



Extreme silicon isotope fractionation due to Si organic complexation: Implications for silica biomineralization

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ARTICLE INFO

Article history:

Received 2 December 2019

Received in revised form 25 March 2020

Accepted 15 April 2020

Available online 5 May 2020

Editor: L. Derry

Keywords:

silicon

equilibrium isotope fractionation

organo-silicon complexes

first principle calculation

three-isotope method

Si coordination change

ABSTRACT

A combination of theoretical predictions and isotopic equilibration experiments using the three-isotope method have been performed to assess Si isotope fractionation among minerals, and aqueous species in the presence of dissolved catechol. Aqueous Si in abiotic ambient temperature aqueous solutions is dominated by the IV-coordinated H_4SiO_4^0 species, but the presence of aqueous catechol provokes the formation of a VI-fold Si-catechol complex. Results show an equilibrium Si fractionation factor of $\sim 19\text{‰}$ between the VI-fold coordinated Si-catechol complex and the IV-fold coordinated aqueous silicic acid, an amplitude never previously observed for silicon. The fractionation between V-fold Si-organo complexes (with diolate, glyconate or methylactate groups) and silicic acid has also been estimated through theoretical predictions to be about -10‰ . These extreme fractionations can be used to improve our ability to interpret the Si isotope compositions of natural solids, and in particular those associated with marine silica biomineralization processes (e.g. sponge spicules).

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1. Introduction

Silicon (Si) enters the biogeochemical cycle through the weathering of silicate minerals, and circulates through the biosphere as dissolved aqueous Si primarily as silicic acid (H_4SiO_4^0). Silicon occurs in numerous plants mostly as phytoliths, which enhance their structural stability and defensive mechanisms (e.g. Kubicki and Heaney, 2003; Poitrasson, 2017 and references therein). In higher organisms, such as animals or humans, it is used for bone or tissue formation (e.g. Jugdaohsingh et al., 2015). In marine environments Si is used by phytoplankton, zooplankton and sponges to form opaline structures, such as frustules, tests or spicules (Kubicki and Heaney, 2003; Hendry and Robinson, 2012; Poitrasson, 2017; Cassarino et al., 2018). Such 'bio-Si' has distinct isotopic signatures with $\delta^{30}\text{Si}$ values ranging from $+3$ to -6.5‰ (Poitrasson, 2017). In general, biogenic solids preferentially uptake light Si isotopes

(e.g. Opfergelt et al., 2006; Hendry and Robinson, 2012; Cassarino et al., 2018). The lightest Si isotope composition reported so far in natural solids, between -5 and -7‰ , has been observed in sponges (Cassarino et al., 2018) and choanoflagellates (Marron et al., 2019). The processes and mechanisms generating these light Si isotope compositions are not yet fully understood (Kubicki and Heaney, 2003; Kinrade et al., 2002; Poitrasson, 2017; Cassarino et al., 2018). One possibility, however, is that the interaction between aqueous Si and organic matter could impact Si isotope fractionation (Kinrade et al., 2002; Cassarino et al., 2018).

Silicon can form aqueous complexes with a number of organic ligands including polyols, saccharides, phenols, pyridine and tropolones (Cella et al., 1980; Sjöberg et al., 1985; Kinrade et al., 2001a; Benner et al., 2003; Kubicki and Heaney, 2003). The formation of such complexes can alter the aqueous Si coordination environment. Past Nuclear Magnetic Resonance (NMR) studies have shown that Si, which usually occurs in natural waters as the IV-coordinated silicic acid (H_4SiO_4^0) complex can form V- and VI-coordinated organosilicon complexes in the presence of aqueous organic ligands such as phenols and polyols (Cella et al., 1980; Kinrade et al., 2001a). Evidence of natural occurring VI-coordinated organosilicon compounds formed *in-vivo* has been provided by the ^{29}Si nuclear resonance study of the fresh water diatom *Navicula*

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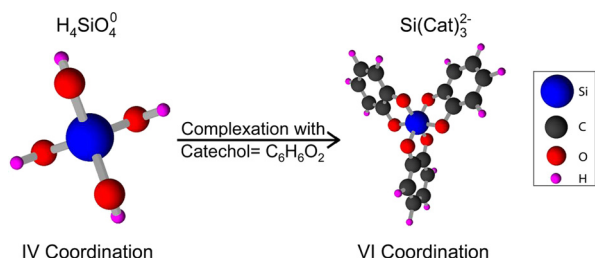


Fig. 1. Schematic illustration of the H_4SiO_4^0 and the SiCat_3^{2-} aqueous species.

pelliculosa (Kinrade et al., 2002). In general, coordination changes have been identified as a primary factor influencing isotopic fractionation (Schauble, 2004). Such is the case for example of boron, with an isotope fractionation of about -27‰ between boric acid (H_3BO_3^0 with trigonal B) and the borate ion (BO_4^- , tetragonal B; e.g. Balan et al., 2018).

This study investigates the effect of the change in Si coordination by aqueous organic Si complex formation on equilibrium Si isotope fractionation in water-rock systems. Catechol ($\text{C}_6\text{H}_4(\text{OH})_2$) is used as a representative aqueous organic ligand, as it readily binds to Si (Barnum, 1970; Pokrovski and Schott, 1998) and changes the common IV-coordinated aqueous Si to a hexacoordinated complex with a 6-membered ring structure as shown in Fig. 1 (Sjöberg et al., 1985; Kinrade et al., 1999). To determine Si isotope equilibrium fractionation between silicic acid and the Si-catecholate complex, this study combines first-principle calculations with experiments performed at 25°C and $\text{pH} \sim 8.8$ at equilibrium between amorphous silica and 0.05 M and 0.08 M catechol solutions using the three-isotope method. The results of this study provide new insight into the effects of aqueous organic complexation on Si isotope equilibrium fractionation in the bio- and hydrosphere.

2. Materials and methods

2.1. Theoretical modelling

To assess the role of changing Si coordination due to aqueous organic complexation on its isotope fractionation properties, both VI-fold and V-fold coordination compounds were considered. These calculations were based on compounds modelled from X-ray determined structures found in the literature. As an example of VI-fold coordinated Si, $\text{Li}_2[\text{Si}(\text{Cat})_3] \cdot 3.5\text{dme}$ was considered (where cat = the catecholate dianion, and dme = dimethoxy ethane $\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-O-CH}_3$; Hahn et al., 1995). For V-fold coordinated Si, three structures were considered, chosen for their different functional groups and coordination polyhedrons: $\text{Li}[\text{Si}(\text{AnErytH}_{-2})_2(\text{OH})] \cdot \text{H}_2\text{O}$ (where AnErytH_{-2} = anhydroerythritol dianions; Benner et al., 1999), $[\text{2}-(\text{Dimethylammonio})\text{ethoxy}]\text{bis}[2\text{-methylactato}(2\text{-})\text{-O}^1, \text{O}^2]$ silicate (compound 7 of Tacke et al., 1999), and $\text{Li}[\text{Si}(\text{OCH}_2\text{CH}_2\text{OH})(\text{OCH}_2\text{CH}_2\text{O})_2]$ (compound 1 of Donh  rl et al., 1998). These structures are assumed to be representative of VI- and V-fold coordinated aqueous Si and will be referred to as SiCat_3^{2-} , SiDio, SiLact and SiGly, respectively.

