

## GEOTRACES inter-calibration of the stable silicon isotope composition of dissolved silicic acid in seawater

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### Abstract :

The first inter-calibration study of the stable silicon isotope composition of dissolved silicic acid in seawater,  $\delta\text{Si-30(OH)}(4)$ , is presented as a contribution to the international GEOTRACES program. Eleven laboratories from seven countries analyzed two seawater samples from the North Pacific subtropical gyre (Station ALOHA) collected at 300 m and at 1000 m water depth. Sampling depths were

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chosen to obtain samples with a relatively low (9 mmol L<sup>-1</sup>, 300 m) and a relatively high (113 mmol L<sup>-1</sup>, 1000 m) silicic acid concentration as sample preparation differs for low- and high-concentration samples. Data for the 1000 m water sample were not normally distributed so the median is used to represent the central tendency for the two samples. Median  $\delta$  Si-30(OH)<sub>4</sub> values of +1.66‰ for the low-concentration sample and +1.25‰ for the high-concentration sample were obtained. Agreement among laboratories is overall considered very good; however, small but statistically significant differences among the mean isotope values obtained by different laboratories were detected, likely reflecting inter-laboratory differences in chemical preparation including pre-concentration and purification methods together with different volumes of seawater analyzed, and the use of different mass spectrometers including the Neptune MC-ICP-MS (Thermo Fisher (TM), Germany), the Nu Plasma MC-ICP-MS (Nu Instruments (TM), Wrexham, UK), and the Finnigan (TM) (now Thermo Fisher (TM), Germany) MAT 252 IRMS. Future studies analyzing  $\delta$  Si-30(OH)<sub>4</sub> in seawater should also analyze and report values for these same two reference waters in order to facilitate comparison of data generated among and within laboratories over time.

## Introduction

The stable isotope composition of silicon in dissolved silicic acid in seawater,  $\delta^{30}\text{Si}(\text{OH})_4$ , is a powerful tool for understanding the silicon cycle in the ocean as it reflects changes in the biological utilization of silicic acid,  $\text{Si}(\text{OH})_4$ , by diatoms in surface water as well as water mass mixing.  $\delta^{30}\text{Si}$  measurements in both  $\text{Si}(\text{OH})_4$  and in biogenic silica are essential to fully understand the marine Si cycle, in particular to characterize Si sources and sinks in order to better constrain the Si budget in the ocean (Tréguer and De La Rocha, 2013). Besides their importance in understanding the present day Si cycle,  $\delta^{30}\text{Si}$  measurements are increasingly being used to assess past changes through the isotopic analysis of Si in biogenic silica within diatom frustules and within sponge spicules from marine sediments (e.g. Reynolds et al., 2008; Maier et al., 2013; Ehlert et al., 2015).

Beginning with the first report of  $\delta^{30}\text{Si}$  measurements in natural waters by De La Rocha et al. (2000), there has been a growing number of publications, especially in the past five years, reporting  $\delta^{30}\text{Si}(\text{OH})_4$  values from marine systems, covering locations in the Southern, Atlantic, Pacific, and Indian Oceans as well as large estuaries (e.g. Cardinal et al., 2005; Reynolds et al., 2006; Cao et al., 2012; de Souza et al., 2012a; Brzezinski & Jones, 2015; Singh et al., 2015; Zhang et al., 2015a). This data set is anticipated to grow as part of the international GEOTRACES program that seeks to understand the global-scale distributions of trace elements and their isotopes in the marine environment (<http://www.geotraces.org>). All Si isotope data obtained by the GEOTRACES and other programs need to be fully comparable in order to better understand Si isotope systematics across the global ocean, and to validate models of the global marine  $\delta^{30}\text{Si}(\text{OH})_4$  distribution (de Souza et al., 2014, 2015; Holzer and Brzezinski, 2015; Gao et al., 2016). However, such efforts are challenged by the lack of seawater reference material of known  $\delta^{30}\text{Si}(\text{OH})_4$  to intercalibrate data generated by different laboratories or within a laboratory through time, as is currently only possible for solid siliceous materials (Reynolds et al., 2007).

The procedures and instrumentation used in stable Si isotope analysis have evolved substantially over the last two decades. The first precise  $\delta^{30}\text{Si}$  measurements of marine dissolved and particulate Si were conducted using a VG Prism gas source isotope ratio mass spectrometer (IRMS) with samples prepared using a manual fluorination line that employed  $\text{F}_2$  gas to convert Si recovered from either seawater or from biogenic silica as solid  $\text{SiO}_2$  to  $\text{SiF}_4$  gas (De La Rocha et al., 1996, 1997). IRMS methods have since been improved with  $\text{SiF}_4$  now produced from acid

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3 decomposition of  $\text{Cs}_2\text{SiF}_6$  in an automated process employing a modified Kiel III carbonate  
4 device and a MAT 252 IRMS (Brzezinski et al., 2006). The first multi-collector inductively  
5 coupled plasma mass spectrometer MC-ICP-MS (Nu Plasma™, Nu Instruments, Wrexham, UK)  
6 measurements were performed by De La Rocha (2002). This method was improved by Cardinal  
7 et al. (2003), who used a dry-plasma mode and Mg doping to correct for mass bias. These early  
8 MC-ICP-MS studies measured  $\delta^{29}\text{Si}$  (calculated from  $^{29}\text{Si}/^{28}\text{Si}$ ; c.f. Eqn. 1) to avoid the  
9 polyatomic interference of  $^{14}\text{N}^{16}\text{O}^+$  on  $m/z$   $^{30}\text{Si}$ , but this interference has since been overcome  
10 by the higher resolving power of new instruments, with all current studies reporting  $\delta^{30}\text{Si}$  values.  
11 However, it is possible to convert between the two values using the relationship  $\delta^{29}\text{Si} = 0.51 \times$   
12  $\delta^{30}\text{Si}$ , assuming pure kinetic isotope fractionation of Si (cf. Reynolds et al., 2007).  $\delta^{30}\text{Si}$  isotope  
13 measurements have now been successfully performed on a Neptune and Neptune *Plus* MC-ICP-  
14 MS (Thermo Fisher™, Germany, e.g. De La Rocha et al., 2011; Zhang et al., 2015b), various  
15 types of MC-ICP-MS produced by Nu Instruments™ (Wrexham, UK), including a Nu Plasma  
16 (e.g. Cardinal et al., 2005), Nu Plasma HR (e.g. Grasse et al., 2013), and the Nu Plasma 1700  
17 high-resolution MC-ICP-MS (e.g. Reynolds et al., 2006), as well as on a Finnigan™ MAT 252  
18 IRMS (e.g. Beucher et al., 2008).

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20 Both mass spectrometry types (MC-ICP-MS and IRMS) produce reliable  $\delta^{30}\text{Si}(\text{OH})_4$  data  
21 with a long-term reproducibility of 0.1 - 0.2 ‰ (2 s. d., e.g. Cardinal et al., 2003; Brzezinski and  
22 Jones, 2015). A major advantage of MC-ICP-MS over current IRMS methods is the  
23 significantly lower sample mass ( $\sim 0.2 \mu\text{mol Si}$ ) required for analysis compared to current  
24 methods using IRMS that require approximately 10 times higher mass, necessitating a much  
25 larger sampling volume which may become prohibitively large for Si-depleted near-surface  
26 waters. On the other hand, IRMS measurements have fewer problems with molecular mass  
27 interferences, given that Si is measured in the form of  $\text{SiF}_3^+$  at  $m/z$  85, 86, 87. Interference from  
28  $\text{SiOF}_2$  with  $^{29}\text{Si}^{18}\text{OF}_2^+$ ,  $^{30}\text{Si}^{17}\text{OF}_2^+$  at  $m/z$  85 and  $^{30}\text{Si}^{18}\text{OF}_2^+$  at  $m/z$  86 is possible and can be  
29 detected by the presence of the same oxyfluorides containing the far more abundant  $^{16}\text{O}$  and  $^{28}\text{Si}$   
30 atoms at  $m/z$  82, 83 and 84. Such interferences are rare with current sample preparation  
31 methods. With MC-ICP-MS, Si is measured as elemental Si with potential polyatomic  
32 interferences from C, H, O and N (e.g.  $^{14}\text{N}_2$ ,  $^{14}\text{N}_2^1\text{H}$ ,  $^{12}\text{C}^{16}\text{O}$ ,  $^{12}\text{C}^1\text{H}^{16}\text{O}$ ,  $^{14}\text{N}^{16}\text{O}$ ) that can bias  
33 beam intensities for  $m/z$   $^{28}\text{Si}$ ,  $^{29}\text{Si}$  and  $^{30}\text{Si}$ . Care must also be taken to eliminate matrix effects  
34 that may be caused by remnants of dissolved organic matter and anions such as sulfate (van den  
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3 Boorn et al., 2009; Hughes et al., 2011). For a detailed comparison between IRMS and MC-ICP-  
4 MS measurements see Reynolds et al. (2007).  
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7 Recent studies of  $\delta^{30}\text{Si}(\text{OH})_4$  distribution in deep waters (>1000 m) in the Atlantic Ocean  
8 by de Souza et al. (2012b) and by Brzezinski and Jones (2015) highlight the need for improved  
9 intercalibration among laboratories measuring  $\delta^{30}\text{Si}(\text{OH})_4$ .  $\delta^{30}\text{Si}(\text{OH})_4$  values at these depths are  
10 expected to be invariant over the relatively short period of time separating these studies, yet  
11 comparison of  $\delta^{30}\text{Si}(\text{OH})_4$  data between these two studies showed a near constant offset of  
12 approximately 0.22 ‰ between samples of comparable silicic acid concentration (see Figure 2 in  
13 Brzezinski and Jones, 2015). Brzezinski and Jones (2015) could not explain the offset, as  $\delta^{30}\text{Si}$   
14 values for solid Si standards reported by both laboratories were in good agreement. Given that  
15 sample preparation methods for samples of solid and dissolved Si differ considerably (Georg et  
16 al., 2006, Reynolds et al. 2006) and in view of the fact that seawater represents a complex matrix  
17 of anions and cations, the use of solid standards, and especially of relatively pure siliceous  
18 materials, cannot account for sample preparation biases arising during the preparation of  
19 seawater samples, motivating the establishment of reference seawaters for this purpose.  
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22 The only inter-laboratory calibration of Si isotope standards to date was conducted with  
23 solid Si material (Reynolds et al. 2007). In that study, 8 groups participated and obtained  
24 consensus mean  $\delta^{30}\text{Si}$  values for high-purity Si solids ( $\delta^{30}\text{Si}_{\text{Diatomite}}$ :  $+1.26 \pm 0.20$  ‰,  $\delta^{30}\text{Si}_{\text{IRMM-018}}$ :  
25  $-1.65 \pm 0.22$  ‰,  $\delta^{30}\text{Si}_{\text{Big Batch}}$ :  $-10.48 \pm 0.54$  ‰, uncertainties are 2 s. d.). Those materials are  
26 now routinely analyzed and reported when presenting Si isotope data from natural waters, diatom  
27 frustules, sponge spicules and minerals. A few rock reference materials are also commonly used  
28 as  $\delta^{30}\text{Si}$  isotopic standards to determine accuracy and reproducibility of solid samples with a  
29 complex matrix, especially BHVO-1 and BHVO-2 (e.g. Abraham et al., 2008; Armytage et al.,  
30 2012). As exemplified by the offsets between studies measuring  $\delta^{30}\text{Si}(\text{OH})_4$  in seawater  
31 discussed above, these standards are of limited use for identifying sample preparation biases  
32 among laboratories analyzing seawater Si isotopes.  
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35 In the following we present the first inter-laboratory calibration study for  $\delta^{30}\text{Si}(\text{OH})_4$   
36 using seawater samples with low ( $\sim 9 \mu\text{mol L}^{-1}$ ) and high ( $\sim 113 \mu\text{mol L}^{-1}$ )  $\text{Si}(\text{OH})_4$  concentration.  
37 The two main goals are to evaluate current reproducibility among laboratories and to establish  
38  $\delta^{30}\text{Si}(\text{OH})_4$  values for the samples so that they can be analyzed and reported as part of future  
39 studies to aid in comparing data generated among and within laboratories over time.  
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## 2 METHODS

### 2.1 Seawater Sampling

The seawater for the intercalibration study was collected at Station ALOHA (22°45'N latitude, 158°00'W longitude) in the North Pacific subtropical gyre. Two large volume seawater samples (60 L each) were collected during the Hawaii Ocean Time series (HOT) cruise 256 (October/November 2013) courtesy of the HOT program using the CTD/rosette sampler aboard the *R/V Kilo Moana* that was equipped with Niskin bottles and a Sea-Bird SBE-9/11 Plus CTD. Samples were collected from 300 m (ALOHA<sub>300</sub>) and 1000 m (ALOHA<sub>1000</sub>) water depth in order to obtain samples with a low and with a high Si(OH)<sub>4</sub> concentration based on the known increase in [Si(OH)<sub>4</sub>] with depth at this location. For each sample seawater from replicate Niskin bottles was pooled in an acid-washed (10% HCl) polyethylene carboy and gravity-filtered into a second acid-washed carboy using AcroPak® filter capsules containing sequential 0.8/0.45µm Supor® membrane filters that had been washed with trace-metal-grade HCl prior to use. Samples were not acidified or preserved as repeated measures of unpreserved samples show no change in either silicic acid concentration or silicon isotopic composition over a period of ten years when kept in the dark (Brzezinski, unpublished).

