

1 Measurement of the Isotopic Composition of dissolved Iron in the Open Ocean

2
3 Lacan¹ F., Radic¹ A., Jeandel¹ C., Poitrasson² F., Sarthou³ G., Pradoux¹ C., Freydier² R.

4
5 ¹: CNRS, LEGOS, UMR5566, CNRS-CNES-IRD-UPS, Observatoire Midi-Pyrénées, 18, Av.
6 E. Belin, 31400 Toulouse, France.

7 ²: LMTG, CNRS-UPS-IRD, 14-16, avenue Edouard Belin, 31400 Toulouse, France.

8 ³: LEMAR, UMR CNRS 6539, IUEM, Technopole Brest Iroise, Place Nicolas Copernic,
9 29280 Plouzané, France.

10
11 *Paper published in Geophysical Research Letters (2008) L24610.*

12 *We acknowledge Geophysical Research Letters and the American Geophysical Union copyright*

13
14 This work demonstrates for the first time the feasibility of the measurement of the isotopic
15 composition of dissolved iron in seawater for a typical open ocean Fe concentration range
16 (0.1-1nM). It also presents the first data of this kind. Iron is preconcentrated using a
17 Nitrioloacetic Acid Superflow resin and purified using an AG1x4 anion exchange resin. The
18 isotopic ratios are measured with a MC-ICPMS Neptune, coupled with a desolvator
19 (Aridus II), using a ⁵⁷Fe-⁵⁸Fe double spike mass bias correction. Measurement precision
20 (0.13‰, 2SD) allow resolving small iron isotopic composition variations within the water
21 column, in the Atlantic sector of the Southern Ocean (from $\delta^{57}\text{Fe}=-0.19$ to $+0.32\text{‰}$).
22 Isotopically light iron found in the Upper Circumpolar Deep Water is hypothesized to result
23 from organic matter remineralization. Shallow samples suggest that, if occurring, an iron
24 isotopic fractionation during iron uptake by phytoplankton is characterized by a fractionation
25 factor, such as: $|\Delta^{57}\text{Fe}_{(\text{plankton-seawater})}| < 0.48\text{‰}$.

26

27 1- Introduction

28 Iron availability has been shown to be the main limitation factor for phytoplankton growth
29 in wide areas of the world ocean, such as in the so-called High Nutrient Low Chlorophyll
30 (HNLC) areas (Southern Ocean, Subarctic and Equatorial Pacific Ocean; see *Boyd* [2007] for
31 a review). In that respect, the iron oceanic cycle is a component of the global carbon cycle and
32 thus of the climate [*Martin and Fitzwater*, 1988]. Despite this importance, our knowledge of
33 the iron (Fe) oceanic cycle remains partial. In particular, significant uncertainties remain
34 about the iron sources to the open ocean. Whereas dust dissolution is traditionally considered
35 as the dominant source [e.g. *Jickells, et al.*, 2005], diagenetic dissolution at the continental
36 margins is proposed to significantly contribute to the Fe content of the open ocean surface
37 waters [*Elrod, et al.*, 2004]. Hydrothermal inputs have also been recently hypothesized as
38 significant contributors for the Fe content of the open ocean surface waters [*Boyle and*
39 *Jenkins*, 2008].

40 The iron isotopic composition (Fe IC) of these sources are different [*Beard and Johnson*,
41 2004; *Severmann, et al.*, 2006]. Iron isotopes are therefore a very promising tool for the study
42 of the iron sources to the ocean [*Zhu, et al.*, 2000; *Beard, et al.*, 2003]. Internal oceanic
43 processes, in particular oxydo-reduction and organic complexation processes, have been
44 shown to fractionate iron isotopes [*Bullen, et al.*, 2001; *Johnson, et al.*, 2002; *Dideriksen, et*
45 *al.*, 2008]. Iron isotopes could therefore also bring new insights into the internal oceanic Fe
46 cycle, such as iron speciation, dissolved/particulate fluxes or biological processes.

