Measurement of the isotopic composition of dissolved iron in the open ocean

F. Lacan,[1,2] A. Radic,[1] C. Jeandel,[1,2] F. Poitrasson,[3] G. Sarthou,[4,5] C. Pradoux,[1,2] and R. Freydier[3,6]

Received 28 August 2008; revised 18 November 2008; accepted 24 November 2008; published 31 December 2008.

[1] This work demonstrates for the first time the feasibility of the measurement of the isotopic composition of dissolved iron in seawater for a typical open ocean Fe concentration range (0.1–1 nM). It also presents the first data of this kind. Iron is preconcentrated using a Nitriloacetic Acid Superflow resin and purified using an AG1x4 anion exchange resin. The isotopic ratios are measured with a MC-ICPMS Neptune, coupled with a desolvator (Aridus II), using a ^{57}Fe-^{58}Fe double spike mass bias correction. Measurement precision (0.13‰, 2SD) allows resolving small iron isotopic composition variations within the water column, in the Atlantic sector of the Southern Ocean (from δ^{57}Fe = −0.19 to +0.32‰). Isotopically light iron found in the Upper Circumpolar Deep Water is hypothesized to result from organic matter remineralization. Shallow samples suggest that, if occurring, an iron isotopic fractionation during iron uptake by phytoplankton is characterized by a fractionation factor, such as: $|\Delta^{57}Fe_{(plankton\text{-}seawater)}| < 0.48‰$.
Citation: Lacan, F., A. Radic, C. Jeandel, F. Poitrasson, G. Sarthou, C. Pradoux, and R. Freydier (2008), Measurement of the isotopic composition of dissolved iron in the open ocean, *Geophys. Res. Lett.*, *35*, L24610, doi:10.1029/2008GL035841.

1. Introduction

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

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

[4] This great potential motivated very numerous Fe isotope studies during the last decade in the marine environment and at the ocean boundaries (ferromanganese crusts, plankton tows, aerosols, sediments, pore waters, suspended particles, rivers, estuaries, hydrothermal vents... [*Zhu et al.*, 2000; *Rouxel et al.*, 2003; *Levasseur et al.*, 2004; *Bergquist and Boyle*, 2006; *de Jong et al.*, 2007]). However, the isotopic composition of the iron dissolved in seawater in the open ocean has never been reported so far, because of the analytical difficulty of such measurement, due to the very low seawater Fe content (typically 1 to 0.1 nM) combined to a concentrated salt matrix. Such a measurement is however of the highest importance, because dissolved iron in seawater is the phase which links all the above listed marine phases. It is, for instance, absolutely necessary to fully exploit phytoplankton or ferromanganese Fe IC.

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

2. Sampling

[6] Four 10 L seawater samples taken during the BONUS/GOODHOPE cruise (Feb–March 2008, RV Marion Dufresne) have been analyzed following the protocol described below. These samples have been taken at station 18 (13°07′E–36°30′S), in the Atlantic sector of the Southern Ocean, north of the subtropical front, from 30 to 4000 m depth. They were collected with acid-cleaned 12-L Go-Flo bottles mounted on a Kevlar wire and tripped by Teflon messengers. The bottles were brought into a trace metal clean container for filtration through 0.4 μm Nuclepore®

[1] LEGOS, Observatoire Midi-Pyrénées, Université de Tolouse, Toulouse, France.
[2] LEGOS, CNRS, Toulouse, France.
[3] LMTG, CNRS, Toulouse, France.
[4] LEMAR, Université Européenne de Bretagne, Rennes, France.
[5] LEMAR, CNRS, Plouzané, France.
[6] Now at Laboratoire HydroSciences Montpellier, Montpellier, France.

0094-8276/08/2008GL035841

membranes (90 mm), within a few hours of collection. The filtration units were entirely made of PTFE. Samples were then acidified onboard to pH $\approx$ 1.8 (bi-distilled HCl).

3. Chemical Separation

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

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

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

[10] The protocol described here is adapted from *Lohan et al.* [2005], using a commercially available Nitriloacetic Acid (NTA) Superflow resin (Qiagen®). The NTA resin is packed in a PTFE column. The 10L sample, filtered and acidified to pH = 1.75, is stored in a LDPE cubitainer. Such pH quantitatively dissociates the iron complexed to the organic ligands [*Lohan et al.*, 2005]. Hydrogen peroxide is added to the sample before the preconcentration to oxidize Fe^{II} to Fe^{III} ([H_2O_2] = 10 μM). The sample is passed through the resin at about 10 ml.min^{-1}. The resin is then rinsed with deionized water. Iron is eluted with 10 ml 1.5 M HNO_3. The column is then washed with 20 ml 1.5 M HNO_3 and stored at pH = 7. The sample is evaporated and re-dissolved in 6 M HCl for the purification step.

