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Stable silicon isotope analysis on nanomole quantities using MC-ICP-MS with a hexapole gas-collision cell

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We demonstrate in this study that a single focusing multiple collector inductively coupled plasma mass spectrometer (MC-ICP-MS) equipped with a hexapole gas-collision cell (GV-instrument® *Isoprobe*) can precisely determine the $\delta^{29}\text{Si}$ (2S.D., 0.2‰) using a total Si consumption of less than 14 nmole (390 ng Si). Testing and evaluation of background, rinse time, and major matrix effects have been performed in a systematic way to establish a procedure to measure $\delta^{29}\text{Si}$ in small quantities. Chemical purification prior to analysis is required to remove potential interferences. For data collected during a four-year period, the average $\delta^{29}\text{Si}$ value of IRMM-018 relative to NBS-28 was found to be -0.95‰ ($n = 23$, 2S.D. 0.16‰) with a 95% confidence interval ($-0.95 \pm 0.028\text{‰}$). The mean $\delta^{29}\text{Si}$ value of the Big-Batch standard was found to be -5.50‰ ($n = 6$, 2S.D. 0.26‰). Although determination of the $\delta^{30}\text{Si}$ measurements is not possible, with our current instrument we demonstrate that this system provides a fast and long-term reliable method for the analysis of $\delta^{29}\text{Si}$ in purified samples with low Si concentration (18 μM Si).

Introduction

Silicon is one of the most abundant elements in the continental crust, 28.8 wt%,¹ and constitutes the backbone of silicate minerals, which are continuously altered by weathering processes. Mass-balance studies of the oceanic Si cycle² have demonstrated that the gross input is primarily derived from the continents (84%) as dissolved silicate (DSi). The largest part by far is supplied by river transport, but eolian transport (7.5%) is also important. Submarine weathering of basalt is an additional source primarily at sea floor hydrothermal areas. As an essential element, silicon fertilizes the seas by stimulating the production of diatoms, which are a key phytoplankton group responsible for fuelling of the pelagic and benthic food webs and dominating the biological carbon sequestration in the oceans.^{3–5} Weathering of continental silicates is also suggested to be a long-term regulator of atmospheric CO_2 by sequestration of CO_2 carbonates during weathering and consecutive storage in the ocean and the deep sea sediments.⁶ The silicon cycle and its variation through time are crucial for the understanding of marine productivity and carbon sequestration and stable silicon isotopes constitute a tool that can be used to study these processes.

Variations in the stable silicon isotope composition (^{28}Si , ^{29}Si , ^{30}Si with abundances of 92.22%, 4.69% and 3.09%, respectively)⁷

have been documented in geological materials since the early 1950s. It has been shown that minerals formed at different temperatures were isotopically lighter (*i.e.* enriched in ^{28}Si) as a function of decreasing crystallization temperature.⁸ Based on theoretical calculations, Grant⁹ predicted a positive correlation between ^{30}Si enrichment and increasing silicon content in rocks. Another study showed that the enrichment of ^{30}Si in coexisting minerals in igneous rocks increases in the mineral order of biotite, quartz, feldspar, and that granitic rocks were enriched the most in ^{30}Si compared to meteorites and mafic rocks.¹⁰ However, like most of the other elements above 20 amu, only small isotopic variations of Si are found in nature (<10‰). Therefore, the analytical methods for determining Si isotope ratios need to have sufficient accuracy and reproducibility to determine silicon isotope ratio variations.

Currently, studies on variations in stable Si isotope ratios are focused on low-temperature processes such as biogenic opal formation,^{11–14} clay formation¹⁵ and chemical weathering processes in groundwater aquifers.^{16,17} Opal formation in the ocean is dominated by diatom assimilation of dissolved silicate from the surrounding aqueous phase to build up their silicified cell wall, a process which occurs in micromole Si concentration environments. The opal formed has an isotope value of about 1‰ lower than the source isotope value of DSi,¹⁸ *i.e.*, the heavier Si isotopes are enriched in surface waters as diatoms preferentially sequester the ^{28}Si to form opal. When diatom growth become Si-limited ($\text{DSi} < 5 \mu\text{mol/l}$) as is often the case in coastal^{19,20} and open ocean marine systems,⁵ the isotope fractionation becomes even higher. Thus, heavier Si isotopes in surface waters might indicate a shift in the ecosystem, which has occurred in many coastal waters from siliceous (diatoms) to non-siliceous phytoplankton species.^{21–23} Therefore, methods addressing stable isotope fractionation during opal formation should be operational on micromole concentrations.