47 This great potential motivated very numerous Fe isotope studies during the last decade in
48 the marine environment and at the ocean boundaries (ferromanganese crusts, plankton tows,
49 aerosols, sediments, pore waters, suspended particles, rivers, estuaries, hydrothermal vents...
50 [*Zhu, et al.*, 2000; *Rouxel, et al.*, 2003; *Levasseur, et al.*, 2004; *Bergquist and Boyle*, 2006; *de*

51 *Jong, et al., 2007*]). However, the isotopic composition of the iron dissolved in seawater in
52 the open ocean has never been reported so far, because of the analytical difficulty of such
53 measurement, due to the very low seawater Fe content (typically 1 to 0.1nM) combined to a
54 concentrated salt matrix. Such a measurement is however of the highest importance, because
55 dissolved iron in seawater is the phase which links all the above listed marine phases. It is, for
56 instance, absolutely necessary to fully exploit phytoplankton or ferromanganese Fe IC.

57 In this paper, we briefly present, for the first time, a protocol allowing the measurement of
58 the isotopic composition of dissolved iron in seawater, for Fe concentrations down to 0.1nM.
59 We also present the first data of the Fe IC of dissolved iron in the open ocean.

60

61 2- Sampling

62 Four 10L seawater samples taken during the BONUS/GOODHOPE cruise (Feb-March
63 2008, RV Marion Dufresne) have been analyzed following the protocol described below.
64 These samples have been taken at station 18 (13°07'E-36°30'S), in the Atlantic sector of the
65 Southern Ocean, north of the subtropical front, from 30 to 4000m depth. They were collected
66 with acid-cleaned 12-L Go-Flo bottles mounted on a Kevlar wire and tripped by Teflon
67 messengers. The bottles were brought into a trace metal clean container for filtration through
68 0.4µm Nuclepore[®] membranes (90mm), within a few hours of collection. The filtration units
69 were entirely made of PTFE. Samples were then acidified onboard to pH≈1.8 (bi-distilled
70 HCl).

71

72 3- Chemical Separation

73 All of the chemical separation procedure is conducted in a trace metal clean lab, equipped
74 with an ISO 4 (class 10) laminar flow hood. Reagents are bi-distilled. All labware is acid
75 cleaned. Blanks of reagents, labware and atmosphere are monitored

76 Fe IC measurement in seawater requires its extraction from the sample matrix, with (i) a
77 high yield (because of its low abundance), (ii) low contamination levels, (iii) no isotopic
78 fractionation or a method for correcting for it, and (iv) a sufficient separation of the elements
79 interfering with Fe isotopes during the spectrometric analysis.

80 Dissolved Fe concentration in open ocean depleted surface waters can be as low as
81 $\sim 0.05\text{nM}$ [Croot, *et al.*, 2004; Blain, *et al.*, 2008]. The minimum amount of iron required to
82 perform a precise isotopic analysis is around 20 to 50 ng [Weyer and Schwieters, 2003, this
83 work; Schoenberg and von Blanckenburg, 2005]. Therefore, analyzing the IC of dissolved Fe
84 in Fe depleted seawater requires the preconcentration of $\sim 10\text{L}$ samples (10L of seawater with
85 $[\text{Fe}] = 0.05\text{nM}$ contain 28ng of Fe).

86 The protocol described here is adapted from Lohan *et al.* [2005], using a commercially
87 available Nitriloacetic Acid (NTA) Superflow resin (Qiagen[®]). The NTA resin is packed in a
88 PTFE column. The 10L sample, filtered and acidified to $\text{pH} = 1.75$, is stored in a LDPE
89 cubitainer. Such pH quantitatively dissociates the iron complexed to the organic ligands
90 [Lohan, *et al.*, 2005]. Hydrogen peroxide is added to the sample before the preconcentration
91 to oxidize Fe^{II} to Fe^{III} ($[\text{H}_2\text{O}_2] = 10\mu\text{M}$). The sample is passed through the resin at about
92 $10\text{ml}\cdot\text{min}^{-1}$. The resin is then rinsed with deionized water. Iron is eluted with 10ml 1.5M
93 HNO_3 . The column is then washed with 20 ml 1.5M HNO_3 and stored at $\text{pH} = 7$. The sample is
94 evaporated and re-dissolved in 6M HCl for the purification step.

