Evaluation of the use of cold plasma conditions for Fe isotopic analysis via multi-collector ICP-mass spectrometry: effect on spectral interferences and instrumental mass discrimination
Evaluation of the use of cold plasma conditions for Fe isotopic analysis via multi-collector ICP-mass spectrometry: effect on spectral interferences and instrumental mass discrimination

Stepan M. Chernonozhkin,†a,b Marta Costas-Rodríguez,†a Philippe Claeysb and Frank Vanhaecke*a

The advantages and disadvantages of using cold plasma conditions in combination with both the standard and the high-transmission (‘jet’) plasma interface and under dry and wet plasma conditions were evaluated in the context of high-precision isotopic analysis of Fe via multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS). When using the standard interface and wet plasma, cold plasma conditions suppressed the occurrence of the polyatomic ions $^{40}\text{Ar}^{14}\text{N}$ and $^{40}\text{Ar}^{16}\text{O}$, but not that of $^{40}\text{Ar}^{16}\text{O}^{+}$. Dry plasma conditions efficiently removed the (hydr)oxide ions, but at the cost of a dramatic increase in the prevalence of $^{40}\text{Ar}^{14}\text{N}$. Thus, interference-free $^{56}\text{Fe}/^{57}\text{Fe}$ measurement can be performed at low mass resolution using cold plasma conditions and the standard plasma interface. No alleviation of the spectral interferences due to Ar-based ions was observed with the ‘jet’ interface with cold plasma conditions. With cold plasma conditions, the instrumental mass discrimination affecting the Fe isotope ratios was mitigated compared to that obtained with hot plasma when the standard interface was used (1.4% per amu versus 3.2% per amu, respectively). This mitigation in instrumental mass discrimination with cold plasma conditions was not observed when the high-transmission interface was used.

1. Introduction

In many contexts, predominantly within geo- and cosmochemistry, but also to an increasing amount in the context of biomedicine, the ability to measure natural variations in the isotopic composition of Fe with high-precision is of crucial importance.1–4 Fe isotope ratios can be measured with high precision using thermal ionization mass spectrometry (TIMS); however, its use is challenged by the low ionization efficiency (for conversion into M$^{+}$ ions) and the necessity of laborious isotope dilution.5 Fe isotopic analysis can be accomplished using negative TIMS via the monitoring of molecular ions,* but it was the introduction of multi-collector ICP-mass spectrometry with its far higher ionization efficiency and sample throughput that caused a breakthrough in this field. However, the occurrence of spectral interferences, predominantly caused by the presence of $^{40}\text{Ar}^{16}\text{O}$, $^{40}\text{Ar}^{14}\text{N}$ and $^{40}\text{Ar}^{16}\text{O}^{+}$, and that of instrumental mass discrimination are inherent disadvantages of MC-ICP-MS. Both issues require proper attention, as they otherwise jeopardize accurate Fe isotope ratio measurements. Many experimental and computational studies focused on the formation of polyatomic ions in ICP-MS.7–9 To suppress the occurrence of Ar-based ions and thus, to alleviate the corresponding spectral interferences, high mass resolution, cold plasma conditions (i.e. operation of the ICP with a low forward power and higher nebulizer gas flow rate), collision/reaction cells and to some extent, aerosol desolvation providing dry plasma conditions, can be used. Multi-collector (MC) ICP-mass spectrometers equipped with a collision/reaction cell did not become widespread, although promising results were obtained for Fe isotope ratios.10,11 Also cold plasma conditions can be relied on to avoid or at least strongly suppress the interference due to overlap of the signals of $^{40}\text{Ar}^{16}\text{O}^{+}$ and $^{56}\text{Fe}$.12,13 However, as a result of the widespread application of sector-field instruments capable of working at higher mass resolution, cold plasma conditions became nearly forgotten.13 Also the drawbacks accompanying the use of cold plasma conditions contributed to this waning success: deterioration of the sensitivity for elements characterized by a high first ionization energy, more pronounced matrix effects and an increased formation of oxide ions. As a result, high mass resolution1 is the typical approach used to avoid spectral overlap in MC-ICP-MS isotopic analysis of Fe nowadays, although cold plasma conditions were successfully used for isotope ratio measurements of Fe,14 Li,15 Mg16 and Cr17 by MC-ICP-MS. Thus, the main aim of this work was to re-evaluate the advantages and disadvantages of cold plasma conditions for high-precision Fe isotope ratio measurements. The effect on the occurrence of interfering ions and the

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extent of instrumental mass discrimination were paid special attention to.

