

Measuring production–dissolution rates of marine biogenic silica by ^{30}Si -isotope dilution using a high-resolution sector field inductively coupled plasma mass spectrometer

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Abstract

Regional and seasonal variability of the Si dissolution:production ratios in the surface ocean have not been well assessed. Here, we propose a new method for determining these rates, using the ^{30}Si -isotopic dilution technique with a high-resolution sector field inductively coupled plasma mass spectrometer (HR-SF-ICP-MS). Relative analytical precision of the isotopic measurement is better than 1%, similar to that obtained by thermal ionization–quadrupole mass spectrometry (TIMS). Accuracy and reproducibility of the isotopic measurements have been checked on artificial and natural solutions by intercomparison between two HR-SF-ICP-MS instruments and one TIMS. Measurements of real Si production and dissolution rates are illustrated for two contrasted situations with an average relative precision of 10%, including one from waters with low Si content ($2\ \mu\text{mol L}^{-1}$), which required an additional purification step by cation exchange chromatography. Si production rate from this later incubation was not significantly different from the one measured by radioactive ^{32}Si . The new method is faster and simpler than TIMS or isotope ratio mass spectrometry (IRMS). Its sensitivity is more than one order of magnitude better than TIMS, and it can cover the whole range of Si concentrations encountered in the ocean.

Introduction

The silicon (Si) biogeochemical cycle is linked to global CO_2 concentrations through chemical weathering of silicate minerals, which transfers carbon dioxide from the atmosphere to the lithosphere (e.g., Wollast and Mackenzie 1983). Si also affects carbon cycling through production of marine siliceous phytoplankton such as diatoms, a group that has an absolute requirement for Si to build their cell wall (the frustule) and contributes from 25% to 75% of the ocean's total primary productivity (e.g., Nelson et al. 1995, Tréguer et al. 1995). As a result, diatoms are a key player in the carbon biological pump (Buesseler 1998, Smetacek 2001) and contribute significantly to atmospheric CO_2 drawdown (Tréguer and Pondaven 2000). They are the only ecologically dominant phytoplankton group requiring silicic acid [$[\text{Si}(\text{OH})_4$; DSi] for growth whose

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availability in surface waters depends on both external inputs (mostly resupply of silicic acid from below the mixed layer or by advection) and internal recycling within the mixed layer. Indeed, very little is known about the exact contribution of this internal recycling to Si(OH)₄ availability in surface waters in different ecosystems on seasonal and annual time scales (Nelson et al. 1995, Tréguer et al. 1995), mainly because accurate biogenic silica (bSiO₂) dissolution rates are still difficult to measure. In 2007, only 56 integrated profiles of the silicon budget (J_D/J_P) in the surface oceans were available (Nelson and Goering 1977b; Nelson and Gordon 1982; Nelson et al. 1981, 1995; Brzezinski and Nelson 1989; Brzezinski et al. 2001, 2003; DeMaster et al. 1996; Beucher et al. 2004a, 2004b). Therefore, the magnitude of the Si-dissolution:production ratio (D:P) and its variability are not well defined. This constitutes a major remaining uncertainty in the global marine silica budget.

Since 1973, simultaneous measurements of the production and dissolution rates of bSiO₂ have been performed using the ³⁰Si-isotopic dilution technique (Goering et al. 1973; Nelson and Goering 1977a, 1977b). Samples from the euphotic layer are spiked with ³⁰Si(OH)₄ and incubated under controlled conditions (mainly temperature and light) for a specified time (usually 24 h). The change in isotopic composition of the biogenic silica is used to estimate the production rate by measuring the enrichment in ³⁰Si of the particulate phase. To assess dissolution rates, the increase in ²⁸Si in the dissolved phase due to the dissolution of initial biogenic silica is measured.

Two different methods to measure the enriched isotopic Si compositions have been used so far. The first one [developed by Goering et al. (1973), Nelson and Goering (1977a, b)] uses a gas source mass spectrometer and measures abundance of SiF₃⁺ ions. This requires the transformation of SiO₂ (bSiO₂) into BaSiF₆ by hydrofluoric acid (HF) attack, then (BaCl₂) precipitation. For dissolved silicon, a prior extraction and purification of Si(OH)₄ into SiO₂ with triethylamine-molybdate is required (De Freitas et al. 1991, De La Rocha et al. 1996), or the use of an ion-exchange resin (Sephadex) and subsequent transformation in BaSiF₆ by Na₂SiF₆ precipitation/HCl dissolution/(BaCl₂) precipitation (Brzezinski et al. 2003). These procedures are time-consuming, and use HF, which is potentially harmful. Corvaisier et al. (2005) proposed an alternative using thermal ionization–mass spectrometry (TIMS) with a quadrupole (THQ; Thermo) to measure SiO₂⁻ ions from pure silica deposits. An alkaline digestion for biogenic silica is first applied. Purification and transformation of Si(OH)₄ into SiO₂ is performed followed by triethylamine-molybdate coprecipitation completed by a mineralization at 1100°C. This method avoids the use of HF and allows accurate blank measurements, although the procedure is still time-consuming.

