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High precision measurement of iron isotopes by plasma source mass spectrometry

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Abstract

Multiple-collector inductively coupled plasma mass spectrometry has been used for the precise measurement of natural variations in the isotopic composition of Fe. The contributions of Ar–O and Ar–N molecular species to the mass spectrum in the Fe mass region are minimised and the repeatability of the ^{57}Fe/^{54}Fe ratio of a sample Fe solution relative to the IRMM-14 Fe isotope standard is better than 100 ppm at 95% confidence. Variations in sample ^{57}Fe/^{54}Fe ratio are expressed as ε^{57}Fe units, which are deviations in parts per 10^4 from the same ratio in the IRMM-14 Fe isotope reference standard. Measurements of ε^{57}Fe are presented for samples of meteoritic iron and terrestrial Fe–oxides and carbonates. (Int J Mass Spectrom 197 (2000) 191–195) © 2000 Elsevier Science B.V.

Keywords: Plasma source mass spectrometry; Fe-isotopes; Stable isotope

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1. Introduction

Natural variations in the stable isotope abundance of light elements such as hydrogen, carbon, and oxygen have been studied systematically for many decades. The results have had a profound influence in many fields of research ranging from the life and biomedical sciences to planetary, earth, and environmental sciences. There have been relatively few attempts to search for and exploit variations in the abundance of the stable isotopes of heavier elements. This has been due in part to analytical difficulties combined with the small magnitude of natural stable isotope fractionation that occurs at higher masses. Thus the stable isotopes of many potentially interesting elements remain relatively unexplored.

The introduction of multiple collector magnetic sector-type mass spectrometers with inductively coupled plasma (ICP) sources has transformed this situation [1–3]. This instrumentation combines the high ionisation efficiency of the Ar-plasma source with the high transmission of magnetic sector mass spectrometer and the capability for multiple collection and high-precision isotope ratio measurement. For example, it has been used successfully for the isotopic analysis of Pb, Hf, W, Cu, and Li [3–9].

Of the transition metals, Fe is a particularly important target for stable isotope studies. This is because it has a relatively high planetary abundance, is biologically utilised, and has relevance to studies of human and animal nutrition. In addition, fractionation of the stable isotopes of Fe at thermodynamic equilibrium is predicted to be as large as 1% in the ^{57}Fe/^{54}Fe ratio [10]. Previous analyses of Fe isotopes include those of

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isotopically enriched Fe by ICP mass spectrometry (ICPMS) [e.g. 11] and a study on the natural variability in Fe isotopes by thermal ionisation mass spectrometry (TIMS). Völkening and Papanastassiou [12], for example, reported Fe-isotope anomalies in carbonaceous chondrite meteorites and more recently Beard and Johnson [13] have claimed mass dependent fractionation of Fe in terrestrial samples.

Developments in multiple-collector (MC) magnetic sector ICPMS have progressed to the point where the natural stable isotope variability in a number of elements with masses less than about 100 u should now become possible. In the particular case of Fe isotope analysis by MC-ICPMS the presence of Ar–O and Ar–N molecular species has been a problem, particularly when aqueous solutions are introduced through a Meinhardt nebuliser. These molecular species interfere with the isotopes of Fe at masses 54, 55, 56, 57, and 58 u.

In this article we report a technique for the isotopic analysis of Fe using a desolvation nebuliser coupled to a Nu Instruments multiple collector ICPMS. The molecular interferences at masses 54 and 57 have been reduced to very low levels and are typically 3×10^{-4} and 1×10^{-4} of ^{54}Fe and ^{57}Fe ion beams, respectively, under normal conditions of analysis, where $^{54}\mathrm{Fe} = 5.0 \times 10^{-11}$ A. At higher signal levels the background contributions are proportionately lower and a method for assessing their contribution is presented. The new technique reported here for Fe-isotope analysis is robust as long as sample and standard Fe are appropriately matched in concentration. The ^{57}Fe/^{54}Fe ratio of the IRMM-14 Fe standard is measured with a repeatability of <100 ppm at 95% confidence level. The technique is applicable to a wide variety of materials and results are presented here for Fe isotopes in iron meteorites and terrestrial Fe–oxide and carbonate samples.