### 2.2 Sample Preparation and Silicon Isotope Measurements

At the University of California Santa Barbara (UCSB), the Si(OH)<sub>4</sub> concentration of each sample was measured as described by Brzezinski and Nelson (1995). Both ALOHA<sub>300</sub> and ALOHA<sub>1000</sub> samples were then aliquoted into 50 mL acid-cleaned polypropylene screw cap tubes, and shipped in groups of 25 tubes each to participating laboratories.

In total, 11 laboratories from 7 countries participated in the study (Table 1). Each group used its own techniques and protocols for sample preparation and Si isotope measurements, as detailed in Table A1. In addition to analyzing the seawater samples, many groups also measured the solid secondary standards Big Batch and Diatomite used in the previous intercalibration of siliceous solids by Reynolds et al. (2007).

All groups used some form of scavenging or precipitation to concentrate Si from the ALOHA<sub>300</sub> sample and to remove major seawater ions (e.g. Na<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>). All groups

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3 followed similar procedures for ALOHA<sub>1000</sub> except for group 10 which did not pre-concentrate  
4 ALOHA<sub>1000</sub>. Several pre-concentration methods were used: i) a MAGnesium Induced Co-  
5 precipitation (MAGIC) method with sodium hydroxide (Karl and Tien, 1992; Georg et al., 2006,  
6 de Souza et al., 2012b); ii) a Mg-induced co-precipitation with purified ammonia (NH<sub>3</sub>·H<sub>2</sub>O,  
7 Zhang et al., 2014) and iii) a TEA-Moly precipitation (De La Rocha et al., 1996) during which Si  
8 is precipitated as a triethylamine silico-molybdate complex. In the following we will refer to the  
9 chemical (NaOH, Ammonia, TEA-Moly) to describe the precipitation method. The most  
10 common precipitation method was NaOH, followed by Ammonia and TEA-Moly precipitation.  
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17 In order to further purify the samples, most groups using magnesium co-precipitation  
18 dissolved the magnesium hydroxide precipitate in a strong acid and then applied column  
19 chromatography, using either a cation exchange resin (AG50W-X8; Dowex 50W-X8, AG50W-  
20 X12, 200 to 400 mesh) or an anion exchange resin (AG1-X8). Samples precipitated as TEA-  
21 Moly were purified by high-temperature combustion to solid SiO<sub>2</sub> in a platinum crucible,  
22 followed by the dissolution of the SiO<sub>2</sub> in HF and the precipitation of the dissolved Si as Cs<sub>2</sub>SiF<sub>6</sub>  
23 (Brzezinski et al., 2006). Depending on the chemical preparation and the mass spectrometer  
24 type, the sample volume needed for Si isotope measurements ranged from 8 mL to 2000 mL for  
25 ALOHA<sub>300</sub> and from 1 mL to 200 mL for ALOHA<sub>1000</sub> with the largest seawater volume being  
26 required for measurements by IRMS. For an overview of the different chemical preparation  
27 methods, see Table 1. More details about chemical preparation and mass spectrometry methods  
28 are given in the appendix (Table A1).  
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39 Si isotope measurements were performed on three different mass spectrometer types  
40 (Table 1). Four groups used a Neptune or Neptune *Plus* MC-ICP-MS (Thermo Fisher™,  
41 Germany), six groups a Nu Plasma MC-ICP-MS (Nu Instruments™, Wrexham, UK; including a  
42 Nu Plasma II MC-ICP-MS and a Nu Plasma 1700 HR-MC-ICP-MS) and one group employed a  
43 MAT 252 IRMS (Finnigan™, now Thermo Fisher™, Germany). The MC-ICP-MS  
44 measurements were performed on solutions containing 10 - 90 μmol L<sup>-1</sup> Si (0.35–2.5 ppm Si),  
45 which resulted in a 2 - 9 V ion beam (on a Faraday cup equipped with a 10<sup>11</sup> Ω resistor) for  
46 elemental Si with *m/z* of 28, the most abundant stable isotope of Si (atom % <sup>28</sup>Si = 92.229 %;  
47 Rosman and Taylor, 1998). Most MC-ICP-MS analyses were carried out in ‘dry plasma mode’  
48 using one of three different desolvating nebulizer systems (CETAC Aridus II™, Nu Instruments  
49 DSN-100™, ESI Apex™) to remove the sample solvent before introduction into the plasma.  
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Only 2 groups employed ‘wet plasma mode’ (Table A1), which avoids possible blank problems with the desolvating nebulizer system, but is less sensitive (De La Rocha, 2002). On the IRMS, samples are loaded into a modified Kiel III carbonate device as solid  $\text{Cs}_2\text{SiF}_6$  (6  $\mu\text{mol}$  Si) and decomposed to  $\text{SiF}_4$  gas with 98 % sulfuric acid. Electron ionization of  $\text{SiF}_4$  in the instrument source creates  $\text{SiF}_3^+$  ions measured at 85, 86 and 87  $m/z$  (De La Rocha et al. 1996, Brzezinski et al. 2006) with a typical voltage of 4 – 8 V (on a Faraday cup with a  $3 \times 10^8 \Omega$  resistor) at 85  $m/z$  corresponding to  $^{28}\text{Si}^{19}\text{F}_3^+$ .

The intensity of the blank was generally below 1% of the sample signal across laboratories (Table A1). All measurements were performed using a standard-sample-bracketing method. For MC-ICP-MS measurements the standard employed was the reference standard NBS28 or an in-house standard that had been calibrated against NBS28. For IRMS measurements samples were run against cryogenically purified commercial  $\text{SiF}_4$  gas which had been calibrated against NBS28. NBS28 (NIST Reference Material 8546) is a silica sand that was obtained by the United States Geological Survey from the Corning Glass Company.

Si isotope compositions are reported in the  $\delta$ -notation using the reference standard NBS28 in parts per thousand,

$$\delta^{30}\text{Si} = \left( \frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right) * 1000 \quad (1)$$

where  $R_{\text{sample}}$  is the measured  $^{30}\text{Si}/^{28}\text{Si}$  ratio of the sample and  $R_{\text{std}}$  is the measured  $^{30}\text{Si}/^{28}\text{Si}$  ratio of the NBS28 standard.

Laboratories pre-concentrated each seawater sample 3 to 10 times. Each pre-concentration was considered to be a replicate when performing statistical tests and when evaluating the external reproducibility for each group (2 s. d., Table 2, A2). The analytical scheme applied to each pre-concentration was as follows: Subsamples of each concentrate were analyzed between 1 and 12 times with the actual number of analyses performed listed as analytical replicates for each pre-concentration in Table A2. Analysis of the subsamples by both IRMS and MC-ICP-MS utilized a standard-sample-bracketing approach, which depending on the laboratory involved 15 to 60 measurements of the subsample bracketed by analyses of the standard. Each set of analytical replicates was averaged providing a mean value for each separate pre-concentration of ALOHA<sub>300</sub> and of ALOHA<sub>1000</sub> performed by each laboratory (Table A2).



Analysis of variance (ANOVA) was used to test for difference among means with post hoc tests performed using Tukey's HSD (honest significant difference) method to control type I error rate across multiple comparisons. For each ANOVA Levene's method was used to test for the equality of variance among factors and the Shapiro-Wilk method was used to test that the residuals from each ANOVA model were normally distributed. A significance level of  $p = 0.05$  was used throughout. Residuals were normally distributed across all tests and will not be discussed further. However, in some cases the variance across factors was found not to be constant. In those cases, differences among means were re-evaluated using Welch's ANOVA that is not reliant on an assumption of homogenous variances among factors with post hoc testing performed using False Discovery Rate procedures (q-FDR, e.g. Benjamini and Hochberg, 1995; Verhoeven et al., 2005). q-FDR controls the expected proportion of type I errors rather than the probability that such errors will occur which can increase statistical power compared to family-wise error rate techniques for handling multiple comparisons (Benjamini and Hochberg, 1995). Statistical analyses were performed using JMP 12 statistical software.

### 2.3 Mg Doping and Sulfate Addition

Except for one laboratory, all measurements on Neptune mass spectrometers were performed with Mg doping of the sample, whereas only group 10 applied Mg doping to samples measured on a Nu Plasma instrument. Cardinal et al. (2003) showed that Mg isotope mass bias is constant relative to Si isotopes during a MC-ICP-MS analytical session and follows an exponential mass fractionation law. Si isotope ratios ( $^{30}\text{Si}/^{28}\text{Si}$  and  $^{29}\text{Si}/^{28}\text{Si}$ ) were corrected for mass bias by adding  $\text{Mg}(\text{NO}_3)_2$  to samples and to standards just prior to measurement (Cardinal et al., 2003; Abraham et al., 2008). Mg is added at a concentration that matches the Si content of standards and samples. Between each measurement of Si isotopes  $^{24}\text{Mg}$  and  $^{25}\text{Mg}$  and/or  $^{26}\text{Mg}$  isotopes are measured in dynamic mode with the same integration time as for Si isotopes. The correction to the  $^{30}\text{Si}/^{28}\text{Si}$  ratio ( $^{30}\text{Si}/^{28}\text{Si}$ )<sub>corr</sub> is calculated as follows:

$$(^{30}\text{Si}/^{28}\text{Si})_{\text{corr}} = (^{30}\text{Si}/^{28}\text{Si})_{\text{meas}} \times (^{30}\text{Si}_{\text{AM}}/^{28}\text{Si}_{\text{AM}})^{\epsilon_{\text{Mg}}} \quad (2)$$

where  $(^{30}\text{Si}/^{28}\text{Si})_{\text{meas}}$  is the measured ratio,  $^{30}\text{Si}_{\text{AM}}$  and  $^{28}\text{Si}_{\text{AM}}$  are the atomic masses of  $^{30}\text{Si}$  and  $^{28}\text{Si}$ .  $\epsilon_{\text{Mg}}$  is then calculated from the beam intensities on masses 26 and 24 as:

$$\varepsilon_{\text{Mg}} = \ln [(^{26}\text{Mg}_{\text{A}}/^{24}\text{Mg}_{\text{A}})/(^{26}\text{Mg}/^{24}\text{Mg})_{\text{meas}}]/[^{26}\text{Mg}_{\text{AM}}/^{24}\text{Mg}_{\text{AM}}] \quad (3)$$

where  $^{26}\text{Mg}_{\text{A}}/^{24}\text{Mg}_{\text{A}}$  is the expected ratio of the natural abundances of the isotopes,  $(^{26}\text{Mg}/^{24}\text{Mg})_{\text{meas}}$  is the measured ratio, and  $^{26}\text{Mg}_{\text{AM}}$  and  $^{24}\text{Mg}_{\text{AM}}$  are the atomic masses of  $^{26}\text{Mg}$  and  $^{24}\text{Mg}$ .

One laboratory (group 2) implemented sulfate doping to overcome the effects of the presence of seawater sulfate ions (Table 1). Van den Boorn et al. (2009) first reported a significant isotopic bias due to the presence of  $\text{SO}_4^{2-}$  in rock samples after a cation chromatographic purification step. Such a bias was also observed by Hughes et al. (2011) on freshwater samples of dissolved Si, although Georg et al. (2006) and de Souza et al. (2012b) observed no significant matrix effect of  $\text{SO}_4^{2-}$  on their MC-ICP-MS analyses of Si isotopes from freshwater and seawater samples. In the present study several tests were made to optimize sulfate doping. For group 2, systematic and constant  $\text{H}_2\text{SO}_4$  additions were performed as for Mg prior to the measurements on the ALOHA<sub>1000</sub> sample and the NBS28 standard at  $1 \text{ mmol L}^{-1}$ , which should largely overcome the amount of seawater  $\text{SO}_4^{2-}$  remaining in the solutions. For the ALOHA<sub>300</sub> sample where group 2 processed 50 mL of seawater, systematic measurements of  $\text{SO}_4^{2-}$  were made via ad-hoc doping to reach  $1 \text{ mmol L}^{-1}$   $\text{H}_2\text{SO}_4$ . Nitric acid and HCl were also added by group 2 to all samples and standards to reach final concentrations of  $0.5 \text{ mol L}^{-1}$  each in order to overcome the influence of residual seawater nitrate and chloride ions.