Here we describe a new method for the simultaneous determination of the rates of production and dissolution of biogenic silica in the marine environment. We used the same

sampling method and the calculation models described in Corvaisier et al. (2005) and Elskens et al. (2007), but we analyzed the isotopic composition by HR-SF-ICP-MS (Element 2) instead of TIMS or IRMS. Our procedure required a different sample processing protocol than the previous ones, but it is easier and two to four times faster, prevents the use of HF, and uses HR-SF-ICP-MS instruments, which are widespread and available in many laboratories.

Materials and procedures

Instrumentation—A standard HR-SF-ICP-MS (Element2; Thermo) was used to measure the Si-isotopic abundances as described in Eqs. 1 and 2 for ³⁰Si and ²⁸Si, respectively.

$$\text{Atom \% } ^{30}\text{Si} = 100 \times \frac{[^{30}\text{Si}]}{[^{28}\text{Si}] + [^{29}\text{Si}] + [^{30}\text{Si}]} \quad (1)$$

$$\text{Atom \% } ^{28}\text{Si} = 100 \times \frac{[^{28}\text{Si}]}{[^{28}\text{Si}] + [^{29}\text{Si}] + [^{30}\text{Si}]} \quad (2)$$

Ionic currents were measured using a secondary electron multiplier in electric scanning mode (E-scan). For accurate determinations, all spectrometric interferences on silicon must be resolved. A mass resolution of 4000 (medium resolution mode of the Element2) is adequate to avoid all possible interferences (Klemens and Heumann 2001). The sample introduction system combined a glass concentric nebulizer (100 μL/min), a glass-jacketed Tracey type cyclonic spray chamber (Glass Expansion), a quartz injector, and a quartz torch (Thermo). This configuration provided the best blank:sample ratio (less than 10%) even when compared with a Teflon PFA sample introduction system. The HR-SF-ICP-MS operating conditions are summarized in Table 1.

A spectrophotometer (Genesys 10S UV, VWR) was used for quantification of biogenic silica and dissolved silicon concentrations, with a colorimetric method according to Grasshoff et

Table 1. Operating conditions of silicon isotope ratio measurements by HR-SF-ICP-MS.

RF power	1210 W
Plasma gas	16 L min ⁻¹
Auxiliary gas flow	1.0–1.3 L min ⁻¹
Nebulizer gas flow	1.0–1.2 L min ⁻¹
Sample uptake rate	100 μL min ⁻¹
Mass resolution	4500
Acquisition mode	Electric scanning
Isotopes measured	²⁸ Si, ²⁹ Si, ³⁰ Si
Detection mode	Pulse counting mode
Search window	80%
Integration window	40%
Integration type	Average
Time per scan	2.64 s
Number of samples per peak	50
Number of replicates	18 (3 runs, 6 passes)
Sensitivity/100 ppb Si	1–2 × 10 ⁶ cps
Blank	0.4–2.0 × 10 ⁵ cps

al. (1983). The relative precision of the method for concentrations of biogenic silica and dissolved silicon was 10% and 2.5%, respectively.

Reagents and standard solutions—All the solutions were prepared with 18 MΩ ultrapure deionized water. All sampling plasticware (flasks, filtration units, decantation funnels, etc.) were precleaned with 3% HCl (Merck, p.a.). The plasticware used for the isotopic measurements were precleaned with acid (2 times with distilled HNO₃ 6.5% [Merck, p.a.], once with HF/HCl 4.5%–3.2% [Merck, Suprapur], and once with bidistilled HNO₃ 6.5% [Merck, p.a.]).

Spike solutions of sodium silicate were prepared after the fusion of ³⁰Si-enriched silica powder (99.62%; Chemgas) with anhydrous sodium carbonate (Merck, Suprapur) (Goering et al. 1973). Hot 0.2 M NaOH (Merck, p.a.) was used for alkaline digestion of biogenic silica and 1 M HCl for neutralization thereafter. Brucite coprecipitation adapted from MAGIC (magnesium induced coprecipitation; Karl and Tien 1992) to pre-concentrate dissolved silicon was performed with 14 M sodium hydroxide. The brucite precipitate was redissolved in 3 M HCl. HNO₃ 65% and 32% was used for the pre-cleaning of the cation-exchange resin. HNO₃ 65% was used to adjust the acidity of the HR-SF-ICP-MS solution matrix. All acids were bidistilled or Suprapur (Merck).

