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Direct determination of Si isotope ratios in natural waters and commercial Si standards by ion exclusion chromatography multi-collector inductively coupled plasma mass spectrometry

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ABSTRACT

Silicon isotope ratios in natural waters and several commercial Si standards were determined by on-line ion exclusion chromatography (IEC) multicollector inductively couple plasma mass spectrometry (MC-ICPMS). As recent studies have shown that mass-independent fractionation (MIF) also exists in MC-ICPMS itself, e.g., Nd, Ce, W, Sr, Ge, Hg and Pb isotopes, the nature of mass bias for Si isotopes was thus investigated. MIF was observed for Si isotopes on both Neptune and Neptune plus MC-ICPMS instruments in this study. Therefore, a standard-sample-standard bracketing (SSB) mass bias correction model which is capable of correcting both mass-dependent and mass-independent bias was employed to obtain accurate Si isotope ratio results in all samples by using NBS28 Si standard as the bracketing standard. Medium resolution was used for all measurements in order to resolve polyatomic interferences on Si isotopes. NBS28 Si standard solutions prepared in nutrient-free seawater and 0.1% NaOH matrix, respectively, were used for the method validation and subjected to the on-line IEC-MC-ICPMS determination of Si isotope ratios. Values of -0.01 ± 0.06 and 0.00 ± 0.06 ‰ (1SD, n=10); and -0.01 ± 0.03 and 0.01 ± 0.06 ‰ (1SD, n=10) for $\delta^{29/28}\text{Si}$ and $\delta^{30/28}\text{Si}$, respectively, were obtained, confirming accurate results can be obtained using the proposed method for natural waters.

Significant variations in Si isotope ratios from -0.72 ± 0.09 to -0.24 ± 0.03 ‰ (1SD, n=10) and -1.36 ± 0.11 to -0.46 ± 0.04 ‰ (1SD, n=10) for $\delta^{29/28}\text{Si}$ and $\delta^{30/28}\text{Si}$, respectively, were found among commercial Si standards of NIST SRM3150, SCP Si and Sigma-Aldrich Si. Values of -0.06 ± 0.07 and -0.20 ± 0.11 ‰ (1SD, n=10) for $\delta^{29/28}\text{Si}$ and $\delta^{30/28}\text{Si}$, respectively, were obtained for the MOOS-3 seawater whereas 0.59 ± 0.11 and 1.19 ± 0.15 ‰ (1SD, n=10) for $\delta^{29/28}\text{Si}$ and $\delta^{30/28}\text{Si}$, respectively, were obtained for the SLRS-5 river water. To the best of our knowledge this is the first report of an application of on-line IEC-MC-ICPMS for the high accuracy and precision determination of Si isotope ratios in natural waters. The reported method provides for a relatively rapid (10 minutes per run) and simple on-line technique, requiring no sample pre-treatment, for the Si isotope ratio measurements.

Keywords: Si isotope ratio, multi-collector inductively coupled plasma mass spectrometry, Ion exclusion chromatography, mass bias, mass-independent fractionation, mass-dependent fractionation

INTRODUCTION

Silicon is the second most common element in the Earth's crust¹ with three stable isotopes. Silicon isotopes have received increasing attention in the last decade due to their applications in various scientific fields. As biogeochemical tracers, Si isotopes have been used for the studying of various processes such as weathering and biological processes occurring in nature, improving our understanding of the global biogeochemical cycle of silicon.²⁻⁹ As a result, significant efforts were made for the development of high accuracy and precision methods for the determination of Si isotope ratios in various sample matrices, such as continental crust, river waters and seawaters. Early studies on Si isotope ratio measurements have been carried out using gas source mass spectrometry (GS-MS)¹⁰⁻¹⁶ which requires complex step of fluorination of silicon and dealing with hazardous gas of F₂ and BrF₅. Furthermore the production of pure fluorine gas and purification of the generated SiF₄ is difficult. The introduction of multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) has allowed the highly precise and accurate determination of Si isotope ratios, significantly advanced the use of Si isotopes as a powerful tool for the studying of various biogeochemical processes^{2-9, 17-18}, and for applications in other disciplines. For example, the high precision and accuracy Si isotope ratio determination has played a significant role in chemistry, as recently illustrated in the high profile atomic weight determination¹⁹⁻²⁰ in ²⁸Si enriched 1-Kg silicon sphere, essential for the estimation of the Avogadro Constant for the purpose of redefinition of new SI unit of kg.²¹

