Chapter 6

An inter-laboratory comparison of Si isotope reference materials *

Abstract

Three Si isotope materials have been used for an inter-laboratory comparison exercise to ensure reproducibility between international laboratories investigating natural Si isotope variations using a variety of chemical preparation methods and mass spectrometric techniques. These proposed standard reference materials are (i) IRMM-018 (a SiO_2 standard), (ii) Big-Batch (a fractionated SiO_2 material prepared at the University of California Santa Barbara), and (iii) Diatomite (a natural diatomite sample originally deposited as marine biogenic opal). All analyses are compared with the international Si standard NBS28 (RM8546) and are in reasonable agreement ($<\pm 0.22$‰ $1\sigma_{SD}$ δ^{30}Si) given the different measurement techniques involved. These methods include both acid and alkaline dissolution/fusion, Si separation using cation exchange, selective co-precipitation, and gas-source *versus* plasma-ionization (high and low resolution) mass-spectrometric techniques. The average δ^{30}Si for Diatomite, IRMM-018, and Big-Batch are +1.26‰, -1.65‰ and -10.48‰, respectively, with corresponding δ^{29}Si values of +0.64‰, -0.85‰ and -5.35‰ for the same standards, respectively.

*Adapted from Reynolds B.C., Aggarwal J., André L., Baxter D., Beucher C., Brzezinski M.A., Engström E., Georg R.B., Land M., Leng M.J., Opfergelt S., Rodushkin I., Sloane H.S., van den Boorn S.H.J.M., Vroon P.Z., Cardinal D. (2007) An inter-laboratory comparison of Si isotope reference materials. *Journal of Analytical Atomic Spectrometry*, 22, 561-568. www.rsc.org.

For the most fractionated standard (Big-Batch), results demonstrate a kinetic mass-dependent fractionation effect for atomic Si (i.e., δ^{29}Si $\sim 0.51 \times \delta^{30}$Si). There is almost no statistical difference between the mean values obtained by each participating laboratory, with the notable exception of the IRMM-018 standard. This effect could be caused by heterogeneity or contamination of this standard. The results for the other two standards indicate that data sets produced using any of the methods employed in this study will have similar precision and differences are limited to 0.2‰ in mean δ^{30}Si values for a given sample between laboratories, or differences of 0.13‰ in mean δ^{29}Si values.

6.1 Introduction

Recently, there has been a renewed interest in the measurement of silicon (Si) isotope variations in natural samples because of the importance of Si in global biogeochemical cycles (Basile-Doelsch, 2006), and its importance as the most abundant non-volatile element in the solar system. Naturally occurring variations in the isotopic composition of Si can be caused by mass-dependent fractionation processes, either kinetic or thermodynamic isotope effects, *via* chemical and biological reactions, or by non-mass-dependent processes from stellar nucleosynthesis and the incorporation of pre-solar grains (see Halliday et al. (2008) and references cited therein). This makes the ability to measure very slight variations in the relative abundances of the three naturally occurring stable isotopes (^{28}Si, ^{29}Si, and ^{30}Si have abundances of 92.23%, 4.67%, and 3.10%, respectively (Barnes et al., 1975)) of interest to a broad range of geoscientific disciplines (Coplen et al., 2002).

Stable isotope variations of Si were first measured over 50 years ago by (Reynolds and Verhoogen, 1953) and (Allenby, 1954), who converted the siliceous minerals into gaseous SiF_4 and assayed this gas in a Nier-type mass spectrometer. These authors used different techniques for the production of the purified gas, measured as SiF_3^+, with a precision of >0.3‰ ($2\sigma_{SD}$). Since these early experiments, the natural variability of the terrestrial Si isotope composition has been inadequately investigated, due mainly to analytical difficulties and the poor reproducibility compared with small natural variations in the ^{30}Si/^{28}Si ratio of only 3.5‰ for terrestrial, igneous and metamorphic rocks, and 6‰ for biogenic opal (Douthitt, 1982), with an error of ±0.2‰ $2\sigma_{SD}$ (Coplen et al., 2002). Furthermore, unlike with oxygen isotopes, careful studies of meteorites and lunar material could not evidently show visible isotopic anomalies, e.g. Epstein and Taylor (1970), with

all of the measured samples falling close to a single mass-fractionation line, although small pre-solar SiC grains contain very anomalous Si isotope compositions (Besmehn and Hoppe, 2003). The relatively small variations observed, as compiled by Douthitt (1982), showed that Si isotopes were probably of little significance in the understanding of igneous processes, whilst the fractionation of aqueous or biological precipitates was limited by an inability to measure dissolved Si isotope compositions. Hence, in the following decade, little work was done to further investigate Si isotope fractionations, see (Ding, 2004). However, the application of Si isotope variations to investigate geochemical cycles has been enhanced by two separate developments. Firstly, the ability to measure the Si isotope composition on a wide range of samples: dissolved and biogenic Si from marine and freshwaters environments (Alleman et al., 2005; André et al., 2006; Cardinal et al., 2005; De La Rocha et al., 2000; Engström et al., 2006; Georg et al., 2006ab; Reynolds et al., 2006a; Varela et al., 2004), soils and plants (Ding et al. (2005b); Opfergelt et al. (2006ab); Chapter 7) as well of altered rocks and soils (André et al., 2006; Basile-Doelsch et al., 2005; Georg et al., 2006b; van den Boorn et al., 2006; Ziegler et al., 2005ab). Secondly, improved gas source isotope ratio mass spectrometer (IRMS) techniques (Brzezinski et al., 2006) and the advancement of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) (Cardinal et al., 2003; Reynolds et al., 2006b) now provide the precision required to better constrain these biogeochemical systems.