One of the most interesting recent advances in MC-ICP-MS is the introduction of high-transmission plasma interfaces (also termed ‘jet’ interface in the case of one manufacturer, Thermo-Scientific), which provide a significantly higher ion extraction efficiency from the plasma. A signal enhancement with a factor of two or higher can be obtained for both heavy (e.g., Sr, Nd, Hf, Pb and U) and light (e.g., Li) elements using the ‘jet’ interface and enhanced pumping of the plasma interface, compared to the standard arrangement in MC-ICP-MS instruments. The ‘jet’ interface in combination with dry plasma conditions, achieved via sample aerosol desolvation (either via membrane desolvation or solvent evaporation techniques), enabled precise measurements of isotope ratios at element concentrations down to 0.5 ng g⁻¹. Overall, an enhanced and thus closer to stoichiometric efficiency from the plasma.

In the other hand, high-sensitivity cone geometries are associated with increased space-charge repulsion within the ion beam and thus, a larger contribution to instrumental mass discrimination in the interface region. Also effects not seen with the standard interface have been reported on. For instance, mass-independent instrumental mass discrimination, associated with the formation of NdO⁻, was observed for Nd when using the ‘jet’ interface. These benefits and limitations of the ‘jet’ interface for high-precision isotopic analysis are yet to be fully addressed.

In view of the above, the potential benefits of cool plasma conditions for high-precision isotopic analysis of Fe were also tested with the high-transmission ‘jet’ interface and with membrane aerosol desolvation.

2. Experimental

2.1. Reagents and materials

Only high-purity reagents and acids were used throughout the experiments. Pro analysis grade HNO₃ (65%, Chem-Lab, Belgium) was further purified through sub-boiling in PFA equipment. Optima-grade HCl (37%, Seastar Chemicals Inc., Canada), trace-metal grade HF (47–51%, Seastar Chemicals Inc., Canada) and ultrapure 9.8 M H₂O₂ (Sigma Aldrich, Belgium) were used as such. Water was purified (to a resistivity ≥ 18.2 MΩ cm) in a Milli-Q Element water purification system (Millipore, France). All the Teflon® recipients, disposable plastic tubes and pipette tips used in the sample preparation were pre-cleaned by soaking in 10% pro-analysis HCl under class-10 clean lab conditions for 48 h.

IRMM-014 (Institute for Reference Measurements and Materials, Belgium) and NIST SRM 986 (National Institute for Science and Technology, USA) certified isotopic reference materials of Fe and Ni, respectively, were used throughout this study. A standard solution of Fe (Inorganic Ventures, The Netherlands) with isotope ratios known from 5 years of in-house measurements was used for the Fe isotope ratio measurements. NIST SRM 997 Tl, NIST SRM 981 Pb, NIST SRM 987 Sr, IRMM-16 Li and NIST SRM 951 B certified isotopic reference materials were used to study the instrumental mass discrimination under different plasma conditions. Reference materials of terrestrial mafic rock were used to validate the MC-ICP-MS measurement protocol using cold plasma conditions. These geological reference materials (GRMs) included PCC-1 peridotite and BHVO-2G basalt (United States Geological Survey, CO, USA), and iron formation IF-G from the Centre de Recherches Pétrographiques et Géochimiques (CRPG, France).

2.2. Acid digestion and Fe chromatographic isolation

Powdered GRMs were digested via two-step microwave-assisted acid digestion in an Ethos One Microwave digestion system (Milestone, Italy). For details of the digestion procedure, the reader is referred to ref. 24. Fe was subsequently chromatographically isolated from the GRM digests using AG MP-1 strong anion exchange resin in HCl medium, as first described in ref. 25 and 26. The purified Fe solutions were then subjected to MC-ICP-MS isotopic analysis.

