Routine isotopic analysis of iron by HR-MC-ICPMS: How precise and how accurate?

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**A B S T R A C T**

High-temperature isotopic variations documented in natural materials span a narrow range and call for precise and accurate isotopic analyses. Precisions better than ±0.03‰ (95% confidence interval) for δ\(^{56}\)Fe have been obtained by High-Resolution Multi-Collector Inductively Coupled Plasma Mass Spectrometry (HR-MC-ICPMS). Whether these uncertainties encompass all sources of error has not been carefully evaluated. The current study examines all parameters that can affect accuracy and precision of Fe isotopic measurements by HR-MC-ICPMS. It is demonstrated that accurate δ\(^{56}\)Fe measurements can be routinely achieved within the quoted uncertainties.

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**1. Introduction**

The field of Fe isotope geochemistry has seen important developments in methodology and scope since the advent of Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) (see recent reviews by Anbar, 2004; Beard and Johnson, 2004; Johnson et al., 2004; Dauphas and Rouxel, 2006). There is now increasing evidence that Fe isotopic variations are not confined to the realm of biology or low temperature aqueous geochemistry but can also occur at high temperature by equilibrium fractionation between minerals and melts (Polyakov and Mineev, 2000; Polyakov et al., 2007; Dauphas et al., 2007; Schuessler et al., 2007; Shahar et al., 2008), by diffusion in solid metal (Mullen, 1961; Roskosz et al., 2006; Dauphas, 2007 and references therein) and silicate melts (Richter et al., 2009), by evaporation/condensation (Wang et al., 1994; Alexander and Hewins, 2004; Dauphas et al., 2004; Tachibana et al., 2007; Zipfel and Weyer, 2007), and by Soret diffusion (Huang et al., in press; Richter et al., 2009). Considering that the Fe isotopic compositions of most geomatials formed at high temperature span a narrow range, important unsettled questions require high precision and accurate analyses. For instance, the Fe isotopic composition of the silicate Earth is still uncertain. While basalts have almost homogeneous δ\(^{56}\)Fe around +0.1‰ (Beard et al., 2003; Schoenberg and von Blankenburg, 2006; Weyer and Ionov, 2007), mantle peridotites have variable compositions averaging ~0‰ (Williams et al., 2005; Schoenberg and von Blankenburg, 2006; Weyer and Ionov, 2007).

Although increasing the number of repeats (n) in High Resolution (HR-) MC-ICPMS reduces the uncertainty related to instability in instrumental mass bias and counting statistics (\(\propto 1/\sqrt{n}\)), many other parameters can affect the precision and accuracy of Fe isotopic analyses (Malinovsky et al., 2003; Schoenberg and von Blankenburg, 2005). These include mass fractionation during column chromatography, incomplete separation of Fe from matrix elements that can cause instrumental mass bias to vary, presence of direct isobars from \(^{54}\)Cr\(^+\) on \(^{54}\)Fe\(^+\) and \(^{58}\)Ni\(^+\) on \(^{58}\)Fe\(^+\) and imperfect matching in acid molarity or Fe concentration between samples and bracketing standards.

A major challenge in making precise and accurate measurements of Fe isotopes arises from incomplete mass separation between Fe and argides, which include interferences of \(^{40}\)Ar\(^{14}\)N\(^+\), \(^{40}\)Ar\(^{16}\)O\(^+\), and \(^{40}\)Ar\(^{18}\)O\(^{1}\)H\(^+\) on \(^{54}\)Fe\(^+\), \(^{56}\)Fe\(^+\), and \(^{58}\)Fe\(^+\), respectively. Several strategies have been employed to address this analytical difficulty and are briefly discussed below. (i) The first method employed for isotopic analysis of Fe by MC-ICPMS relies on desolvating nebulization to increase the ratio of Fe/argide (Belshaw et al., 2000; Anbar et al., 2000; Zhu et al., 2002, de Jong et al., 2007). Nevertheless, this brute-force method is incapable of eliminating all interferences and careful matching between standard and sample ion intensities during bracketing is essential. (ii) The GV IsoProble MC-ICPMS is equipped with a hexapole collision cell, which is primarily used to thermalize the incoming ions before introduction into the magnetic sector. It also serves the purpose of breaking down molecules such as argides through interaction with the collision gas, a mixture of Ar and H\(_2\) for Fe isotopes (Beard et al., 2003; Rouxel et al., 2003; Dauphas et al., 2004). (iii) Operating the MC-ICPMS at reduced power (cold plasma) can also drastically reduce...
argide interferences (Kehm et al., 2003). The main drawback of this technique, however, is that it promotes formation of CaOH+, which can interfere with 57Fe+ peak. (iv) Medium to high mass-resolving power on the Thermo Scientific Neptune, Nu-Plasma HR, and Nu Plasma 1700 are used to separate argide interferences from Fe isotopes (Malinovsky et al., 2003; Weyer and Schwieters, 2003; Arnold et al., 2004; Poitrasson and Freydié, 2005; Schoenberg and von Blankenburg, 2005; Williams et al., 2005; Borrok et al., 2007). Precisions of better than 0.04‰ are achievable with this method.

In the current study, we evaluate the variables that can affect the accuracy of Fe isotope measurements using HR-MC-ICPMS. Error bars in Fe isotopic geochemistry have been traditionally ascribed based on either the long-term external reproducibility of geostandards or the dispersion of replicate analyses of a solution during a session of measurements. In the following, we present a method, which is also applicable to other isotope systems, to take into account both sources of analytical uncertainties. We demonstrate that δ56Fe can be measured accurately at a precision of ~0.03‰ in rocks and minerals.