2.1.1. First-principle calculations of equilibrium Si isotope fractionation factors

The equilibrium fractionation of silicon isotopes between two phases is obtained by combining the β -factors of both phases. The β -factor corresponds to the isotopic fractionation factor between Si atoms in a phase compared to it as a perfect gas. This quantity can be computed within the harmonic approximation from the vibrational frequencies of the phase of interest (Bigeleisen and Mayer, 1947). Details of the calculation of the β -factor of quartz and of

dissolved H_4SiO_4^0 with the harmonic approximation are given in M  heut et al. (2007) and Dupuis et al. (2015), respectively. The β -factors of hypervalent Si model structures in the present study were computed from their phonon frequencies at the Γ -point according to equation (5) of Dupuis et al. (2015). The phonon frequencies were computed from first-principles using density functional theory (DFT; Hohenberg and Kohn, 1964; Kohn and Sham, 1965). The calculation was based on two exchange-correlation functionals: that of Perdew, Burke and Ernzerhof (PBE; Perdew et al., 1996), and the vdW-DF2 non-local functional (Lee et al., 2010). It used a plane-wave basis set, and atomic pseudopotentials as implemented in the Quantum Espresso package (Giannozzi et al., 2009). The pseudopotentials used for Si, O and H are described in the electronic annexes of M  heut et al. (2007). The pseudopotential used for Li was taken from the PSLibrary (Dal Corso, 2014). The pseudopotential used for C was taken from F  ger et al. (2018). Electronic wave-functions were expanded in plane-waves up to an energy cutoff $\varepsilon_{\text{cut}} = 80$ Ry and the charge density cut-off is set to $4 \varepsilon_{\text{cut}}$. The electronic structure calculation was performed at the Γ -point of the first Brillouin zone for Si-catecholate (SiCat_3^{2-}), and at the Baldereschi point (Baldereschi, 1973) for Si-diolate (SiDio), Si-lactate (SiLact) and Si-glyconate (SiGly). Phonon frequencies were computed using linear response theory (Baroni et al., 2001) and the Quantum Espresso package (Giannozzi et al., 2009). The calculated structural properties (Table A.1), vibrational properties (Fig. A.2) and the derived fractionation properties (Figs. A.1, A.3, A.4) are discussed in detail in the Supplemental Information A.

2.1.2. Speciation calculations

Speciation calculations for all aqueous solutions used in this study were performed using the PHREEQC code (Parkhurst and Appelo, 2013) together with its llnl thermodynamic database. The equilibrium constant for the amorphous SiO_2 dissolution reaction of the llnl database was changed to match that reported by Stamm et al. (2019); this value was obtained on the same amorphous SiO_2 powder ($\text{SiO}_{2,\text{am}}$) as used in the present study. Furthermore the dissociation constants of aqueous catechol from Sillen and Martell (1971) and the formation constant of the Si-catechol complex from Pokrovski and Schott (1998) summarized in the Supplemental Table B.1 were added to the llnl database.

The equilibrium fractionation factor between the aqueous solution and amorphous silica depends on the Si speciation of the solution, and the individual fractionation factors, $\alpha_{i-\text{SiO}_{2,\text{am}}}^{x/28}$, of each of the i th Si aqueous species with respect to amorphous silica. The Si isotopic fractionation factor between the solution and amorphous silica is the weighted sum of the fractionation factors of each species such that (Zhang et al., 1995):

$$10^3 \ln \alpha_{\text{fluid-SiO}_{2,\text{am}}}^{x/28} = \sum_i (x_i \times 10^3 \ln \alpha_{i-\text{SiO}_{2,\text{am}}}^{x/28}) \quad (1)$$

where x_i refers to the mole fraction of the subscripted Si aqueous species present in the fluid. Note that Si isotopic fractionation between the fluid and $\text{SiO}_{2,\text{am}}$, $\Delta^x \text{Si}_{\text{fluid-SiO}_{2,\text{am}}}$ is approximately related to $\alpha_{\text{fluid-SiO}_{2,\text{am}}}^{x/28}$ by

$$\Delta^x \text{Si}_{\text{fluid-SiO}_{2,\text{am}}} \approx 10^3 \ln \alpha_{\text{fluid-SiO}_{2,\text{am}}}^{x/28} \quad (2)$$

2.2. Experimental approach

2.2.1. Experimental design

The three-isotope method was used to determine the equilibrium isotopic fractionation factor between aqueous catechol solutions and $\text{SiO}_{2,\text{am}}$. This method permits the determination of the degree of isotopic exchange (F) between the solid and its coexisting aqueous solution after adding a ^{29}Si tracer to the aqueous

phase. A detailed description of this method is given in previous studies (e.g. Matsuhisa et al., 1978; Stamm et al., 2019). In brief the equilibrium isotopic composition of amorphous silica ($\delta^{30}\text{Si}_{\text{SiO}_2,\text{am}}$) and the fluid ($\delta^{30}\text{Si}_{\text{fluid}}$) were obtained from the linear extrapolation of $\delta^{30}\text{Si}$ values to 100% isotope exchange. This extrapolation was facilitated by plotting of measured $\delta^{30}\text{Si}_{\text{fluid}}$ and $\delta^{30}\text{Si}_{\text{SiO}_2,\text{am}}$ as a function of the degree of isotopic exchange F . F was calculated using

$$F = \frac{(\delta_t - \delta_i)}{(\delta_e - \delta_i)} \quad (3)$$

where δ_t denotes $\delta^{29}\text{Si}$ of the fluid at any time t during the reaction, and δ_i and δ_e describe the initial and equilibrium $\delta^{29}\text{Si}$ value of the fluid, respectively; δ_e was deduced iteratively from mass balance considerations. A detailed description of these mass balance calculations is given by Stamm et al. (2019).

All isotope equilibration experiments performed in this study were conducted at bulk chemical equilibrium but isotopic disequilibrium conditions to minimize the potential effect of kinetics on the isotopic fractionation. The experiments were performed within experimental series consisting of two steps as described below.

2.2.2. Starting materials

All experiments were performed using Alfa Aesar® 100 mesh hydrated silicic acid powder. Ultrafine particles were removed from the powder by sedimentation using the approach of Pokrovski and Schott (1998). Specifically, 50 g of the powder was suspended in $>18.2 \Omega$ de-ionized Milli-Q® water by stirring in a 1 dm³ glass beaker. The solid was sedimented and then the fluid phase decanted. This was repeated until the supernatant became clear within the first 5 min. The powder was subsequently oven dried, and placed into a desiccator while cooling.

Two aqueous solutions, one containing 0.05 mol/kg and the other 0.08 mol/kg catechol were prepared by dissolving Merck® pyrocatechol ($\text{C}_6\text{H}_4(\text{OH})_2$) into a NH_4Cl – NH_3 pH-buffer solution. The buffer solution was prepared from de-ionized Milli-Q® water, suprapur Merck® NH_4Cl salt and Merck® 25% NH_3 solution and contained 0.1 mol/kg NH_4Cl and 0.36 mol/kg NH_3 .

