ligands in  
807 the Central North Pacific as determined by a new competitive ligand equilibration/adsorptive  
808 cathodic stripping voltammetric method, *Marine Chemistry*, 50(1-4), 117-138.  
809 doi:10.1016/0304-4203(95)00031-1

810 Sedwick, P. N., T. M. Church, A. R. Bowie, C. M. Marsay, S. J. Ussher, K. M. Achilles, P. J.  
811 Lethaby, R. J. Johnson, M. M. Sarin, and D. J. McGillicuddy (2005), Iron in the Sargasso Sea  
812 (Bermuda Atlantic Time-series Study region) during summer: Eolian imprint, spatiotemporal  
813 variability, and ecological implications, *Global Biogeochemical Cycles*, 19(4), GB4006.  
814 doi:10.1029/2004gb002445

815 Sedwick, P. N., E. R. Sholkovitz, and T. M. Church (2007), Impact of anthropogenic  
816 combustion emissions on the fractional solubility of aerosol iron: Evidence from the Sargasso  
817 Sea, *Geochemistry, Geophysics, Geosystems*, 8(10), Q10Q06. doi:10.1029/2007gc001586

818 Séguret, M. J. M., M. Koçak, C. Theodosi, S. J. Ussher, P. J. Worsfold, B. Herut, N.  
819 Mihalopoulos, N. Kubilay, and M. Nimmo (2011), Iron solubility in crustal and  
820 anthropogenic aerosols: The Eastern Mediterranean as a case study, *Marine Chemistry*,  
821 126(1-4), 229-238. doi:10.1016/j.marchem.2011.05.007

822 Shaffer, G., S. M. Olsen, and J. O. P. Pedersen (2009), Long-term ocean oxygen depletion in  
823 response to carbon dioxide emissions from fossil fuels, *Nature Geoscience*, 2(2), 105-109.  
824 doi:10.1038/ngeo420

825 Shelley, R., P. N. Sedwick, T. Bibby, P. Cabedo-Sanz, T. M. Church, R. J. Johnson, A.  
826 Macey, C. Marsay, E. R. Sholkovitz, and S. J. Ussher (2012), Controls on dissolved cobalt in  
827 surface waters of the Sargasso Sea: Comparisons with iron and aluminum, *Global*  
828 *Biogeochemical Cycles*, 26(2), GB2020. doi: 10.1029/2011GB004155

829 Sholkovitz, E. R., P. N. Sedwick, and T. M. Church (2009), Influence of anthropogenic  
830 combustion emissions on the deposition of soluble aerosol iron to the ocean: Empirical  
831 estimates for island sites in the North Atlantic, *Geochimica et Cosmochimica Acta*, 73(14),  
832 3981-4003. doi:10.1016/j.gca.2009.04.029

833 Sholkovitz, E. R., P. N. Sedwick, T. M. Church, A. R. Baker, and C. F. Powell (2012),  
834 Fractional solubility of aerosol iron: Synthesis of a global-scale data set, *Geochimica et*  
835 *Cosmochimica Acta*, 89(0), 173-189. doi:10.1016/j.gca.2012.04.022

836 Stramma, L., G. C. Johnson, J. Sprintall, and V. Mohrholz (2008), Expanding oxygen-  
837 minimum zones in the tropical oceans, *Science*, 320(5876), 655-658.  
838 doi:10.1126/science.1153847

839 Tagliabue, A., L. Bopp, O. Aumont, and K. R. Arrigo (2009), Influence of light and  
840 temperature on the marine iron cycle: From theoretical to global modeling, *Global*  
841 *Biogeochemical Cycles*, 23(2), GB2017. doi: 10.1029/2008gb003214

842 Takeda, S., and A. Tsuda (2005), An in situ iron-enrichment experiment in the western  
843 subarctic Pacific (SEEDS): Introduction and summary, *Progress in Oceanography*, 64(2-4),  
844 95-109. doi: 10.1016/j.pocean.2005.02.004

845 Taylor, S. R., and S. M. McLennan (1995), The geochemical evolution of the continental  
846 crust, *Reviews of Geophysics*, 33(2), 241-265. doi:10.1029/95rg00262

847 Ussher, S. (2005), Determination of dissolved iron speciation in the North East Atlantic  
848 Ocean by flow injection chemiluminescence, PhD thesis, School of Geography, Earth and  
849 Environmental Sciences, Plymouth University, Plymouth, UK.

850 Ussher, S. J., E. P. Achterberg, G. Sarthou, P. Laan, H. J. W. de Baar, and P. J. Worsfold  
851 (2010), Distribution of size fractionated dissolved iron in the Canary Basin, *Marine*  
852 *Environmental Research*, 70(1), 46-55. doi: 10.1016/j.marenvres.2010.03.001

853 Ussher, S. J., E. P. Achterberg, C. Powell, A. R. Baker, T. D. Jickells, R. Torres, and P. J.  
854 Worsfold (2013), Impact of atmospheric deposition on the contrasting iron biogeochemistry  
855 of the North and South Atlantic Ocean, *Global Biogeochemical Cycles*. doi:  
856 10.1002/gbc.20056

857 Whitney, F. A., H. J. Freeland, and M. Robert (2007), Persistently declining oxygen levels in  
858 the interior waters of the eastern subarctic Pacific, *Progress in Oceanography*, 75(2), 179-  
859 199. doi:10.1016/j.pocean.2007.08.007

860 Wozniak, A. S., R. U. Shelley, R. L. Sleighter, H. A. N. Abdulla, P. L. Morton, W. M.  
861 Landing, and P. G. Hatcher (2013), Relationships among aerosol water soluble organic  
862 matter, iron and aluminum in European, North African, and Marine air masses from the 2010  
863 US GEOTRACES cruise, *Marine Chemistry*, 154(0), 24-33.  
864 doi:10.1016/j.marchem.2013.04.011

865 Wu, J., E. Boyle, W. Sunda, and L.-S. Wen (2001), Soluble and colloidal iron in the  
866 oligotrophic North Atlantic and North Pacific, *Science*, 293(5531), 847-849.  
867 doi:10.1126/science.1059251

868 Wu, J., R. Rember, and C. Cahill (2007), Dissolution of aerosol iron in the surface waters of  
869 the North Pacific and North Atlantic oceans as determined by a semicontinuous flow-through  
870 reactor method, *Global Biogeochemical Cycles*, 21(4), n/a-n/a. 10.1029/2006gb002851

871 Zhu, X. R., J. M. Prospero, and F. J. Millero (1997), Diel variability of soluble Fe(II) and  
872 soluble total Fe in North African dust in the trade winds at Barbados, *Journal of Geophysical*  
873 *Research: Atmospheres*, 102(D17), 21297-21305. doi: 10.1029/97jd01313

874 Zhuang, G., R. A. Duce, and D. R. Kester (1990), The Dissolution of Atmospheric Iron in  
875 Surface Seawater of the Open Ocean, *Journal of Geophysical Research*, 95(C9), 16207-  
876 16216. doi:10.1029/JC095iC09p16207  
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879 7. Tables  
880

881 **Table 1.** Total trace metal masses<sup>a</sup> contained in aerosol subsamples and atmospheric loading of trace metals in sampled air<sup>b</sup>.  
882

