Chapter 5

Isotopic determinations on BHVO-1 and BHVO-2 reference materials *

Abstract

We report silicon isotopic analyses of rock standards BHVO-1 and BHVO-2 using a Nu Plasma Multi Collector (MC)-ICP-MS, upgraded with a new adjustable entrance slit to obtain medium resolution, as well as a stronger primary pump and newly designed sampler and skimmer cones ("B" cones). These settings combined with the use of collector slits allow to reach a resolution sufficient to overcome the $^{14}N^{16}O$ and $^{14}N_2$ interferences overlying the ^{30}Si and the ^{28}Si peaks respectively in the previous set-up. This enables accurate measurement of both $\delta^{30}Si$ and $\delta^{29}Si$. The δ value is expressed in per mil variation relative to the NBS28 quartz standard. Based on data acquired from numerous sessions spread over a period of six months apart, we propose a recommended average $\delta^{30}Si$ of -0.33 ± 0.05‰ and -0.29 ± 0.11‰ ($2\sigma_{SEM}$) for BHVO-1 and BHVO-2, respectively. Our BHVO grand mean silicon isotope composition ($\delta^{30}Si = -0.31\pm0.06$‰) is significantly more negative than the only published value for BHVO-2, but is in very good agreement with the recently established average value of ocean island basalts (OIB) confirming the conclusion that the OIB reservoir has a distinct isotopic composition from the solar reservoir as sampled by chondrites.

*Adapted from Abraham K., Opfergelt S., Fripiat F., Cavagna A.-J., de Jong J. T. M., Foley S., André L., Cardinal D. (2008) $\delta^{30}Si$ and $\delta^{29}Si$ determinations on BHVO-1 and BHVO-2 reference materials via new configuration on Nu Plasma Multi Collector (MC)-ICP-MS. *Geostandards and Geoanalytical Research*, in press.

5.1 Introduction

During the last decade, there has been a renewed interest in the measurement of silicon (Si) isotope variations in water and biological samples because of the importance of Si in global biogeochemical cycles through its incorporation in diatoms (Alleman et al., 2005; Cardinal et al., 2005 2007; De La Rocha et al., 1998; Fripiat et al., 2007; Georg et al., 2006b; Varela et al., 2004) and its pathways in plants (Ding et al. (2005b); Opfergelt et al. (2006b); Chapter 7). The interest has been recently extended to water-rock interaction and core formation processes focused on various mineral and rock samples: clays (Ziegler et al., 2005ab), cherts (André et al., 2006; Robert and Chaussidon, 2006), silcretes (Basile-Doelsch et al., 2005), metabasalts (André et al., 2006), metasediments (André et al., 2006), basalts, lherzolites and meteorites (Georg et al., 2007b).

Naturally occurring mass fractionation processes between aquatic dissolved Si and biological/ mineral Si-rich phases are generally limited (max. 1.5‰) (Alleman et al. (2005); Georg et al. (2007c); Méheut et al. (2007); Opfergelt et al. (2006b); Chapter 7) producing rather small variations in the relative abundances of the three naturally occurring stable isotopes (^{28}Si, ^{29}Si and ^{30}Si). Improved gas source isotope ratio measurement (IRMS) techniques (Brzezinski et al., 2006) and the advance of MC-ICP-MS now provide the required precision to constrain aquatic and biological systems. This has been confirmed recently by an inter-laboratory Si isotope comparison of three pure silica reference materials (Carignan et al., 2004; Reynolds et al., 2007) (Chapter 6): (1) IRMM-018 (a SiO_2 standard); (2) Big-Batch (an artificial SiO_2 material) and (3) a diatomite sample (natural opal sample). These comparisons demonstrated that published δ^{30}Si data can be reliably compared between laboratories within 0.2‰ precision for pure silicon materials.

Chemically more complex specimens like soils and rocks require appropriate analytical dissolution and elemental separation/purification procedures, which may differ between laboratories. As yet, there are no cross-calibration data available to assess the accuracy of the whole Si isotopic analytical procedure on these matrices. So far only two U.S. Geological Survey (USGS) reference materials AGV-2 (andesite, Oregon) and BHVO-2 (Hawaiian basalts) have been analysed for Si isotopes (van den Boorn et al., 2006). Their δ^{30}Si measurements (at -0.01 ± 0.24‰ and -0.09 ± 0.31‰, $2\sigma_{SD}$, respectively) fall outside the 95% confidence intervals of representative rocks from the basaltic rock range of upper mantle lherzolites (δ^{30}Si = -0.37 ± 0.05‰, n=4, $2\sigma_{SD}$,