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Until recently, Si isotope data in the literature have been limited, largely due to analytical difficulties. The traditional method of analysing Si isotope ratios is by fluorination of silicon and introducing the resulting SiF₄ gas into a gas-source isotope ratio mass spectrometer (IRMS).^{10,11,24} A new preparation method using the acid decomposition of Cs₂SiF₆ followed by the analysis of IRMS²⁵ improved the precision compared with the previous IRMS method. However, this technique is fairly complicated and requires a potentially hazardous preparation process.

The development of multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has opened up new possibilities for the determination of stable silicon isotopes with a precision comparable with that of IRMS.^{26–30} The major advantages with ICP source mass spectrometry is that the sample preparation is simplified and less hazardous, and it requires shorter analytical time and smaller sample size compared to gas-source IRMS.

Stable Si isotope measurements using MC-ICP-MS has mainly utilised double-focusing mass spectrometers with high mass resolution, *i.e.* $m/\Delta m > 1000$, to overcome the problem with polyatomic interferences derived from the ICP source. Instrumentation used for high-resolution analysis includes the *NuPlasma HR*, the *NuPlasma 1700* from NU instruments® and the *Neptune* from ThermoFisher®.^{26,30,31}

In this study, we have established a technique to analyse stable silicon isotopes using a single-focusing low-resolution ($m/\Delta m \sim 450$) MC-ICP-MS, the *IsoProbe* from GV instruments®. This instrument is equipped with a hexapole collision cell, which works as an energy filter. The technique permits higher sensitivity and less consumption of Si compared to the double-focusing high-resolution MC-ICP-MS.^{26,31,32} Below, we present detailed investigations of matrix effects, polyatomic interferences as well as instrument memory and background. Moreover, we document the long-term performance over four years using international standard materials.

Experimental

Si isotope standards

It is important that the standard materials used are well documented so that results from different sample measurements can be normalized and properly compared. Therefore, several standard materials with different isotope compositions have been introduced to compile data on silicon isotopes. Previously, the standard to which samples were compared with was the Caltech Rose Quartz³³ followed by the RM8564-NBS28-Silica Sand (National Institute of Standards and Technology); the latter is labelled in the following as NBS-28. NBS-28 is nowadays widely used as an universally accepted zero reference material for silicon isotopes, and has a similar Si isotope composition to that of Caltech Rose Quartz.³⁴ Other standard materials such as the Big-Batch and diatomite with an isotopic composition different than NBS-28 have been produced and used as secondary reference materials.^{16,17,30–32} An additional reference material, IRMM-018, has shown a larger than expected variation in isotopic compositions, which might be due to heterogeneity in this material.^{31,32,35}

Sample preparation

Solid materials obtained as part of the inter-laboratory comparison of Si isotope reference materials published by Reynolds *et al.*³⁰ have been prepared and used throughout this study. This included the standard material NBS-28 and IRMM-018, and the isotopically highly enriched (both in ²⁹Si and ³⁰Si) material called Big-Batch (prepared at UCSB, University of California Santa Barbara, and initially originated from a commercial Na-metasilicate).