However, MC-ICPMS suffers mass bias²²⁻²³; raw isotope amount ratios measured by MC-ICPMS can deviate from their true values in a range of one to a few percent levels, and up to 25% for Li per atomic mass unit. Therefore, proper correction of mass bias is crucial to obtain accurate isotope ratios by MC-ICPMS. In general, mass bias in MC-ICPMS is treated as mass-dependent fractionation (MDF) and is corrected by numerous mass-dependent fractionation models (e.g., linear law, power law, exponential law and Russell law)²³. Among these, the Russell law based on Eq. 1 is the most popular:

$$R^{i/j} = r^{i/j} \cdot \left(\frac{m_j}{m_i}\right)^f \quad (1)$$

where r and R are the measured and the true isotope amount ratios, respectively, m_i and m_j are nuclide masses of the isotopes of interest, and f is the mass bias factor. However, recent studies²⁴⁻³⁰ have shown mass-independent fractionation (MIF) exists within MC-ICPMS for a quite few isotope systems including Sr Nd, Ce, W, Ge, Hg and Pb. Consequently, biased ratio results may occur when traditional mass-dependent models, such as Russell's law, are used directly to correct MIF in MC-ICPMS²⁸⁻²⁹. Thus, it's of importance to investigate the nature of mass bias of Si isotopes within MC-ICPMS in order to obtain accurate results by selecting suitable mass bias correction models. In addition to instrumental mass bias, matrix-dependent non-spectral mass discrimination caused by changes in sample composition and fluctuations in mass bias within the ICP through time also present a significant hindrance. To properly correct for these effects, separation of analyte from sample matrix is generally necessary. For Si matrix separation, off-line column separation using either cation exchange resin 50W-X12 or anion exchange resin AG1-X8 have been employed^{2-9, 17-18}. Unfortunately, off-line column separation is usually time-consuming. Therefore, the object of this study was to evaluate the feasibility of using an ion exclusion chromatography (IEC) with MC-ICPMS for the on-line determination of Si isotope ratios in natural waters or other samples. In addition, the nature of mass bias for Si isotopes in MC-ICPMS itself was investigated since MIF can significantly influence the choice of mass bias correction models for Si isotope ratio measurements. To the best of our knowledge, this is the first report of direct on-line determination of Si isotope ratios in nature waters by IEC-MC-ICPMS.

EXPERIMENTAL SECTION

Instrumentation. An Agilent high pressure liquid chromatography (HPLC) 1200 Series (Agilent Technologies Canada Inc., Mississauga, Ontario, Canada) with an ion exclusion column ICE-AS1 (9 mm id x 250 mm) from Thermo Fisher Scientific (Waltham, MA, USA) was used for the on-line column

separation of the analyte from sample matrix. The coupling of LC to MC-ICPMS was accomplished by directing the eluent from the column to the nebuliser of the MC-ICPMS through a 1 m length of PEEK tubing (0.13 mm id, 1.59 mm od). The eluent was 0.01% HCl at a flow rate of 0.80 mL min⁻¹.

A Thermo Fisher Scientific (Bremen, Germany) Neptune at National Research Council Canada and a Neptune plus MC-ICPMS at China University of Geosciences (Wuhan, China) both equipped with nine Faraday cups and a combination of cyclonic and Scott-type spray chambers with a perfluoroalkoxy self-aspirating nebulizer MCN50 (Elemental Scientific, Omaha, NE, USA) operating at 50 μ L min⁻¹ were used for all measurements in the investigation of the nature of mass bias of Si isotopes. Medium resolution was used for all measurements. A PFA ST nebulizer ES-2040 (Elemental Scientific; Omaha, NE, USA) operating at 0.80 mL min⁻¹ was used for the on-line Si isotope ratio measurements by IEC-MC-ICPMS. A plug-in quartz torch with a quartz injector and a Pt guard electrode were used. In addition, X skimmer cone was also used for Si isotope amount ratio measurements as improved sensitivity can be obtained.

Reagents and Solutions. Hydrochloric acid was purified by subboiling distillation of reagent grade feedstock in a quartz still prior to use. Environmental grade HF was purchased from Anachemia Science (Montreal, Quebec, Canada). Deionized water (DIW) was obtained from a Nanopure ion exchange reverse osmosis system (Barnstead/Thermolyne, Boston, MA, USA). High-purity sodium hydroxide (99.9995+ %) made by Fluka was purchased from Sigma-Aldrich (Oakville, ON, Canada). NBS28 Silica sand was purchased from Institute for Reference Materials and Measurements (Retieseweg, Geel, Belgium). Stock solution of NBS28 Si (770 μ g g⁻¹) was prepared by dissolution of appreciate amount of SiO₂ in 1 mL HF, followed by dilution with DIW. SRM3150 silicon stock solution at 10.458 $\pm$ 0.032 mg g⁻¹ (U, 95% confidence interval) was purchased from National Institute of Standards and Technology (NIST, Gaithersburg, MD USA). A working standard solution of SRM3150 at 553.54 μ g g⁻¹ was prepared by dilution of the stock in DIW. A 1000 μ g ml⁻¹ silicon stock solution was purchased from

SCP science (Baie D'Urfé, Quebec, Canada). A high purity metal of Si (99.999%+) was purchased from Sigma-Aldrich (Oakville, ON, Canada) and a 1000 $\mu\text{g g}^{-1}$ stock solution was prepared by dissolution of Si metal in 2 mL HF, followed by dilution with DIW.