One laboratory (group 1) treated samples with ultraviolet light/ozone to remove dissolved organic carbon (DOC; Table 1) as Hughes et al. (2011) revealed significant biases in  $\delta^{30}\text{Si}$  data when DOC concentrations significantly exceeded those of dissolved Si.

### 3 Results

The seawater samples collected from 300 m (300.21 decibar pressure,  $13.37^\circ\text{C}$ , salinity 34.311) and 1000 m (1021.65 decibar pressure,  $3.88^\circ\text{C}$ , salinity 34.467) at Station ALOHA resulted in the desired range of  $\text{Si}(\text{OH})_4$  concentrations with measured concentrations of  $9.18 \pm 0.05 \mu\text{mol L}^{-1}$  and  $112.8 \pm 0.5 \mu\text{mol L}^{-1}$  for ALOHA<sub>300</sub> and ALOHA<sub>1000</sub>, respectively.

In total, 11 laboratory groups participated in the seawater intercalibration study. The  $\delta^{30}\text{Si}(\text{OH})_4$  values for ALOHA<sub>300</sub> and ALOHA<sub>1000</sub> from each laboratory were in good overall agreement. Average values from individual laboratories for ALOHA<sub>300</sub> ranged from  $+1.46 \text{ ‰}$  to

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3 +1.94 ‰, with a mean value of  $+1.68 \pm 0.35$  ‰ (2 s. d., results from 9 groups).  $\delta^{30}\text{Si}(\text{OH})_4$   
4 values for ALOHA<sub>1000</sub> ranged between +1.10 ‰ and +1.45 ‰ with a mean of  $+1.24 \pm 0.20$  ‰ (2  
5 s. d., results from 11 groups; Fig. 1, Table 2). Normal probability plots of the laboratory group  
6 means for each sample were highly linear with  $R^2 \geq 0.95$  (Fig. 2). Shapiro's tests confirmed that  
7 the group averages for ALOHA<sub>300</sub> were normally distributed ( $W = 0.966$ ,  $p = 0.21$ , where  $H_0$  is  
8 that the data are from a normal distribution); however, group means for ALOHA<sub>1000</sub> were not  
9 ( $W = 0.954$ ,  $p = 0.036$ ). In the latter case the median or modal value may be better measures of  
10 central tendency. Median values and interquartile deviations, i.e.  $0.5 \times$  (75% quartile – 25%  
11 quartile), for ALOHA<sub>300</sub> and ALOHA<sub>1000</sub>, are  $+1.66 \pm 0.13$  ‰ and  $+1.25 \pm 0.06$  ‰ respectively  
12 (Table 2) with corresponding modal values of 1.66 and 1.22. Values obtained for Big Batch and  
13 Diatomite by each group that measured these materials (Table A3) were within the uncertainty  
14 bounds of the values established by Reynolds et al. (2007).  
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24 The reproducibility of measurements for the seawater samples within individual groups  
25 ranged from 0.04 ‰ to 0.24 ‰ for the standard deviations and 0.06 ‰ to 0.13 ‰ for the  
26 interquartile deviations with the larger variation generally obtained for ALOHA<sub>300</sub> (Fig. 1, Table  
27 2). For each sample testing for statistically significant differences in the mean isotope values  
28 obtained by each group is confounded as all groups used a single mass spectrometer type  
29 negating the use of a two-way ANOVA to simultaneously test for differences among groups and  
30 among mass spectrometer types. Testing for differences in the mean isotope values across groups  
31 was thus restricted to tests among laboratories using the same mass spectrometer type. Tests for  
32 differences among sample preparations methods reveal no significant sample preparation effect  
33 (see below) so the effect of preparation was subsumed in the mean square error when examining  
34 differences among laboratory groups.  
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44 Considering groups that used a Neptune mass spectrometer the ANOVA revealed  
45 significant differences among mean values across groups for ALOHA<sub>1000</sub> ( $F = 27.2$ , d. f. = 3,  $p <$   
46  $0.001$ ), but not for ALOHA<sub>300</sub> ( $F = 0.30$ , d.f. = 1,  $p = 0.59$ , note only two groups measured  
47 ALOHA<sub>300</sub> using a Neptune) indicating the presence of small, but statistically significant, biases  
48 between laboratories for ALOHA<sub>1000</sub>. However, Levene's test showed unequal variances across  
49 groups for both ALOHA<sub>300</sub> ( $F = 8.85$ , d.f. = 1,  $p = 0.012$ ) and for ALOHA<sub>1000</sub> ( $F = 3.35$ , d.f. = 3,  
50  $p = 0.045$ ) so that the results of the ANOVA should be interpreted with caution. When these  
51 data were re-evaluated using Welch's ANOVA the presence of significant differences among  
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3 means for ALOHA<sub>1000</sub> (F= 38.2, d.f. = 3, p <0.0004) and the lack of any significant differences  
4 among groups for ALOHA<sub>300</sub> (F = 0.374, d.f. = 1, p = 0.55) were confirmed. Post hoc tests  
5 (Table A4) revealed that differences among laboratories were not consistent between the two  
6 seawater samples.  
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10 A similar analysis investigating differences among groups using Nu Plasma mass  
11 spectrometers showed significant differences among means for both ALOHA<sub>300</sub> (F = 34.5, d.f. =  
12 5, p < 0.001) and ALOHA<sub>1000</sub> (F = 6.90, d.f. = 5, p = 0.0004). In both cases the assumption of  
13 equality of variances was met (Levine: F= 0.765, d.f. = 5, p = 0.58 and F = 0.421, d.f. = 5, p =  
14 0.83 for ALOHA<sub>1000</sub> and ALOHA<sub>300</sub>, respectively). Similar to the case for the Neptune, post hoc  
15 tests (Table A5) showed that the pattern of significant differences among group means for the Nu  
16 Plasma shifted between ALOHA<sub>300</sub> and ALOHA<sub>1000</sub>. The shifting biases among groups seen for  
17 both instruments is also seen in the change in rank order of the mean isotope values obtained by  
18 each group between the ALOHA<sub>1000</sub> and ALOHA<sub>300</sub> samples (Fig. 1).  
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26 An indicator for the quality of  $\delta^{30}\text{Si}$  measurements is given by the slope of the  
27 relationship between  $\delta^{30}\text{Si}$  and  $\delta^{29}\text{Si}$  values, as any polyatomic interferences during MC-ICP-MS  
28 measurements would lead to an offset from predicted equilibrium or kinetic fractionation line.  
29 Least squares linear regression between  $\delta^{30}\text{Si}(\text{OH})_4$  and  $\delta^{29}\text{Si}(\text{OH})_4$  produces a slope of  $0.5188 \pm$   
30  $0.0184$  (s.e.,  $R^2 = 0.98$ ; Fig. 3). Repeating the analysis using reduced major axis model II  
31 regression that gives equal weight to errors in both  $\delta^{29}\text{Si}(\text{OH})_4$  and  $\delta^{30}\text{Si}(\text{OH})_4$  yields a slope of  
32  $0.5131 \pm 0.0040$  (s.e.,  $R^2 = 0.98$ ).  
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39 Figure 4 shows the  $\delta^{30}\text{Si}(\text{OH})_4$  data for all measurements grouped by mass spectrometer  
40 type (Fig. 4a, 4b) and by co-precipitation method (Fig. 4c, 4d). Considering mass spectrometer  
41 types the Neptune and Nu Plasma types are replicated across groups while the IRMS is not as  
42 IRMS was used by a single group. Thus statistical analysis of mass spectrometer type was only  
43 possible for Neptune and Nu Plasma types. Furthermore, as each laboratory used a single mass  
44 spectrometer the data from the same group are not independent. To account for this lack of  
45 independence an ANOVA with Neptune and Nu Plasma as main effects was performed on the  
46 average values obtained by each group weighted by the number of measurements contributing to  
47 each mean. Those results show no significant differences between the results obtained on the  
48 Neptune versus the Nu Plasma for ALOHA<sub>300</sub> (F = 0.687, d.f. = 1, p = 0.44) and likewise for  
49 ALOHA<sub>1000</sub> (F = 3.75, d.f. = 1, p = 0.089). In qualitative terms the values obtained by IRMS are  
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3 nearly identical to those obtained using the Nu Plasma for ALOHA<sub>1000</sub>, but they appear lower  
4 than the averages for either the Nu Plasma or Neptune for ALOHA<sub>300</sub>. That difference is driven  
5 by one low value of +1.36 ‰ measured by IRMS (Table A2). If that value is considered an  
6 outlier the resulting mean for IRMS becomes closer to that for the other two mass spectrometer  
7 types, +1.52 ‰ (Figure 4).  
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12 ANOVAs evaluating the effect of different precipitation methods showed no differences  
13 among NaOH, Ammonia or TEA-moly procedures for ALOHA<sub>1000</sub> ( $F = 0.27$ , d. f. = 2,  $p = 0.77$ ),  
14 but a significant difference for ALOHA<sub>300</sub> ( $F = 4.7$ , d. f. = 2,  $p = 0.014$ ) driven by a lower mean  
15 value for TEA-moly precipitation compared to the other two methods (Table 3, Figure 4). For  
16 ALOHA<sub>300</sub> the significant differences between precipitation methods are driven by one outlier  
17 value mentioned above (Table A2). When that value is removed from the analysis no significant  
18 differences among precipitation methods ( $F = 2.4$ , d. f. = 2,  $p = 0.10$ ) are found for ALOHA<sub>300</sub>.  
19 We are quick to point out that the ANOVA used to detect differences among precipitation  
20 methods necessarily incorporated the effects of groups and of mass spectrometer type into the  
21 mean square error as the experimental design is confounded so that these results should be  
22 viewed with caution. One group, Group 6, utilized both NaOH and Ammonia co-precipitation  
23 methods allowing a direct comparison of methods for this one group. Here too there was no  
24 significant difference between precipitation methods ( $F = 0.61$ , d.f. = 1,  $p = 0.49$ ).  
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## 37 **4 Discussion**