The exploitation of MC-ICP-MS offers two major advantages over IRMS: firstly, faster analytical protocols (both chemical processing and analysis time), including repeated analyses, and secondly, much smaller sample sizes. However, MC-ICP-MS also has disadvantages, including lower internal precision on isotopic measurement compared with dual-inlet IRMS, potential "matrix effects" and significant polyatomic interferences resulting from the plasma source. Few comparisons of Si isotope variations between IRMS and MC-ICP-MS analyses have been made (Cardinal et al., 2003) but they show agreement between methods of *ca.* 0.2‰. The present paper demonstrates that, despite recent problems concerning the composition of IRMM-018 (Ding et al., 2005a; Reynolds et al., 2006b; Valkiers et al., 2005), δ^{30}Si and δ^{29}Si compositions measured using a wide variety of chemical preparation methods and mass spectrometric techniques all give consistent results and that there is no systematic bias induced by measurement instrumentation.

Stable isotope fractionation can be assessed using only two isotopes, but different mass-dependent fractionation laws apply for kinetic, equilibrium, and experimentally observed instrumental mass-fractionation.

However, to resolve differences between these fractionation laws, as observed for oxygen, iron and magnesium (Galy et al., 2002a; Malinovsky et al., 2003; Miller, 2002; Young et al., 2002), there must be considerable mass-fractionation and three isotopes must be measured to extremely high precision. Hence, most natural Si isotope variations can be reported as variations in either $^{30}Si/^{28}Si$ or $^{29}Si/^{28}Si$ (or even $^{30}Si/^{29}Si$), and are expressed in δ-notation ; variations relative to the international Si standard NBS28 (RM #8546) in per mille (‰). For mass-dependent fractionation, the enrichment of ^{30}Si is almost twice the enrichment of ^{29}Si when normalised to ^{28}Si, resulting in the fact that $\delta^{30}Si$ variations are roughly twice those of $\delta^{29}Si$, for any given fractionation. Given similar precisions on the measured $^{30}Si/^{28}Si$ and $^{29}Si/^{28}Si$ ratios, the relative error on $\delta^{30}Si$ variations are less than those of $\delta^{29}Si$, which is why natural Si isotope variations are typically expressed as $\delta^{30}Si$. However, the analyses of $^{30}Si/^{28}Si$ ratios using some MC-ICP-MS are problematic due to more pronounced polyatomic interferences on mass 30, so a number of laboratories can only determine the $\delta^{29}Si$ values. Precision for MC-ICP-MS methods are comparable to that obtained by IRMS.

6.2 Samples and methods

In order to compare stable Si isotope variations between different laboratories and measurement techniques, it was decided that three materials should be used so that variations could be observed for natural samples which were both distinctly light and distinctly heavy compared with the international Si isotope standard reference material NBS28 (RM8546), and also highly fractionated. To ensure easy distribution and similar sample preparation protocols of all the standards, the chosen standards were required to be distributed as powdered SiO_2, just like NBS28. Although several laboratories have their own in-house standards (typically a commercially available Si powder), these were not used as they had $\delta^{30}Si$ values similar to NBS28. The three materials chosen were (i) IRMM-018, a SiO_2 standard, (ii) a natural diatomite sample termed "Diatomite", and (iii) a highly fractionated SiO_2 material termed "Big-Batch" (Brzezinski et al., 2006; Cardinal et al., 2003). Although the European Si standard IRMM-018 was commercially available, in order to address the possibility of sample heterogeneity given a large discrepancy between previously published $\delta^{30}Si$ values (Coplen et al., 2002; Ding et al., 2005a; Reynolds et al., 2006b; Valkiers et al., 2005), sub-samples of IRMM-018 were distributed from ETH Zürich to all

Table 6.1: Summary of the different methods used by each group for the preparation of the standard materials and the mass-spectrometric techniques for determining the relative Si isotope composition.