Nutrient-free seawater was purchased from Ocean Scientific International Ltd. (Surrey, UK). Seawater CRM MOOS-3 and river water SLRS-5 were obtained National Research Council Canada (Ottawa, ON, Canada) and used as test samples. MOOS-3 was collected in the North Atlantic Ocean at a depth of 200 m as described by Hioki *et al.*³¹. SLRS-5 was collected from Ottawa River at the city of Ottawa's Britannia water purification plant as stated in the certificate.

Sample preparation and analysis for the study of the nature of mass bias of Si isotopes in MC-ICPMS. Sample preparation was conducted in a Class-100 clean room. Replicate solutions of 2-15 $\mu\text{g g}^{-1}$ Si were prepared by diluting the Si stock in DIW for the Si isotope ratio measurements by MC-ICPMS. Optimization of the Neptune or Neptune Plus MC-ICPMS was performed daily as recommended by the manufacturer. The instruments were tuned to achieve high possible sensitivity while maintaining flat top square peaks and stable signals in order to ensure accurate measurements. In addition, measurements were started after at least 1 hour warm-up time of the instruments. Typical operating conditions of MC-ICPMS are summarized in Table 1. The gain on each Faraday cup was monitored daily to ensure normalization of its efficiency. In addition, the "Virtual Amplifier" design was employed for all measurements in order to eliminate any bias caused by uncertainties in the gain calibration of amplifiers³². Samples were introduced into the plasma through a peristaltic pump pumping at a flow rate of 50 $\mu\text{L min}^{-1}$. Intensities of the Si isotopes obtained from the blank solution of DIW were subtracted from those of all samples. In general intensities of the Si isotopes measured in the blank solution were at least four to five orders of magnitude lower than those obtained from standard solutions. Static runs were employed to simultaneously measure three Si isotopes using the Faraday cup

configuration shown in Table 1. 10 to fifteen measurements were made for each standard solution of triplicate solutions prepared over duration of 5-8 hours. It is noteworthy that shorter measurement time can be used with similar results. Numbers for blocks and cycles were adjusted to result in a total of 10 minutes measurement time for each run.

Table 1. Typical MC-ICPMS operating conditions

Instrument settings	
Rf power	1120 W
Plasma Ar gas flow rate	16.0 L min ⁻¹
Auxiliary Ar gas flow rate	1.00 L min ⁻¹
Ar carrier gas flow rate	0.915 L min ⁻¹
Sampler cone orifice (nickel)	1.00 mm
Skimmer cone orifice (nickel)	0.88 mm
Lens settings	Focus: -704 V; X deflection: 0.61 V; Y deflection: 2.43 V; Shape: 205 V; Rot Quad 1: 1.95 V; Foc Quad 1: -19.89 V; Rot Quad 2: 0.05 V; Focus Offset: 50.00 V
Data acquisition parameters	
Zoom Optics	Focus Quad: 0 V and Dispersion Quad: 0 V
Scan type	Static
Faraday cup configuration	L3 (²⁸ Si); C (²⁹ Si); H3 (³⁰ Si)
Mass resolution, $m/\Delta m$ at 5 and 95%	~4000
Sensitivity	3.8 V/ppm for ²⁸ Si,
Blank signal	0.006 V for ²⁸ Si,
Signal integration time	16.777 s for MC-ICPMS, 0.524 s for IEC-MC-ICPMS
Number of integrations	1
Blocks/Cycles	3/12 for MC-ICPMS, 1/1125 for IEC-MC-ICPMS
Agilent HPLC 1200 Series	
Column	ICE-AS1 (9 mm id x 250 mm)
Mobile phase A	0.01% HCl

Isocratic elution	100% A
Injection volume	100 μ L

Sample Preparation and Analysis for the determination of Si isotope ratios by IEC MC-ICPMS.

