Silicon isotope ratio measurements by inductively coupled plasma tandem mass spectrometry for alteration studies of nuclear waste glasses

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Figure

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Fig.1

Fig.2

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7 4 **Silicon isotope ratio measurements by inductively coupled plasma tandem**
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9 5 **mass spectrometry for alteration studies of nuclear waste glasses**
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Abstract

High-level long-lived nuclear waste arising from spent fuel reprocessing is vitrified in silicate glasses for final disposal in deep geologic formations. In order to better understand the mechanisms driving glass dissolution, glass alteration studies, based on silicon isotope ratio monitoring of ^{29}Si -doped aqueous solutions, were carried out in laboratories.

In this work were explored the capabilities of the new type of quadrupole-based ICP-MS, the Agilent 8800 tandem quadrupole ICP-MS/MS, for accurate silicon isotope ratio determination for alteration studies of nuclear waste glasses. In order to avoid silicon polyatomic interferences a new analytical method was developed using O_2 as the reaction gas in the Octopole Reaction System (ORS), and silicon isotopes were measured in mass-shift mode. A careful analysis of the potential polyatomic interferences on SiO^+ and SiO_2^+ ion species was performed, and we found that SiO^+ ion species suffer from important polyatomic interferences coming from the matrix of sample and standard solutions (0.5M HNO_3). For SiO_2^+ no interferences were detected and thus these ion species were chosen for silicon isotope ratio determination. A number of key settings for accurate isotope ratio analysis like, detector dead time, integration time, number of sweeps, wait time offset, memory blank and instrumental mass fractionation, were considered and optimized. Particular attention was paid to the optimization of abundance sensitivity of the quadrupole mass filter before the ORS. We showed that poor abundance sensitivity leads to a significant shift of the data away from the Exponential Mass Fractionation Law (EMFL) due to the spectral overlaps of silicon isotopes combined with different oxygen isotopes (i.e. $^{28}\text{Si}^{16}\text{O}^{18}\text{O}^+$, $^{30}\text{Si}^{16}\text{O}^{16}\text{O}^+$). The developed method was validated by measuring a series of reference solutions with different ^{29}Si enrichment. Isotope ratio trueness, uncertainty and repeatability were found to be $<0.2\%$, $<0.5\%$ and $<0.6\%$, respectively. These performances meet the requirements of the studies of nuclear glasses alteration and open up possibilities to use this method for precise determination of silicon content in natural samples by Isotope Dilution.

1. Introduction

Vitrification of liquid effluents issued from the reprocessing of spent nuclear fuel is considered to be the best solution for long-term immobilization of radionuclides[1]. Minor actinides and fission products in countries which have chosen the reprocessing of spent fuel are confined in borosilicate glasses. Those materials are considered particularly suitable for final disposal in deep, low permeable, geologic formations[2-4]. Work is still in progress to better understand the physical and chemical mechanisms of glass behavior under repository conditions[5, 6]. Water is considered to be the main cause of glass package corrosion and processes influencing the glass dissolution rate[7-13] must be understood sufficiently well to estimate the performance of nuclear waste glass in its disposal environment over geologic time scales. In this context, isotopic tracers are considered a powerful tool as they are able to trace ion exchanges between the solution and the glass[7, 14-16]. They are used to determine the contribution of the solution and the glass to the isotopic composition of the alteration layers. To this end, recent studies focused on leaching solutions containing amorphous silica highly enriched in ^{29}Si [7, 16] in which silicon isotope ratio evolution is monitored at regular time intervals.

For silicon isotope ratio measurements, gas source Isotope Ratio Mass Spectrometry (IR-MS)[17] was the predominant technique, but it has been shown that Multi Collection Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) offers important advantages[18, 19]. The latter technique offers faster analytical protocols (both sample preparation and analysis time), and much smaller samples are required. However, one of the largest drawbacks in mass spectrometry coupled with a plasma source is the occurrence of polyatomic interferences deteriorating isotope ratio accuracy. The presence of a plethora of polyatomic interferences for silicon isotopes has been well documented[18, 20-22], and some of the most prominent are related to $^{14}\text{N}_2^+$, $^{14}\text{N}_2\text{H}^+$ and $^{14}\text{N}^{16}\text{O}^+$, which significantly overlay the $^{28}\text{Si}^+$, $^{29}\text{Si}^+$ and $^{30}\text{Si}^+$ peaks, respectively. Silicon isotope polyatomic interferences originate from reactions of the sample solvent (i.e. diluted HNO_3) and entrained atmospheric gases in the plasma, and thus they cannot be removed by chemical purification of the analyzed samples.

In order to overcome this problem and to achieve accurate isotope ratio measurements, MC-ICP-MS with high-resolution capabilities was used[20, 23-25]. In the same context, High Resolution sector field ICP-MS (HR-ICP-MS) was also employed for the determination of silicon concentrations by isotope dilution[26, 27]. An hexapole collision/reaction cell based MC-ICP-MS was also used for silicon isotope ratio measurements in low resolution[28]. However, $^{14}\text{N}^{16}\text{O}^+$ interference on $^{30}\text{Si}^+$ was not resolved, and only $^{29}\text{Si}^+ / ^{28}\text{Si}^+$ ratios were measured.