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

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

4. Mass Spectrometric Analysis

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

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

[15] The double spike is added to the acidified sample at least 12 h before the preconcentration to allow the homogenization of the double spike with the sample. After preconcentration and purification, the sample is dissolved in $\sim$0.7 ml 0.3 M HNO_3, for the spectrometric analysis.

[16] Each sample is bracketed with an IRMM-14 certified reference material (mixed with the double spike), relative to which the sample IC is calculated. Each measurement session includes measurements of the ETH (Eidgenössische Technische Hochschule Zürich) in-house hematite standard (named HemSTD hereafter [*Poitrasson and Freydier*, 2005], mixed with the double spike), every 1.5 hours in order to monitor accuracy and precision of the instrument. Instrumental blanks (0.3 M HNO_3), and Cr and Ni interferences are monitored and corrected for. They are most of the time lower than 0.1% (with maximum values reaching 0.5%). The Fe IC is finally corrected for the blank of the overall procedure, which Fe IC is taken to be that of the igneous rocks.

5. Validation

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

[18] The total yield of the chemical Fe preconcentration and purification is determined as follows. A 10 L seawater sample, taken at $\sim$40 m depth at the Dyfamed site (Northwest Mediterranean), is filtered (SUPOR® 47 mm, 0.8 μm), then acidified and spiked with a solution of ^{57}Fe (for the determination of its Fe concentration by isotopic dilution). The sample is then taken through the entire procedure. The resulting Fe is measured on the quadrupole ICPMS, both by the isotopic dilution method and the external calibration method (combined with a sensitivity correction with indium as an internal standard). The former allows determining the initial sample concentration, whereas the latter allows determining the Fe quantity recovered after the purification. Comparison of both quantities allows calculating the total

Table 1. Faraday Cup Configuration and Isotopic Abundances of Fe and Elements That 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

yield of the procedure. This has been measured repeatedly, at each chemistry session. Total Fe yield is 92 ± 10% (1SD, n = 5). Achieving a 100% yield is not critical, however, since we add a double spike before the chemical procedure.

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

[20] The three ratios δ^{56}Fe, δ^{57}Fe and δ^{58}Fe (usual δ notation, relative to ^{54}Fe) are measured with the same accuracy and the same internal and external precisions per atomic mass unit (see below and Table 2). In the following the Fe IC are reported as δ^{57}Fe, relative to IRMM-14.

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

[22] External precision and accuracy of the Fe IC measurement were tested in different ways. First, the measurement of variable amounts of the HemSTD (relative to IRMM-14) allowed estimating the capabilities of our instrument, configuration and data reduction, for variable Fe consumption. These results are reported in Figure 1. The known Fe IC of HemSTD is δ^{57}Fe(HemSTD) = 0.75 ± 0.14‰ (2 SD, n = 55 unpooled analyses, [*Poitrasson and Freydier*, 2005]). Taking into account all of our measurements, which correspond to Fe consumptions ranging from 200 to 25 ng per analysis, we find: δ^{57}Fe(HemSTD) = 0.79 ± 0.13‰ (2 SD, n = 40, over a period of 4 months). For the measurements with the lowest Fe quantity, corresponding to a Fe consumption of 25 ng, we find δ^{57}Fe(HemSTD) = 0.81 ± 0.16‰ (2 SD, n = 7). The accuracy is estimated from the deviation (absolute value of the difference) of the measurements from the known value. That deviation is on average δ^{57}Fe = 0.06 ± 0.08‰ (2 SD, n = 40), with a maximum value of 0.14‰.

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

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

6. Fe Concentration

[25] Together with the measurement of the Fe isotopic composition, the double spike method provides precise and accurate determination of the Fe concentration (as shown with a simple spike by *de Jong et al.* [2008]). The detection limit, defined as three times the standard deviation of the blank (7.5 ng, 3 SD, n = 5, cf. section 4), is 13 pM when preconcentrating 10 L of sample. The precision, mostly limited by the blank variability (5 ng 2 SD, n = 5), is 9% for

Table 2. Isotopic Composition of Dissolved Fe From a Seawater Column[a]

Sampling Bottle Number	Depth (m)	[Fe] nM	δ^{56}Fe	2SE	δ^{57}Fe	2SE	δ^{58}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[b]	4000	0.550	0.23	0.052	0.34	0.077	0.44	0.102	91
B1[b]	4000	0.550	0.20	0.039	0.30	0.057	0.39	0.076	91

[a]Bonus Goodhope Cruise. February 22nd 2008. Station 18. 13°07′E–36°30′S. Cast GOFLO-8. Each line corresponds to distinct chemical separation and spectrometric measurement, except where noted.
[b]Only the spectrometric measurement was duplicated (the chemical separation was the same).

