

Purification, Recovery, and Laser-Driven Fluorination of Silicon from Dissolved and Particulate Silica for the Measurement of Natural Stable Isotope Abundances

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A procedure for the purification, recovery, and determination of isotopic abundances of silicon from biogenic and lithogenic particulate matter and dissolved silicic acid is reported. Purification involves the reaction of acid molybdate with dissolved silicon in natural waters or that produced by the dissolution of particulate silica by hydrofluoric acid. The resulting silicomolybdic acid is then quantitatively precipitated by reaction with triethylamine hydrochloride. The silicon is recovered as silicon dioxide through stepwise combustion of the dried precipitate. Fluorination of the product for isotopic analysis is accomplished by laser heating under pure fluorine generated by the decomposition of a fluorine-based salt. The resulting silicon tetrafluoride is separated from hydrogen fluoride and other fluorination byproducts cryogenically using a variable-temperature cold trap. Yields for silicon recovery are 99.9% for precipitation and greater than 95% for the purification/fluorination procedure. Reproducibility of the isotopic composition for pure quartz granules processed through the procedure is $\pm 0.1\%$ for $\delta^{30}\text{Si}$.

Although a substantial body of data on silicon isotope natural abundances in both terrestrial and lunar rocks (e.g., refs 1 and 2) exists, few measurements have been reported for biogenic silica, and none have been reported for dissolved silicon in natural waters. $\delta^{30}\text{Si}$ values reported for diatomite and sponge spicules³ indicate that the range of isotopic variation seen in biogenic silica (6.2‰) is significantly greater than that seen in igneous rocks (1.1‰), suggesting that biogenic silica formation fractionates silicon isotopes.

In order to confirm the fractionation of silicon isotopes during biogenic silica formation and to further explore the biogeochemistry of silicon through variations in its isotopic natural abundances, we devised a method to quantitatively recover and purify silicon from both particulate silica and from dissolved silicon in marine or fresh waters. We modified the procedure described

by DeFreitas et al.⁴ so that it delivers the recovered silicon with negligible contamination by extraneous silicon. A vacuum fluorination system was devised to liberate silicon from the purified SiO_2 by laser heating⁵ under pure F_2 to produce SiF_4 gas for isotopic analysis.⁶ Additionally, we have adapted the use of a pure fluorine generator⁷ and a variable-temperature cold trap⁸ to the silicon fluorination procedure.

In this paper, we present our methods for silicon recovery and fluorination, as well as report our initial measurements of silicon isotopic ratios in quartz standards, diatom silica, and dissolved silicon from seawater.

EXPERIMENTAL SECTION

Reagents. All reagents were made using deionized distilled water (D4700 NANOpure System, Barnstead/Thermolyne) and reagent grade chemicals (Fisher Scientific, ACS certified unless otherwise noted).

Triethylamine Molybdate (TEA-moly). Four grams of ammonium molybdate was dissolved in 500 mL of water. Next, 25 mL of concentrated HCl was added and mixed before the addition of 7.67 g of triethylamine hydrochloride (Sigma). This reagent was stored in a dark polypropylene bottle and allowed to sit for 7 days, during which time trace contaminant Si precipitates (Table 1). The reagent was then filtered through a 0.4 μm PCTE filter (Poretics) before use. Filtered reagent, if kept in a dark container, remains stable for 1–2 months.

Silicon Extraction and Purification. The first step in silicon recovery from particulate silica (biogenic or quartz) is its solubilization in aqueous solution. At least three simple techniques exist for this: fusion of SiO_2 with Na_2CO_3 to form water-soluble sodium silicate, dissolution in HF, or dissolution in NaOH. We do not recommend fusion with Na_2CO_3 due to incomplete silicon recoveries (<98% in all our tests). NaOH is ineffective for the dissolution of mineral silica. Thus, we dissolved our silica in 2.5 M HF in polystyrene centrifuge tubes. A sufficient volume of HF must be added to keep the final concentration of fluosilicate ions below

(1) Tilles, D. *J. Geophys. Res.* **1961**, *66*, 3003–3014.

(2) Taylor, H. P., Jr.; Epstein, S. *Earth Planet. Sci. Lett.* **1970**, *9*, 208–210.

(3) Douthitt, C. B. *Geochim. Cosmochim. Acta* **1983**, *46*, 1449–1458.