Group. No.	Group.	Authors	Ion source	Mass Spectrometry	Preparation technique	References
1	IGMR, ETH Zürich	Ben C. Reynolds, R. Bastian Georg	ICP	NuPlasma 1700	Alkali fusion and ion-exchange	Georg et al. (2006ab) Reynolds et al. (2006ab)
2	Keck Labs, UCSC	Jugdeep Aggarwal	ICP	Neptune	See Reynolds et al. (2006b)	
3	MRAC, Belgium	Damien Cardinal, Sophie Opfergelt Luc André	ICP	NuPlasma (low-res.)	HCl-HF dissolution Dry plasma, Mg doping	Alleman et al. (2005) André et al. (2006) Cardinal et al. (2003 2005) Opfergelt et al. (2006ab)
4	Analytica AB, Luleå, Sweden	Douglas Baxter, Emma Engström, Ilia Rodushkin	ICP	Neptune	HNO_3-HF dissolution	Engström et al. (2006)
5	Marine Science, UCSB	Mark Brzezinski, Charlotte Beucher	Duel-inlet Gas-Source	Kiel III MAT 252	HF dissolution, then $CsSiF_6$ precipitation	De La Rocha et al. (1996 1997) De La Rocha et al. (2000 1998) Ziegler et al. (2005ab) Brzezinski et al. (2002)
6	Stockholm, Sweden	Magnus Land	ICP	IsoProbe (low-res.)	$LiBO_2$ fusion and HCl dissolution	
7	NERC Isotope Labs, UK	Melanie Leng, Hilary Sloane	Gas-Source	Finnigan MAT 253	Based on O_2 method	Leng and Barker (2006)
8	FALW, VU, Netherlands	Sander van den Boorn, Pieter Vroon	ICP	Neptune	Alkali dissolution and ion-exchange	van den Boorn et al. (2006)

the participating laboratories (under verbal agreement from IRMM). The previously published results for the highly fractionated standard Big Batch were initially prepared by Christina De La Rocha and Mark Brzezinski at the Marine Science Institute of the University of California Santa Barbara, as precipitated triethylamine silicomolybdate from a dissolved sodium metasilicate (De La Rocha et al., 1996). For the inter-comparison exercise, a new batch of powdered SiO_2 was produced, and distributed by Mark Brzezinski, from multiple combustions and subsequent crushing and mixing of the same precipitated triethylamine silicomolybdate. Unfortunately, the combustion does not fully remove all the molybdate, and the Big Batch standard actually contains about 1.5 ppm Mo (van den Boorn et al., 2006), which may not be separated from Si during the chemical preparation during dissolution or cation-exchange chromatography and thus lead to potential matrix effects (see later). The Diatomite Standard was also prepared and distributed by Mark Brzezinski, and from a 1 kg sample of purified diatomite with the trade name Celpure®, donated by the Celite Corporation of Lompoc, California. The three distributed standards are all relatively pure SiO_2, but with variable amounts of water, so are not crystographically identical. Additional milligram sized samples of the Big Batch and Diatomite standards are available from Mark Brzezinski.

In terms of sample and standard preparation, each group has developed its own techniques and protocols suitable for its own instrumentation, as shown in Table 6.1. We will use the term group rather than laboratory as, although only one mass spectrometer has been used in each case, workers participating within each group may come from several laboratories. The details for all of these analytical methods are published elsewhere, see Table 6.1. However we will briefly review the advances in chemical preparation and mass-spectrometric techniques.

6.3 Advances in mass spectrometry

6.3.1 IRMS

Silicon isotope analysis by IRMS usually involves conversion of the sample to SiF_4 gas (De La Rocha et al., 1996; Ding, 2004; Douthitt, 1982; Epstein and Taylor, 1970), for example using fluorine compounds, and heat to convert SiO_2 to O_2 and SiF_4, as also used for the measurement of silica oxygen, see (Leng and Barker, 2006). The SiF_4 is converted to beams of SiF_3^+ ions by electron bombardment in the ion source of the mass spectrometer, the intensities of which are measured at 85, 86, 87 m/z. The procedure is difficult because of the use of dangerous fluorine

based compounds, but once samples are prepared analysis by dual inlet IRMS is highly reliable and has high internal precision. The results for IRMS analyses in this paper were produced using the fluorination method (BrF_5) and a MAT 253 isotope ratio mass spectrometer (at NIGL, Nottingham) and the Cs_2SiF_6 method (UCSB, California) using a modified Kiel III carbonate device attached to a MAT 252 isotope ratio mass spectrometer.

The new IRMS method eliminates the need to use F_2 or BrF_5 to produce SiF_4 (Brzezinski et al., 2006). Samples are converted to solid Cs_2SiF_6 using simple chemical procedures and SiF_4 is a product of the acid decomposition of Cs_2SiF_6. Several commercially available inlet systems operate on the principle of acid decomposition of solids for the analysis of carbonates. Minor modification of these systems can make them suitable for the analysis of isotopes of Si (Brzezinski et al., 2006). Cs_2SiF_6 is loaded directly into these systems with the acid decomposition performed mechanically, allowing for relatively rapid automated analysis.

6.3.2 MC-ICP-MS

Initial measurements of Si isotopes using MC-ICP-MS used a "wet-plasma" sample introduction technique, with 0.25 M HF (De La Rocha, 2002). Unfortunately, this technique produced very poor sensitivity, poor temporal stability of instrumental mass-bias and severe memory effects, so that the analytical precision was poor. Relative Si isotope variations are measured using a standard-sample-standard bracketing technique that requires identical conditions in the measurement solutions and plasma source between samples and standards, and minimum drift in the instrumental mass-bias with time. Failure to ensure identical conditions, for instance the presence of additional cations in the analyte, can lead to "matrix-effects" and incorrect determination of relative isotopic compositions. However, when correctly implemented, this bracketing technique effectively eliminates the errors from instrumental background and amplifier corrections, since these should affect both sample and standard in an identical manner. A refined analytical technique was developed by Cardinal et al. (2003), with a "dry-plasma" sample introduction using a desolvating nebulization system and Mg external doping for mass bias correction. This technique introduced very dilute acids, with HF below 0.01 M, in order to increase the sensitivity and stabilize instrumental mass-bias over time.