The solid samples of standards were prepared by fusion with LiBO₂ and digested in HCl. About 42.5 mg SiO₂ was mixed with 150 mg LiBO₂ in a graphite crucible and fused at 1000 °C for 30 minutes. After cooling, the formed glass pearl was digested in 20 ml 2.5 M HCl on a shaking table, resulting in a solution containing 35.4 mM Si. This solution was immediately diluted 50 times with 0.075 M HCl, yielding a stock solution with a concentration of 0.7 mM Si in 0.12 M HCl, which was stored in acid-cleaned high-density polyethylene bottles. It is important to keep the Si concentration in samples below about 2 mM Si to avoid polymerization during storage.³⁶ After four-year storage, the Si concentration in the stock solution was still 0.7 mM Si, indicating that polymerization did not influence the concentration during this period. Water used for dilution was obtained from a Millipore® Milli-Q water purification system. The stock solution was diluted to 18 μM Si in 0.12 M HCl for Si isotope measurements.

The Big-Batch standard material contains about 1.5 μg/g Mo^{30,37} as a result from the preparation process using a molybdate co-precipitation technique, which may cause potential matrix effects. Screening of our stock solution by ICP-OES showed that there was about 4 μM Mo. Furthermore about 2.6 mM Li and 2.6 mM B was present in the Si solution.

Instrumentation

All the isotope measurements were carried out in the Laboratory of Isotope Geology at the Swedish Museum of Natural History using an *IsoProbe* MC-ICP-MS. The operating conditions of the instrument are summarized in Table 1. The ions generated in the plasma are introduced into the hexapole collision cell, where they collide/react with a collision gas. This reduces the energy spread from about 15 V to less than 1 V, and makes the ions suitable, after acceleration, for direct entry into the mass spectrometer. The collision cell also reduces the presence of ions interfering with the measured Si isotopes by collisions between the ions and the collision gas as described below. The low energy spread of the ions allows the refocused beam width to be less than the width of the collector slits, leading to the flat-topped peaks required for accurate isotope ratio measurements. A large variety of gases and gas mixtures can be used in the collision cell and for isotope ratio measurement noble gases such as Ar are frequently used. For optimal transmission of light isotopes, Helium is selected as a collision gas.³⁸

A typical torch material is quartz, but for the Si isotope measurements we used a torch in which the outer tube of the torch is made of sialon, an aluminium–silicon–oxynitride alloy, which has a high wear resistance, good durability and low contamination potential. The inner part of the torch is made of

Table 1 Instrument settings

Multi-collector settings		
Cup		Mass
Axial		²⁸ Si
High 3		²⁹ Si
High 6		³⁰ Si
^a Denoted values of these parameters are kept constant during one entire measurement, but it may vary between different measurements in this given range.		
ICP parameters		
	Values	Units
High tension ^a	6000~6020	V
Cooling Ar flow ^a	14	l/min
Intermediate Ar flow ^a	0.95~1.05	l/min
Collision He flow ^a	8~9.9	l/min
Neb 1 gas flow ^a	50~60	μl/min
Hexapole RF amplitude ^a	30~50	%
Outer tube of torch	Syalon	—
Inner tube of torch	Alumina	—
Cone	Nickel	—
Cetac® Aridus settings		
Spray Chamber	95	°C
Desolvator	160	°C
Sweep gas flow ^a	3.60~3.80	ml/min
N ₂ gas flow	0	ml/min

pure aluminium, which not only has extremely high-temperature stability and wear resistance, but also helps to provide protective atmospheres at high temperature to eliminate contamination or impurity.

The Si concentrations both in the standard and unknown solution were kept at about 18 μM. The solution was introduced into the plasma using a Cetac® Aridus desolvating nebulizer with a sample uptake rate of approximate 50–60 μL/min. A ^{28}Si signal of 8~10 V was usually obtained, but the ^{28}Si signal could occasionally decrease to ~7 V during measurements. The formation of gaseous SiCl_4 can be neglected in water-rich solution.