2. Analytical methods

Fe-isotope analysis is made potentially difficult by the large differences in isotope abundances between ^{56}Fe and minor isotopes, and the presence of molecular interferences. Accurate Fe-isotope ratio measurement by MC-ICPMS is possible only if potentially interfering molecular species and any other contributions to the background are eliminated or reduced to manageable proportions. Normal practice with ICPMS involves introduction of samples in dilute HNO_3 solution—a procedure that provides a source of both O and N to the Ar plasma, particularly when using a Meinhardt-type nebuliser. The resulting contributions of ArO^+ and ArN^+ to the Fe mass spectrum may preclude precise Fe-isotope ratio measurements on multiple collector instruments. In this study, techniques that minimise the contributions from ArO^+ and ArN^+ have been developed, and the techniques developed focus on the high precision measurement of ^{57}Fe/^{54}Fe ratios.

2.1. Sample preparation

All standards and samples were prepared in dilute acid solution and introduced into the plasma through a modified Cetac MCN 6000 desolvating nebuliser. This device was operated without a flow of N_2 gas in order to minimise the formation of ArN^+ species. The formation of Ar–N molecular species was reduced further through the use of HCl rather than HNO_3 solutions. Memory effects from the Cetac MCN 6000 nebuliser were occasionally severe, but this was remedied through the installation of additional thermal insulation in the nebuliser chamber to avoid condensation.

Samples of meteoritic iron and terrestrial Fe–oxide and carbonate minerals were dissolved in 6 M HCl and purified using a two-step precipitation of Fe(III) hydroxide with NH_3, then prepared in 0.1% HCl solution for mass spectrometric analysis.

2.2. Mass spectrometry

Fe-isotope ratios were measured using a Nu Instruments MC-ICPMS. This mass spectrometer is a double focussing magnetic sector instrument with variable dispersion ion optics and a fixed array of 12 Faraday collectors [4]. For the measurement of ^{57}Fe/^{54}Fe ratios, $^{57}\mathrm{Fe}^+$ (~91.8 at. %) is positioned either to pass through a gap in the collector array or to be collected in a Faraday equipped with a 10^{10} Ω resistor. $^{57}Fe^+$ (~2.1 at. %) and $^{54}Fe^+$ (~5.9 at. %) are collected in Faraday collectors using 10^{11} Ω resistors.

Mass discrimination in the Fe mass region is approximately 3%/u and may be corrected with reference to either an external or an internal standard. In this work correction is made relative to the IRMM-14 Fe-isotope standard using the sample-standard bracketing technique. A series of measurements were performed using Cu as an internal dopant, and the measured $^{65}Cu/^{63}Cu$ ratios were used to correct the $^{57}Fe/^{54}Fe$ for mass discrimination. However this technique offered no improvement in the repeatability of $^{57}Fe/^{54}Fe$ ratio measurement over the standard-sample bracketing method and has not been adopted as a routine procedure.

Samples and standards were introduced into the mass spectrometer in 0.1 M HCl with matched Fe concentrations. The accuracy to which they must be matched depends upon the instrument sensitivity. Under optimised conditions, where $^{54}Fe^+ \geq 5.0 \times 10^{-11}$ A, then as detailed below, it is unnecessary to match sample and standard Fe concentrations to better than about 20%. If Cr is present then there will be an isobaric interference on ^{54}Fe. Therefore, Cr is monitored at mass 52, and a correction made at mass 54 as necessary. In no case in this study did this correction exceed 25 ppm of the $^{54}Fe^+$ intensity.

3. Results

In most cases it is convenient to express the $^{57}Fe/^{54}Fe$ ratio of a sample as a deviation from the same ratio in the reference standard as follows:

$$\varepsilon^{57}\mathrm{Fe} = [(^{57}\mathrm{Fe}/^{54}\mathrm{Fe})_{\mathrm{sample}}/(^{57}\mathrm{Fe}/^{54}\mathrm{Fe})_{\mathrm{standard}} - 1.0] \times 10^4$$

The material used as Fe-isotope reference standard is IRMM-14.

