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Measurement of silicon stable isotope natural abundances via multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS)

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[1] Widespread utilization of silicon isotope ratio variations ($\delta^{29}\text{Si}$ and $\delta^{30}\text{Si}$) as a geochemical and paleoceanographic tracer has been hampered by the hazardous nature of the analysis, which requires the use of a fluorinating gas. Multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) provides a safer means of silicon isotope analysis. High backgrounds, long rinsing and sample introduction times, and interferences are significant difficulties. It is possible to work around these obstacles, and the measurement of $\delta^{29}\text{Si}$ may be done to a precision averaging $\pm 0.1\%$. The $\delta^{30}\text{Si}$, which cannot be measured directly due to a NO interference at mass 30, may be extrapolated from the theoretically derived and empirically verified relationship, $\delta^{30}\text{Si} = 1.93\delta^{29}\text{Si}$. Biological materials (sponge spicules and diatoms) measured via MC-ICP-MS yielded $\delta^{30}\text{Si}$ values in the ranges expected from the prior analysis of similar samples by the method of fluorination.

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1. Introduction

[2] Natural variations in the abundance of the stable isotopes of silicon are useful for the study of the silicon geochemistry of terrestrial and lunar rocks [e.g., Tilles, 1961a, 1961b; Taylor and Epstein, 1970; Douthitt, 1982; Ding et al., 1996] and as a tracer of silica cycling in the ocean [De La Rocha et al., 1998, 2000]. Silicon isotopes are fractionated during silica biomineralization [De La Rocha et al., 1997] and as a result biogenic

materials may exhibit a silicon isotopic composition considerably different from that of igneous or metamorphic materials [Douthitt, 1982; Ding et al., 1996]. Silicon isotopes might also be fractionated during weathering and clay formation [De La Rocha et al., 2000; Zeigler et al., 2000].

[3] Despite the plethora of topics awaiting investigation, relatively little silicon isotope work has been accomplished in the 50 years since the measurement was introduced [Reynolds and Verhoogen,



1953; Allenby, 1954; Grant, 1954]. This is largely due to the fact that the high precision analysis of silicon isotope ratios has required the use of an extremely hazardous fluorinating gas, such as BrF_5 or F_2 [Taylor and Epstein, 1962; De La Rocha et al., 1996; Ding et al., 1996]. Introduction of a safer method would open up the field of silicon isotope biogeochemistry to many researchers. Toward this end, a technique has been devised for the measurement of silicon isotope ratio variations via plasma source mass spectrometry, which does not require the reaction of silica with a highly reactive gas.

2. Analytical Methods

2.1. Sample Preparation

[4] Solutions were made up in deionized distilled water (Milli-Q), and all acids used were of Analar grade (Merck), which had a lower silicon blank than quartz-distilled acids. All silica samples and standards were dissolved in 0.25 M HF, with Si concentrations kept below 40 mM to avoid formation of the volatile SiF_4 [De La Rocha et al., 1996]. The standards, NBS28 and 99.995% pure silica (Alfa Aesar) adopted as the working standard, were used without further cleaning. Diatom sediment samples were cleaned prior to dissolution following Mortlock and Froelich [1989]. Sponge spicules were ashed at 350°C to removed organics before dissolution. After dissolution in HF, samples were diluted to 10 ppm Si (in the form of SiF_6) in 0.12 M HCl, which resulted a final total HF content of 25 mM.

2.2. Mass Spectrometry

[5] The silicon isotopic composition of sample solutions was measured on a multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) manufactured by Nu Instruments Ltd. This mass spectrometer combines a double-focusing Nier-Johnson analyzer with variable dispersion ion optics, allowing the use of a fixed static array of Faraday collectors [Belshaw et al., 1998]. RF power was set at 1200 W, and samples were introduced through an HF-resistant PFA nebulizer, an HF-resistant, low-volume spray chamber, and a ceramic and alumina fully demountable torch (all

from Glass Expansion) in order to avoid high silicon blanks associated with quartz nebulizers, spray chambers, and torches. Desolvation of solutions containing Si and F resulted in the disappearance of silicon (most likely as SiF_4 gas) and was thus rejected as method of sample introduction for Si analysis.

