High-Precision Determination of the Isotopic Composition of Dissolved Iron in Iron Depleted Seawater by Double Spike Multicollector-ICPMS

Francois Lacan,* Amandine Radic,† Marie Labatut,‡ Catherine Jeandel,‡ Franck Poitrasson,‡ Geraldine Sarthou,§ Catherine Pradoux,† Jerome Chmeleff,‡ and Remi Freydier‡

LEGOS (CNRS-CNES-IRD-UPS) and LMTG (CNRS-IRD-UPS), Observatoire Midi Pyrenees, 14 av Edouard Belin, 31400 Toulouse, France, and LEMAR (CNRS-IRD-UBO), Institut Universitaire Europe´en de la Mer, place Nicolas Copernic, 29280 Plouzané, France

This work demonstrates the feasibility of the measurement of the isotopic composition of dissolved iron in seawater for an iron concentration range, 0.05–1 nmol L⁻¹, allowing measurements in most oceanic waters, including Fe depleted waters of high nutrient low chlorophyll areas. It presents a detailed description of our previously published protocol, with significant improvements on detection limit and blank contribution. Iron is preconcentrated using a nitrioloactic acid superflow resin and purified using an AG 1 × 4 anion exchange resin. The isotopic ratios are measured with a multicollector-inductively coupled plasma mass spectrometer (MC-ICPMS) Neptune, coupled with a desolvator (Ardis II or Apex-Q), using a ⁵⁷Fe–⁵⁸Fe double spike mass bias correction. A Monte Carlo test shows that optimum precision is obtained for a double spike composed of approximately 50% ⁵⁷Fe and 50% ⁵⁸Fe and a sample to double spike quantity ratio of approximately 1. Total procedural yield is 91 ± 25% (2SD, n = 55) for sample sizes from 20 to 2 L. The procedural blank ranges from 1.4 to 1.1 mg, for sample sizes ranging from 20 to 2 L, respectively, which, converted into Fe concentrations, corresponds to blank contributions of 0.001 and 0.010 nmol L⁻¹, respectively. Measurement precision determined from replicate measurements of seawater samples and standard solutions is 0.08‰ (δ⁵⁶Fe, 2SD). The precision is sufficient to clearly detect and quantify isotopic variations in the oceans, which so far have been observed to span 2.5‰ and thus opens new perspectives to elucidate the oceanic iron cycle.

Iron (Fe) availability has been shown to be the main limiting factor for phytoplankton growth in wide areas of the world ocean, such as the so-called high nutrient low chlorophyll (HNLC) areas (Southern Ocean, Subarctic, and Equatorial Pacific Ocean). In that respect, the iron oceanic cycle is a component of the global carbon cycle and thus of the climate. Despite this importance, our knowledge of the iron oceanic cycle remains partial. Several sources of iron to the open ocean have been proposed and are currently being debated. Whereas dust dissolution was traditionally considered as the dominant source, sediment dissolution at the continental margins is proposed to significantly contribute to the Fe content of the open ocean surface waters. Hydrothermal inputs have recently also been hypothesized as significant contributors to the Fe content of the open ocean surface waters. The iron isotopic compositions (Fe IC) of these sources appear to be different. In the following, the Fe IC are reported as δ⁵⁶Fe = [(⁵⁶Fe/⁵⁴Fe)sample/ (⁵⁶Fe/⁵⁴Fe)IRMM-14] × 10⁶. Atmospheric and crustal Fe IC are δ⁵⁶Fe = 0.07 ± 0.02‰, 2SD for the crust (34). Pore waters of sediments deposited on shelves and upper slopes display much more negative Fe IC (−3.4 < δ⁵⁶Fe < −1.8 for samples just below the seawater interface at three sites between 150 and 500 m

depth\textsuperscript{15,16}, while mid-oceanic ridge hydrothermal fluids are characterized by $\delta^{56}$Fe $\approx 0.4$ (values ranging from $\delta^{56}$Fe $= -0.7$ to $-0.1$\textsuperscript{17–19}). These distinct isotopic signatures suggest that iron isotopes could be a very useful tool to better quantify the iron sources to the ocean.\textsuperscript{17,20}

