

New sample preparation techniques for the determination of Si isotopic compositions using MC-ICPMS

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Abstract

Techniques for the purification of Si for the determination of its natural stable isotopic composition have in the past been based on the requirements for gas-source mass-spectrometry, rather than MC-ICPMS. For high precision analyses by MC-ICPMS it is essential to have very pure solutions and in this paper a new technique is presented for the separation and purification of Si from natural samples to improve the determination of isotope ratios. A method has been optimised based on alkaline fusion followed by ion-exchange chromatography. The application to natural samples, such as river water samples and silicate mineral/rock samples is demonstrated. Alkali fusion avoids the use of hydrofluoric acid (HF), which introduces difficulties for the determination of Si isotope ratios using MC-ICPMS. By eliminating HF a 30–40% increase in sensitivity is achieved as well as a marked enhancement of mass bias stability leading to a factor of 2 improvement in reproducibility. The cation-exchange method enables processing of very small samples (3.6 µg Si) and a rapid and effective separation of Si from other cationic species. The overall recovery of Si during the entire procedure is better than 98% and no Si isotope fractionation is generated. Matrix tests demonstrate that this method is suitable for silicates, and that typical sulphate and nitrate abundances of river waters have no effect on measured Si isotope composition. The latter aspect is vital for analysis of river waters since the technique does not separate dissolved Si (silicic acid) from ambient anionic species. Overall, the new method presents a faster, safer and more reliable way to measure Si isotopes via MC-ICPMS.

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1. Introduction

Most studies published so far on silicon (Si) isotopes have been carried out using gas source mass spectrometry (GS-MS) (Douthitt, 1982; De La Rocha et al., 1996, 1997, 1998, 2000; Ding et al., 2003, 2004; Varela et al., 2004; Ding et al., 2005). The determination of Si isotope ratios

by GS-MS requires the fluorination of silicon as mass-ratios are measured as SiF_3^+ ions. Fluorination occurs within a vacuum line, either as the direct fluorination of purified SiO_2 (Allenby, 1954) or by the thermal decomposition of Ba_2SiF_2 (Reynolds and Verhoogen, 1953a). Sample preparation is complicated and time consuming, and requires the use of hazardous chemicals such as BrF_5 or F_2 (De La Rocha et al., 1996; Ding, 2004). With the advent of multi-collector inductively coupled plasma mass-spectrometry (MC-ICPMS) these problems

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can be avoided, facilitating the establishment of Si isotopes as a standard method in isotope geology and biogeochemistry. However, Si must be introduced to the plasma as an aerosol, so the sample preparation has to produce pure solutions (typically mildly acidic) of silicic acid rather than purified SiO₂ or Ba₂SiF₂. Indeed, the purity requirements in order to avoid ‘matrix’ problems during mass-spectrometric analysis are probably more acute for analysis using MC-ICPMS.

It has been shown that MC-ICPMS can be used to determine accurate and precise Si-isotope ratios (De La Rocha, 2002; Cardinal et al., 2003). The ability to replicate measurements easily leads to higher precision and confidence concerning the measured isotope ratios. Unfortunately, the analysis of Si isotopes via MC-ICPMS has a major analytical difficulty; it is hampered by polyatomic interferences of CO⁺, N₂⁺, NO⁺ and SiH⁺ in the Si mass spectrum. The large ¹⁴N¹⁶O⁺ interference on ³⁰Si⁺ at normal “low-resolution” prevents the measurement of all three stable Si isotopes, such that stable isotope variations can only be based on the ²⁹Si/²⁸Si ratio. By using a high-resolution MC-ICPMS, like the *NuPlasma 1700* (built by Nu Instruments Ltd., UK for ETH Zürich), it is possible to resolve polyatomic interferences to both, the low and high mass side of the Si⁺ peaks and to measure all three Si isotope masses simultaneous (Halliday et al., in press). Using the high-resolution capacity of the *NuPlasma 1700* MC-ICPMS and applying a standard-sample-standard bracketing technique we are able to determine relative Si isotope variations of samples with a long-term external reproducibility of ±0.14‰ (2σ_{SD}) for the ³⁰Si/²⁸Si and better than ±0.10 ‰ (2σ_{SD}) for the ²⁹Si/²⁸Si (Reynolds et al., 2006b).

Another problem with MC-ICPMS measurements is that major difficulties are encountered with the use of hydrofluoric acid (HF). Published methods have so far introduced Si as the SiF₆²⁻(aq) ions, but the presence of excess fluoride ions impair the plasma ionisation, and can lead to loss of volatile SiF₄ during sample introduction. We found the presence of HF within the sample solutions is associated with a significant loss of beam intensity and mass-bias stability. Furthermore, the use of HF requires special safety considerations and the need for special HF-resistant sample introduction equipment. This paper presents a separation procedure for Si from waters and geological materials without the use of HF, making the measurement of Si isotopes safer, faster and more reliable.