Georg et al. (2007b)), terrestrial mafic and ultramafic igneous rocks (δ^{30}Si = −0.4‰, Douthitt (1982)), ocean island basalts (OIB) (δ^{30}Si = −0.37±0.06‰, n=5, $2\sigma_{SD}$, Georg et al. (2007b)) and bulk Iceland basalt value (δ^{30}Si = −0.35±0.10‰, n=2, $2\sigma_{SD}$, Georg et al. (2007c)). The compilation with Douthitt Si rock data needs no correction, since the Caltech Rose Quartz reference material is shown to be similar to NBS28 (Georg et al., 2007b). These differences may reflect either analytical artefacts or natural variations that are known to affect other trace or isotopic ratios in andesitic or basaltic rocks. The first aim of this contribution is to answer this question by providing additional measurements on both BHVO-1 and BHVO-2 OIB standards using a different sample preparation and analytical methodology.

One of the largest drawbacks in MC-ICP-MS analysis is the occurrence of interferences of isobaric polyatomic ions, inhibiting correct analysis of various elements with m/z<100, notably Fe and Si. The interferences are mostly molecular species derived from reactions in the plasma and cannot be avoided by chemical purifications. In particular, the analysis of δ^{30}Si on a conventional Nu Plasma instrument was so far impossible because of the insufficient resolution of the $^{14}N^{16}O$ interference overlying the ^{30}Si peak. δ^{30}Si was calculated from δ^{29}Si using theoretical multiplying factors based either on kinetic (δ^{30}Si = 1.96*δ^{29}Si) or equilibrium (δ^{30}Si = 1.93*δ^{29}Si) simplified mass-dependent fractionation law, based on an approximation valid for small ranges of isotopic fractionations (Johnson et al., 2004). In order to eliminate these interferences and to obtain high precision measurements, the Nu Plasma MC-ICP-MS was upgraded with a new high quality adjustable entrance slit, newly designed B-type cones (as opposed to the regular A-type cones) and a more powerful primary pump. The second objective of this paper is to demonstrate precise and accurate δ^{30}Si analyses on a conventional Nu Plasma in high resolution mode.

5.2 Instrumental

5.2.1 New configuration of the Nu Plasma mass spectrometer

The measurements were performed on a Nu Plasma MC-ICP-MS (Nu Instruments, Wrexham UK, described in detail by Belshaw et al. (1998)) at the Université Libre de Bruxelles (Belgium). For δ^{30}Si analyses our Nu Plasma instrument has been upgraded with the combination of two sets of adjustable slits (entrance and collector slits), high transmission B cones and a new vacuum rotary pump (BOC Edwards E2M80), in order

to accomplish a compromise between complete interference separation, flat-topped peak shape and sufficient signal intensity on all Si stable isotopes: ^{28}Si, ^{29}Si and ^{30}Si.

A newly designed **entrance slit** was installed in 2006 with three selectable slit narrower width settings: 0.3mm, 0.05mm and 0.03mm, corresponding to true low (∼400m/Δm), medium (∼1500m/Δm) and high resolution (∼3000m/Δm). For Si isotope measurements, this slit was set at medium resolution. A higher resolution mode reduces the transmission and overall sensitivity. Contrary to the Nu Plasma HR, our Nu Plasma is not equipped with so-called "Alpha" slits, used to reduce beam aberrations, which could cause a blurred peak image at the detector. As an alternative to improve the peak shape, the edge-resolving power was improved by setting the High Voltage 5 lens at 0V. This led to steeper peak edges and improved peak top flatness. However, sensitivity is further reduced by a factor of approximately 2.

Two **collector slits** were installed in 2001 on the Nu Plasma instrument at ULB in Brussels in front of the L4 and H5 Faraday cups, where respectively ^{28}Si and ^{30}Si are measured. They were used to clip the interfering $^{14}N_2$ and $^{14}N^{16}O$ ion beams from the ^{28}Si and ^{30}Si beams to achieve full separation from the interference and to help peak-centering the instrument in dynamic mode (Figure 5.1).

The data acquisition was done in high resolution mode. The peak centering is performed according to the 10% valley rule on ^{28}Si or ^{30}Si. The source slit is set to give medium resolution, while the collector slit is optimized each session to give spatially resolved beams on the collector. The interfered parts of the beams are clipped by the collector slits on the high mass end of the peaks. Given that $^{14}N_2$ and $^{14}N^{16}O$ are slightly heavier than ^{28}Si and ^{30}Si and do not enter the detector, this allows only the analyte beam to enter the Faraday cup. In doing so the signal for each isotope is measured at the mid-point of the analyte peak. This configuration can be used when all interfering species are located at the high-mass side of the peak. As there is no collector slit on the axial Faraday cup where ^{29}Si is measured, this does not allow full separation of analyte and interference peaks (10% valley). This isotope is analysed in the so-called "pseudo-high resolution mode", i.e. ^{29}Si peak is wider than ^{28}Si and ^{30}Si but measurement is performed on the lower mass side of the peak where no interference is present (Figure 5.1).