Other uncertainties remain about the Fe internal oceanic cycle, in particular concerning the fluxes between the different Fe species in the water column, notably the soluble, colloidal, and particulate phases. Transfers between these phases include numerous processes, such as dissolution, oxidation followed by precipitation, photoreduction, sorption, complexation with organic ligands, biological uptake, and bacterial remineralization. None of these processes has been directly investigated in oceanic conditions regarding Fe isotopic fractionation so far. However several \textit{in situ} and \textit{in vitro} studies in other media (e.g., fresh water) have been realized (dissolution,\textsuperscript{13,21} oxidation followed by precipitation,\textsuperscript{12,22} sorption,\textsuperscript{23,24} siderophore complexation,\textsuperscript{25} and uptake by plants\textsuperscript{26}). Some of these processes and associated Fe isotopic fractionations may complicate the use of Fe isotopes as a tracer of iron sources in the open ocean. On the other hand, they may provide new insights into the internal oceanic Fe cycle, such as iron speciation, dissolved/particulate fluxes, or biological processes. In such a context, multiparametric and multi-isotopic approaches and a better description of laboratory determined isotopic fractionation factors in realistic open oceanic conditions may be useful.

This great potential motivated very numerous Fe isotope studies during the past decade in the marine environment and at the ocean boundaries (ferromanganese crusts, plankton tows, aerosols, sediments, pore waters, suspended particles, rivers, estuaries, hydrothermal vents\textsuperscript{20,27–30}). However, because of the analytical difficulty of such measurement, the only data of the isotopic composition of the iron dissolved in seawater in the open ocean published so far to our knowledge are those obtained with the protocol described here.\textsuperscript{31} Ranges of values have been reported in the San Pedro Basin ($\delta^{56}$Fe $= -1.82\%$) and in the Western Subtropical North Atlantic ($\delta^{56}$Fe $= +0.3\%$ to $+0.7\%$).\textsuperscript{32} Finally, the samples used in the present study have dissolved Fe (DFe) IC in the following ranges, $\delta^{56}$Fe $= -0.13$ to $+0.27$ in the South East Atlantic (Cape Basin), $\delta^{56}$Fe $= -0.49$ to $-0.19$ in the Atlantic sector of the Southern Ocean Antarctic zone, $\delta^{56}$Fe $= +0.22$ to $+0.40$ in the Western and Central Equatorial Pacific, and $\delta^{56}$Fe $= +0.41$ to $+0.52$ in the Western Subtropical North Atlantic. Documenting the IC of DFe is extremely important because dissolved iron in seawater is the phase which links all the above listed marine phases. It is, for instance, necessary to exploit phytoplankton or ferromanganese Fe IC. Before being able to measure the Fe IC of the different Fe forms included in the operationally defined “dissolved” form (e.g., colloids, nanoparticles, and free ionic Fe), the measurement of the dissolved pool is a major step forward.

DFe concentration in open ocean depleted surface waters can be as low as $\sim 0.02\text{ nmol L}^{-1}$ (nM),\textsuperscript{32} and reach a typical value of 0.6 nM at depth.\textsuperscript{7} The minimum amount of iron required to perform a precise isotopic analysis (i.e., typical precision $<0.1\%$ 2SD) is around 20 ng (refs 33 and 34 and this work). Therefore, analyzing the DFe IC in Fe depleted seawater requires the preconcentration of $\sim 20$ L samples (20 L of seawater with [Fe] $= 0.02\text{ nmol L}^{-1}$ contain 22 ng of Fe). Twelve years ago, a Fe preconcentration method based on Mg(OH)\textsubscript{2} precipitation was published.\textsuperscript{35} This method appeared promising for the analysis of the Fe IC because of its low blank level. However, it produces rather voluminous precipitates, which are difficult to handle. De Jong et al.\textsuperscript{29} managed to measure the DFe IC of seawater in the North Sea using such coprecipitation. However this method was restricted to samples smaller than 2 L, with a procedural blank of $\sim 10$ ng, which, converted into Fe concentration, corresponds to a blank contribution of 0.9 nM (10 ng in 2 L). It was therefore unsuitable for open ocean Fe concentrations. We also tested this method at LEGOS but gave up because of the volume of the precipitate that was excessively large for further chromatographic purification. Then, adapting a protocol for the preconcentration of 2 mL seawater samples for the determination of its DFe concentration,\textsuperscript{36} we developed a protocol for the analysis of the DFe IC, using a commercially available nitriolacetic acid (NTA) superflow resin (Qiagen), packed in a column, that allowed the measurement of 10 L samples with a blank of 8 ng.\textsuperscript{37} This blank contribution, of 0.014 nM, allowed measuring samples with [DFe] > 0.14 nM (i.e., blank contribution <10%) but was unsuitable for HLNC area surface waters, which concentrations are often around 0.05 nM. The use of the same resin in a bulk extraction technique was then reported on 1 L samples, with a blank of 1.1 ng.\textsuperscript{38} Although
the use of a smaller volume facilitates sampling and handling issues and although the absolute value of that blank was significantly reduced compared to previous studies, when scaled to the sample volume, the blank contribution of that technique, 0.020 nM (1.1 ng in 1 L), was slightly larger than that of Lacan et al. (2008).31

In this paper, we present a detailed description of the protocol briefly presented in Lacan et al.,31 with significant improvements on detection limit and blank contribution. This protocol allows the measurement of the isotopic composition of dissolved iron in seawater, for Fe concentrations down to 0.05 nM (blank contribution of 0.001 nM).