Replicate solutions of 2-10 $\mu\text{g g}^{-1}$ were prepared by diluting their respective stocks of NIST SRM3150 Si, Sigma-Aldrich Si and SCP Si in DIW. Individual solution of NBS28 in DIW containing a similar concentration of Si was prepared and used as the bracketing standard for each Si sample. River water SLRS-5 (pH 4) and seawater MOOS-3 were used directly without any pre-treatment for Si ratio measurements by IEC MC-ICPMS. Corresponding solutions of NBS28 in DIW and in Nutrient-free seawater containing similar concentrations of Si were prepared and used as the bracketing standards for SLRS-5 and MOOS-3, respectively. No significant amount of dissolved silicate was found in the nutrient-free seawater.

Neptune MC-ICPMS was used for the online Si isotope ratio measurements. Optimization of the Neptune MC-ICPMS was the same as described above but without use of the “Virtual Amplifier” since the transit signal was of interest. After the optimization, LC was connected to the nebuliser of MC-ICPMS through a 1 m length of PEEK tubing (0.13 mm id, 1.59 mm od). Sample gas was fine-tuned again by monitoring back ground Si signals in the 0.01% HCl eluent. Samples and corresponding NBS28 standard solutions were transferred to precleaned 1 mL polypropylene autosampler vials (Agilent Technologies Canada Inc., Mississauga, ON, Canada) for injections. A 100 μ L of each sample and standard was injected onto the IEC MC-ICPMS in the sequence of NBS28-sample-NBS28. Static run were employed to simultaneously measure three Si isotopes using the Faraday cup configuration shown in Table 1. At the end of the chromatographic run, the acquired raw data were transferred to an off-line computer for further processing using Excel software. Instead of using peak areas of three Si isotopes to generate measured ratios of $^{29}\text{Si}/^{28}\text{Si}$ and $^{30}\text{Si}/^{28}\text{Si}$, a more precise calibration³³⁻³⁵ based on linear

regression of transient intensities of three Si isotopes arising from the Si peak was used to derive its ratios.

RESULTS AND DISCUSSION

Evaluation of the nature of Si isotope fractionation in MC-ICPMS. To achieve accurate Si ratio measurements, medium resolution was employed to resolve potential polyatomic interferences such as $^{12}\text{C}^{16}\text{O}^+$, $^{14}\text{N}_2^+$, $^{28}\text{Si}^1\text{H}^+$, $^{13}\text{C}^{16}\text{O}^+$, $^{12}\text{C}^{16}\text{O}^1\text{H}^+$, $^{14}\text{N}^{15}\text{N}^+$, $^{14}\text{N}_2^1\text{H}^+$, $^{14}\text{N}^{16}\text{O}^+$, $^{13}\text{C}^{16}\text{O}^1\text{H}^+$, $^{14}\text{N}^{15}\text{N}^1\text{H}^+$ on Si isotopes by measuring at the left shoulders and the center of flat region of the peaks of analyte isotopes. As shown in Figure 1, for Si isotope ratio measurements, typically at 28.967 Da for the center cup of ^{29}Si instead of at the peak center was used, consequently the signals for all three Si isotopes could be acquired free of any interference. At the end of daily measurement session, a mass scan was performed again and no significant change in measurement point was observed, confirming accurate measurements.

Figure 1. Medium resolution mass scan of a $0.5 \mu\text{g g}^{-1}$ Si solution. Green line is ^{28}Si ; red line is ^{29}Si and purple line is ^{30}Si .

Various methods have been applied to evaluate the nature of isotope fractionation. The three-isotope plot approach, known as the δ' - δ' plot, has been successfully applied to ascertain the nature of isotope fractionation^{27, 36-38} where δ' is calculated from the Eq. 2.

$$\delta' = \ln\left(\frac{R_{\text{sample}}^{ij}}{R_{\text{std}}^{ij}}\right) \cdot 1000 \quad (2)$$

Currently there are no uniform mass dependent fractionation laws which can describe the instrumental mass bias observed in MC-ICPMS. In general, the slope, $\beta_{\text{experiment}}$, obtained from the $^{ij}\delta'$ vs $^{kj}\delta'$ plot of three isotopes of all measurements is compared to the expected “theoretical” slopes of common mass-dependent fractionation functions, such as kinetic mass-dependent law, equilibrium mass-dependent law, Russell’s law or generalized power law³⁷⁻³⁹. When $\beta_{\text{experiment}}$ differs significantly from the expected “theoretical” slopes of mass-dependent fractionation functions, it indicates mass independent fractionation. Calculation of theoretical slopes of the above popular mass-dependent fractionations are outlined below:

$$\beta_{\text{Theor-kinetic}} = \frac{\ln\left(\frac{m_j}{m_i}\right)}{\ln\left(\frac{m_j}{m_k}\right)} \quad (3)$$