(4) DeFreitas, A. S. W.; McCulloch, A. W.; McInnes, A. G. *Can. J. Chem.* **1991**, *69*, 611–614.

(5) Sharp, Z. D. *Geochim. Cosmochim. Acta* **1990**, *54*, 1353–1357.

(6) Taylor, H. P., Jr.; Epstein, S. *Bull. Geol. Soc. Am.* **1962**, *73*, 461–480.

(7) Asprey, L. B. *J. Fluorine Chem.* **1976**, *7*, 359–361.

(8) Des Marais, D. J. *Anal. Chem.* **1978**, *50*, 1405–1406.

Table 1. Percent of Silicon Removed from TEA-moly Reagent after Cleaning As Measured Using ^{32}Si as a Tracer^a

reaction time (in days)	CPM ^{32}Si /mL	% Si removed
0	84.9 ± 0.2	
2	5.8 ± 0.1	93.2 ± 0.1
7	0.6 ± 0.1	99.3 ± 0.1
12	0.3 ± 0.1	99.6 ± 0.1

^a Errors are standard deviations.

40 mM. Recoveries decline from 100% at greater concentrations, possibly due to the volatilization of SiF_6 with potential isotopic fractionation of the sample. Quartz pieces weighing 1–10 mg required up to 4 weeks to dissolve. Dissolution of >90% of biogenic silica from diatoms in 2.5 M HF was observed to occur in 30 min, but biogenic samples were allowed to dissolve for a minimum of 3 days before proceeding. Samples of dissolved silicon in 2.5 M HF were diluted by a factor of 325 to avoid interference from F^- with subsequent reaction chemistry.⁹

The dissolved silicon from the HF digests (~200 μM) or that occurring naturally in seawater (~50–100 μM) was precipitated by the addition of 60 mL of cleaned TEA-moly reagent per 100 mL of sample solution. Formation of the precipitate occurs in two steps. Monomeric silicic acid reacts with molybdate to form silicomolybdic acid. The silicomolybdate then reacts with the triethylamine to form the insoluble triethylamine silicomolybdate, $((\text{CH}_3\text{CH}_2)_3\text{NH})_4\text{SiMo}_{12}\text{O}_{40}$.⁴

After 24 h, the precipitated triethylamine silicomolybdate was collected on a 0.4 μm PCTE filter and rinsed three times with a mixture of 6 parts cleaned TEA-moly and 10 parts water to remove traces of salts (from seawater) and F^- . Each filter with its retained precipitate was placed in a platinum crucible and dried overnight in air at 60 °C. Once dry, samples were combusted in a furnace to produce SiO_2 . Furnace temperature was initially ramped at 10 °C min^{-1} to 350 °C and held there for 0.6 h to remove organics before being raised 30 °C min^{-1} to 1000 °C for 6 h to volatilize Mo.⁴

X-ray diffraction analysis indicated the white powder remaining after combustion is a mixture of cristobalite and tridymite, which are polymorphs of SiO_2 . The silicon content of this powder, as measured colorimetrically¹⁰ after fusion in Na_2CO_3 and subsequent dissolution in water, was $101.0 \pm 2.8\%$ of that expected for SiO_2 , indicating a high purity for the end product. The purified SiO_2 was then fluorinated by reaction with F_2 as described below.

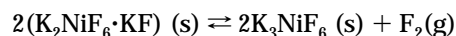
Fluorination. Figure 1 shows a schematic diagram of the fluorination vacuum line used for the fluorination of silica samples for silicon isotope analysis. The line consists of two portions: a metal section for fluorination and a glass section for yield determination and sample collection. The metal side is made of nickel (Ni 200) tubing joined with stainless steel Swagelok compression fittings and contains a pure fluorine generator,⁷ the sample reaction chamber (Metra, Inc.; Model B2810ZS), and a variable-temperature trap.⁸ A tank of N_2 (Linde Specialty Gases) plumbed into the metal section is used to pressurize the sample chamber for sample loading and melting. A tank of F_2 (Air

Products) provides the commercial fluorine for charging the pure fluorine generator. The glass section of the line consists of a 4 U-tube multitrap to collect SiF_4 distilled from the metal side, a capacitance manometer (Vacuum General, Model CMLA-21) calibrated to measure the micromoles of SiF_4 produced, and a site for the sealing of samples into borosilicate tubes for mass spectrometry. The vacuum pump on the metal side of the line is an Alcatel 2012CP1 equipped with fluorine-resistant Viton fittings and lubricated with a perfluorinated polyether (Fomblin). The glass side of the line is fitted with a mercury diffusion pump in line with an Alcatel 2004A vacuum pump which is lubricated with 100% neutral paraffinic oil (Fisher).