2.3. Instrumentation

Iron isotope ratios were measured using a Thermo Scientific (Germany) Neptune multi-collector ICP-MS unit, equipped with a Pfeiffer (Germany) OnTool™ Booster 150 dry interface pump (130 m₃ h⁻¹ pumping speed). Fe isotope ratios were measured using 8 different instrument setups, realized via a combination of cold or hot plasma conditions, dry or wet plasma conditions and standard or ‘jet’ interface. Cold plasma conditions were obtained by a gradual decrease of the plasma RF power, optimization of the ICP torch position, and corresponding reduction of the nebulizer gas flow rate. The latter is needed to optimize the position of the zone with the highest analyte ion density to that of the sampling cone of the interface so as to achieve maximum sensitivity for Fe. Either high-transmission ‘jet’ Ni interface cones or ‘standard’ Ni interface cones were used to test the effect of an enhanced interface transmission efficiency on spectral interferences and the extent of instrumental mass discrimination. A 100 μl min⁻¹ concentric nebulizer with a double spray chamber with Scott-type and cyclonic sub-units or with an Aridus II desolvating nebulizer system (Teledyne CETAC Technologies Inc., USA) was used to study the effect of wet and dry plasma conditions. Detailed instrument settings are shown in Table 1.

2.4. MC-ICP-MS measurements and correction for instrumental mass discrimination

All sample solutions were prepared in 3% HNO₃. Depending on the instrument configuration, the Fe solutions were diluted to a final concentration between 50 ng ml⁻¹ and 1 μg ml⁻¹ in order to obtain similar intensities with the different configurations. The NIST SRM 986 Ni isotopic reference material was added to all samples and standards in a concentration equal to that of Fe to serve as an internal standard relied on for internal mass discrimination correction. Concentrations of samples and bracketing standards were fitted to within ±3%. The measurements of Fe isotope ratios were carried out in a sample-standard bracketing (SSB) sequence with the IRMM-
014 Fe isotopic reference material as an external standard. Correction for instrumental mass discrimination was performed according to the model proposed by Baxter et al. The model of Baxter corrects for both the mass- and time-dependent contributions to the instrumental mass discrimination. After this correction, the Fe isotope ratios are converted into delta notations, calculated following eqn (1) and relative to the bracketing isotopic reference material IRMM-014; here x denotes 56 or 57.

\[
\delta^{54}_{/54}\text{Fe} = \left( \frac{^{54}\text{Fe} / ^{54}\text{Fe}_{\text{corr,smp}}}{^{54}\text{Fe} / ^{54}\text{Fe}_{\text{corr,IRMM-014}}} - 1 \right) \cdot 1000
\]  

(1)

| Instrument settings, data acquisition parameters and multi-collector detector configuration for the Thermo Scientific Neptune MC-ICP-MS instrument used for Fe isotopic analysis at different instrument settings |

<table>
<thead>
<tr>
<th>Instrument settings</th>
<th>Hot plasma conditions</th>
<th>Cold plasma conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution mode</td>
<td>Medium</td>
<td>Medium, low</td>
</tr>
<tr>
<td>RF power, W</td>
<td>1260 (^{a})</td>
<td>600</td>
</tr>
<tr>
<td>Gas flow rates (^{a}), l min(^{-1})</td>
<td>Cool 15</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Auxiliary 0.8</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>Nebulizer 0.997</td>
<td>0.570</td>
</tr>
<tr>
<td>Dry plasma (Teledyne Cetac Technologies Aridus II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas flow rates (^{a}), l min(^{-1})</td>
<td>Nebulizer 0.680</td>
<td>0.580</td>
</tr>
<tr>
<td></td>
<td>Sweep Ar 4.85</td>
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</tr>
<tr>
<td></td>
<td>(N_2) 0.008</td>
<td>0</td>
</tr>
<tr>
<td>Spray chamber temperature, °C</td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>Membrane desolvator temperature, °C</td>
<td>160</td>
<td>160</td>
</tr>
</tbody>
</table>

