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Determination of Stable Silicon Isotopes Using Multi-Collector Inductively Coupled Plasma Mass Spectrometry

ZHANG An-Yu[1,2,*], ZHANG Jing[2], ZHANG Rui-Feng[2], XUE Yun[2]

[1] School of Resources and Environment Science, East China Normal University, Shanghai 200062, China
[2] State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Shanghai 200062, China

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Abstract: An instrumental analysis method for stable silicon (Si) isotope ratios using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) was established in this study. In dry plasma mode, silicon isotopes suffered from the spectral polyatomic interferences of C, N, O and H at medium resolution. The sample gas flow had significant effect on the Si sensitivity and signal stability. Moreover, higher sample gas flow led to higher production of $^{14}N^{16}O$. Consistent $\delta^{29}Si$ and $\delta^{30}Si$ within 0.04 ‰ (1σ) was obtained over a mass range of ca. 0.009 amu at the lower mass side of Si at medium resolution. The concentration between the samples and standards was matched within 20% to obtain accurate mass bias correction using standard-sample-bracketing correction (SSB) method. The measurements were not sensitive to the acid molarity and Cl matrix. An internal precision better than 8 ppm (1σ) was achieved for $^{29}Si/^{28}Si$ and $^{30}Si/^{28}Si$ by taking an integration time of 8 s. The long-term reproducibility of 0.06‰–0.10‰ (2σ, $n = 20$) was obtained for $\delta^{29}Si$ and $\delta^{30}Si$ by repeated analysis of the silicon reference materials, whilst the determined isotopic value for GBW04421 and GBW04422 were in good agreement with the recommended values, suggesting the precision and robustness of this method. The measured silicon isotopic values of fresh waters (river and lake waters), saline waters and seawater demonstrated the capability of this method to trace the biogeochemical processes of silicon in natural waters.

Key Words: Multi-collector; Silicon isotopes; Inductively coupled-plasma mass spectrometry

1 Introduction

Silicon (Si) is the second only to oxygen in abundance in the earth's surface, accounting for 27.6% of the continental crust by weight. The Si cycle processes in the natural environment, for example, the silicate weathering and photosynthesis of diatoms, are closely linked to the global carbon cycle, and exert far-reaching impact on the partial pressure of atmospheric CO_2 at different time scales[1,2]. Si has three stable isotopes of atomic mass unit ^{28}Si, ^{29}Si and ^{30}Si, with abundance of 92.23%, 4.67% and 3.10%, respectively[3]. Measurement of the isotopic composition of dissolved silicon (DSi) in natural waters (such as river water, seawater and groundwater) can be applied to trace the biogeochemical cycles of Si, for example, the chemical weathering of silicate

minerals[4], the bio-mineralization of DSi by vegetation and diatoms, etc.

Si isotopes were initially measured using gas source mass spectrometry (IRMS) by converting it as SiF_4 gas and determined as SiF_3^+. High precision was achieved using this technique. However, special safety consideration should be taken for the fluorination process. More importantly, large sample amount required by the instrumental analysis limited the application of this method in Si-depleted samples (such as surface seawaters). Recently, the rapid development of multi-collector inductively coupled mass spectrometry (MC-ICP-MS) enabled the precise measurement of isotopic composition with reduced sample amount. The major factors that hamper the precision and accuracy of analysis included the spectral interference and mass discrimination correction[5]. With

respect to Si, all three stable isotopes suffered from the polyatomic interferences of C, H, O and N[6], which might originate from the solvents and atmosphere. Especially, the high production of $^{14}N^{16}O$ using wet plasma might even prevent the measurement of ^{30}Si[7]. The instrumental mass bias in ICP-MS was primarily contributed by the so-called space-charge-effect and nozzle effect[8], and was usually corrected by applying standard-sample-bracketing (SSB) method. However, the matrix composition, concentration match between the samples and standards, as well as the instrumental setting could cause the variation of mass bias.

In this study, the factors influencing the determination of Si isotopes by MC-ICP-MS, including polyatomic interferences, instrumental parameters, sample acidity and matrix composition, were systematically evaluated. The precision and accuracy of instrumental analysis were verified using different Si isotope reference materials. Additional samples collected from typical natural water were also analyzed to demonstrate the capability of this method in resolving small Si isotopic variations in natural environments.