Interferences

The Si isotope ratio measurement using MC-ICP-MS is usually affected by mass bias, isobaric interferences, and matrix effects. Potential isobaric interferences include $^{14}\text{N}_2$ and $^{12}\text{C}^{16}\text{O}$ on the ^{28}Si peak, $^{14}\text{N}^{15}\text{N}$ and $^{12}\text{C}^{16}\text{O}^1\text{H}$ on the ^{29}Si peak and $^{14}\text{N}^{16}\text{O}$ on the ^{30}Si peak. The mass resolution on our *Isoprobe* is too low ($m/\Delta m \sim 450$) to fully resolve the polyatomic interferences, but they could be reduced by using the hexapole collision cell. The three Si isotopes are influenced by the interfering ions, but compared to the atomic ions the polyatomic ions are slightly heavier and they mainly affect the peaks on the high-mass side (Fig. 1). By adjusting the measurement position to the low-mass side, a well defined flat-top peak can be found for ^{28}Si and ^{29}Si (Fig. 1). However, due to a relatively large isobaric interference from $^{14}\text{N}^{16}\text{O}$ on the smallest peak, ^{30}Si , no flat area can be defined and we are thus not able to measure this isotope (Fig. 1).

Fig. 1 Mass scans with the signals in volts for the ^{28}Si , ^{29}Si and ^{30}Si peaks and possible isobaric interferences from polyatomic ions using 18 μM Si solutions. The isobaric interferences are given and marked by the shade area as well as their contribution to the signal in volts. The dashed vertical lines on low and high mass side show the positions for test measurements of Si isotope ratios, and the area between them is the measurement position.

Keeping the measurement position stable is important and this was tested by determination of the $^{29}\text{Si}/^{28}\text{Si}$ ratio at two positions, one on the low mass side and the other on the high mass side, of the flat area for ^{28}Si and ^{29}Si . The $^{29}\text{Si}/^{28}\text{Si}$ ratio was measured and it was found that the ratios determined on both sides of the measurement position (marked in Fig. 1) differ from the ratio determined at the measurement position. This demonstrates that it is necessary to reduce the isobars to a minimum and carefully adjust the position of the peak before data collection.

By using the hexapole as a reaction cell we can reduce the isobaric interferences to obtain sufficient peak flatness to measure the $^{29}\text{Si}/^{28}\text{Si}$ ratio. This is similar to what Moureau *et al.*³⁹ have demonstrated when injecting N_2O in a reaction cell to remove the isobaric interference ^{92}Zr for ^{92}Mo efficiently and thus make it possible to accurately measure Mo isotope ratios also by using an *Isoprobe*.

Measurement procedure

An individual measurement of a standard/sample consisted of 5 blocks and 12 cycles per block, with the integration time of 10 seconds for each cycle. Before each measurement the inlet system was rinsed for 180 seconds with 0.12 M HCl. After the rinsing, there was an uptake period of 180 seconds before data acquisition commenced. In total it took about 13 minutes to measure one standard/sample. With an uptake flow of 50~60 μL/min, the

amount of Si consumed during the measurement was approximately 14 nmol (390 ng).

In order to obtain the relative Si isotope variation, we used the standard-sample-standard bracketing technique. This method is frequently applied for determination of isotope ratio using MC-ICP-MS but requires identical matrix conditions in the sample and standard solutions.³⁹ Each sample was measured using the standard-sample-standard bracketing technique including nine brackets, *i.e.*, nine individual measurements. Before and after each measurement, a blank solution was introduced for 210 seconds and measured with an integration time of 60 seconds. It took approximately 160 minutes to acquire each reported isotope ratio, which was the average value calculated from nine brackets with two times the standard deviation (2S.D.) or at 95% confidence interval.

Instrument drift

When using the *Isoprobe* for isotope ratio determination, a drift in the ratio during the measurement period is commonly observed. This drift can be both in the upward or downward direction, *i.e.*, increasing or decreasing ratios with time. Typically a systematic variation towards a single direction was observed (Fig. 2). Fig. 2a shows the machine upward drift in an individual measurement, which was the case for most of the analyses, and Fig. 2b illustrates the downward drift. The drift in the $^{29}\text{Si}/^{28}\text{Si}$ ratio appeared not only in individual measurements, but was also observed during the entire analysis using the standard-sample-standard bracketing technique (Fig. 3). The systematic drift in the ion beam signal is independent of the integration time. This type of drift in the isotope ratio is frequently observed also for other heavier elements such as S and Pb, but can mostly be

Fig. 2 (a) example of upward and (b) downward drift in the measured $^{29}\text{Si}/^{28}\text{Si}$ ratios from two individual measurements including 60 cycles. The dotted lines show the 95% confidence interval and the solid line shows the linear trend.