By combining the advantages of modern high-resolution MC-ICPMS and a simplified chemical preparation method, Si isotopes should be within reach of a broader scientific community. Thus, Si isotopes can become a powerful and widely used tool for diverse fields such as

weathering studies and soil science, marine biology, oceanography, and plant physiology, leading to a significant improvement in our understanding of the global biogeochemical cycle of silicon.

2. Experiments

2.1. Instrumentation

Elemental concentrations were measured using a Varian ICP-OES at the Institute of Terrestrial Ecology, Soil Chemistry of ETH Zürich. Silicon concentrations were measured colorimetrically by the molybdenum-blue method using a photospectrometer.

Silicon isotopic compositions were mainly determined using the *NuPlasma 1700* high-resolution MC-ICPMS with a Nu DSN-100 desolvating nebuliser introduction system (Nu Instruments, Wrexham, UK). Sample uptake was via a self-aspirating 6 mm microflow PFA-nebuliser with variable uptake rates between 60 and 80 μl/min. In order to lower the background of Si to below 1 ppb, the dry aerosol was introduced into the plasma using a semi-demountable torch equipped with an alumina injector. In addition to the standard setup the consistency between different analytical approaches was evaluated with a conventional *NuPlasma* MC-ICPMS at low mass resolution and a Cetac ARIDUS desolvating nebuliser. Table 1 gives an overview of the instrument operating conditions.

Table 1
Operating conditions for the used MC-ICPMS instruments, Nu plasma 1700 and Nu plasma

Parameter	Nu plasma 1700	Nu plasma
	IGMR – isotope lab at ETH Zurich	
RF power	1300 W	1300 W
1st acceleration potential	6 kV	4 kV
Sampler cone	“experimental” WA cone (Nu Instruments)	
Skimmer cone	“experimental” WA cone (Nu Instruments)	
Coolant flow rate (Ar)	13 l/min	13 l/min
Auxiliary flow rate (Ar)	0.9–0.75 l/min	0.9–1.0 l/min
Nebulizer	Self aspirating 6 mm microflow PFA (Elemental Scientific Inc.)	
Nebulizer uptake rate	60–80 μl/min	50 μl/min
Mass-resolution (10% valley)	~2000	~400
Cup configuration	L7 (²⁷ Al), L4 (²⁸ Si), H1 (²⁹ Si), H6 (³⁰ Si)	L5 (²⁸ Si), Ax (²⁹ Si), H6 (³⁰ Si)
Desolvating device	DSN-100 (Nu Instruments)	Cetac ARIDUS

2.2. Reagents and samples

All acids were distilled by sub-boiling in Savillex Teflon elbows. Solutions were made up using deionised water from a MilliQ-element (Millipore) system, referred to here as “MQ-e” ($18.5 \text{ M}\Omega \text{ cm}^{-1}$), and were stored in pre-cleaned PTFE bottles. Two silica (SiO_2) samples were used to check for Si yields during the different procedural steps and for accuracy of Si isotopic compositions. These were an in-house Si(IV)oxide powder and the IRMM-018 silica standard. The international silica standard NBS-28 was used as the international ‘zero-point’ reference material. In order to test sample matrix-effects, an in-house standard was doped with various metal oxide and carbonate powders to produce typical cation compositions of the following silicate minerals: almandine, albite, pyrope, K-feldspar and clinopyroxene (Table 2). All solid silica samples were first ground and powdered using a Si-free boron-carbide mortar and pestle prior to the alkaline fusion procedure.

River water samples were filtered through $0.45 \mu\text{m}$ Millipore cellulose acetate filters directly at the sampling site and acidified with HCl to a pH of 2–3 the same day in the lab. Filtered and acidified samples were stored in pre-cleaned polyethylene canisters.

The fusion procedure required solid NaOH pellets and silver (Ag) crucibles. The NaOH (analytical grade, Merck) had a Si blank of about 5 ppm, which is insignificant compared to the amount of sample material used.

The Ag crucibles were made in-house from 99.99% pure Ag sheet.

2.3. Alkaline fusion of silicates using solid NaOH

In order to avoid the use of HF, a key issue of this study, an alkaline fusion was used to dissolve silicates instead of attacking them with HF. The idea was to transform solid silicate samples into an aqueous and HF-free solution and process them through chemistry as if they were water samples. To comply with these requirements a fusion procedure was deployed using a solid sodium hydroxide (NaOH) flux. Sodium hydroxide was preferred over other fluxes such as lithium metaborate and alkaline carbonates, because it provides the simplest composition and, by neutralisation with HCl, it just forms NaCl and H_2O . Fusions with alkaline fluxes have a long tradition in analytical chemistry and are especially used when silicate minerals and rocks are analysed for their Si content. Prior to fusion the sample powder was mixed with the flux in a metal crucible, typically composed of Pt, Ag, Ni or Au. The crucible material depends on the flux used, with Ag being more resistant to NaOH dissolution. Above a certain temperature the flux melted and the sample powder dissolved completely. For example, silicate rocks, mineral separates and biogenic silica samples were totally dissolved. The resulting “fusion cake” was subsequently dissolved in a weakly acidic solution. This fusion procedure can be applied to a variety of silicate mineral and rock samples and is the standard method for preparation of silicate minerals for the determination of Si concentrations. An overview of different fusion procedures and their applications is given in Potts (1987). The application of alkaline fluxes prior to Si isotope ratio measurements has been considered in numerous studies (Reynolds and Verhoogen, 1953b; Tilles, 1961; Yeh and Epstein, 1978; Douthitt, 1982), and so should not be regarded as a totally new technique.