2 Experimental

2.1 Reagents and instruments

Three Si isotope reference materials (NBS28, GBW04421 and GBW04422) were prepared using the alkaline fusion procedure[9]. Approximately 214.8 mg Si reference material and 757.1 mg Na_2CO_3 solid (99.99%) were taken and mixed in a platinum crucible; the mixture was fused in the muffle furnace at 950 °C for 1 h. After cooling, the fusion cake was dissolved with 1 M HCl (30% Supra, Merck) and diluted to 100 mL in plastic volumetric flask. Then the solution was transferred into clean HDPE bottle and stored at 4 °C. Solutions of 500 ng mL^{-1}Si was prepared by diluting the stock solution using MQ-water (18.2 MΩ cm, Millipore) for instrumental analysis.

2.2 Sample collection and pre-treatment procedure

Natural water samples (river water, saline water, seawater and lake water) were collected and filtered through 0.4 μm polycarbonate membranes. The filtrate was stored in clean polyethylene bottles and acidified to pH 2 with hydrochloric acid.

Fresh water samples with DSi > 20 μM were purified using the cation exchange resin (Dowex 50W-X8, 200–400 mesh, H$^+$-form, Sigma Aldrich) for Si isotopes determination, the remaining samples were prepared using the modified single magnesium induced co-precipitation method followed by the resin purification[10]. DSi concentration for these samples was measured using colorimetric method[11] on a SAN Skalar Plus continuous flow analyzer.

2.3 Instrumental analysis

Isotopic analysis was performed by NEPTUNE MC-ICP-MS (Thermo Fisher, Germany). All three Si isotopes ^{28}Si, ^{29}Si and ^{30}Si were detected simultaneously in static mode at medium resolution. To attenuate the formation of polyatomic interference, the sample solution was introduced in a dry plasma mode using 100 μL min^{-1} PFA nebulizer (Thermo Fisher Scientific) attached to Apex-IR desolvating system (Elemental Scientific, without membrane module) to reduce the introduction of H_2O, CO_2, O_2 and N_2 into the torch. Instrumental parameters were optimized using the Si-containing solution prior to sample analysis on a daily basis. The typical settings are listed in Table 1.

Mass bias of Si isotopes was usually corrected by applying a SSB method or Mg-doping internal correction. As the fractionation coefficients for Mg and Si were reported to be not equal and vary between different analytical sessions, normally additional SSB technique was required when using the Mg-doping procedure[7,12]. In addition, the detection of Si and Mg isotopes using a dynamic peak jumping would extend the measurement duration and reduce the sample throughout. Therefore, the SSB procedure was applied to correct the Si isotope mass bias, the results were expressed in delta notation relative to NBS28 and calculated as follows:

$$\delta^x Si(\text{‰}) = [\frac{(^x Si/^{28} Si)_{Sample}}{(^x Si/^{28} Si)_{Standard}} - 1] \times 1000 \qquad (1)$$

where, x= 29 or 30.

3 Results and discussion

3.1 Spectral interferences

As shown in Fig.1, the polyatomic interferences were clearly identified through the mass scan of Milli-Q water at medium resolution in dry plasma mode. An interference-free

Table 1 Instrumental setting for Si isotope determination using NEPTUNE MC-ICP-MS

MC-ICP-MS parameters	
Resolution	Medium Resolution
Cup configuration	^{28}Si(L3)-^{29}Si(L1)-^{30}Si(H3)
Sample introduction	PFA nebulizer (100 μL min^{-1}), Apex-IR
Apex-IR temperature	100 °C/4 °C
Skimmer cone	X-cone (0.8 mm)
Sample gas	0.94 –0.98 L min^{-1}
Cool gas	16 L min^{-1}
Auxiliary gas	1.0 L min^{-1}
RF power	1250 W
Data acquisition	1 block × 30 cycle
Idle time	3 s
Instrumental blank	^{28}Si 6–15 mV
Si concentration	500 ng mL^{-1}
Si sensitivity	3–5 V mL μg^{-1}