EXPERIMENTAL SECTION

Sampling. Seawater samples of 10–20 L were collected with acid-cleaned 12 L Go-Flo bottles mounted on a trace metal clean rosette or directly on a Kevlar wire. The Go-Flo bottles were brought into a trace metal clean container for filtration through 0.45 μm Nuclepore membranes (90 mm), within a few hours of collection. Filtration was performed from the Go-Flo bottles (pressurized with 0.02 μm filtered nitrogen), through PFA filtration units (Savillex), directly into a 20 L flexible LDPE container (with PP closure; Fillaud). Samples were then acidified onboard (1.7 mL L⁻¹ of seawater of 9 M HCl, twice distilled in a Picotrace sub-boiling distillation system) and stored double bagged.

Chemical Separation General Points. All of the chemical separation procedure was conducted in a trace metal clean lab, equipped with an ISO 4 (class 10) laminar flow hood. High-purity reagents were used (either twice distilled at LEGOS or commercially available). All labware was acid cleaned. Blanks of reagents, labware, and atmosphere were monitored.

Fe IC measurement in seawater requires the Fe 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.

Most of the tests described below were performed on 10 L samples, but the method has also been validated for sample volumes ranging from 2 to 20 L.

Preconcentration. A volume of 1.2 mL of NTA resin is packed in a FEP column (homemade with FEP tubings and frits; 9.6 mm internal diameter, 16.5 mm length, cf. Figure 1). Before the first use, the resin is washed with 50 mL of 1.5 M HNO₃ during 30 min and rinsed with deionized water (DW) until pH rises back to that of the DW (pH ∼ 6). The sample, filtered and acidified (pH = 1.75), is stored in a LDPE container. Such a pH dissociates the iron complexed to the organic ligands.36 Hydrogen peroxide is added to the sample 30 min before the preconcentration to oxidize Fe²⁺ to Fe³⁺ ([H₂O₂] = 10 μmol L⁻¹).36 The sample is lifted to the top of a shelf. The container is connected to the top of the column through FEP tubings (6.3 mm internal diameter). The base of the column is connected to the waste. The NTA column lies roughly 130 cm below the sample container so that the gravity flow through the column is around 10 mL min⁻¹. A 10 L seawater sample passes through the column in about 17 h. The column is then disconnected from the preconcentration tubings and placed in a laminar flow hood. Then, 30 mL of DW are run through the column to remove traces of salt. The iron is eluted with 10 mL of 1.5 M HNO₃. The column is then washed with 10 mL of 1.5 M HNO₃ and stored at pH = 7. The column can be reused to preconcentrate up to a total of 20 L of seawater. The sample is evaporated under a class-100 laminar flow hood (using acid inert hot plates set to temperatures between 90 and 60 °C) and redissolved in 6 M HCl for the purification step.

Purification. Fe is then purified from the remaining salts using an AG 1×4 anionic resin, following a protocol adapted from Strelow.38 Before the first use, the resin is washed as follows. The resin is put in a vial filled with 1 M HCl. It is shaken a few seconds. Once the resin has settled, the supernatant is decanted. The vial is refilled and the procedure is repeated three times. Then 0.5 mL of resin is packed in a homemade heat shrinkable PTFE column, having an internal diameter of 4 mm. The resin is then washed with the following sequence, repeated twice: 5 mL of 0.1 M HF, 7 mL of 6 M HCl mixed with 0.001% H₂O₂ and 7 mL of 7

Figure 1. Photograph of the preconcentration setup (two simultaneous preconcentrations). The small white boxes indicate the positions of the NTA columns. The NTA column is enlarged in the top left insert, where the NTA resin can be seen between the two frits.

double spike method allows correcting for potential isotope fractionation during chemical separation, provided that the fractionation law is the same during chemical separation and within the spectrometer.\textsuperscript{20} This assumption is currently made.\textsuperscript{40,41} The use of a double spike also allows the determination of the Fe concentration using the isotopic dilution method.