For the NaOH fusion (Riley, 1958; Walsh et al., 1981), we used 1–20 mg of the powdered silicate material and ~200 mg of the solid NaOH flux. Fusion was carried out in Ag crucibles for 10 min at $730 \text{ }^\circ\text{C}$ in a muffle furnace. After slight cooling, the crucibles and fusion cake were dropped directly into 30-ml Teflon vials containing 20 ml MQ-e water, in which the resulting fusion cake dissolves. To aid dissolution an ultrasonic probe was used to agitate the water for a few minutes. After 24 h, the crucible contents were washed through PTFE funnels into a weakly acidified solution with a molarity of 0.12 (HCl is typically used to avoid additional NO^+ formation in the

Table 2
Artificial mineral cationic compositions, metal-oxide and metal carbonate powders were used

Matrix	Metal	wt (g)	wt.%
Albit	Na_2CO_3	0.696	3.67
	CaCO_3	0.667	3.51
	Al_2O_3	3.87	20.39
	SiO_2	13.75	72.43
	Total:	18.983	
K-feldspar	K_2CO_3	1.17	12.34
	Al_2O_3	1.84	19.41
	SiO_2	6.47	68.25
	Total:	9.48	
Pyrop	MgO	2.92	29.29
	Al_2O_3	2.56	25.68
	SiO_2	4.49	45.04
	Total:	9.97	
Almandin	Fe_2O_3	2.15	27.49
	Al_2O_3	2.05	26.21
	SiO_2	3.62	46.29
	Total:	7.82	
Clinopyroxene	MgO	3.53	36.21
	Fe_2O_3	0.26	2.67
	SiO_2	5.96	61.13
	Total:	9.75	

SiO_2 is the PuraTronic Si(IV)oxide by AlfaAesar.

plasma, but HNO_3 can be used as well). To ensure the fusion cake is completely transferred the crucibles are rinsed several times with water. The ratio of flux to acid is approximately 3.1 ml of a 10 N HCl or 2.2 ml of a 14 N HNO_3 for 200 mg NaOH flux. Final solutions of 0.5 to 1 l are stored in pre-cleaned FEP bottles, with Si concentrations between 1 and 20 ppm.

2.4. Chromatographic separation of Si

One way to separate Si from ambient ionic species is via ion-chromatography using an anion-exchange resin, as initially demonstrated by Wickbold (1959) and then used more recently for the purpose of Si isotope measurements (Engström et al., 2006). To make Si exchangeable with the anion resin it needs to be converted to the weak divalent acid H_2SiF_6 that dissociates to the exchangeable anionic species SiF_6^{2-} . The Si recovery is in excess of 97% and Si becomes effectively separated from ambient ionic species. This method, however, requires the use of HF and thus does not meet with our requirements for an HF-free final solution.

The ion-chromatography presented here is instead based on a cation-exchange process. The prevailing species of dissolved Si in natural waters is essentially non-ionic monosilicic acid $\text{Si}(\text{OH})_4$, that is in equilibrium with the anionic silicate species H_3SiO_4^- for the pH range from 2 to 8. Cation-exchange columns will not retain either Si species. The Si separation and purification is achieved using the BioRad cation exchange resin DOWEX 50W-X12 (200–400 mesh) in H^+ form, filled to a 1.8 ml resin bed in BioRad columns. The resin is pre-cleaned by rinsing it several times with HCl and HNO_3 and MQ-e water, as detailed in Table 3. Before loading the sample on the resin, the eluting water is checked for neutral pH to ensure complete removal of any acids. Since the prevailing Si species do not bind to the resin the elute is simply MQ-e water. The cation exchange resin effectively retains all the ambient cationic species.