2. Chemical separation of iron

All chemical protocols used for Fe isotopic analyses rely on the partition behavior of Fe with anion-exchange resin in HCl medium (Strelow, 1980). Matrix and interfering elements are eluted with concentrated HCl while Fe, which forms strong anion chloride-complexes, is retained on the resin. Iron is subsequently eluted at lower HCl molarity. Protocols using AG MP-1 anion exchange resin can be found in Maréchal et al. (1999), Archer and Vance (2004), Brantley et al. (2004), Borrok et al. (2007) and de Jong et al. (2007). Protocols using AG1-X8, -X4 or -X8 are described in Rouxel et al. (2003), Dauphas et al. (2004), Poitrasson and Freydié (2005), Schoenberg and von Blankenburg (2005), Dideriksen et al. (2006), and Thompson et al. (2007).

Here we used the separation protocol described by Dauphas et al. (2004, 2007). Typically 2–10 mg of powdered sample is subjected to the sequence of acid addition and heating and evaporations presented in Table 1. The purification procedure of column chromatography is repeated twice to ensure complete elimination of the matrix. After elution of Fe from the second column, the solution is dried down under a heat lamp, taken up in ~100 μL of 15.3 M HNO3 and evaporated to dryness to eliminate chloride complexes. The dried Fe residue is finally dissolved in 10 mL of 0.3 M HNO3 (an ultrasonic bath is often used at this step to ascertain complete dissolution). The 0.3 M HNO3 comes from a large batch that also serves for preparation of IRMM-014 and blanks used in standard bracketing and on peak zero correction. This ensures perfect matching in acid molarity between all analyzed solutions, which is critical for accurate isotopic analyses. At this point, Fe is ready for isotopic measurement by MC-ICPMS. It must be noted that the chromatographic procedure described herein does not allow for quantitative separation of Cu and Zn from Fe, which can be a problem for certain matrices, such as sulfides. To mitigate this problem, Schoenberg and von Blankenburg (2005) introduced an iron hydroxide precipitation step by basification with NH4OH.

3. Mass spectrometry

Iron isotopic analyses were performed with a Thermo Scientific Neptune HR-MC-ICPMS (see Wieser and Schwieters, 2005 for a description of the instrument). The mass-resolution of the instrument is controlled with a set of three switchable slits (250 μm, 30 μm, and 16 μm width) located before the electrostatic analyzer. Measurements were performed in both medium-resolution (MR) and high-resolution (HR) modes. In these two modes, the Fe+ peaks are resolved from argide interferences as flat-topped shoulders on the low mass side of argide peaks (Weyer and Schwieters, 2003). The mass resolution is defined as m/Δm (50, 100, and 500 m/z), where m and Δm are the masses measured at 5% and 95% intensity peak heights (see Weyer and Schwieters, 2003, for details). Mass resolutions are equal to ~8500 and ~11,000 for MR and HR, respectively. The ion transmission efficiency of the instrument for Fe is reduced by a factor of ~8 from LR to MR and another factor of ~2 from MR to HR. The δ notation (in ‰), δFe = [(Fe/Fe)sample/(Fe/Fe)IRMM-014]−1×10^6, is used throughout the current study. IRMM-014 is a pure Fe metal reference material (Taylor et al., 1992) that has a Fe isotopic composition identical to chondrites (Dauphas and Rouxel, 2006). Unless otherwise noted, the pair of isotopes reported is 56Fe/54Fe (i = 56). In the course of this study, the stock solution of IRMM-014 used during sample-standard bracketing was renewed. The δ56Fe and δ54Fe of the new batch of IRMM-014 normalized to the old batch are ~0.004 ± 0.009‰ and 0.001 ± 0.015‰ (95% ci), respectively. This confirms the conclusion of Dauphas et al. (2004) that IRMM-014 has homogeneous isotopic composition at the 0.01‰ level. Except for a series of tests aimed at estimating the influence of acid molarity on isotopic ratios, all analyzed solutions were in 0.3 M HNO3. An enclosed SC-2 sample changer installation (autosampler) equipped with an ULPA filter unit was used throughout this study. Most analyses were performed with the Thermo Scientific Stable Introduction System (SIS), which combines quartz cyclonic and Scott-type spray chambers. A few tests were also performed with the Apex-Q + Spiro TMD desolvating inlet system from Elemental Scientific Inc. operated with addition of N2 (~10 mL/min). The introduction of N2 increases the sensitivity of the Apex + Spiro inlet system but it also increases the level of interferences on 54Fe from 40Ar14N+. The temperatures of cooler (multipass condenser) and heater (cyclonic spray chamber) were set at 2 °C and 100 °C, respectively. A 50–100 μL/min PFA Teflon self-aspirating micronebulizer was used with both SIS and Apex-Q. The virtue of the Apex-Q + Spiro relative to SIS is that it drastically reduces oxides and increases Fe sensitivity. However, instrumental mass fractionation is less stable and achieving optimal tuning conditions is more daunting with the Apex-Q + Spiro than with the SIS. Therefore, using the SIS is recommended unless low quantities of Fe are analyzed. The sampler and skimmer cones are made of Ni, yet the contribution of 59Ni from the cones on 56Fe is negligible (Dauphas et al., 2004). Two cone geometries are available for the Neptune; the standard (H) and high-sensitivity (X). X-cones can increase transmission by a factor of 3 relative to H-cones (Weyer and Schwieters, 2003), which can be important for samples containing little Fe. H-cones were exclusively used in this study.