The isotopes $^{57}$Fe and $^{58}$Fe are chosen for the double spike because they have the two lowest natural abundances among the Fe isotopes. This allows optimizing the beam intensities of all Fe isotopes, which is critical for samples with very low Fe content. Data reduction is performed using the iterative approach of Siebert et al.\textsuperscript{40} Assuming that the natural and artificial (during chemical separation and within the spectrometer) fractionations are mass dependent, a single analysis of the sample--double spike mixture is sufficient to determine the true sample Fe IC.

The $^{57}$Fe--$^{58}$Fe double spike is prepared from two monoisotope solutions ($^{57}$Fe solution with the following abundances $^{56}$Fe = 0.18\%, $^{57}$Fe = 92.57\%, $^{58}$Fe = 5.33\%, and $^{59}$Fe = 1.92\% and a $^{58}$Fe solution with the following abundances $^{56}$Fe = 0.04\%, $^{57}$Fe = 0.07\%, $^{55}$Fe = 8.22\%, and $^{59}$Fe = 91.7\%). The isotopic composition of the double spike and the double spike to sample mixing ratio are optimized to minimize error propagation during data reduction.

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. A preliminary determination or an estimation of the sample Fe concentration is therefore necessary. After preconcentration and purification, the sample is dissolved in $\sim$0.7 mL of 0.3 M HNO$_3$ for the spectrometric analysis. The exact volume is determined depending on the spectrometer uptake flow rate (varying between $\sim$50 and 120 $\mu$L min$^{-1}$, cf. Table 1), in order to maximize beam intensities.

Each measurement session begins with repeated measurements of the ETH (Eidgenössische Technische Hochschule Zürich) in-house hematite standard\textsuperscript{42} (named ETH-STD hereafter; mixed with the double spike), relative to IRMM 14 (mixed with the double spike). The ETH-STD (mixed with the double spike) is then run every 80 min in order to monitor accuracy and precision of the instrument. Each measurement is bracketed with an instrumental blank (0.3 M HNO$_3$ used to dissolve the standards and samples). Acquisition times are set to 25 cycles.

\begin{table}[h]
\centering
\caption{Operation Parameters of the ThermoFinnigan Neptune MC-ICPMS at the Observatoire Midi Pyrenees}
\begin{tabular}{|c|c|}
\hline
\textbf{Parameter} & \textbf{Value} \\
\hline
rf power & $1200$ W \\
acceleration voltage & $10$ kV \\
mass analyzer pressure & $1.0 \times 10^{-8}$ mbar \\
transmission lens & $-2000$ V \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Faraday Cup Configuration and Isotopic Abundances of Fe and Elements That Can Produce Isobaric Interferences with Fe}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
& \multicolumn{2}{c|}{nominal mass} & \multicolumn{2}{c|}{isotope abundance (\%)} & \multicolumn{2}{c|}{Fe} & \multicolumn{2}{c|}{Ni} \\
\hline
& 53 & 54 & 56 & 57 & 58 & 60 & 61 & 68.3 & 26.1 & 1.13 \\
\hline
collector configuration & L4 & L2 & L1 & H1 & H2 & H3 & H4 \\
\hline
\end{tabular}
\end{table}
of 8.4 s for samples (and standards) and 10 cycles of 8.4 s for blanks. Uptake time is set to the minimum, here 55 s, in order to save as much sample as possible for the acquisition. Wash time is set to the minimum (20 s) for the samples (because they follow blanks), whereas it is set to 150 s for blanks in order to wash traces of Fe remaining from the previous sample (or standard). The absence of memory effect after such a wash is monitored between each sample (or standard) by checking that the 10 cycles of each blank do not display a decreasing trend. The average beam intensities of the bracketing instrumental blanks are also subtracted to the sample beam intensities. $^{54}$Cr and $^{58}$Ni interferences are subtracted from the $^{53}$Cr and $^{60}$Ni beams, taking into account the instrumental mass fractionation for Fe, determined by the double spike mass fractionation correction. Instrumental blanks and interferences 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.$^{43}$

RESULTS AND DISCUSSION

Isotopic Analysis Optimization. Two desolvators, the Aridus II and the Apex-Q (without membrane) were used. Instrumental isotopic fractionation was found much more stable with the Apex-Q (typical mass bias variations of 0.05% over 10 h) than with the Aridus II (mass bias variation up to 1% over 10 h). The Apex-Q and Aridus II provided sensitivities ~5 and 3 times higher than the stable introduction system (SIS, Elemental Scientific Inc.), respectively (taking into account sample uptake rates). The Apex Q (without membrane) is therefore now preferred because of its more stable mass fractionation and higher sensitivity relative to the Aridus II.