Silicon isotope ratio determination by quadrupole ICP-MS (ICP-QMS) has not yet been reported to our knowledge. The lack of high resolution capabilities of the ICP-QMS makes silicon isotope ratio analysis quite complex. However, ICP-QMS has been widely employed for total silicon determination in a large variety of sample matrices. The isotope $^{28}\text{Si}^+$ was mainly used; and to alleviate the problem of polyatomic interferences, Dynamic Reaction Cell (DRC)[29-31], Collision Reaction Interface (CRI)[32, 33], and Octopole Reaction System (ORS)[34, 35] with different gases (NH_3 , O_2 , CH_4 , H_2 , He) were used.

Recently, Agilent Technologies developed a new ICP-MS using a tandem quadrupole mass filter (ICP-MS/MS)[36, 37]. This new instrument is equipped with an ORS which is placed between the two quadrupole mass filters. When the MS/MS mode is activated, the first quadrupole prevents all off-mass ions from entering the cell, offering superior potential to deal with spectral overlaps in reaction mode.

Since the commercialization of the ICP-MS/MS, several scientific works with very interesting analytical results have been published, and a tutorial review is given by Balcaen et al.[38]. With this new instrument, and by using O_2 as the reaction gas, total silicon determination was facilitated[39-42] due to a more efficient control of polyatomic interferences compared to a single quadrupole collision/reaction cell-based ICP-QMS. Moreover, with the ICP-MS/MS, more than one isotope can be used for total silicon determination; Amais *et al.*[40] investigated the potential use of $^{28}\text{Si}^{16}\text{O}^+$ and $^{29}\text{Si}^{16}\text{O}^+$ ion species, and Aureli *et al.*[41] successfully used the three silicon isotopes for silicon content determination of silica nanoparticles. In both cases, calibration curves of the respective silicon isotopes were used supposing silicon natural isotope abundance in samples and standard solutions.

However, although ICP-MS/MS was already used for isotope ratio measurements[37, 43-48], silicon isotope ratio determination has not yet been reported with this technique.

The main objective of this work is to explore the potential of the tandem quadrupole ICP for silicon isotope ratio determination for alteration studies of nuclear glasses. In the present study, we report a novel analytical method which takes into account a number of key settings for accurate silicon isotope ratio analysis like, polyatomic interferences, detector dead time, integration time, number of sweeps, wait time offset, memory blank and instrumental mass fractionation. For the validation of the method, a series of reference solutions with different ^{29}Si enrichment levels were used. The detailed analytical development of the method is presented below.

Experimental

2.1 Instrumentation

The Agilent 8800 ICP-MS/MS (Agilent Technologies, Tokyo, Japan) used in this work has recently been installed at the LT2S laboratory of the Institut de Radioprotection et de Sûreté Nucléaire (IRSN). O_2 was used as the reaction gas in the ORS, and silicon isotope ratio measurements were performed in mass shift mode ($^x\text{Si}^{16}\text{O}_2^+$). The O_2 was introduced through the 4th inlet line. A Peltier-cooled (2°C) Scott-type spray chamber with a PFA nebulizer (0.1 mL min⁻¹, ESI, USA) was used as the introduction system. In order to avoid discrete noise components caused by rotation of the peristaltic pump, the self-aspiration mode was used for the sample introduction to the ICP-MS/MS. All of the experimental parameters were optimized daily with a pure silicon test solution (100 ng g⁻¹) in order to obtain the optimum signal-to-background ratio of $m/z = 60$. Typical sensitivity and stability (Relative Standard Deviation, %RSD) values measured for 5 min at $m/z=60$ are $\sim 8 \times 10^5$ counts per second (cps) / ppm ($\mu\text{g g}^{-1}$) and $\sim 0.9\%$, respectively (1 sigma). Before each analytical session, a peak center mass calibration at $m/z=60$ (for the quadrupole mass filter after the ORS) was performed. It should be noted that peak center calibration is crucial for high order reaction product ions[49]. For all isotope measurements, the pulse counting mode was ensured. Typical instrumental settings and measurement parameters used throughout the experiments are summarized in Table 1.

2.2 Samples and reagents

Two silicas were used for the preparation of reference solutions and for silicon isotope ratio measurements: i) the Chemgas silica material, highly enriched in ^{29}Si ($^{28}\text{Si} < 0.01\%$, $^{29}\text{Si} = 99.4\%$, $^{30}\text{Si} = 0.6\%$), with $^{29}\text{Si}/^{30}\text{Si} = 165.7(8)$ and, ii) the standard reference material IRMM-018a[50] ($^{28}\text{Si} = 92.22036\%$, $^{29}\text{Si} = 4.68730\%$, $^{30}\text{Si} = 3.09234\%$), which for this work represents the natural silicon isotope abundance. The $^{29}\text{Si}/^{28}\text{Si}$ and $^{30}\text{Si}/^{28}\text{Si}$ isotope ratio values of IRMM-018a are equal to 0.0508272(40) and 0.0335320(42), respectively. For silica digestion, the alkali fusion method was used with KOH (Suprapur) flux and nickel crucibles. All dilutions were performed with 0.5 M (mol L⁻¹) HNO₃ obtained from Ultrapur (60 %) nitric acid and de-ionized water (18.2 MΩ.cm Milli Q system, Millipore, USA). The same acid was used as the blank solution and also for the instrument-washing procedure between standards and samples. Sample purification was performed using BioRad AG50 X-12 (200-400 mesh) cation exchange resin. For instrument-tuning and oxygen flow rate optimization in the ORS, a solution of 100 ng g⁻¹ of VWR pure silicon solution was used. For all measurements, Ultrapur O₂ gas 5.2 quality (99.9992% purity) was injected in the ORS.