The **"Big 80" (BOC Edwards E2M80 vacuum rotary pump)** with a capacity of $80 m^3 h^{-1}$ was installed for a better vacuum in the expansion chamber to improve the transmission and balance the loss of sensitivity related to the medium resolution mode. The Big 80 evacuates the interface region between the sampler and skimmer cones.

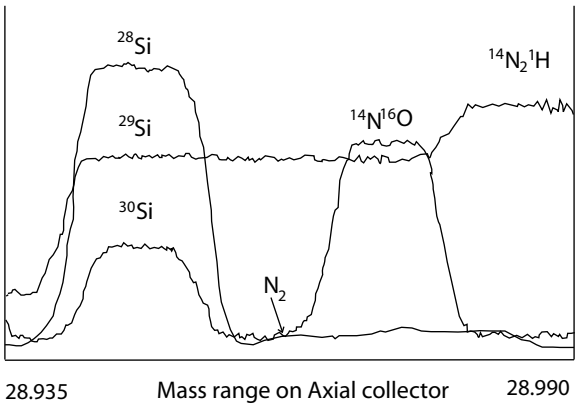

Figure 5.1: Magnet scan of an acid blank solution (1.25ppm Si, 0.7ppm Mg). Abscissa characterises the magnet scan mass range on the Axial collector. Ordinate indicates signal intensity (different scales per curve, ^{28}Si-peak ∼17mV, ^{29}Si-peak ∼1.4mV and ^{30}Si-peak∼0.8mV). Interferences were identified by calculation of Δm (Reed et al., 1994). The ^{29}Si-peak is not separated from its $^{14}N_2{}^1H$ interference due to the absence of a collector slit in front of the Axial collector. Given that the analysis is centred on the ^{28}Si or ^{30}Si peak, the measurements of ^{29}Si take place on the interference-free left side of the ^{29}Si-peak. Note that the $^{14}N_2{}^1H$ interference is much higher, as in Cardinal et al. (2003), who reported insignificant levels (<0.1mV), probably related to the use of the Big80 pump in combination with B-cones, causing a higher transmission of plasma-entrained atmospheric nitrogen into the mass spectrometer.

It improves the vacuum to approximately 1mbar in comparison to the standard E2M28 rotary pump of 28m^{3}h^{-1} (2mbar). Furthermore, higher sensitivity is obtained by running in dry plasma conditions using a Cetac Aridus desolvating sample introduction system in combination with B-type cones with a slightly different geometry than regular A-type cones: B-type skimmer is characterised by a flatter tip and B-type sample cone by a smaller interior angle compared to former A-type design. Sample desolvation greatly reduces potential polyatomic isobaric interferences. The sensitivity on Si decreases with increasing resolution and decreasing entrance slit width.

5.2.2 Analytical conditions

The measurements were carried out using the standard sample bracketing technique in dry plasma mode. The isotopic variations were expressed as δ-values in per mil deviation from a reference material

(NBS28 or in house standard: $pSiO_2$ or Quartz Merck). We applied mass bias correction using external Mg doping and measured Si and Mg in dynamic mode. Typical operation conditions for Si isotope analysis on this instrument are reported in Cardinal et al. (2003) except that a single analysis is now split in 4 blocks of 15 runs instead of 3 blocks of 20 runs (5 second integration) (Table 5.1). Peak centering is now required before each block as the narrower plateau of ^{28}Si and ^{30}Si in high resolution results in an increased sensitivity to magnet drift during the measurement.