Sample collection, spiking, and incubation—As described in Corvaisier et al. (2005), a variable volume of seawater, dictated by the initial Si content (usually 6 L), was collected in the euphotic layer. The only difference between the sampling procedure described in Corvaisier et al. (2005) and ours resided in the fact that we sampled an additional ~2 L of seawater to have a natural silicon isotopic standard (i.e., not spiked with ³⁰Si) to be processed along with the samples. This unspiked sample was immediately filtered (0.4 μm; Nuclepore PC membrane) to separate bSiO₂ from DSi. The membrane was dried at room temperature under a laminar flow hood or at 50°C in an oven, and the filtrate was directly preconcentrated. These samples were used later as analytical standards for natural biogenic and dissolved silicon isotopic composition to correct for the matrix effect inducing instrumental mass bias (see next section).

The 4-L sample aliquot was spiked with ³⁰Si in the form of Na₂SiO₃ solution, in a proportion usually lower than 10% of the ambient DSi concentration. This minimized the perturbation on the natural DSi contents and provided sufficient sensitivity for the isotopic measurements.

After ³⁰Si spiking and gentle mixing, 2 L was immediately filtered and processed to characterize the initial conditions.

The second half of the 4-L aliquot was poured into a polycarbonate flask and incubated either at temperature and light conditions simulating those prevailing in situ (on deck incubation) or in laboratory controlled conditions (in vitro incubation), usually for 24 h. At the end of the incubation period, the sample was filtered and treated as described above to characterize the final variables of the incubation.

Digestion of biogenic silica—The material collected on the polycarbonate membranes was digested in one step with 0.2 M NaOH during 40 min at 100°C followed by neutralization with 1 M HCl (Ragueneau et al. 2005).

A fraction of the digested sample was used to measure bSiO₂ concentration, whereas another one was diluted to ~100 ppb Si in a bidistilled 0.65% HNO₃ solution for the isotopic measurement.

Preconcentration of dissolved silicon—This preconcentration was achieved with a protocol adapted from the MAGIC method (Karl and Tien 1992): a quantitative scavenging of Si(OH)₄ by the brucite [Mg(OH)₂] precipitate was obtained by adding 1 mL of 14 M NaOH in 1 L seawater. Brzezinski et al. (2003) report that this method does not fractionate at the precision level usually required for isotopic dilution experiments, and Cardinal et al. (2005) have shown it is even suitable for measurements of natural Si isotopic composition. The precipitate was recovered by filtration (0.8 μm; PC membrane Nuclepore) or by centrifugation and then redissolved in 4.3 mL of 3 M HCl. This step enhanced the Si:salinity ratio of the redissolved solution and reduced the Si-requirement of the whole method, because the maximum salinity of the solution that can be introduced in the mass spectrometer is ~2‰ (see below). An aliquot of this solution was then diluted to ~100 ppb Si in 0.65% HNO₃ and run for the isotopic measurement.

Chromatographic purification of dissolved silicon—As the Si-requirement is controlled both by the maximum salinity (2‰) of the solution that can be introduced in the HR-SF-ICP-MS (mostly to avoid clogging of the cones) on the one hand and by the initial content of DSi in seawater on the other, the minimal DSi content in seawater should be ~2.8 μmol L⁻¹ for measurement without purification. This estimation takes into account an average HR-SF-ICP-MS sensitivity of 1.10⁶ cps/100 ppb Si in solution (Table 1) and a salinity of the MAGIC solution of 80 ± 8‰ by liter of coprecipitated seawater (average of 132 measurements). For bSiO₂, due to the low salinity (~10‰) of the alkaline digestion solution and the important Si concentration factor of this step (400 times for 2 L filtrated), the Si-requirement was not controlled by the salinity of the digested bSiO₂ solutions for the range of bSiO₂ concentrations encountered in the ocean. In the case of DSi < 2.8 μmol L⁻¹, the salinity constraint could be overcome by applying a purification step using the cation-exchange chromatography developed by Georg et al. (2006) for the natural silicon isotopic composition measurements. The Si separation and purification were achieved with 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 was precleaned by several rinses with HCl, HNO₃, and ultrapure deionized water (18 MΩ), as detailed in Table 2 and described in Georg et al. (2006). Before loading the sample, the eluted water was checked for neutral pH to ensure complete removal of any acid. Because the prevailing Si species do not bind to the resin, the elutant is water and silicic acid, allowing complete Si

Table 2. Separation scheme (Georg et al. 2006) of the cation-exchange chromatography applied to the MAGIC solution with low Si content (BioRad AG 50W-X12, 1.8 mL resin bed).

Separation stage	Solution matrix	Volume, mL
Precleaning	3N HCl	3
Precleaning	6N HCl	3
Precleaning	7N HNO ₃	3
Precleaning	10N HCl	3
Precleaning	6N HCl	3
Precleaning	3N HCl	3
Rinse	MQ-e	8
		(pH should be neutral)
Sample load	Diluted MAGIC solution	2–4 µg Si
Elution	MQ-e ^a	2

^aMQ-e is ultrapure deionized water.

recovery, the cation-exchange resin retaining effectively all the ambient cationic species (Georg et al. 2006).