Aerosol sample	Sample period	Total mass of trace metal in aerosol subsample (ng)							Concentration of trace metal in sampled air (pmol m <sup>-3</sup> )						
		Al	Fe	V	Ni	Cu	Pb	Sb	Al	Fe	V	Ni	Cu	Pb	Sb
AER 1	13 Jul. to 20 Aug. 2009	16,200 ±700	9,180 ±300	41.0 ±0.4	17.0 ±0.6	14.8 ±0.4	18.0 ±0.6	2.65 ±0.2	8,800 ±400	2,400 ±70	12 ±0.1	4.3 ±0.2	3.4 ±0.1	1.3 ±0.04	0.32 ±0.02
AER 2	27 Sept. to 11 Oct. 2010	21,000 ±500	12,300 ±100	82.0 ±5	32.0 ±1	31.1 ±3	28.8 ±0.5	5.21 ±0.01	9,400 ±200	2,700 ±30	19 ±1	6.6 ±0.2	5.9 ±0.5	1.7 ±0.03	0.52 ±0.001
AER 3	22 Feb. to 8 Mar. 2010	30,000 ±900	18,600 ±200	169 ±40	76.0 ±10	92.9 ±30	146 ±30	24.6 ±1	12,000 ±400	3,600 ±30	36 ±8	14 ±2	16 ±4	7.6 ±2	2.2 ±0.1
AER 4	11 Oct. to 13 Dec. 2010	8,840 ±900	4,870 ±100	73.0 ±4	31.0 ±1	47.5 ±3	75.0 ±9	14.4 ±0.3	1,700 ±200	460 ±10	7.5 ±0.4	2.8 ±0.1	3.9 ±0.2	1.9 ±0.2	0.62 ±0.01

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884 <sup>a</sup>Total mean masses (ng) of aluminum (Al), iron (Fe), vanadium (V), nickel (Ni), copper (Cu), lead (Pb) and antimony (Sb) in triplicate subsamples of each aerosol sample.  
885 Standard deviations from mean masses ( $\pm 1 \sigma$ ) represent masses of metals determined for three subsamples of the same aerosol sample.  
886 <sup>b</sup>Mean concentrations (pmol m<sup>-3</sup>) of Al, Fe, V, Ni, Cu, Pb and Sb in sampled air calculated using total mean masses of trace metals in each aerosol subsample and the total  
887 volume of air passed through each sample filter over the sampling period. Standard deviations from mean concentrations ( $\pm 1 \sigma$ ) represent the uncertainty of trace metals  
888 mean mass measurements only.  
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896 **Table 2.** Trace metal to aluminum mass ratios<sup>a</sup> and trace metal enrichment factors relative to upper continental crust abundances<sup>b</sup>.  
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Aerosol sample	Mass ratio						Enrichment factors					
	Fe/Al	V/Al	Ni/Al	Cu/Al	Pb/Al	Sb/Al	Fe	V	Ni	Cu	Pb	Sb
AER 1	0.568 ±0.06	0.00254 ±0.00004	0.00105 ±0.00006	0.000917 ±0.00004	0.00111 ±0.00006	0.000164 ±0.00002	1.3 ±0.1	3.4 ±0.05	4.2 ±0.2	2.9 ±0.1	4.5 ±0.2	66 ±7
AER 2	0.584 ±0.01	0.00391 ±0.0003	0.00152 ±0.00008	0.00148 ±0.0002	0.00137 ±0.00003	0.000248 ±0.000001	1.3 ±0.02	5.2 ±0.5	6.1 ±0.3	4.8 ±0.6	5.5 ±0.1	100 ±0.4
AER 3	0.620 ±0.008	0.00563 ±0.002	0.00253 ±0.0005	0.00310 ±0.001	0.00486 ±0.002	0.000820 ±0.00007	1.4 ±0.02	7.5 ±2	10 ±2	10 ±4	20 ±6	330 ±30
AER 4	0.551 ±0.02	0.00826 ±0.0007	0.00351 ±0.0003	0.00537 ±0.0005	0.00848 ±0.002	0.00163 ±0.00005	1.3 ±0.05	11.0 ±1	14 ±1	17 ±1	34 ±6	660 ±20

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899 <sup>a</sup>Iron/aluminum (Fe/Al), vanadium/aluminum (V/Al), nickel/aluminum (Ni/Al), copper/aluminum (Cu/Al), lead/aluminum (Pb/Al) and antimony/aluminum (Sb/Al) mass  
 900 ratios calculated by dividing the total mean mass of each trace metal with the total mean mass of aluminum in each aerosol subsample. Standard deviations from mean mass  
 901 ratios ( $\pm 1 \sigma$ ) represent the uncertainty of trace metals mean mass measurements only.

902 <sup>b</sup>Iron (Fe), vanadium (V), nickel (Ni), copper (Cu), lead (Pb) and antimony (Sb) enrichment factors were calculated by dividing trace metal/aluminum mass ratios of aerosol  
 903 samples by trace metal/aluminum ratios found in the upper continental crust. Abundances of trace metals in the upper continental crust taken from *Taylor and McLennan*  
 904 [1995] and used to calculate mass ratios (Fe/Al = 0.4, V/Al = 0.0007, Ni/Al = 0.0002, Cu/Al = 0.0003, Pb/Al = 0.0002 and Sb/Al = 0.000002). Standard deviations from  
 905 mean enrichment factors ( $\pm 1 \sigma$ ) represent the uncertainty of trace metals mean mass measurements only.

906 **Table 3.** The mean total (nmol) of dissolved iron (dFe), colloidal iron (cFe) and soluble iron (sFe) leached from  
 907 aerosol samples AER 1, AER 2, AER 3 and AER 4 during three replicate leaches with seawater<sup>a</sup>.  
 908

Aerosol sample	Seawater condition	Total Fe leached from aerosols (nmol)			Colloidal proportion of dFe (%)
		dFe	cFe	sFe	
AER 1	25 °C	0.9 ±0.4	0.7	0.20	77%
AER 1	4 °C	0.7 ±0.2	0.6	0.037	94%
AER 1	Ambient (25 °C, pH 8.0, oxygenated)	0.8 ±0.4	0.8	0.016	98%
AER 1	Acidified (pH 7.6)	0.6 ±0.2	0.5	0.043	92%
AER 2	25 °C	2.4 ±0.4	2.3	0.15	94%
AER 2	4 °C	2.8 ±0.4	2.3	0.41	85%
AER 2	Ambient (25 °C, pH 8.0, oxygenated)	2.6 ±0.3	2.5	0.09	97%
AER 2	Acidified (pH 7.6)	1.7 ±0.3	1.6	0.052	97%
AER 2	Anoxic	2.0 ±0.3	1.9	0.060	97%
AER 3	25 °C	4.3 ±1.6	4.2	0.12	97%
AER 3	4 °C	3.3 ±1.1	3.1	0.22	93%
AER 3	Ambient (25 °C, pH 8.0, oxygenated)	4.3 ±1.3	4.2	0.16	96%
AER 3	Acidified (pH 7.6)	4.7 ±1.9	4.6	0.11	98%
AER 4	25 °C	2.5 ±0.5	2.2	0.23	91%
AER 4	4 °C	2.2 ±1.0	2.0	0.15	93%
AER 4	Ambient (25 °C, pH 8.0, oxygenated)	2.4 ±0.6	2.3	0.055	98%
AER 4	Acidified (pH 7.6)	2.2 ±0.7	2.1	0.055	97%
AER 4	Anoxic	2.8 ±0.7	2.8	0.043	98%