[6] Beams of masses 28, 29, and 30 were monitored on the innermost, axial, and outermost Faraday collectors, respectively. Backgrounds for each sample were monitored using 0.12 M HCL solutions containing the same amount of HF as the sample in question. The measured backgrounds were then subtracted from the peak intensities of the sample. Instrumental mass fractionation was corrected for by standard-sample-standard bracketing.

[7] Isotope ratio variations are reported as δ values, either $\delta^{29}\text{Si}$ or $\delta^{30}\text{Si}$, generally calculated as

$$\delta = 1000 \times \frac{R_{\text{sam}} - R_{\text{std}}}{R_{\text{std}}} \text{‰}, \quad (1)$$

where R_{sam} and R_{std} are ratios of the heavier isotope to lighter isotope (e.g., $^{29}\text{Si}/^{28}\text{Si}$ or $^{30}\text{Si}/^{28}\text{Si}$) of a sample and standard, respectively.

3. Results and Discussion

3.1. Signal Intensity

[8] A 10 ppm silicon solution at natural abundance introduced into the plasma at 0.29 mL per minute produces 4.5 V of signal on the major isotope (28) after blanks have been subtracted (see section 3.3), or 3.4×10^7 counts per second per ppm. This is 4–13% of the transmission observed on this machine for elements of similar mass (Figure 1). This cannot be entirely due to the high first ionization potential of silicon (8.15 eV) as the first ionization potential of boron, which produces 2.8×10^8 cps/ppm, is slightly higher (8.3 eV). The high first ionization potentials of fluorine and chlorine (17.4 and 13 eV) may be suppressing the ionization of silicon.

3.2. Interferences

[9] There are three potential obstacles to high precision measurement of isotope ratio variations.

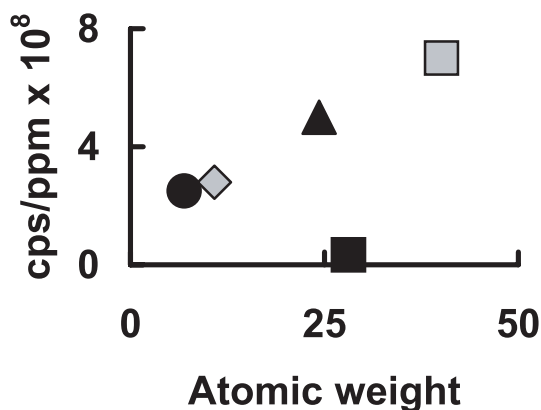


Figure 1. Counts per second (cps) per ppm observed for lithium (black circle), boron (grey diamond), magnesium (black triangle), silicon (black square), and calcium (grey square).

The first is the possible presence of interferences on the masses of interest. The second is the overestimation of sample peak intensities due to high blank levels. And the third is isotopic fractionation during the transmission of sample through the mass spectrometer. Care must be taken in each of these areas during the measurement of silicon isotope ratios by MC-ICP-MS. There are interferences on masses 28 and 30 from $^{14}\text{N}_2$ and $^{14}\text{N}^{16}\text{O}$. Introduction of silicon destabilizes the plasma, causing a period of drift in the mass bias, the slope of which is variable. Background levels of silicon are relatively high. Despite these difficulties, however, silicon isotope ratio variations may be measured by MC-ICP-MS as precisely and accurately as by SiF_4 gas source mass spectrometry, in a more time consuming but remarkably less hazardous manner.

[10] Scans of the background at masses 28, 29, and 30 show peaks associated with silicon as well as interferences from species such as $^{14}\text{N}_2$ and $^{14}\text{N}^{16}\text{O}$ (Figure 2). The interference at mass 29 (Figure 2b) contributes 2 mV to a total 6 mV background. This interference is only 0.8% of the typical sample beam intensity of 0.1–0.24 V and does not visibly affect the sample peak shape (Figure 3). Similarly, the interference at mass 28 (Figure 2a), which at 5 mV of a total 35 V background is only 0.1% of the 4.5 V sample beam intensity and also has a negligible impact on sample peak shape (Figure 3).

[11] At mass 30, however, the interference appears to significantly interfere with the determination of the peak intensity. Comprising the bulk of the 10 mV background (Figure 2c), this interference is 6% of the sample peak intensity of 0.17 V. The peak top at mass 30 is not flat but slopes appreciably in both blank solutions (Figure 2c) and in solutions containing 10 ppm Si (Figure 3), making it difficult to precisely quantify the intensity of either during analysis.