The widths of the medium and high resolution (MR and HR) slits were changed by Thermo Scientific in 2008, from 30 and 16 $\mu$m to 50 and 18 $\mu$m, respectively. Until 2008, an unused MR slit (30 $\mu$m) and a HR slit (16 $\mu$m) lead to typical mass resolution ($m$/$\Delta m$ of the peak side 5% to 95% peak height, measured on $^{56}$Fe) of 9000 and 13 000, respectively, which allowed resolving polyatomic interferences. This is now extremely difficult with the new MR slit width (50 $\mu$m), leading to typical resolutions of 7400. The HR slit (18 $\mu$m) is thus now almost always preferred, although it reduces the transmission. A 30 $\mu$m width slit would provide better performance but is no more commercially available today.

The optimization of the isotopic composition of the double spike and the double spike to sample mixing ratio, in order to minimize error propagation during data reduction, was performed using a Monte Carlo method ($N = 160$), in which (i) the proportion of the $^{57}$Fe solution in the double spike varied from 10 to 90% and (ii) the mixing ratio, defined as the mass proportion of double spike relative to the total amount of Fe in the mixture (double spike + sample), varied from 5 to 98%. The results are displayed in Figure 2. They show that the minimum errors are obtained with (i) a proportion of the $^{57}$Fe solution in the double spike lying between 40 and 90% and (ii) a mixing ratio lying between 30 and 70%. The double spike was therefore made with 55% of the $^{57}$Fe solution and 45% of the $^{58}$Fe solution. The precise double spike isotopic composition was measured relative to IRMM-14 using a combination of the measurements of (i) both solutions doped with Ni and normalized with the interelement exponential normalization method$^{44}$ and (ii) the double spike measured pure.$^{45}$ Its isotopic ratios relative to the IRMM-14 certified ones are $^{56}$Fe/$^{54}$Fe = 32.957 ± 0.050, $^{57}$Fe/$^{54}$Fe = 615.17 ± 0.96, $^{58}$Fe/$^{54}$Fe = 525.52 ± 0.97 (2 SD). The amount of double spike added was chosen so that the mixing ratio (defined above) was about 50%.

Blanks. The blank of the whole procedure was measured in different ways. First, the pH of 300 mL of DW was adjusted to 3.0 (2 SD). The amount of double spike added was chosen so that the pH of 300 mL of DW was adjusted to 3.0 (2 SD). The amount of double spike added was chosen so that the pH of 300 mL of DW was adjusted to 3.0 (2 SD). The amount of double spike added was chosen so that

Figure 2. Error propagation during the double spike mass bias correction calculated with a Monte Carlo method. A true Fe IC of a sample is calculated by fractionating the IRMM-14 using an exponential mass fractionation law, in which the coefficient is chosen from −0.1 to 0.1 to simulate a realistic natural Fe IC. A true double spike Fe IC is calculated by mixing the $^{57}$Fe and $^{58}$Fe solutions. The true Fe IC of the mixture is calculated. An instrumentally biased Fe IC of the mixture is calculated (using an exponential mass fractionation law, in which the coefficient is chosen similar to those observed in our instrument, typically between 1 and 1.5). Each ratio of the latter Fe IC is then perturbed by multiplying it by (1 + $x$), where $x$ is a value randomly chosen in the following intervals: ±1 × 10$^{-5}$; ±2 × 10$^{-5}$; and ±2 × 10$^{-5}$ for the $^{54}$Fe/$^{56}$Fe, $^{57}$Fe/$^{56}$Fe, and $^{58}$Fe/$^{56}$Fe ratios, respectively. The double spike mass bias correction algorithm is then used to calculate back the true Fe IC of the sample from the perturbed ratios. The deviation (absolute value of the difference) between the known true IC and the calculated true IC is calculated. Such a calculation is performed in the different cases shown in the figure (variable IC of the double spike and variable proportion of double spike in the mixture). In each case, it is performed 160 times (in order to smooth out the variability due to the random perturbations). The mean value of the 160 samplings is reported in the figure as the “deviation from the true value”. Note that values along the ordinate axis are arbitrary, since they depend on arbitrary perturbation magnitudes. The “DS” curve (white, line) shows the case of the double spiked used in the present study.


Analytical Chemistry, Vol. 82, No. 17, September 1, 2010 7107
quadrupole ICPMS (Agilent 7500, with a collision cell in He mode) or on the MC-ICPMS (mass fractionation corrected for by standard bracketing). This blank (preconcentration + purification) was initially 8.0 ng when the method was first developed, then progressively reduced to 2.9 ± 1.6 ng (2SD, n = 8), and is now 1.04 ± 0.6 ng (2SD, n = 6). This very significant improvement is the result of the progressive replacement of HDPE and LDPE labware by Teflon labware (FEP, PTFE, and PFA) and increased care in handling. The blank of each step of the protocol were also measured individually: NTA preconcentration and AG 1×4 purification blanks are found to amount to 0.40 ± 0.25 and 0.64 ± 0.35 ng (2SD, n = 6), respectively. The H₂O₂ blank is negligible (∼1 pg).