909  
 910 <sup>a</sup>25 °C seawater, 4 °C seawater, ambient seawater from the pH and de-oxygenation experiment (25 °C, pH 8.0,  
 911 oxygenated), acidified seawater (pH 7.6, sparged with air enriched in carbon dioxide) and anoxic seawater  
 912 (sparged with nitrogen gas for leaches 3 and 4). Standard deviations ( $\pm 1 \sigma$ ) from mean total Fe leached from  
 913 replicate subsamples of the same aerosol sample shown for dFe.  
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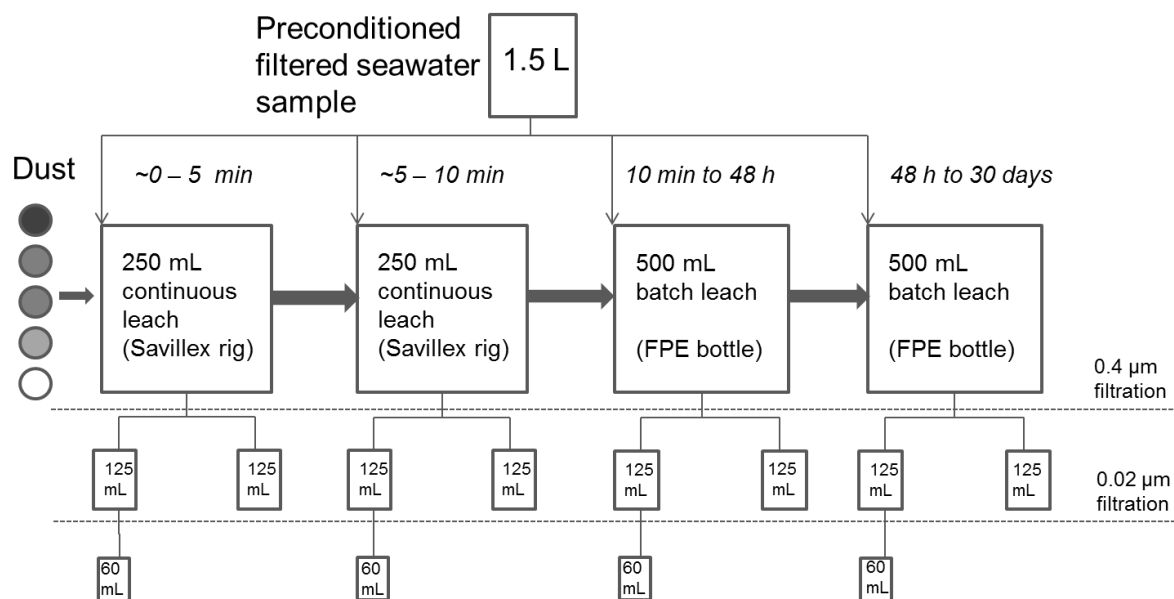
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926 8. Figures  
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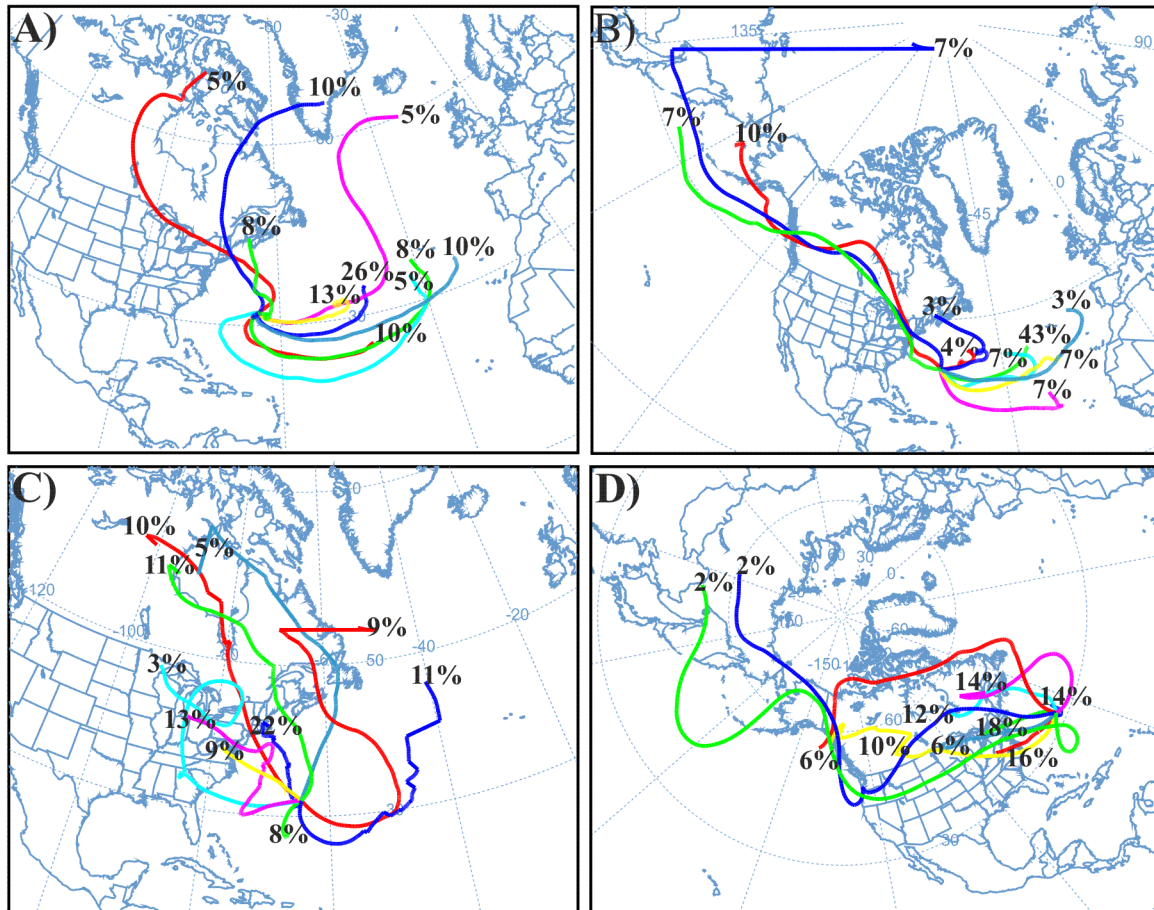
929 **Figure 1.** Summary of aerosol leaching method. Leach 1 and 2 were continuous leaches carried out using a  
930 Savillex filtration tower, and leach 3 and 4 were batch leaches carried out in 500 mL fluorinated polyethylene  
931 (FPE) bottles. All seawater leachate samples were filtered through 0.4 μm and 0.02 μm pore size filters to  
932 define the size distribution of dissolved iron species in solution.