This chromatographic method allows relatively small amounts of sample to be processed. Per ion-exchange column only $\sim 3.6 \mu\text{g}$ Si of the sample material are separated, so the sample volume loaded depends on the initial Si concentration, e.g. for river water samples with Si concentrations of 1–2 ppm, 1–2 ml of water are used. The amount of Si used is approximately 80 times less than the 300 μg load used for the anion exchange approach (Engström et al., 2006). The elute volume depends on the loaded volume but should be at least once the resin bed volume, around ~ 2.0 ml. The total elute is typically diluted to 6 ml, so that the final solution has a Si concentration of 0.6 ppm (21 μM). An example of the

Table 3

Separation scheme considering the preparation of an acidified river water sample with a Si concentration of 1.8 ppm

Separation scheme for a river water sample (1.8 ppm Si)		
BioRad AG 50W-X12, 1.8 ml resin bed		
Separation stage	Solution matrix	Volume (ml)
Pre-cleaning	3 N HCl	3 ml
Pre-cleaning	6 N HCl	3 ml
Pre-cleaning	7 N HNO_3	3 ml
Pre-cleaning	10 N HCl	3 ml
Pre-cleaning	6 N HCl	3 ml
Pre-cleaning	3 N HCl	3 ml
Rinse	MQ-e	6 ml (pH should be neutral)
Sample load	Acidified water sample	2 ml (or equal to 3.6 μg Si)
Elution	MQ-e	2 ml
	Final Si elution	4 ml
Dilution to running concentration	MQ-e	2 ml
Result		6 ml at 600 ppb Si

separation scheme is given in Table 3. This separation scheme is used to process both fused solutions and acidified river water samples. The latter being directly loaded onto the resin as no pre-treatment is required prior to the chromatographic procedure. The preparation time is short, in that a set of river water samples can be completely processed through the columns within 4 h, including pre-cleaning steps (see Table 3).

2.5. Mass-spectrometry

The direct measurement of all stable Si isotopes by MC-ICPMS requires high-resolution mass-spectrometry in order to resolve Si^+ ions from polyatomic interferences of similar mass, in particular $^{14}\text{N}^{16}\text{O}^+$ interferences on the $^{30}\text{Si}^+$ ion beam (De La Rocha, 2002; Cardinal et al., 2003). We have analysed Si isotopes using the high-resolution capacity of the NuPlasma 1700 (Nu Instruments, UK) MC-ICPMS at ETH Zürich (Halliday et al., in press). A mass-resolution of 2000 ($m/\Delta m$ at 10% peak valley) allows for a separation of the three Si^+ ion beams from all major polyatomic interferences including $^{12}\text{C}^{16}\text{O}^+$, $^{14}\text{N}^{14}\text{N}^+$, $^{14}\text{N}^{15}\text{N}^+$, $^{14}\text{N}^{14}\text{N}^+\text{H}^+$ and $^{14}\text{N}^{16}\text{O}^+$. The unique high resolving power of the NuPlasma 1700 allows for the isolation of interferences to both the high and low mass sides of the Si^+ peak while maintaining flat-topped peaks. Furthermore, SiH^+ and Fe^{2+} interferences can be resolved. All three Si peaks are measured simultaneously in static mode with Faraday collectors equipped with $10^{11} \Omega$ resistors. The mass bias of the NuPlasma 1700 is very stable with a drift in $^{30}\text{Si}/^{28}\text{Si}$ of standard

solutions of <1‰ over 60 h. It is corrected for by standard-sample bracketing. Silicon isotope data are reported as deviations of $^{30}\text{Si}/^{28}\text{Si}$ and $^{29}\text{Si}/^{28}\text{Si}$ from the international standard NBS-28 in parts per thousand (the standard delta notation $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$) as follows:

$$\delta^{30}\text{Si} = \left[\frac{(^{30}\text{Si}/^{28}\text{Si})_{\text{sample}} - (^{30}\text{Si}/^{28}\text{Si})_{\text{NBS-28}}}{(^{30}\text{Si}/^{28}\text{Si})_{\text{NBS28}}} \right] \times 1000$$

External mass bias correction using Mg isotopes (Cardinal et al., 2003; Engström et al., 2006) was evaluated and rejected due to the significant differential behaviour of Si and Mg isotopes within the plasma. The NuPlasma 1700 has an array of 16 Faraday detectors equipped with independently adjustable collector slits and achieves sufficient mass dispersion to measure the Si and Mg isotopes simultaneously at high resolution in static mode. However, variation in the Mg mass-bias does not correct adequately for variable Si mass-bias at the *sub*-permil level. Adding Mg produces a matrix-effect that causes instability in the mass bias with larger drift in Mg than Si.

In order to address whether the new preparation techniques can be easily applied to other MC-ICPMS instruments, we compared two different analytical setups of MC-ICPMS, attached with different desolvating units. Beside the standard combination of the NuPlasma 1700 attached to the DSN-100, a second setup used was a combination of a standard NuPlasma attached to a Cetac ARIDUS desolvating unit (also at the Zürich Radiogenic Isotope Geochemistry Laboratory). Different sets of sampler and skimmer cones were used with the same semi-demountable torch, equipped with an alumina injector. A PFA nebuliser with a lower uptake rate of only 50 $\mu\text{l}/\text{min}$ (as compared with a standard uptake rate of 60–80 $\mu\text{l}/\text{min}$) was used on the NuPlasma. Silicon isotope data could not be acquired at high resolution on the standard NuPlasma, although more recent versions of this instrument have some such capability. As a result the measurements are only based on deviations of the $^{29}\text{Si}/^{28}\text{Si}$ ratios and noted as $\delta^{29}\text{Si}$. Both MC-ICPMS instruments are equipped with an 80 l/min rotary pump for evacuating the space between the sampler and skimmer cones, which enhances the machine sensitivity. Each sample is measured several times and the results reported are based on a dataset consisting of multiple δ -values. One δ -value consists, according to the standard-sample bracketing protocol, of one sample measurement normalised to the average of two adjacent standard measurements. One measurement represents 25 cycles with 8 s integration time for each cycle. The background from the Faraday detector noise is evaluated by de-

flecting the beam in the electrostatic analyzer for 30 s prior to each measurement.