Instrumental mass fractionation is large in MC-ICPMS (between 3.5 and 5.5‰/amu for Fe, see Fig. 2 of Dauphas and Rouxel, 2006). Excluding double spike (Johnson and Beard, 1999; Balci et al., 2006; Dideriksen et al., 2006; Fantle and Bullen, 2009), three strategies have been developed for correcting instrumental mass fractionation during MC-ICPMS analysis: (i) Ni-doping, (ii) Cu-doping, and (iii) standard bracketing (Bielshaw et al., 2000, Malinovsky et al., 2003; Arnold et al., 2004, Dauphas et al., 2004; Schoenberg and von Blankenburg, 2005; also see Albarède and Beard, 2004, for a detailed review of this topic).

Table 1

<table>
<thead>
<tr>
<th>Sample dissolution and Fe column chemistry protocols.</th>
</tr>
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<tbody>
<tr>
<td>• Addition of 1 mL of 28.8 M HF + 0.5 mL 15.3 M HNO3 + 1 drop 11.3 M HClO4</td>
</tr>
<tr>
<td>• Heating in close beakers at 100 °C for 5 h</td>
</tr>
<tr>
<td>• Evaporation, addition of 0.75 mL of 10.2 M HCl + 0.25 mL 15.3 M HNO3 + 1 drop 11.3 M HClO4</td>
</tr>
<tr>
<td>• Heating and evaporation. Addition of 500 μL 6 M HCl</td>
</tr>
<tr>
<td>• Disposable Bio-Rad Poly-Prep polyethylene columns filled with 1 mL of AG1-X8 200-400 mesh Cl-form anion exchange resin (resin bed length 2.0 cm, diameter 0.8 cm)</td>
</tr>
<tr>
<td>• The resin is conditioned with 10 mL of HClO4, 10 mL of 0.4 M HCl, 5 mL of H2O, and 2 mL of 6 M HCl</td>
</tr>
<tr>
<td>• The samples in ~250 μL 6 M HCl are loaded on the column</td>
</tr>
<tr>
<td>• Most matrix and interfering elements are eluted with 8 mL (0.5 + 0.5 + 1 + 3 + 4) of 0.4 M HCl</td>
</tr>
<tr>
<td>• Iron is recovered in a Teflon beaker by passing 9 mL (0.5 + 0.5 + 1 + 3 + 4) of 0.4 M HCl</td>
</tr>
<tr>
<td>• The solution is dried down and the column procedure is repeated a second time with new resin.</td>
</tr>
</tbody>
</table>
Instrumental mass bias in MC-ICPMS is adequately described by the exponential law (Maréchal et al., 1999), which relates the measured isotopic ratio \( r \) to the true ratio \( R \) and the relative mass difference of the isotopes (\( \Delta m/m \)):

\[
r = R(1 + \Delta m/m)^{\beta},
\]

where \( \beta \) represents the instrumental mass bias and is a free parameter. In standard-bracketing with element doping, a fixed amount of Ni or Cu of known isotopic composition is added to the sample and the standard solutions. \( \beta \) is calculated for Ni or Cu using Eq. (1). The fractionation corrected ratio for Fe is subsequently computed from the measured ratio assuming that \( \beta_{\text{Fe}} = \beta_{\text{Ni,Cu}} \). In reality \( \beta_{\text{Fe}} \neq \beta_{\text{Ni,Cu}} \) (e.g., Maréchal et al., 1999; Woodhead, 2002; Archer and Vance, 2004) and the exponential law may not be completely adequate in describing instrumental mass fractionation (e.g., Vance and Thirwall, 2002; Wombacher and Rehkämper, 2003).

It is therefore critical to bracket sample analyses by measurements of the IRMM-014 Fe reference material doped with the same amount of Ni or Cu and reduced in the same manner. In standard bracketing without element doping, the instrumental mass bias is computed for the two reference standards \( \hat{\beta}_{\text{STD1}, \text{STD2}} \) using \( R = 15.6986 \) in Eq. (1); Taylor et al., 1992) that bracket the sample. The average of these two values is used to correct the sample analysis for instrumental mass fractionation (\( \hat{\beta}_{\text{SAMPLE}} = 0.5\hat{\beta}_{\text{STD1}} + 0.5\hat{\beta}_{\text{STD2}} \)). In both cases, the isotopic ratios are then reported in \( \delta \)-notation relative to the IRMM-014.

The advantage of the Ni-doping method is that both Fe and Ni (60 and 61) isotopes can be measured at the same time, i.e., no peak jumping is involved. In addition, Ni is easily separated from Fe during the column chemistry. Poitrasson and Freydid (2005) pointed out that keeping the \( ^{61}\text{Ni}^{+} \) signal above 500 mV is essential for precise analyses because uncertainty in the measurement of \( ^{61}\text{Ni} \) (1.13% of total Ni) propagates unfavorably to the corrected Fe isotope ratios. The main drawback of this method is that it generates a major interference on \( ^{58}\text{Fe} \) (0.2819 atom % of total iron) from \( ^{58}\text{Ni} \) (68.27 atom % of total Ni). This is not a problem if the laws of mass-dependent fractionation solely govern variations of isotopic ratios. However, non-mass-dependent isotopic variations may arise from photochemistry in aqueous systems or incomplete mixing of the products of stellar nucleosynthesis in meteorites (Völkkening and Papenastassiou, 1989; Dauphas et al., 2004, 2008). Another difficulty is that while Fe and Ni isotopes can be measured at the same time, our collector setting does not allow \( ^{52}\text{Cr}^{+} \) to be measured simultaneously with \( ^{58}\text{Ni}^{+} \) and the contribution of \( ^{52}\text{Cr}^{+} \) on \( ^{58}\text{Fe}^{+} \) cannot be controlled. For these reasons, this scheme was not utilized (Malinovský et al., 2003, Schoenenn and von Blanckenburg, 2005; Poitrasson and Freydid, 2005, provide ample details on how to implement this correction scheme).