For a real seawater sample, the blank from the sample acidification needs to be considered (more acid is used than for 300 mL of DW). The acid used here was obtained at LEGOS by two consecutive distillations (PicoTrace sub-boiling distillation system). Its Fe concentration was 10 × 10⁻¹² g g⁻¹ (i.e., 0.18 nmol L⁻¹) for a HCl concentration of 9 M (this is similar to the cleanest commercially available HCl to our knowledge). The acid quantity (for such a molarity) required to lower the seawater pH to 1.75 is 1.7 mL/L of seawater. This leads to an acidification blank corresponding to 0.3 pM, i.e., about 1.5% of the natural iron in the most depletions waters (0.02 nM). Acid purity has to be carefully monitored since much higher blanks may be found in some HCl solutions, even twice distilled.

Filtration and storage blanks also have to be considered. They are however difficult to estimate. For that purpose, we compared the Fe concentrations determined with the present protocol with those obtained independently from duplicate samples (same location but successive casts) with well established techniques, using a different filtration (e.g., Sartobran capsules), different containers (e.g., 60 mL bottles), and flow injection analysis.

The former concentrations were found lower than or equal to the latter. This implies that filtration and storage blanks of the present protocol are negligible or at least as good as those of the well-established techniques. Moreover, this validates the entire protocol (including sampling, filtration, acidification, storage, preconcentration, purification, and spectrometric analysis) regarding blank issues. This was tested for sample sizes up to 20 L and Fe concentrations down to 0.05 nM (compared to 10 L and 0.1 nM in Lacan et al.).

In total, the procedural blank is therefore the sum of (i) 1.04 ng coming from the preconcentration and purification steps and (ii) the acidification blank that depends on sample size. It ranges from 1.4 to 1.1 ng, for sample sizes ranging from 20 to 2 L, respectively, which converted into Fe concentrations, corresponds to total blank contributions of 0.001 and 0.010 nmol L⁻¹, respectively.

The isotopic composition of the total procedural blank is unknown (in particular that coming from the acidification). Our attempts to measure it were unfruitful because of the too low Fe quantities. However NTA blanks have been reported with δ⁵⁶Fe ranging from −0.5 and +0.5‰, converging toward igneous rock Fe IC as the blank increased. In order to correct for the procedural blank contribution to the measured ratios, it was therefore assumed that it is characterized by the IC of igneous rocks. The implication of a deviation from that value can be estimated. It depends on the Fe content of the sample. For instance, for a 10 L sample with a Fe concentration of 0.05 nM, i.e., 56 ng of Fe, if the blank Fe IC deviates from the assumed value by less than 3.7‰, then the blank correction would imply a bias lower than 0.08‰ (the measurement precision, cf. below) on the final result.

Yields. The total yield of the chemical Fe preconcentration and purification was determined as follows. A 10 L seawater sample, taken at ~40 m depth at the Dyfamed site (Northwest Mediterranean), was filtered (SUPOR 47 mm, 0.8 μm), then acidified, and spiked with a solution of ⁵⁷Fe (for the determination of its Fe concentration by isotopic dilution). The sample was then taken through the entire procedure. The resulting Fe was 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). After correction for the blank contribution, the isotopic dilution method allowed determining the initial concentration of the sample and the external standard method allowed determining the Fe quantity recovered after the purification. Comparison of both quantities allowed calculating the total yield of the procedure. This has been measured repeatedly at each chemistry session. The total Fe yield is 92 ± 25% (2SD, n = 55). This value confirms, with much more data, what was previously established in Lacan et al. who reported 92 ± 20% (2SD, n = 5). Note that achieving a 100% yield is not necessary since a double spike is added before the chemical procedure. The preconcentration and purification step yields were also measured separately, with similar techniques. The purification step is quantitative (100% yield for Fe), whereas the preconcentration step yield is 92%. Where the method was tested for samples volumes up to 10 L only in Lacan et al., we also performed yield measurements on 20 L samples in the present study, which are found to be 98 ± 9% (2SD, n = 2).