$$\beta_{\text{Theor-Equilibrium}} = \frac{\frac{1}{m_i} - \frac{1}{m_j}}{\frac{1}{m_k} - \frac{1}{m_j}} \quad (4)$$

$$\beta_{\text{Theor-Russell}} = \frac{\ln\left(\frac{m_j}{m_i}\right)}{\ln\left(\frac{m_j}{m_k}\right)} \quad (5)$$

$$\beta_{\text{general-power}} = \frac{m_i^n - m_j^n}{m_k^n - m_j^n} \quad (6)$$

Where n is the discrimination exponent from -2 to +2 in Eq. 6. When $n \rightarrow 0$, it becomes Russell's law. When $n=1$, it becomes the power law. Since only the slope, not the intercept, is the subject of this investigation, the nature of isotope fractionation in MC-ICPMS can thus be ascertained by use of a simplified three isotope-plot of natural logarithms of two measured isotope amount ratios, $\ln r^{i/j}$ vs $\ln r^{k/j}$, as demonstrated in a recent study²⁸. The slope, $\beta_{\text{experiment}}$, of the $\ln r^{i/j}$ vs $\ln r^{k/j}$ plot of three isotopes of all measurements is obtained by using the SLOPE or LINEST function in Excel. The major advantage of this approach is that MIF can be verified without resorting to a "true" or "absolute" isotopic composition of standard.

Under normal MC-ICPMS operating conditions and with use of a pair of standard sample and H skimmer cones, a slope generated in the three-isotope plot for Si and their respective "predicted" mass-dependent slopes (calculated from Eqs 3-6) are shown in Figure 2. The slope obtained for isotope ratios involving ^{29}Si deviated significantly and consistently from their respective theoretical values. For example, a maximum value of $\beta_{\text{exp}} = 0.650 \pm 0.008$ (U, $k=1$) was obtained for the slope of $\ln r^{29/28}$ vs $\ln r^{30/28}$ plot, significantly different from theoretical values of 0.5009, 0.5092, 0.5092 and 0.5178 based on power law, Russell's law, kinetic law and equilibrium mass-dependent law, respectively, indicating MIF for ^{29}Si . The observed MIF for ^{29}Si isotope could not be explained by simple measurement artifacts since intensities for three isotopes were in a range of 0.85 to 25 V which were subtracted by intensities (0.3-7 mV) obtained in the blank and the same standard solution (from NIST SRM3150) was used to establish each $\ln r^{29/28}$ vs $\ln r^{30/28}$ plot. In addition, medium resolution mode was used to ensure free from any potential polyatomic interferences as shown in Figure 1. Furthermore, subsequent experiments of measuring Si standard solutions prepared from another Si standard (SCP) produced similar values of 0.537 ± 0.006 (U, $k=1$) to 0.716 ± 0.010 (U, $k=1$) for the slopes of β_{exp} generated from $\ln r^{29/28}$ vs $\ln r^{30/28}$ plots.

Figure 2. Typical three-isotope plot for silicon arising from measurements acquired over a 5-8 hour period. Error bars are 1SD at $n=3$ at each point. Solid lines represent predicted mass-dependent fractionation lines as given by the Eqs. 3-6. All nuclide masses were obtained from the 2003 Atomic Mass Evaluation report⁴⁰.

In addition, over the three-month period encompassing Oct. 2013 to Jan. 2014, many sets of the $\ln r^{29/28}$ vs $\ln r^{30/28}$ log-linear regressions were acquired, each yielding the respective slope. During this period instrument was optimized daily by a same and experienced operator to ensure high sensitivity, flat top square peaks and stable signals. Of these data obtained using H skimmer cone, 18 high-quality sets exhibiting the coefficient of determination r^2 larger than 0.99 are summarized in Figure 3a. Clearly relative small variations in the obtained experimental slopes of $\ln^{29/28}r$ vs $\ln^{30/28}r$ were evident in data obtained in a same day (for example, three points on Day H1) wherein significant day-to-day variations in the obtained experimental slopes were evident. As shown in Figure 3a, results obtained on Day H4

were on the predicted mass-dependent line, but the instrument settings were not significantly different from settings on days before or after.

Figure 3. Time-series plot of the silicon three-isotope regression slopes. Slope according to the Russell's law is shown as solid line (Eq. 5). Isotope ratio $^{30/28}\text{Si}$ is used as reference and uncertainties are given as $U = ku$ where $k = 1$.