In contrast to the low resolution mode (Cardinal et al., 2003), the analyte concentrations were doubled (1.7-2.5ppm Si, 0.9-1.25ppm Mg, for an uptake rate of 100 μl.min^{-1}) to compensate for the loss of sensitivity at medium resolution mode. Conversely, in order to minimize the use of HF, which induces a loss of Si in the desolvator (Cardinal et al., 2003; Georg et al., 2006b), the HF/HCl content has been reduced by a factor of $\sim$2 compared to the procedure of Cardinal et al. (2003). Acid molarities of the running solutions were usually in the range of 0.7-1.2 mM for both HF and HCl. Si-rich sample solutions were diluted and spiked with Mg in order to reach approximately a 1:1 voltage intensity ratio (^{28}Si: ^{24}Mg) at the mass spectrometer (Cardinal et al., 2003). The Mg/Si intensity ratios range between 1.01 and 1.34 and was generally not varying from more than $\pm$ 3% between a sample and standard. Indeed HF, HCl, Mg and Si contents of the running solutions were adjusted daily and kept constant throughout each analytical session. The δ-values are expressed relative to NBS28 or with acid attack digested in-house standards Quartz Merck and $pSiO_2$. The average values of -0.03 ± 0.06‰ ($\delta^{29}Si$) and -0.04 ± 0.11‰ ($\delta^{30}Si$) for $pSiO_2$ (n=10, $1\sigma_{SD}$) and -0.01 ± 0.07‰ ($\delta^{29}Si$) and 0.00 ± 0.03‰ ($\delta^{30}Si$) for Quartz Merck (n=2, $1\sigma_{SD}$) confirm that the in-house standards measured versus NBS28 are not significantly different from zero. The $pSiO_2$ was already used and calibrated as an internal in-house standard by Cardinal et al. (2003).

5.3 Experimental

5.3.1 Standard preparation

Secondary Si isotope reference materials Diatomite and Big Batch were dissolved using single step HF-HCl dissolution at atmospheric pressure (Cardinal et al., 2003) in order to check the accuracy of the new MC-ICP-MS configuration on these previously inter-compared standards (Reynolds et al. (2007); Chapter 6). For each aliquot we dissolved about 800 μg silicate-powder with HCl ($\sim$1 M) - HF ($\sim$2.3 M). After dissolution

Table 5.1: Operation conditions for the used MC-ICPMS instrument Nu Plasma.

Parameter	Running conditions
RF power	1350 W
Acceleration voltage	4 kV
Plasma mode	Dry plasma
Introduction system	Cetac ARIDUS (I) desolvator
Coolant gas flow rate	13 l/min
Auxiliary gas flow rate	0.7 l/min
Nebulizer gas flow rate	0.9 l/min
Nebulizer type	100 μl/min PFA microconcentric nebulizer (ESI)
Aridus sweep gas flow rate	3.5 - 4.0 l/min
PFA Spray chamber temperature	105°C
Membrane temperature	160°C
Running concentrations	Si = 1.7-2.5 ppm, Mg = 0.9-1.25 ppm
Intensity yields	^{28}Si = 5-7 V
Backgrounds on HCl-HF (∼1mM) running solutions	^{28}Si ∼ 40 mV, ^{24}Mg ∼ 5 mV
Washout time	7 minutes
Stabilisation time before analyse	7 minutes
Cup configuration	L4(^{28}Si), Ax(^{29}Si), H5(^{30}Si); L5(^{24}Mg), Ax(^{25}Mg), H6(^{26}Mg)

the solution is diluted to reach a ∼100 ppm Si solution with acid content of ∼0.05 M and ∼0.04 M for HCl and HF respectively.

BHVO-1 and BHVO-2 USGS Hawaiian rock standards were taken from the same location from the surface layer of a pahoehoe lava that overflowed from the Halemaumau crater in late 1919 (cf. Flanagan et al. (1976)). They thus should be considered as two aliquots from the same lava flow. Because the low pressure HF/HCl acid attacks were inefficient in dissolving rock samples, aliquots of BHVO powders were digested using an alkaline flux attack procedure adapted from the techniques proposed by Georg et al. (2006b). The generated glass is easily dissolvable in low concentration acids (Georg et al., 2006b). A series of tests were performed to determine the appropriate flux for the alkaline fusion method. In addition to $LiBO_2$ we tested alternative fluxes like Cs_2CO_3 and Na_2CO_3 for the fusion step, but they resulted in poor yields of recovery of about 60 to 90% and were therefore thought to potentially fractionate the Si isotopes. Therefore the fusion step was

carried out with $LiBO_2$ as the most appropriate flux due to providing the highest yield (>98%, see below). About 5 mg silicate powder was mixed with 30 mg of $LiBO_2$ flux in a platinum crucible. After one hour of melting at 1000°C, the fusion beads were quickly quenched in 50 ml double distilled 5% HNO_3 (0.8 M) to inhibit crystallization and avoid potential Si isotope fractionation that might result from such a process. Silicon was purified through its quantitative coprecipitation with triethylamine-molybdate (TEA) (De La Rocha et al., 1996). The pure cristobalite was dissolved with HCl (∼1 M) - HF (∼2.3 M) solution. The same alkaline procedure was also applied to the diatomite standard and four quartz Merck aliquots (Table 5.2) in order to compare results from acid and alkaline attacks.