Per column, 2 to 3.6 µg Si was loaded and purified by ion-exchange chromatography in about 12 h, including all precleaning steps. The number of samples processed simultaneously depends on the number of available columns (usually 20–30).

One aliquot of the elutant was taken and diluted to ~100 ppb Si in a bidistilled 0.65% HNO₃ solution for the isotopic measurement.

Isotopic measurements—The solutions of ~100 ppb Si in bidistilled 0.65% HNO₃ were analyzed by HR-SF-ICP-MS to determine the silicon isotopic abundances. A single analysis took 4.5 min (2 min uptake time and 2.5 min analysis) and included 18 measurements (Table 1).

We applied the blank/standard/sample bracketing technique to correct for the instrumental mass bias (induced by matrix and temporal drift) using the linear law. Because the standard (which is the initial unspiked aliquot of the same sample) and the sample have exactly the same matrix, any matrix bias is avoided by the bracketing technique. The blank (ultrapure deionized water [18 MΩ] with bidistilled 0.65% HNO₃) was subtracted from the sample. A complete analysis (2 blanks, 2 standards, 1 sample) was achieved in less than 20 min, and an autosampler can be used. No memory effect was observed, since each spiked sample was bracketed with a standard bearing a natural isotopic composition and no significant difference was observed between two standards.

Determinations of production and dissolution rates—To calculate the flux rates (production and dissolution of biogenic silica, respectively, ρ_p and ρ_D) from those measurements, it is necessary to postulate a model. Until now two different models existed, the linear one-compartment model described for production (Nelson and Goering 1977a) and dissolution (Nelson and Goering 1977b), and the nonlinear two-compartment

model described in Beucher et al. (2004a), de Brauwere et al. (2005), and Elskens et al. (2007).

The one-compartment model from Nelson and Goering (1977a, b) is described for production and dissolution rates by Eqs. 3 and 4, respectively:

$$\rho_p = [\text{bSiO}_2] \cdot \frac{\text{Atom } \% \text{ }^{30-28}\text{Si-bSiO}_{2(t)}}{t \cdot \text{Atom } \% \text{ }^{30-28}\text{Si-DSi}_{(0)}}, \quad (3)$$

$$\rho_D = [\text{DSi}] \cdot \frac{\text{Atom } \% \text{ }^{30-28}\text{Si-DSi}_{(0)} - \text{Atom } \% \text{ }^{30-28}\text{Si-DSi}_{(t)}}{t \cdot \text{Atom } \% \text{ }^{30-28}\text{Si-DSi}_{(0)}}, \quad (4)$$

where [DSi] and [BSiO₂] are the dissolved and biosilica contents, respectively (in µmol L⁻¹); ³⁰⁻²⁸Si-DSi and ³⁰⁻²⁸Si-bSiO₂ are the abundances of ³⁰⁻²⁸Si in DSi and bSiO₂ phases, respectively (in atom %). For Eqs. 3, 4, 7, and 8, the abundances represent the abundance in excess, i.e. measured minus natural abundances. Subscripts 0 and *t* refer to initial and final samples (*t* is incubation time).

It is noted, however, that two different analytical solutions were gathered whether considering the sample concentration at the beginning or at the end of the incubation. To correct for these changes in concentration, Nelson and Goering (1977a, b) recommend using the geometric mean when calculating the rates.

The nonlinear two-compartment model from Beucher et al. (2004a) is described by Eqs. 5–8:

$$[\text{DSi}]_{(t)} = [\text{DSi}]_{(0)} + (\rho_D - \rho_p) \cdot t, \quad (5)$$

$$[\text{bSiO}_2]_{(t)} = [\text{bSiO}_2]_{(0)} + (\rho_p - \rho_D) \cdot t, \quad (6)$$

$$\text{Atom } \% \text{ }^{30-28}\text{Si-DSi}_{(t)} = \text{Atom } \% \text{ }^{30-28}\text{Si-DSi}_{(0)} \cdot \left(1 + \frac{\rho_D - \rho_p}{[\text{DSi}]_{(0)}} \cdot t\right)^{\frac{\rho_D}{\rho_D - \rho_p}}, \quad (7)$$

$$\text{Atom } \% \text{ }^{30-28}\text{Si-bSiO}_{2(t)} = \frac{\text{Atom } \% \text{ }^{30-28}\text{Si-DSi}_{(0)} \cdot [\text{DSi}]_{(0)} \cdot \left(1 - \left(1 + \frac{\rho_D - \rho_p}{[\text{DSi}]_{(0)}} \cdot t\right)^{\frac{\rho_p}{\rho_D - \rho_p}}\right)}{[\text{bSiO}_2]_{(0)} + (\rho_p - \rho_D) \cdot t} \quad (8)$$

These parameters were constrained by the requirement to fit mass and isotopic balances of the dissolved and the particulate phases (i.e., four equations for two unknowns, ρ_D and ρ_p), the best solution being found iteratively by minimizing the cost function for the four equations simultaneously. This model takes into account both isotope dilution and concentration changes occurring in the course of incubation, which can induce biases in the estimations (Elskens et al. 2007).