Fig. 3 (a) examples of upward and (b) downward drift in two measurements of $^{29}\text{Si}/^{28}\text{Si}$ for IRMM-018 vs. NBS-28 and Big-Batch vs. NBS-28. (a) Nine points with the NBS-28 measured 5 times and (b), IRMM-018/Big-Batch as unknown solutions was measured 4 times. Both graphs show the linear trend.

effectively corrected using the standard-sample-standard bracketing technique.

Mass discrimination or mass bias is observed in all mass spectrometric techniques and can generally be described as the time dependent deviation between observed and “true value”. In ICP-MS the mass bias is the result of a number of processes in the plasma and in the transmission through the ion optical system.⁴⁰ Generally the mass bias decreases with increasing mass and is most pronounced for the light isotopes.⁴¹ The applied standard-sample-standard bracketing technique can be used to compensate for mass bias, matrix interferences and backgrounds.²⁸ However, this requires that the signals obtained from both the standard and the samples are equally high and that the blank solutions have the same matrix as the analytical solution.

The reported delta values in per mil units were calculated according to Equation 1,

$$\delta^{29}\text{Si} = \left(\frac{\left(\frac{^{29}\text{Si}}{^{28}\text{Si}} \right)_{\text{sample}}}{\left(\frac{^{29}\text{Si}}{^{28}\text{Si}} \right)_{\text{standard}}} - 1 \right) \cdot 1000 \quad (\text{Equation 1})$$

Matrix effects

Matrix effects are caused by the presence of additional ions, such as Na^+ , Mg^{2+} , Al^{3+} , Ca^{2+} , K^+ , in the Si solution. These ions can affect the stability of the ion beam signal and lead to inaccurate results. Presence of Na^+ in the analytical solution is known to suppress the ion beam of the analyte, *i.e.* Si. In this study, we made a detailed study of the effect of increasing concentration of Mg^{2+} in the analytical solution on the $\delta^{29}\text{Si}$ value. Aluminium,

the most abundant metal in the earth crust, might also be a potential problem causing matrix effects. To examine these possible interferences on the $\delta^{29}\text{Si}$ value, a series of measurements with varying concentrations of Mg and Al were performed by adding these elements to the IRMM-018 standard solution. The experiments were performed in 2005 and repeated using different machine settings during 2008/09.

The presence of Mg shown as an increased Mg/Si ratio (Fig. 4) seems to increase the spread in the $\delta^{29}\text{Si}$ value even though the average value of each measurement was similar. At high Mg/Si ratio, >1 , the $\delta^{29}\text{Si}$ seems to decrease towards lower values and the precision also seems to decrease. This might be due to changing conditions in the plasma when the ion strength is increasing.

In contrast to Mg, the presence of Al causes a substantial effect on the $\delta^{29}\text{Si}$ value and larger errors (Fig. 5). At Al/Si weight ratios as low as 0.1, the $\delta^{29}\text{Si}$ is lowered by $>0.7\text{‰}$. In addition to these detailed investigations of the effects of Mg and Al, we have observed that Si intensity can be greatly reduced in solutions with high concentrations of Na^+ and Ca^{2+} , which might also cause poor measurement accuracy. However, this effect on the $\delta^{29}\text{Si}$ has not been quantitatively determined.

The formation of $^{26}\text{MgH}_2^+$, $^{27}\text{AlH}^+$ and $^{27}\text{AlH}_2$ are potential problems in that they cause isobaric interferences. However, the formation of metal hydrides is likely to be small and can most

likely be omitted. In addition, van den Boorn *et al.*⁴² reported that anionic species, such as SO_4^{2-} , could also cause a substantial matrix effect on the Si isotope measurement.