2.2.3. Step 1: equilibration of the reactive aqueous solutions with amorphous SiO_2

Experiments in this study were performed within two distinct series. One series was performed with an aqueous 0.05 mol/kg catechol solution and the other with a 0.08 mol/kg catechol solution prepared as described above. These solution compositions were chosen as they were likely to contain high percentages of Si bound in VI-coordinated aqueous complexes. Each aqueous solution (200 mL) was first equilibrated with 3 g of washed amorphous SiO_2 powder (SiO_2,am) in a closed polypropylene (PP) bottle. The closed bottles were placed in a constantly shaking thermostatic bath at 25 °C. The aqueous solutions were regularly sampled over 10 days. The short equilibration period was chosen as aqueous catechol decomposes or reacts with ammonia over time (Barnum, 1972). The pH and concentration of the aqueous solutions were measured immediately after sampling. The aqueous Si concentrations of the fluid samples were determined by colorimetry. When the measured pH and Si concentrations of the sampled solutions attained a constant value, chemical equilibrium was assumed to be reached. The equilibrated aqueous solutions were then filtered with Teflon syringe filters (Merck® 0.2 μm).

2.2.4. Step 2: isotopic exchange experiments

To employ the three-isotope method, the chemical equilibrated solutions were enriched with a small quantity of ^{29}Si isotope tracer solution having an initial composition of 0.21% ^{28}Si , 99.76% ^{29}Si ,

and 0.03% ^{30}Si , to obtain starting reactive fluids having a $\delta^{29}\text{Si}$ $\sim 23\text{‰}$. To ensure that these fluids were still at equilibrium with SiO_2,am after adding the spike, the pH and Si concentrations of these spiked fluids were measured. The isotope exchange experiments in this study were conducted in two series consisting of 8 individual closed system experiments and lasted up to 7 days. The short duration of the experiments avoids the decomposition of the aqueous catechol. By performing individual closed system experiments, solids and fluids could be collected and analysed after selected experiment durations. For the individual experiments, ~ 0.30 g of freshly pre-washed SiO_2,am powder with a known Si isotope composition was placed in 10 ml polypropylene reactors together with 10 ml of the prepared ^{29}Si enriched aqueous catechol solution. The reactors were wrapped in aluminium foil, to avoid light, and placed in an orbital shaker to be constantly mixed at 25 °C. To verify that the reactors were indeed closed, they were weighted at the beginning and end of each experiment. The experiments were terminated at pre-chosen times. Once an experiment was complete, the reactor was centrifuged for 20 min at 4500 rpm. The supernatant was then separated from the powder and filtered with Merck® 0.2 μm Teflon syringe filters. The pH and Si concentrations of the recovered aqueous solutions were measured just after sampling. These solutions were then immediately prepared for column chromatography to avoid any isotopic fractionation during decomposition of the organic ligand. The powders were washed and filtered with de-ionized Milli-Q® water, oven dried at 40 °C, then stored prior to Si isotopic analysis.

2.3. Analytical methods

2.3.1. Characterization of SiO_2,am powder

The washed SiO_2,am powder, and the SiO_2,am powder collected from the longest duration experiments were characterized using a JEOL JSM-7800F Prime scanning electron microscope (SEM) and a JEOL JEM-ARM200F Cold FEG transmission electron microscope (TEM), both located at the Raimond Castaing Microcharacterization Centre (Toulouse, France). Some representative images are shown in Fig. 2. The average grain size of the cleaned silicic acid powder was 23 ± 7 nm ($n = 100$, S.D.) as determined using TEM images and the ImageJ software package (Schindelin et al., 2012). The water content of the powder was determined to be 7.86% by thermogravimetric analysis using a Mettler Toledo® ATG/DSC1. This is consistent with the chemical formula $\text{SiO}_2 \bullet 0.28 \text{H}_2\text{O}$.

The specific surface area of the washed SiO_2,am powder used in the experiments was determined to be 195.6 m²/g with an estimated uncertainty of $\pm 10\%$ using a Quantachrome Autosorb-1MP, together with the nitrogen multipoint BET method (Brunauer et al., 1938).

2.3.2. Characterization of aqueous solutions

The pH of all aqueous solutions was determined using a Metrohm® 913 pH Meter connected to a standard glass microelectrode. The electrode was calibrated using certified Orion Thermo Scientific® buffers, and yielded an uncertainty of 0.05 pH unit (2 SD).

Aqueous silicon concentrations were determined by the molybdate blue method (Truesdale and LeCorre, 1975) using a Bran & Luebbe® analyser-III colorimeter coupled to a Seal XY-2 autosampler and a Technicon analyser II mixing unit. The Si concentrations of the measurements ranged from 0.1 to 10 ppm, with a long-term reproducibility within 3% and a quantification limit of 0.04 ppm. To exclude possible uncertainties in measured Si concentrations introduced by the presence of catechol, aqueous solutions with known Si concentration were prepared, doped with 0.05 M and 0.08 M catechol, and measured at the same time as the experimental so-

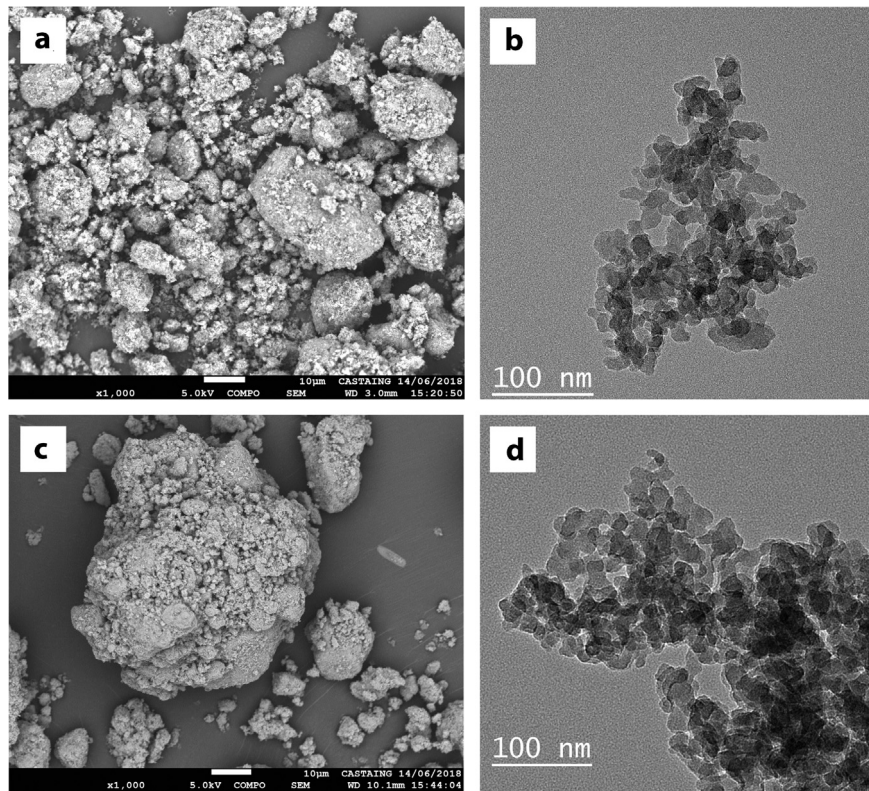


Fig. 2. Representative images of amorphous SiO_2 powders. A. SEM image of starting powder showing agglomerates of SiO_2 grains. B. TEM image of starting powder showing rounded ~ 21 nm SiO_2 grains. C. Representative SEM image of reacted silica powder. D. TEM image with 40 000x magnification of powder reacted at $T \sim 25^\circ\text{C}$, $\text{pH} \sim 6$.

lutions. No effect of the presence of aqueous catechol was observed on the analyses.