3. Results and discussion

The new separation and purification technique for Si based on NaOH fusion and ion exchange chemistry avoids problems associated with the use of HF. We will show that this has two major advantages: (1) HF-free solutions are more stable with respect to instrumental mass-bias, enabling better reproducibility for standard-sample bracketing and thus higher precision, and (2) HF-free solutions gain 30% to 40% higher Si beam intensity compared to solutions with equivalent Si concentrations containing HF.

3.1. Silicon recovery and elution profile

The recovery of Si for the fusion procedure has been estimated using standard materials, natural pure quartz and garnet with a known proportion of SiO_2 (Table 4). The recovery during the fusion procedure, estimated on these different silicate materials averages $99.4 \pm 2.6\%$

Table 4
Si recovery (in %) for the fusion procedure and the column chromatography

NaOH fusion		Column chromatography	
Material	Recovery (%)	Material	Recovery (%)
NBS-28	99.6	NBS-28	99.4
NBS-28	105.1	NBS-28	97.6
IRMM-018	105.0	NBS-28	100.2
IRMM-018	100.9	NBS-28	101.2
Quartz	99.2	NBS-28	102.0
Quartz	96.9	NBS-28	102.4
Quartz	97.1	NBS-28	102.2
Quartz	96.0	B_03/04 river	100.4
Quartz	99.0	B_03/04 river	99.2
Quartz	95.5	Coop H ₂ O	100.0
Quartz	100.8	Coop H ₂ O	97.1
Quartz	98.2	Coop H ₂ O	97.4
Garnet	100.4	Coop H ₂ O	100.0
Garnet	98.5	T_05/04 river	100.1
Garnet	99.7	T_05/04 river	101.4
Garnet	100.4	T_05/04 river	100.9
Garnet	98.2	T_05/04 river	101.2
Garnet	98.1	T_05/04 river	99.5
Average	99.4	Average	100.1
S.D.	2.6	S.D.	1.6
<i>n</i>	18	<i>n</i>	18

SiO_2 wt.% data of the garnets represent ion-probe analyses and were taken from (Clechenko and Valley, 2003). The recovery of the column chromatography has been determined using standards and water samples. Beside standard materials natural silicates, such as quartz and garnets were used to assess the Si recovery of the fusion.

($\pm 1\sigma_{SD}$, $n=18$). Given the uncertainties on the Si concentration, the initial sample weight and sample heterogeneities of $\pm 2\%$, this is consistent with fully quantitative recovery.

The prevailing Si species after fusion exhibit no affinity for cation exchange resin and thus Si is quantitatively recovered through the chromatographic procedure. The measured Si recovery through column separation (Table 4) is $100.1 \pm 1.6\%$ ($\pm 1\sigma_{SD}$, $n=18$), and the eluted sample is free of all major cations (Na, Ca, K, Mg, Al) and free of trace metals (Fe, Ni, Mo). The separation efficiency is demonstrated by the elution curves of two samples that were loaded onto the pre-cleaned cation exchange resin (Fig. 1); Si is not retained by the resin and migrates straight through the column and nearly 70% of the loaded Si is already recovered while the sample load is still infiltrating the resin bed. The last 30% is eluted with 2 ml of MQ-e water. The elution scheme in Fig. 1 also demonstrates that the subsequent 4 ml of elution with MQ-e is free of Si and cations. The separation peak for Si is thus clearly delimited, with no breakthrough of any cations into the Si eluant. This demonstrates a complete separation of Si from the ambient cation matrix. The cationic species first start to migrate through the resin as soon as an acidic solution is used as the eluting matrix, such as 3 N HCl as shown in Fig. 1.

However, it is worth considering that the preparation technique does not separate Si from other anions, which would also pass directly through the cation-exchange column. These anions could potentially cause a matrix-effect during analysis by MC-ICPMS. The elution