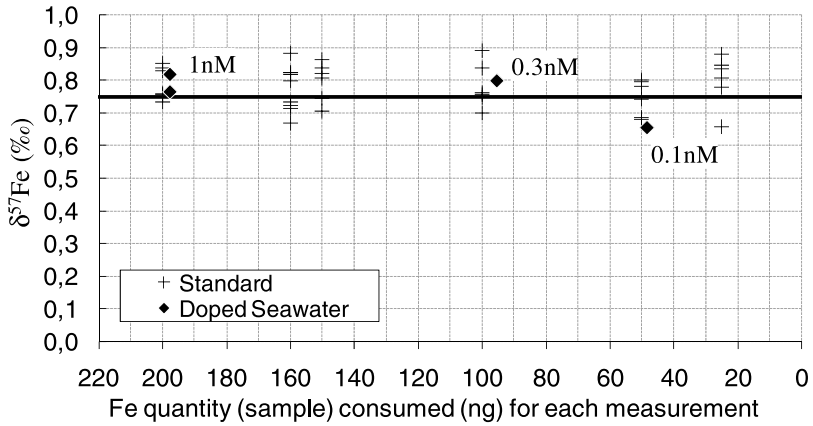

Figure 1. Fe IC of the HemSTD, measured directly (crosses) and after having being mixed to 10 L seawater samples from which most of the iron had been previously removed (diamonds). The thick line represents the known Fe IC of the HemSTD.

seawater samples with [Fe] = 0.1 nM, 2% for [Fe] = 0.5 nM, and lower than 1% for [Fe] > 1 nM.

7. Results and Discussion

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

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

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

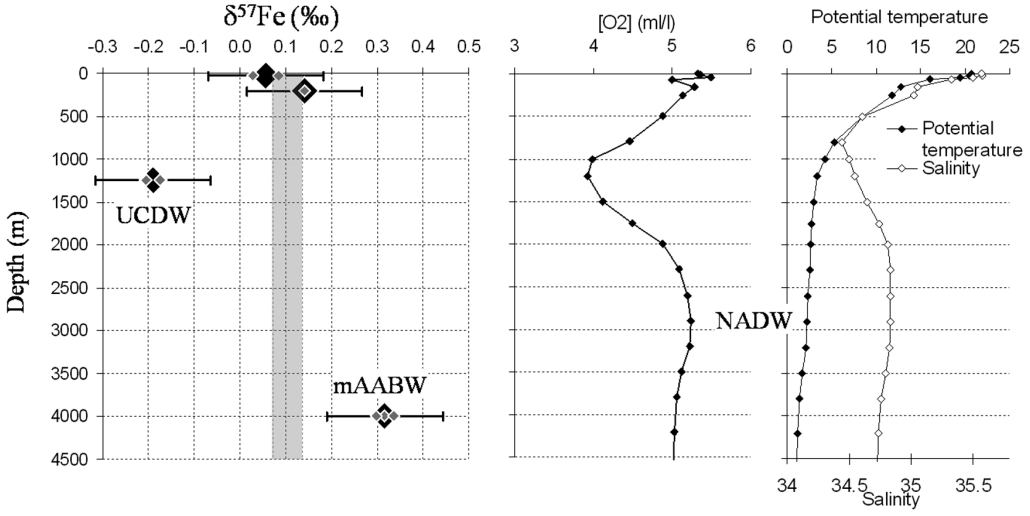

Figure 2. Fe isotopic composition, dissolved oxygen concentration, potential temperature and salinity profiles at station 18 of the Bonus/Goodhope cruise (2008). (left) Gray diamonds represent individual analyses, black diamonds represent the average of the replicate analyses. Error bars are the external precision of the measurements (2 SD = 0.13‰, cf. section Validation). The gray area represents the Fe IC of igneous rocks (±2 SD, [*Poitrasson*, 2006]). (middle and right) Hydrographic data (onboard raw data).