^{29}Si nuclear magnetic resonance (NMR) was used to verify the presence of the Si-catecholate (SiCat_3^{2-}) complex in the aqueous solutions. Two 1.8 mM ^{29}Si solutions were prepared, one at $\text{pH} = 10.1$ without catechol and the second at $\text{pH} = 8.9$ with a catechol concentration of 0.05 mol/kg to match the experiments. In NMR glass tubes, 300 μl of the ^{29}Si solutions were mixed with 300 μl D_2O as a solvent. NMR measurements were carried out at 298 K using a Bruker® AVANCE III HD 500 spectrometer at the ICT Institut de Chimie in Toulouse. The spectrometer was set at 11.7 T and a resonating frequency of 99.35 MHz for ^{29}Si using a 5 mm Z-gradient BBO Prodigy cryoprobe. The ^{29}Si NMR chemical shifts are reported in ppm relative to the SiMe_4 internal standard. An echoing pulse program (spin-echo for X nuclei with 1 H inverse gated decoupling) was used with a relaxation delay of 20 s. The acquisition time for the solution without catechol was 0.5 h with 96 scans, whereas the acquisition time for the catechol was 17.75 h with 3072 scans.

2.3.3. Data reporting and Si isotope analysis

Silicon isotope compositions were measured on all aqueous solutions and solids sampled from the isotope exchange experiments, as well as the initial solid, the non-spiked chemical equilibrated aqueous solutions, and the spiked initial aqueous solutions. The silicon isotope compositions in this study are expressed using the standard δ -notation in per mil (‰) relative to the international NBS-28 standard (NIST RM-8546) as defined by:

$$\delta^x\text{Si} = \left[\frac{(^x\text{Si}/^{28}\text{Si})_{\text{sample}}}{(^x\text{Si}/^{28}\text{Si})_{\text{NBS-28}}} - 1 \right] \times 1000 \quad (4)$$

where x denotes the mass of Si, either ^{29}Si or ^{30}Si , and $(^x\text{Si}/^{28}\text{Si})_{\text{sample}}$ refers to the molar ratio of the Si with mass x to that of mass 28 in the sample.

The fractionation between an aqueous fluid and a solid ($\alpha_{\text{fluid-solid}}^{x/28}$) is defined either as

$$\alpha_{\text{fluid-solid}}^{x/28} = \frac{(^x\text{Si}/^{28}\text{Si})_{\text{fluid}}}{(^x\text{Si}/^{28}\text{Si})_{\text{solid}}} \quad (5)$$

or as

$$\Delta^x\text{Si}_{\text{fluid-solid}} = \delta^x\text{Si}_{\text{fluid}} - \delta^x\text{Si}_{\text{solid}} \quad (6)$$

Note that $\Delta^x\text{Si}_{\text{fluid-solid}}$ is approximately related to $\alpha_{\text{fluid-solid}}^{x/28}$ by Eqn. (2).

The uncertainty in retrieved Si isotope fractionation factors is calculated from the error propagation function given by

$$E\Delta^x\text{Si}_{\text{fluid-solid}} = \left[(E\delta^x\text{Si}_{\text{fluid}})^2 + (E\delta^x\text{Si}_{\text{solid}})^2 \right]^{1/2} \quad (7)$$

where $E\Delta^x\text{Si}_{\text{fluid-solid}}$ is the uncertainty of the Si isotope fractionation factor, and $E\delta^x\text{Si}_{\text{fluid}}$ and $E\delta^x\text{Si}_{\text{solid}}$ are the analytical error of the indicated analysis of the fluid and solid, respectively. Note that uncertainties due to the extrapolation of Si compositions to 100% of isotope exchange are taken into account.

To determine their isotopic compositions, SiO_2 am powders were prepared by an initial calcination of 1–5 mg of each powder at 500°C (Cornu et al., 1999) and then using the alkali fusion method of Zambardi and Poitrasson (2011). The sampled aqueous solutions were prepared for isotope analysis by a combination of calcination, similar to the approach of Cornu et al. (1999) for soils, and the alkali fusion method of Zambardi and Poitrasson (2011). In detail, five ml of aqueous solution was evaporated in silver crucibles (XRF scientific, Montreal, Canada). The remaining Si and organic residue were then calcined by heating the crucibles

in a furnace at 500 °C for 4 h, destroying all remaining organic residue, leaving only the Si of the solution behind. After cooling, ~200 mg of Merck® NaOH pellets were weighted into the crucibles. The crucibles were capped and placed into a furnace heated at 720 °C for 10 min. After cooling to room temperature, the crucibles were placed into 30 ml Savillex® Teflon beakers filled with 15 ml Milli-Q® water to dissolve the SiO₂ am powder. The resulting aqueous solutions were transferred after 24 hours into 30 ml polypropylene bottles and diluted with Milli-Q® water to 20 ml and subsequently acidified with ~10 N bi-distilled HCl to a pH of 1.5.

All samples were purified prior to Si isotope analysis by cation exchange chromatography using 2 ml of Bio-Rad® AG50W-12X cationic resin filled into 10 ml Bio-Rad® polypropylene columns. The resin was initially cleaned as described in Georg et al. (2006). After cleaning, 2 ml of the liquid samples were loaded onto the column, directly collected, and eluted twice with 2 ml Milli-Q® water. The collected fluids were then diluted and acidified to obtain a 3 ppm Si solution and a total HCl concentration of 0.05 mol/kg. The overall Si recovery was determined to be between 90 and 100%. The ²⁸Si signal of the procedural blank was found to be less than 3% of the total signal, which can be considered negligible. This was confirmed by assuming a signal bias of 3%, within a −1‰ to +1‰ signature range as shown in Supplemental Table B.2. For the solids, the maximum bias effect on the isotopic signature is <0.04‰, which is four times less than the measured 2 SD uncertainty.

Silicon isotope ratios were determined using the Thermo Scientific Neptune® MC-ICP-MS located at the Laboratoire Géosciences Environnement Toulouse (GET), France. Measurements were performed under wet plasma conditions in medium resolution. A Thermo SIS system was used together with a double-pass cyclonic spray chamber to inject the samples into the spectrometer. Instrumental mass bias drift was corrected using sample-standard bracketing combined with Mg addition as an internal standard. Measurements of ²⁵Mg/²⁴Mg ratios were performed in the dynamic mode. Russell's exponential law (Russell et al., 1978) was used to further correct for the mass bias drift.

To ensure the accuracy and precision of the isotopic analysis, the BHVO-2 reference material was repeatedly measured during each run. The results yielded $\delta^{30}\text{Si} = -0.25 \pm 0.16\text{‰}$, and $\delta^{29}\text{Si} = -0.13 \pm 0.08\text{‰}$ (2 S.D, $n = 48$), which is in close agreement with the measured BHVO-2 values of Savage et al. (2014).