scheme for the river water sample shown in Fig. 1, demonstrates that aqueous anionic species, such as SO_4^{2-} , are eluted with Si. We tested whether the presence of sulphates or nitrates has an impact on the accuracy of the Si isotope measurements. An aliquot of NBS-28 was taken and doped with a sulphate solution, made up to be 50 ppm in SO_4^{2-} and processed through the chromatographic procedure. The doped NBS-28 solution yielded a $\delta^{30}\text{Si}$ value of $-0.04 \pm 0.15\%$ ($\pm 2\sigma_{SD}$, $n=11$), demonstrating no significant isotopic offset for a solution with a $\text{SO}_4^{2-}/\text{Si}$ molar ratio of ~ 14.4 . We also tested for matrix-effects from nitrates by doping a NBS-28 aliquot with 0.1 N HNO_3 (much higher than the natural NO_3^- content of river waters). This test revealed a $\delta^{30}\text{Si}$ of $-0.03 \pm 0.07\%$ ($\pm 2\sigma_{SD}$, $n=6$) and shows that excess NO_3^- does not impact on the Si isotope composition. That low anion contents, excluding F^- , do not introduce significant matrix effects is not surprising given that the amount of anions added during acidification is by far in excess of the original concentration of anions in river waters, which thus become negligible. However, for samples with higher concentrations of dissolved solids and corresponding higher contents of anions, such as seawater and brines, a pre-concentration step for Si prior to the chromatographic procedure is a more suitable approach to avoid possible matrix problems. We utilise a co-precipitation of Si on (oxy-)hydroxides in slightly alkali solutions. This procedure has been used to concentrate dissolved Si and P from seawater (Karl and Tien, 1992; Brzezinski et al., 2003), as the co-precipitate or adsorption is quantitative (Cardinal et al., 2005; Reynolds et al., 2006a).

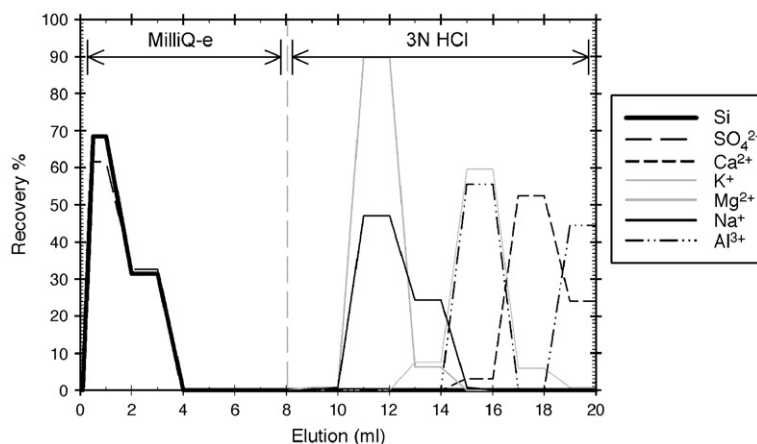


Fig. 1. Elution curves for an acidified river water sample using the BioRad DOWEX 50W-X12 cation exchange resin. Silicon is quantitatively recovered during the load step and the first elution step using MQ-e water. The Si elution is quite delimited and there is no tailing from any cation peak as long as MQ-e water is used as the eluting matrix. Cations start to move through the resin when an acidic elution matrix is used. The elution scheme is similar for silicate samples, only the interfering SO_4^{2-} is not present.

3.2. Silicon background and Sensitivity

Fusion blanks were assessed using 200 mg of solid NaOH in empty crucibles. The melt cakes were dissolved in 20 ml MQ-e and acidified with 3.1 ml of a 10 N HCl and diluted up to 45 ml. The Si concentration of these solutions was below 2 ppb. This low blank level makes it possible to process small silicate samples with sizes of only 0.1–1 mg (Georg et al., 2005).

The very rapid washout performance of the DSN-100 meant that the Si blank on the mass-spectrometer could be reduced to below 20 mV prior to each measurement (corresponding to <2 ppb Si in the analyte). A washout procedure of 150 s after measurement was sufficient to reduce the Si background to this adequate level. The ion beam to background ratio is on the order of 500, and no memory effects or build-up of Si background were observed even over several consecutive days of analysis (in fact background usually improved over time).

One major advantage of HF-free sample solutions is the enhanced sensitivity. Setting the *NuPlasma 1700* MC-ICPMS to a mass-resolution ($m/\Delta m$) of 2000 (10% valley definition) is associated with a decrease in sensitivity of nearly 50%. This reduced sensitivity can be compensated by either higher analyte concentration or sample uptake rate. Our method shows an enhanced sensitivity and enables relatively low Si concentrations to be run. Compared to solutions containing HF we achieve between 30% and 40% higher sensitivity with a similar setup. The actual instrument sensitivity varies, but typical analyte concentrations of 500 to 600 ppb Si and uptake rate of 60–80 $\mu\text{l}/\text{min}$ provides a total Si beam of ~ 8 V, whilst running in high-resolution mode. This sensitivity of ~ 13 V/ppm Si at 0.1 ml/min uptake is about 3 times higher than published results using a Neptune (Thermo Electron Corp., Bremen) MC-ICPMS in similar high-resolution mode (Engström et al., 2006).