Under normal operating conditions, as well as the efficient ionization of cations, there is also the production of interfering polyatomic ions,

either within the plasma or in the interface region. Assuming a typical $^{28}Si^{+}$ intensity of 60 pA on an instrument equipped with a desolvating nebulizer (Cardinal et al., 2003; Georg et al., 2006b), the polyatomic species $^{14}N^{2}H^{+}$ and $^{14}N^{16}O^{+}$ would typically result in signals corresponding to at least 0.7% and 5% of the $^{29}Si^{+}$ and $^{30}Si^{+}$ ion beams, respectively. For instruments using conventional "wet-plasma" sample introduction systems (Engström et al., 2006), the magnitude of these spectral interferences on the silicon isotopes would be even more pronounced. Although some of these interferences can be corrected for (Cardinal et al., 2003), the polyatomic interference on mass 30 prevents accurate measurement of $^{30}Si/^{28}Si$ ratios compared with $^{29}Si/^{28}Si$. However, polyatomic ions are slightly heavier than atomic ions of the same nominal mass in this region of the mass spectrum, a fact that can be exploited using high-resolution ion optics to separate the Si^{+} ion beams from potential polyatomic interferences (Halliday et al., 2008). This requires the ability to resolve ion beams which differ by less than 1‰ in mass (usually expressed as requiring a mass-resolution ($m/\Delta m$) in excess of 1000), and has been demonstrated for Si isotope analyses using higher resolution MC-ICP-MS instruments (Engström et al., 2006; Reynolds et al., 2006b) utilized by groups participating in this study. A new chemical preparation technique has also been developed independently by two groups to avoid HF in sample solutions, which has been shown to enhance sensitivity and minimize mass-bias variations (Georg et al., 2006b; Reynolds et al., 2006b; van den Boorn et al., 2006).

6.4 Results

There are a variety of ways to compare different isotope results generated within and between laboratories, and so we will first describe the statistical approach taken here. For Si isotope analyses, the internal errors on individual measurements are much lower than the reproducibility among measurements. For the standard-sample-standard bracketing approach used in MC-ICP-MS analysis there are a number of ways in which to propagate measurement error on the standard and sample, leading to discrepancies between reported internal errors. A simplified approach is taken here; we assume that the errors for individual measurements of $\delta^{30}Si$ and $\delta^{29}Si$ values are much smaller than the measurement reproducibility and that they are equal for all measurements from all groups. While this is not strictly true, it is a fair approximation as it does not lead to a significant bias in the distribution of the reproducibility reported for each group, or the collectively pooled data.