3. Results

3.1. First-principle calculations of equilibrium fractionation factors

To assess the role of changing Si coordination due to aqueous organic complexation on its isotope fractionation properties, both VI-fold and V-fold coordination compounds were considered (see Methods). A goal of this study was to determine the Si isotope fractionation of these compounds relative to amorphous silica, the predominant naturally forming Si-oxide solid formed at ambient temperature. The modelling of amorphous silica, however, is difficult because its structure and composition, in particular its degree of hydration is poorly defined. The Si equilibrium fractionation factors were thus calculated between these species and either quartz or dissolved H₄SiO₄⁰, which represent two compositional end-members of amorphous silica. The quality of isotopic predictions based on DFT depend on the accuracy of the calculated frequencies. For a large number of ^{IV}Si materials, it was shown that PBE functionals underestimate frequencies by 5%, leading to a 5–10% underestimation of Si fractionation properties depending on temperature (Méheut et al., 2009). The resulting uncertainties for quartz are discussed in Supplemental Information A for both

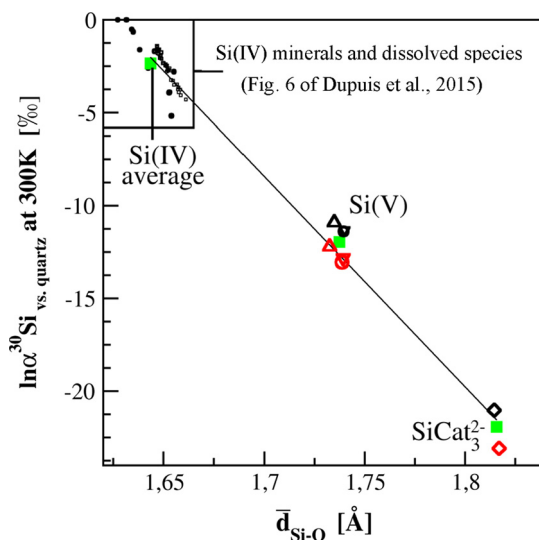


Fig. 3. Theoretical equilibrium Si isotopes fractionation factors relative to quartz of Si-diolate (SiDio, open upward pointing triangle), Si-methylactate (SiLact, open downward pointing triangle), Si-glyconate (SiGly, open circle) and Si-catecholate (SiCat₃^{2−}, open diamond), plotted as a function of the mean Si-O distance of the aqueous complex, and comparison with minerals and dissolved species with IV-fold Si coordination (upper left insert). For a more detailed description of the insert, we refer the reader to Fig. 6 of Dupuis et al. (2015). Outside of the insert, black and red symbols correspond to the results of PBE and vdW-DF2 calculations, respectively. The three average points of the Si(IV) minerals (PBE calculations only), and of the Si(V) and Si(VI) compounds (both PBE and vdW-DF2 calculations are considered) are reported (green squares). The regression line going through these three points has the equation $\ln \alpha = -113 * (\bar{d}_{\text{Si-O}} - 1.626)$.

the PBE and vdW-DF2 functionals. Results show that the fractionation properties of quartz calculated using either functional yield nearly identical results. The compounds considered in these calculations other than quartz, are molecular crystals where weak dispersion forces play an important role differently from previous calculations on silicate minerals (Méheut et al., 2007, 2009; Méheut and Schauble, 2014; Huang et al., 2014). Previous calculations were based on the PBE (Perdew et al., 1996) or LDA (Perdew and Zunger, 1981) functionals, which by their construction essentially miss dispersion effects. Improved functionals, meant to better account for dispersion, have been designed to account for these effects. Notably, the vdW-DF2 non-local functional (Lee et al., 2010) was also considered in this study. The calculated Si isotope fractionation of investigated compounds relative to quartz is plotted as a function of Si-O bond distance in Fig. 3. This figure shows that the vdW-DF2 functional, designed to take into account dispersion forces better than PBE, gives identical Si-O distances, but slightly larger Si isotope fractionations with respect to quartz. As discussed in Supplemental Information A, it is difficult to verify the relative accuracy of the vdW-DF2 functional owing to the lack of comparable direct measurements. Consequently, the difference between the results obtained using the two functionals were used to estimate the error of these calculations. Resulting calculations give at 25 °C $\Delta_{\text{eq}}^{30}\text{Si}_{\text{SiCat}_3^{2-}\text{-quartz}} = -21.9 \pm 1.2\text{‰}$, $\Delta_{\text{eq}}^{30}\text{Si}_{\text{SiDio}\text{-quartz}} = -11.7 \pm 0.6\text{‰}$, $\Delta_{\text{eq}}^{30}\text{Si}_{\text{SiGly}\text{-quartz}} = -11.7 \pm 0.9\text{‰}$, $\Delta_{\text{eq}}^{30}\text{Si}_{\text{SiLact}\text{-quartz}} = -12.2 \pm 0.7\text{‰}$. The equations describing these fractionations as a function of temperature are listed in Table 1. Combining these values with values of the silicic acid-quartz equilibrium Si isotopes fractionation (Dupuis et al., 2015) $\Delta_{\text{eq}}^{30}\text{Si}_{\text{H}_4\text{SiO}_4^0\text{-quartz}} = -2.10\text{‰}$ at 25 °C, provides the following Si isotope equilibrium fractionation factors among these compounds and aqueous silicic acid: $\Delta_{\text{eq}}^{30}\text{Si}_{\text{SiCat}_3^{2-}\text{-H}_4\text{SiO}_4^0} = -19.8 \pm 1.2\text{‰}$ and $\Delta_{\text{eq}}^{30}\text{Si}_{\text{SiDio}\text{-H}_4\text{SiO}_4^0} = -9.6 \pm 0.6\text{‰}$ (see Fig. 4).

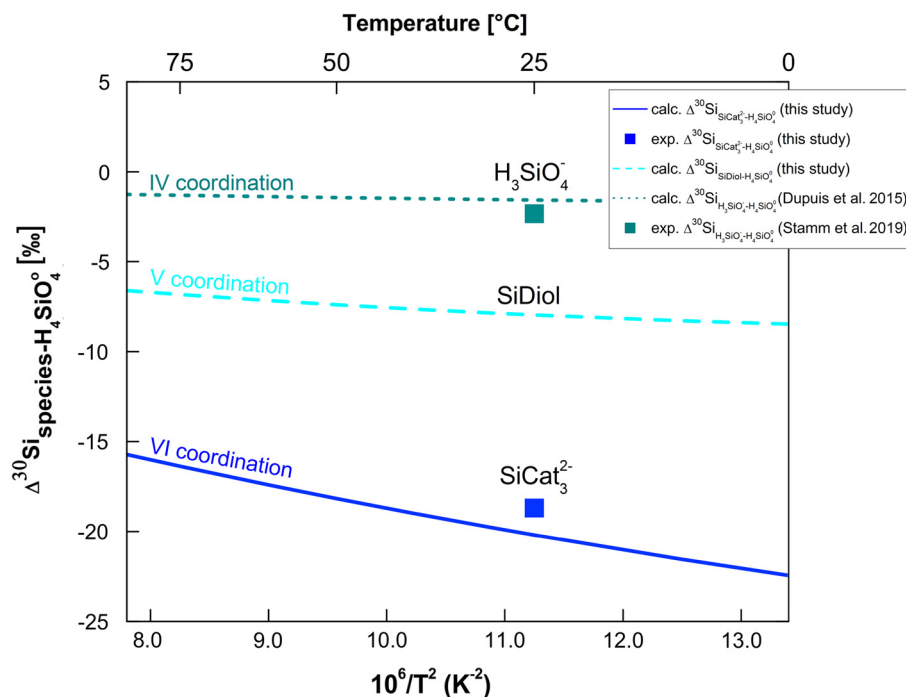


Fig. 4. Results of ab initio calculations, showing the evolution of the equilibrium fractionation factors between Si-catecholate (SiCat_3^{2-}) and silicic acid (H_4SiO_4^0 ; solid line), Si-diolate (SiDiol) and H_4SiO_4^0 (dashed line), and H_3SiO_4^- and silicic acid (dotted line) as a function of temperature. Experimental results are shown by square symbols.