The comparison and the precision of the two models are outside the scope of this article; a detailed discussion on these issues is developed in Elskens et al. (2007).

The development of radioactive ³²Si isotope method (Tréguer et al. 1991, Brzezinski and Phillips 1997) has significantly improved the measurements of biogenic silica production rates but is not able to measure dissolution rates. When

Table 3. Average ³⁰⁻²⁸Si isotopic abundance, with absolute and relative standard deviations of the same solution (after MAGIC preconcentration step) without and with chromatographic purification.

	³⁰ Si ± SD, atom %	RSD, %	²⁸ Si ± SD, atom %	RSD, %	n
Without chromatographic purification ^a	6.37 ± 0.04	0.60	89.12 ± 0.05	0.05	10
With chromatographic purification ^b	6.40 ± 0.04	0.26	89.09 ± 0.04	0.05	17

The resin was loaded with 500 µL solution diluted to 4 mL. RSD, relative standard deviation. ^aTen measurements performed during six analytical sessions over a 4-month period; ^b17 measurements performed during six analytical sessions over a 2-month period.

production rates are calculated from ³²Si, dissolution rates can be calculated only if the ³⁰Si method is coupled to the ³²Si method. In such a case, Eq. 4 must be used (as in Brzezinski et al. 2001, 2003).

Assessment

Chromatographic purification step—Table 3 compares the ³⁰⁻²⁸Si-isotopic abundances for one solution after MAGIC preconcentration step with and without chromatographic purification. The results show that there was no significant difference, providing evidence that the purification step did not introduce any measurable isotopic bias, as initially shown by Georg et al. (2006).

Incubation experiments used to determine production and dissolution rates—Two contrasted incubations, including one that required a chromatographic purification step, have been conducted to test the precision and the accuracy of this analytical method. For incubation 1, a 500-mL laboratory culture of diatoms *Chaetoceros brevis* was grown at 3°C in F/2 medium (Veldhuis and Admiraal 1987; except for saline matrix, which was natural seawater) and a 16:8 h light:dark cycle under light intensity of 120 µmol quanta m⁻² s⁻¹ in an incubation cabinet (RUMED). Three weeks after the inoculation, the incubation was spiked with ³⁰Si for 24 h. For incubation 2 (needing the purification step), a ³⁰Si-spiked 4-L culture of natural seawater sample at 1% light level in the Antarctic Polar Frontal Zone south of Tasmania was left for 24 h in an on-deck incubator (SAZ-SENSE cruise onboard the R/V *Aurora Australis*, summer 2007). The initial and final DSi and bSiO₂ concentrations of these incubations are given in Table 4. The incubations were processed as described above.

In the case of incubation 2, the spike addition represents about +20% of the ambient DSi concentration, i.e., larger than the targeted spiking rate (<10%) to avoid an artifact due to the

Table 4. Initial and final bSiO₂ and DSi concentrations of incubations 1 and 2 used to test the method.

	DSi ± SD, µmol L ⁻¹	bSiO ₂ ± SD, µmol L ⁻¹
Incubation 1		
Initial	30.4 ± 0.8	9.5 ± 0.9
Final	24.9 ± 0.8	14.4 ± 1.4
Incubation 2		
Initial	1.98 ± 0.04	1.31 ± 0.13
Final	2.08 ± 0.04	0.89 ± 0.09

possible disturbance of the ambient DSi availability. This over-spiking is because during an oceanographic cruise, the DSi contents of the actual seawater sampled for incubations are usually not available at the time of spiking; previous data have to be used. During SAZ-SENSE, we used the most recent nutrient value available, which was generally analyzed from Niskin samplings performed 1 day before ours. As implemented during a more recent cruise, it is possible to have actual DSi analyses within 30 min after Niskin sampling using an on-board autoanalyzer. This ensures that the amount used for spiking is systematically less than 10%. As explained below, however, the larger ³⁰Si addition in incubation 2 does not seem to have increased the measured biogenic silica production rates.

Reproducibility—Table 5 shows the results and reproducibility in ³⁰⁻²⁸Si abundance (atom %) of the two incubations and of artificial and natural solutions. The chromatographic step for incubation 2 was fully duplicated (Table 5), and there was no significant difference between the duplicates. The reproducibility of the ³⁰⁻²⁸Si isotopic abundance was better than 1% and 0.2% for n ≥ 3 and similar to the one obtained by Corvaisier et al. (2005) (Table 5). Several Monte Carlo simulations have been run (n = 1000, using a normal distribution) to have an alternative evaluation of the precision of the ³⁰Si isotopic abundance measurements (after the different instrumental corrections). The relative precision obtained was typically 0.5%–1.5%, well in the range of reproducibility (Table 5). Because reproducibility was improved to better than 1% with n ≥ 3, we recommend performing isotopic measurements in triplicate.