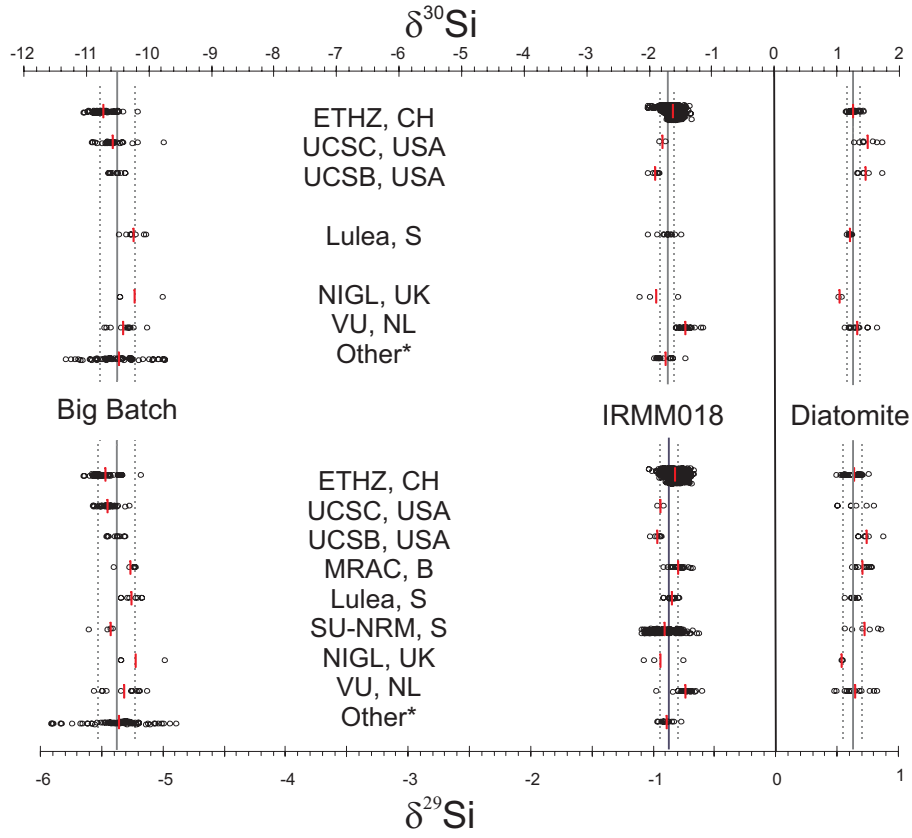

Figure 6.1: Summary of all of the results from each group, upper panel for δ^{30}Si and lower panel for δ^{29}Si, scaled to allow direct correlation between these two units. There is no δ^{30}Si data available from MRAC and SU-NRM due to the mass spectrometry used. *Other refers to previously analysed preparation of Big Batch (see Table 6.2) and for a different sample of IRMM-018 obtained by and run at VU, Amsterdam. Grey lines mark the pooled mean values (solid) and $\pm$ 1σ_{SD} from the mean (broken), see Table 6.2.

The collected data from the eight groups taking part (Table 6.1) are shown in Figure 6.1 and Table 6.2. Note that when a silica dissolution step is required (i.e., when using MC-ICP-MS), each group has performed at least three separate dissolutions for every reference material. The measured Si isotope composition for single analyses of Diatomite range from +0.47 to +0.85‰ δ^{29}Si or +0.99 to +1.70‰ δ^{30}Si, whilst for IRMM- 018 the δ^{30}Si and δ^{29}Si values range from -1.13 to -2.16‰ and -0.61 to -1.10‰, respectively. However, ranges are biased by

the inclusion of statistical outliers (or anomalies), and thus do not reflect how well the measured values may be compared between laboratories. Despite the wide range from individual data points, the mean results from each group are in good agreement (Figure 6.1), with a marked overlap in the measured isotope ratios for each standard from each group.

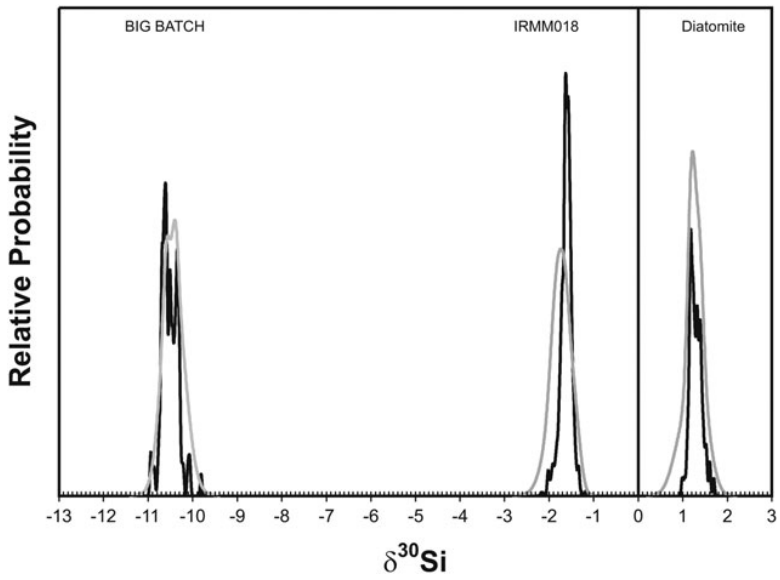

Figure 6.2: Probability density function (pdf) of the δ^{30}Si results from all groups for all 3 standards, using both equal weighting for each data point (black line) and equal weight for each group (grey line).

The data can be compiled to form a probability density function (pdf), so that the shape of the distribution can be easily observed, as is shown in Figure 6.2. However, this can be realized in two separate ways, either (i) by weighting all the data points equally or (ii) by weighting the averages for each group equally. The results of both approaches are illustrated in the figure. For the large number of analyses obtained, we would expect the data to be normally distributed around an average value, and in describing the data and reproducibility in terms of standard deviations (σ_{SD}) and standard errors (σ_{SEM}, standard error of the mean) one would be defining this to be the case. However, as is shown in Figure 6.2, the data are not normally distributed in a Gaussian or bell-shaped curve, so the modal and arithmetic mean (or average) of each population is not exactly the same. That is to say, the peak in the pdf is not in the middle of the distribution. Thus, by describing

Table 6.2: Summary of all of the results from each group, in rank order of mean δ^{29}Si value for each standard. Pooled data is weighted according to the precision of the 95% confidence limit (c.l.). Data shown in grey when the number of measurements (n) was small ($n < 6$), which leads to 95% c.l. $\ll$ 1 σ_{SD} (one standard deviation of the mean), and a mean value that is poorly constrained. * Denotes results from a previously analysed preparation of Big Batch, and a separate supply of IRMM-018 to VU.