The sensitivity at low-resolution mode on the standard *Nu Plasma* is naturally much higher (60 V/ppm Si at 0.1 ml/min uptake). This is >60 times higher than achieved with a wet-plasma assembly (De La Rocha, 2002) and 5 times higher than for solutions containing HF running in dry-plasma mode (Cardinal et al., 2003) for the same type of MC-ICPMS (a *NuPlasma*). It should be noted that the sensitivity also depends on the capacity of the turbo pump that evacuates the region between sampler and skimmer cone and the design of the used cones. Both, the Nu Instruments “experimental WA cones” and the 80 l/min pumps used in this study improve the overall machine sensitivity.

3.3. Reproducibility, precision and accuracy

In order to demonstrate the performance of our new method we have chosen the European Si Standard IRMM-018 and compared a sample prepared using the method described in this paper to a sample prepared by direct dissolution in HCl–HF acids following Cardinal et al. (2003). The differences between the prepared aliquots are the acid matrix and the Si concentration. The HCl–HF aliquots had a Si concentration of 1 ppm and an associated intensity of ~ 4.5 V/ppm Si, whereas the HF-free aliquots had a concentration of 600 ppb and an associated intensity of ~ 7.5 V/ppm. Each IRMM-018 aliquot was measured on two different sessions (Fig. 2). The results display good agreement between the two preparation methods, with similar mean $\delta^{30}\text{Si}$ values of -1.63% and -1.62% . Hence, we conclude that there is no significant isotope fractionation effect induced during either the fusion or the column chemistry. The direct comparison between both sample preparation techniques shows that the HF-free solutions can be reproduced to a greater precision, as the HF-free solutions provides rather more stable measuring conditions for the MC-ICPMS. By

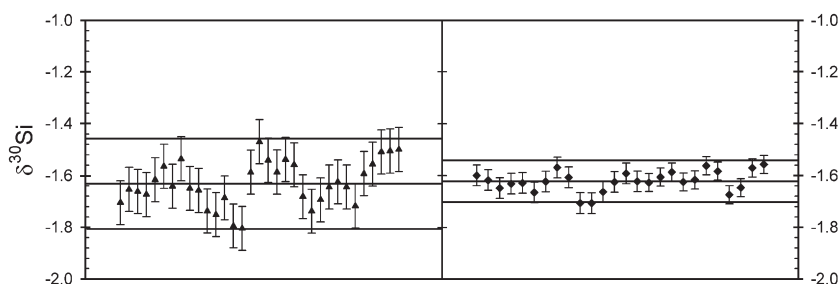


Fig. 2. Comparison of two IRMM-018 aliquots: one digested with HCl–HF (\blacktriangle) and one processed according to the combined fusion and ion chromatographic procedure (\blacklozenge). Both aliquots yield the same Si isotope composition ($\delta^{30}\text{Si} = -1.63\%$ and -1.62%). The reproducibility of the HF-free solution is twice as good as the HCl–HF solution. Black lines denote $2\sigma_{\text{SD}}$ and the ^{30}Si mean. Running conditions: HCl–HF solution: 1 ppm Si, beam intensity: 4.5 V/ppm – HF-free solution: 0.6 ppm Si, beam intensity: 7.5 V/ppm.

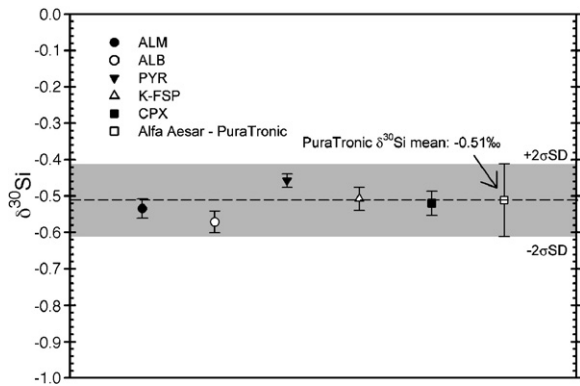


Fig. 3. The mixed mineral compositions agree with the $\delta^{30}\text{Si}$ value of the in-house standard. Errors on mineral samples are given in 95% S.E.M. The grey shaded field indicates the $2\sigma_{\text{SD}}$ of the in-house standard. ALM=almandine, ALB=albite, PYR=pyrope, K-FSP=K-feldspar, CPX=clinopyroxene, matrix composition see in Table 2.

changing from HCl–HF solutions to HCl only we could improve the reproducibility by a factor of 2.

The long-term reproducibility of over 300 measurements of the IRMM-018 standard was $\pm 0.14\text{‰}$ ($2\sigma_{\text{SD}}$) for $\delta^{30}\text{Si}$ values and $\pm 0.10\text{‰}$ ($2\sigma_{\text{SD}}$) for $\delta^{29}\text{Si}$ values (Reynolds et al., 2006b). The standard data were acquired during 16 sessions between November 2004 and August 2005 and represent the first long-term evaluation of $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ data of a Si isotope reference material to be published. Since all standards were processed through the chemical separation procedure prior to each session, this standard reproducibility also includes the repeatability of the applied ion-chromatography procedure. Thus the ion-exchange chemistry is highly reproducible. The reproducibility of multiple sample