General Performances of the AG 1×4 Column. In order to better understand the behavior of the AG 1×4 resin, it was tested using multielemental standard solutions (quantities around 10–100 ng for most elements, up to a few micrograms for major elements such as Si or Ca). The multielemental standard was evaporated, redissolved in 0.5 mL of 6 M HCl mixed with 0.001% H₂O₂, and loaded onto the resin. The concentrations of the different elements in the successive elution solutions were measured with the Agilent 7500 ICPMS. Table 3 displays the yields for the different elements. The test was replicated six times. The results were always the same (within instrument precision, typically of 2%), which shows the robustness of this protocol. This test shows that the column is very efficient at separating most of the elements from the Fe fraction, notably major ions such as Na, Mg, or Ca. Only U and Ga are quantitatively eluted together with Fe and to a lower extent Sb and In, which are partially eluted together with Fe.

Matrix. The performance of the chemical separation was also assessed by the measurement of the matrix in which the Fe is eluted. This was determined similarly to the yield determinations. A 10 L Dyfamed seawater sample was first preconcentrated with the NTA column. The elemental composition of the preconcentrated sample was then measured on the quadrupole ICPMS. Most
of the elements (those measurable with the ICPMS technique) were measured. The amount of solid residue eluted with the Fe weighs only about 70 µg. Therefore, 99.999 98% of the total dissolved solids of the initial 10 L seawater sample (350 g) are rejected. Most of the residue (>90%) is composed of Mg, Na, and Ca. It also contains traces of V, Mo, Sb, K, Sr, Cu, Ti, Ga, Sn, B, U, and Al.

The same measurements were performed after the purification step. At this stage, the elements eluted together with Fe are mostly Ca, Ga, and Sb (~ 90, 30, and 20 ng, respectively). There are also traces of U, B, and Mg. In total, the matrix solid residue weighs ~150 ng. No traces of Cr, Ni, or Zn could be detected within the Fe fraction. The separation of Ni and Cr was found as efficient for 20 L samples as for 10 L samples (other elements not measured). The concentrations of matrix ions in the final solution for MC-ICPMS are a function of the volume used to dissolve the sample. For a typical volume of 600 µL, the above quantities yield to 150, 50, and 33 ppb, for Ca, Ga, and Sb, respectively. These results differ from what is obtained from a multielemental standard solution (Table 3) because they reflect the initial matrix of seawater, which some of the major elements (e.g., Mg and Ca) are still present in the Fe fraction even if they are found at undetectable levels in the tests performed with standard solutions.

**Precision and Accuracy.** The three ratios \( \delta^{56}\text{Fe}, \delta^{57}\text{Fe}, \) and \( \delta^{58}\text{Fe} \) are measured with the same accuracy and the same internal and external precisions per atomic mass unit. Internal precision of the measurements is typically 0.06‰ \( (\delta^{56}\text{Fe}; 2SE = 2SD/\sqrt{n}, \text{where SE and SD stand for standard error and standard deviation, respectively}) \). This value is lower than the external precisions reported below. Except rare instances in which internal precision is larger than external precision, external precision, rather than internal precision, determines the measurement precision and is described below.

Precision and accuracy of the Fe IC measurement were tested in different ways. First, the measurement of variable amounts of the ETH-STD (relative to IRMM-14) allowed estimating the capabilities of our instrument, configuration, and data reduction for variable Fe consumptions. These results are reported in Figure 3. The Fe IC of the ETH-STD has been measured in several laboratories with different instruments. Its mean value from the data obtained in the different laboratories is \( \delta^{56}\text{Fe}(\text{ETH-STD}) = \)

\[
\begin{array}{ccccccc}
\text{Li, B, Na, Mg, Al, P, K, Ca, Sc, Ti, V,} & 3.5 \text{ mL of 6 M HCl} & 3 \text{ mL of 1 M HCl} & 3 \text{ mL of 0.1 M HF} & 7 \text{ mL of 6 M HCl} & 7 \text{ mL of 7 M HNO}_3 & \text{total} \\
+ 0.001% \text{ H}_2\text{O}_2 & & + 0.001% \text{ H}_2\text{O}_2 & + 0.001% \text{ H}_2\text{O}_2 & & & \\
& & & & & & \\
\text{Cr, Mn, Co, Ni, Cu, Ge, As, Rb, Sr, Y,} & 100 & 0 & 0 & 0 & 0 & 100 \\
\text{Nb, Rh, Ag, Cs, Ba, REE, Hf, Ta, Ph, Th} & & & & & & \\
\end{array}
\]

[a] Not determined.
As shown in Lacan et al., accuracy and precision were also estimated using ETH-STD-doped seawater samples that had previously been stripped of their Fe content with NTA columns. The results are reported in Figure 3. They show that the measurements of the Fe IC of the doped seawater samples are as precise and accurate as those performed directly on the standard solutions. This validates the overall procedure for 10 L seawater samples with Fe concentrations ranging from 0.1 to 0.1 nM. Concerning 20 L samples, with [Fe] down to 0.05 nM, we showed above that the recovery, the blanks, and the purification were equivalent to (or better than) those obtained with 10 L samples with [Fe] down to 0.1 nM. The Fe quantity obtained from such a sample (20 L, 0.05 nM) after purification is 51 ng (taking into account the chemistry yield), which is enough for the isotopic measurement. These results, together with the above-described validation of the overall procedure for 10 L seawater samples with [Fe] down to 0.1 nM, validate the overall protocol for 20 L samples with [Fe] down to 0.05 nM.