2.3 Sample preparation

Around 10 mg of Chemgas and 200 mg of IRMM-018a were mixed with KOH (Suprapur) and melted at 600°C. The proportion of the mixture between the silica powder and the KOH flux used in this work is mSiO₂ / mKOH ~ 1/10. Potassium hydroxide was preferred over other fluxes such as lithium metaborate and alkaline carbonates because it provides the simplest composition and is easy to eliminate with ion-exchange resin. After alkali fusion, de-ionized water and diluted HNO₃ (0.5 M) was added into the digested materials in order to yield final solution concentrations of 100 ppm and 200 ppm for the Chemgas and the IRMM-018a, respectively. The solutions are then stored in chemically inert PTFE vessels.

Five reference solutions with different ^{29}Si enrichment were fabricated by gravimetric mixing of the Chemgas and the IRMM-018a solutions. Values of the reference solutions are presented in table 2. The $\delta^{29}\text{Si}$ ($\delta^{29}\text{Si} = [(^{29}\text{Si}/^{28}\text{Si})_{\text{sample}} / (^{29}\text{Si}/^{28}\text{Si})_{\text{IRMM-018a}} - 1] \times 1000$) of the mixing solutions was adjusted roughly to 10 ‰, 30 ‰, 50 ‰, 70 ‰ and 100 ‰. This isotope composition of the reference solutions was chosen because of the same order of magnitude with the silicon isotope ratio variation, which is observed for alteration studies of nuclear glasses[15].

$\delta^{30}\text{Si}$ in the mixing solutions is lower than 0.1 ‰. Isotope ratio uncertainties of the reference solutions were calculated by using the binary mixing equation and by propagating uncertainties of the isotope ratios, of the weights of the solutions as well as of their concentrations. Uncertainty propagation was performed using Monte Carlo simulations.

Before silicon isotope ratio analysis, reference solutions and the IRMM-018a were purified using BioRad AG50 X-12 (200-400 mesh) cation exchange resin, as described in detail by Georg *et al*[23].

2. Results and discussion

3.1 Mass-shift method for interference-free silicon isotope detection

As previously mentioned, accurate silicon isotope measurements by plasma source spectrometers is hampered by the presence of polyatomic interferences. As for this work, since diluted HNO_3 (0.5 M) is the matrix of standards and samples, the generated major polyatomic interferences will contain N, O and H. A list of the major potential silicon interferences (after Engström *et al*. [20]) is presented in table 3. In order to overcome this problem, oxygen was chosen as the reaction gas in the ORS. The reaction of Si^+ with O_2 is an O-atom transfer reaction ($\text{Si}^+ + \text{O}_2 \rightarrow \text{SiO}^+ + \text{O}$) and is slightly endothermic[51]. Typically endothermic reactions do not occur spontaneously. However, the plasma source and collisional processes in the cell provide additional energy, which promotes the reaction, enabling the O_2 mass-shift method to be applied.

In the mass-shift mode, the first quadrupole (Q1) works as a unit mass filter allowing only ions with $m/z = 28, 29$ and 30 entering the ORS to react with O_2 . The second quadrupole (Q2) selects ions with $m/z = 44, 45$ and 46 , corresponding to the ions of $^{x}\text{Si}^{16}\text{O}^+$. The oxygen flow in the ORS was optimized by controlling both the signal intensity and the signal-to-background ratio at $m/z = 44$, and the optimum flow was found at 0.26 mL min^{-1} .

In order to investigate if $m/z = 44, 45$ and 46 are free of polyatomic interferences, 0.5 M HNO_3 blank solution was measured, and count rate ratios ($\text{cps}_{45} / \text{cps}_{44}$, $\text{cps}_{46} / \text{cps}_{44}$) were reported in a three isotope plot and compared to the Exponential Mass Fractionation Law (EMFL, Fig.1). The EMFL expresses the kinetic isotope fractionation[52] and was used as an indicator of data quality as unresolved interferences should cause ratios to be shifted away from the EMFL. For the calculation of the EMFL, the IRMM-018a reference values were used. Typical count rates for cps_{44} , cps_{45} , cps_{46} , in blank solution were found to be $\sim 8.6 \times 10^3$, $\sim 6.0 \times 10^2$ and $\sim 18.5 \times 10^3$, respectively and typical $^{28}\text{Si}^{16}\text{O}^+$ signal for 100 ng g^{-1} of Si was $\sim 9 \times 10^5 \text{ cps}$.