Subsequent experiments using Jet sample and X skimmer cones were also conducted to investigate the magnitude of MIF for Si isotopes for a comparison purpose. Optimization of the

instrument was performed by the same operator to ensure high sensitivity, flat top square peaks and stable signals, similar to that using H cone. Compared to the standard H cone, sensitivity for Si improved about three-fold with the use of X cone. Results are shown in Figure 3b for the observed slopes of $\ln^{29/28}r$ vs $\ln^{30/28}r$ obtained in different days. Similarly, MIF in ^{29}Si isotope using X cone were varied significantly from the day-to-day and slightly varied during a same day. The maximum MIF observed for ^{29}Si isotope using X cone stayed roughly at same level as that observed using H cone. The above findings of day-to-day variations in MIF are possibly due to different daily plasma conditions and cone conditions (including different geometric of cones) that produced varying degrees of mass biases, similar to that observed recently for Sr isotopes²⁹.

Si isotope ratio measurements in commercial Si standards by MC-ICPMS. Based on the above finding of MIF within MC-ICPMS for Si isotopes, standard-sample bracketing (SSB) mass bias correction approach which is capable of correcting for both MDF and MIF was selected in this study by monitoring a standard solution prior to and after the introduction of the sample. In order to obtain accurate isotope ratio results, matrix matching between the sample and the standard solution is required with use of SSB mass bias correction model²³. Currently, NBS28 is frequently used as the standard to derive δ -values of Si isotope ratios in various samples, although absolute values for Si isotope ratios in NBS28 are not available. However, under stable instrument conditions, short measurement time and matrix matching sample and standard, measured raw ratios instead of mass bias corrected ratios can be directly used to calculate the δ -value of Si isotope ratio, as detailed elsewhere²³.

$$\delta^{i/28}\text{Si} = \left(\frac{r_{\text{sample}}^{i/28}}{r_{\text{NBS28}}^{i/28}} - 1 \right) \cdot 1000 \quad (7)$$

where $r_{\text{sample}}^{i/28}$ and $r_{\text{NBS28}}^{i/28}$ are measured ratio in the sample and the average measured ratio of two adjacent bracketing standard solution, respectively. Since the bracketing standard stock solution

NBS28 was made from SiO₂ in 1% HF and sample stocks of NIST SRM3150, SCP Si and Aldrich Si were made from Na₂SiO₃·9H₂O in DIW, NH₄SiF₆ in DIW with trace HF and Si metal in 2 % HF acid, respectively, thus simple dilution of the standard and sample stocks may lead to miss matched matrix between the standard and sample, resulting inaccurate results. As shown in Figure 4, matrix Na concentration induced a significant change in $\delta^{29/28}\text{Si}$ and $\delta^{30/28}\text{Si}$ values, the higher the Na concentration, the larger the change in $\delta^{29/28}\text{Si}$ and $\delta^{30/28}\text{Si}$ values. Sever signal suppression was noted for Si isotopes when Na concentration increased above 1000 ppm.

Figure 4. Effect of matrix Na concentration on measured $\delta^{i/28}\text{Si}$ in 5 $\mu\text{g g}^{-1}$ Si solutions with different amounts of Na added against a pure 5 $\mu\text{g g}^{-1}$ Si solution. $\blacktriangle$: $\delta^{29/28}\text{Si}$; $\blacksquare$: $\delta^{30/28}\text{Si}$; error bar is 1SD and n=5.

This observation highlights the need of matching of sample matrix in both standard and sample when SSB model is used. Indeed, both $\delta^{29/28}\text{Si}$ and $\delta^{30/28}\text{Si}$ values went back to 0.00 ± 0.04 and 0.00 ± 0.05 ‰

(mean and 1SD, n=10) when the standard and the sample were prepared at 5 $\mu\text{g g}^{-1}$ Si from NBS28 stock in a same matrix, such as in 0.1% NaOH heavy matrix.

It is of interest to measure Si isotope ratios in current commercially available Si materials such as NIST SRM3150, SCP Si and Aldrich Si against NBS28 to verify if there is any isotope variation among these standards. To avoid any potential matrix effect, the bracketing standard NBS28 and samples of NIST SRM3150, SCP Si and Aldrich Si were prepared at 5 $\mu\text{g g}^{-1}$ in 0.1% NaOH. Results obtained are shown in Table 2. Clearly, significant difference was detected in Si isotopic compositions in these commercially available Si standards. This observation could be very useful when comparisons of Si isotope ratio results calculated against different Si standards and from different research labs are needed.