Standard	Group no.	**GROUP**	Rank	δ^{30}**Si**	95% c.l. SEM	1σ_{SD}	n	δ^{29}**Si**	95% c.l. SEM	1σ_{SD}	n
IRMM-018	5	UCSB	1	**-1.86**	0.07	0.11	14	**-0.95**	0.03	0.06	14
IRMM-018	7	NIGL	2	**-1.89**	0.81	0.32	3	**-0.95**	0.42	0.17	3
IRMM-018	2	UCSC	3	**-1.79**	0.59	0.07	2	**-0.95**	0.35	0.04	2
IRMM-018	6	SU-NRM	4	n/a				**-0.91**	0.02	0.10	157
IRMM-018	4	Luleå	5	**-1.71**	0.09	0.14	12	**-0.85**	0.03	0.04	12
IRMM-018	1	ETHZ	6	**-1.61**	0.01	0.11	493	**-0.82**	0.01	0.06	493
IRMM-018	3	MRAC	7	n/a				**-0.80**	0.03	0.06	21
IRMM-018	8	VU	8	**-1.41**	0.05	0.11	25	**-0.73**	0.03	0.05	24
IRMM-018*	8	VU, new		**-1.74**	0.08	0.14	14	**-0.90**	0.03	0.05	14
IRMM-018	8	VU, both		**-1.62**	0.04	0.13	39	**-0.80**	0.03	0.10	39
IRMM-018		**POOLED**		**-1.65**	**0.01**	**0.11**	**563**	**-0.85**	**0.01**	**0.07**	**740**
Diatomite	7	NIGL	1	**+1.02**	0.32	0.04	2	**+0.54**	1.53	0.17	2
Diatomite	2	UCSC	2	**+1.46**	0.15	0.16	7	**+0.63**	0.10	0.11	7
Diatomite	4	Luleå	3	**+1.17**	0.03	0.03	6	**+0.63**	0.03	0.03	8
Diatomite	1	ETHZ	4	**+1.23**	0.03	0.08	31	**+0.63**	0.02	0.06	30
Diatomite	8	VU	5	**+1.29**	0.09	0.15	13	**+0.64**	0.07	0.11	13
Diatomite	3	MRAC	6	n/a				**+0.70**	0.04	0.06	11
Diatomite	6	SU-NRM	7	n/a				**+0.72**	0.12	0.12	6
Diatomite	5	UCSB	8	**+1.38**	0.04	0.08	23	**+0.71**	0.04	0.04	23
Diatomite		**POOLED**		**+1.26**	**0.02**	**0.10**	**82**	**+0.64**	**0.02**	**0.07**	**100**
Big Batch	2	UCSC	1	**-10.64**	0.05	0.15	38	**-5.46**	0.02	0.06	42
Big Batch	6	SU-NRM	2	n/a				**-5.43**	0.11	0.10	6
Big Batch	1	ETHZ	3	**-10.58**	0.04	0.07	18	**-5.39**	0.02	0.05	18
Big Batch	5	UCSB	4	**-10.39**	0.04	0.07	23	**-5.31**	0.04	0.04	23
Big Batch	8	VU	5	**-10.44**	0.13	0.20	12	**-5.32**	0.09	0.15	12
Big Batch	3	MRAC	6	n/a				**-5.27**	0.07	0.07	6
Big Batch	4	Luleå	7	**-10.29**	0.12	0.14	8	**-5.26**	0.06	0.07	8
Big Batch	7	NIGL	8	**-10.27**	0.98	0.40	3	**-5.23**	0.52	0.21	3
Big Batch*	3	MRAC		n/a				**-5.29**	0.02	0.04	23
Big Batch*	5	UCSB		**-10.56**	0.07	0.17	23	**-5.39**	0.04	0.09	23
Big Batch*	1	ETHZ		**-10.48**	0.18	0.50	34	**-5.39**	0.11	0.31	34
Big Batch		**POOLED**		**-10.48**	**0.04**	**0.27**	**159**	**-5.35**	**0.02**	**0.15**	**198**

the data in terms of a mean, plus/minus a standard deviation, we are not accurately reflecting the underlying data, and the given values can be somewhat biased by the way the data is amassed. A better approach would be to quantify the quartile or 90% confidence limits of the observed distributions in order to quantify the reproducibility of the Standards (Table 6.3). For Big Batch these δ^{30}Si ranges are from -10.77 to -10.23‰, and -10.64 to -10.38‰ for the 90% range and 50% (quartile) range, respectively, weighting each point equally, or from -10.81 to -10.04‰, and -10.60 to -10.29‰ for the 90% range and 50% (quartile) range, respectively, weighting each group equally. The modal δ^{30}Si value, or average, is between -10.53 and -10.45‰, depending upon the weighting used, as is shown in Table 6.3. Even for this highly fractionated standard, all groups have data within these relatively narrow quartile ranges.

Table 6.3: Summary of the collective distribution of δ^{30}Si and δ^{29}Si values for each standard, based on either weighting all the data points equally or by weighting the averages for each group equally.