All sample preparation steps were carried out in a clean environment. Procedural blanks were prepared for all samples and found to contain non-measurable quantities of Si (with a sample: blank ratio >350). Concentrations were measured by ICP-AES after fusion to calculate Si recovery (Table 5.3) and before Si-purification in order to check the absence of major elements and Mo contaminants. Our average calculated yield was 100.9 ± 2.9% ($1\sigma_{SD}$).

5.4 Results

Results for Diatomite and Big Batch secondary reference material are reported in Table 5.2 and Figure 5.2. For the silica standard Diatomite the average delta value of +0.64 ± 0.05‰ and +1.25 ± 0.07‰ ($1\sigma_{SD}$) for δ^{29}Si and δ^{30}Si, respectively with a δ^{30}Si/δ^{29}Si of 1.95 are in good agreement with the recommended values from the recent inter-laboratory comparison (+0.64 ± 0.07‰ and +1.26 ± 0.10‰, $1\sigma_{SD}$; Reynolds et al. (2007); Chapter 6)). No significant difference was observed between samples prepared by acid and alkaline attack, including for Quartz Merck showing that the alkaline flux procedure does not introduce any analytical bias relative to those obtained with our previous acid procedure (Cardinal et al., 2003). For the Big Batch standard, we obtained values of −5.38 ± 0.05‰ (δ^{29}Si, $1\sigma_{SD}$) and −10.53 ± 0.07‰ (δ^{30}Si, $1\sigma_{SD}$) with a δ^{30}Si/δ^{29}Si of 1.96, which also fits closely to the recommended values (−5.35 ± 0.15‰ and −10.48 ± 0.27‰, $1\sigma_{SD}$, Reynolds et al. (2007); Chapter 6). These accurate results demonstrate clearly the high data quality of the δ^{30}Si measurements with our new alkaline fusion procedure and the upgraded configuration of the Nu Plasma MC-ICP-MS.

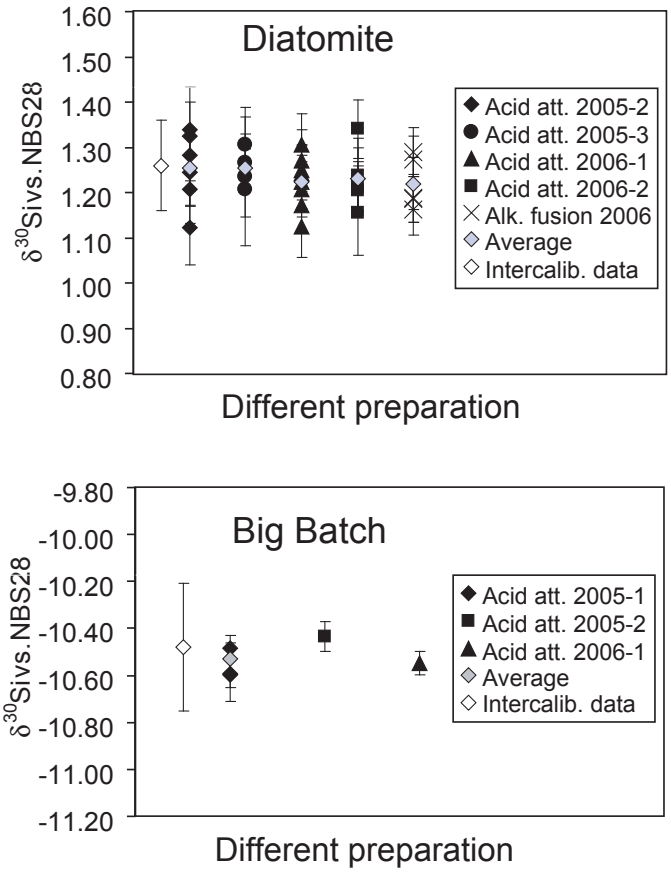

Figure 5.2: Individual analyses of Diatomite and Big Batch prepared in different years and by different methods (alkaline fusion and acid attack) are indicated by black symbols, with error bars showing the 1σ std. error. Open diamonds on the left side of each figure represent the mean of inter-calibrated standard (Reynolds et al. (2007); Chapter 6); their error bars stand for $1\sigma_{SD}$. Grey coloured points indicate the average values of accordant values, with error bars characterising $1\sigma_{SD}$. Alkaline attack analysis corresponds to different chemical preparations.