95 Fe is then purified from the remaining salts using an AG1x4 anionic resin, using a
96 protocol adapted from Strelow [1980]. Half a ml of resin is packed in a PTFE column. The
97 sample is loaded onto the resin in 0.5ml 6M HCl mixed with 0.001% H_2O_2 . Most of the
98 elements are first eluted with 3.5ml 6M HCl mixed with 0.001% H_2O_2 . Iron is then eluted
99 with 3ml 1M HCl mixed with 0.001% H_2O_2 . The elements remaining in the resin are washed
100 with HF 0.1M, then 6M HCl mixed with 0.001% H_2O_2 and 7M HNO_3 .

101 Briefly, for the whole chemical procedure (preconcentration and purification), the yield
102 for iron is $92\pm 10\%$, the Fe blank is $8.0\pm 2.5\text{ng}$ and all interfering elements are quantitatively
103 removed. This protocol is simple, since it is composed of a single preconcentration column
104 (that could be carried out on board) and a single purification column.

105

106 4- Mass spectrometric analysis

107 A Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) Neptune
108 (Thermo Scientific[®]), coupled with a desolvating nebulizer system (CETAC Aridus II[®]) is
109 used. The medium mass resolution allows resolving the polyatomic interferences on masses
110 54 and 56 (e.g. ArN, ArO, ArOH, CaO, [Weyer and Schwieters, 2003]). The desolvator
111 provides a sensitivity ~ 3 times higher than the Stable Introduction System (SIS, Elemental
112 Scientific Inc). "X" skimmer cones were also employed to enhance the sensitivity. The very
113 low Fe content of the samples requires the use of such devices. The Collector configuration is
114 indicated in Table 1. This setting allows measuring all stable Fe isotopes as well as
115 monitoring Cr and Ni, which can produce isobaric interferences with Fe.

116 The mass fractionation occurring within the spectrometer and potentially during the
117 chemical separation are corrected for with a ^{57}Fe - ^{58}Fe double spike, assuming that both
118 fractionations are mass dependent and are described by the same fractionation law [Russel, *et*
119 *al.*, 1978; Siebert, *et al.*, 2001; Dideriksen, *et al.*, 2003]. Data reduction is performed using the
120 iterative approach of Siebert *et al.* [2001] from a single analysis of the sample-spike mixture.

121 The double spike is added to the acidified sample at least 12h before the preconcentration
122 to allow the homogenization of the double spike with the sample. After preconcentration and
123 purification, the sample is dissolved in ~ 0.7 ml 0.3M HNO_3 , for the spectrometric analysis.

124 Each sample is bracketed with an IRMM-14 certified reference material (mixed with the
125 double spike), relative to which the sample IC is calculated. Each measurement session

126 includes measurements of the ETH (Eidgenössische Technische Hochschule Zürich) in-house
127 hematite standard (named HemSTD hereafter, [Poitrasson and Freydier, 2005], mixed with
128 the double spike), every 1.5 hour in order to monitor accuracy and precision of the instrument.
129 Instrumental blanks (0.3M HNO₃), and Cr and Ni interferences are monitored and corrected
130 for. They are most of the time lower than 0.1% (with maximum values reaching 0.5%). The
131 Fe IC is finally corrected for the blank of the overall procedure, which Fe IC is taken to be
132 that of the igneous rocks.