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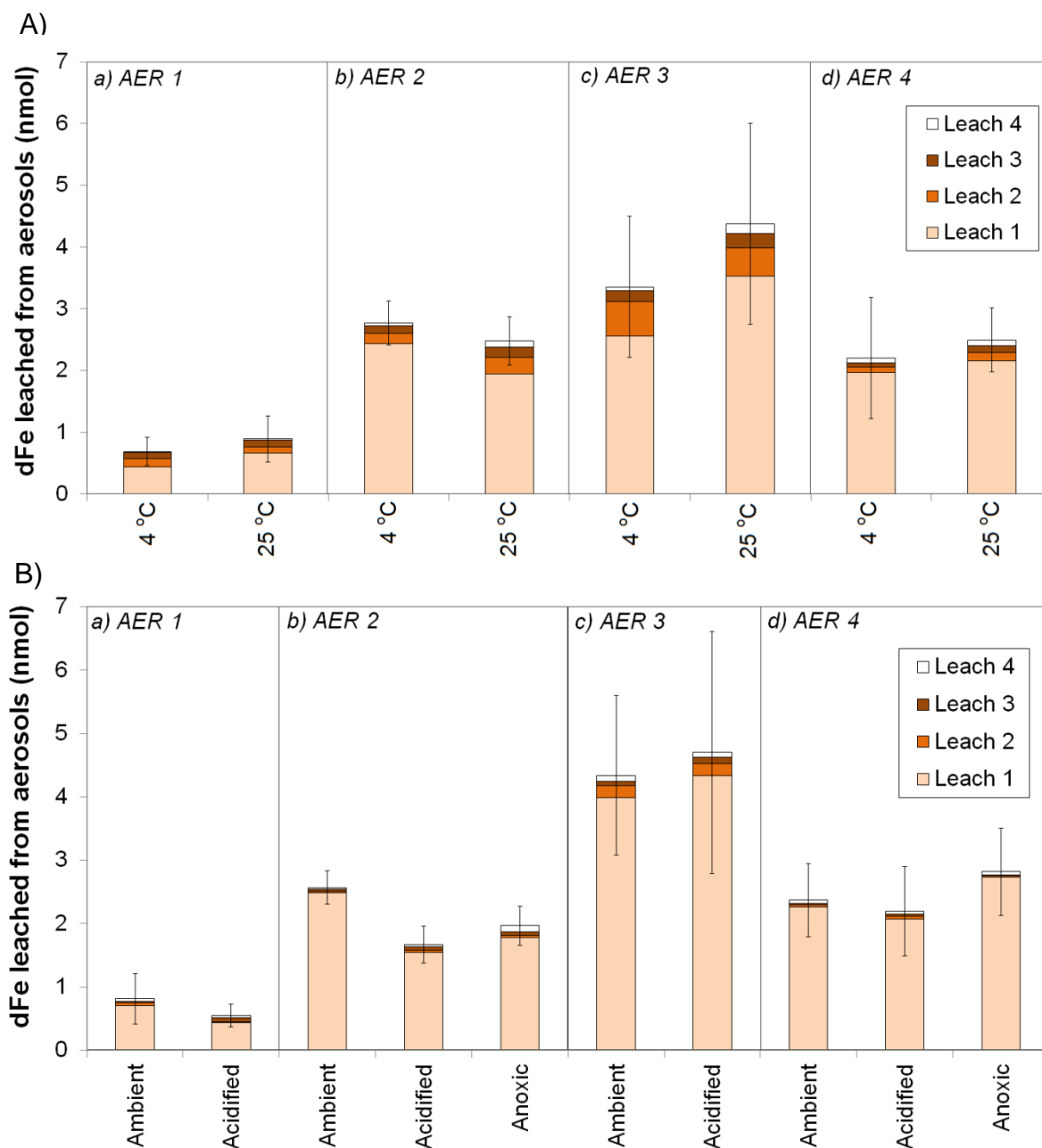


937

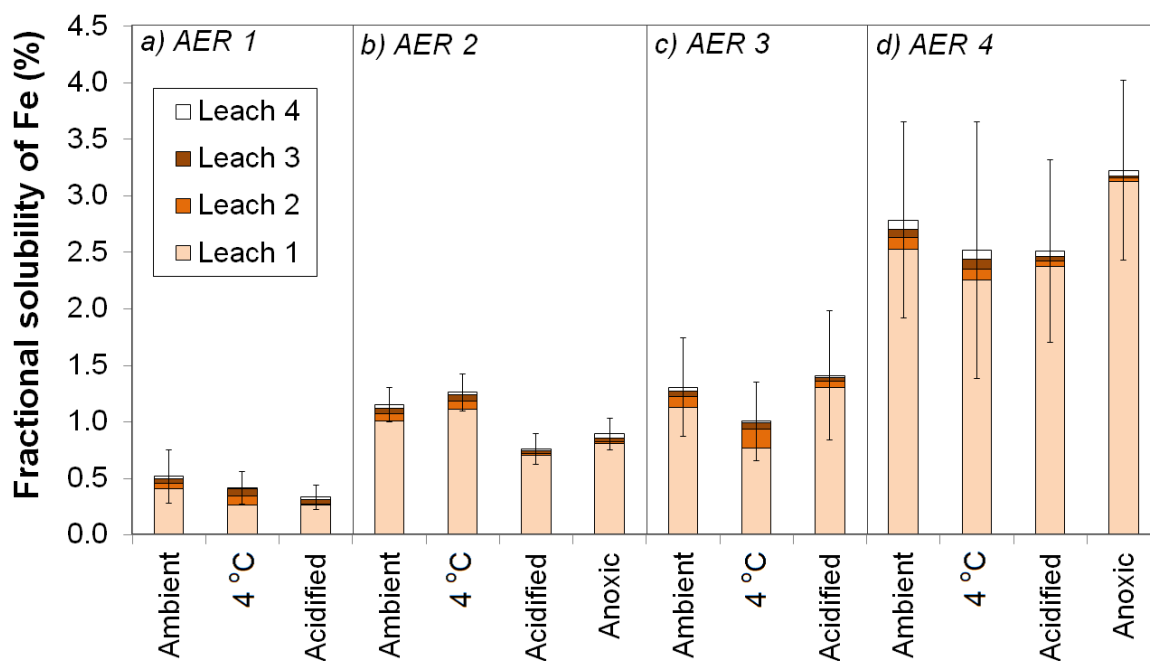
938 **Figure 2.** Mean air mass back-trajectory clusters generated from daily 500 m 10 day back trajectories from  
 939 Tudor Hill using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model for the  
 940 following sampling periods: A) 13 July to 20 August 2009 (AER 1), B) 27 September to 11 October 2010 (AER  
 941 2), C) 22 February to 8 March 2010 (AER 3) and D) 11 October to 13 December 2010 (AER 4). Ten mean back  
 942 trajectory clusters are shown for each sample with the proportion of total trajectories used in each cluster shown  
 943 beside each mean back trajectory cluster. **UPDATE BACK TRAJECTORY 'C' AND ASSOCIATED**  
 944 **DISCUSSION**