The BHVO-1 and BHVO-2 dataset is given in Table 5.3. The average values of BHVO-1 and BHVO-2 are identical at -0.17 ± 0.03‰ for δ^{29}Si and -0.33 ± 0.05‰ and -0.29 ± 0.11‰ ($2\sigma_{SEM}$) for δ^{30}Si, respectively. The reproducibility of BHVO measurements is slightly inferior to that obtained for the mono-elemental materials (Diatomite and Big Batch), probably due to the alkaline fusion step, to the purification procedure or to a combination of both, which induces additional variability for

Table 5.2: Bulk average isotopic compositions for Diatomite and Big Batch: (1) prepared by acid attack and alkaline fusion (this study) and (2) from the inter-laboratory comparison (Reynolds et al. (2007); Chapter 6) and average isotopic composition of Quartz Merck digested by alkaline attack (Quartz Merck is not a inter-compared standard in Reynolds et al. (2007) (Chapter 6)). Standard deviation is expressed in $1\sigma_{SD}$ as for respective literature value. Attention should be paid to the standard deviation of inter-laboratory comparison where variability is also resulting from different laboratories using different methodologies and instrumentations.

Isotope standard	δ^{29}Si (‰)	**st.dev** ($1\sigma_{SD}$)	**n**	δ^{30}Si (‰)	**st.dev** ($1\sigma_{SD}$)	**n**	**ratio** δ^{30}/δ^{29}
Diatomite							
This study	+0.64	0.05	24	+1.25	0.07	24	1.95
Reynolds et al. (2007)	+0.64	0.07	100	+1.26	0.10	82	1.97
Big Batch							
This study	-5.38	0.05	5	-10.53	0.07	5	1.96
Reynolds et al. (2007)	-5.35	0.15	198	-10.48	0.27	159	1.96
Quartz Merck							
This study	+0.00	0.07	2	-0.01	0.12	2	-

samples with more complex matrix. Considering that BHVO-1 and BHVO-2 are derived from the same rock sampled at the same location, we use their grand mean as the representative isotopic composition of the BHVO lava flow (see Table 5.3). These grand mean values (δ^{29}Si = -0.17 ± 0.10‰ and δ^{30}Si = -0.31 ± 0.20‰, $2\sigma_{SD}$) fall within the error brackets of the previous data on BHVO-2 (δ^{29}Si = -0.03 ± 0.17‰ (n=14, $2\sigma_{SD}$) and δ^{30}Si = -0.09 ± 0.31‰ (n=14, 2σ)) by van den Boorn et al. (2006). Besides, our δ^{30}Si BHVO estimate is fully consistent with the average value of 4 Ocean Island Basalt (OIB) samples by Georg et al. (2007b) (δ^{30}Si = -0.37 ± 0.06‰, $2\sigma_{SEM}$). In contrast, it slightly differs from Ziegler et al. (2005b) evaluation of a Hawaiian basalt (δ^{30}Si = -0.5‰), that relies on a single measurement and cannot thus be used as an actual reference value.

The 3-isotope plot shown in Figure 5.3 on all standards Diatomite, BHVO-1, BHVO-2 and Big Batch is an additional way to demonstrate high data quality and the interference-free determination of δ^{30}Si and δ^{29}Si. The slope of 0.510, mostly driven by the Big Batch set of data, is not significantly different from the one in Reynolds et al. (2007) (Chapter 6) observed on Big Batch, Diatomite and IRMM018 (0.511). This slope is again in close agreement with kinetic fractionation law (0.509), as expected for large isotopic fractionation process such as the one likely

Table 5.3: Delta values, precision and recovery of individual BHVO-1 and BHVO-2 analysis. The recovery noted here was achieved by concentration measurements after the fusion. N.a. stands for not analysed. 1 σ error stands for the single delta values of the data. Standard deviation of average values is expressed in $2\sigma_{SEM}$. All data biasing more than $2\sigma_{SEM}$ away from their mean of δ^{29}Si were rejected and are not shown in this table (n=3 for BHVO-1 and n=4 for BHVO-2).