For incubations 1 and 2, the reproducibilities of production and dissolution rates given by the models are shown in Table 6 and were similar to the ones obtained by Corvaisier et al. (2005). These standard deviations are satisfactory given the usual temporal and/or spatial range of the production and dissolution rates measured in coastal and/or open ocean ecosystems (Nelson and Goering 1977a, b; Nelson et al. 1981; Nelson and Gordon 1982; Brzezinski and Nelson 1989; Nelson et al. 1995; Brzezinski et al. 2001, 2003; DeMaster et al. 1996; Beucher et al. 2004a, b). The two different models described above give similar precision, as described in Elskens et al. (2007), independently if we use ³⁰Si or ²⁸Si (Table 6). In the case of the two-compartment model, incubation 1 has a much larger relative uncertainty (30%–50%) on Si dissolution rate compared to incubation 2 (8%), despite the fact that absolute errors are comparable (0.03 versus 0.02 µmol L⁻¹ d⁻¹,

Table 5. Average ³⁰⁻²⁸Si isotopic abundances with absolute and relative standard deviations.

	³⁰ Si ± SD, atom %	RSD, %	²⁸ Si ± SD, atom %	RSD, %	<i>n</i>
HR-SF-ICPMS (RMCA)					
Incubation 1					
DSi initial	10.33 ± 0.05	0.44	85.30 ± 0.05	0.06	10
DSi final	10.21 ± 0.03	0.33	85.45 ± 0.05	0.06	10
bSiO ₂ final	5.72 ± 0.06	1.01	89.71 ± 0.04	0.05	10
Incubation 2					
DSi initial	22.02 ± 0.19	0.85	74.18 ± 0.12	0.16	4
	22.03 ± 0.13	0.60	74.17 ± 0.12	0.16	3
DSi final	19.45 ± 0.09	0.48	76.64 ± 0.13	0.13	4
	19.35 ± 0.06	0.81	76.73 ± 0.13	0.13	3
bSiO ₂ final	3.61 ± 0.03	0.89	91.74 ± 0.07	0.07	8
RMCA natural standard	3.09 ± 0.01	0.42	92.23 ± 0.03	0.03	30
Artificial solution	4.00 ± 0.02	0.58	91.36 ± 0.03	0.03	8
HR-SF-ICPMS (IUEM)					
Artificial solution	4.03 ± 0.02	0.50			12
TIMS (IUEM)					
12 IUEM natural standard	3.07 ± 0.02	0.65			30

HR-SF-ICPMS data from incubations 1 and 2 were measured during several analytical sessions spread over several months (*n*, number of measurements). The two different rows for DSi initial and DSi final of incubation 2 represent complete chemical duplicates (i.e., including chromatography step). The natural standards (seawater for RMCA [Royal Museum for Central Africa, Tervuren, Belgium] and NaSiO₃ from Corvaisier et al. 2005 for IUEM [Institut Universitaire Européen de la Mer, Brest, France]) are the average of 30 successive measurements within the same analytical session. Note that natural ³⁰Si and ²⁸Si abundances are 3.09 and 92.23 atom %, respectively (Rosman and Taylor 1998); abundances of artificial standards are 4.00 and 91.35 atom %, respectively (see text). RSD, relative standard deviation.

Table 6. Production (ρ_p) and dissolution (ρ_D) rates with standard deviations for incubations 1 and 2 with the ³⁰⁻²⁸Si method; production and dissolution rates for both one-compartment model (model 1) (initial, final, and mean concentration values [Nelson and Goering 1977a,b]) and two-compartment model (model 2) (Beucher et al. 2004a, de Brauwere et al. 2005, Elskens et al. 2007); production rates for incubation 2 is also given by the ³²Si method (Tréguer et al. 1991, Leynaert 1993).

Model	³⁰ Si		²⁸ Si			
	$\rho_p \pm SD,$ $\mu\text{mol L}^{-1} \text{ day}^{-1}$	$\rho_D \pm SD,$ $\mu\text{mol L}^{-1} \text{ day}^{-1}$	$\rho_p \pm SD,$ $\mu\text{mol L}^{-1} \text{ day}^{-1}$	$\rho_D \pm SD,$ $\mu\text{mol L}^{-1} \text{ day}^{-1}$		
Incubation 1						
³⁰ Si	2	5.43 ± 0.57	0.11 ± 0.03	5.59 ± 0.56	0.18 ± 0.09	
³⁰ Si	1	Initial	3.43 ± 0.39	0.58 ± 0.02	3.47 ± 0.35	0.66 ± 0.02
³⁰ Si	1	Final	5.18 ± 0.59	0.47 ± 0.02	5.24 ± 0.53	0.54 ± 0.01
³⁰ Si	1	Mean	4.31 ± 0.27	0.52 ± 0.03	4.35 ± 0.22	0.60 ± 0.03
Incubation 2						
³⁰ Si	2	0.032 ± 0.004	0.246 ± 0.019	0.058 ± 0.004	0.241 ± 0.019	
³⁰ Si	1	Initial	0.036 ± 0.004	0.273 ± 0.011	0.036 ± 0.004	0.274 ± 0.007
³⁰ Si	1	Final	0.024 ± 0.003	0.287 ± 0.012	0.024 ± 0.003	0.288 ± 0.007
³⁰ Si	1	Mean	0.030 ± 0.006	0.280 ± 0.017	0.030 ± 0.006	0.281 ± 0.013
³² Si	—	0.027 ± 0.003				