**Wet plasma (pneumatic nebulization)**

| Sample uptake | Pumped via a peristaltic pump, 0.1 ml min\(^{-1}\) |
| Nebulizer     | Concentric, 100 \(\mu\)l min\(^{-1}\) |
| Spray chamber | Double, cyclonic and Scott-type sub-units |

**Interface**

| Interface pump | ‘Standard’ interface |
| Sampling cone  | High-efficiency dry interface pump (130 m\(^3\) h\(^{-1}\) pumping speed) |
| Skimmer cone   | ‘Jet’ interface |

| Skimmer cone          | H-type Ni skimmer (0.8 mm actual orifice \(\phi\)) |
|                       | X-type Ni skimmer (0.7 mm actual orifice \(\phi\)) |

| Data acquisition | Static; multi-collection |
| Idle time, s      | 3 |
| Integration time, s | 4.194 |
| Number of integrations | 1 |
| Number of blocks  | 9 |
| Number of cycles per block | 5 |

**Cup configuration for Fe isotope ratio measurements**

<table>
<thead>
<tr>
<th>Cup</th>
<th>(L_4)</th>
<th>(L_2)</th>
<th>(L_1)</th>
<th>(C)</th>
<th>(H_1)</th>
<th>(H_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclide</td>
<td>(^{54}\text{Fe})</td>
<td>(^{56}\text{Fe})</td>
<td>(^{57}\text{Fe})</td>
<td>(^{58}\text{Fe}, ^{58}\text{Ni})</td>
<td>(^{60}\text{Ni})</td>
<td>(^{62}\text{Ni})</td>
</tr>
<tr>
<td>Amplifier</td>
<td>(10^{11}\ \Omega)</td>
<td>(10^{11}\ \Omega)</td>
<td>(10^{11}\ \Omega)</td>
<td>(10^{11}\ \Omega)</td>
<td>(10^{11}\ \Omega)</td>
<td>(10^{11}\ \Omega)</td>
</tr>
</tbody>
</table>

\(^{a}\) Parameters optimized on a daily basis for the highest sensitivity and stability.
3. Results and discussion

An overview of the results obtained using the instrument configurations: cold/hot plasma conditions, wet/dry plasma and standard/jet interface cones (8 different conditions) is presented in Table 2. These results are discussed in more detail in the next paragraphs.

### 3.1. Wet plasma conditions

The peak profiles at the m/z ratios of 54, 56 and 57 obtained with wet plasma conditions and for different instrument settings are shown in Fig. 1. Fig. 1(A and B) presents peak profiles at the m/z ratios of 54, 56 and 57 measured in medium mass resolution mode (MR, m/Δm = 4500 with Δm being the difference between the masses where the signal intensity is 5% and is 95% of the plateau intensity, respectively) with standard interface cones and with hot (A) and cold (B) plasma conditions, respectively. With hot plasma conditions and at low mass resolution (LR, m/Δm ≈ 300), the peaks of 54Fe, 56Fe and 57Fe suffer from overlap with those of the Ar-based polyatomic ions 40Ar14N+ and 40Ar16O1H+, respectively. MR allows the separation of the Fe signals (separate plateau) from the polyatomic ion, enabling interference-free Fe isotope ratio measurements (A). A reduction of the plasma RF power from 1260 W down to 600 W efficiently suppresses the signals of 40Ar14N+ and 40Ar16O+ with this setup. Complete absence of these interferences with cold plasma conditions is confirmed by accurate 56Fe/54Fe isotope ratio measurement at LR. The 56Fe/54Fe isotope ratios measured for our in-house isotopic standard with cold plasma conditions in LR (δ56/54Fe = 0.452 ± 0.020SD, n = 5) and MR (δ56/54Fe = 0.450 ± 0.034SD, n = 5) are in agreement with the corresponding 2 year average (δ56/54Fe = 0.450 ± 0.030SD, 2SD, n = 200).