133

134 5- Validation

135 The blank of the whole procedure was determined by applying the above described
136 protocol to 100ml deionized water in place of a sample. This blank was measured repeatedly
137 at each chemistry session (by isotopic dilution, either on a quadrupole ICPMS, Agilent 7500,
138 with a collision cell in He mode, or on the MC-ICPMS; mass fractionation corrected for by
139 standard bracketing). Its value is 8.0 ± 2.5 ng (1SD, n=5).

140 The total yield of the chemical Fe preconcentration and purification is determined as
141 follows. A 10L seawater sample, taken at ~40m depth at the Dyfamed site (Northwest
142 Mediterranean), is filtered (SUPOR[®] 47mm, 0.8 μ m), then acidified and spiked with a solution
143 of ⁵⁷Fe (for the determination of its Fe concentration by isotopic dilution). The sample is then
144 taken through the entire procedure. The resulting Fe is measured on the quadrupole ICPMS,
145 both by the isotopic dilution method and the external calibration method (combined with a
146 sensitivity correction with indium as an internal standard). The former allows determining the
147 initial sample concentration, whereas the latter allows determining the Fe quantity recovered
148 after the purification. Comparison of both quantities allows calculating the total yield of the
149 procedure. This has been measured repeatedly, at each chemistry session. Total Fe yield is

150 92±10% (1SD, n=5). Achieving a 100% yield is not critical, however, since we add a double
151 spike before the chemical procedure.

152 The performance of the chemical separation was also assessed by the measurement of the
153 matrix in which the Fe is eluted (after processing of a 10L seawater sample). Most of the
154 elements (those measurable with the ICPMS technique) were measured on the quadrupole
155 ICPMS. The elements eluted together with Fe, are mostly Ca, Ga and Sb (~ 90, 30 and 20 ng,
156 respectively). In total, the matrix solid residue weights ~150ng and no traces of Cr, Ni or Zn
157 could be detected.

158

159 The three ratios $\delta^{56}\text{Fe}$, $\delta^{57}\text{Fe}$ and $\delta^{58}\text{Fe}$ (usual δ notation, relative to ^{54}Fe) are measured
160 with the same accuracy and the same internal and external precisions per atomic mass unit
161 (see below and Tab. 2). In the following the Fe IC are reported as $\delta^{57}\text{Fe}$, relative to IRMM-14.

162 Internal precision of the measurements is typically lower than 0.1‰ ($\delta^{57}\text{Fe}$; $2\text{SE}=2\text{SD}/\sqrt{n}$,
163 where SE and SD stand for standard error and standard deviation, respectively). This is lower
164 than the external precisions reported below.

165 External precision and accuracy of the Fe IC measurement were tested in different ways.
166 First, the measurement of variable amounts of the HemSTD (relative to IRMM-14) allowed
167 estimating the capabilities of our instrument, configuration and data reduction, for variable Fe
168 consumption. These results are reported in Figure 1. The known Fe IC of HemSTD is
169 $\delta^{57}\text{Fe}(\text{HemSTD})= 0.75\pm 0.14\text{‰}$ (2SD, n=55 unpooled analyses, [Poitrasson and Freydier,
170 2005]). Taking into account all of our measurements, which correspond to Fe consumptions
171 ranging from 200 to 25ng per analysis, we find: $\delta^{57}\text{Fe}(\text{HemSTD})=0.79\pm 0.13\text{‰}$ (2SD, n=40,
172 over a period of 4 months). For the measurements with very low Fe contents, with Fe
173 consumption of 25ng, we find $\delta^{57}\text{Fe}(\text{HemSTD})=0.81\pm 0.16\text{‰}$ (2SD, n=7). The accuracy is
174 estimated from the deviation (absolute value of the difference) of the measurements from the

175 known value. That deviation is on average $\delta^{57}\text{Fe}=0.06\pm 0.08\%$ (2SD, n=40), with a maximum
176 value of 0.14%.