respectively). This low dissolution rate might be explained by the characteristics of incubation 1: an exponentially growing monospecific culture at low temperature (3°C) free of bacteria and grazers.

Sensitivity—To test empirically if this new method can actually measure a ³⁰Si isotopic difference of 1%, ³⁰Si tracer in increasing amounts was added to the same pre-concentrated

seawater. A set of six solutions ranging from 8.05 to 8.30 atom % ³⁰Si was prepared (with a ~0.5 % relative ³⁰Si isotopic abundance difference between two consecutive solutions) and analyzed in triplicate (Table 7). This table shows that the samples with relative differences of 1% have significantly different measured atom % ³⁰Si abundances. This empirical demonstration agrees with the reproducibility better than 1% in Table 5.

Table 7. Triplicates (analyzed during the same session) of the same batch of preconcentrated seawater spiked with increasing ³⁰Si amounts.

³⁰ Si ± SD, atom %	²⁸ Si ± SD, atom %
8.04 ± 0.03	87.52 ± 0.04
8.07 ± 0.05	87.50 ± 0.05
8.11 ± 0.03	87.44 ± 0.01
8.16 ± 0.03	87.40 ± 0.03
8.21 ± 0.03	87.36 ± 0.02
8.29 ± 0.06	87.27 ± 0.07

The relative difference between two consecutive solutions prepared is 0.5%, and the abundances measured follow this trend as expected. The measurements are significantly different for a difference of 1% (e.g., between solutions 1 and 3, 2 and 4, etc.).

The results for the atom % ²⁸Si values (which are the preferred abundances used for calculation Si dissolution rates with the one-compartment model) present the same trends (Table 7) with smaller relative atom % ³⁰Si abundance variations. Overall, Table 7 shows that we are able to differentiate absolute abundance changes at the level of ~ 0.1 atom % ³⁰⁻²⁸Si.

Accuracy—The results for the RMCA standards (natural seawater) showed that the accuracy of the isotopic abundances is good, because our average measured on 30 analyses is exactly the one expected from the crustal abundance (Table 5). It has been further confirmed on artificial solutions prepared by mixing a natural isotopic solution (prepared from dissolution of Na₂SiF₆) with the spike solution (Table 5). The solution was measured on two different HR-SF-ICP-MS instruments (RMCA and IUEM) following the same analytical procedure and gave 4.00 ± 0.02 and 4.03 ± 0.02 atom %, respectively, which agreed with calculated ³⁰Si abundance of this solution (4.00%). A third assessment for accurate measurement has been made from the comparison with a parallel incubation using ³²Si performed during the SAZ-SENSE cruise by K. Leblanc (COM, Marseille) following the method developed by Tréguer et al. (1991) and Leynaert et al. (1993). The production rate obtained with the ³²Si method on parallel incubation 2 was 0.027 ± 0.003 μmol L⁻¹ Si day⁻¹ (Table 6), which was in agreement with our estimate (0.032 ± 0.004 μmol L⁻¹ Si day⁻¹ for the two-compartment model and 0.030 ± 0.006 μmol L⁻¹ Si day⁻¹ for the one-compartment model). Moreover, this good agreement between ³²Si and ³⁰Si methods for incubation 2 provides further evidence that the overspiking of 20% with ³⁰Si did not affect the production rates.

This is in the lower range of Si-production rates measured in the world ocean. Although this comparison cannot be regarded as an absolute evidence of accuracy, their convergence provides good confidence for the whole ³⁰Si methodology. The analyses are currently underway for the 24 ³⁰Si spiked incubations performed in parallel with ³²Si incubations during SAZ-SENSE. The preliminary results are particularly encouraging, since for 24 incubations we obtain a slope of 1.0 with

$r^2 = 0.80$ (not shown). This whole dataset will then permit a better comparison between the two approaches.