On the other hand, Sharma et al. (2001), Kehm et al. (2003), and Arnold et al. (2004) advocated the use of Cu-doping. Nevertheless, the mass-dispersion in the collector array of the Neptune is not wide enough to allow analysis of the 4 stable isotopes of Fe and 2 isotopes of Cu (63 and 65) at the same time. Two sequences must therefore be used, making peak jumping unavoidable. As is the case with the Ni-doping scheme, isotopic analyses with Cu-doping are potentially less sensitive to matrix effects, which can improve accuracy. However, the duration of the measurements is significantly extended, more Fe is consumed, and in Cu-rich samples, one must ascertain complete removal of Cu during the chemistry. Although tests using Cu-doping were performed on selected samples to validate the quality of the measurements, the standard-bracketing method was preferred for most tests and measurements (also see Schoenenn and von Blanckenburg, 2005).

The Neptune MC-ICPMS at the University of Chicago is equipped with 9 Faraday collectors connected to an array of one 1012 \( \Omega \), seven 1011 \( \Omega \), and one 1010 \( \Omega \) amplifiers. With the standard-bracketing method, \( ^{54}\text{Fe} \), \( ^{56}\text{Fe} \), \( ^{57}\text{Fe} \), and \( ^{58}\text{Fe} \) were measured on L2, C, H1, and H2 Faraday collectors. Possible isobaric interferences from Cr and Ni were monitored at masses \( ^{57}\text{Cr} \) and \( ^{60}\text{Ni} \) on L4 and H4 Faraday collectors, respectively. All measurements were performed in medium and high mass resolution. Isobaric interferences of \( ^{40}\text{Ar}^{14}\text{N} \), \( ^{40}\text{Ar}^{16}\text{O} \), \( ^{40}\text{Ar}^{16}\text{O}^{1} \text{H} \), and \( ^{40}\text{Ar}^{38} \) on \( ^{54}\text{Fe} \), \( ^{56}\text{Fe} \), and \( ^{58}\text{Fe} \), were resolved by measuring iron isotopes as flat-topped peak shoulders. The ion intensities of \( ^{57}\text{Cr} \) and \( ^{60}\text{Ni} \) were measured at the center of the peaks. High-intensity measurements of minor isotopes became possible by measuring the high-abundance \( ^{56}\text{Fe}^{+} \) with a 1012 \( \Omega \) amplifier. The low intensity \( ^{60}\text{Ni}^{+} \) signal, on the other hand, was measured with a 1013 \( \Omega \) amplifier (settling time ~3 s) to reduce the Johnson noise/signal ratio (Wieser and Schwieters, 2005). The washout time with 0.45 M HNO3 between samples and standards was 90 s. The take-up time was 60 s. The mass spectrometer baseline was measured with the beam defocused for 30 cycles of 1.05 s each. Before a sequence of analysis, a clean 0.3 M HNO3 solution was measured under conditions identical to sample measurements (e.g., same number of cycles and integration time). The ion intensities of this solution were subtracted from all sample/standard measurements (On Peak Zero, OP2). The idle time was set to 3 s. Iron isotopes were acquired in a single block consisting of 25 cycles of 8.389 s each. The Fe concentrations of samples and standards ranged between 2 to 5 ppm at a sensitivity of 5 to 13 V/ppm in MR on \( ^{56}\text{Fe} \) with a 50–100 \( \mu \)l/min nebulizer.

All measurements for the Cu-doping tests were made in HR. The same amounts of pure Cu were added to the sample and standard solutions to reach a constant concentration of ~5 ppm, with a sensitivity of 2 V/ppm on \( ^{63}\text{Cu} \). The sample \( \delta\text{Fe} \) values were computed relative to bracketing IRMM-014 also doped with the same level of Cu. It is well documented that \( \beta_{\text{Cu}} \neq \beta_{\text{Fe}} \), so sample-standard bracketing is critical. The measurements were performed in 25 cycles of 2 sequences. The first sequence was identical to the standard-bracketing method and a 3 s idle time was used between each sequence. In the second sequence, \( ^{63}\text{Cu} \) and \( ^{65}\text{Cu} \) were measured on C and H2 Faraday collectors. The integration times were 8.389 s for both Fe and Cu samples. The relative mass dispersion between \( ^{63}\text{Cu} \) and \( ^{65}\text{Cu} \) was different from that of \( ^{58}\text{Fe} \) and \( ^{56}\text{Fe} \), which was corrected by adjusting the dispersion lens to ~−75 V. To correct aberrations in the Cu peak shape, the focus lens was also adjusted to ~10 V, which resulted in square peak shapes appropriate for Cu isotopic measurement. The lenses switched between Fe and Cu mode on a timescale of ~10 s. No peak centering was required during the analysis because hysteresis was not observed at any time. In other words, the center of peak measurement consistently returned to the appropriate position on the flat-topped iron peak shoulder.