945

946

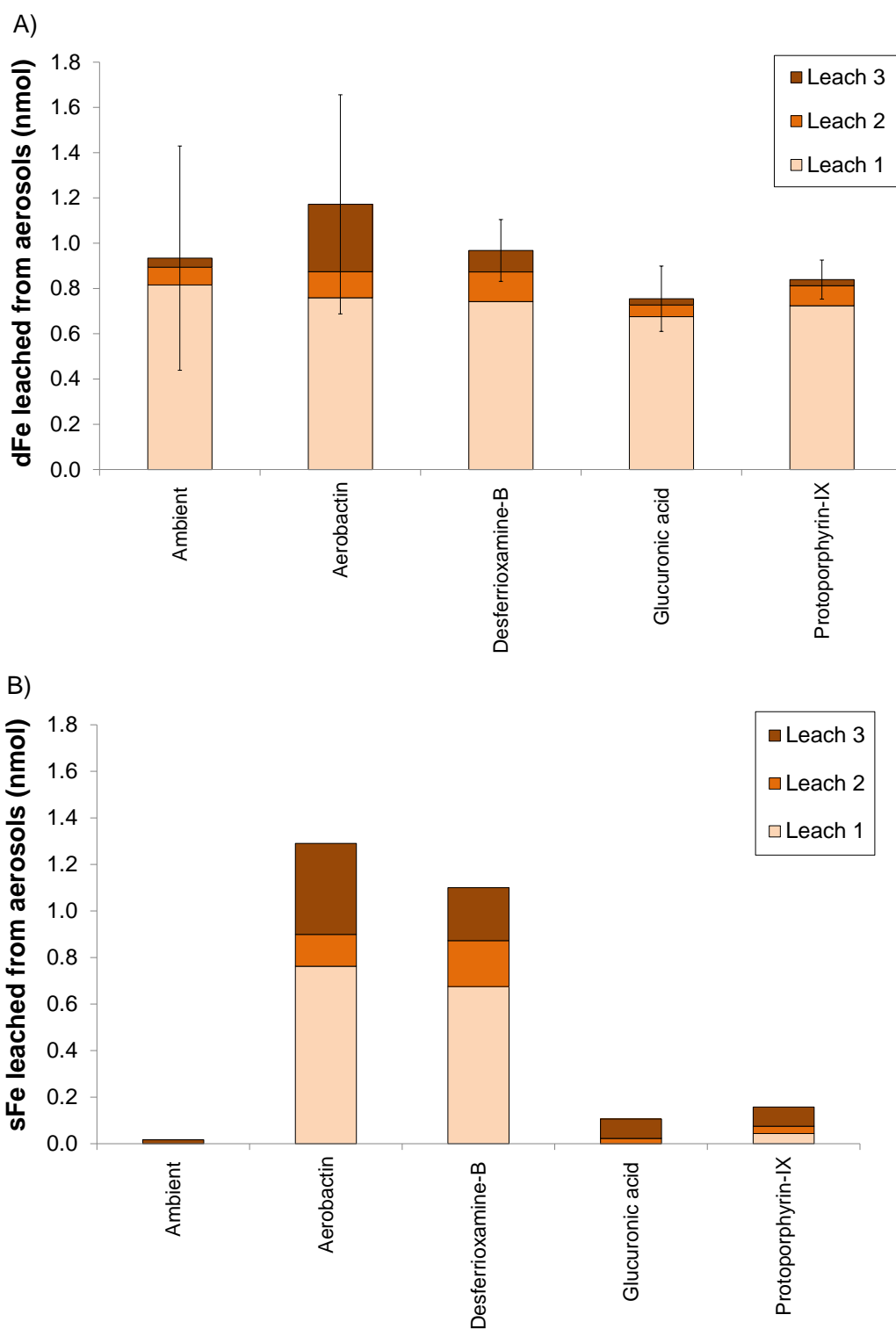


947 **Figure 3.** The mean total dissolved iron (dFe, nmol) leached from aerosol samples AER 1, AER 2, AER 3 and  
 948 AER 4 during three replicate leaches with A) 4 °C and 25 °C seawater and B) ambient seawater (25 °C, pH 8.0,  
 949 oxygenated), acidified seawater (pH 7.6, sparged with air enriched in carbon dioxide) and anoxic seawater  
 950 (sparged with nitrogen gas for leaches 3 and 4). Error bars represent the standard deviation ( $\pm 1 \sigma$ ) on the mean  
 951 total dFe leached from replicate subsamples of the same aerosol sample. Segments of each bar show the amount  
 952 of dFe leached during each sequential aerosol leach (i.e., leaches 1 – 4). Sequential leaches 1, 2, 3 and 4  
 953 represent the following time periods seawater was exposed to aerosols: 0 – 5 min, 5 – 10 min, 10 min – 48 h and  
 954 48 h – 30 days, respectively.



955

956 **Figure 4.** Fractional solubility (%) of iron (Fe) from aerosol samples AER 1, AER 2, AER 3 and AER4 leached  
 957 with ambient seawater (combined mean of the temperature experiment and pH and de-oxygenation experiment,  
 958 25 °C, pH 8.0, oxygenated), 4 °C seawater, acidified seawater (pH 7.6, sparged with air enriched in carbon  
 959 dioxide) and anoxic seawater (sparged with nitrogen gas for leaches 3 and 4). Error bars represent the standard  
 960 deviation ( $\pm 1 \sigma$ ) on the mean fractional solubility of Fe leached from replicate subsamples of the same aerosol  
 961 sample. Segments of each bar show the fractional solubility of each sequential aerosol leach (i.e., leaches 1 – 4).  
 962 Sequential leaches 1, 2, 3 and 4 represent the following time periods seawater was exposed to aerosols: 0 – 5  
 963 min, 5 – 10 min, 10 min – 48 h and 48 h – 30 days, respectively.