BHVO-1	**Date of analysis**	δ^{29}Si (‰)	**st. error** (1σ)	δ^{30}Si (‰)	**st. error** (1σ)	**Recovery (%)**
BHVO-1 1	6/07/2006	-0.18	0.03	n.a.	n.a.	102.4%
BHVO-1 3	7/07/2006	-0.25	0.03	n.a.	n.a.	99.3%
BHVO-1 1	23/10/2006	-0.10	0.04	n.a.	n.a.	103.1%
BHVO-1 2	23/10/2006	-0.16	0.04	n.a.	n.a.	98.8%
BHVO-1 b-I	15/01/2007	-0.12	0.04	-0.28	0.06	101.0%
BHVO-1 2	24/02/2007	-0.26	0.03	-0.41	0.05	106.2%
BHVO-1 3	24/02/2007	-0.18	0.03	-0.29	0.06	99.9%
BHVO-1 1	24/02/2007	-0.17	0.04	-0.22	0.05	102.8%
BHVO-1b-II	7/03/2007	-0.20	0.05	-0.37	0.08	103.0%
BHVO-1a-I	9/03/2007	-0.12	0.05	-0.31	0.09	98.0%
BHVO-1a-Li	10/03/2007	-0.17	0.04	-0.41	0.06	105.0%
		δ^{29}Si (‰)	**2σSEM**	δ^{30}Si (‰)	**2σSEM**	**Recovery (%)**
average	**BHVO-1**	**-0.17**	**0.03**	**-0.33**	**0.05**	**101.7 ± 2.6 (1σ)**

BHVO-2	**Date of analysis**	δ^{29}Si (‰)	**st. error** (1σ)	δ^{30}Si (‰)	**st. error** (1σ)	**Recovery (%)**
BHVO-2 1	24/10/2006	-0.24	0.03	n.a.	n.a.	99.0%
BHVO-2 3	24/10/2006	-0.16	0.04	n.a.	n.a.	102.5%
BHVO-2 2	16/01/2007	-0.11	0.03	-0.17	0.05	99.5%
BHVO-2 3	23/02/2007	-0.10	0.04	-0.22	0.08	95.4%
BHVO-2 1	23/02/2007	-0.15	0.04	-0.19	0.06	102.5%
BHVO-2 1	24/02/2007	-0.23	0.04	-0.44	0.06	102.1%
BHVO-2 2	24/02/2007	-0.26	0.03	-0.47	0.05	95.2%
BHVO-2b-II	9/03/2007	-0.12	0.03	-0.22	0.07	101.0%
		δ^{29}Si (‰)	**2σSEM**	δ^{30}Si (‰)	**2σSEM**	**Recovery (%)**
average	**BHVO-2**	**-0.17**	**0.04**	**-0.29**	**0.11**	**99.7 ± 2.9 (1σ)**

		δ^{29}Si (‰)	**2σSEM**	δ^{30}Si (‰)	**2σSEM**	**Recovery (%)**
average	**BHVO-total**	**-0.17**	**0.03**	**-0.31**	**0.06**	**100.9 ± 2.9 (1σ)**

to have led to the Big Batch isotopic signature.

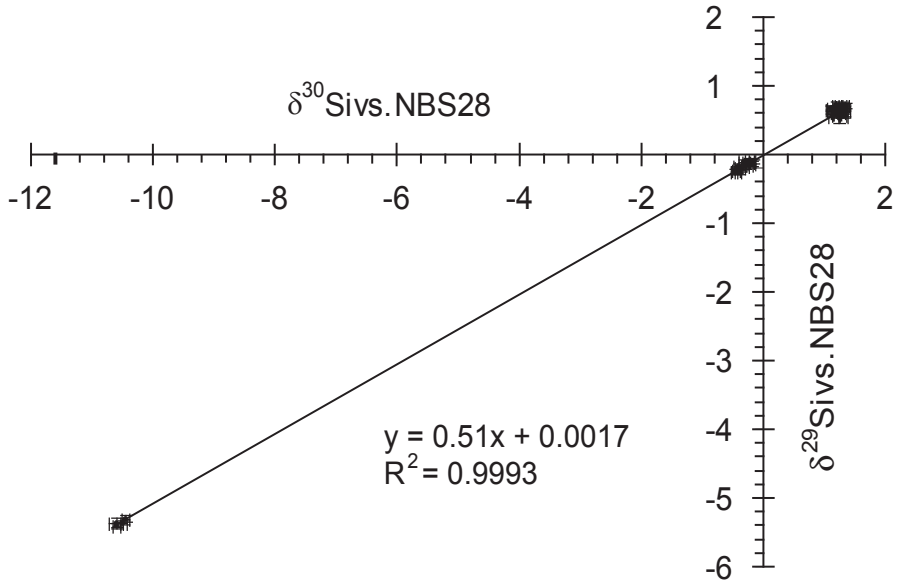

Figure 5.3: Three isotope plot of δ^{29}Si versus δ^{30}Si for all standards Diatomite, BHVO-1, BHVO-2 and Big Batch with linear regression line (error bars indicate $1\sigma_{SD}$). All groups of standards fall along a mass dependent line. The best fit line with an intercept of zero has an gradient of 0.510 which is principally controlled by the kinetic fractionation of Big Batch (Reynolds et al. (2007); Chapter 6).