The standard-sample sequences were repeated \( n \) times (typically 5 ≤ \( n \) ≤ 9). Data processing was performed offline. In a sequence consisting of standard \( (i−1) \), sample \( (i−1) \), standard \( (i) \), sample \( (i) \), standard \( (i+1) \), sample \( (i+1) \), the isotopic composition of the \( i \)th sample repeat is \( \delta\text{Fe}_{\text{sample}}(i) = \frac{R_{\text{Sample}}(i)/(0.5\hat{\beta}_{\text{STANDARD}}(i) + 0.5\hat{\beta}_{\text{STANDARD}}(i+1)) − 1 \times 10^{3}}{\hat{\beta}_{\text{STANDARD}}(i+1)} \). The reported isotopic compositions are the averages of \( n \) repeat analyses.

\[
\delta\text{Fe}_{\text{sample}} = \frac{\sum_{i=1}^{n} \delta\text{Fe}_{\text{sample}}(i)}{n}.
\]
instrumental uncertainty is that there are many more standard analyses than samples and the standard deviation is better known. For instance, in a session of 5 sample analyses repeated 9 times each, the number of standard brackets \( m \) is 44. The uncertainty on the sample \( \delta^{56}\text{Fe} \) analysis is therefore:

\[
\sigma^2_{\text{MassSpec}} = \frac{1}{n} \sum_{i=1}^{m} \left[ \delta^{56}\text{Fe}_{\text{standard(i)}} \right]^2 / m,
\]

where \( n \) represents the number of sample measurements, as we are interested in the uncertainty of the average of \( n \). For \( n = 9 \) replicate analyses of the sample solution, \( \sigma^2_{\text{MassSpec}} \) is the standard deviation of all the standard \( \delta^{56}\text{Fe} \) values measured in that session divided by \( 3 (\sqrt{n}) \). Instrumental uncertainty only represents a part of the total uncertainty, which must be assessed by examining the external reproducibility of the analyses.

4. Optimization of isotopic analyses

Several parameters such as the peak position, acid molarity, Fe concentration, presence of matrix elements or isobaric interferences can influence the quality of isotopic analyses. We explored these factors in order to establish a robust and optimized method that can be used routinely for high-precision Fe isotope measurements.

4.1. Shoulder peak plateau in medium-resolution (MR) mode

Malinovsky et al. (2003) tested how the flatness of the peak shoulder in HR mode can affect the precision and accuracy of isotopic analyses. They showed that highly reproducible results can be obtained over a mass range of ~0.01 provided the Faraday cups are properly aligned. Iron isotopic analyses can degrade the HR slit very rapidly by ion milling and thereby reduce the mass resolution. Because the MR slit blocks a smaller fraction of the incoming ions, it has a longer lifetime in terms of the number of analyses that can be performed. Weyer and Schwierset al. (2003) looked at the same issue in MR and showed that consistent \( \delta^{56}\text{Fe} \) within 0.06% (2\(\sigma\)) ratios can be obtained over a mass range of 0.005 (~100 ppm). In the following we improve the results reported by Weyer and Schwie (2003) to higher precision \( \delta^{56}\text{Fe} \) (0.02 to 0.03%, 2\(\sigma\)). A 5 ppm solution of Fe was introduced into the mass spectrometer using the SIS. A sequence was established where the Fe isotopic composition was measured alternatively at the center and off-center of the Fe shoulder peak. The On Peak Zero (OPZ) used for all analyses was taken at the center (during routine analyses only one OPZ is measured at the beginning of a sequence). The center was selected visually, as would be done during a routine analysis. Six off-center measurements were performed, spanning a mass interval of 0.006 amu. We computed the \( \delta^{54}\text{Fe} \), \( \delta^{57}\text{Fe} \), and \( \delta^{58}\text{Fe} \) values for off-center analyses relative to the bracketing center measurements. The results are shown in Fig. 1. Expectedly, as the mass positions approach the argide peaks, tailing leads to erroneous \( \delta^{56}\text{Fe} \) and \( \delta^{57}\text{Fe} \) values. Uncertainties also tend to increase, as the position gets further away from the center, due to fluctuations in argide/Fe ratio and/or peak position. Overall, consistent measurements were achieved with minimum uncertainties of ~0.02% for \( \delta^{56}\text{Fe} \), 0.043% for \( \delta^{57}\text{Fe} \), and 0.187% for \( \delta^{58}\text{Fe} \) (2\(\sigma\)) over a mass interval of 0.003 amu. These observations indicate that it is preferable to position the mass slightly to the left (~0.001 amu) of what visually appears to be the center of the Fe shoulder peak plateau.

4.2. Concentration matching between samples and standards

With the first generation of MC-ICPMS, where Fe isotopic analyses depended on the use of a desolvating nebulizer to reduce argide interferences, it was absolutely crucial to match the concentration of samples and standards (Belshaw et al., 2000; Anbar et al., 2000; Zhu et al., 2002). In the Neptune, three strategies help eliminate the effect of argide interferences. Clearly the most important factor is the use of MR or HR modes. Subtraction of OPZ ion intensities can also help.
reduce the influence of tailing from argide peaks, if present. Finally, matching the concentration between samples and standards can also play a role in improving accuracy. Schoenberg and von Blanckenburg (2005) studied this aspect by bracketing standard measurements by analyses of the same standard but with a Fe concentration that was deliberately mismatched. These authors concluded that $\delta^{56}\text{Fe}$ was not affected by mismatch between the concentration of Fe in the standard and the sample as long as the difference was less than a factor of 2. Examination of Fig. 4 from Schoenberg and von Blanckenburg (2005) however reveals a statistically significant positive correlation between $\delta^{56}\text{Fe}$ and $C_{\text{sample}}/C_{\text{standard}}$. We performed similar tests in both MR and HR modes using the SIS and Apex-Q at different ion intensities of the reference solution (5, 25 and $38 \times 10^{-11}$ A ($\text{n}^{56}\text{Fe}$). The measurements reveal that indeed, individual sample analyses do not depart from the standard isotopic compositions when $0.5 < C_{\text{sample}}/C_{\text{standard}} < 2$ (Fig. 2). Nevertheless, there seems to be a negative correlation between $\delta^{56}\text{Fe}$ and the degree of mismatch between the sample and standard. In MC-ICPMS, concentration matching within 5% is easily achieved, which is sufficient to obtain accurate analyses within ~0.03‰ on $\delta^{56}\text{Fe}$. Under these conditions, only one OPZ analysis needs to be made per session.