### 38 *4.1 General Results*

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40 We present the first inter-laboratory study comparing the stable silicon isotope  
41 composition of dissolved Si(OH)<sub>4</sub> in seawater. Samples with both a relatively low and a  
42 relatively high Si(OH)<sub>4</sub> concentration were used to evaluate the influence of varying degrees of  
43 Si pre-concentration and varying matrix to analyte ratios. The results from the 11 laboratories  
44 were in good agreement for both samples, despite the use of different sample preparation and  
45 purification methods and different mass spectrometer models (Nu Plasma versus Neptune) and  
46 types (MC-ICP-MS versus IRMS). The mean  $\delta^{30}\text{Si}(\text{OH})_4$  values for ALOHA<sub>300</sub> and ALOHA<sub>1000</sub>  
47 were  $+1.68 \pm 0.35$  ‰ and  $+1.24 \pm 0.20$  ‰ (2 s. d.), respectively (Fig. 1, Table 2). Given that the  
48 data for ALOHA<sub>1000</sub> are not normally distributed a better representation of the central tendency is  
49 the median. Median values and interquartile deviations for ALOHA<sub>300</sub> and ALOHA<sub>1000</sub>, are  
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3 +1.66 ± 0.13 ‰ and +1.25 ± 0.06 ‰ respectively (Table 2). Modal values are nearly identical  
4 (within 0.03 ‰) of corresponding median values (Table 2).  
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7 The slope of the least squares fit of  $\delta^{30}\text{Si}(\text{OH})_4$  versus  $\delta^{29}\text{Si}(\text{OH})_4$  relationship, 0.5188 is  
8 statistically indistinguishable from the theoretical value of 0.5178 for equilibrium control of  
9 fractionation ( $t = 0.302$ , d. f. = 19,  $p = 0.38$ ; Thiemens, 1999, Young et al. 2002) and significantly  
10 higher than those for kinetic fractionation, i.e. 0.5047 or 0.5092 depending on whether elemental  
11 Si or  $\text{SiO}_2$  is fractionating, respectively ( $t = 4.26$ , d. f. = 19,  $p = <0.0001$  for Si and  $t = 2.90$ , d. f.  
12 = 19,  $p < 0.0001$  for  $\text{SiO}_2$ , Young et al. 2002). The slope of the reduced major axis regression,  
13 0.5131, is statistically indistinguishable from both the theoretical value for equilibrium fraction ( $t$   
14 = 1.17, d. f. = 19,  $p = 0.13$ ) and the kinetic fractionation of  $\text{SiO}_2$  ( $t = 0.94$ , d. f. = 19,  $p = 0.97$ ),  
15 but it was statistically larger than the theoretical value for the kinetic fractionation of elemental  
16 Si ( $t = 2.10$ , d. f. = 19,  $p < 0.00001$ ). For reference the Bonferroni corrected  $p$  value for these six  
17 comparisons is 0.008. Thus, the data lack the precision necessary to discriminate between  
18 control by equilibrium or kinetic fractionation. Ultimately, the fractionation of  $\text{Si}(\text{OH})_4$  in the sea  
19 should be kinetically controlled given the strong role of biology in the process (Nelson et  
20 al.1995).  
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23 The tight relationship between  $\delta^{30}\text{Si}(\text{OH})_4$  and  $\delta^{29}\text{Si}(\text{OH})_4$  relationship does indicate  
24 insignificant isobaric interference problems during Si isotope analysis. External reproducibility  
25 (2 s. d.) during this study (0.20 ‰ and 0.35 ‰ for ALOHA<sub>1000</sub> and ALOHA<sub>300</sub>, respectively)  
26 were similar to those obtained during the inter-laboratory comparison of Si isotopes in pure  
27 siliceous solid materials by Reynolds et al. (2007), where 2 s. d. uncertainty values of 0.22 ‰,  
28 0.16 ‰ and 0.54 ‰ were obtained for the standards IRMM-018, Diatomite and Big Batch,  
29 respectively. Analyzing both ALOHA<sub>300</sub> and ALOHA<sub>1000</sub> as a routine part of future studies of  
30 seawater Si isotopes will allow potential biases to be quantified, facilitating comparisons among  
31 data sets.  
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33 The suite of methodologies used to analyze the isotopic composition of Si in the  
34 seawater samples all yielded robust results. Comparison of the data obtained from the low and  
35 high concentration samples suggests that further improvement may be possible. Overall  
36 ALOHA<sub>1000</sub> shows a better reproducibility ( $\pm 0.20$  ‰ s.d., 0.05 ‰ i.q.d) than ALOHA<sub>300</sub> ( $\pm 0.35$   
37 ‰ s.d., 0.13 ‰ i.q.d.) among laboratories and within each laboratory (Fig. 1, Table 2). Small,  
38 but statistically significant, differences in the mean isotope values among laboratories were  
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3 detected for both samples (Table A4). Moreover, the number and magnitude of significant  
4 differences changed between the low and high concentration samples (Table A4). Together  
5 these results imply that differences in how the two samples were processed marginally  
6 influenced the results.  
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10 The main difference in sample preparation between ALOHA<sub>300</sub> and ALOHA<sub>1000</sub> was the  
11 larger sample volume processed for ALOHA<sub>300</sub> (Table A1). The volume of seawater used for  
12 pre-concentration scales inversely with the Si(OH)<sub>4</sub> concentration in the sample such that larger  
13 volumes are processed for samples with low Si concentration. To the extent that they are not  
14 removed during the chromatographic purification of Si, the carryover of seawater ions (e.g.  
15 Mg<sup>2+</sup>, Na<sup>+</sup>, Ba<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) will be a function of the sample volume processed, altering the ratio  
16 of these ions to the analyte Si in the final sample which may produce matrix effects during  
17 measurements (see Methods). As most groups use a cation exchange resin as the final  
18 purification step (Table 1), residual anions are likely present.  
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26 Another possible cause of the larger variance of the measurements of ALOHA<sub>300</sub> could  
27 be the higher DOC to Si ratio in the shallow sample. Any element remaining in the solution  
28 analyzed can compete with analyte for ionization within the plasma and thus can potentially  
29 induce a matrix effect on isotopic mass bias. Hughes et al. (2011) showed that a DOC:Si mass  
30 ratio (as C:Si) above 0.6 can interfere with  $\delta^{30}\text{Si}$  measurements. DOC concentrations measured  
31 on the same cruise and at the same depths as sampled for Si isotopes were 48 and 37  $\mu\text{mol C L}^{-1}$   
32 for ALOHA<sub>300</sub> and ALOHA<sub>1000</sub>, respectively (C. A. Carlson, pers. com.), which are three orders  
33 of magnitude lower than in the samples analyzed by Hughes et al. (2011). However, DOC/Si  
34 mass ratios (C/Si) were 2.2 and 0.1 for ALOHA<sub>300</sub> and ALOHA<sub>1000</sub>, respectively. Those ratios  
35 imply a potential for interference from DOC in ALOHA<sub>300</sub> if DOC is concentrated at the same  
36 efficiency as Si during the sample pre-concentration procedure. Detailed investigations into  
37 these and other possible interferences may improve the analytical precision obtained for low  
38 concentration samples.  
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#### 50 51 *4.2 Potential Instrument Biases*

52 Measurements on the Neptune (mean = +1.18 ± 0.18 ‰) and the Nu Plasma (mean = +1.28 ±  
53 0.18 ‰) show a slight and only marginally significant (p = 0.089) offset for ALOHA<sub>1000</sub> with the  
54 values from the Neptune being lower by 0.1 ‰. For ALOHA<sub>300</sub> the mean value on the Neptune  
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3 is also lower than on the Nu Plasma by 0.1‰ (Table 3), but in this case the difference is far from  
4 statistically significant given the larger variance of the measurements for the shallow sample.  
5 One possible explanation for this offset could be the applied Mg doping of the sample, which is  
6 mainly conducted for measurements on the Neptune (except for group 11), to correct for the  
7 instrumental mass bias (Cardinal et al. 2003). This possibility was investigated by examining the  
8 results for Group 11, which performed Si isotope analysis on a Neptune without Mg doping. The  
9 mean value for this group was slightly higher  $+1.27 \pm 0.05$  ‰ (2s.d.), than the Neptune mean.  
10 Only one group (Group 10) applied Mg doping using a Nu Plasma, which resulted in a mean  
11 value of  $+1.45 \pm 0.17$  ‰, higher than the average  $\delta^{30}\text{Si}$  value of  $+1.28 \pm 0.18$  ‰ obtained by  
12 groups using the Nu Plasma without Mg doping. The results are thus inconclusive, and it is not  
13 clear whether Mg doping or an instrument bias caused the small offset between the results from  
14 the Neptune and Nu Plasma instruments.  
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24 The average  $\delta^{30}\text{Si}(\text{OH})_4$  value from IRMS match the average from the Nu Plasma for  
25 ALOHA<sub>1000</sub>, but they are lower than both the Nu Plasma or Neptune data for ALOHA<sub>300</sub>. It is  
26 difficult to draw firm conclusions from these similarities and differences given the very large  
27 difference in the volume of seawater processed for measurement by IRMS compared to the other  
28 instrument types (Table 3).  
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#### 35 *4.3 Possible Improvement of Chemical Preparation and $\delta^{30}\text{Si}$ Measurements*

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37 There are several approaches to reduce “matrix effects” in MC-ICP-MS measurements  
38 caused by remnants of DOC and seawater ions in samples (Cardinal et al., 2007, Hughes et al.,  
39 2011). Methods that further reduce the ion concentrations (cations and anions) may thus be  
40 beneficial or ion concentrations in the sample solution could be measured and the samples doped  
41 prior to measurement, though the latter may be cumbersome for studies with large numbers of  
42 samples. Alternatively, a sequential cation-anion-exchange chromatography purification  
43 procedure, such as has been tested by some groups for  $\delta^{30}\text{Si}(\text{OH})_4$  (N. Estrade, pers. comm.),  
44 may be a promising approach. Closset (2015) showed that the contribution of  $\text{Cl}^-$  originating  
45 from seawater can be neglected when HCl is used to dissolve the brucite produced during Mg co-  
46 precipitation as the  $\text{Cl}^-$  from the acid is present in large excess (up to  $0.5 \text{ mol L}^{-1}$ ) compared to  
47 remaining  $\text{Cl}^-$  from seawater. Similarly, the occurrence of  $\text{NO}_3^-$  in seawater is negligible when  
48  $\text{HNO}_3$  ( $0.5 \text{ mol L}^{-1}$ ) is used as a solvent in both the samples and standards. In the present study  
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3 group 2 employed a mixture that was 0.5 mol L<sup>-1</sup> HCl, 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> and 1 mmol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>  
4 to simultaneously compensate for the presence of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>.  
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7 The concentration of SO<sub>4</sub><sup>2-</sup> ions remaining after chemical purification of the Si (i.e. not  
8 collected by cation exchange resin) depends on the volume of seawater used for the NaOH and  
9 Ammonia methods. There is, however, no simple relationship between total sample volume  
10 processed and final SO<sub>4</sub><sup>2-</sup> concentration, since most seawater is discarded during the pre-  
11 concentration procedure. Some laboratories also observed that the presence of high SO<sub>4</sub><sup>2-</sup>  
12 (higher than 0.5 mmol L<sup>-1</sup>) may cause a negative shift in the baseline of <sup>29</sup>Si and <sup>30</sup>Si due to the  
13 high <sup>32</sup>S signal. More importantly, this impact will directly alter the Si<sup>+</sup> signal intensity and is  
14 different from the matrix effect, and cannot be corrected using the matrix-match approach  
15 (Zhang A., data unpublished). The influence of residual ions also varies with the number of co-  
16 precipitations employed as the two-step NaOH process developed by Reynolds et al. (2006)  
17 significantly reduces the final seawater volume from which Si is stripped compared to a one step  
18 co-precipitation. Furthermore, a general treatment of seawater sample with ultra violet light,  
19 ozone or peroxide to reduce the influence of dissolved organic matter, as already suggested by  
20 Hughes et al. (2011) may be beneficial.  
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23 The IRMS method is largely free of “matrix effects”. Interference from SiOF<sub>2</sub> is rare as a  
24 significant signal at *m/z* 83 that would indicate the presences of the compound (see above) are  
25 rarely observed. The major challenge with the Cs<sub>2</sub>SiF<sub>6</sub> IRMS method is the large sample size  
26 required compared to MC-ICP-MS. When less than 5 μmoles of Cs<sub>2</sub>SiF<sub>6</sub> are analyzed the  
27 resulting δ<sup>30</sup>Si values are significantly biased to higher values (Brzezinski et al., 2006). This is  
28 not a limitation of the instrument, as the Kiel III/ MAT 252 combination is capable of analyzing  
29 at least an order of magnitude lower amount of Si. The reason for the apparent fractionation of  
30 small samples is unknown. Overcoming this limitation would allow seawater sample volumes  
31 similar to those currently employed for MC-ICP-MS analysis. The lower limit of sample size  
32 would then essentially only be determined by the mass of Si necessary to quantitatively  
33 precipitate Cs<sub>2</sub>SiF<sub>6</sub>.  
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#### 51 52 53 *4.4 Best Practices during MC-ICP-MS Measurements*

54 The major challenges during MC-ICP-MS measurements leading to lower accuracy and  
55 precision are i) molecular interference at *m/z* <sup>28</sup>Si (<sup>14</sup>N<sub>2</sub>, <sup>12</sup>C<sup>16</sup>O), <sup>29</sup>Si (<sup>14</sup>N<sub>2</sub><sup>1</sup>H, <sup>12</sup>C<sup>1</sup>H<sup>16</sup>O<sup>15</sup>N<sup>14</sup>N)  
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3 and  $^{30}\text{Si}$  ( $^{14}\text{N}^{16}\text{O}$ ) and ii) variable mass-dependent fractionation in the instrument (mass-bias, see  
4 also Cardinal et al. 2003). To handle possible problems with interfering compounds the matrix  
5 blank should not exceed 1% of the sample sensitivity and it should be routinely measured and  
6 subtracted from the measurement signal. Furthermore the achieved resolving power (10% peak  
7 valley definition) of the mass spectrometer should be above 3500 in order to clearly separate  
8 molecular interference masses. All of these issues are also influenced by operating condition  
9 (“plasma conditions”), non-analyte composition of the particular sample (“matrix effect”) and  
10 the amount of material that is introduced into the instrument (“mass-load effect”), which is  
11 determined by the Si concentration introduced into the instrument by the sample gas flow. A  
12 study by Zhang et al. (2015b) also demonstrated that the sample gas flow has an effect on the  
13 production of polyatomic ions besides its obvious effects on sensitivity and stability. The  
14 importance of the energetic/thermal “plasma conditions” during ICP-MS measurements for  
15 precise and accurate stable isotope measurements was recently shown by Fietzke et al. (2015).  
16 Therefore, in addition to the elemental purity of the sample and the Si concentration introduced  
17 into the instrument, plasma conditions should be monitored carefully in order to improve the  
18 accuracy and precision of  $\delta^{30}\text{Si}$  measurements. This may require allowing the instrument to  
19 stabilize for several hours before measurements.  
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#### 35 *4.5 Recommendations*