[12] Without the flat sample peak top, it was found to be impossible to measure the 30/28 ratio of a solution more precisely than $\pm 10 \times 10^{-6}$, which translates into an error of $\pm 0.3\%$ associated with only one of the three ratio determinations required for the analysis of isotope ratio variations by the

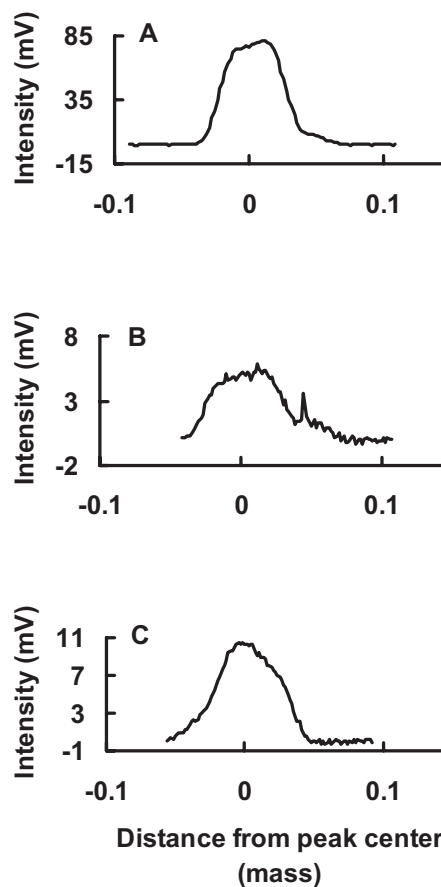


Figure 2. Intensities of backgrounds (with baselines subtracted) for a 0.12 M HCl plus 25 mM HF solution on masses (a) 28, (b) 29, and (c) 30 in the axial collector.

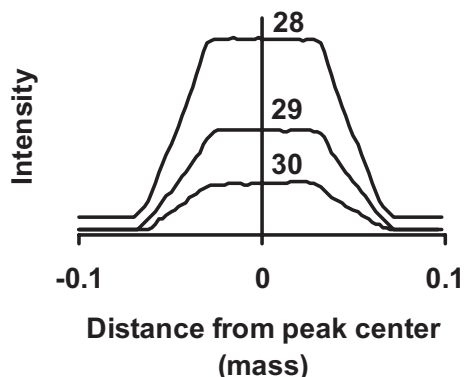


Figure 3. Peak shapes collected simultaneously on masses 28, 29, and 30 for a 10 ppm Si solution. Peaks are plotted of different scales. Peak heights in this scan are 2.5 V for 28, 0.13 V for 29, and 0.09 V for 30.

standard-sample-standard bracketing technique (see section 3.3).

3.3. Backgrounds

[13] In addition to the interferences on masses 28, 29, and 30 from nitrogen compounds, there are potentially high background levels of silicon to contend with. Quartz sample introduction components, silicone tubing, seals, and gaskets, and quartz-distilled waters and reagents (or those stored in glass bottles) may all serve as significant sources of background silicon. The background observed on mass 28 with a quartz torch, Scott-type spray chamber, and Meinhard nebulizer was several volts. Adoption of nonsilica sample introduction components (a polypropylene cyclonic spray chamber, a PFA nebulizer, and a fully demountable ceramic and alumina torch) dropped the 28, 29, and 30 backgrounds (subtracting out interference peaks) down as low as 35 mV, 4 mV, and less than 3 mV. Accumulation of silica on the cones and in the sample introduction system may cause silicon backgrounds to rise over the course of analyses (e.g., from 35 mV to as much as 200 mV on 28). Usually, however, 28 backgrounds plateau around 100 mV after the first few hours of analysis and do not increase even over several consecutive days of analysis.

[14] Significant reduction of the 35 mV background on mass 28 may be difficult. Some of the back-

ground may be removed through distillation of HCl, HF, and deionized, distilled water in FEP or PTFE stills. The silicon nitride outer tube of the demountable torch, although quite refractory, may serve as a source of background silicon levels. The alumina portions of the torch contain less than 1% silicon by weight and may also be serving as a source. The polypropylene spray chamber and associated O rings may both contain silicon at ppb levels. The PFA nebulizer contains less than 1 ppb silicon.