4.3. Influence of matrix elements on instrumental mass fractionation

Although our chemistry is highly efficient at eliminating most common rock forming elements, certain transition elements that are present in appreciable quantities in Fe-bearing rocks can persist after chromatography. This is true in particular for Cu, which follows Fe throughout the chemistry. Such elements can affect the accuracy of the isotopic analyses by modifying the value and the stability of instrumental mass fractionation. Schoenberg and von Blankenburg (2005) examined the influence of Cu, Zn, Cd, and Co on Fe isotopic analyses on a Neptune MC-ICPMS. They found that even when the concentrations of these elements reach 50% of Fe concentration, no significant deviation of $\delta^{56}\text{Fe}$ is observed within ~0.06‰.

We have extended the range to higher matrix concentrations. Solutions of 1 to 5 ppm Fe were mixed with up to ~100 ppm Co, Ni, Cr, and Cu. These solutions were then analyzed by bracketing with pure Fe solutions. The resulting $\delta^{56}\text{Fe}$ are plotted in Fig. 3A as a function of the concentration of the matrix element (this is easily converted to a ratio to iron by dividing by 1 to 5 ppm). We do not report $\delta^{56}\text{Fe}$ for the Cr-doping test because there is a direct isobaric interference of $^{54}\text{Cr}$ on $^{56}\text{Fe}$.
4.4. Correction of isobaric interferences from $^{54}$Cr and $^{68}$Ni together with the study of Schoenberg and von Blanckenburg (2005) below ~10 ppm (Element/Fe accuracy of isotopic analyses, as long as their concentration is kept within ~1%), which can be achieved easily.

$^{54}$Fe. Instead, $2 \times \delta^{57/56}$Fe is reported, which should be similar to $\delta^{56}$Fe for mass-dependent fractionation. All doping solutions have normal $^{56}$Fe within 0.1‰ up to matrix concentrations of ~10 ppm but error bars seem to increase with increasing matrix concentrations, reflecting greater instability of instrumental mass bias. Because Cu is not easily separated during the chemistry, particular attention was paid to this element. Iron has normal isotopic composition within 0.035‰, Gramlich et al., 1989). The fractionated $^{54}$Cr/$^{53}$Cr and $^{58}$Ni/$^{60}$Ni ratios are easily separated during the chemistry, particular attention was paid to this element. Iron has normal isotopic composition within 0.035‰, Gramlich et al., 1989). Even in HR mode, Cr and Ni interferences cannot be resolved from Fe. However, one can correct these interferences by analyzing the ion intensities of $^{53}$Cr and $^{60}$Ni. The data reduction proceeds as follows. At first, $\beta$ is calculated for the sample or standard based on the $^{53}$Fe/$^{56}$Fe ratio. This $\beta$ is then used to compute fractionated $^{54}$Cr/$^{53}$Cr and $^{58}$Ni/$^{60}$Ni ratios assuming that $\beta_{53Cr} = \beta_{53Ni} = \beta_{56Fe}$ and using unfractoned ratios $^{54}$Cr/$^{53}$Cr = 0.24890 (Shields et al., 1966) and $^{58}$Ni/$^{60}$Ni = 2.59607 (Gramlich et al., 1989). The fractionated $^{53}$Cr/$^{53}$Cr and $^{58}$Ni/$^{60}$Ni ratios are then combined with measured $^{53}$Cr and $^{60}$Ni intensities to estimate and subtract isobaric interferences on $^{54}$Fe and $^{58}$Fe. In order to test this correction scheme and evaluate its potential limitations, we have analyzed the isotopic composition of Fe mixed with various levels of Cr and Ni (Fig. 3B). The $\delta^{54/56}$Fe value is normal within 0.08‰ up to $^{54}$Cr/$^{56}$Fe = 0.04. This ratio corresponds to a correction of 40‰. When the $^{54}$Cr/$^{56}$Fe ratio reaches 0.7 (700‰), the correction begins to break down ($\delta^{54/56}$Fe $\approx$ 0.6‰), most likely because the mass bias obtained from $^{54}$Fe/$^{56}$Fe is not appropriate for Cr (and Ni). The $\delta^{58/56}$Fe value remains normal within uncertainties (± 0.5‰) for Ni, as long as the $^{58}$Ni/$^{56}$Fe ratio is kept below ~0.05 (50‰). Erroneous negative $\delta^{58/56}$Fe are observed for higher $^{58}$Ni/$^{56}$Fe ratios. Better corrections can be obtained by artificially modifying the $^{54}$Cr/$^{53}$Cr and $^{58}$Ni/$^{60}$Ni ratios to eliminate isotopic anomalies on $\delta^{56/54}$Fe and $\delta^{58/54}$Fe, which is a practical way of accounting for the fact that $\beta_{54Fe} \neq \beta_{56Cr}$.