Table 2. Si isotope ratio results in commercial high purity Si materials

Sample ID	MC-ICPMS (mean, SD, n=10)	
	$\delta^{29/28}\text{Si}$	$\delta^{30/28}\text{Si}$
NIST SRM3150	-0.22±0.04	-0.43±0.06
SCP Si	-0.60±0.06	-1.26±0.11
Aldrich Si	-0.70±0.02	-1.38±0.04
Sample ID	IEC-MC-ICPMS (mean, SD, n=10)	
	$\delta^{29/28}\text{Si}$	$\delta^{30/28}\text{Si}$
NIST SRM3150	-0.24±0.03	-0.46±0.04
SCP Si	-0.65±0.06	-1.21±0.07
Aldrich Si	-0.72±0.09	-1.36±0.11

Si isotope ratio measurements by on-line IEC MC-ICPMS. For samples with heavy matrix such as seawater or river water, it is practically impossible to match all matrix elements between these samples and the bracketing standard solution of NBS28 through addition of a common matrix such as Na as used earlier for commercial Si standards. Thus, an on-line column separation using IEC for the total Si determination reported in a previous study⁴¹ was adapted in this study for the determination of Si isotope

ratios. To improve sensitivity, X skimmer cone was used. As shown in Figure 1, silicate peak was found at retention time 360s for the MOOS-3 seawater by IEC SF-ICPMS. Same eluting conditions⁴¹ of 0.01% HCl as eluent at a flow rate of 0.80 mL min⁻¹ were used in this study.

Figure 5. Chromatogram of an injection of 100 μ L MOOS-3 seawater; ^{28}Si (solid black line), ^{29}Si (dash line) and ^{30}Si (solid grey line).

Instead of using peak areas of three Si isotopes to generate measured ratios of $^{29}\text{Si}/^{28}\text{Si}$ and $^{30}\text{Si}/^{28}\text{Si}$, a more precise calibration³³⁻³⁵ based on linear regression of transient intensities of all three Si isotopes was used to derive Si ratios. As shown in Figure 6, slopes of ^{29}Si and ^{30}Si versus ^{28}Si plots using 100 % Si peak (335-415 seconds) represent the measured ratios of $^{29}\text{Si}/^{28}\text{Si}$ and $^{30}\text{Si}/^{28}\text{Si}$, respectively. These measured ratios in the sample and bracketing standard were then used to derive δ -values of Si isotope ratios using Eq. 7.

Figure 6. Intensities of ^{29}Si and ^{30}Si versus intensity of ^{28}Si for the chromatographic Si peak (data from 100 % peak used) obtained for MOOS-3 seawater by IEC-MC-ICPMS. Slope of each linear regression represents corresponding Si isotope ratios of $^{29}\text{Si}/^{28}\text{Si}$ and $^{30}\text{Si}/^{28}\text{Si}$, respectively.

In general, signal intensity plays an important role in the measurement precision. To compare measurement precisions between on-line IEC-MC-ICPMS and direct nebulization MC-ICPMS analyses, NBS28 Si solutions at concentrations of 1, 2, 5, 10 and 15 $\mu\text{g g}^{-1}$ in DIW were measured. Same NBS28 Si solution was used as the bracketing standard accordingly. Results are summarized in Table 3. As expected, standard deviation from replicate measurements of Si isotope ratios decreased as Si isotope intensity increased and then leveled off when ^{28}Si intensity increased above 10 V. No significant difference was found in precisions of Si isotope ratios measured by IEC-MC-ICPMS and direct

nebulization MC-ICPMS when ^{28}Si signal in NBS28 Si solution was great than 10 V, confirming precise measurements can be obtained with on-line IEC-MC-ICPMS and linear regression of transient intensities of all three Si isotopes for generating measured Si isotope ratios.

Table 3. Si isotope ratio results in NBS28 Si solutions

Sample ID	MC-ICPMS (mean, SD, n=10)	
	$\delta^{29/28}\text{Si}$	$\delta^{30/28}\text{Si}$
1 $\mu\text{g g}^{-1}$	0.00±0.07	-0.01±0.07
2 $\mu\text{g g}^{-1}$	-0.01±0.04	0.01±0.04
5 $\mu\text{g g}^{-1}$	0.00±0.02	-0.01±0.03
10 $\mu\text{g g}^{-1}$	0.01±0.03	0.00±0.02
15 $\mu\text{g g}^{-1}$	ND (^{28}Si signal too high)	
Sample ID	IEC-MC-ICPMS (mean, SD, n=10)	
	$\delta^{29/28}\text{Si}$	$\delta^{30/28}\text{Si}$
1 $\mu\text{g g}^{-1}$	-0.01±0.11	0.01±0.14
2 $\mu\text{g g}^{-1}$	0.01±0.08	-0.01±0.10
5 $\mu\text{g g}^{-1}$	0.00±0.04	0.01±0.05
10 $\mu\text{g g}^{-1}$	-0.01±0.02	0.00±0.03
15 $\mu\text{g g}^{-1}$	0.00±0.03	0.01±0.02

