

**SILICON ISOTOPE ANALYSIS IN SULFUR AND IRON-RICH SAMPLES BY MC-ICP-MS.** X. Chen<sup>1</sup>, T. J. Lapen<sup>1</sup>, R. Andreasen<sup>2</sup>, and H. S. Chafetz<sup>1</sup>, <sup>1</sup>Department of Earth and Atmospheric Sciences, University of Houston, Houston, TX 77204 (xchen28@uh.edu), <sup>2</sup>Department of Geoscience, Aarhus University, Denmark.

**Introduction:** High-precision silicon isotope analysis by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) requires quantitative extraction and purification of silicon from matrices that can cause spectral interferences and/or changes in instrumental mass fractionation (IMF). Recent studies used an alkaline fusion technique at 730°C employing pure NaOH flux to decompose the sample [1]. A similar method uses solid NaOH monoxide to decompose sample material at ~200°C [2]. Both methods utilized cation-exchange chromatography to quantitatively recover silicon and separate it from other cations in the sample solution. These methods have been applied to various natural samples such as igneous rocks [3], lunar rocks [4], and meteorites [5-9].

The combination of alkaline digestion and ion chromatography allows fast and effective sample preparation with high silicon yield. It also avoids the use of HF or generation of volatile SiF<sub>4</sub>. However, samples with complex matrices may cause unexpected results, especially meteorite samples. For example, studies have shown that when silicate rock samples were digested, the resultant solution is typically brownish [10,11], probably due to the precipitation of Fe hydroxide, in contrast to clear solutions produced by high purity silicon samples such as Diatomite and the SiO<sub>2</sub> standard NBS-28. It has been demonstrated that Fe hydroxides selectively adsorb light silicon isotopes, inducing significant isotopic fractionation in the solution prior to ion chromatography [12].

Another issue is that the cation-exchange chromatography does not separate any of the anion species, which may cause significant changes in instrumental mass fractionation compared to pure Si standards. Georg et al. [1] investigated the effect of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> by doping standard Si solutions with sulfate or nitrates and observed no significant isotopic offset when compared to undoped solutions. However, van den Boorn et al. [10] showed significant offset (up to 1.4 ‰) when SO<sub>4</sub>/Si ratio (wt.) exceeds 0.02.

Several purification processes have been proposed to remove S that include ignition of sample at 1350°C [10] and addition of Ba to form BaSO<sub>4</sub> precipitates [13]. However, ignition requires special equipment and the products from ignition usually form sinters that are difficult to recover. Adding Ba may not completely remove all of the sulfate. Instead of removing the S, doping both samples and bracketing standards to the same S/Si ratios has been suggested for sulfate-rich

rocks and river water samples [14]. The aims of this study are to test whether S doping can yield accurate and precise Si isotope ratio measurements and to investigate methods that eliminate the formation of Fe hydroxides which can induce offsets in measured  $\delta^{30}\text{Si}$  values. We propose sample preparation and analytical methods that seems to eliminate potential issues with variable S/Si ratios in measured Si solutions and address the issue of Fe hydroxide precipitation that fractionates Si in sample solutions prior to ion-exchange chromatography. These methods are applied to a variety of well characterized samples and standards.

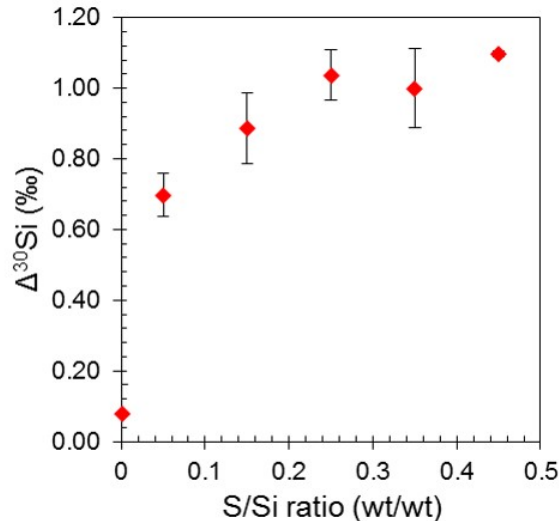
**Experimental:** The effect of S was investigated by doping a pure Si standard solution (PlasmaCal) with various amounts of a sulfate standard (in H<sub>2</sub>SO<sub>4</sub> form) to achieve S/Si weight ratios from 0 to 0.45 (molar ratios 0 to 0.39), similar to the range of van den Boorn et al. [10]. To test the effect of Fe oxide/hydroxide precipitations and the feasibility of the S doping technique, 3 commonly measured silicon isotope reference standards and 4 meteorite samples with various matrices and Fe contents were used: BHVO-2 (basalt, USGS), BIR-1a (basalt, USGS), Diatomite (opal standard), Allende (carbonaceous chondrite, Smithsonian), NWA 3134 (enstatite chondrite), NWA 1068 (shergottite), and EET 87520 (eucrite). Among all the samples measured, Allende has the most abundant S content of up to 2 wt.%. Both Allende and NWA 3134 contain significant amounts of Fe. The same types of meteorites have been extensively measured for Si isotopes by various laboratories [3-9], allowing accurate assessment for the new procedure. Samples were measured in 3 groups: (1) S-undoped, Fe untreated; (2) S-doped, Fe untreated; and (3) S-doped, Fe treated.