As can be seen in figure 1, signal ratios for HNO_3 0.5 M (green squares) are not in good agreement with the EMFL. If the recorded signals at $m/z = 44, 45$ and 46 were generated only by $^{x}\text{Si}^{16}\text{O}^+$ species, $\text{cps}_{45, 46} / \text{cps}_{44}$ signal ratios correspond to $^{29, 30}\text{Si}^{16}\text{O}^+ / ^{28}\text{Si}^{16}\text{O}^+$ ratios, which should be in good agreement with the EMFL (silicon could come from blank impurities and/or instrument silicon-containing materials with natural isotope composition close to the IRMM-018a in both cases). The high $\text{cps}_{46} / \text{cps}_{44}$ ratios relative to the EMFL clearly point to the presence of an important interference at $m/z = 46$. $^{14}\text{N}^{16}\text{O}^+$ ion species, formed in the plasma after passing through the first quadrupole filter ($m/z = 30$), can react with O_2 in the ORS, forming $^{14}\text{N}^{16}\text{O}_2^+$ which interferes with $^{30}\text{Si}^{16}\text{O}^+$ at $m/z = 46$. In order to control the dependence of $^{14}\text{N}^{16}\text{O}_2^+$ formation against HNO_3 concentration, two HNO_3 solutions with different concentrations (0.1 M and 1 M) were fabricated from 60% Ultrapur HNO_3 , and each solution was measured twice. From figure 1, it is clear that higher HNO_3 concentrations favor not only $^{14}\text{N}^{16}\text{O}_2^+$ formation but also a polyatomic interference at $m/z = 45$. In fact, the same applies to $^{14}\text{N}_2^{16}\text{O}^+$ and $^{14}\text{N}^{15}\text{N}^{16}\text{O}^+$ ion species ($m/z = 29$) which are formed in the plasma and can react with O_2 in the ORS, producing $^{14}\text{N}_2^{16}\text{O}^{16}\text{H}^+$ and $^{14}\text{N}^{15}\text{N}^{16}\text{O}^+$ which interfere with $^{29}\text{Si}^{16}\text{O}^+$ at $m/z = 45$. It should be noted that even if $^{14}\text{N}_2^{16}\text{O}^{16}\text{H}^+$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}^+$ and $^{14}\text{N}^{16}\text{O}_2^+$ are potentially the dominant interferences in this work, to a lesser extent, $^{14}\text{N}_2^+$ and

$^{12}\text{C}^{16}\text{O}^+$ ($m/z = 28$) can react with O_2 producing $^{14}\text{N}_2^{16}\text{O}^+$ and $^{12}\text{C}^{16}\text{O}_2^+$ at $m/z = 44$, interfering with $^{28}\text{Si}^{16}\text{O}^+$ ion species at $m/z = 44$.

The potential formation of polyatomic interferences at $m/z = 44$, 45 and 46 was based on the summary table of polyatomic interferences in ICP-MS after Thomas W. May and Ray H. Wiedmeyer[21].

Therefore, on shifting m/z from 28, 29, 30 to 44, 45, 46, we observed that $^x\text{Si}^{16}\text{O}^+$ ion species are still affected by polyatomic interferences. Thus, this method was not satisfactory for silicon isotope ratio measurements. Moreover, it is worth mentioning that the dependence of the polyatomic interferences with the HNO_3 concentration makes their control between different standards and samples complicated and thus their correction quite complex.

Another product ion of the silicon reaction with O_2 is the $^x\text{SiO}_2^+$. The potential use of silicon dioxide for silicon isotope ratio measurements was investigated using the mass shift mode. The Q1 was settled at $m/z = 28$, 29, 30 and the Q2 at $m/z = 60$, 61, 62. For the oxygen flow optimization in the ORS, the signal intensity and the signal-to-background ratio at $m/z = 60$ were monitored, and the optimum flow was found at 0.24 mL min^{-1} . To control the presence of polyatomic interferences at $m/z = 60$, 61 and 62, the same procedure described previously was performed. Typical counts rates in blank solution (HNO_3 0.5 M) can be found in section 3.4. As can be seen in figure 1, signal ratios for all HNO_3 solutions are in good agreement with the EMFL, and no dependence of signal ratios with HNO_3 concentration was observed. This confirms that $m/z = 60$, 61, 62 are free of polyatomic interferences, and therefore, $^x\text{SiO}_2^+$ ion species were chosen for silicon isotope ratio determination.

$^{28}\text{SiO}_2^+$ was already used for total silicon concentration determination in complex matrices allowing for the improvement of detection limits relative to that obtained for silicon monoxide[39, 42].

Isobaric interferences at $m/z = 44$, 45, 46 and $m/z = 60$, 61, 62 ($^{44,46}\text{Ca}^+$, $^{45}\text{Sc}^+$, $^{46}\text{Ti}^+$, $^{60,61,62}\text{Ni}$) as well as their oxides (i.e. $^{44,46}\text{Ca}^{16}\text{O}^+$, $^{45}\text{Sc}^{16}\text{O}^+$, $^{46}\text{Ti}^{16}\text{O}^+$) were not considered because even if traces of these elements were still present in samples and standards after chemical purification, they were discarded from Q1 mass filter. Some of these interferences are presented in table 3.

A schematic representation of the operating principle of the tandem mass spectrometer for silicon isotope ratio measurement as well as the added value of the silicon isotope measurement as $^{x}\text{Si}^{16}\text{O}_2^+$ ion species are shown in figure 2.

3.2 Optimization of data acquisition parameters for isotope ratio measurements.

A number of key settings for accurate silicon isotope ratio measurements were tested and optimized. The reliability of the detector dead time (adjusted by the manufacturer at 31.8 ns) was controlled using silicon solutions with different concentrations (between 100 ng g⁻¹ and 700 ng g⁻¹). No significant variation of the $^{29,30}\text{Si}^{16}\text{O}_2^+ / ^{28}\text{Si}^{16}\text{O}_2^+$ ratios with the silicon concentration was observed, and thus no reevaluation of the detector dead time was needed.