4.5. Acid molarity

Malinovsky et al. (2003) showed that the molarity of the acid used to dilute the samples can affect instrumental mass fractionation for Fe. They observed an increase of $\delta^{56}$Fe with increasing HNO$_3$ concentration. Correcting mass fractionation by doping with Ni, however, eliminates the observed trend. The potential effect of acid molarity on the quality of Fe isotopic analyses was studied as follows. Standards in 0.15 to 0.9 M HNO$_3$ were bracketed with standards in 0.3 M HNO$_3$. Tests were performed with both the SIS (5 ppm Fe) and the Apex-Q + Spiro (1 ppm Fe). In both cases, very large isotopic variations with changing acid molarity were measured (Fig. 4). Note that the uncertainty also seems to increase with increasing acid molarity. The use of a desolvating nebulizer does not seem to considerably improve this problem. It is therefore critical to match the molarity of the sample and standard whenever the standard bracketing method is applied. The best results are achieved by using the same batch of acid to dilute all solutions, including standards (IRMN-014) and blanks. Effort must be also directed towards eliminating evaporative loss during the course of sample preparation and analyses, which can change the molarity of the remaining solution (e.g., use an ultrasonic bath rather than a hot plate to dissolve the iron residue).

4.6. Cu-doping

Details on how to implement Cu-doping method for instrumental mass fractionation correction are given by Sharma et al. (2001), Kehm
dissolution (assuming that the powder is homogeneous) to isotopic measurement. This will help better estimate the external reproducibility. However, it is also desirable to incorporate the instrumental uncertainty when reporting results. This can be easily achieved by writing the standard deviation of the data as the quadratic sum of the standard deviation associated with instability of the mass spectrometer ($\sigma_{\text{MassSpec}}$, Eq. (3)), the standard deviation corresponding to the distribution in $\delta^{56}\text{Fe}$ of the material being analyzed ($\sigma_{\text{Natural}}$), and a standard deviation ($\sigma_{\text{Unknown}}$) that accounts for all other sources of variability associated with the analytical procedure (Humayun and Clayton, 1995; Rehkämper and Halliday, 1999):

$$\sigma_{\text{Data}} = \sigma_{\text{MassSpec}} + \sigma_{\text{Natural}} + \sigma_{\text{Unknown}}^2$$  

(4)

In order to estimate $\sigma_{\text{Unknown}}$, the Fe isotopic compositions of geostandard powders were analyzed. The starting materials have homogeneous $\delta^{56}\text{Fe}$ with $\sigma_{\text{Natural}} = 0$. For a set of $k$ replicate analyses, one can compute the Mean Squared Weighted Deviates (MSWD or reduced $\chi^2$),

$$\text{MSWD} = \frac{1}{k-1} \sum \frac{(X_i - \bar{X})^2}{\sigma_{\text{MassSpec},i}^2 + \sigma_{\text{Unknown}}^2}$$

(5)

where $\bar{X}$ is the weighted average. Note that in this equation, $\sigma_{\text{MassSpec}}$ depends on the sample while $\sigma_{\text{Natural}}$ is fixed. If the analytical uncertainty has been properly estimated, the dispersion of the data around the average should be explained by $\sigma_{\text{MassSpec}}$ and the MSWD should be around unity. Otherwise, the measurements would call for a positive $\sigma_{\text{Unknown}}$. The isotopic compositions of 23 replicates of the BHVO-1 geostandard were measured over a period of a year using the SIS (Fig. 6). The MSWD associated with these 23 replicates is 2.52. This is outside the 95% confidence interval of 0.5–1.7 given by $\chi^2$ statistics. The MSWD can be brought down to unity by adjusting $\sigma_{\text{Unknown}}$ to 0.011. Similarly, for $\delta^{57}\text{Fe}$, one can compute $\sigma_{\text{Unknown}}^{57}\text{Fe}=0.012$. For

### Table 2

<table>
<thead>
<tr>
<th>Geostandard</th>
<th>$\delta^{56}\text{Fe}$</th>
<th>$\delta^{56}\text{Fe}_{\text{MassSpec}}$</th>
<th>95% CI</th>
<th>$\delta^{57}\text{Fe}$</th>
<th>$\delta^{57}\text{Fe}_{\text{MassSpec}}$</th>
<th>95% CI</th>
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<tr>
<td>Geostandard matrix+IRMM014</td>
<td>Allende a</td>
<td>0.004</td>
<td>0.011</td>
<td>0.031</td>
<td>0.004</td>
<td>0.017</td>
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<td>Allende b</td>
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<td>0.015</td>
<td>0.038</td>
<td>−0.025</td>
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<td>0.028</td>
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<td>AC-E b</td>
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<td>0.011</td>
<td>0.031</td>
<td>−0.014</td>
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<td>BCR-2 a</td>
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<td>0.028</td>
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<td></td>
<td>BCR-2 b</td>
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<td>0.008</td>
<td>0.028</td>
<td>−0.017</td>
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<td>DTS-2 a</td>
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<td>0.009</td>
<td>0.028</td>
<td>0.017</td>
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<tr>
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<td>IF-G a</td>
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<td>0.011</td>
<td>0.031</td>
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<td>IF-G b</td>
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<td>0.009</td>
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<td>−0.018</td>
<td>0.014</td>
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<td>0.023</td>
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<td>0.025</td>
<td>0.393</td>
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<tr>
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<td>0.006</td>
<td>0.164</td>
<td>0.009</td>
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</table>