Standard	Equal	Composition	Modal value	Quartile range		90% range	
	Weighting			lower	upper	lower	upper
IRMM-018	datapoints	δ^{30}Si	-1.61	-1.68	-1.54	-1.85	-1.44
IRMM-018	groups	δ^{30}Si	-1.73	-1.88	-1.58	-2.12	-1.36
IRMM-018	datapoints	δ^{29}Si	-0.84	-0.90	-0.79	-1.01	-0.72
IRMM-018	groups	δ^{29}Si	-0.88	-0.96	-0.80	-1.10	-0.70
Diatomite	datapoints	δ^{30}Si	+1.27	+1.19	+1.38	+1.11	+1.54
Diatomite	groups	δ^{30}Si	+1.25	+1.13	+1.39	+0.85	+1.61
Diatomite	datapoints	δ^{29}Si	+0.66	+0.61	+0.71	+0.51	+0.79
Diatomite	groups	δ^{29}Si	+0.65	+0.58	+0.72	+0.47	+0.85
Big Batch	datapoints	δ^{30}Si	-10.53	-10.64	-10.38	-10.77	-10.23
Big Batch	groups	δ^{30}Si	-10.45	-10.60	-10.29	-10.81	-10.04
Big Batch	datapoints	δ^{29}Si	-5.38	-5.46	-5.30	-5.55	-5.20
Big Batch	groups	δ^{29}Si	-5.34	-5.43	-5.25	-5.56	-5.10

As the number of measurements (n) is not the same between groups, the mean can be biased to either the groups from which more data has been analysed or those which have produced less. Rather than use either of these extremes for creating an average or mean δ-value, we have weighted the contribution from each group by their individual reproducibility (the 95% confidence-limit (c.l.) of each group's dataset). The error on this mean δ-value is estimated using normal theory, where the total pooled variance (σ_p^2) is the sum of the variance from within each group normalized to the degrees of freedom (n-1). Statistical differences between the means from each group and each other group,

and the overall mean (termed pooled value) are evaluated using Scheffé adjustment on a Bonferroni method at the 95% c.l. ($p < 0.05$), see Table 6.2 (Uitenbroek, 1997). This corrects for the likelihood that given enough comparisons there is likely to be some significant difference arising from the application of simple pair-wise comparisons (like the Student's T-test).

6.5 Discussion

As shown in Figure 6.1 and Table 6.2, the average results from each group are typically within 1 standard deviation (σ_p) of the pooled mean, implying that all groups obtained consistent results for both δ^{30}Si and δ^{29}Si values for all three standards. As these groups employ distinctive methods (including acid/ alkaline dissolution/fusion, Si separation using cation exchange, selective co-precipitation, as well as fluorination techniques) there does not appear to be any significant mass fractionation associated with any of the methods. Furthermore, the good agreement between gas-source and plasma ionization (both in high and low resolution) mass spectrometric techniques excludes the possibility of a systematic bias in the determined Si isotope composition induced by measurement instrumentation. This confirms the previously published conclusion that there is no systematic offset between MC-ICPMS and IRMS (Cardinal et al., 2003). The published data from a previous comparison of Big Batch are presented in Table 6.2 (denoted by Big Batch*) along with the unpublished results from the analysis of the same sample solution at ETH, which further illustrates the agreement between instruments.

An indicator of data quality is given by the correlation between measured δ^{30}Si and δ^{29}Si values, as unresolved interferences or problems in the Si isotope analyses should cause isotope ratios to be shifted away from that expected from terrestrial mass-dependent fractionation. As is shown in Figure 6.3, there is an excellent correlation between δ^{30}Si and δ^{29}Si values for all the mean values reported from each group ($R^2 = 0.99996$, excluding Diatomite from UCSC, which appears to have an interference problem, discussed below). Furthermore, the slope of this line depends upon the fractionation process: for an equilibrium fractionation the gradient should equal 0.518, whilst for kinetic fractionation it would depend upon the Si species considered and gives values from 0.509 for Si atoms to 0.505 for SiO_2. The best-fit line, with an intercept of zero, has a gradient of 0.511 which is principally controlled by the composition of Big Batch, and implies that the

fractionation induced in the formation of this standard was kinetically controlled and did not take place under equilibrium conditions. This is expected as the equilibrium conditions generally lead to smaller isotope fractionation effects.