The effect of the integration time and the number of sweeps per replicate on the isotope ratio precision was also investigated. The isotope ratio precision was expressed as the Relative Standard Deviation (%RSD) of the $^{29}\text{Si}^{16}\text{O}_2^+ / ^{28}\text{Si}^{16}\text{O}_2^+$ ratio for 10 replicates. For all these tests, a solution of 400 ng g⁻¹ of IRMM-018a was used. This concentration was chosen because it is close to that which was used for reference solution measurements. First, the integration time of the $^{29}\text{Si}^{16}\text{O}_2^+$ was varied and that of $^{28}\text{Si}^{16}\text{O}_2^+$ was kept constant at 1 s. During the optimization tests of the integration time, the number of sweeps was fixed at 1 and for this reason the integration time is the dwell time of the detected ion species.

As expected, the increase of the integration time significantly improved the %RSD of $^{29}\text{Si}^{16}\text{O}_2^+ / ^{28}\text{Si}^{16}\text{O}_2^+$ ratio, and the improvement follows the counting statistics law (Fig. 3a).

The counting statistics law is described by the following equation:

$$\% \text{RSD} = 100 \times \sqrt{(1/c_{29} + 1/c_{28})} \quad (1)$$

where c_{29} and c_{28} are the total counts (cps $\times$ integration time) for $^{29}\text{Si}^{16}\text{O}_2^+$ and $^{28}\text{Si}^{16}\text{O}_2^+$ respectively. As can be seen from the counting statistic law (Fig. 3a), integration times higher than 6 s result in a slight improvement of the %RSD. For this reason, and in order to keep the total analysis time as low as possible, 6 s was chosen as the integration time for both $^{29}\text{Si}^{16}\text{O}_2^+$ and $^{30}\text{Si}^{16}\text{O}_2^+$ as their abundances are similar. In the same context, the increase of the $^{28}\text{Si}^{16}\text{O}_2^+$ integration time beyond 1 s does not bring a significant improvement of the %RSD (figure 3a, dashed lines), and thus, 1 s was chosen as the integration time for $^{28}\text{Si}^{16}\text{O}_2^+$.

Then the integration times were kept constant (6 s for $^{29,30}\text{Si}^{16}\text{O}_2^+$ and 1 s for $^{28}\text{Si}^{16}\text{O}_2^+$), and the number of sweeps per replicate was varied. The role of the sweeps is to rapidly scan the different isotopes (ion species) in order to approximate a simultaneous measurement. As can be seen in figure 3b, the number of sweeps does not significantly influence the ratio %RSD, and 20 sweeps per replicate was chosen for silicon isotope ratio measurements. With this number of sweeps, the dwell time of $^{29,30}\text{Si}^{16}\text{O}_2^+$ and $^{28}\text{Si}^{16}\text{O}_2^+$ was 0.3 s and 0.05 s respectively.

Particular attention was paid to the optimization of the Wait Time Offset (WTO). The WTO is an additional wait time to the Q1 settling time, compensating for the slowdown of the ions in the ORS and giving the system time to arrive at steady state conditions[47, 53]. Different values of WTO were tested; and as can be seen in figure 4, no significant influence on the $^{29,30}\text{Si}^{16}\text{O}_2^+ / ^{28}\text{Si}^{16}\text{O}_2^+$ ratio was noticed. A WTO of 3 ms was selected for this work.

No replicates were performed for the measurements which were used for the optimization of the data acquisition parameters and ratio uncertainties presented in figure 4 were calculated following the next equation: $2 \times SD / \sqrt{n}$, where SD is the Standard Deviation and n the number of replicates per measurement, in this case $n = 10$.

3.3 Optimization of the abundance sensitivity

Several measurements of the IRMM-018a standard solution (400 ng g⁻¹) were performed, and silicon dioxide ratios were reported in a three-isotope plot (Fig. 5, blue dots). As can be seen, the data are significantly shifted away from the EMFL. As silicon measurement in its dioxide form is not suffering from polyatomic interferences, the influence of the abundance sensitivity of the Q1 mass filter was examined to explain this shift.

Abundance sensitivity is one of the most important figures of merit in a mass spectrometer system for precise isotope determination. It describes the signal contribution of the peak tail of a high-abundance isotope with mass M at neighboring masses ($M \pm 1$, $M \pm 2$, etc.). Although abundance sensitivity is influenced by several factors (design of the quadrupole rods[54], frequency of the power supply, etc.), kinetic energy of the ions, as they enter the quadrupole, operating vacuum[55] and peak resolution, has the biggest impact.