Geostandard matrix+IRMM014 correspond to sample matrices mixed with IRMM-014 iron. These samples have $\sigma_{\text{MassSpec}}=0$, demonstrating that the measurements are accurate. The geostandards agree with recommended values (Dauphas and Rouxel, 2006). $\sigma_{\text{MassSpec}}$ corresponds to the standard deviation from the mass spectrometer (typically, replicate analyses obtained on a single day). The 95% CI (confidence interval) integrates our knowledge of the long-term reproducibility of BHVO-1 (Section 5) a and b represent 2 aliquots of IRMM-014 mixed with sample matrices processed independently through the chemistry.
Over the past several years, important developments have been made in terms of analytical precision. Therefore, systematic biases that could not be detected before may be revealed as the precision improves. In order to test whether the measurements are accurate, we have proceeded in a similar manner as that described in Bermin et al. (2006) and Dauphas et al. (2007). Powdered geostandards (Allende CV3 chondrite, AC-E granite, BCR-2 basalt, DTS-2 dunite, and IF-G banded iron formation) with previously documented Fe isotopic compositions (see the compilation in Dauphas and Rouxel, 2006) were passed through a first column of anion exchange. Both Fe and the matrix were recovered. The matrix was passed through a second column to completely eliminate any Fe that may have persisted through the first column. The Fe-free matrix was doped with 50 μg of IRMM-014 and then split into 2 aliquots (a and b in Table 2 and Fig. 7). Each fraction was treated by 2 columns following the procedure described in Section 2. The sample Fe eluted from the first column was passed through a second column. To summarize, three Fe solutions were generated from the original geostandard solution. The geostandard matrix + IRMM-014 tests indicate that the measurements are highly accurate.

The results obtained on geostandards were also compared with those published in the literature (Fig. 7B). δ56Fe values of 0.647 ± 0.027, 0.091 ± 0.027, 0.017 ± 0.027, 0.002 ± 0.027, and 0.322 ± 0.027% were measured for IF-G, BCR-2, DTS-2, Allende, and AC-E, respectively. This compares very well with published values of 0.631 ± 0.019, 0.064 ± 0.034, 0.022 ± 0.041, −0.011 ± 0.047, 0.289 ± 0.024% (see compilation in Dauphas and Rouxel, 2006). Overall, the results from these tests demonstrate that δ56Fe can be measured accurately with a precision of less than ±0.03‰ (95% confidence interval).

6. Double-spike vs. sample-standard bracketing

Double-spike (58Fe–54Fe or 58Fe–57Fe have been used) is an approach that was not investigated in this study but has the potential to yield precise and accurate Fe isotopic analyses by TIMS (Johnson and Beard, 1999; Fantle and Bullen, 2009) or MC-ICPMS (Balci et al., 2006; Dideriksen et al., 2006, 2007, 2008) with a high sample throughput. The main advantage of the double spike is that the instrumental mass fractionation can be efficiently corrected. Dideriksen et al. (2006, 2007, 2008) reported a dispersion (2SD) of standard δ56Fe values of ±0.06‰. This is similar to what can be achieved by standard-sample bracketing but the measurements of Dideriksen et al. were acquired with a Thermoelemental Axiom instrument, which provides no intrinsic capability to resolve argide interferences. Balci et al. (2006) reported external reproducibilities (2SD) of ±0.07‰ on a Neptune HR-MC-ICPMS. Whether better precisions can be achieved with such instruments remains to be explored. One major drawback of the double-spike technique is that the search for Fe anomalies in meteorites may be hindered (Völk Rinke and Papanastassiou, 1989; Dauphas et al., 2008). Iron-58 was produced in massive stars together with 56Fe (1/2=1.49 My) by neutron-capture reactions and as such, it represents a useful proxy to probe the distribution of 58Fe in the protoplanetary disk (Dauphas et al., 2008). An additional limitation is that the double-spike method does not allow one to study the form of the mass-fractionation.
law, which may provide clues on the mechanisms underlying isotopic fractionation (Young et al., 2002).

7. Conclusion

A protocol was developed for routine analyses of the Fe isotopic compositions of common natural materials. Iron is purified using a two-step anion exchange column scheme. Iron isotopes are then analyzed by HR-MC-ICPMS. A number of parameters that can affect the accuracy and precision of δ^{56}Fe measurements were identified and examined:

1. The samples were introduced into the mass spectrometer using the Standard Introduction System (a 50 µl/min Teflon nebulizer with a cyclonic + Scott spray chamber). For samples with high Fe content, utilizing an Apex-Q + Spiro inlet system did not offer any advantage over a conventional wet-introduction system. Medium resolution and standard Ni H-cones provided adequate intensities for high-precision measurements with ~2 ppm Fe solutions.

2. The analyte concentrations of the sample and the reference material (IRMM-014) were matched within 5%. Tests reveal that concentration was not critical to acquiring accurate analyses. This disagrees with the results of Malinovsky et al. (2003) but is in agreement with Schoenberg and von Blanckenburg (2005).

3. Matching in acid molarity between samples and standards is critical to achieving accurate measurements. Batches of blank and reference material were prepared together with samples with the exact same molarity (HNO₃ 0.3 M).

4. The measurements were not sensitive to the presence of other transition elements in the solution, as long as their concentrations remained below ~10 ppm (Element/Fee)⁻².

5. Measurement of each solution was repeated 5 to 9 times. This allowed the uncertainty associated with instability in instrumental mass fractionation to be reduced to less than 0.02% for δ^{56}Fe. However, precision may not be limited by instrument instability per se, but rather by the overall external reproducibility. Taking that into account, a precision of ~0.03‰ (95% confidence interval) can be routinely obtained.

6. The accuracy of Fe isotopic analyses was tested by measuring IRMM-014 mixed with Fe-free matrix from geostandards. The average δ^{56}Fe is ~−0.0045 ± 0.0094‰, demonstrating that δ^{56}Fe measurements are accurate within the quoted uncertainties.

This study complements the earlier efforts of Weyer and Schwieters (2003), Malinovsky et al. (2003), Arnold et al. (2004), Poitrasson and Freydlid (2005) and Schoenberg and von Blanckenburg (2005) by demonstrating that accurate isotopic analyses with precisions of less than 0.03‰ on δ^{56}Fe can be achieved routinely on HR MC-ICPMS. This opens up exciting avenues of research in high temperature Fe isotope geochemistry.

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