measurements during a single session is usually better than $\pm 0.10\text{‰}$ for $\delta^{30}\text{Si}$ and $\pm 0.07\text{‰}$ for $\delta^{29}\text{Si}$ ($2\sigma_{\text{SD}}$). We are thus limited in our precision by our long-term standard reproducibility. Thus, our limiting precision (95% S.E.M.) can be estimated from the number of replicates (n) using this long-term reproducibility (95% S.E.M. = ~ 2.5 S.E. for $n=7$). For 11 repeated measurements our limiting precision is $\pm 0.04\text{‰}$ on $\delta^{30}\text{Si}$ and $\pm 0.03\text{‰}$ on $\delta^{29}\text{Si}$ ratios. This high precision facilitates the resolution of even small variations in the Si isotope composition of natural samples, such as the seasonal variation of the dissolved Si in river samples (Georg et al., in press).

As there is no Si isotope rock standard yet available, in order to check the effects of sample matrix we doped our in-house Si standard to achieve artificial mineral matrixes and processed these through the entire procedure, including fusion and ion-chromatography. The results from the doped and pure samples all reproduce the $\delta^{30}\text{Si}$ composition of $-0.51 \pm 0.1\text{‰}$ ($\pm 2\sigma_{\text{SD}}$, $n=12$) (Fig. 3), demonstrating that our method is suitable for natural silicate samples and does not introduce Si isotope fractionations.

A comparison of measurements obtained on different MC-ICPMS instruments is limited by polyatomic interferences on mass ^{30}Si on the standard *NuPlasma*. However, we can compare the $^{29}\text{Si}/^{28}\text{Si}$ ratios relative to the standard NBS-28. The results shown on Fig. 4 demonstrate that the analyses of 3 different aliquots of the same sample (river water sample) are consistent between two distinct analytical set-ups. Thus, the sample preparation method described here is suitable for different types of MC-ICPMS.

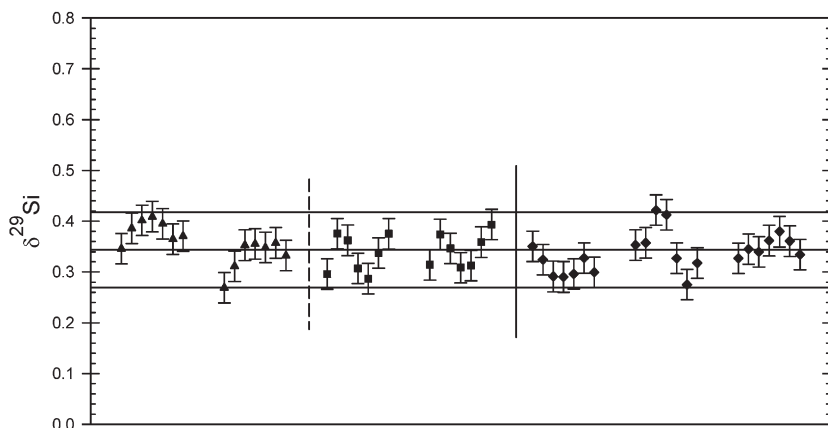


Fig. 4. The comparison between different analytical setups shows that the new method is highly reproducible and can be applied to different analytical setups. Aliquots 1 (▲) and 2 (■) measured on a standard *NuPlasma* attached to a Cetac ARIDUS, aliquot 3 (◆) was measured on the *NuPlasma 1700* attached to the DSN-100. All measurements give a mean $\delta^{29}\text{Si}$ of $+0.34\text{‰}$ and a reproducibility of $\pm 0.07\text{‰}$ ($2\sigma_{\text{SD}}$). Running conditions: *NuPlasma*, low resolution (~ 400): 250 ppb Si, beam intensity: ~ 30 V/ppm – *NuPlasma 1700*, high resolution (~ 2000): 0.6 ppm Si, beam intensity: ~ 12.5 V/ppm.

4. Conclusion

The new method detailed here represents a robust, fast and reliable way to determine accurate and precise Si isotope ratios of natural samples using MC-ICPMS. By avoiding the use of HF, it is possible to obtain higher sensitivity and mass-bias stability, which ultimately results in improved precision. Cations that introduce matrix-effects in the mass-spectrometer can be effectively removed using a cation exchange procedure. Indeed, this method is the most effective way of excluding the potential problems of matrix-effects from additional cations. Anionic species that are not separated from Si and could represent a potential problem are shown to not affect our results for river water samples with natural sulphates and nitrates or for silicate samples. River waters contain these anionic species, though in extremely low abundances compared to the dominant anion in the analyte from acidifying our samples (~0.1 M Cl⁻). For samples that contain higher concentration of anions, such as seawater and brines, a pre-concentration of Si prior to the cation exchange process can be easily completed using quantitative co-precipitation on MgOH. Since silicate minerals and rocks do generally not contain high amounts of anionic species, except sulphur-rich samples, this new method is well suited for the determination of Si isotope ratios in natural materials.

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