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3 328 Although sequential transmission of silicon isotopes into the ORS prevents spectral overlaps
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5 329 due to the presence of different oxygen isotopes[44] (i.e. $^{28}\text{Si}^{16}\text{O}^{18}\text{O}^+$, $^{30}\text{Si}^{16}\text{O}^{16}\text{O}^+$), accurate
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7 330 silicon isotope ratio measurement can be hampered by the contribution of $^{28}\text{Si}^+$ peak tailing on
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9 331 $^{29}\text{Si}^+$ and $^{30}\text{Si}^+$ (at M+1 and M+2). During $^{29}\text{Si}^+$ and $^{30}\text{Si}^+$ ion transmission through Q1mass
10 332 filter, a small amount of $^{28}\text{Si}^+$ enters the ORS and, $^{28}\text{Si}^{16}\text{O}^{17}\text{O}^+$ ($m/z = 61$) interferes with
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12 333 $^{29}\text{Si}^{16}\text{O}^{16}\text{O}^+$ ($m/z = 61$) shifting the data to the right and, $^{28}\text{Si}^{16}\text{O}^{18}\text{O}^+$ ($m/z = 62$) and
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14 334 $^{28}\text{Si}^{17}\text{O}^{17}\text{O}^+$ ($m/z = 62$) interfere with $^{30}\text{Si}^{16}\text{O}^{16}\text{O}^+$ ($m/z = 62$) shifting the data upwards (Fig.5).
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16 335 Therefore, $^{28}\text{Si}^+$ peak tail in high masses can explain the shift of the ratio data away from the
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20 337 When the ORS is pressurized with O_2 , the analyzer pressure increases from $\sim 2.4 \times 10^{-4}$ Pa (no
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22 338 gas in the ORS) to $\sim 6.3 \times 10^{-4}$ Pa (with 0.24 mL min^{-1} of O_2 in the ORS). It is well accepted
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24 339 that a lower vacuum in the analyzer can lead to more collisions between gas molecules and
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26 340 ions, resulting in a higher spread in kinetic energy of the ions and therefore more of a tail
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28 341 mainly at the low mass side of the main peak[55]. As our aim was to work in optimum
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30 342 condition of signal-to-background ratio, the O_2 flux was maintained at the same value and, no
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32 343 investigations were carried about the operating vacuum of the instrument.

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34 344 Parameters influencing the peak resolution and the kinetic energy of the ions entering the
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36 345 quadrupole were explored and optimized. The *Q1 Mass Offset*, *Q1 Mass Gain* and *Extract 2*,
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38 346 were settled in order to minimize $^{28}\text{Si}^+$ peak tailing contribution on $^{29}\text{Si}^+$ and $^{30}\text{Si}^+$. With the
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40 347 first two parameters, the peak resolution was improved from ~ 0.8 amu to ~ 0.57 amu (at 10%
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42 348 of peak high). The last parameter allowed the reducing of the ion kinetic energy, which leads
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44 349 to an increase in the residence time of ions in the quadrupole mass analyzer and results in
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46 350 improved mass separation. After parameter optimization, data fit well with the EMFL (Fig. 5,
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48 351 red dots), confirming that Q1 abundance sensitivity was efficiently improved. However, it
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50 352 should be noted that peak tailing improvement was accompanied by a sacrifice in sensitivity
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52 353 of about 15%. Sensitivity performance, presented in section 2.1 (Instrumentation), has taken
53 354 into account abundance sensitivity optimization.

3.4 Memory blank and instrumental mass fractionation

For memory blank, a washing procedure to reduce signal intensities was applied after every sample or standard. This procedure included a short pre-wash of the auto-sampler probe for 10 s with 0.5 M HNO₃ and a wash for 2 min with the same acid. After washing, silicon dioxide intensities were measured for 0.5 M HNO₃ blank solution and then corrected to sample and standard measurements. Typical intensities for ²⁸Si, ²⁹Si, ³⁰Si¹⁶O₂⁺ in blank solution were found to be ~ 800 cps, ~ 40 cps and ~ 30 cps, respectively. The wash procedure effectively reduces signal intensities to the original blank values. Procedural blank intensities were found to be at the same level with that of HNO₃ blank solution.

The sample-standard bracketing procedure (standard solution (IRMM-018a) – sample (²⁹Si-enriched reference solutions) – standard solution (IRMM-018a)) was adopted to correct for instrumental mass fractionation. To do this, the exponential mass fractionation law[56] was used:

$$R_{\text{true}} = R_{\text{meas}} (m_1 / m_2)^\beta$$

where R_{true} and R_{meas} are the true and measured isotope ratios for isotopes 1 and 2, with m_1 and m_2 being their respective atomic masses, and β , the mass fractionation factor. The β factors were calculated for both ²⁹Si / ²⁸Si and ³⁰Si / ²⁸Si ratios (in ^xSiO₂⁺ form) of the IRMM-018a standard solution ($\beta_{29/28}$, $\beta_{30/28}$). These factors were used for the correction of the isotope fractionation for the respective ratios (²⁹Si/²⁸Si, ³⁰Si/²⁸Si) of the reference solutions.

3.5 Isotope composition determination of ²⁹Si-enriched reference solutions

The developed method described above was applied to measure isotope composition in a series of reference solutions with different ²⁹Si enrichment (Table 2). Silicon isotope ratio measurements were found to be in good agreement with the values of the reference solutions (zeta-score < 2, according to ISO 13528[57]) that allowed for the validation of our method (Fig. 6).

Each measurement consisted of fifteen consecutive replicates and every solution was measured three times in order to estimate the method repeatability which was calculated as the %RSD for the three measurements.