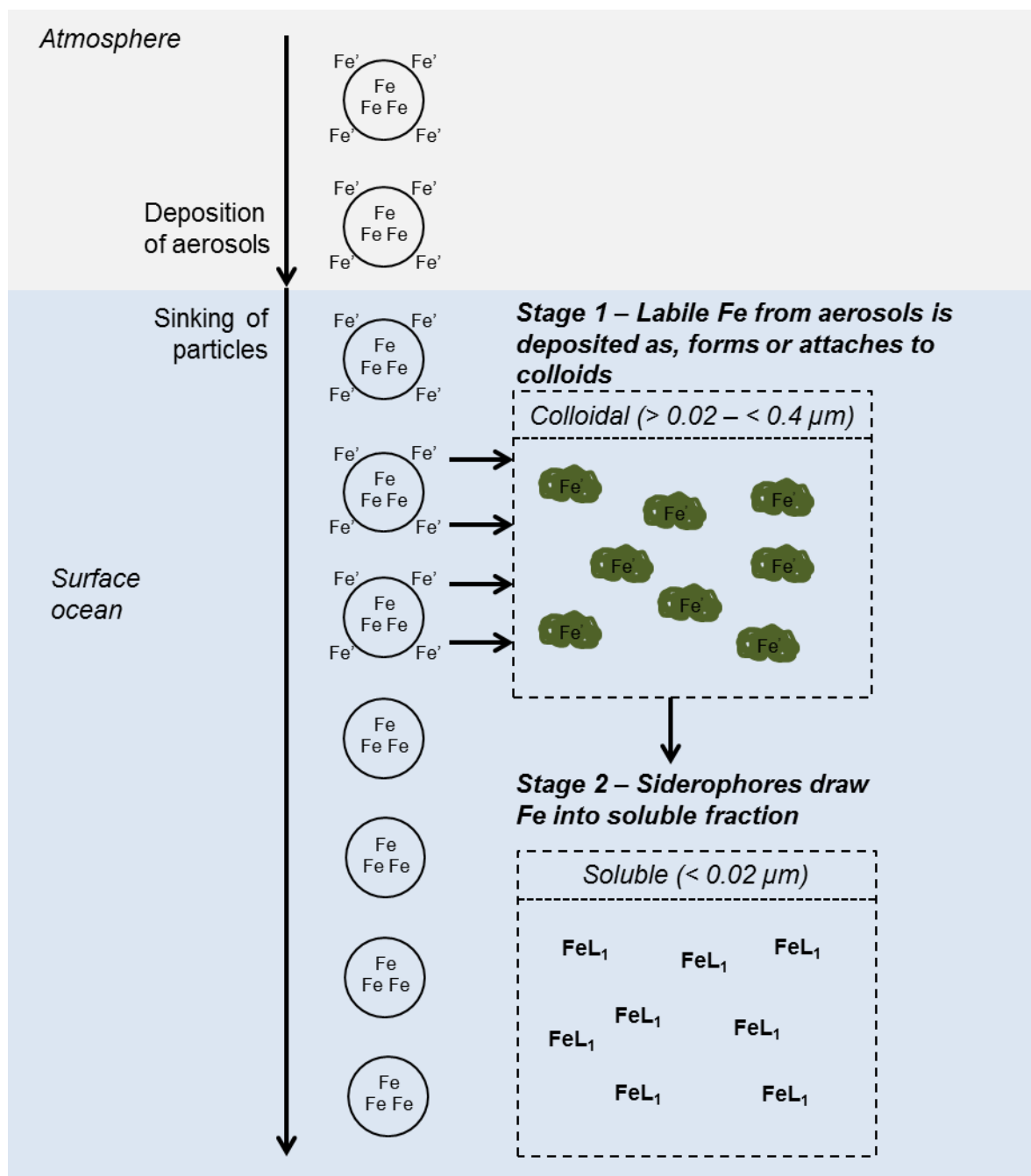


964

965 **Figure 5.** The mean total amount (nmol) of A) dissolved iron (dFe), and B) soluble iron (sFe) leached from  
 966 aerosol sample AER 1 into ambient seawater and seawater amended with various Fe-binding organic ligands  
 967 (aerobactin, desferrioxamine-B, glucuronic acid and protoporphyrin-IX). Error bars of A represent the standard  
 968 deviation ( $\pm 1 \sigma$ ) on the mean total dFe leached from replicate subsamples of the same aerosol sample. No error  
 969 bars are shown in B, as replicate leaches were not performed. In both A and B, segments of each bar show the  
 970 amount of dFe leached during each sequential aerosol leach (i.e., leaches 1 – 3). Sequential leaches 1, 2 and 3  
 971 represent the following time periods seawater was exposed to aerosols: 0 – 5 min, 5 – 10 min, and 10 min – 48  
 972 h, respectively. Leach 4 was not performed in this experiment.

973





974

975 **Figure 6.** A conceptual model for the dissolution of aerosol iron (Fe) in surface ocean waters, which proposes a  
 976 two-stage mechanism. Fe = refractory Fe species, Fe' = labile Fe species, FeL<sub>1</sub> = L<sub>1</sub> Fe-ligand complexes.  
 977

978 Dear Dr. Ussher:

979

980 Thank you for your manuscript submission entitled "The impact of changing surface ocean  
981 conditions on the dissolution of aerosol iron" [Paper #2014GB004921] to Global Biogeochemical  
982 Cycles. I have now received the Associate Editor's recommendation and 3 reviews of your  
983 manuscript.

984

985 All three reviewers find that this study is potentially an important contribution to understanding  
986 aerosol iron input to the ocean and is potentially publishable in GBC. All three provide detailed  
987 comments, though most require relatively minor changes/clarifications of the text. Please respond  
988 to all of the reviewer comments in your revision.

989

990 The feedback provided in the reviewer assessments of your manuscript is important and should be  
991 taken into account as you complete your revision. I encourage you to submit a suitably revised  
992 version of your manuscript within 30 days of receipt of this letter.

993

994 Upon submission, we will need to receive the following:

995

996 1. A response to reviewer file that lists each of the comments and describes how the manuscript  
997 has/has not been modified in response to those comments.

998

999 2. A copy of the manuscript with the changes noted (e.g., highlighted, "track changes," italics or bold  
1000 changes). Please upload the article with tracked/highlighted changes as a response to reviewer file.

1001

1002 3. A copy of the revised manuscript with the changes incorporated.

1003

1004 4. All files in publication-ready formats.

1005 \*\*\*Publication-ready formats for article files are limited to Word and LaTeX (Excel is also acceptable  
1006 for tables only). Figure files must be individually uploaded as .eps, .tif, .jpg, or .pdf files. A full list of  
1007 acceptable files for publication can be found at [http://publications.agu.org/author-resource-](http://publications.agu.org/author-resource-center/author-guide/acceptable-file-formats)  
1008 [center/author-guide/acceptable-file-formats](http://publications.agu.org/author-resource-center/author-guide/acceptable-file-formats); please refer to the columns labeled "Publication" in  
1009 the tables on this page.

1010

1011 \*\*\*Please ensure that the figures and text you send are final. After your final figure and text files  
1012 have been accepted by the editor, they will be forwarded to Wiley for production.

1013

1014 When you are ready to submit your revision, please login to your account ([http://gbc-](http://gbc-submit.agu.org/cgi-bin/main.plex)  
1015 [submit.agu.org/cgi-bin/main.plex](http://gbc-submit.agu.org/cgi-bin/main.plex)), and click "Revise 2014GB004921."

1016

1017 I look forward to receiving your revised manuscript. If you have any questions, please contact the  
1018 editor's assistant at [gbc@agu.org](mailto:gbc@agu.org).

1019

1020 Sincerely,

1021

1022 Susan Trumbore

1023 Editor

1024 Global Biogeochemical Cycles

1025

1026 -----IMPORTANT INFORMATION-----

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1028 1. Combine figure parts or provide separate captions

1029 2. Provide copyright permissions for reprinted figures and tables

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1035

1036 For any additional questions, see Author Resources at

1037 <http://publications.agu.org/author-resource-center> or reply with your question to this e-mail.

1038 -----

1039 Reviewer #1 (Comments to Author):

1040

1041 Title: Impact of changing ocean conditions on the dissolution of aerosol iron

1042 Authors: Mathew Fishwick, Peter Sedwick, Maeve Lohan, Paul Worsfold, Kristen Buck, Tom Church,  
1043 Simon Usher

1044

1045 The manuscript describes the influence of several seawater parameters (pH, temperature, dissolved  
1046 oxygen, and organic iron-binding ligands) on the dissolution of bulk aerosol iron as observed during a  
1047 series of aerosol leaching experiments conducted on samples collected in Bermuda, using seawater  
1048 (amended and un-amended) collected within the deep chlorophyll maximum near BATS. These  
1049 parameters were chosen and are appropriate for investigating effects of changes in ocean conditions  
1050 expected in the near-future, and which have the potential to alter the dissolution of aerosol iron  
1051 after deposition in surface waters. The authors' choice of experimental conditions provides insight  
1052 into the effect of single variables on dissolution and size partitioning of the solubilized aerosol Fe. A  
1053 conceptual model describing the dissolution of aerosol Fe in seawater is also presented.

1054 The manuscript is a well-organized and clearly written. The experimental design is logical, and  
1055 results provide additional data to support previous notions regarding aerosol Fe dissolution in  
1056 surface waters (e.g. aerosol type is the key aspect controlling the observed variability in the  
1057 fractional aerosol Fe solubility), as well as new insight into soluble aerosol Fe species (e.g. L1-type  
1058 ligands influence the size partitioning of Fe after dissolution). The authors have considerable  
1059 experience studying various aspects of Fe marine biogeochemistry, and these data contribute  
1060 towards understanding of atmospheric Fe input to the ocean and informs modelers of important  
1061 parameters to consider when modeling this input.

1062 I recommend the manuscript is accepted for publication at GBC. Below are suggested minor  
1063 revisions that should be addressed prior to publication. Hopefully these comments will be useful.

1064

1065 General Comments/Suggestion

1066 The title and abstract appropriately reflect the findings of the study.

1067 The introduction provides a good background on the subject and places aerosol Fe dissolution into a

1068 global context.

1069 The Methods section is easy to follow. A few areas could use clarification/additional information  
1070 (see Specific Suggestions).

1071 Results are clearly communicated, and their interpretation is reasonable. Some suggestions are  
1072 provided in the specific comments below.

1073 Given the team's expertise in Fe speciation, inclusion of redox speciation in the initial leachate would  
1074 have contributed towards the conceptual model presented. Its omission, however, does not lessen  
1075 the insights gained by the study.