Table 1

Fits of $1000\ln\alpha^{30}\text{Si}_{\text{SiCat}_3^{2-}\text{-silica}}$ and $\alpha^{30}\text{Si}_{\text{SiDiol-silica}}$ based on $ax^2 + bx^3$, with $x = 10^3/T(\text{K})$. The resulting fits are the average of the PBE, and the vdW-DF2 calculations. The uncertainties correspond to the difference between the two results.

System	T (°C)	Fit parameters		Uncertainties	
		a	b	a	b
SiCat - quartz	0-1100	-3.16	0.354	0.14	-0.011
SiCat - H_4SiO_4	0-50	-3.11	0.392	0.14	-0.011
SiDiol - quartz	0-1100	-1.73	0.205	0.08	-0.008
SiDiol - H_4SiO_4	0-50	-1.54	0.248	0.08	-0.008
SiGly - quartz	0-1100	-1.86	0.226	0.11	-0.010
SiGly - H_4SiO_4	0-50	-1.81	0.268	0.11	-0.010
SiLact - quartz	0-1100	-1.74	0.195	0.08	-0.005
SiLact - H_4SiO_4	0-50	-1.69	0.237	0.08	-0.005

3.2. Experimentally determined equilibrium Si isotope fraction factors between aqueous silicic acid and the aqueous Si-catecholate complex

The results of first-principle calculations described above suggest a large Si isotope fractionation due to aqueous Si-organic ligand complexing. To validate the results of these first-principle calculations, isotope exchange experiments at bulk chemical equilibrium were performed to measure the equilibrium Si isotope fraction factor between aqueous silicic acid (H_4SiO_4^0) and the aqueous Si-catecholate complex (SiCat_3^{2-}). The presence of the aqueous Si-catecholate complex was confirmed by NMR measurements. The spectra of two representative 1.8 mM silica solutions are shown in Supplemental Fig. B.1a and b. The NMR spectrum of the solution containing 0.05 mol/l catechol shows a clear shift of the ^{29}Si peak to 144.2 ppm, compared to 72.3 ppm in the catechol-free solution. This confirms that silicon is mainly present in the form of the VI-coordinated Si-catecholate anion in the solution containing 0.05 mol/l catechol.

In the first step of the experiments, the reactive aqueous solutions were chemically equilibrated with pre-washed amorphous $\text{SiO}_2\text{,am}$ powder. The chemical evolution of these fluids during this first equilibration step can be seen in the Supplemental Table B.2. After attainment of $\text{SiO}_2\text{,am}$ -fluid chemical equilibrium, the solids

and fluids were separated and a ^{29}Si spike was added to the fluid. Some of the original pre-washed $\text{SiO}_2\text{,am}$ powder was added to the spiked fluid, which was then in chemical equilibrium but isotopic disequilibrium with the $\text{SiO}_2\text{,am}$ powder. For each series, 8 individual closed system experiments were prepared, and stopped after pre-chosen time intervals (Table 2).

The water content of the silica powder recovered from the longest experiments of each series decreased slightly from 7.86% to 6.54%. The grain size of the solids did not change but their BET surface area was 10–15% lower than that of the starting powder. These changes could result from some minor Ostwald ripening of the amorphous silica grains during the experiments; however, the post experiment solids appear unchanged by the isotope exchange experiments under scanning electron microscope (SEM) and transmission electron microscope (TEM). Representative images are shown in Fig. 2.

The pH and Si concentration of the aqueous 0.05 mol/kg catechol fluid remained constant during the isotope exchange experiments as shown in Fig. 5. The aqueous 0.08 mol/kg catechol experiments however, show an initial decrease of pH from 8.9 to 8.7, and a decrease in dissolved Si concentration of 9%, but this stabilised after 6 hours. The longest duration experiment of the 0.05 and 0.08 mol/kg catechol experiment series showed a decrease of $\sim 10\%$ in dissolved Si concentration likely due to slight catechol oxidation. These two fluids were not considered in the retrieval of equilibrium isotope fractionation factors.

The temporal evolution of the Si isotopic compositions of the aqueous fluids and solids during the two 7-day of isotopic exchange experimental series are shown in Fig. 5. In both experimental series, the $\delta^{29}\text{Si}$ values of the fluids and solids shown in Fig. 5 a and b mirror one another consistent with Si isotope exchange at bulk chemical equilibrium. The ^{29}Si concentrations of the enriched fluids decrease rapidly during the first 3 h and the corresponding $\delta^{29}\text{Si}$ value of the solids increase. A similar trend is exhibited by the $\delta^{30}\text{Si}$ values shown for both experiments in Fig. 5. All chemical and isotopic compositions of the fluids and solids are listed in Table 2.

Table 2

Summary of the results of the isotopic exchange experiments performed in this study. Uncertainties of the isotopic measurements are expressed as 2 SD (Standard Deviation) and 2 SE (Standard Error). The 2 SE is computed following the relation: $SE = \frac{SD}{\sqrt{(n-1)}} \times t$, where n denotes the number of measurements performed and t denotes the Student t-factor. δ_{eq} represents the equilibrium isotopic composition of ^{29}Si and F denotes the degree of isotopic exchange. ^a denotes the spiked initial solution.