Finally, replicate analyses of real seawater samples (including distinct chemical separations and spectrometric measurements) provide an integrated estimate of the measurement precision. A total of 9 duplicate and 2 triplicate analyses (24 analyses in total) were performed (compared to 3 duplicate in Lacan et al.). Results are shown in Figure 5. The weighted (3 for triplicate and 2 for duplicate) average value of 2 standard deviations calculated for each individual replicate is δ⁵⁶Fe = 0.07‰ and 2.9‰ for the DFe IC and concentration, respectively.

Fe Concentration. Secondarily, together with the measurement of the Fe isotopic composition, the double spike method provides a precise and accurate determination of the Fe concentration (as shown with a simple spike). The detection limit, defined as 3 times the standard deviation of the blank (0.9 ng, 3SD, n = 6, cf. above), is 1.65 pmol L⁻¹ when preconcentrating 10 L samples. As for the IC, the precision of the concentration measurement is determined from the replicate analyses of seawater samples (Figure 5). Reproducibility is 2.9% on average (2SD, with a maximum discrepancy between replicate of 9.7%). This precision has been determined from samples containing from 22 to 390 ng of DFe. No clear trend appeared between reproducibility and Fe content. Although not adapted to high-resolution Fe concentration analyses (due to the large sample volumes required), the present technique provide accurate and very precise Fe concentration data, with a very low detection limit.

CONCLUSIONS

This work demonstrates the feasibility of the measurement of the isotopic composition of dissolved iron in seawater for Fe concentration as low as 0.05 nmol L⁻¹, with a precision of 0.08‰ (δ⁵⁶Fe, 2 standard deviations) and a total procedural blank ranging from 1.4 to 1.1 ng, for sample sizes ranging from 20

---

**Figure 4.** Results of a blind test. Measurements performed following the protocol of Poitrasson and Freydier. Sample 1, δ⁵⁶Fe = −0.540 ± 0.034 (2SE, n = 9); sample 2, δ⁵⁶Fe = +0.237 ± 0.035 (2SE, n = 6). (−) measurement performed following the protocol presented in this study; sample 1, δ⁵⁶Fe = −0.539 ± 0.072 (2SD, n = 3); sample 2, δ⁵⁶Fe = +0.276 ± 0.017 (2SD, n = 3).

**Figure 5.** Reproducibly of the measurement determined from replicate analyses of real seawater samples (including distinct chemical separations and spectrometric measurements). The weighted (3 for triplicate and 2 for duplicate) average value of 2 standard deviations calculated for each individual replicate is δ⁵⁶Fe = 0.07‰ and 2.9‰ for the DFe IC and concentration, respectively.

---

to 2 L respectively, which converted into Fe concentrations correspond to blank contributions of 0.001 to 0.010 nmol L\(^{-1}\), respectively.

Iron is preconcentrated using a column of nitriloacetic acid superflow resin and purified using a column of AG 1×4 anion exchange resin. The preconcentration procedure has the advantage of being entirely closed, which prevents contamination from the air. Although not tested so far, it could therefore be performed onboard.

The isotopic ratios are measured with a MC-ICPMS Neptune, coupled with a desolvator (Aridus II or better Apex-Q), using a \(^{57}\text{Fe} - ^{58}\text{Fe}\) double spike mass bias correction. The range of variation observed in the ocean so far being of about 2.5‰, the measurement precision is only about 3% of this range. Such measurements therefore allow for the detection of small variations in the oceanic dissolved Fe isotopic composition and thus open new perspectives for the study of the many facets of the oceanic Fe cycle, such as its sources and sinks and its redox and/or biological cycles.

**ACKNOWLEDGMENT**

The CNRS (French National Center for Scientific Research) is thanked for supporting this study. Candaudap is thanked for his help with the quadrupole ICPMS. We thank L. Coppola for providing the Dyfamed seawater. We thank three anonymous reviewers, who greatly helped improve this manuscript.

Received for review January 28, 2010. Accepted June 25, 2010.

AC1002504