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37 The intercalibration results show a very good precision within all participating groups  
38 taking into account the external reproducibility of the individual measurements. However, small  
39 but statistically significant differences among mean values across groups were observed for both  
40 samples. Such differences can be rigorously quantified through routine analysis of these  
41 reference waters as part of future studies of  $\delta^{30}\text{Si}(\text{OH})_4$  distributions in the ocean. This is  
42 particularly important for international programs such as GEOTRACES for which global data  
43 from multiple laboratories are often combined for analysis. It is recommended that future studies  
44 analyzing  $\delta^{30}\text{Si}(\text{OH})_4$  in seawater also analyze ALOHA<sub>300</sub> and ALOHA<sub>1000</sub> and report these  
45 results to facilitate and evaluate comparability of data between laboratories. While the use of  
46 ALOHA samples is needed to validate the seawater processing procedures, analytical conditions  
47 and instrument stability should first be checked for each analytical session by measuring  
48 secondary reference materials such as Diatomite and Big Batch (Reynolds et al., 2007) which are  
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3 more readily available. ALOHA samples, Diatomite and Big Batch can be obtained from Mark  
4 Brzezinski at UCSB. Finally, a plan for reference water renewal must be developed to facilitate  
5 intercalibration efforts in the future.  
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Figure Captions:

Figure 1.  $\delta^{30}\text{Si}(\text{OH})_4$  results from all groups for ALOHA<sub>300</sub> (open circles) and ALOHA<sub>1000</sub> (filled circles). The long black vertical solid line indicates the mean value of all measurements for ALOHA<sub>1000</sub> and the long dashed line that for ALOHA<sub>300</sub>. The data points represent the individual  $\delta^{30}\text{Si}(\text{OH})_4$  values from Table A2. Short vertical solid lines are the means obtained by individual laboratories for the two samples. Uncertainty in the mean for all measurements for each sample (2 s. d.) is indicated by the horizontal bars at the top of the figure.

Figure 2. Z scores as a function of  $\delta^{30}\text{Si}(\text{OH})_4$  for ALOHA<sub>300</sub> (open circles) and ALOHA<sub>1000</sub> (filled circles).

Figure 3. Plot of  $\delta^{30}\text{Si}(\text{OH})_4$  versus  $\delta^{29}\text{Si}(\text{OH})_4$  for ALOHA<sub>300</sub> (open circle) and ALOHA<sub>1000</sub> (filled circle; error bars are 2 s. d.). Solid line is the result of least-squares linear regression with a slope of  $0.5188 \pm 0.0184$  (s.e.,  $R^2 = 0.98$ ). The lower and upper 95 % confidence intervals are given as dashed black lines. The kinetic fractionation line has a slope of 0.5092 (intercept of zero) for Si (dashed red line) and the equilibrium fractionation line has a slope of 0.5178 (intercept of zero) for Si (solid red line). Regression line obtained by analysis using reduced major axis model II regression yields a slope of  $0.5131 \pm 0.0040$  (s.e.,  $R^2 = 0.98$ ; not displayed in the figure).

Figure 4. Boxplots showing  $\delta^{30}\text{Si}(\text{OH})_4$  data sorted by different mass spectrometer types for a) ALOHA<sub>300</sub> and for b) ALOHA<sub>1000</sub>. Data sorted by different precipitation methods for c) ALOHA<sub>300</sub> and d) ALOHA<sub>1000</sub>. On the boxplots the median values (black) and the mean values (grey) are displayed. For ALOHA<sub>300</sub> a) and c) show data for IRMS and TEA-Moly with (grey boxplot) and without outlier (black boxplot). Here, the mean value (which equals the median) is indicated by a superscript star. The value next to each boxplot indicates the median (black) and the mean (grey), respectively. The number of included data points (n) is given below each boxplot. Raw data are presented in Table 3

Table 1: Summary of the different participating laboratory groups and methods for sample preparation and mass spectrometry.

No.	Lab	Country	Responsible person	Sample Introduction	Mass spectrometry	Precipitation Method	Further preparation	Extras	References
1	MPI Oldenburg	Germany	Claudia Ehlert, Katharina Pahnke	Wet-plasma	Neptune <i>Plus</i>	NaOH	Cation Exchange Resin (AG50W-X8)	H <sub>2</sub> O <sub>2</sub> /UV treatment/Mg doping	Georg et al. 2006; Hughes et al. 2011
2	LOCEAN/LSCE	France	Damien Cardinal, Ivia Closset, Jill Sutton	Apex, Dry-plasma	Neptune <i>Plus</i>	NaOH	Cation Exchange Resin (AG50W-X8)	Mg/SO <sub>4</sub> <sup>2-</sup> Doping	Karl and Tien 1992; Georg et al. 2006; Hughes et al. 2011
3	Unité de Recherche Géosciences Marines, IFREMER and Université de Brest	France	Jill Sutton	Apex, Dry-plasma	Neptune	TEA-Moly	Anion Exchange Resin (AG1-X8)	Mg doping	Cardinal et al. 2005; Engström et al. 2006; De La Rocha et al. 2006; De LaRocha et al. 2011
4	ETH Zürich	Switzerland	Florian Wetzel, Gregory de Souza	DSN-100, Dry-plasma	Nu Plasma 1700	NaOH	Cation Exchange Resin (AG50W-X8)		Georg et al. 2006; deSouza et al. 2012
5	Swedish Museum of Natural History	Sweden	Per Andersson, Xiaole Sun	Wet-plasma	Nu Plasma II	NaOH	Cation Exchange Resin (AG50W-X8)		Georg et al. 2006; Sun et al. 2014
6	GEOMAR Helmholtz Institute for Ocean Research	Germany	Patricia Grasse, Martin Frank	Aridus II, Dry-plasma	Nu Plasma II	NaOH/NH <sub>4</sub>	Cation Exchange Resin (AG50W-X8)		Karl and Tien 1992; Georg et al. 2006; Zhang et al. 2014
7	University of British Columbia	Canada	Nicolas Estrade	Aridus II, Dry-plasma	Nu Plasma 1700	NH <sub>4</sub>	Cation Exchange Resin (AG50W-X8)		Karl and Tien 1992; Zhang et al. 2014
8	University of California Santa Barbara	US	Janice Jones, Patricia Grasse, Mark Brzezinski	Dual-inlet gas-source	Kiel III MAT 252	TEA-Moly	HF dissolution, then CsSiF <sub>6</sub> precipitation		De LaRocha et al. 1996; Brzezinski et al. 2006
9	Xiamen University	China	Minhan Dai, Zhouling Zang	Dry-plasma	Nu Plasma II	NaOH	Cation Exchange Resin (AG50W-X8)		Karl and Tien 1992; Georg et al. 2006
10	Research Center for Eco-Environmental Sciences, CAS Beijing	China	Qian Liu	DSN-100, Dry-plasma	Nu Plasma II	NaOH	Cation Exchange Resin (Dowex50W-X8)		Karl and Tien 1992; Georg et al. 2006
11	State Key Laboratory of Estuarine and Coastal Research, Shanghai	China	Anyu Zhang	Dry-plasma	Neptune	NH <sub>4</sub>	Cation Exchange Resin (Dowex50W-X8)		Georg et al. 2006; Zhang et al. 2014; Zhang et al. 2015

Table 2: Summary of mean Si isotope values ( $\delta^{30}\text{Si}$ ,  $\delta^{29}\text{Si}$ ), the associated  $2\sigma$  analytical uncertainty (2 s.d.), number of chemical preparations (N) and the number of measurements (n) obtained by each laboratory group for ALOHA<sub>300</sub> and ALOHA<sub>1000</sub>. Overall mean, uncertainty about the mean (2 s.d.), median as well as the interquartile deviation (IQD) for all groups are given at the bottom of the table. NaN indicates data not available (for a compilation of all measurements see Table A2).

Group No.	Aloha <sub>300</sub>							Aloha <sub>1000</sub>						
	$\delta^{30}\text{Si}$	2 s.d.	$\delta^{29}\text{Si}$	2 s.d.	$\delta^{29}\text{Si}/\delta^{30}\text{Si}$	N	n	$\delta^{30}\text{Si}$	2 s.d.	$\delta^{29}\text{Si}$	2 s.d.	$\delta^{29}\text{Si}/\delta^{30}\text{Si}$	N	n
1	NaN	NaN	NaN	NaN	NaN	NaN	NaN	1.10	0.07	0.63	0.07	0.57	4	4
2	1.66	0.10	0.84	0.05	0.50	6	12	1.10	0.07	0.56	0.02	0.51	5	15
3	NaN	NaN	NaN	NaN	NaN	NaN	NaN	1.16	0.16	0.59	0.09	0.51	3	9
4	1.64	0.13	0.87	0.05	0.53	4	12	1.17	0.20	0.62	0.10	0.53	3	12
5	1.51	0.12	0.80	0.08	0.53	3	11	1.23	0.08	0.64	0.04	0.52	4	15
6	1.78	0.18	0.89	0.18	0.50	6	6	1.26	0.12	0.68	0.09	0.54	5	5
7	1.92	0.08	1.02	0.12	0.53	5	14	1.25	0.07	0.65	0.07	0.52	6	31
8	1.46	0.17	0.75	0.09	0.51	3	10	1.29	0.04	0.66	0.02	0.51	4	25
9	1.94	0.12	0.99	0.08	0.51	8	16	1.31	0.15	0.68	0.09	0.52	10	20
10	1.53	0.17	0.79	0.11	0.52	3	9	1.45	0.17	0.76	0.16	0.53	3	9
11	1.69	0.24	0.85	0.17	0.50	8	8	1.27	0.05	0.65	0.03	0.51	8	72
<b>Mean</b>	<b>1.68</b>		<b>0.87</b>		<b>0.52</b>			<b>1.24</b>		<b>0.65</b>		<b>0.52</b>		
<b>2 s.d.</b>	<b>0.35</b>		<b>0.10</b>					<b>0.20</b>		<b>0.10</b>				
<b>Median</b>	<b>1.66</b>		<b>0.85</b>					<b>1.25</b>		<b>0.65</b>				
<b>Modal Value</b>	<b>1.66</b>		<b>0.85</b>					<b>1.22</b>		<b>0.65</b>				
<b>IQD</b>	<b>0.13</b>		<b>0.05</b>					<b>0.05</b>		<b>0.02</b>				

Table 3: Statistics for  $\delta^{30}\text{Si}(\text{OH})_4$  values sorted by different instrument types and precipitation methods (for details see Appendix 2). NaN denotes sample not available.