The results of δ56/54Fe measurements with cold plasma conditions at LR and with the standard interface in the geological reference materials PCC-1 (3 replicate sample preparations, 0.029 ± 0.085SD, 0.015 ± 0.048SD, and 0.016 ± 0.080SD, SD, n = 4), BHVO-2G (2 replicate sample preparations, 0.076 ± 0.100 and 0.071 ± 0.063, SD, n = 4) and IF-G (3 replicate sample preparations, 0.597 ± 0.608SD, 0.608 ± 0.054SD, and 0.660 ± 0.041SD, SD, n = 4) are in agreement with the corresponding literature values (see Fig. 2). The results obtained for the in-house isotopic standard and the geological reference materials clearly indicate that application of cold plasma conditions at LR can be an alternative to the traditionally applied MR with a hot plasma when using the standard interface and pneumatic nebulization for sample introduction.
At the same time, cold plasma conditions cannot fully remove the $^{40}$Ar$^{16}$O$^{+}$ ions, not even by reducing the RF power to values lower than 600 W. As a result, the $^{57}$Fe/$^{54}$Fe ratio can only be measured in MR. Transition to the cold plasma conditions is associated with a 2-fold loss in sensitivity, a re-optimization of the nebulizer and auxiliary gas flow rates and torch position. At the same time, when using LR and cold plasma conditions, a small gain in Fe sensitivity is achieved as compared to MR and hot plasma conditions.

Critically, after transition to cold plasma conditions, also the voltages of the focus lens array need to be re-tuned substantially to achieve maximum sensitivity and ensure signal stability. Although we didn’t directly monitor the amount of all the Ar-based ions (Ar$^{+}$ and Ar-containing polyatomic ions), extracted into the mass spectrometer from the ICP, the necessity to change the voltages of the focusing lens array seems to indicate a lower amount of extracted Ar species ions with cold than with hot plasma conditions.

Fig. 1(C and D) presents the peak profiles at $m/z$ ratios of 54, 56 and 57 measured with the high-transmission ‘jet’ interface cones and with hot and cold plasma conditions, respectively. Based on one year of experience with Fe isotopic analysis using the ‘jet’ and standard interface configurations in our group, an approximately two-fold improvement in isotope ratio measurement precision is observed when switching to the high-transmission ‘jet’ interface ($\delta^{56/54}$Fe = 0.450 ± 0.030$^{\text{m}}$ versus $\delta^{56/54}$Fe = 0.450 ± 0.070$^{\text{m}}$, $n = 17$). In comparison with standard interface cones, the sensitivity achieved with the ‘jet’ interface is 2-fold higher. At the same time, the higher ion transmission efficiency is associated with a significantly higher level of Ar-based spectral interferences, as can be seen in Fig. 1(C). With the ‘jet’ interface, however, the occurrence of Ar-based polyatomic ions is not suppressed as a result of operating the ICP under cold plasma conditions, such that Fe isotope measurements absolutely require a higher mass resolution under these conditions, see Fig. 1(D). At the same time, conversion to cold plasma conditions is associated with a 3-fold decrease in Fe sensitivity, which renders application of cold plasma conditions with high-transmission ‘jet’ interface cones futile.
needs to be tuned conditions, an N\textsubscript{2} the 40\textsubscript{Ar}14\textsubscript{N}\textsuperscript{+} signal. It makes application of LR impossible as the reference isotope, su

standard deviation of 4 replicate measurements of sample solution.

-0.8 \quad -0.4 \quad 0.0 \quad 0.4 \quad 0.8

\begin{align*}
\delta^{56/54}\text{Fe}_{\text{BMM-014}} \quad \%_{\text{oo}}
\end{align*}

\begin{align*}
\text{IF-G, Marin-Carbonne et al. 2011} \quad \bullet
\end{align*}

\begin{align*}
\text{IF-G, Dauphas et al. 2004} \quad \bullet
\end{align*}

\begin{align*}
\text{IF-G, Craddock & Dauphas. 2011} \quad \bullet
\end{align*}

\begin{align*}
\text{IF-G, this work} \quad \bullet
\end{align*}

\begin{align*}
\text{BHVO-2G, Oeser et al. 2014} \quad \Delta
\end{align*}

\begin{align*}
\text{BHVO-2G, this work} \quad \Delta
\end{align*}

\begin{align*}
\text{PCC-1, Dauphas et al. 2009} \quad \triangle
\end{align*}

\begin{align*}
\text{PCC-1, Craddock & Dauphas 2011} \quad \triangle
\end{align*}