Table 6 allows comparison of the two different models in terms of accuracy. First, the use of ³⁰Si or ²⁸Si to calculate the rates gives values without significant difference. For incubation 1, the two-compartment model gives higher production rate and lower dissolution rates. It is in agreement with Elskens et al. (2007), who discuss (1) potential underestimation of the production rate by the one-compartment model, as it does not take into account the increase of DSi due to the dissolution of biogenic silica, and (2) overestimation of the dissolution rate, as it does not take into account the decrease of DSi due to the production of biogenic silica. For incubation 2, the two models gave production rates without significant difference. In contrast, the one-compartment model seems to overestimate the dissolution rate, as discussed above.

Si-requirement—The Si-requirement, as defined above, was controlled by both the maximum salinity (2‰) of the solution that could be introduced in the HR-SF-ICP-MS and the initial content of Si in seawater. For 1 L sample, the detection limit of HR-SF-ICP-MS method is more than one order of magnitude better than when using the TIMS (Table 8). To obtain the same sensitivity with a TIMS, incubation volumes of 16 L would be necessary, which is unrealistic to handle. The detection limit in Table 8 covers the whole range of Si content encountered in the ocean, since the DSi contents are commonly below 0.5 μmol L⁻¹ in the oligotrophic areas such Sub-Tropical Gyres and Sub-Antarctic Zone in late summer. In the case of biogenic silica, values are frequently less than 0.5 μmol L⁻¹ in diatoms' nongrowth period in the productive areas and almost every time in the oligotrophic areas.

Discussion

This new HR-SF-ICP-MS method improves significantly compared to the two former methods using TIMS (Corvaisier et al., 2005) or IRMS (Goering et al. 1973; Nelson and Goering 1977a, b) because it is two, three, or four times quicker (for dissolved silicon with chromatographic purification step, dissolved silicon without chromatographic purification step, and biogenic silica, respectively) and improves the sensitivity by more than one order of magnitude. Indeed, a complete analysis takes ~20 min (blank/standard/sample/standard/blank) and can be processed with an autosampler. The chemical preparation for DSi can be completely processed on board (MAGIC-preconcentration) when the Si-content of the seawater is more than 2.8 μmol L⁻¹. If not, a complete set of samples (depending on the number of columns available, usually 20–30) can be purified in one working day using the cation-exchange chromatography developed by Georg et al. (2006). For bSiO₂, a simple alkaline digestion is applied (Ragueneau et al. 2005). In the case of the preexisting methods for DSi and bSiO₂, the chemical preparation of a limited set of samples takes several days (Goering et al. 1973; Nelson and Goering, 1977a, b; Brzezinski et al. 2001, 2003; Corvaisier et al. 2005). HR-SF-ICP-MS are now

Table 8. Comparison of detection limits for HR-SF-ICPMS and TIMS as a function of volume sampled.

	Volume, L		
	2	1	0.5
HR-SF-ICP-MS			
DSi, $\mu\text{mol L}^{-1}$, without chromatographic purification	2.80	2.80	2.80
DSi, $\mu\text{mol L}^{-1}$, with chromatographic purification	0.04	0.07	0.14
bSiO ₂ , $\mu\text{mol L}^{-1}$	0.05	0.09	0.18
TIMS			
DSi, $\mu\text{mol L}^{-1}$	0.50	1.00	2.00
bSiO ₂ , $\mu\text{mol L}^{-1}$	0.50	1.00	2.00

These theoretical estimations take into account an average HR-SF-ICP-MS sensitivity of 1.10%/100 ppb (Table 1), the salinity of the MAGIC solution of 80 ± 8‰ per L seawater coprecipitated (average of 132 measurements), the salinity of alkaline digestion (~10‰), the salinity of solution purified by chromatography, which is less than 0.1‰ (8 measurements), the concentration factor of the alkaline digestion and the MAGIC solution (± 400 and 50 respectively), and the Si-requirement per ion-exchange column (2.0–3.6 $\mu\text{g Si}$).

widespread, which will help to expand the biogenic silica production–dissolution dataset, which is currently poorly documented. Ultimately, this method will help to improve quantifications of the silicon budget in the surface ocean.

Comments and recommendations

The analytical method presented here could be easily applicable to measure Si fluxes in environments extremely different from the sole system of marine diatoms. The most direct application would be for studies on freshwater environments (limnology and rivers), where diatoms can also play a major role (Alleman et al. 2005). No chromatographic or MAGIC preconcentration steps are to be expected on such samples, since salinity is low and DSi contents are usually high. This method could also expand the studies of Si adsorption–desorption processes in batch experiments on sediments (e.g., Van Cappellen et al. 2002) and soils (Delstanche et al. 2009). It should permit more particularly the measurement of low rates on short time scales. Finally, we foresee potential applications to trace the origin and fate of Si in the course of complex processes such as reverse weathering in sediments (Michalopoulos and Aller 2004), formation of chemical complexes like hydroxyaluminosilicates (e.g., Doucet et al. 2001), or Si uptake, transport, and precipitation within higher organisms such as plants (e.g., Opfergelt et al. 2006, Carneiro et al. 2008).

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