Purified silica samples, 15–100 μmol of Si, are loaded into 0.5 cm deep wells drilled into a cylindrical nickel (Ni 200) plate. A 22 W CO_2 laser coaxial with a 3 mW HeNe sighting laser (Melles Griot) is mounted on a motorized x - y translation stage and set to fire through a BaF_2 window⁵ (Figure 1) on the top of reaction chamber. An NEC color CCD camera (Model NX18A) mounted atop a 0.7–3.0 \times dissection scope on an x - y translation stage provides a view of the sample plate through a sapphire viewport positioned 45° off of the vertical axis, as illustrated in Figure 1 and ref 5. The front side of each well on the nickel sample plate is milled to an angle of 45° to eliminate blind spots due to the inclination of the viewport.

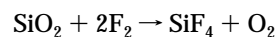
After sample loading, the reaction chamber and vacuum line are evacuated for several hours. Pieces of pure quartz may be fluorinated at this point, but the finely powdered silica that has been purified through precipitation and combustion sputters during fluorination. Sputtering is eliminated by melting the powder under 1 atm of N_2 into lumps of glass that then fluorinate in a controlled fashion. The CO_2 laser is set for a beam width of 0.8 ms and a pulse period of 0.9 ms. The intensity of the laser beam at this setting is raised from zero to near maximum levels slowly during lasing. Melting the silica with a continuous beam is avoided as partial vaporization of the sample can occur. After the melting of samples the reaction chamber is evacuated and pumped for several hours.

Purified fluorine for sample reaction is generated inside the vacuum line (Figure 1) by heating potassium hexafluoronickelate (Ozark-Mahoning Co.) which decomposes at ~350 °C to produce F_2 .⁷



Fluorination of the nickel compound and the subsequent evolution of F_2 follow Rumble et al.¹¹ except that during generator charging we do not monitor the reaction rate, but rather stop fluorination when there is no longer any observable drop of F_2 pressure.

Samples are fluorinated under 0.1 atm of purified F_2 that has been passed through a liquid nitrogen trap (cold trap 1 on Figure 1). Silica samples react with F_2 upon being heated by the laser set to fire a continuous beam:



Lasing of the 1–3 mg samples takes approximately 10–20 min, during which the intensity of the continuous laser beam is varied

(9) Eggimann, D. W.; Betzer, P. R. *Anal. Chem.* **1976**, *48*, 886–890.

(10) Strickland, J. D.; Parsons, T. R. *A Practical Handbook of Seawater Analysis*; Fisheries Research Board of Canada: Ottawa, ON, Canada, 1972; pp 65–70.

(11) Rumble, D.; Hoering, T. C.; Palin, J. M. *Geochim. Cosmochim. Acta* **1993**, *57*, 4499–4512.