\begin{align*}
\text{PCC-1, Fehr et al. 2008} \quad \bullet
\end{align*}

\begin{align*}
\text{PCC-1, this work} \quad \bullet
\end{align*}

![Fig. 2 Results from 56\textsuperscript{Fe}/54\textsuperscript{Fe} isotope ratio measurement of the geological reference materials PCC-1, BHVO-2G and IF-G as obtained under cold plasma conditions and at LR. The reference values correspond to the values reported in (ref. 11, 40–44). The error bars represent the internal measurement precision, expressed as the standard deviation of 4 replicate measurements of sample solution.](image)

3.2. Dry plasma conditions

Dry plasma conditions were achieved using the Teledyne Cetac Aridus II membrane desolvating nebulizer. This device utilizes a PFA C-type nebulizer (100 \textmu l min\textsuperscript{-1}) and a heated spray chamber, combined with a PTFE membrane desolvator unit. This combination provides an increase in sensitivity due to a more efficient analyte transfer into the plasma and a reduction in solvent-based interferences (e.g., oxide, hydride and hydroxide ions). The desolvation unit was operated with a 4.85 l min\textsuperscript{-1} Ar sweep gas flow rate (at 160 °C). The N\textsubscript{2} gas flow rate needs to be tuned finely. It was found that with hot plasma conditions, an N\textsubscript{2} flow rate of about 10 ml min\textsuperscript{-1} provides the highest Fe sensitivity, while with cold plasma conditions, the highest sensitivity was achieved at a near-to-zero N\textsubscript{2} flow rate. Aerosol desolvation provided a 7-fold improvement in the sensitivity for Fe with hot plasma conditions in comparison to pneumatic nebulization. Fig. 1(E and F) presents peak profiles at the m/z ratios of 54, 56 and 57 with hot and cold plasma conditions, respectively, when using standard interface cones and dry plasma conditions. The 40\textsuperscript{Ar}16\textsuperscript{O} and 40\textsuperscript{Ar}16\textsuperscript{O}1\textsuperscript{H}\textsuperscript{+} signals were successfully removed, rendering the signals of 56\textsuperscript{Fe} and 57\textsuperscript{Fe} interference-free, but the signal from 54\textsuperscript{Fe}, typically used as the reference isotope, suffers from significant overlap with the 40\textsuperscript{Ar}14\textsuperscript{N}\textsuperscript{+} signal. It makes application of LR impossible under such conditions (except for the 57\textsuperscript{Fe}/56\textsuperscript{Fe} isotope ratio). This 40\textsuperscript{Ar}14\textsuperscript{N}\textsuperscript{+} peak most probably originates from air inside the nebulizer and spray chamber of the Teledyne Cetac Aridus II or entrained within the ICP, because it is present even when the N\textsubscript{2} gas flow is switched off.

Conversion to cold plasma conditions is associated with a 1.5-fold loss in sensitivity compared to hot plasma conditions. In contrast to wet plasma conditions, the 40\textsuperscript{Ar}14\textsuperscript{N}\textsuperscript{+} interference peak is not fully removed by conversion to cold plasma conditions, although it is reduced significantly. This Ar\textsuperscript{N}\textsuperscript{+} interference makes it impossible to measure at LR under cold plasma/dry plasma/standard interface conditions.