1076

1077 Specific Suggestions

1078 Line 170. Provide length of time for seawater storage. **Seawater storage time (< 3 months) now  
1079 added to the manuscript.**

1080 Line 172. Were the ligand characteristics determined in the freshly collected, filtered seawater, or  
1081 after storage? Is the concentration of excess strong ligand in the seawater at the time of the  
1082 experiments known? **CSV-CLE was undertaken at the time of leaching experiments. This has been  
1083 added to the manuscript.**

1084 Line 176. AER 2 and AER 3 are numbered out of chronological sampling order, but I can't see a  
1085 reason for this. It might be easier for the reader if the sample collected during Feb/Aug 2010 were  
1086 labeled AER2, and the sample collected during Sept/Oct 2010 were labeled AER 3. **The order of  
1087 samples follows the order of anthropogenic influence and we believe by ordering it in this allows for  
1088 a clearer discussion of the influence of source on dissolution. The sample ordering has not been  
1089 changed in the manuscript.**

1090 Line 186. Aerosol storage time can affect dissolution. Like me, others might be curious about the  
1091 longest time aerosols were stored. **Storage time (6 – 24 months) added now added to the  
1092 manuscript.**

1093 Lines 207-209. Provide the reasoning behind the choice of excess ligand concentrations in the  
1094 amended seawater. **The choice of ligand concentrations by based on the concentration typically  
1095 observed in surface waters of the North Atlantic. We wanted to ensure a clear response in aerosol  
1096 Fe complexation and therefore amended seawater to unsure a great excess of ambient  
1097 concentrations. This justification has been added to the manuscript.**

1098 Lines 229 -233. State whether wall adsorption of Fe during leaches 3 and 4 was considered. If  
1099 considered, how was it determined? **Wall adsorption of Fe during batch leaches (leaches 3 and 4)  
1100 was considered during the experimental set up. Fischer *et al.* (2007) identify that Fe adsorption to  
1101 container material can be significant, depending on the container material. Therefore the choice of  
1102 bottle material is important. Séguret *et al.* (2011) found that when fluorinated polymer containers  
1103 were used, adsorption to the container walls was negligible. FPE is typically used for CSV-CLE analysis  
1104 specifically to avoid competition for Fe between wall surfaces and ligands. Therefore, it was decided  
1105 to use FPE bottles for batch leaches to minimise the effect of wall adsorption as much as possible. As  
1106 a further measure, FPE bottles were first preconditioned for 24-72 h with BATS seawater in order to  
1107 allow major cations to adsorb to any charged surfaces of the bottles before they were exposed to  
1108 leached Fe. Moreover, previous studies (e.g. Buck *et al.*, 2006 and Wu *et al.* 2007) have shown  
1109 leaching of Fe from aerosols occurs rapidly (i.e. < 5 mins) and therefore it is unlikely that, following  
1110 two continuous leaches, the aerosol filter was able to saturate 500 mL of seawater in the following  
1111 batch leaches. In these low iron conditions, the seawater leachate will be likely 'out compete'  
1112 container walls for iron.**

1113 Line 279. Provide FI-CL value for SAFe and GEOTRACES samples. FI-CL values for reference seawater  
1114 now added to manuscript.

1115 Lines 289-290. List relevant elements included in QC Standard 4. Elements have now been listed in  
1116 the manuscript.

1117 Lines 313-318. Move description of AER 4 back trajectories after description of AER 3. If AER 2 and  
1118 AER 3 labels are switch, switch description here accordingly. This has now been moved.

1119 Line 328. "Cu" is listed twice. This has now been amended in manuscript.

1120 Line 344. Replace "the four different aerosol samples" with "AER 1 - AER 4". This makes it clear that  
1121 the sentence is referring to the four samples and not to subsamples in the four leaches. This has now  
1122 been amended in manuscript and made clearer to understand.

1123 Line 345. To clarify, replace "four sequential leaches" with "four sets of sequential leaches". The four  
1124 sequential leaches refers to leach 1 (0-5 min), leach 2 (5-10 min), leach 3 (10 min to 48 hr) and leach  
1125 4 (48 hr to 30 day) rather than the four aerosols. We have clarified this in the text of the manuscript  
1126 now.

1127 Line 355. "Wu, 2007" could be added to reference. Reference added to manuscript.

1128 Lines 359-360: Replace "the four different aerosol samples" with "AER 1 - AER 4". This has now been  
1129 amended in manuscript and made clearer to understand.

1130 Lines 374-375: Replace "the four different aerosol samples" with "AER 1 - AER 4" This has now been  
1131 amended in manuscript and made clearer to understand.

1132 Line 406: "Aguilar-Islas et al., 2010" could be added to reference. Reference added to manuscript.

1133 Lines 476 - 480: The variability observed in the leaches can reflect the variability of the punched  
1134 subsamples. 3% variability in bulk aerosol Fe can sufficiently account for the observed variability in  
1135 the leaches, considering the fractional solubility for all samples was ~ 3% or less. Our statement on  
1136 the cause of the variability between leaches assumes the fractional solubility of Fe will not change  
1137 between subsamples of the same aerosol sample (only the total amount of Fe) and therefore a 3%  
1138 change in total Fe contained on a filter will only change the amount of Fe leached by 3%, whereas  
1139 the RSD observed between replicate leaches exceeded 50% in some cases. I think your point  
1140 highlights the possibility that Fe species may not be loaded onto the filter paper evenly and  
1141 therefore the fractional solubility of subsamples of the same sample may differ. This is a possibility  
1142 and has been included as an explanation for the observed variability in dFe in replicate leaches.

1143 A point that needs to be clarified in the methods is whether the leached aerosol subsamples were  
1144 digested, and fractional solubility calculated by matching specific punched subsample analyses, or if  
1145 separate replicate punches were used for bulk analysis. Good point. Both digestion and leaching  
1146 methods are destructive and therefore, unfortunately, the same aerosol filter cannot be used. We  
1147 have added this point in the methods to be clear.

1148 Lines 481-501. These 2 paragraphs might be better integrated. They seem a bit repetitive.  
1149 Paragraph starting on line 481 describes the total sFe concentrations of seawater amended with  
1150 ligands and leads quite nicely onto paragraph starting on 501 deals, which goes on to describe the  
1151 size partitioning of Fe in solution.

1152 Line 510: Specify "un-complexed" before "in sufficient" This has now been amended in manuscript.

1153 Lines 522-528: I would suggest that aerosol type (soil dust vs. combustion) would also play a role in  
1154 whether colloids form after dissolution or are deposited. Aerosols Fe in the colloidal size class is  
1155 likely being deposited on surface water from combustion sources, since this type of aerosols exists  
1156 mostly in the fine size fraction. Buck et al., 2010 showed considerable DI soluble Fe coming from the  
1157 smaller size fractions of aerosols collected with their impactor when anthropogenic aerosols were

1158 present in the sample. Although the impactor does not separate particles base on their geometric  
1159 diameter, the smaller aerodynamic diameter of fine aerosols they collected were 0.098 and 0.056  
1160 um, and could potentially contain Fe colloids. **A paragraph has been added to the manuscript to  
1161 consider aerosol composition and size as a factor in determining whether colloidal Fe is delivered by  
1162 aerosols or forms in seawater following deposition.**

1163

1164 Tables & Figures:

1165 Tables 1-3: Switch sample name for AER 2 and AER 3 if changed in the text. **Not amended in  
1166 manuscript. See above.**