[15] Given the rapid rise and plateau of the background at 100 mV as 10 ppm Si samples are run, it may not make sense to invest much time in eliminating the initial 35 mV of background. The approach that was taken with this work instead was the precise quantification and subtraction of the background from the sample signal. This is possible because once a reasonable washout of the previous sample has been achieved, the backgrounds are relatively stable over a period of time longer than that required for the analysis of one sample (Figure 4). There is some infrequent pulsing seen in the signal (possibly due to condensation on the tip of the nebulizer), but this fluctuation in 28 intensities of only 0.01 to 0.02 V represents a potential error of less than 1% of the sample intensity. Backgrounds measured at different times over the course of a typical working day might vary by a total of 0.05 V on mass 28.

[16] The most critical aspect to determining the level of silicon background appears to be the rinsing away of the previous sample. Although the overwhelming majority of the background from the previous sample washes out in the first minute

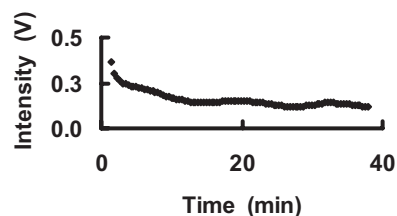


Figure 4. Intensity of the background on mass 28 for a 0.12 M HCl plus 25 mM HF solution over the time required for the measurement of the 29/28 ratio of a sample or standard.

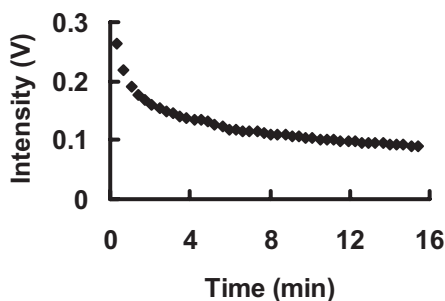


Figure 5. Washout of the sample signal as monitored on mass 28. Initial measurement of 2.7 V (of sample) has been omitted from the plot in favor of showing details at lower intensities.

of rinsing (Figure 5), 13–15 min may be required to reach baseline levels. Sample washout times are much shorter immediately after the nebulizer and spray chamber have been cleaned.

[17] For silicon isotope analysis, a 5 min rinse prior to the measurement of backgrounds has been adopted. The measured backgrounds are then subtracted from the sample peaks measured next. Measurement of machine zeros is not necessary as they cancel out from the signal during the subtraction of the backgrounds.

3.4. Measurement by Standard-Sample-Standard Bracketing

[18] Long sample introduction times are required prior to the measurement of sample peak intensities. Peak intensity ratios (e.g., 29/28) drift for 10–25 min after sample introduction before level-

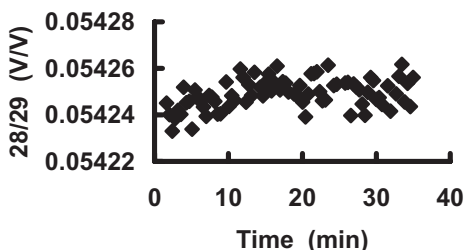


Figure 6. Ratios of the volts of signal at masses 29 and 28 for a 10 ppm Si solution in 0.12 M HCl + 25 mM HF over time from the point of first introduction to the plasma.

ling off (Figure 6). The slope and exact duration of this drift is variable from run to run. It may be that silicon and fluorine unsettle the plasma. Both elements possess high first ionization potentials, and this in conjunction with the strength of the Si-F bond (600 kJ/mol) may work to lower the temperature of the plasma, which silicon in the sample solutions enters as SiF₆.

[19] It is impossible to precisely remove the imprint of the mass bias by bracketing a sample measurement between two measurements of a standard when the mass bias is drifting as much as seen in Figure 6. Delta values calculated from such data are reproducible to no better than 0.5‰ and are generally much worse than that. However, the period of drift in the ratios appears to be a temporary diversion of the mass bias from a baseline value that is stable over several hours. It becomes possible to use the standard-sample-standard bracketing scheme of isotope ratio mass spectrometry to correct for mass bias, provided that ratios are measured after the cessation of drift following the start of sample introduction. For example, the average of 40 ratios (20 second integrations) taken 22–36 min after sample introduction yields ²⁹Si/³⁰Si ratio values stable over the course of the day (Figure 7) and displaying exceptional internal precision (2σ standard error ranges from 2 × 10⁻⁶ to 4 × 10⁻⁶). These values are stable to within 0.05‰ between consecutive standards, even over such a large time difference.