Sample digestion was carried out using the alkaline fusion technique adapted from Georg et al. [1]. Si isotope analysis was conducted at medium resolution using a *Nu Plasma II* MC-ICP-MS at University of Houston following the methods detailed by Georg et al. [1]. The results are reported with  $\delta$  notation relative to NBS-28.

#### **Results and Discussion:**

*S-doped standards.* The results of the S-doped PlasmaCal standards clearly show a strong correlation between the shifts in  $\delta^{30}\text{Si}$  values and the S/Si ratios (Fig. 1). Also observed during this test is the increase in ion intensity caused by higher S/Si ratios. A significant shift of  $\delta^{30}\text{Si}$  values (expressed as  $\Delta^{30}\text{Si}$ ) relative to undoped standards was observed when S/Si ratios

are  $> 0.05$ . Samples with S/Si ratios between 0.25 and 0.45 show almost the same magnitude of shifts (*ca.* +1.1‰), indicating the maximum offset is likely reached when the S/Si ratio is higher than 0.25, which also corresponds to 60%-70% increase in total Si ion intensity. These findings are in good agreement with previous studies [10,14].



**Figure 1.** Effect of S on silicon-isotope measurements.  $\Delta^{30}\text{Si}$  represents shift in  $\delta^{30}\text{Si}$  values of S-doped standard relative to pure standard.

*S-induced effect in rock samples.* Sulfur-rich samples that are not artificially doped with S yield variable and anomalous  $\delta^{30}\text{Si}$  values (Table 1). Chondrite samples show the largest offset to heavier  $\delta^{30}\text{Si}$  values. The two achondrite samples show moderate offsets, whereas the basalt standards do not show such a shift in their  $\delta^{30}\text{Si}$  values. This is expected because chondrites have the highest relative S abundance, and terrestrial basalts have relatively low S contents of 168 ppm [15]. Allende has a S/Si ratio of *ca.* 0.1, which corresponds to *ca.* 0.80‰ shift in  $\delta^{30}\text{Si}$  value based on the S-doped standards experiments (Fig. 1). Thus, for accurate and precise measurement of Si isotopic composition in high S/Si content rocks, the S/Si should be adjusted to a fixed value ( $>0.5$  wt/wt) for all samples and bracketing standards.

*Evaluation of the sample preparation procedures and the effect of Si adsorption onto Fe hydroxide precipitates.* After the flux-fusion and dissolution of the sample, the solution can precipitate Fe hydroxides if the pH is too high. The hydroxides adsorb Si, resulting in solutions with heavier Si. In this experiment, samples were acidified directly to pH 2 to 3 using 6 M HCl. The final solution of the two basalt standards appeared to have formed a small amount of tannish to

light-brownish precipitates. The two chondrite samples had the highest content of brownish precipitates, which is expected because the chondrites have the highest Fe contents. It appeared that directly bringing down the solution pH to 2 to 3 cannot eliminate the precipitation of Fe hydroxide. Additional steps suggested by Zambardi and Poitrasson [11] were also tested but failed to produce clear solutions. Significant shifts in Si isotope ratios were observed in Fe-rich samples Allende and NWA 3134 (Table 1) as compared to literature values.

*Fe-treatment.* A new step is proposed to eliminate the precipitation of Fe hydroxides prior to ion-exchange chromatography. This is done by acidifying the solution with HCl to a pH  $< 1$ . This step dissolves all of the Fe hydroxides resulting in clear solutions. Prior to loading on ion-exchange columns, the pH was adjusted to a range of 2 to 3 by slowly adding a 1 M NaOH solution. This step did not result in any Fe hydroxide precipitates.

Sample	S-undoped	S-doped	S-doped
	Fe-untreated	Fe-untreated	Fe-treated
	$\delta^{30}\text{Si}$ ( $\pm 2\text{SE}$ )	$\delta^{30}\text{Si}$ ( $\pm 2\text{SE}$ )	$\delta^{30}\text{Si}$ ( $\pm 2\text{SE}$ )
BHVO-2	-0.17 (0.20)	-0.23 (0.06)	-0.27 (0.03)
BIR-1a	-0.30 (0.15)		-0.33 (0.03)
Allende	0.64 (0.31)	-0.09 (0.10)	-0.42 (0.04)
NWA 3134	0.57 (0.29)	-0.31 (0.08)	-0.52 (0.03)
NWA 1068	-0.15 (0.19)	-0.43 (0.09)	-0.37 (0.03)
EET 87520	-0.12 (0.36)	-0.41 (0.08)	-0.46 (0.05)
Diatomite			1.25 (0.04)

**Table 1.**  $\delta^{30}\text{Si}$  values for 3 groups of measurements. Uncertainties are given as 2SE.

**Conclusion:** S and Fe can cause significant shifts in  $\delta^{30}\text{Si}$  values. The results from S-doped and Fe-treated samples agree well with previous studies [4-9].

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