Among all the configurations studied, the combination of membrane desolvation (dry plasma) and the high-transmission ‘jet’ interface with hot plasma conditions provides the highest sensitivity for Fe. Similarly to the situation with the standard interface cones, the signals of the Ar\textsuperscript{O} and ArOH\textsuperscript{+} ions are fully removed by membrane desolvation. However, this configuration results in an even higher level of 40\textsuperscript{Ar}14\textsuperscript{N}\textsuperscript{+}, which saturates the faraday cup detector with a 10\textsuperscript{11} Ω amplifier, rendering measurements at LR impossible. Although this interferring peak is resolved in MR, 56\textsuperscript{Fe}/54\textsuperscript{Fe} isotope ratio measurements were still not adequate (δ\textsuperscript{56/54}\textsuperscript{Fe} = 0.522 ± 0.041\textsubscript{oo}, SD, n = 5, compared with the reference value of 0.450 ± 0.030\textsubscript{oo}). This is likely the result of an insufficient abundance sensitivity of the instrument to avoid the influence of the tail of the huge 40\textsuperscript{Ar}14\textsuperscript{N}\textsuperscript{+} peak on the plateau of the 54\textsuperscript{Fe}\textsuperscript{+} signal. At the same time, 57\textsuperscript{Fe}/56\textsuperscript{Fe} ratios measured in MR were within the range expected for the in-house standard (δ\textsuperscript{57/56}\textsuperscript{Fe} = 0.220 ± 0.053\textsubscript{oo}, SD, n = 5, compared with the reference value of 0.228 ± 0.017\textsubscript{oo}).

Conversion to cold plasma conditions when using the high-transmission ‘jet’ interface and dry plasma conditions leads to a 10-fold drop in the sensitivity compared to that with hot plasma conditions. Although the occurrence of 40\textsuperscript{Ar}14\textsuperscript{N}\textsuperscript{+} is not fully avoided by cold plasma conditions, it is suppressed enough to allow 54\textsuperscript{Fe}\textsuperscript{+} to be measured in MR mode. When the N\textsubscript{2} gas flow rate in the membrane desolvator is decreased in order to provide the highest sensitivity, a small 40\textsuperscript{Ar}16\textsuperscript{O}\textsuperscript{+} interference peak. This small interference can be removed fully when the N\textsubscript{2} flow rate is optimized, but in the latter case, the overall Fe sensitivity is compromised.

3.3. Instrumental mass discrimination

Instrumental mass discrimination is an inherent drawback of MC-ICP-MS and it refers to a mass-dependence of the transmission efficiency of the ions of the target element’s isotopes\textsuperscript{22,28} from the ICP ion source to the detector. Typically, ions of the heavier of two isotopes are transmitted more efficiently than the ions of the lighter one. While the extent of mass discrimination is in the 1% per amu range at mid-mass, there is a stronger effect for light elements (up to several % per amu). Coulomb repulsion (space-charge effects) and scattering effects within the ion beam were previously suggested to be the main contributors to the instrumental mass discrimination,\textsuperscript{31} although other effects were also described.\textsuperscript{32,33} Various strategies to correct for instrumental mass discrimination are efficiently used,\textsuperscript{28,34,35} but reducing the extent of discrimination would possibly allow achieving even higher precisions for isotope ratio measurements and possibly avoid the need for target element isolation in many cases. Ar is the major component of the ICP discharge and its ions and excited atoms transfer the RF energy to the analyte via charge transfer and penning ionization. After charge separation, the Ar\textsuperscript{+} ions
It was found that when operating the ICP under cold plasma conditions (600 W), when the presence of Ar-based species in the beam is expected to be lower, the extent of instrumental mass discrimination observed for IRMM-014 solution of Fe (2.8% for $^{56/54}$Fe or 1.4% per amu) is lower than in the case of hot plasma conditions (6.4% for $^{56/54}$Fe or 3.2% per amu), as indicated in Fig. 3(A). This observation is in agreement with the observed effect for U on Pb isotope ratios reported earlier in the literature. However, with the high-transmission ‘jet’ interface and wet plasma conditions, the magnitudes of instrumental mass discrimination with cold and hot plasma conditions are nearly similar. This unexpected behavior with the ‘jet’ interface might be a result of the extraction of a higher number of Ar-based ions from the plasma by the high-transmission interface, thus rendering the effect of changing over to cold plasma conditions negligible.