177 Accuracy and precision were then estimated using natural seawater. Ten liter filtered
178 seawater samples (Dyfamed site, 40m depth, $[\text{Fe}]=5\text{nM}$), were processed 3 to 4 times through
179 the NTA column, in order to remove most of their Fe content. The samples were then doped
180 with variable amounts of HemSTD: 550ng, 165ng and 55ng, which corresponds to Fe
181 concentrations of 1, 0.3 and 0.1nM. The samples were allowed to homogenize for 12 hours.
182 Their Fe IC are then measured following the above described protocol. The Fe IC measured is
183 corrected for the contributions of i) the chemistry blank and ii) the Fe remaining in the
184 samples before doping (both are considered having the Fe IC of the igneous rocks). The
185 results are reported in Figure 1. They show that the measurements of the Fe IC of the doped
186 seawater samples are as precise and accurate as those performed directly on the standard
187 solutions. This validates the overall procedure for seawater samples with Fe concentrations
188 ranging from 1 to 0.1nM, which represent a typical range found in the open ocean.

189 Finally, replicate analyses of real seawater samples provide an integrated estimate of the
190 measurement precision. From 3 duplicate analyses, the mean discrepancy between duplicates
191 is found to be 0.04‰ ($\delta^{57}\text{Fe}$), with a maximum discrepancy of 0.06‰ (cf. gray symbols in
192 Fig. 2). These values are lower than the external precision reported above for HemSTD.
193 Therefore, in the following, the external precision reported above for HemSTD (0.13‰ 2SD,
194 n=40) will be considered to best characterize the measurement uncertainty.

195

196 6- Fe concentration

197 Together with the measurement of the Fe isotopic composition, the double spike method
198 provides precise and accurate determination of the Fe concentration (as shown with a simple
199 spike in [De Jong, et al., 2008]). The detection limit, defined as three times the standard

200 deviation of the blank (7.5ng, 3SD, n=5, cf section 4), is 13 pM when preconcentrating 10 L
201 of sample. The precision, mostly limited by the blank variability (5ng 2SD, n=5), is 9% for
202 seawater samples with [Fe]=0.1nM, 2% for [Fe]=0.5nM, and lower than 1% for [Fe]>1nM.

203

204 7- Results and discussion

205 Four BONUS/GOODHOPE samples were analyzed following the above described
206 protocol. Once back in the home laboratory, the double spike was added to the samples. Then,
207 3 of them were split into two duplicates, and analyzed. The results are reported in Table 2 and
208 displayed in Figure 2.

209 The range of variation is 0.51 ‰, with values ranging from $\delta^{57}\text{Fe}=-0.19$ to $+0.32\text{‰}$. This
210 range is small compared to that found in the environment, of the order of 5‰ [*Beard and*
211 *Johnson, 2004*]. However, the variations are significant, considering the measurement
212 precision (0.13‰, 2SD external precision).

213 The two shallower samples are located at 30 and 200 m depth, in the chlorophyll
214 maximum and just below the euphotic zone, respectively. Their Fe IC ($\delta^{57}\text{Fe}=0.06$ and
215 0.14‰ , respectively) are undistinguishable from the crustal value ($\delta^{57}\text{Fe}=0.10\pm 0.03\text{‰}$ 2SD
216 [*Poitrasson, 2006*]). At 1250m depth, the sample is located in the core of the Upper
217 Circumpolar Deep Water (UCDW), characterized by an oxygen minimum resulting from
218 organic matter remineralization (see Fig. 2). The UCDW Fe IC is $\delta^{57}\text{Fe}=-0.19\text{‰}$. At 4000m
219 depth, the sample is located between the cores of the North Atlantic Deep Water (NADW)
220 and of the Antarctic Bottom Water (AABW). Its hydrographic and nutrient properties (in
221 particular its silicate content, not shown here), compared to that of the NADW and AABW
222 allow estimating that it is composed of roughly 80% AABW and 20% NADW (it is identified
223 as mAABW, for modified AABW, in Fig. 2). Its Fe IC is $\delta^{57}\text{Fe}=+0.32\text{‰}$.