[20] Repeated measurement of ²⁹Si/²⁸Si of working standard against NBS-28 over five weeks was

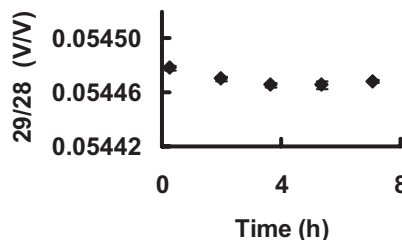


Figure 7. Ratio of signal intensities (in volts) at masses 29 and 28 determined for a working standard introduced into the plasma once every 1.7 hours over a day of analysis.

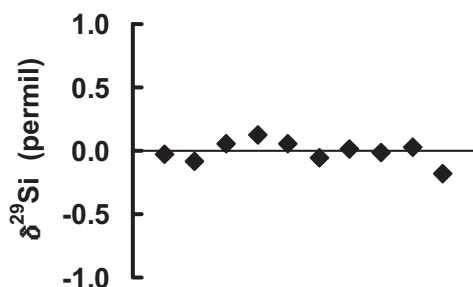


Figure 8. Reproducibility of the $\delta^{29}\text{Si}$ of the working standard measured against NBS-28. Analyses were carried out between 4 October and 11 November 2001.

reproducible (standard deviation of 10 analyses) to $\pm 0.09\text{‰}$ (Figure 8), which compares well with the long-term $\delta^{29}\text{Si}$ reproducibility of NBS-28 of $\pm 0.04\text{‰}$ by the fluorination method (C. De La Rocha, unpublished data, 1996). Analysis of biological and geological samples suggests that the reproducibility of natural samples is also on average $\pm 0.1\text{‰}$ (see section 3.6). Diatoms from a deep-sea sediment sample gave a $\delta^{29}\text{Si}$ value in reasonable agreement with the value determined by the fluorination method (0.54‰ by MC-ICP-MS versus 0.43‰ by fluorination).

[21] One drawback to standard-sample-standard method of mass bias correction is that it is slow. The combination of 5 min of rinse before measurement of a blank prior to each analysis and then 22 min of sample introduction time before roughly 15 min of sample measurement means that the collection of data for one $^{29}\text{Si}/^{28}\text{Si}$ ratio, be it sample or standard, requires ~ 40 min. Thus 2 hours is required to complete one set of standard-sample-standard determinations. This is much greater than the period required for standard-sample-standard analysis on dual-inlet isotope ratio mass spectrometers (where the cycle may be completed multiple times in just a few minutes). This time period is also much greater than that previously utilized on MC-ICP-MS machines for measurement of isotope ratios of other elements, such as calcium [Halicz *et al.*, 1999].

[22] One obvious possibility for shortening the time required for the measurement of silicon isotope

natural abundances by MC-ICP-MS would be by tracking the mass bias from the fractionation of the isotopic ratios of magnesium (masses 24–26) spiked into the sample solutions. However, considering the order of magnitude difference in the transmission of silicon and magnesium through the machine (Figure 1), it is unlikely that the mass fractionations of the two elements are closely equivalent.

3.5. Extrapolation of $\delta^{30}\text{Si}$ from $\delta^{29}\text{Si}$ Based on Mass-Dependent Fractionation Laws

[23] It would be best to report Si isotope data as $\delta^{30}\text{Si}$ rather than as $\delta^{29}\text{Si}$ to facilitate comparison with previously reported data [e.g., Taylor and Epstein, 1970; Douthitt, 1982; Ding *et al.*, 1996; De La Rocha *et al.*, 1996, 1997, 1998, 2000]. Unfortunately, owing to the presence of $^{14}\text{N}^{16}\text{O}$ at mass 30, we are not able to precisely measure $\delta^{30}\text{Si}$. However, $\delta^{30}\text{Si}$ may be extrapolated from $\delta^{29}\text{Si}$, provided that the samples have been subject only to mass-dependent isotope fractionation.