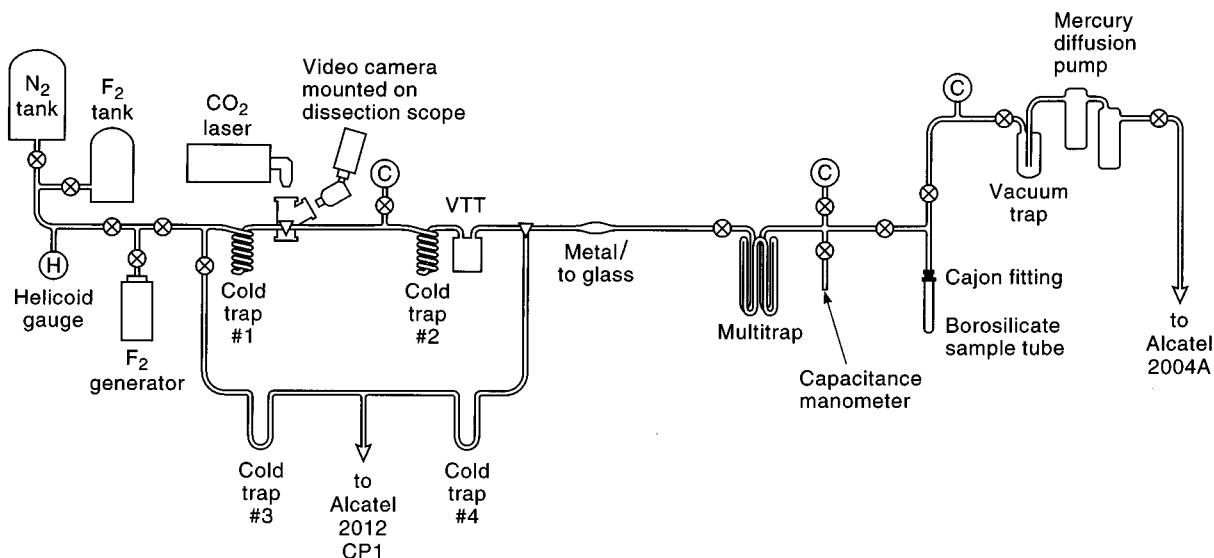


Figure 1. Schematic of silicon fluorination vacuum line. Convectron vacuum gauges are denoted by ©. Valves are represented by ⊗ and ∇.

between zero and maximum intensity to maintain controlled, continuous fluorination. When lasing has been completed, the resulting SiF_4 is collected in a coil cooled to -195°C with liquid nitrogen (cold trap 2 on Figure 1). O_2 and excess F_2 are then pumped away through the coil.

Any water present either in the silica or in the reaction chamber during fluorination will form HF, which may in turn form SiF_4 by etching the walls of the glass section of the line. Traps cooled to liquid nitrogen temperature will collect both SiF_4 and HF, and so will not serve to separate them. In order to separate them, SiF_4 (and any HF present) is transferred from cold trap 2 into the variable-temperature trap,⁸ which has been cooled to at least -183°C with liquid nitrogen. Remaining noncondensibles are pumped away through the trap. The variable-temperature trap is then heated to -140°C , distilling SiF_4 to the glass side of the line where it is collected at liquid nitrogen temperature in the multitrap (Figure 1). Tests indicate that SiF_4 quantitatively distills out of the trap at this temperature, but HF remains behind.

The liquid nitrogen on the multitrap where the sample is frozen is replaced by a dry ice–2-propanol slush. SiF_4 distills from the multitrap to the capacitance manometer, where the micromoles of sample gas are determined. Samples are distilled into borosilicate tubes, sealed, and analyzed on a VG Prism mass spectrometer.

Commercially produced SiF_4 (Matheson Gas Products) is used as a reference gas during mass spectrometry, and isotopic values are reported relative to the CalTech Rose Quartz Standard (RQS). δ values are calculated as

$$\delta^{30}\text{Si} = [(R_{\text{sam}}/R_{\text{RQS}}) - 1] \times 10^3\text{‰}$$

where R is the ratio of ^{30}Si to ^{28}Si in the sample or standard.

Safe Handling of Fluorine. Fluorine is a highly toxic and reactive gas; it is imperative to handle fluorine in a safe and controlled manner. Fluorine cylinders should be stored inside a gas cabinet or other suitable barricade. We also recommend housing the fluorine generator (which is pressurized to 2 atm of F_2 during charging) inside a continuously running fume hood. Exhaust from the pump on the metal side of the line, as well as

from the pump on the glass side, must be discharged well into the hood, and a toxic gas monitor and alarm (e.g., Series 6200/2 toxic gas monitor with Model 4562 F_2 gas sensor/transmitter; Exidyne Instrumentation Technologies, Exton, PA) should be mounted outside of the hood but within the working area.

RESULTS AND DISCUSSION

Reagent Cleaning and Quantitative Recovery of Si. There are several steps in our purification procedure during which the isotopic ratios of silicon might be altered due to incomplete reactions or the addition of contaminating silicon to the samples. First, significant contaminating Si may be present in the HF and TEA-moly reagents. Second, if the formation of the triethylamine silicomolybdate is not quantitative, isotopic fractionation could occur during precipitation. Third, and finally, if any silicon volatilizes over the course of combustion the potential for fractionation exists. In order for our purification procedure to be applicable to natural abundance work none of these artifactual effects can occur.