Isotope ratio uncertainties were calculated for each individual measurement by propagating uncertainties of the mass fractionation factors ($\beta_{29/28}$, $\beta_{30/28}$) and of the measured silicon ratios (calculated using $2 \times \text{SD} / \sqrt{15}$). The detailed equation for uncertainty propagation used in this work can be found in Section 5 of the Supplementary Information by Gourgiotis et al.[58]. The method repeatability and the isotope ratio uncertainties were calculated for a coverage factor $k = 2$.

This method allowed achieving isotope ratio trueness, uncertainty and repeatability at <0.2%, <0.5%, <0.6%, respectively. Reference solution repeatability was similar to repeatability obtained for the IRMM-018a (0.2 % and 0.4 % for ^{29,30}Si/²⁸Si, n = 16) during the analytical protocol for the measurement of the reference solutions (~4h). These performances are similar to those obtained for silicon isotope measurements by HR-ICP-MS for silicon Isotope Dilution[27]. Average values of, isotope ratios, uncertainties, zeta-score, repeatability and trueness can be found in table 4.

3.6 Conclusion

This is the first time where silicon isotope ratio measurements were performed by quadrupole-based ICP-MS and more specifically by ICP-MS/MS. In order to avoid silicon polyatomic interferences, oxygen was used as the reaction gas in the ORS, and silicon isotope determination was performed in mass-shift mode using SiO_2^+ ion species. A number of key parameters for accurate isotope ratio measurements were carefully evaluated and corrected. With this new method, isotope ratio uncertainties, trueness and repeatability were found to be <0.5%, <0.2% and <0.6%, respectively. The method performances meet the requirements for nuclear glasses studies and more generally for investigations of silicate dissolution rates based on isotope doping[59].

We believe that this method can be seen as a valid alternative for HR-ICP-MS and be easily transferred to other application fields like geosciences, i.e. for precise silicon content determination in natural samples by Isotope Dilution (ID).

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Tables

ICP-MS/MS

Sample Introduction System

Nebulizer	PFA Micro-Concentric (ESI)
Spray chamber	Scott (quartz)
Torch	One-piece (quartz)
Sample gas (L min ⁻¹)	0.88
Ar makeup gas (L min ⁻¹)	0.36
Liquid uptake (μL min ⁻¹)	~150

ICP-MS/MS conditions

RF power (W)	1550
Plasma gas flow rate (L min ⁻¹)	15
Auxiliary flow rate (L min ⁻¹)	0.9
Extract 1 and 2 (V)	-3, -195
Q1 and 2 Mass Gain	152, 126
Q1 and 2 Mass Offset	131, 128
O ₂ reaction gas flow rate (mL min ⁻¹)	0.24
Sensitivity on ²⁸ Si ¹⁶ O ₂ ⁺ (cps ppm ⁻¹)	~8×10 ⁵
Signal on ²⁸ Si ¹⁶ O ₂ ⁺ for HNO ₃ 0.5M (cps)	~800

Acquisition parameters

Peak shape (points)	1
Integration time for ^{28, 29, 30} Si ¹⁶ O ₂ ⁺ (s)	1, 6, 6
Number of sweeps per replicate	20
Number of replicates per sample	15

Table 1. ICP-MS/MS operating conditions

$\delta^{29}\text{Si}$ (‰)	$^{29}\text{Si} / ^{28}\text{Si}$	$^{30}\text{Si} / ^{28}\text{Si}$
~10	0.051352(15)	0.0335349(85)
~30	0.052392(29)	0.0335414(81)
~50	0.053434(45)	0.0335481(91)
~70	0.054494(56)	0.0335541(85)
~100	0.056047(79)	0.0335635(87)

Table 2. Isotope ratio values of the reference solutions used for the method validation. All uncertainties are expressed for a coverage factor $k=2$.

m/z	Isotopes/molecules of interest	Interferences	
		Isobaric	Polyatomic
28	$^{28}\text{Si}^+$		$^{14}\text{N}_2^+, ^{12}\text{C}^{16}\text{O}^+$
29	$^{29}\text{Si}^+$		$^{14}\text{N}_2^1\text{H}^+$
30	$^{30}\text{Si}^+$		$^{14}\text{N}^{16}\text{O}^+$
44	$^{28}\text{Si}^{16}\text{O}^+$	$^{44}\text{Ca}^+$	$^{14}\text{N}_2^{16}\text{O}^+, ^{12}\text{C}^{16}\text{O}_2^+$
45	$^{29}\text{Si}^{16}\text{O}^+$	$^{45}\text{Sc}^+$	$^{14}\text{N}_2^{16}\text{O}^1\text{H}^+, ^{14}\text{N}^{15}\text{N}^{16}\text{O}^+$
46	$^{30}\text{Si}^{16}\text{O}^+$	$^{46}\text{Ca}^+, ^{46}\text{Ti}^+$	$^{14}\text{N}^{16}\text{O}_2^+, ^{46}\text{Ca}^{16}\text{O}^+, ^{46}\text{Ti}^{16}\text{O}^+$
60	$^{28}\text{Si}^{16}\text{O}_2^+$	$^{60}\text{Ni}^+$	$^{44}\text{Ca}^{16}\text{O}^+$
61	$^{29}\text{Si}^{16}\text{O}_2^+$	$^{61}\text{Ni}^+$	$^{45}\text{Sc}^{16}\text{O}^+$
62	$^{30}\text{Si}^{16}\text{O}_2^+$	$^{62}\text{Ni}^+$	$^{46}\text{Ti}^{16}\text{O}^+$

Table 3. List of potential polyatomic and isobaric interferences for silicon isotopes and $^x\text{SiO}_x^+$ ion species. Only major interferences for silicon isotopes are noted (after Engström *et al*[20].). Potential polyatomic interferences for the $^x\text{SiO}_x^+$ ion species were found in the paper of May T. W. and Wiedmeyer R. H.[21].