[24] From a model of molecules as simple harmonic oscillators the difference in fractionation among isotope ratios in multiisotope systems may be calculated [Criss, 1999]. The relationship between $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ in a given sample should be

$$\delta^{30}\text{Si} = \delta^{29}\text{Si} \times (29/30) \times \frac{(30 - 28)}{(29 - 28)} = \delta^{29}\text{Si} \times 1.93. \quad (2)$$

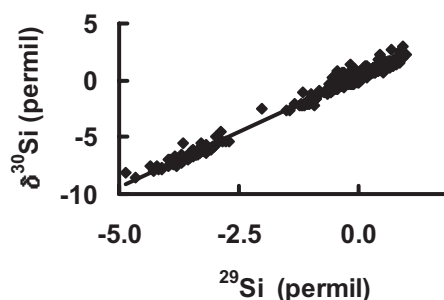


Figure 9. Plot of $\delta^{30}\text{Si}$ versus $\delta^{29}\text{Si}$ of samples measured by vacuum line fluorination coupled with gas source isotope ratio mass spectrometry. The line shown is $y = 1.93x + 0.24$ ($r^2 = 0.99$).

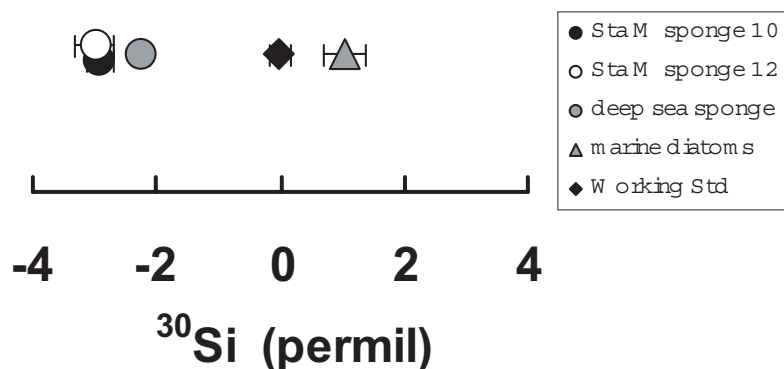


Figure 10. The $\delta^{30}\text{Si}$ values for various samples analyzed by MC-ICP-MS. Samples include spicules from three deep-sea sponges, marine diatoms from a sediment core, and a high purity working standard. Error bars are standard deviations on two measurements, except in the case of the working standard where it is based on 10 measurements.

A plot of 582 samples measured over the course of 3 years via laser-fluorination (De La Rocha, published and unpublished data, 1997) displays exactly this relationship (Figure 9). Samples analyzed cover the range from river and ocean and hydrothermal waters, reagent grade silica, commercially produced SiF_4 gas, naturally produced quartz, and diatoms grown in laboratory culture, obtained from deep sea sediments, and collected live from the ocean. These results suggest that $\delta^{29}\text{Si}$ values measured by MC-ICP-MS may be converted to $\delta^{30}\text{Si}$ values using equation (2).

3.6. Analysis of Geological Materials

[25] Figure 10 and Table 1 display $\delta^{30}\text{Si}$ values extrapolated from $\delta^{29}\text{Si}$ values measured by MC-ICP-MS for several geological samples and a working standard. The geological samples include sedimentary marine diatoms from the Quaternary

and modern deep-sea sponges. Measured $\delta^{30}\text{Si}$ values fall into the ranges expected for all samples, lending support to the use of MC-ICP-MS for the analysis of silicon isotope ratio variations.

[26] Values for sponge spicules (-2.3‰ to -3.0‰) fall within the range of -1.2‰ to -3.7‰ previously reported for sponge spicules [Douthitt, 1982]. The high purity working standard is identical in isotopic composition to NBS-28, a result identical to that by the fluorination method (De La Rocha, unpublished data, 1997).