The background silicon content of 2.5 M HF was determined via molybdate blue spectrophotometry.¹⁰ The amount of HF used to dissolve 100 μmol of SiO_2 (2.5 mL) contains 1.5 nmol of silicon. Introduction of that amount of silicon, corresponding to 0.0015% of the sample mass, should not significantly affect isotopic ratios.

Uncleaned TEA-moly reagent contains 1 nmol of silicon/mL of reagent. If uncleaned TEA-moly were used to precipitate silicon in seawater, for example, 0.6% of the silicon recovered would come from the reagent. Fortunately, the pH of undiluted TEA-moly reagent (1.2) resides in the reactive range (pH 1–4) for silicomolybdic acid formation.¹² Silica present in the TEA-moly reagent itself will precipitate as triethylamine silicomolybdate and can be removed through filtration. The concentration of contaminant silicon in the uncleaned reagent is significantly smaller than the silicon content of samples, which results in the precipitation of silicon from the reagent taking longer than the 24 h required to completely precipitate a sample (see below).

To assay the amount of time required for precipitation of contaminating silicon, a fresh batch of uncleaned reagent was

(12) Grasshoff, K. *Deep-Sea Res.* **1964**, *11*, 597–604.

Table 2. Percent of Dissolved Silicon Precipitated from 100 mL of Solution after 24 h Using ^{32}Si as a Tracer^a

solution	μmol of Si	CPM ^{32}Si /mL initial	CPM ^{32}Si /mL of filtrate after 24 h	% Si precip
deionized distilled water	100	358.4 ± 0.3	0.3 ± 0.1	99.9 ± 0.0
seawater	10	269.7 ± 0.3	0.3 ± 0.1	99.9 ± 0.0

^a Errors are standard deviations.

Table 3. Percent Recovery of Dissolved Silicon as SiO_2 Extracted from 100 mL Samples^a

solution	μmol of Si	mean % recovery
deionized distilled water	100	97.9 ± 4.1
	10	95.4 ± 2.4
seawater	10	95.7 ± 2.3

^a Errors are standard deviations.

spiked with the radioisotope ^{32}Si (42 000 Bq/ μg Si; Los Alamos National Laboratories) and the disappearance of radioactivity from solution monitored through time. ^{32}Si is a low-level β -emitter with a half-life of roughly 133 years.¹³ Aliquots of the TEA-moly reagent were removed and filtered every few days. Radioactivity remaining in the filtrate was measured via Cerenkov counting of the daughter product of ^{32}Si , ^{32}P , on a Beckman scintillation counter (LS 5000TA). Filtrate was allowed to sit for the four months required to attain secular equilibrium between ^{32}Si and ^{32}P before counts were taken. Filtration after 7 days removed 99.3% of the ^{32}Si (Table 1). Thus filtration of the TEA-moly seven days after preparation decreases the contaminant silicon in the reagent to 7 pmol of Si/mL of reagent. At this level, the amount contaminant silicon in silicon recovered from seawater would be less than 0.0006%.

^{32}Si was similarly used to trace the precipitation of silicon in 10 and 100 μmol solutions of dissolved silicon made up in 100 mL of seawater or deionized distilled water. In both cases silicon is quantitatively removed from solution within 24 h (Table 2).

Silicon recoveries from the combustion of the triethylamine silicomolybdate precipitate were assayed gravimetrically. Dried precipitate was weighed into a tared crucible before combustion. The weight of the SiO_2 remaining after combustion was then compared to the weight expected from the weight of precipitate combusted. Recoveries averaged $102.5 \pm 1.0\%$, indicating that no silicon is being lost due to volatilization during the combustion process. Such an analysis assumes that the SiO_2 produced by combustion is relatively pure. Direct measurement of the silicon content of the end product (101.0% of that expected by weight of the SiO_2 end product; see above) indicates that this is a valid assumption.