224 Detailed interpretation of these few data, at a single station, would be premature and
225 speculative. We can however propose hypotheses, which will require to be tested with more
226 data in future works. Plankton tows have been measured at one site in the Equatorial Atlantic
227 (Amazon plume). They are characterized by $\delta^{57}\text{Fe}=-0.36\text{‰}$ [Bergquist and Boyle, 2006]. The
228 isotopically light dissolved Fe found in the UCDW could therefore reflect the
229 remineralization of organic matter (resulting from the degradation of such plankton cells) in
230 this water mass.

231 Surface (30m depth) iron depletion relative to subsurface concentrations (200m depth) is
232 42%. In the hypothesis of the occurrence of Fe fractionation during Fe uptake by
233 phytoplankton, the present data allow estimating an upper limit for the fractionation factor
234 (according to Rayleigh distillation), above which a Fe IC variation would have been
235 measurable (larger than twice the present data precision, i.e.: 0.26‰). If the difference
236 between the Fe IC of phytoplankton and that of seawater in which it grows is equal to
237 $\pm 0.48\text{‰}$, then a 42% depletion should generate a difference of $\pm 0.26\text{‰}$ in the seawater
238 relative to the initial value. Since no difference is observed between the 30 and 200 m depth
239 samples, these data could suggest that, if occurring, a potential Fe isotopic fractionation
240 during Fe uptake by phytoplankton could be characterized by a fractionation factor, such as:

$$241 \quad |\Delta^{57}\text{Fe}_{(\text{plankton-seawater})}| < 0.48\text{‰}.$$

242 Much more data are needed to propose more reliable interpretations of these results. They
243 will be acquired in the framework of GEOTRACES.

244

245 Acknowledgements: The CNRS (French National Center for Scientific Research) is thanked for
246 its investment in this project. We thank two anonymous reviewers. M. Boye and S. Speich are
247 thanked for having organized the Bonus/GoodHope Project and cruise. We thank the Crew
248 and Captain of R/V Marion Dufresne. We thank the Go-Flo sampling team: J. Bown, M.

249 Boye, E. Bucciarelli, F. Chever and B. Wake. F. Candaudap and J. Chmeleff are thanked for
250 their help with the ICPMS.

251

252 References

253

254 Beard, B. L., and C. M. Johnson (2004), Fe isotope variations in the modern and ancient earth
255 and other planetary bodies, in *Geochemistry of Non-Traditional Stable Isotopes*, edited, pp.
256 319-357.

257 Beard, B. L., C. M. Johnson, K. L. Von Damm, and R. L. Poulson (2003), Iron isotope
258 constraints on Fe cycling and mass balance in oxygenated Earth oceans, *Geology*, *31*, 629–
259 632.

260 Bergquist, B. A., and E. A. Boyle (2006), Iron isotopes in the Amazon River system:
261 Weathering and transport signatures, *Earth Planet. Sci. Lett.*, *248*, 54-68.

262 Blain, S., G. Sarthou, and P. Laan (2008), Distribution of dissolved iron during the natural
263 iron-fertilization experiment KEOPS (Kerguelen Plateau, Southern Ocean), *Deep Sea*
264 *Research Part II: Topical Studies in Oceanography*, *55*, 594-605.

265 Boyd, P. W., et al. (2007), Mesoscale iron enrichment experiments 1993-2005: Synthesis and
266 future directions, *Science*, *315*, 612-617.

267 Boyle, E., and W. J. Jenkins (2008), Hydrothermal Iron in the Deep Western South Pacific,
268 *Geochim. Cosmochim. Acta*, A107.

269 Bullen, T. D., A. F. White, C. W. Childs, D. V. Vivit, and M. S. Schulz (2001),
270 Demonstration of significant abiotic iron isotope fractionation in nature, *Geology*, *29*, 699–
271 702.

272 Croot, P. L., K. Andersson, M. Ozturk, and D. R. Turner (2004), The distribution and
273 specification of iron along 6 degrees E in the Southern Ocean, *Deep-Sea Research Part II-*
274 *Topical Studies in Oceanography*, 51, 2857-2879.