5.5 Discussion

Our BHVO grand mean (δ^{30}Si = -0.31 ± 0.06‰, $2\sigma_{SEM}$) is significantly heavier than the chondritic reservoir (δ^{30}Si = -0.55 ± 0.08‰, Molini-Velsko et al. (1986); δ^{30}Si = -0.58 ± 0.06‰, ($1\sigma_{SD}$), Georg et al. (2007b)), but is consistent with the average compositions of upper mantle spinel lherzolites, recent OIB basalts (both at -0.37 ± 0.06‰, Georg et al. (2007b)) and bulk Iceland basalts (δ^{30}Si = -0.35 ± 0.10‰, $2\sigma_{SD}$, Georg et al. (2007c)). Four processes may be invoked to account for the non-chondritic δ^{30}Si signature within OIBs. First, water-rock interactions may have modified Si isotopic compositions of altered rocks (e.g., Ziegler et al. (2005ab)), which can be discounted considering the lack of any surface weathering on BHVO standards

(Flanagan et al., 1976). Second, Si-rich rocks from the continental crust and sedimentary components derived from them bear heavier signatures (δ^{30}Si = -0.07 ± 0.05‰) (André et al., 2006; Ding et al., 1996; Douthitt, 1982), indicating that crustal contamination may shift the Si isotopic compositions of basaltic melts towards more positive δ^{30}Si values. This hypothesis can obviously be disregarded for Hawaii, which lies within an oceanic plate. Third, the BHVO δ^{30}Si signature might mirror a widespread mantle-derived geochemical feature related to the incorporation of Si as a light element in the core during the early history of the Earth as proposed by Georg et al. (2007b). Finally, the BHVO δ^{30}Si signature might reflect recycling of old oceanic crust through the mantle. Indeed, much of the trace element and isotopic variability observed in Hawaiian basalts has been attributed to mantle sources that contain various proportions of old (∼3 Ga) recycled oceanic basaltic crust with or without sediments (e.g. Hofmann (1986)). Because highly silicified early Archaean metabasalts bear heavy Si isotopic compositions (δ^{30}Si $>$ 0 ‰, André et al. (2006); Abraham et al. (2007)), their recycling through the mantle is a process by which mantle sources with superchondritic signatures (δ^{30}Si $>$ -0.55‰) might be generated. The feasibility of such a scenario may be evaluated through a simple (SiO_2-δ^{30}Si) mass balance using a lherzolitic chondritic mantle with a silica content circa 45 wt% and the 3.47Ga "Barberton Silicified Basalts" (BSB: 70$<$ SiO_2 $<$75wt%, +0.4‰$<$ δ^{30}Si $<$+0.6‰) as the recycled component. With those end-members, the offset of +0.24‰ between the Hawaiian basalts and the chondritic reservoir requires between 13% (for SiO_2=75wt%, δ^{30}Si = +0.6‰ in BSB) and 28% (for SiO_2=70wt%, δ^{30}Si = +0.4‰ in BSB). These percentages match well the recent estimates of recycled inputs in the source of Hawaian basalts (∼16wt%, Sobolev et al. (2007)). Therefore, Si isotopes might have some potential in tracing early oceanic crust recycling in the source of OIBs. To decipher whether crustal recycling or core formation (or both) is the ultimate cause of the non-chondritic OIB composition will need further detailed examination based on larger Si-isotopic datasets on various basaltic rock populations with improving accuracy and reproducibility. After accurate inter-laboratory calibration, BHVO-1 and BHVO-2 rock standards may serve as ideal reference materials to test new appropriate sample preparation procedures and provide insights to answer this question.

5.6 Conclusions

We have demonstrated that accurate and precise δ^{30}Si data can be acquired on a Nu Plasma MC-ICP-MS. A new simple alkaline flux digestion method followed by purification by TEA coprecipitation has been tested successfully on secondary reference materials (Big Batch and Diatomite). This $LiBO_2$ alkaline fusion method seems to be suitable also for chemically more complex samples like soils and rocks, since it produces consistent and reproducible silicon isotopic signatures. We provide the second silicon isotope characterization of international basaltic rock standards, BHVO-1 and BHVO-2. Our δ^{30}Si values agree with isotope signatures of average Ocean Island Basalts, (Georg et al., 2007b) and are just inserted in the middle of previous Hawaiian basalt estimates by Ziegler et al. (2005a) and van den Boorn et al. (2006). As no certified rock standard exist so far for silicon isotopic composition, our study is a first step to fill this gap. Further isotopic determinations of the BHVO standard through inter-calibration should now be carried out.