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Table 1. Identity and $\delta^{30}\text{Si}$ of Samples Presented in Figure 10

Sample	ID	Locality/Source	$\delta^{30}\text{Si}$
Sponge 10	<i>Hyalonema bianchoratum</i> (hexactinellid)	station M, NE Pacific ($34^\circ 45'\text{N}$, $123^\circ 00'\text{W}$, 4100 m depth)	-2.9 ± 0.2
Sponge 12	<i>Hyalonema bianchoratum</i> (hexactinellid)	station M, NE Pacific ($34^\circ 45'\text{N}$, $123^\circ 00'\text{W}$, 4100 m depth)	-3.0 ± 0.3
Deep-sea sponge	unknown hexactinellid	unknown	-2.3 ± 0.1
Marine diatoms	101 cm, core E50-11	LGM Southern Ocean	$+0.1 \pm 0.4$
WORKING Standard	99.995% SiO_2	Alfa Aesar (Johnson Matthey)	0.0 ± 0.2



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References

- Allenby, R. J., Determination of the isotopic ratios of silicon in rocks, *Geochim. Cosmochim. Acta*, **5**, 40–48, 1954.
- Belshaw, N. S., P. A. Friedman, R. K. O’Nions, M. Frank, and Y. Guo, A new variable dispersion double-focusing plasma mass spectrometer with performance illustrated for Pb isotopes, *Int. J. Mass. Spectrom.*, **181**, 51–58, 1998.
- Criss, R. E., *Principles of Stable Isotope Distribution*, 254 pp., Oxford Univ. Press, New York, 1999.
- De La Rocha, C. L., M. A. Brzezinski, and M. J. DeNiro, Purification, recovery, and laser-driven fluorination of silicon from dissolved and particulate silica for the measurement of natural stable isotope abundances, *Anal. Chem.*, **68**, 3746–3750, 1996.
- De La Rocha, C. L., M. A. Brzezinski, and M. J. DeNiro, Fractionation of silicon isotopes by marine diatoms during biogenic silica formation, *Geochim. Cosmochim. Acta.*, **61**, 5051–5056, 1997.
- De La Rocha, C. L., M. A. Brzezinski, M. J. DeNiro, and A. Shemesh, Silicon-isotope composition of diatoms as an indicator of past oceanic change, *Nature*, **395**, 680–683, 1998.
- De La Rocha, C. L., M. A. Brzezinski, and M. J. DeNiro, A first look at the distribution of the stable isotopes of silicon in natural waters, *Geochim. Cosmochim. Acta.*, **64**, 2467–2477, 2000.
- Ding, T., S. Jiang, D. Wan, Y. Li, J. Li, H. Song, Z. Liu, and X. Yao, *Silicon Isotope Geochemistry*, 125 pp., Geol. Publ. House, Beijing, China, 1996.
- Douthitt, C. B., The geochemistry of the stable isotopes of silicon, *Geochim. Cosmochim. Acta*, **46**, 1449–1458, 1982.
- Grant, F. S., The geological significance of variations in the abundances of the isotopes of silicon in rocks, *Geochim. Cosmochim. Acta*, **5**, 225–242, 1954.
- Halicz, L., A. Galy, N. S. Belshaw, and R. K. O’Nions, High-precision measurement of calcium isotopes in carbonates and related materials by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS), *J. Anal. Atmos. Spectrom.*, **14**, 1835–1838, 1999.
- Mortlock, R. A., and P. N. Froelich, A simple method for the rapid determination of biogenic opal in pelagic marine sediments, *Deep Sea Res.*, **36**, 1415–1426, 1989.
- Reynolds, J. H., and J. Verhoogen, Natural variations in the isotopic constitution of silicon, *Geochim. Cosmochim. Acta*, **3**, 224–234, 1953.
- Taylor, H. P., Jr., and S. Epstein, Relationships between $^{18}\text{O}/^{16}\text{O}$ ratios in coexisting minerals of igneous and metamorphic rocks, part I, Principles and experimental results, *Bull. Geol. Soc. Amer.*, **73**, 461–480, 1962.
- Taylor, H. P., Jr., and S. Epstein, Oxygen and silicon isotope ratios of lunar rock 12013, *Earth Planet. Sci. Lett.*, **9**, 208–210, 1970.
- Tilles, D., Natural variations in isotopic abundances of silicon, *J. Geophys. Res.*, **66**, 3003–3014, 1961a.
- Tilles, D., Variations of silicon isotope ratios in a zoned pegmatite, *J. Geophys. Res.*, **66**, 3015–3020, 1961b.
- Ziegler, K., O. A. Chadwick, E. F. Kelly, and M. A. Brzezinski, Silicon isotope fractionation during weathering and soil formation: Preliminary experimental results (abstract), *Goldschmidt J. Conf. Abstr.*, **5**, 1135, 2000.