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

[30] Surface (30 m depth) iron depletion relative to subsurface concentrations (200 m depth) is 42%. In the hypothesis of the occurrence of Fe fractionation during Fe uptake by phytoplankton, the present data allow estimating an upper limit for the fractionation factor (according to Rayleigh distillation), above which a Fe IC variation would have been measurable (larger than twice the present data precision, i.e., 0.26‰). If the difference between the Fe IC of phytoplankton and that of seawater in which it grows is equal to ±0.48‰, then a 42% depletion should generate a difference of ±0.26‰ in the seawater relative to the initial value. Since no difference is observed between the 30 and 200 m depth samples, these data could suggest that, if occurring, a potential Fe isotopic fractionation during Fe uptake by phytoplankton could be characterized by a fractionation factor, such as: $|\Delta^{57}Fe_{(plankton\text{-}seawater)}| < 0.48‰$.

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

[32] **Acknowledgments.** The CNRS (French National Center for Scientific Research) is thanked for its investment in this project. We thank two anonymous reviewers. M. Boye and S. Speich are thanked for having organized the Bonus/GoodHope Project and cruise. We thank the Crew and Captain of R/V Marion Dufresne. We thank the Go-Flo sampling team: J. Bown, M. Boye, E. Bucciarelli, F. Chever and B. Wake. F. Candaudap and J. Chmeleff are thanked for their help with the ICPMS.

References

Beard, B. L., and C. M. Johnson (2004), Fe isotope variations in the modern and ancient earth and other planetary bodies, in *Geochemistry of Non-Traditional Stable Isotopes, Rev. Mineral. Geochem.*, vol. 55, edited by C. M. Johnson, B. L. Beard, and F. Albarède, pp. 319–357, Mineral. Soc. of Am., Washington, D. C.

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

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

Blain, S., G. Sarthou, and P. Laan (2008), Distribution of dissolved iron during the natural iron-fertilization experiment KEOPS (Kerguelen Plateau, Southern Ocean), *Deep Sea Res., Part II*, *55*, 594–605.

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

Boyle, E., and W. J. Jenkins (2008), Hydrothermal iron in the deep western South Pacific, *Geochim. Cosmochim. Acta*, *72*, A107.

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

Croot, P. L., K. Andersson, M. Ozturk, and D. R. Turner (2004), The distribution and specification of iron along 6°E in the Southern Ocean, *Deep Sea Res., Part II*, *51*, 2857–2879.

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

de Jong, J., V. Schoemann, D. Lannuzel, J. L. Tison, and N. Mattielli (2008), High-accuracy determination of iron in seawater by isotopoe dilution multiple collector inductively coupled plasma mass spectrometry (ID-MC-ICP-MS) using nitrilotriacetic acid chelating resin for preconcentration and matrix separation, *Anal. Chim. Acta*, *623*, 126–139.

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

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

Elrod, V. A., W. M. Berelson, K. H. Coale, and K. S. Johnson (2004), The flux of iron from continental shelf sediments: A missing source for global budgets, *Geophys. Res. Lett.*, *31*, L12307, doi:10.1029/2004GL020216.

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

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

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

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

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

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

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

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

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

Schoenberg, R., and F. von Blanckenburg (2005), An assessment of the accuracy of stable Fe isotope ratio measurements on samples with organic and inorganic matrices by high-resolution multicollector ICP-MS, *Int. J. Mass Spectrom.*, *242*, 257–272.

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

Siebert, C., T. F. Nägler, and J. D. Kramers (2001), Determination of molybdenum isotope fractionation by double-spike multicollector inductively coupled plasma mass spectrometry, *Geochem. Geophys. Geosyst.*, *2*(7), 1032, doi:10.1029/2000GC000124.

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

Weyer, S., and J. B. Schwieters (2003), High precision Fe isotope measurements with high mass resolution MC-ICPMS, *Int. J. Mass Spectrom.*, *226*, 355–368.

Zhu, X.-K., R. K. O'Nions, Y. Guo, and B. C. Reynolds (2000), Secular variation of iron isotopes in North Atlantic Deep Water, *Science*, *287*, 2000–2002.

R. Freydier, Laboratoire HydroSciences Montpellier, F-34095 Montpellier CEDEX 5, France.

C. Jeandel, F. Lacan, C. Pradoux, and A. Radic, LEGOS, Observatoire Midi-Pyrénées, Université de Tolouse, 14, avenue Edouard Belin, F-31400 Toulouse, France. (francois.lacan@legos.obs-mip.fr)

F. Poitrasson, LMTG, CNRS, 14–16, avenue Edouard Belin, F-31400 Toulouse, France.

G. Sarthou, LEMAR, CNRS, Place Nicolas Copernic, F-29280 Plouzané, France.