²⁹ Si / ²⁸ Si	$\delta^{29}\text{Si}$ (‰)				
	~10	~30	~50	~70	~100
Ratio value	0.05145(20)	0.05241(22)	0.05339(17)	0.05450(19)	0.05598(20)
% Uncertainty	0.38	0.42	0.32	0.35	0.36
% Repeatability (n=3)	0.013	0.087	0.30	0.17	0.016
% Trueness	0.19	0.03	-0.08	0.01	-0.12
Zeta-score	0.98	0.16	0.50	0.06	0.62
³⁰ Si / ²⁸ Si					
Ratio value	0.03354(13)	0.03357(15)	0.03352(13)	0.03359(13)	0.03361(14)
% Uncertainty	0.38	0.44	0.39	0.39	0.41
% Repeatability (n=3)	0.40	0.54	0.11	0.23	0.26
% Trueness	0.015	0.09	-0.08	0.11	0.14
Zeta-score	0.08	0.38	0.43	0.55	0.66

Table 4. Average values of isotope ratios, uncertainty, repeatability and trueness for different silicon reference materials. Zeta-score was expressed according to ISO 13528[57]. Isotope ratio uncertainties were calculated by taking into account uncertainties of the mass fractionation factors ($\beta_{29/28}$, $\beta_{30/28}$) and the measured silicon ratios. Isotope ratio repeatability was calculated as the %RSD for three measurements of the same solution. Trueness is expressed as the difference between the average isotope ratio and the values of the reference solutions. Uncertainty and repeatability are expressed for a coverage factor $k = 2$.

Figure captions

Figure 1. Three-isotope plot for $^x\text{Si}^{16}\text{O}^+$ (open squares) and $^x\text{Si}^{16}\text{O}_2^+$ (open circles) ion species in Ultrapur HNO_3 solutions with different concentrations. $^x\text{Si}^{16}\text{O}^+$ ratios are shifted away from the Exponential Mass Fractionation Law (EMFL) due to important polyatomic interferences. The good agreement of the $^x\text{Si}^{16}\text{O}_2^+$ ratios with the EMFL points to the absence of polyatomic interferences. Uncertainties of the ratios were calculated following the next equation: $2 \times \text{SD} / \sqrt{n}$, where SD is the Standard Deviation and n the number of replicates per measurement, in this case $n = 10$.

Figure 2. Simplified schematic representation of the operating principle of the tandem mass spectrometer for silicon isotope ratio measurements, showing the advantageous use of $^x\text{Si}^{16}\text{O}_2^+$ ions species compared to $^x\text{Si}^{16}\text{O}^+$.

Figure 3. Evolution of the Relative Standard Deviation (%RSD) of $^{29}\text{Si}^{16}\text{O}_2^+ / ^{28}\text{Si}^{16}\text{O}_2^+$ ratio measurements (red dots) for: (a) different integration times for $^{29}\text{Si}^{16}\text{O}_2^+$ and 1 s for $^{28}\text{Si}^{16}\text{O}_2^+$ and (b) different number of sweeps and fixed integration times (6 s for $^{29}\text{Si}^{16}\text{O}_2^+$ and 1 s for $^{28}\text{Si}^{16}\text{O}_2^+$). Solid and dashed lines represent the counting statistics law for different integration times for $^{28}\text{Si}^{16}\text{O}_2^+$.

Figure 4. $^{29,30}\text{Si}^{16}\text{O}_2^+ / ^{28}\text{Si}^{16}\text{O}_2^+$ ratios as a function of different Wait Time Offset. Uncertainties of the ratios were calculated following the next equation: $2 \times \text{SD} / \sqrt{n}$, where SD is the Standard Deviation and n the number of replicates per measurement, in this case $n = 10$.

Figure 5. Three-isotope plot for $^{29,30}\text{Si}^{16}\text{O}_2^+ / ^{28}\text{Si}^{16}\text{O}_2^+$ ratios before (blue dots) and after (red dots) abundance sensitivity optimization. For these measurements, a solution of 400 ng g^{-1} of the IRMM-018a was used. The solid line represents the Exponential Mass Fractionation Law (EMFL). Uncertainties of the ratios were calculated following the next equation: $2 \times \text{SD} / \sqrt{n}$, where SD is the Standard Deviation and n the number of replicates per measurement, in this case $n = 15$.

Figure 6. Measurements of reference solutions with different ^{29}Si enrichment (red dots). Each solution was measured three times. Solid lines represent values of the referent solutions and dashed lines their uncertainties. Isotope ratio uncertainties were calculated for each individual measurement by propagating uncertainties of the mass fractionation factors and of the measured silicon ratios. All uncertainties are expressed for a coverage factor $k = 2$. Values of isotope ratios, uncertainties, zeta-score, the method repeatability and trueness can be found in table 4.