<b>Grouped by Instrument</b>						
	<b>Aloha<sub>300</sub></b>			<b>Aloha<sub>1000</sub></b>		
	<b>Neptune</b>	<b>Nu</b>	<b>IRMS</b>	<b>Neptune</b>	<b>Nu</b>	<b>IRMS</b>
<b>Median</b>	1.64	1.81	1.51	1.15	1.28	1.28
<b>Mean</b>	1.68	1.78	1.46	1.18	1.28	1.29
<b>2 s.d.</b>	0.19	0.36	0.17	0.18	0.18	0.04
<b>Min</b>	1.52	1.45	1.36	1.07	1.08	1.27
<b>Max</b>	1.86	2.05	1.52	1.30	1.55	1.31
<b>N</b>	14	29	3	20	31	4

<b>Grouped by Precipitation</b>						
	<b>Aloha<sub>300</sub></b>			<b>Aloha<sub>1000</sub></b>		
	<b>MAGIC</b>	<b>Ammonia</b>	<b>TEA-Moly</b>	<b>MAGIC</b>	<b>Ammonia</b>	<b>TEA-Moly</b>
<b>Median</b>	1.69	1.82	1.51	1.25	1.27	1.27
<b>Mean</b>	1.73	1.78	1.46	1.24	1.26	1.23
<b>2 s.d.</b>	0.34	0.30	0.17	1.25	0.06	0.16
<b>Min</b>	1.45	1.52	1.36	1.07	1.20	1.10
<b>Max</b>	2.05	1.97	1.52	1.55	1.30	1.31
<b>N</b>	30	13	3	32	16	7

Table A1: Detailed Overview of chemical preparation and measurement methods (1/5; Nu Plasma)

Group	4	5	6	7	9	10
Sample Vol. (Aloha <sub>300</sub> )	50 ml	50ml	30ml	12ml	15ml	15ml
Sample Vol. (Aloha <sub>1000</sub> )	10 ml	10ml	10ml	12ml	10ml	10ml
Precipitation Method	MAGIC	MAGIC	MAGIC	MAGIC	MAGIC	MAGIC
	Sodium hydroxide	Ammonium Hydroxid	Ammonium & Sodium Hydroxid	Ammonium Hydroxid	Sodium Hydroxid	Ammonium Hydroxid
Column Chemistry	Cation Exchange Resin	Cation Exchange Resin	Cation Exchange Resin	Cation Exchange Resin	Cation Exchange Resin	Cation Exchange Resin
	AG50W-X8, 200-400 mesh	AG50W-X12	AG50W-X8, 200-400 mesh	AG50W-X8, 200-400 mesh	AG50W-X8, 200-400 mesh	Dowex50W-X8
Amount Si (µg) introduced into machine	2.5 µg	0.6 to 1.6 µg	2.5 µg	1.4 µg		1.8 µg
Mg Doping (yes/no)	no	no	no	no	no	yes
Extras		Aloha <sub>300</sub> evaporated after column to double concentration	Aloha <sub>300</sub> evaporated after column to double concentration			
Co-precipitation for Aloha <sub>1000</sub> and Aloha <sub>300</sub>	2.5 µg	0.6 to 1.6 µg	2.5 µg	1.4 µg		1.8 µg

Table A1: Detailed Overview of chemical preparation and measurement methods (2/5; Nu Plasma)

Group	4	5	6	7	9	10
<b>Mass spectrometer</b>	Nu plasma (1700) HR-MC-ICP-MS	Nu plasma (II) MC-ICP-MS	Nu plasma (II) MC- ICP-MS	Nu plasma (1700) HR-MC-ICP-MS	Nu plasma (II) MC-ICP-MS	Nu plasma (II) MC- ICP-MS
<b>Sample introduction</b>	Desolvator DSN- 100; PFA nebulizer; ~75µL/min uptake rate	wet plasma glass nebulizer ~100µL/min uptake rate	Desolvator Cetac Aridus II PFA nebulizer ~70µL/min uptake rate	Desolvator Cetac Aridus II PFA nebulizer, ~100µL/min uptake rate	Desolvation Nebulizer System PFA nebulizer ~80µL/min uptake rate	DeSolvation Nebulizer (DSN-100) PFA nebulizer ~70 µL/min uptake rate
<b>Cones</b>	common Ni cones	common Ni cones	common Ni cones	common Ni cones	common Ni cones	common Ni cones
<b>Torch</b>	semi-demountable quartz torch	glass	glass	glass	glass	glass
	alumina injector					
<b>Measurement mode</b>	high resolution	medium resolution; m/Δm 4000-7000	medium resolution	high resolution	medium resolution	medium resolution
<b>Standard-Sample- Bracketing</b>	yes	yes	yes	yes	yes	yes
	smp. repeated 5 times	smp. repeated 3 times	smp. repeated 4-5 times	smp. repeated 3 times	smp. repeated 4-5 times	smp. repeated 3 times
	1 block, 36 cycles of 5sec each	2 blocks, 20 cycles	1 block, 60 cycles	1 block, 25 cycles , 10 sec	1 block, 20 cycles	4 block, 15 cycles
<b>Measurement intensity (<sup>28</sup>Si)</b>	6-7 V	2-3.5 V/ppm	4 V	9 V for 0.35 ppm Si	6 V	5.5 V/ppm
<b>Blanks (<sup>28</sup>Si)</b>	10 to 30 mV	10-30 mV	10 to 30 mV	40-100 mV, measured by OPZ	50 to 80 mV	16 to 36 mV

Table A1: Detailed Overview of chemical preparation and measurement methods (3/5; Neptune)

Group	1	2	3	11
Sample Vol. (Aloha <sub>300</sub> )	-	50ml	-	8ml
Sample Vol. (Aloha <sub>1000</sub> )	10ml	10ml	100mL	1ml
Precipitation Method	MAGIC	MAGIC	Triethylamine silicomolybdate	MAGIC
	Sodium Hydroxide	Sodium Hydroxide	Sodium Hydroxide	Ammonium Hydroxid
Column Chemistry	Cation Exchange Resin	Cation Exchange Resin	Anion Exchange Resin	Cation Exchange Resin (Dowex 50W-X8)
	(AG50W-X12, 200-400 mesh)	(AG50W-X12, 200-400 mesh)	(AG1-X8)	
Amount Si (µg) introduced in the machine	0.6 ppm	7 µg	1.2 µg	2.5 µg
Mg Doping (yes/no)	yes	yes	Yes	no
Extras	treatment with H <sub>2</sub> O <sub>2</sub> /UV light	sulfate doping; anion concentration checked; Aloha <sub>300</sub> evaporated after column to double concentration	Combustion of precipitate in platinum crucibles Dissolution of purified SiO <sub>2</sub> in HF	no
Co-precipitation for Aloha <sub>1000</sub> and Aloha <sub>300</sub>	yes/yes	yes/yes	yes/yes	yes/yes

Table A1: Detailed Overview of chemical preparation and measurement methods (4/5; Neptune)

Group	1	2	3	11
Mass spec	Neptune Plus MC-ICP-MS (Thermo-Fisher, Germany)	Neptune Plus MC-ICP-MS (Thermo-Fisher, Germany)	Thermo Scientific Neptune MC-ICP-MS	Neptune MC-ICP-MS
Sample introduction	Wet Plasma; Quartz spray chamber; PFA nebulizer; ~70µL/min uptake rate	Desolvator APEX (ESI); PFA nebulizer; 100 µL/min uptake rate	Desolvator Apex (ESI); PFA nebulizer; 100µL/min uptake rate	Apex-IR; PFA nebulizer; ~100µL/min; uptake rate
Cones	H-skimmer, Jet-sampler (Ni cones)	Nickel X-Skimmer cone Standard Ni-Sample cone	common Ni cones	Standard sampling cone X skimmer cone
Torch	glass	Quartz + alumina injector	glass	glass
Measurement mode	medium resolution standard-sample bracketing smp repeated 3 times 1 block, 30 cycles	medium resolution standard-sample bracketing smp repeated 2-3 times 3 blocks, 20 cycles per block	medium resolution standard-sample bracketing >3 replicates 1 block, 25 cycles	medium resolution standard-sample bracketing smp repeated 3 times 1 block, 30 cycles, 8s integration time
Measurement intensity ( <sup>28</sup> Si)	8 V	6 V	12 V	2.5 to 3 V
Blanks ( <sup>28</sup> Si)	20 to 30 mV	10 to 50 mV	10 to 30 mV	10 to 20 mV



Table A1: Detailed Overview of chemical preparation and measurement methods (5/5; IRMS)

Group	8
Sample Vol. (Aloha <sub>300</sub> )	2000ml
Sample Vol. (Aloha <sub>1000</sub> )	200ml
Precipitation Method	TEA Moly
Column Chemistry	no column chemistry
Mg Doping (yes/no)	no
Extras	Combustion of precipitate in platinum crucibles Dissolution of purified SiO <sub>2</sub> in HF, precipitation as Cs <sub>2</sub> SiF <sub>6</sub>
Instrument Setting	
Mass spec	Finnigan Mat 252 IRMS
Introduction	modified Kiel III inlet system 98% Sulfuric Acid decomposition of Cs <sub>2</sub> SiF <sub>6</sub> to SiF <sub>4</sub>
Cones	
Torch	
Measurement mode	standard-sample bracketing >3 replicates 1 block, 20 cycles, 8s integration time
Amount Si introduced in the machine	6μmol
Measurement intensity ( <sup>28</sup> SiF <sub>3</sub> <sup>+</sup> )	2V to 8V
Blanks ( <sup>28</sup> SiF <sub>3</sub> <sup>+</sup> )	No blank

Table A2: Measurements of  $\delta^{30}\text{Si}(\text{OH})_4$  and  $^{29}\text{Si}(\text{OH})_4$  by each laboratory group for ALOHA<sub>1000</sub>. The means of analytical replicates,  $\delta^{30}\text{Si}$  and  $\delta^{29}\text{Si}$ , and associated 2 sigma standard deviations where analytical replicates are defined as replicate analyses from the same chemical preparation. Averages across chemical preparations within a laboratory group are given by  $\delta^{30}\text{Si\_mean}$  and  $\delta^{29}\text{Si\_mean}$  with associated 2 sigma standard deviations, 2sd\_mean. N and n denote the total number of chemical preparations and analytical replicates for each laboratory group, respectively. NaN indicates data not available.

Group	$\delta^{30}\text{Si}$	2 s.d.	$\delta^{29}\text{Si}$	2 s.d.	$^{29/30}\text{Si}$	n	$\delta^{30}\text{Si}$ mean	2 s.d. mean	$\delta^{29}\text{Si}$ mean	2 s.d. mean	N	n
Aloha 1000m	[‰]	[‰]	[‰]	[‰]	[‰]	analyt. replicate	[‰]	[‰]	[‰]	[‰]		
<b>1</b>	1.15	0.02	0.68	0.07	0.59	<b>1</b>	1.10	0.07	0.63	0.07	<b>4</b>	<b>4</b>
	1.07	0.05	0.62	0.04	0.58	<b>1</b>						
	1.09	0.08	0.61	0.03	0.56	<b>1</b>						
	1.08	0.07	0.61	0.06	0.56	<b>1</b>						
<b>2</b>	1.15	0.01	0.56	0.04	0.49	<b>3</b>	1.10	0.07	0.56	0.02	<b>5</b>	<b>15</b>
	1.09	0.04	0.55	0.01	0.51	<b>2</b>						
	1.07	0.01	0.57	0.05	0.53	<b>3</b>						
	1.07	0.06	0.55	0.03	0.51	<b>4</b>						
	1.12	0.06	0.57	0.04	0.51	<b>3</b>						
<b>3</b>	1.14	0.08	0.59	0.05	0.52	<b>3</b>	1.16	0.16	0.59	0.09	<b>3</b>	<b>9</b>
	1.10	0.00	0.55	0.06	0.50	<b>3</b>						
	1.25	0.09	0.64	0.08	0.51	<b>3</b>						
<b>4</b>	1.28	0.13	0.66	0.08	0.52	<b>6</b>	1.17	0.20	0.62	0.10	<b>3</b>	<b>12</b>
	1.17	0.07	0.62	0.09	0.53	<b>3</b>						
	1.08	0.13	0.56	0.07	0.52	<b>3</b>						
<b>5</b>	1.19	0.19	0.66	0.10	0.55	<b>5</b>	1.23	0.08	0.64	0.04	<b>4</b>	<b>15</b>
	1.20	0.32	0.62	0.07	0.52	<b>3</b>						
	1.27	0.08	0.66	0.04	0.52	<b>3</b>						
	1.25	0.13	0.62	0.14	0.50	<b>4</b>						
<b>6</b>	1.27	0.10	0.68	0.07	0.53	<b>1</b>	1.26	0.12	0.68	0.09	<b>5</b>	<b>5</b>
	1.28	0.11	0.68	0.13	0.53	<b>1</b>						
	1.18	0.23	0.67	0.16	0.57	<b>1</b>						
	1.22	0.22	0.62	0.07	0.51	<b>1</b>						
	1.33	0.37	0.74	0.12	0.56	<b>1</b>						
<b>7</b>	1.29	0.08	0.70	0.04	0.54	<b>8</b>	1.25	0.07	0.65	0.07	<b>6</b>	<b>31</b>
	1.28	0.08	0.62	0.11	0.48	<b>9</b>						
	1.27	0.09	0.66	0.04	0.52	<b>5</b>						
	1.25	0.10	0.65	0.06	0.52	<b>3</b>						
	1.22	0.19	0.66	0.23	0.54	<b>3</b>						
	1.20	0.17	0.60	0.19	0.50	<b>3</b>						
<b>8</b>	1.27	0.11	0.64	0.06	0.51	<b>12</b>	1.29	0.04	0.66	0.02	<b>4</b>	<b>25</b>
	1.29	0.10	0.66	0.05	0.51	<b>6</b>						
	1.27	0.02	0.65	0.01	0.51	<b>2</b>						
	1.31	0.11	0.67	0.06	0.51	<b>5</b>						

Table A2 continued: Measurements of  $\delta^{30}\text{Si}(\text{OH})_4$  and  $^{29}\text{Si}(\text{OH})_4$  by each laboratory group for ALOHA<sub>1000</sub>.