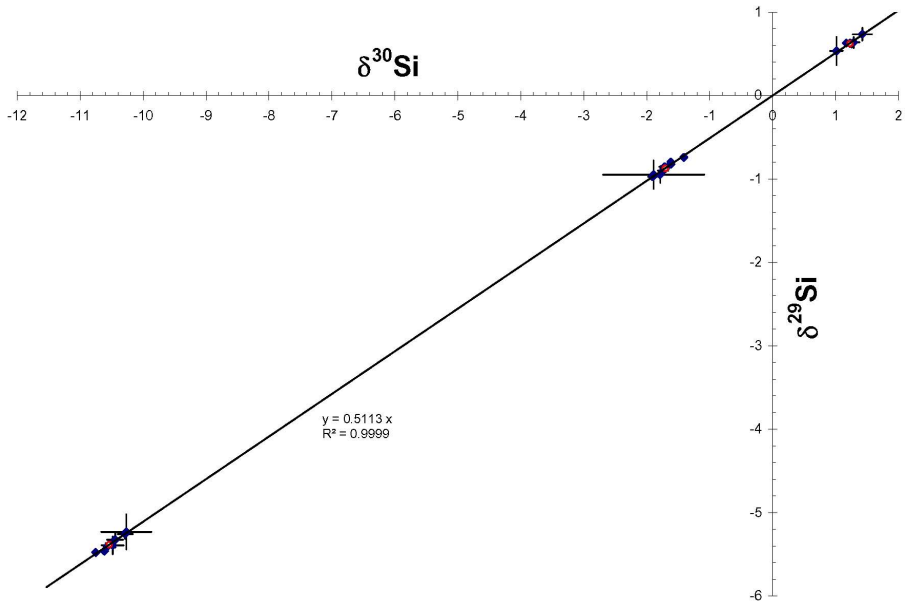

Figure 6.3: Three isotope plot of δ^{29}Si *versus* δ^{30}Si (error bars are $1\sigma_{SD}$). Means from all groups for all standards fall along a mass-dependent fractionation array (excluding Diatomite from UCSC), with a slope of 0.511, in close agreement with kinetic isotope fractionation of Si of 0.5092.

However, despite the generally good agreement, in detail there is some divergence in the mean results from each group beyond the internal reproducibility of the data. This lower reproducibility between groups compared with within groups is typical for most analytical measurements, but it ultimately limits the reliability of comparing datasets published by different groups. Even though published internal precisions may be below 0.1‰, there may remain problems with comparing data from different groups to this level of accuracy. From this inter-laboratory comparison, using the quartile range from individual measurements, it would appear that differences between reported results should be limited to 0.20‰ δ^{30}Si for a given sample and 0.13‰ for δ^{29}Si.

We can quantify the statistical significance of the apparent offsets between participating groups by applying a Bonferroni method to test

for significant differences between the mean values reported from each group. Mean results are significant at the 0.05 (or 95% confidence) level if they differ by more than the following (see Table 6.2): IRMM-018 δ^{30}Si >0.18‰, δ^{29}Si >0.11‰; Big Batch δ^{30}Si >0.44‰, δ^{29}Si >0.22‰;Diatomite δ^{30}Si >0.20‰, δ^{29}Si >0.13‰. Excluding means based on a small number of duplicate analyses ($n < 6$), there are no statistical differences between groups for either the Big Batch or Diatomite standard, apart from one notable exception. This exception is the mean δ^{30}Si value of Diatomite from UCSC compared with Lulea, but given that both groups report exactly the sample δ^{29}Si values and that the high δ^{30}Si values from UCSC do not fit on the terrestrial mass-dependent fractionation array shown in Figure 6.3, this UCSC δ^{30}Si data can be clearly seen as anomalous (probably due to a small interference problem on mass 30).

There are several statistical differences in the mean value of IRMM-018 between groups including two different analyses of IRMM-018 from one participating group (VU), see also (van den Boorn et al., 2006). The statistical differences are unlikely to result from a systematic error, given the agreement for the other two standards, and are possibly due to contamination by dust during handling or heterogeneity within the standard material itself. The mean from UCSB is distinct from the means VU, ETHZ and MRAC, which could be taken to suggest a slight discrepancy in the result between gas-source mass spectrometry and MC-ICP-MS techniques, but may equally be simply due to chance. We thus recommend against future use of IRMM-018 as a calibration standard. Indeed, given that IRMM has stopped selling IRMM-018 and replaced it with IRMM-018a, which may be similar to NBS28, this standard is essentially obsolete. Therefore, NBS28 should remain the primary reference material for Si isotope studies (δ^{30}Si = δ^{29}Si = 0) and we recommend the use of Big Batch and Diatomite as secondary reference materials to check accuracy of methods and new analytical studies.

6.6 Conclusions

All chosen methods for both sample preparation and mass spectrometric techniques give consistent results for both δ^{30}Si and δ^{29}Si values for the samples Diatomite and Big Batch distributed by Mark Brzezinski (UCSB). These methods include dissolution/fusion, cation exchange, co-precipitation and decomposition, and fluorination techniques: in addition, we have used two different types of mass spectrometry,

plasma-ionization (both in high and low resolution) and gas source. Published data can be reliably compared between laboratories at the 0.2‰ accuracy for δ^{30}Si values (2 σ_{SD}), although internal reproducibility within each participating laboratory is generally better than this. Statistical differences between the mean values reported by each group for neither Big Batch nor Diatomite are significant (excluding poorly constrained data). However, they are significant for the IRMM-018 standard. As the Si isotopic compositions of the other standards are in agreement, this difference is unlikely to be a systematic error and is possibly due to heterogeneity of the powder or laboratory contamination of the IRMM-018 standard.

The calibration between δ^{30}Si and δ^{29}Si values are in complete agreement with a mass-dependent fractionation between the standards, with $\delta^{29}\text{Si} = 0.51 \times \delta^{30}\text{Si}$ (or $\delta^{30}\text{Si} = 1.96 \times \delta^{29}\text{Si}$), allowing for easy calculation of δ^{30}Si values from given δ^{29}Si values and *vice versa*. The mean δ^{30}Si values from the collectively pooled data for the three standards are +1.26‰, -1.65‰ and -10.48‰ for Diatomite, IRMM-018 and Big-Batch, respectively.