3.1. Spectral interference

Spectral interferences on Fe isotopes include $^{54}Cr^+$ and $^{40}Ar^{14}N^+$ on ^{54}Fe and $^{40}Ar^{17}O^+$ on ^{57}Fe. Contributions from Cr^+ are negligible in the case of the IRMM-14 and Romil solutions, but in any case are routinely monitored at $^{52}Cr^+$. The contributions of $^{40}Ar^{14}N^+$ and $^{40}Ar^{17}O^+$ at 54 and 57 u, respectively, have been determined using a Fe-free 0.1 M HCl solution and are typically $<10^{-14}$ and $<10^{-15}$ A, respectively. The contribution of $^{40}Ar^{14}N^+$ at mass 54 in Fe-bearing solutions is of crucial importance and is examined in Fig. 1(a). The anticipated effect of this interference at mass 54 on ε^{57}Fe has been calculated as a function of parameters C' and f. C' is the ratio of the Fe concentration in a sample solution over that in the standard solution, whereas f is the fractional contribution of the interfering ion at mass 54 for a fixed concentration of Fe in the standard solution. The modelling is simplified by assuming that both sample and standard have identical real ε^{57}Fe values, and that there is no interfering signal at mass 57. Thus in Fig. 1(a), $\varepsilon^{57}\mathrm{Fe} = 0$ when the effect of the interfering signal at mass 54 is zero. The modelling results shown in Fig. 1(a) demonstrate that: (1) the true ε^{57}Fe value can be obtained when the Fe concentrations in both sample and standard solution are identical, no matter how large the interfering signal at mass 54 is; (2) even where the interfering signal at mass 54 is very small, its effect on ε^{57}Fe may be significant, particularly where C' is much less than 1.0; (3) the extent to which the Fe concentration of a sample may be varied relative to that of the standard depends upon the relative intensity of the interfering signal (parameter f) and the analytical precision. Fig. 1(b) shows the results of a series of measurements of ε^{57}Fe in Romil "sample" solutions with different Fe concentrations, relative to Romil "standard" Fe solution at 20 ppm. The Romil sample Fe solutions used vary from 5 to 40 ppm, and are equivalent to C' values ranging from 0.25 to 2. The dependence of ε^{57}Fe on Fe concentration observed from these measurements [Fig. 1(b)] is very similar to the predicted dependence shown in Fig. 1(a). The similarity between the predicted and the actual measured values demonstrates that the assump-

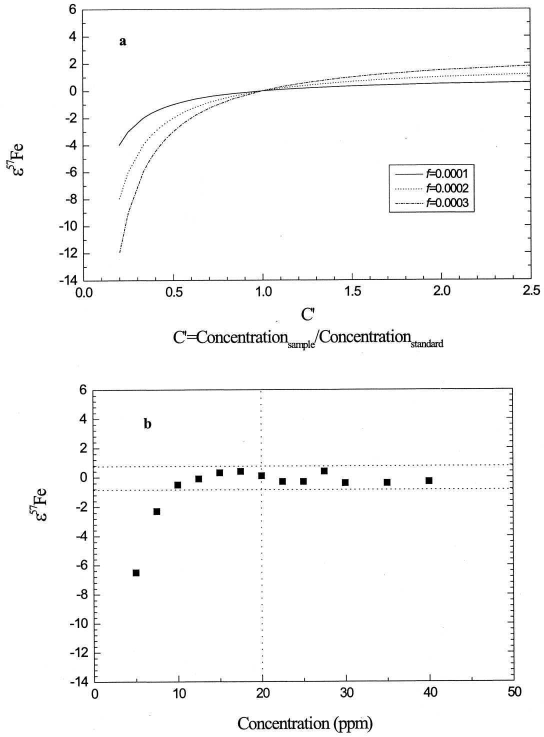

Fig. 1. (a) Calculation of the effect of an interfering signal (such as $^{40}Ar^{14}N^{+}$) at mass 54 on the measured ε^{57}Fe of a sample. Model calculations have been performed at different values of $f = 1 \times 10^{-4}$, $f = 2 \times 10^{-4}$, and $f = 3 \times 10^{-4}$, where f is the fractional contribution of the interfering signal at mass 54 to the ^{54}Fe ion beam intensity at a given concentration of the standard. C' is the ratio of Fe concentration in "sample" relative to that in the "standard". Both sample and standard are assumed to have identical true ε^{57}Fe values. Therefore, the deviation in the ε^{57}Fe value as a function of f and C' are due solely to the interfering signal at mass 54. These calculations show that even though the interfering signal is very small, its effect on the ε^{57}Fe value can still be significant when the difference in Fe concentration between sample and standard is large. (b) Measurement of ε^{57}Fe values in Romil sample Fe solutions with concentration ranging from 5 to 40 ppm, relative to Romil "standard" Fe solution at 20 ppm. The two dotted horizontal lines bracket the measurement repeatability at the 2σ level as defined in Fig. 2. The dotted vertical line indicates the Fe concentration in the standard Romil solution.