1167 Table 3: For improved readability add lines between AER # sets of samples **Tables are formatted  
1168 according to the GBC guidelines, which does not have any horizontal lines between rows.**

1169 Figures 2-5: Switch AER 2 and AER 3 labels are switched in the text. **Not amended in manuscript. See  
1170 above.**

1171 Figure 6: Add to Stage 1 text "is deposited as," before "forms or attaches...". **Text added to figure.**

1172 Add to conceptual model information about source. In Atmosphere portion: "Soil Aerosol" could

1173 include more Fe inside circle and less Fe'outside. "Anthropogenic Aerosol" could include less Fe

1174 inside circle and more Fe' outside. In "Surface Ocean" top portion 2 of the circles could be "Soil

1175 Aerosol" and 1 "Anthropogenic Aerosol". **This is a very good suggestion to illustrate a greater**

1176 **proportion of labile Fe in combustion aerosols in comparison to mineral aerosols. However, we have  
1177 chosen to keep the figure as it is for simplicity.**

1178

1179

1180 Reviewer #2 (Comments to Author):

1181

1182 Excellent, yet brief review of aerosol inputs, solubility and iron binding ligands in seawater. The

1183 introduction does a very good job putting all the pieces of a complex interaction together in an

1184 appropriately referenced and clearly written section.

1185

1186

1187

1188 Line 198... dissolved (not dissolve). **This has now been amended in manuscript.**

1189

1190 Line 205, consider re-wording... These ligands were intended to simulate the range of iron-binding

1191 ligands that exist in open ocean waters. Omit the reference to use by phytoplankton, etc... **This has**

1192 **now been amended in manuscript.**

1193

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1196 The manuscript is satisfyingly replete with analytical methods... I appreciate this, yet it could be

1197 shortened somewhat in this section if necessary.

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1200 The discussion and conclusion sections are well anchored in the results of this experiment and the

1201 conceptual model is believable, yet, as the authors point out, there are alternatives that seem

1202 plausible as well.

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One potential weakness of the manuscript is the assignment of anthropogenic influence over the elemental composition of the aerosols. I understand the argument of enrichment of anthropogenic elements as being an indicator, but there are also strong variations in elemental composition from one weathering basin to another. A simple crustal abundance approach is appealing but simplistic. **The paragraph on enrichment factors (line 340) has been re-worded slightly to stress that enrichment factors only an indicator of anthropogenic influence.**

In brief, I believe this paper will make an important contribution and point the way towards some interesting studies that will help modelers to forecast a more accurate assessment of changing land/ocean conditions as influenced by anthropogenic forcing.

Reviewer #3 (Comments to Author):

This is a very nice paper that describes some very thorough and illuminating studies of the controls on iron solubility at Bermuda. The analytical work reported appears to be of a very high standard, from an excellent research group. I have no doubt the paper should be published and I have only some minor suggestions.

The Bermuda site is particularly useful because it is subject to quite a significant change in aerosol type between anthropogenic and crustal sources, allowing the effect of this difference to be evaluated. However, as the authors do note on line 548, the importance of anthropogenic iron as a global source of iron to the ocean is probably dwarfed by dust sources, although this does require further study. Thus while the statement on line 103 is probably correct, the environmental significance of such an increase is unclear. **Text added to the manuscript to stress that any increase in combustion sources is not likely to be significant in the global context, considering the likely continued dominance of mineral aerosols.**

The issue of the controls on solubility of iron has been reviewed rather well by Baker and Croot 2010 and the authors here might use this as a source to help rationalise their experiments which elegantly test some of the mechanisms Baker and Croot consider. **This importance reference has now been added to the manuscript.**

In the abstract (line 59) and later in the text the authors use the phrase "size distribution of soluble aerosol iron" and I was tripped up by this each time I read it because of the large amount of work done on aerosol size distribution, whereas the authors mean the colloidal/dissolved split of aerosol iron after it has dissolved in seawater. They might want to rephrase this to avoid confusing others. **This phrase has been re-worded to include mention of size distribution in seawater or solution.**

P7 It is not clear how long aerosol samples were collected for. I think based on what is written later

1248 there are actually only 4 samples collected each over a period of a week to 10 days, but when I first  
1249 read the paragraph line 174-186 I assumed they had daily samples. Assuming that there are only 4  
1250 samples used for the experiments, then some caution about the representativeness of the results  
1251 might be appropriate. **The filters were left on the sampler for the entire periods of sampling (ranging**  
1252 **from 14 to 63 days). The number of days has now been added to the manuscript, along with volume**  
1253 **of air sampled.**

1254 Line 223-226. I would suggest that the authors might justify their choice of leaching times in terms of  
1255 the lifetime of particles in the surface ocean and other biogeochemical processes. I don't disagree at  
1256 all with the timescales they have used, but they can indicate that the longest time is about how long  
1257 an aerosol particle spends in the surface ocean. **Justification for these leach times has now been**  
1258 **added to the manuscript.**

1259 Line 248-253. Whenever I have contemplated experiments such as these I have worried that the  
1260 surface area of the filter may produce adsorption effects. The way blanks have been conducted here  
1261 I think does allow the authors to confirm that there appears to be no blank effect revealed either as  
1262 an increase or decrease in iron concentration.

1263 Line 325-329. Conventionally small enrichment factors have often been considered uncertain given  
1264 the variability of crustal concentration, so perhaps the authors should be cautious about EF values  
1265 less than 10. **Sentence stating the all samples were enriched in Fe, V, Ni, Cu, Pb and Sb removed**  
1266 **from the manuscript.**

1267 P14 There seems to be some repetition lines 355- 358 and 370-373. **The first discusses dFe and the**  
1268 **second leads on to discuss sFe and size distribution. There is some repetition in the wording but we**  
1269 **feel it is important to be clear in the description what mean total Fe is and therefore have kept the**  
1270 **working similar to avoid confusion.**

1271 A second point on this page and later (e.g. line 387-390) the authors several times comment on  
1272 differences (here between 4 and 25oC) and then say the differences are not significant. If the  
1273 differences are not significant I don't think you can usefully really note the differences at all. **The**  
1274 **commentary on differences has now been removed from the manuscript.**

1275 Line 378-380 The anoxic experiment is useful but I suspect on this time scale this is effectively an  
1276 inorganic experiment and describes the lack of impact of lower oxygen on the inorganic conversion  
1277 of FeIII to FeII. Probably more relevant to the global iron cycle is the bacterial reduction of iron  
1278 which is probably precluded here. At a more general level too, while the experiments described here  
1279 are very impressive and useful, they do not consider the role of the bacterial and planktonic  
1280 community in solubilising iron from aerosol particles. I think this latter point needs to be  
1281 acknowledged in the discussion of the mechanism of aerosol iron solubility on p20. **It has been**  
1282 **acknowledged in the manuscript that the mechanism is missing biological interactions.** I think the  
1283 proposed mechanism is OK as a hypothesis but it needs to be clear that it is that. **It had been made**  
1284 **clear in the manuscript that it is a hypothesis.** Aggregation and disaggregation of colloidal ligands  
1285 may play a role (line 500). More generally it seems to me that as iron dissolves from aerosol there is  
1286 a complex (and time varying) competition between different sinks for that  
1287 iron including complexation by ligands, inorganic precipitation and biological uptake. Clearly the  
1288 authors demonstrate that ligands play a key role, but we do know that from the higher solubility of  
1289 iron in the real ocean compared to its inorganic solubility. The value of the work reported here is to  
1290 emphasise again that this interaction is key and that the role of temperature, pH and oxygen is  
1291 minor.

1292