Recoveries of SiO_2 over the combined precipitation and combustion procedures fall into the mid to upper 90% range (Table 3). Because we have demonstrated quantitative recovery at each step in the procedure, this loss of product must be mechanical in nature (spillage, adhesion of precipitate to the reaction bottle, adhesion of the combusted SiO_2 to the platinum crucible, or

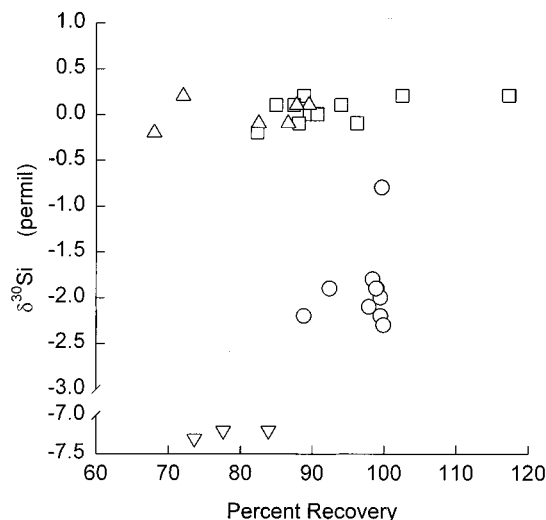


Figure 2. $\delta^{30}\text{Si}$ for pure and precipitated silica vs percent recovery as SiF_4 . Pieces of pure silica are denoted by circles. Granules of pure silica are represented by squares. Granules that have been precipitated are designated as triangles. Diatom silica is represented by inverted triangles.

passage of some of the precipitated triethylamine silicomolybdate through the 0.4 μm filter during collection). The triethylamine silicomolybdate precipitate is extremely adhesive, and visible amounts remain on the walls of the reaction bottle and on the walls of the filter tower after processing. Such mechanical losses should not result in isotopic fractionation.

Fluorination Yields and Isotopic Results. Figure 2 shows measured isotopic values vs recoveries from the fluorination procedure for pieces (3–12 mm) of 99.99% SiO_2 (Aldrich), granules (–40 mesh) of 99.995% SiO_2 (Alfa Aesar), granules after dissolution and purification via our procedure, and purified diatom silica. The biogenic silica was obtained from batch cultures of diatoms grown with sodium metasilicate (Fisher) as the dissolved silicon source for biomineral formation. The sodium metasilicate reagent is depleted in ^{30}Si relative to all other materials analyzed, and thus the diatom silica has more negative $\delta^{30}\text{Si}$ value than the other silica plotted in Figure 2.

Percent recoveries for the fluorination procedure are reported relative to the weight of SiO_2 (assuming 100% purity) placed into the nickel sample holder for lasing. Recoveries for the pieces, which, unlike granules or powders, could be weighed accurately on a Cahn 25 electrobalance, average $97.4 \pm 3.5\%$. Slightly lower recoveries for the granules ($92.9 \pm 9.4\%$), granules after dissolution and purification ($81.1 \pm 8.2\%$), and dissolved and purified diatom silica ($78.4 \pm 4.2\%$) are possibly due to weighing errors and difficulties in completely lasing all of the small particles of silica in a sample well.

Although such incomplete recoveries could result in isotopic fractionation, we do not believe this is happening. There is no trend between $\delta^{30}\text{Si}$ and percent yield of SiF_4 (Figure 2). The nearly identical isotopic values obtained for unmodified and precipitated granules (0.1 ± 0.1 vs $0.0 \pm 0.1\%$) demonstrate that it is possible to extract, recover, and purify silicon from particulate and dissolved silica without altering the silicon isotope ratios significantly.

Isotopic Analysis of Seawater $\text{Si}(\text{OH})_4$. To demonstrate the utility of our method for preparing samples of naturally occurring dissolved silicon for isotopic analysis, two samples of seawater

(13) Hofmann, H. J.; Bonani, G.; Suter, M.; Wölfl, W.; Zimmermann, D.; von Gunten, H. R. *Nucl. Instrum. Methods* **1990**, *B52*, 544–551.

were taken from a depth of 4000 m at Hawaiian Ocean Time-series Station ALOHA (22°45' N; 158°00' W) in the Pacific Ocean. We measured dissolved silicon $\delta^{30}\text{Si}$ in the two samples. Isotopic values agreed to within 0.1‰ (i.e., 1.5‰ vs 1.4‰), indicating that we can measure $\delta^{30}\text{Si}$ on seawater-dissolved silicon with the same precision as we can measure it on reagent grade samples.

CONCLUSIONS

Laser-based fluorination of silica to produce SiF_4 for mass spectrometry represents a valuable new method for the analysis of silicon isotopic ratios from natural samples. This method, coupled with a quantitative procedure to recover and purify silicon as silica, allows us not only to measure $\delta^{30}\text{Si}$ in a more precise and less time-consuming fashion than has been done previously but to measure it on dissolved silicon species as well.

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