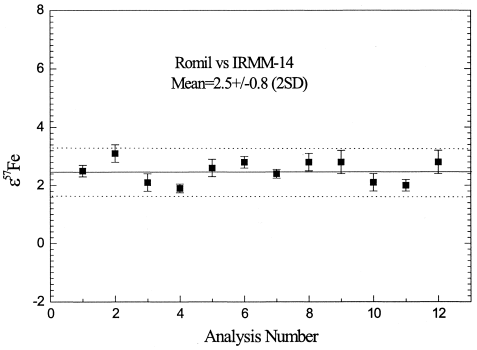

Fig. 2. Repeatability of ^{57}Fe/^{54}Fe ratio measurements. Romil Fe solution relative to IRMM-14 Fe-isotope reference standard. The average ε^{57}Fe value for Romil defined by the repeated analyses over a period of a few months is 2.5 ± 0.8 (2 s.d.).

tions adopted for the simple model must be very close to the real situation, and the interfering signal at mass 54 is indeed very small during analysis for the working conditions used. Also, from Fig. 1(b) it is deduced that the concentrations of Fe in sample and standard solutions may differ by ± 50% with a negligible introduction of error into the ε^{57}Fe value relative to the measurement repeatability achieved (see Sec. 3.2).

It will be important to ascertain this optimum operating regime on different instruments with possibly different sensitivities and background characteristics.

3.2. Iron standard repeatability

The procedure adopted for the measurement of ^{57}Fe/^{54}Fe ratios has been evaluated through the repeated measurement of the Romil Fe solution versus the IRMM-14 Fe reference standard over a period of a few months. The results for 12 separate analyses of the Romil Fe solution are shown in Fig. 2 from which the repeatability of measurements may be assessed. The average ε^{57}Fe values obtained for Romil Fe is 2.5 ± 0.8 (2 s.d.).

3.3. Meteorite and terrestrial ε^{57}Fe values

Samples of meteorite metallic Fe, massive hematite (Fe_2O_3), and sedimentary siderite ($FeCO_3$) have been analysed in duplicate following the procedures described above, and the results are presented in Table 1. The two meteorite Fe samples have ε^{57}Fe values close to 1.0, whereas the siderites are close to −5 and the hematites range from −2 to 11 in ε^{57}Fe. The duplicate analyses agree well within the errors,

Table 1
Fe-isotope results of terrestrial and extraterrestrial samples[a]

Sample number	Name	Description	ε^{57}Fe
Mt42	Iron meteorite	Type IIIA, Carthage	0.9 ± 0.8
Mt42, Dup.			1.4 ± 0.8
Mt46	Iron meteorite	Type IIIA, Thunda	0.6 ± 0.8
Mt46, Dup.			1.1 ± 0.8
OUM848	Hematite	Specular, Mt. Vesuvius, Italy	−2.0 ± 0.8
OUM848, Dup.			−1.2 ± 0.8
OUM859	Hematite	Massive, Marquette, Lake Superior	11.5 ± 0.8
OUM859, Dup.			10.9 ± 0.8
OUM3836	Siderite	North Pennines, UK	−5.3 ± 0.8
OUM3836, Dup.			−5.8 ± 0.8
OUM22159	Siderite	Wheal Maudlin, Cornwall, UK	−5.5 ± 0.8
OUM22159, Dup.			−5.7 ± 0.8

[a] Errors quoted are based on the measurement repeatability at the 2σ level shown in Fig. 2.

which are based upon the long term repeatability shown in Fig. 2.

4. Conclusions

The new technique reported here for Fe-isotope analysis using MC-ICPMS offers approximately an order of magnitude improvement in repeatability over previously published data, and offers the potential for studies of Fe-isotope fractionation in geochemical, cosmochemical, and biological samples. The technique is both sensitive and rapid—sample sizes as small as 2×10^{-5} g Fe may be readily analysed at high precision.

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