Exp.	time (d)	pH	Si-conc. (ppm)	S _{BET} (m ² /g)	solution						amorphous SiO ₂						δ _{eq} ²⁹ Si (‰)	F _{sol.}	ln(1-F)
					δ ³⁰ Si (‰)	2SD (‰)	2SE (‰)	δ ²⁹ Si (‰)	2SD (‰)	2SE (‰)	δ ³⁰ Si (‰)	2SD (‰)	2SE (‰)	δ ²⁹ Si (‰)	2SD (‰)	2SE (‰)			
0.05 M Catechol																	−7.70		
SigC0.05-0	0	8.9	343	195.6	−8.60	0.27	0.22	−4.42	0.06	0.05	−0.04	0.20	0.09	−0.01	0.15	0.07			
SigC0.05-0 S ^a	0	8.9	345		−8.40	0.32	0.26	21.31	0.14	0.11	−0.04	0.20	0.09	−0.01	0.15	0.07		0.000	0.00
SigC0.05-1	0.125	8.9	300		−10.83	0.12	0.10	7.87	0.02	0.02	−0.02	0.04	0.05	0.56	0.05	0.06		0.463	−0.62
SigC0.05-2	0.25	8.9	295		−11.37	0.08	0.07	7.81	0.03	0.02	0.06	0.16	0.10	0.60	0.08	0.05		0.466	−0.63
SigC0.05-3	0.5	8.9	321		−11.93	0.40	0.50	9.97	0.19	0.23	0.06	0.08	0.05	0.53	0.03	0.02		0.391	−0.50
SigC0.05-4	1	8.8	331		−13.04	0.34	0.42	5.82	0.09	0.11	0.17	0.16	0.10	0.72	0.07	0.05		0.534	−0.76
SigC0.05-5	1.5	8.9	314		−13.55	0.20	0.24	5.51	0.06	0.07	0.21	0.13	0.16	0.70	0.03	0.03		0.545	−0.79
SigC0.05-6	3	8.8	315		−14.17	0.29	0.36	3.00	0.13	0.17	0.13	0.06	0.07	0.86	0.03	0.04		0.631	−1.00
SigC0.05-7	5	8.9	318	−14.20	0.05	0.06	2.04	0.03	0.04	0.12	0.02	0.03	0.89	0.10	0.12		0.664	−1.09	
SigC0.05-8	7	8.8	293	174.7	−14.20	0.31	0.39	1.37	0.08	0.09	0.15	0.16	0.10	0.90	0.03	0.02		0.688	−1.16
0.08 M Catechol																	−7.53		
SiC 0.08 0	0	8.9	612	195.6	−5.73	0.24	0.19	−2.90	0.06	0.05	−0.04	0.20	0.09	−0.01	0.15	0.07			
SiC 0.08 0 S ^a	0	8.9	599		−5.70	0.15	0.12	22.92	0.02	0.02	−0.04	0.20	0.09	−0.01	0.15	0.07		0.000	0.00
SiC 0.08 1	0.125	8.8	565		−7.86	0.17	0.13	11.28	0.09	0.07	0.06	0.16	0.07	0.97	0.11	0.05		0.382	−0.48
SiC 0.08 2	0.25	8.8	558		−8.88	0.27	0.22	11.33	0.09	0.07	0.17	0.23	0.11	0.94	0.10	0.05		0.381	−0.48
SiC 0.08 3	0.5	8.7	547		−10.21	0.23	0.19	12.80	0.15	0.12	0.21	0.22	0.10	0.78	0.11	0.05		0.332	−0.40
SiC 0.08 4	1	8.7	547		−10.97	0.14	0.11	9.57	0.06	0.05	0.28	0.09	0.04	1.04	0.07	0.03		0.438	−0.58
SiC 0.08 5	1.5	8.7	535		−11.59	0.16	0.13	9.27	0.04	0.03	0.41	0.08	0.04	1.11	0.09	0.04		0.448	−0.59
SiC 0.08 6	3	8.7	540		−12.28	0.09	0.07	7.16	0.07	0.06	0.36	0.20	0.09	1.21	0.17	0.08		0.518	−0.73
SiC 0.08 7	5	8.7	533	−12.63	0.14	0.11	6.26	0.06	0.04	0.42	0.16	0.07	1.40	0.11	0.05		0.547	−0.79	
SiC 0.08 8	7	8.7	496	165.6	−13.04	0.03	0.02	5.41	0.08	0.06	0.45	0.09	0.05	1.39	0.06	0.03		0.575	−0.86

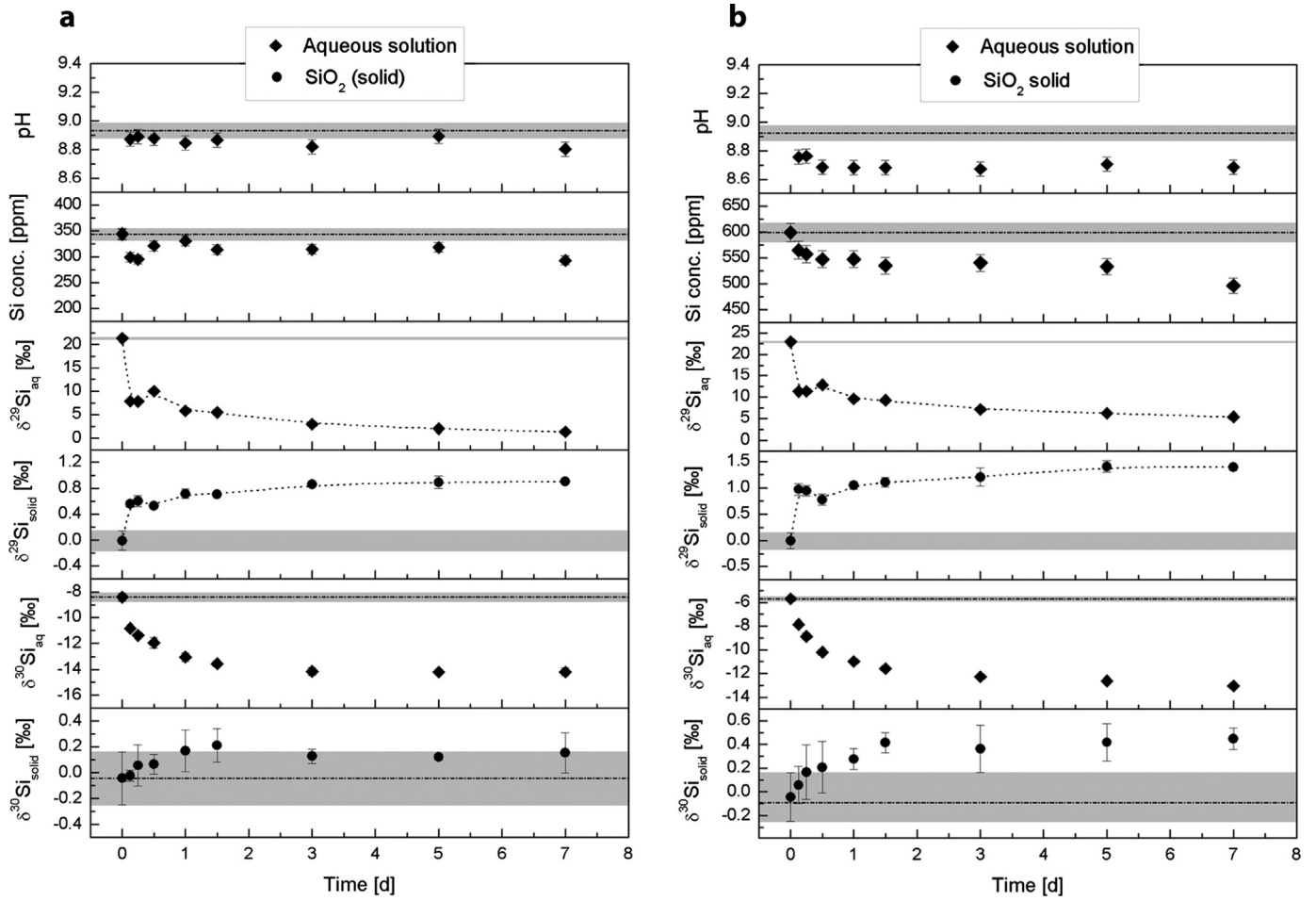


Fig. 5. Plots of pH, Si concentrations and isotopic compositions of solids and aqueous solutions over time during the isotopic exchange experiments. The 2 S.D. uncertainties of data points are denoted by the error bars. Initial values are represented by dashed lines with their 2 S.D. error envelope. A. 0.05 M catechol experiment, B. 0.08 M catechol experiment.