As shown in Figure 4 earlier for the Na matrix effect study, biased values of -1.59 ± 0.12 and -3.40 ± 0.12 ‰ (1SD, n=5) for $\delta^{29/28}\text{Si}$ and $\delta^{30/28}\text{Si}$, respectively, were obtained when matrix was not matched, as the sample in 0.1% NaOH and the standard in DIW. To validate the proposed on-line IEC-MC-ICPMS method, same sample of NBS28 Si at $5 \mu\text{g g}^{-1}$ in 0.1% NaOH was measured against the standard of NBS28 Si at $5 \mu\text{g g}^{-1}$ in DIW. Values of -0.01 ± 0.03 and 0.01 ± 0.06 ‰ (1SD, n=10) for $\delta^{29/28}\text{Si}$ and $\delta^{30/28}\text{Si}$, respectively, were obtained, in agreement with expected zero for δ values, confirming the accuracy of the method. Furthermore, three commercially available high purity Si materials of NIST SRM3150, SCP Si and Aldrich Si at $5 \mu\text{g g}^{-1}$ in DIW were also measured against

NBS28 at $5 \mu\text{g g}^{-1}$ in DIW using IEC-MC-ICPMS. As shown in Table 2, results obtained using IEC-MC-ICPMS are in good agreement with results obtained by direct nebulization MC-ICPMS measurements with matrix matching between the sample and standard in 0.1% NaOH, confirming the accuracy of the method.

The online IEC-MC-ICPMS method was applied for the determination of Si isotope ratios in SLRS-5 river water and MOOS-3 seawater. To avoid any possible plasma instability induced by very heavy matrix of seawater, a solution of NBS28 containing similar concentration of Si prepared in Nutrient-free seawater was used as the bracketing standard. To validate this on-line IEC-MC-ICPMS method for the seawater analysis, NBS28 Si at $5 \mu\text{g g}^{-1}$ in Nutrient-free seawater was measured against itself. Values of -0.01 ± 0.06 and 0.00 ± 0.06 ‰ (1SD, n=10) for $\delta^{29/28}\text{Si}$ and $\delta^{30/28}\text{Si}$, respectively, were obtained, in agreement with expected value of zero, and confirming the accuracy of the method for the determination of Si isotope ratios in heavy matrix seawater. For the final determination of Si isotope ratios in river and seawater samples, ten measurements were made on each sample under optimized experimental conditions. Values of -0.06 ± 0.07 and -0.20 ± 0.11 ‰ (1SD, n=10) for $\delta^{29/28}\text{Si}$ and $\delta^{30/28}\text{Si}$, respectively, were obtained for the MOOS-3 seawater whereas 0.59 ± 0.11 and 1.19 ± 0.15 ‰ (1SD, n=10) for $\delta^{29/28}\text{Si}$ and $\delta^{30/28}\text{Si}$, respectively, were obtained for the SLRS-5 river water. Results obtained in natural waters in this study using on-line IEC-MC-ICPMS are in line with these reported in other river and seawater samples using column separation^{2, 4-6, 8-9}.

CONCLUSION

An accurate, precise and direct method is described for the determination of Si isotope ratios in commercial Si standards and natural waters by on-line IEC MC-ICPMS. The reported method provides for a relatively rapid (10 minutes per run) and simple on-line technique which requires no sample pre-treatment. Mass-independent fractionation was found for Si isotopes within MC-ICPMS itself in this

study. Although results obtained in this study are from two similar MC-ICPMS instruments, namely Neptune (NRC) and Neptune plus (China University of Geosciences), however, we do not believe the observed MIF is only unique with Neptune MC-ICPMS since MIF was also reported using IsoProbe MC-ICPMS and Nu MC-ICPMS for Nd^{24} , Ce^{25} and Sr^{29} . Consequently, the standard-sample bracketing mass bias correction model was selected to obtain accurate results. The proposed on-line IEC-MC-ICPMS method with use of linear regression of transient intensities of Si isotopes for data reduction is capable of providing compatible measurement precisions of Si isotope ratios to that obtained by direct nebulization MC-ICPMS. Significant differences in Si isotope ratios were not only found in several Si standards tested but also in natural waters. These observations further confirm that such data may provide a useful tool for studying a wide variety of chemical, geological and biological processes in nature. To the best of our knowledge this is the first report of the application of on-line IEC-MC-ICPMS for the high precision determination of Si isotope ratios in natural waters.

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