**Fig. 3** Plots of isotope ratios measured using a Neptune MC-ICP-MS unit operated under 8 different instrument settings: hot/cold and dry/wet plasma conditions and standard/jet interface.Measured raw isotope ratios are presented in ln-scale for (A) Fe and Ni isotope ratios measured in IRMM-14 and NIST SRM 986, respectively, (B) Pb and Tl isotope ratios measured in NIST SRM 981 and NIST SRM 997, respectively (C) B isotope ratios measured in NIST SRM 951, (D) Li isotope ratios measured in IRMM SRM 16 and (E) Sr isotope ratios measured in NIST SRM 987. All the ratios presented are raw data – i.e. not corrected for instrumental mass discrimination. The arrows indicate the direction of the change in instrumental mass discrimination when the plasma power is decreased.
less significant. After 1 year of experience with the ‘jet’ interface, we have also observed that its regular application leads to an at least 2-fold faster degradation of the resolution slits compared to the standard interface, even though target analyte intensities are kept the same. We associate this observation with an increased amount of Ar-based ions extracted from plasma by the ‘jet’ interface. An indirect confirmation of our assumption concerning the effect that Ar-based species exert on the extent of instrumental mass discrimination observed for Fe is that when the strongest effect of switching over to cold plasma conditions on instrumental mass discrimination is observed (with standard interface cones and under wet plasma conditions), the voltages of the focusing lens array had to be re-tuned more significantly in order to achieve the highest intensity for Fe+.

Differently to Fe and Ni, both heavier elements Sr, Pb and Tl (Fig. 3(B and E)) and lighter ones Li and B (Fig. 3(C and D)) were found to suffer a larger extent of instrumental mass discrimination with cold plasma conditions than with hot plasma ones. This observation suggests that the prevailing mechanisms of mass discrimination are potentially different for Fe and the other elements evaluated. This indicates that the mechanisms behind instrumental mass discrimination have not been fully unraveled yet and systematic experimental and modeling studies should be carried out under different conditions to obtain a more profound insight into the underlying mechanisms.11

4. Conclusions

In the standard configuration (standard interface cones and sample introduction via pneumatic nebulization), cold plasma conditions can efficiently suppress/remove 40Ar16O+ and 40Ar14N+ ions, but not 40Ar18O+H+. Once the differences from 40Ar16O+ and 40Ar14N+ are fully removed by cold plasma conditions, accurate 56Fe/54Fe measurement can be accomplished at LR, providing a gain in intensity, at the cost of the possibility to monitor the 57Fe isotope. As additionally demonstrated by 56Fe/54Fe isotope ratio measurement of several geological reference materials, application of cold plasma conditions at LR can be an alternative to MR under hot plasma conditions.

Application of membrane desolvation nebulization (dry plasma) efficiently removes oxide-based interferences, but leads to a substantial increase in the 40Ar14N+ signal intensity. This peak of 40Ar14N+ can be suppressed with cold plasma conditions to some extent, but not fully removed.

Application of the high-efficiency ‘jet’ interface provides a higher sensitivity owing to a higher ion transmission efficiency, but it also significantly enhances the level of spectral interferences. None of the relevant interferences can be fully removed by application of cold plasma conditions with the ‘jet’ configuration of the plasma interface.

Overall, conversion from hot to cold plasma conditions is associated with a lower extent of instrumental mass discrimination for Fe, except with the ‘jet’ interface, with which the mass discrimination is nearly equal for hot and cold plasma conditions. Unexpectedly, this is not the case for the other isotopic systems studied, which again opens the questions concerning the processes giving rise to instrumental mass discrimination in MC-ICP-MS. For Fe, it is tempting to suggest that this effect might result from the introduction of fewer Ar-based ions into the mass spectrometer, which would alleviate space-charge effects to some extent. The fact that the voltages of the focusing lens array have to be re-optimized substantially seems to be an indirect indication of a significant change in the ion beam composition after switching from hot to cold plasma conditions.

Acknowledgements

The Flemish Research Foundation FWO-Vlaanderen is acknowledged for financial support through research project“GOZ3014N”, Marta Costas-Rodriguez thanks FWO-Vlaanderen for her post-doctoral grant. Frank Vanhaecke and Stepan Chernonozhkin acknowledge the research project funding by the Planet Topers, Interuniversity Attraction Poles Program initiated by the Belgian Science Policy Office (BELSPO).

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