Group	$\delta^{30}\text{Si}$	2 s.d.	$\delta^{29}\text{Si}$	2 s.d.	$^{29/30}\text{Si}$	n	$\delta^{30}\text{Si}$ mean	2 s.d. mean	$\delta^{29}\text{Si}$ mean	2 s.d. mean	N	n
Aloha 1000m	[‰]	[‰]	[‰]	[‰]	[‰]	analyt. replicate	[‰]	[‰]	[‰]	[‰]		
<b>9</b>	1.32	0.08	0.69	0.01	0.52	<b>2</b>	1.31	0.15	0.68	0.09	<b>10</b>	<b>20</b>
	1.35	0.07	0.74	0.13	0.55	<b>2</b>						
	1.42	0.16	0.69	0.14	0.49	<b>2</b>						
	1.30	0.11	0.67	0.04	0.51	<b>2</b>						
	1.35	0.21	0.70	0.06	0.52	<b>2</b>						
	1.33	0.01	0.72	0.07	0.54	<b>2</b>						
	1.15	0.07	0.63	0.03	0.55	<b>2</b>						
	1.24	0.07	0.64	0.24	0.51	<b>2</b>						
	1.34	0.11	0.60	0.11	0.45	<b>2</b>						
	1.31	0.14	0.73	0.10	0.55	<b>2</b>						
<b>10</b>	1.39	0.09	0.70	0.04	0.50	<b>3</b>	1.45	0.17	0.76	0.16	<b>3</b>	<b>9</b>
	1.55	0.18	0.85	0.08	0.55	<b>3</b>						
	1.41	0.12	0.74	0.07	0.52	<b>3</b>						
<b>11</b>	1.26	0.11	0.62	0.08	0.50	<b>9</b>	1.27	0.05	0.65	0.03	<b>8</b>	<b>72</b>
	1.25	0.14	0.66	0.07	0.52	<b>9</b>						
	1.23	0.16	0.64	0.08	0.52	<b>9</b>						
	1.27	0.10	0.65	0.12	0.51	<b>9</b>						
	1.30	0.11	0.67	0.08	0.52	<b>9</b>						
	1.28	0.23	0.66	0.09	0.51	<b>9</b>						
	1.30	0.16	0.66	0.09	0.50	<b>9</b>						
	1.28	0.16	0.66	0.10	0.52	<b>9</b>						

Table A2: Measurements of  $\delta^{30}\text{Si}(\text{OH})_4$  and  $^{29}\text{Si}(\text{OH})_4$  by each laboratory group for ALOHA<sub>300</sub>. The means of analytical replicates,  $\delta^{30}\text{Si}$  and  $\delta^{29}\text{Si}$ , and associated 2 sigma standard deviations where analytical replicates are defined as replicate analyses from the same chemical preparation. Averages across chemical preparations within a laboratory group are given by  $\delta^{30}\text{Si\_mean}$  and  $\delta^{29}\text{Si\_mean}$  with associated 2 sigma standard deviations, 2sd\_mean. N and n denote the total number of chemical preparations and analytical replicates for each laboratory group, respectively. NaN indicates data not available.

Group	$\delta^{30}\text{Si}$	2 s.d.	$\delta^{29}\text{Si}$	2 s.d.	$^{29,30}\text{Si}$	n	$\delta^{30}\text{Si}$ mean	2 s.d. mean	$\delta^{29}\text{Si}$ mean	2 s.d. mean	N	n
Aloha 300 m	[‰]	[‰]	[‰]	[‰]	[‰]	analyt. replicate	[‰]	[‰]	[‰]	[‰]		
2	1.75	0.02	0.83	0.03	0.48	2	1.66	0.10	0.84	0.05	6	12
	1.64	0.01	0.87	0.05	0.53	2						
	1.62	0.04	0.86	0.01	0.53	2						
	1.65	0.02	0.81	0.05	0.49	2						
	1.67	0.03	0.81	0.02	0.49	1						
	1.63	0.06	0.85	0.04	0.52	3						
4	1.56	0.06	0.87	0.09	0.55	3	1.64	0.13	0.87	0.05	4	12
	1.60	0.12	0.83	0.02	0.52	3						
	1.66	0.12	0.86	0.01	0.52	3						
	1.71	0.09	0.90	0.03	0.53	3						
5	1.52	0.17	0.76	0.07	0.50	4	1.51	0.12	0.80	0.08	3	11
	1.56	0.18	0.84	0.14	0.53	4						
	1.45	0.08	0.81	0.05	0.56	3						
6	1.95	0.37	0.98	0.19	0.50	1	1.78	0.18	0.89	0.18	6	6
	1.76	0.27	0.90	0.17	0.51	1						
	1.76	0.30	0.86	0.19	0.49	1						
	1.75	0.07	0.74	0.16	0.42	1						
	1.68	0.37	0.98	0.12	0.58	1						
	1.81	0.38	0.91	0.22	0.50	1						
7	1.92	0.13	0.98	0.05	0.51	2	1.92	0.08	1.02	0.12	5	14
	1.97	0.02	1.05	0.11	0.53	3						
	1.95	0.08	1.07	0.01	0.55	3						
	1.87	0.30	0.94	0.32	0.50	3						
	1.89	0.07	1.07	0.08	0.57	3						
8	1.51	0.05	0.77	0.05	0.51	3	1.46	0.17	0.75	0.09	3	10
	1.52	0.04	0.77	0.02	0.51	1						
	1.36	0.09	0.69	0.04	0.51	6						
9	1.90	0.01	0.95	0.06	0.50	2	1.94	0.12	0.99	0.08	8	16
	2.05	0.16	1.06	0.08	0.52	2						
	1.90	0.57	0.98	0.21	0.51	2						
	1.94	0.01	0.94	0.10	0.48	2						
	2.02	0.42	1.04	0.11	0.51	2						
	1.91	0.10	1.00	0.24	0.52	2						
	1.89	0.27	0.99	0.14	0.53	2						
	1.95	0.27	1.01	0.10	0.52	2						

Table A2 continued: Measurements of  $\delta^{30}\text{Si}(\text{OH})_4$  and  $^{29}\text{Si}(\text{OH})_4$  by each laboratory group for ALOHA<sub>300</sub>.

Group	$\delta^{30}\text{Si}$	2 s.d.	$\delta^{29}\text{Si}$	2 s.d.	$^{29/30}\text{Si}$	n	$\delta^{30}\text{Si}$ mean	2 s.d. mean	$\delta^{29}\text{Si}$ mean	2 s.d. mean	N	n
Aloha 300 m	[‰]	[‰]	[‰]	[‰]	[‰]	analyt. replicate	[‰]	[‰]	[‰]	[‰]		
<b>10</b>	1.52	0.04	0.77	0.02	0.51	<b>3</b>	1.53	0.17	0.79	0.06	<b>3</b>	<b>9</b>
	1.45	0.05	0.77	0.02	0.53	<b>3</b>						
	1.61	0.07	0.82	0.06	0.51	<b>3</b>						
<b>11</b>	1.61	naN	0.88	naN	0.55	<b>1</b>	1.69	0.24	0.85	0.17	<b>8</b>	<b>8</b>
	1.82	naN	0.97	naN	0.54	<b>1</b>						
	1.73	naN	0.90	naN	0.52	<b>1</b>						
	1.52	naN	0.71	naN	0.46	<b>1</b>						
	1.60	naN	0.77	naN	0.48	<b>1</b>						
	1.76	naN	0.91	naN	0.52	<b>1</b>						
	1.86	naN	0.85	naN	0.46	<b>1</b>						
	1.61	naN	0.80	naN	0.50	<b>1</b>						

Table A3: Summary of mean Si isotope values ( $\delta^{30}\text{Si}$ ,  $\delta^{29}\text{Si}$ ), the associated  $2\sigma$  analytical uncertainty (2 s. d.) and the number of measurements (n) obtained by each laboratory group for the secondary standards Big Batch and Diatomite. The overall mean and the uncertainty about the mean (2 s. d.) as well as the median and the interquartile deviation (IQD) for all groups are given at the bottom of the table. NaN indicates data not available.

Group	Big Batch					Diatomite				
	$\delta^{30}\text{Si}$	2 s.d.	$\delta^{29}\text{Si}$	2 s.d.	n	$\delta^{30}\text{Si}$	2 s.d.	$\delta^{29}\text{Si}$	2 s.d.	n
1	-10.61	0.08	-5.42	0.07	18	1.25	0.11	0.64	0.09	15
2	NaN	NaN	NaN	NaN	NaN	1.26	0.14	0.66	0.12	14
3	-10.48	0.34	NaN	NaN	3	NaN	NaN	NaN	NaN	NaN
4	NaN	NaN	NaN	NaN	NaN	1.25	0.13	NaN	NaN	19
5	-10.67	0.16	-5.43	0.10	5	1.23	0.05	0.63	0.04	4
6	-10.64	0.22	-5.43	0.10	34	NaN	NaN	NaN	NaN	NaN
7	-10.50	0.08	-5.36	0.06	3	NaN	NaN	NaN	NaN	NaN
8	-10.51	0.23	-5.35	0.11	25	1.27	0.16	0.66	0.07	5
9	-10.48	0.08	NaN	NaN	2	NaN	NaN	NaN	NaN	NaN
10	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN
11	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN
Mean	<b>-10.56</b>		<b>-5.40</b>			<b>1.25</b>		<b>0.65</b>		
2 s.d.	<b>0.16</b>		<b>0.08</b>			<b>0.03</b>		<b>0.03</b>		
Median	<b>-10.51</b>		<b>-5.42</b>			<b>1.25</b>		<b>0.65</b>		
IQD	<b>0.07</b>		<b>0.04</b>			<b>0.01</b>		<b>0.01</b>		

Table A4: Statistical Analysis of Differences in differences in  $\delta^{30}\text{Si}(\text{OH})_4$  among groups using Neptune spectrometers. Groups not connected by same letter are significantly different.

ALOHA <sub>1000</sub>					
	Tukey		False Discovery Rate		Mean
Group	Column A	Column B	Column A	Column B	$\delta^{30}\text{Si}(\text{OH})_4$
11	A		A		1.27
2		B	A	B	1.16
3		B		B	1.10
1		B		B	1.10
ALOHA <sub>300</sub>					
	Tukey				
Group	Column A	Column B			
11	A				1.69
2	A				1.66

Table A5: Statistical Analysis of Differences in differences in  $\delta^{30}\text{Si}(\text{OH})_4$  among groups using Nu Plasma mass spectrometers. Groups not connected by same letter are significantly different.