The Li and B ($67.5\text{ }\mu\text{M}$ Li and $65\text{ }\mu\text{M}$ B) in the $18\text{ }\mu\text{M}$ Si solution of the fused standards materials were not removed. However, we cannot exclude the possibility for a matrix effect from those elements on the Si isotope ratio. This was avoided by addition of Li and B to all solutions to keep the Li and B concentrations on the same level and thus affect the plasma in a similar way. We adjusted the amount of Li and B in the samples and measured the elemental concentrations by ICP-OES before Si isotope analysis to assure that the matrix of Li and B were properly adjusted.

Clearly, the presence of alkali metal and alkaline earth metals as well as Al ions in the analytical solution could severely affect the precision and accuracy of the Si isotope ratio measurements. Also other species including both cations and anions could be a potential problem for high precision Si isotope measurements. Therefore it is crucial to remove interferences and isobars by chemical purification prior to the measurements. Alternatively, matrix effects from elements like Li and B, which are hard to quantitatively remove by column chemistry, could be eliminated by determining and adjusting the concentrations in samples.

Background and rinse time test

Since the variations in $\delta^{29}\text{Si}$ values between samples are likely to be small, even a tiny amount of Si from a previous standard/sample remaining in the nebuliser and the analytical system could potentially affect the measured ratio. The system was rinsed using 0.12 M HCl between each individual measurement but the effectiveness of this cleaning needed to be tested thoroughly. The rinse time was investigated by measuring IRMM-018 relative to NBS-28 and the results show that a rinse time of at least 150 seconds between samples is necessary to remove the previous samples. A rinse time of 180 seconds was applied to ensure that the entire system was clean. We efficiently eliminated the instrument memory effects and could reach an error of $\delta^{29}\text{Si}$ less than 0.2‰ (2S.D.).

Instrumental background is mainly derived from the analysed solutions, but the build-up of impurities on the cones as well as on the transfer optics over time also contributes to the background. We investigated the background contribution by using a 180 s rinse time and conducting blank determinations at the beginning and end of each measurement. The observed background contributed up to approximately 2.5‰ on the ^{28}Si and ^{29}Si intensities. The background was found to be similar before and after the analysis. Part of this background comes from build-up of impurities in the inlet area of the instrument. By careful cleaning it could be reduced to about 0.6‰ . However, during a session of measurements the background was generally found to be stable and could be corrected using the standard-sample-standard bracketing technique.

Results and discussion

Long-term reproducibility

To determine our ability to precisely measure and reproduce the $\delta^{29}\text{Si}$ value using a MC-ICP-MS equipped with a collision cell, we

Fig. 4 Testing the influence of varying ions in the matrix on the $\delta^{29}\text{Si}$ by using increasing Mg/Si weight ratios. Data were collected both in 2005 and 2008/09, respectively. The used Si concentration was $71\text{ }\mu\text{M}$ in 2005 and $18\text{ }\mu\text{M}$ in 2008/09.

Fig. 5 Testing the influence of varying ions in the matrix on the $\delta^{29}\text{Si}$ by using increasing Al/Si weight ratios. Data were collected both in 2005 and 2008/09, respectively. The used Si concentration was $71\text{ }\mu\text{M}$ in 2005, and $18\text{ }\mu\text{M}$ in 2008/09.

Fig. 6 The $\delta^{29}\text{Si}$ measured in IRMM-018 relative to NBS-28. Section 1 was performed in 2005 and Section 2 was measured in 2008/09. The same solutions and the same machine were used in both sections although the settings of the machine varied between these two periods. Each point represents the average value of nine brackets in one measurement.