275 De Jong, J., V. Schoemann, D. Lannuzel, J. L. Tison, and N. Mattielli (2008), High-accuracy
276 determination of iron in seawater by isotopoe dilution multiple collector inductively coupled
277 plasma mass spectrometry (ID-MC-ICP-MS) using nitrilotriacetic acid chelating resin for pre-
278 concentration and matrix separation, *Analytica Chimica Acta*, 623, 126-139.

279 de Jong, J., et al. (2007), Precise measurement of Fe isotopes in marine samples by multi-
280 collector inductively coupled plasma mass spectrometry (MC-ICP-MS), *Analytica Chimica*
281 *Acta*, 589, 105-119.

282 Dideriksen, K., J. Baker, S. L. S. Stipp, and H. M. Williams (2003), Fe Isotope analysis by
283 multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) using ^{58}Fe -
284 ^{54}Fe double spike, *Geophysical Research Abstracts*, 5, 06718.

285 Dideriksen, K., J. A. Baker, and S. L. S. Stipp (2008), Equilibrium Fe isotope fractionation
286 between inorganic aqueous Fe(III) and the siderophore complex, Fe(III)-desferrioxamine B,
287 *Earth Planet. Sci. Lett.*, 269, 280-290.

288 Elrod, V. A., W. M. Berelson, K. H. Coale, and K. S. Johnson (2004), The flux of iron from
289 continental shelf sediments: A missing source for global budgets, *Geophys. Res. Lett.*, 31,
290 doi:10.1029/2004GL020216.

291 Jickells, T. D., et al. (2005), Global iron connections between desert dust, ocean
292 biogeochemistry, and climate, *Science*, 308, 67-71.

293 Johnson, C. M., J. L. Skulan, B. L. Beard, H. Sun, K. H. Nealson, and P. S. Braterman (2002),
294 Isotopic fractionation between Fe(III) and Fe(II) in aqueous solutions, *Earth Planet. Sci. Lett.*,
295 195, 141-153.

296 Levasseur, S., M. Frank, J. R. Hein, and A. Halliday (2004), The global variation in the iron
297 isotope composition of marine hydrogenetic ferromanganese deposits: implications for
298 seawater chemistry?, *Earth Planet. Sci. Lett.*, *224*, 91-105.

299 Lohan, M. C., A. M. Aguilar-Islas, R. P. Franks, and K. W. Bruland (2005), Determination of
300 iron and copper in seawater at pH 1.7 with a new commercially available chelating resin,
301 NTA Superflow, *Analytica Chimica Acta*, *530*, 121-129.

302 Martin, J. H., and S. E. Fitzwater (1988), Iron deficiency limits phytoplankton growth in the
303 north-east Pacific subarctic., *Nature*, *331*, 341-343.

304 Poitrasson, F. (2006), On the iron isotope homogeneity level of the continental crust, *Chem.*
305 *Geol.*, *235*, 195-200.

306 Poitrasson, F., and R. Freydier (2005), Heavy iron isotope composition of granites determined
307 by high resolution MC-ICP-MS, *Chem. Geol.*, *222*, 132-147.

308 Rouxel, O., N. Dobbek, J. Ludden, and Y. Fouquet (2003), Iron isotope fractionation during
309 oceanic crust alteration, *Chem. Geol.*, *202*, 155-182.

310 Russel, W. A., D. A. Papanastassiou, and T. A. Tombrello (1978), Ca isotope fractionation on
311 the Earth and other solar system materials., *Geochim. Cosmochim. Acta*, *42*, 1075-1090.

312 Schoenberg, R., and F. von Blanckenburg (2005), An assessment of the accuracy of stable Fe
313 isotope ratio measurements on samples with organic and inorganic matrices by high-
314 resolution multicollector ICP-MS, *International Journal of Mass Spectrometry*, *242*, 257-272.