ALOHA <sub>1000</sub>				
Group	Tukey			Mean $\delta^{30}\text{Si}(\text{OH})_4$
	Column A	Column B	Column C	
10	A			1.45
9		B		1.31
6		B	C	1.26
7		B	C	1.25
5		B	C	1.23
4			C	1.18
ALOHA <sub>300</sub>				
9	A			1.94
7	A			1.92
6		B		1.78
4			C	1.64
10			C	1.53
5			C	1.51



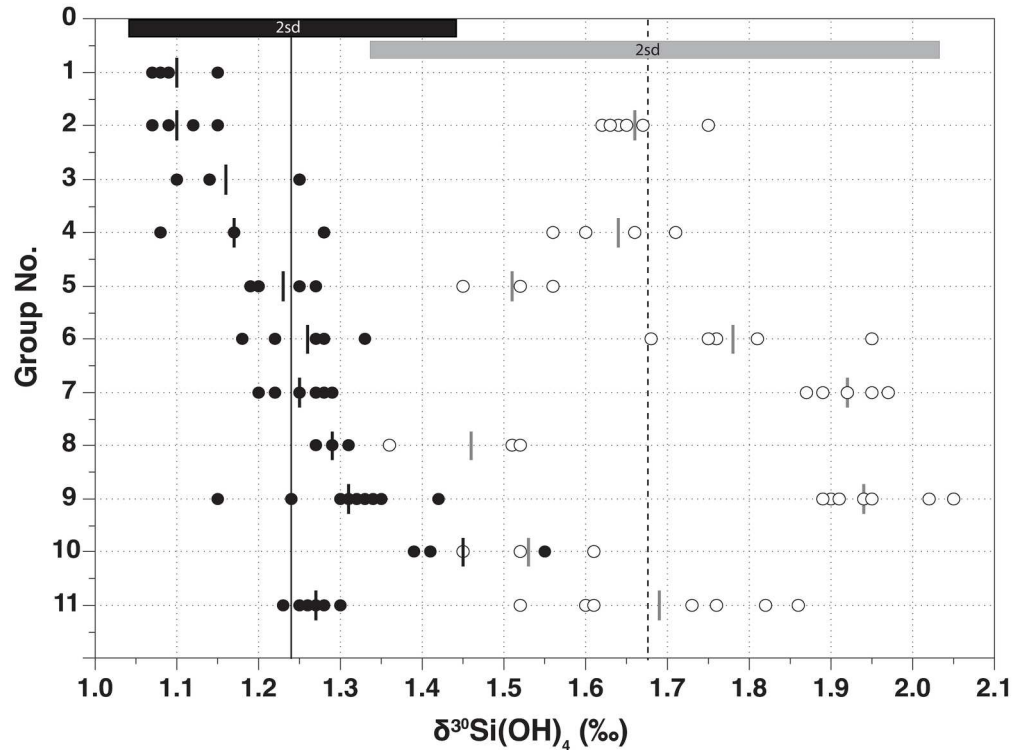


Figure 1.  $\delta^{30}\text{Si}(\text{OH})_4$  results from all groups for ALOHA<sub>300</sub> (open circles) and ALOHA<sub>1000</sub> (filled circles). The long black vertical solid line indicates the mean value of all measurements for ALOHA<sub>1000</sub> and the long dashed line that for ALOHA<sub>300</sub>. The data points represent the individual  $\delta^{30}\text{Si}(\text{OH})_4$  values from Table A2. Short vertical solid lines are the means obtained by individual laboratories for the two samples. Uncertainty in the mean for all measurements for each sample (2 s. d.) is indicated by the horizontal bars at the top of the figure.

Fig. 1

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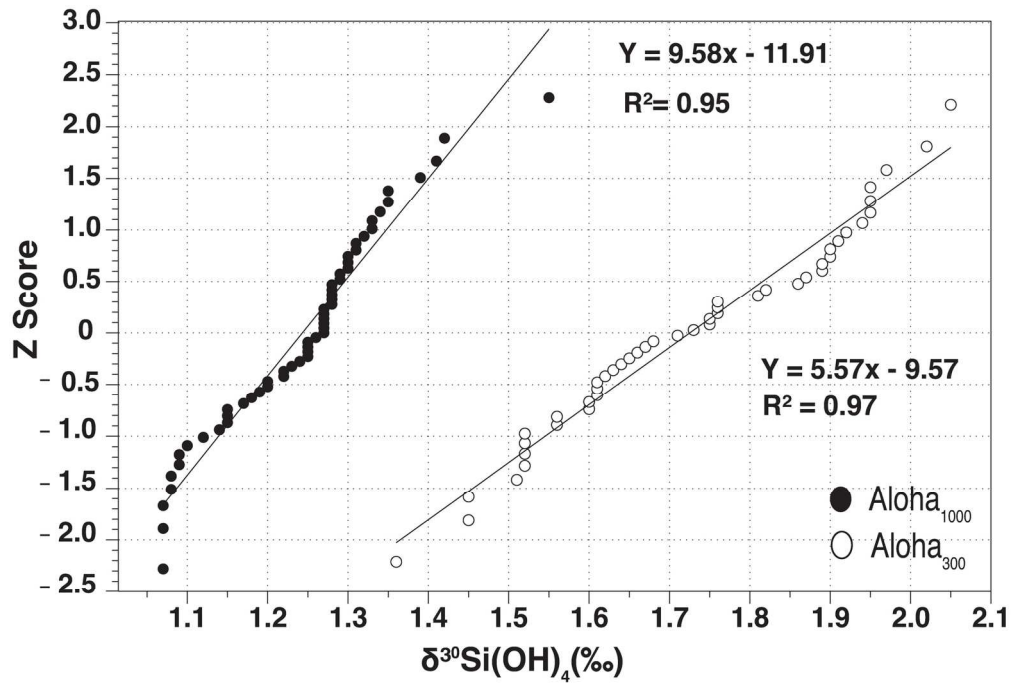


Figure 2. Z scores as a function of  $\delta^{30}\text{Si}(\text{OH})_4$  for ALOHA<sub>300</sub> (open circles) and ALOHA<sub>1000</sub> (filled circles).  
 Fig. 2  
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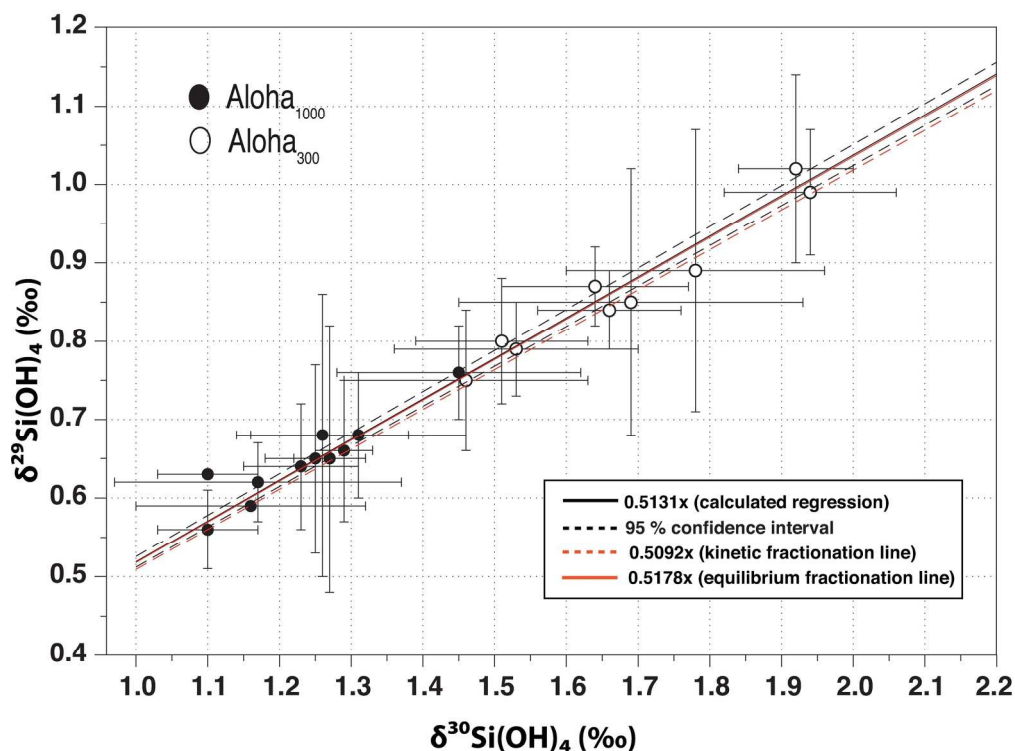


Figure 3. Plot of  $\delta^{30}\text{Si}(\text{OH})_4$  versus  $\delta^{29}\text{Si}(\text{OH})_4$  for ALOHA300 (open circle) and ALOHA<sub>1000</sub> (filled circle; error bars are 2 s. d.). Solid line is the result of least-squares linear regression with a slope of  $0.5188 \pm 0.0184$  (s.e.,  $R^2 = 0.98$ ). The lower and upper 95 % confidence intervals are given as dashed black lines. The kinetic fractionation line has a slope of 0.5092 (intercept of zero) for Si (dashed red line) and the equilibrium fractionation line has a slope of 0.5178 (intercept of zero) for Si (solid red line). Regression line obtained by analysis using reduced major axis model II regression yields a slope of  $0.5131 \pm 0.0040$  (s.e.,  $R^2 = 0.98$ ; not displayed in the figure).

Fig. 3

176x131mm (300 x 300 DPI)

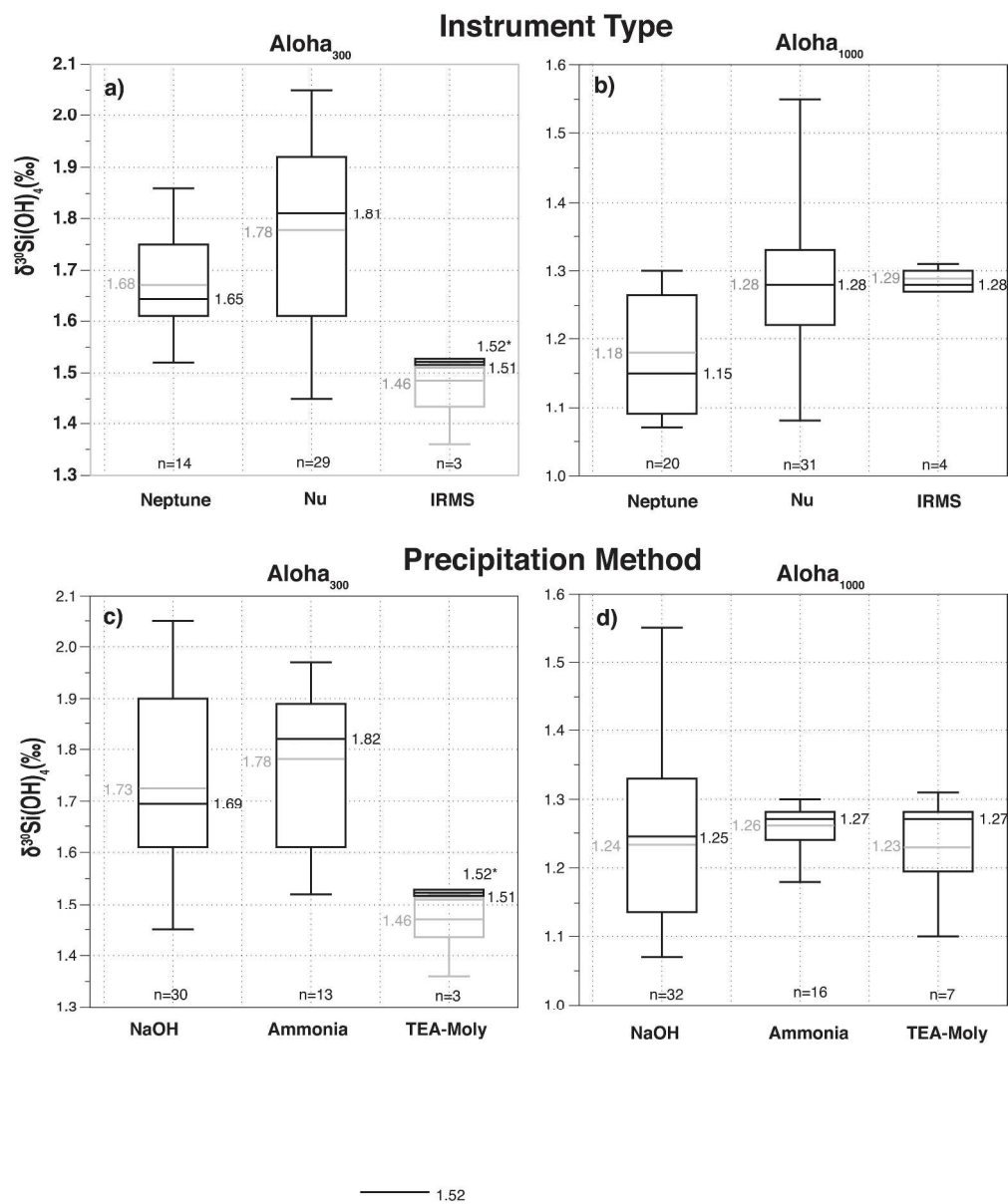


Figure 4. Boxplots showing  $\delta^{30}\text{Si}(\text{OH})_4$  data sorted by different mass spectrometer types for a) ALOHA<sub>300</sub> and for b) ALOHA<sub>1000</sub>. Data sorted by different precipitation methods for c) ALOHA<sub>300</sub> and d) ALOHA<sub>1000</sub>. On the boxplots the median values (black) and the mean values (grey) are displayed. For ALOHA<sub>300</sub> a) and c) show data for IRMS and TEA-Moly with (grey boxplot) and without outlier (black boxplot). Here, the mean value (which equals the median) is indicated by a superscript star. The value next to each boxplot indicates the median (black) and the mean (grey), respectively. The number of included data points (n) is given below each boxplot. Raw data are presented in Table 3

Fig. 4  
334x402mm (300 x 300 DPI)