Fig. 7 The $\delta^{29}\text{Si}$ measured in the Big-Batch relative to NBS-28. The two sections are the results measured in 2005 and 2008/09. Each point represents the average value of nine brackets in one measurement.

have analysed the IRMM-018 and the Big Batch standard. The data have been obtained in periods during 2005 and from October 2008 to August 2009 (Fig. 6 and 7). Data from measurements of IRMM-018 relative to NBS-28 are reported in Fig. 6, comprising the first measurement period in 2005 with the integration time of 5 and 7 seconds and the second in 2008/2009 with the integration time of 10 seconds. The data for IRMM-018 comprising the entire period has been examined statistically using a two sample t-test assuming equal variance and normally distributed errors to test whether the measured results in both periods were similar. No statistically distinct difference between the two periods could be found ($p \leq 0.0014$, $n = 23$).

Table 2 Summary of the results in this study and comparison with other published data

Standard	$\delta^{29}\text{Si}$ (‰)	2S.D.	n
IRMM-18	-0.95	0.16	21
IRMM-18 ^a	-0.85	0.14	740
Big-Batch	-5.51	0.25	6
Big-Batch ^a	-5.35	0.3	198
Big-Batch ^b	-5.39	0.3	28
Big-Batch ^c	-5.39	0.17	15

^a Inter-laboratory calibrated Si isotope values.³⁰ ^b Measurements from van den Boorn *et al.*³⁷ ^c Measurements from Chmeleff *et al.*³¹

The results for both the IRMM-018 and the Big-Batch are summarised in Table 2 along with literature data. The average $\delta^{29}\text{Si}$ value for IRMM-018 during the entire four-year period was found to be -0.95‰ (2S.D. 0.16‰) with a 95% confidence interval of $\pm 0.028\text{‰}$. The results are in agreement with the value of -0.85‰ (2S.D., 0.14‰) obtained in the inter-calibration study by Reynolds *et al.*³⁰ The precision (2S.D.) for a reported $\delta^{29}\text{Si}$ value is typically between 0.1 and 0.2‰ , although smaller and larger errors (0.061 to 0.27‰) occurred occasionally, most probably caused by machine random errors during measurements.

Similar to IRMM-018, we have also analysed the Big-Batch standard and our mean $\delta^{29}\text{Si}$ value was found to be -5.50‰ (2S.D., 0.26‰ , Fig. 7). This can be compared to previously published values of -5.39‰ (2S.D., 0.17‰),³¹ -5.39‰ (2S.D., 0.3‰)³⁷ and -5.35‰ (2S.D., 0.3‰) reported by Reynolds *et al.*³⁰ in the inter-calibration study (Table 2).

The amount of Si consumed during one measurement was approximate 400 ng per sample. This is comparable with other methods using double-focusing high-resolution MC-ICP-MS consuming between 200 and 500 ng Si,^{26,30,31} but lower than the 3 μg Si typically used by a double-focusing low-resolution MC-ICP-MS.²⁸ The sensitivity for ^{28}Si was found to be ~ 18 V/36 μM Si (1 mg/L), which is >3 times higher than 5 ± 0.5 V/36 μM observed by Engström *et al.*²⁷ and slightly higher than ~ 13 V/36 μM reported by Georg *et al.*²⁶ using a high-resolution MC-ICP-MS. Clearly, our method yields high signals using small amounts of Si which can produce $\delta^{29}\text{Si}$ values with a precision similar to other methods.

Conclusion

This study demonstrates that by using a single focusing low-resolution MC-ICP-MS equipped with a hexapole gas-collision cell, we can precisely and accurately measure the $\delta^{29}\text{Si}$ (2S.D., 0.2‰) with a total Si consumption of less than 14 nmol (390 ng Si). Analysis of the same standard material performed during 2005 and 2008/09 gave a similar precision and accuracy. Given that the instrument's hardware and settings have been partly changed during the last four years, the reproducibility in $\delta^{29}\text{Si}$ is found to be stable. For precise measurement of $\delta^{29}\text{Si}$ values it is necessary to use a Si solution with low concentrations of interference ions to avoid matrix effects. Thus, chemical purification to remove these interferences of the Si solution prior to analysis is required. Alternatively, matrix effects from elements like Li and B, which are not easy to remove by using ion-exchange, can be eliminated by determining and adjusting the concentrations in samples and standards to the same level.

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