315 Severmann, S., C. M. Johnson, B. L. Beard, and J. McManus (2006), The effect of early
316 diagenesis on the Fe isotope compositions of porewaters and authigenic minerals in
317 continental margin sediments, *Geochim. Cosmochim. Acta*, *70*, 2006-2022.
318 doi:2010.1016/j.gca.2006.2001.2007.

319 Siebert, C., T. F. Nägler, and J. D. Kraners (2001), Determination of molybdenum isotope
320 fractionation by double-spike multicollector inductively coupled plasma mass spectrometry,
321 *Geochem. Geophys. Geosyst.*, 2, 2000GC000124.

322 Strelow, F. W. E. (1980), Improved separation of iron from copper and other elements by
323 anion-exchange chromatography on a 4% cross-linked resin with high concentrations of
324 hydrochloric acid, *Talanta* 27, 727-732.

325 Weyer, S., and J. B. Schwieters (2003), High precision Fe isotope measurements with high
326 mass resolution MC-ICPMS, *International Journal of Mass Spectrometry*, 226, 355-368.

327 Zhu, X.-K., R. K. O’Nions, Y. Guo, and B. C. Reynolds (2000), Secular Variation of Iron
328 Isotopes in North Atlantic Deep Water, *Science*, 287, 2000-2002.

329

330 Table 1

Faraday cup configuration and isotopic abundances of Fe and elements than can produce isobaric interferences with Fe								
Nominal mass		53	54	56	57	58	60	61
Isotope abundance (%)	Cr	9.5	2.37					
	Fe		5.8	91.7	2.2	0.28		
	Ni					68.3	26.1	1.13
Collector configuration		L4	L2	L1	H1	H2	H3	H4

331

332 Table 2

Isotopic composition of dissolved Fe from a seawater column. Bonus Goodhope Cruise. February 22nd 2008. Station 18. 13°07'E-36°30'S. Cast GOFLO-8.									
Sampling bottle #	Depth (m)	[Fe] nM	$\delta^{56}\text{Fe}$	2SE	$\delta^{57}\text{Fe}$	2SE	$\delta^{58}\text{Fe}$	2SE	Fe consumed per analysis (ng)
B10	30	0.159	0.06	0.056	0.09	0.084	0.11	0.110	52
B10	30	0.170	0.02	0.108	0.03	0.161	0.04	0.213	22
B6	200	0.282	0.09	0.037	0.14	0.055	0.19	0.072	158
B3	1250	0.577	-0.14	0.035	-0.20	0.053	-0.27	0.070	162
B3	1250	0.577	-0.12	0.056	-0.18	0.083	-0.23	0.110	164
B1	4000	0.539	0.21	0.064	0.32	0.095	0.42	0.126	91
B1*	4000	0.550	0.23	0.052	0.34	0.077	0.44	0.102	91
		0.550	0.20	0.039	0.30	0.057	0.39	0.076	91

* : Each line corresponds to distinct chemical separation and spectrometric measurement, except the two last lines, for which only the spectrometric measurement was duplicated (the chemical separation was the same).

333 Figure Captions

334

335 Figure 1: Fe IC of the HemSTD, measured directly (crosses) and after having being mixed to
336 10L seawater samples from which most of the iron had been previously removed
337 (diamonds). The thick line represents the known Fe IC of the HemSTD.

338

339 Figure 2: Fe IC, dissolved oxygen concentration, potential temperature and salinity profiles at
340 station 18 of the Bonus/Goodhope cruise (2008). Left panel: gray diamonds represent
341 individual analyses, black diamonds represent the average of the replicate analyses.
342 Error bars are the external precision of the measurements ($2SD=0.13\text{‰}$, cf. section
343 Validation). The gray area represents the Fe IC of igneous rocks ($\pm 2SD$, [*Poitrasson*,
344 2006]). Middle and right panels: Hydrographic data from the bathysonde (onboard raw
345 data).