3.3. Retrieval of silicon equilibrium isotope fractionation factors

To determine the equilibrium fractionation factors between the experimental fluids and the $\text{SiO}_2\text{,am}$ powder ($\Delta_{eq}^{30}\text{Si}_{fluid-SiO_2,am}$), the isotopic compositions $\delta^{30}\text{Si}$ of the fluids and the amorphous silica powder were first plotted as a function of the degree of isotopic exchange, F , (see the materials and methods section for details) as shown in Fig. 6. F values range from 0 to 1, where 1 indicates that 100% of the isotopes are exchanged between fluid and $\text{SiO}_2\text{,am}$ powder, and isotopic equilibrium is reached. It can be seen that at the end of the experimental series, from 60 to 70% of the equilibrium fractionation value was attained (Fig. 6 a and b). The three-isotope method allows the determination of the equilibrium fractionation factor $\Delta_{eq}^{30}\text{Si}_{fluid-SiO_2,am}$, by extrapolation of the isotopic compositions of the fluid and $\text{SiO}_2\text{,am}$ to $F = 1$ (Matthews et al., 1983). The overall $\Delta_{eq}^{30}\text{Si}_{fluid-SiO_2,am}$ generated from the experiments performed in this study from the experimental series run in the 0.05 mol/kg catechol solutions was $-16.38 \pm 1.71\text{‰}$, and that obtained from the experiments run in the presence of 0.08 mol/kg catechol was $-18.01 \pm 3.43\text{‰}$.

The equilibrium fractionation factor between the fluid and amorphous silica is the weighted sum of the equilibrium fractionation factors between the Si aqueous species present in the solution and amorphous silica (see Eqn. (1)). In the experiments performed in this study, silicic acid and the Si-catecholate complex (SiCat_3^{2-}) were the only Si aqueous species present in solution as shown by the results of speciation calculations with the

PHREEQC code (Parkhurst and Appelo, 2013) listed in Table 3. The equilibrium Si isotope fractionation between SiCat_3^{2-} and H_4SiO_4^0 , $\Delta_{eq}^{30}\text{Si}_{\text{SiCat}_3^{2-}-\text{H}_4\text{SiO}_4^0}$, could therefore be derived by modifying Eqn. (1) to

$$\Delta_{eq}^{30}\text{Si}_{fluid-SiO_2,am} = x_{\text{H}_4\text{SiO}_4^0} \Delta_{eq}^{30}\text{Si}_{\text{H}_4\text{SiO}_4^0-SiO_2,am} + x_{\text{SiCat}_3^{2-}} \Delta_{eq}^{30}\text{Si}_{\text{SiCat}_3^{2-}-SiO_2,am} \quad (8)$$

and

$$\Delta_{eq}^{30}\text{Si}_{\text{SiCat}_3^{2-}-\text{H}_4\text{SiO}_4^0} = \Delta_{eq}^{30}\text{Si}_{\text{SiCat}_3^{2-}-SiO_2,am} - \Delta_{eq}^{30}\text{Si}_{\text{H}_4\text{SiO}_4^0-SiO_2,am} \quad (9)$$

where x_i stands for the mole fraction of the i th aqueous Si species. Using the equilibrium isotope fractionation factors between the fluid and $\text{SiO}_2\text{,am}$ determined in this study and between H_4SiO_4^0 and $\text{SiO}_2\text{,am}$ determined by Stamm et al. (2019), the equilibrium fractionation factor between SiCat_3^{2-} and H_4SiO_4^0 , $\Delta_{eq}^{30}\text{Si}_{\text{SiCat}_3^{2-}-\text{H}_4\text{SiO}_4^0}$, can be derived for both catechol fluids (see Table 3). Taken together they provide an equilibrium isotope fractionation factor between the SiCat_3^{2-} and H_4SiO_4^0 aqueous species, $\Delta_{eq}^{30}\text{Si}_{\text{SiCat}_3^{2-}-\text{H}_4\text{SiO}_4^0}$ of $-18.69 \pm 0.49\text{‰}$. This value is in close agreement with that determined with the first-principle calculations as shown in Fig. 4.

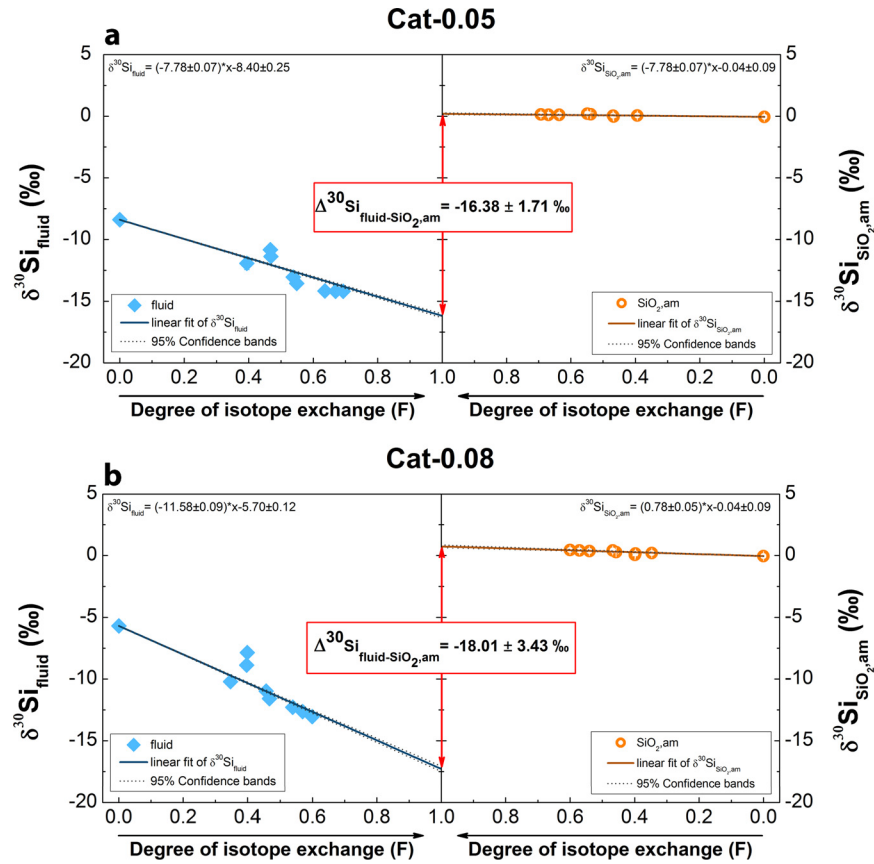


Fig. 6. The isotopic composition of the solids (SiO_2,am) and aqueous fluids as a function of the degree of isotope exchange (F) during the isotope exchange experiments. a) 0.05 M catechol experiment (Cat-0.05), and b) 0.08 M catechol experiment (Cat-0.08).

4. Discussion

4.1. Effect of aqueous Si coordination on its fractionation properties: First-principle calculations

Fig. 3 shows the relationship between the coordination of the Si species, its mean Si-O bond distance ($\bar{d}_{\text{Si-O}}$) and the computed equilibrium Si isotopic fractionation with respect to quartz. This relationship was previously discussed for the case of compounds containing IV-fold Si (Méhaut and Schauble, 2014; Dupuis et al., 2015). Here, a regression based on IV, V and VI coordination (see Fig. 3) leads to:

$$\Delta^{30}\text{Si}_{\text{silicate-qtz}}(\text{at } 300^\circ\text{K}) = -113 * (\bar{d}_{\text{Si-O}} - 1.626) \quad (10)$$

4.2. Equilibrium Silicon isotope fractionation in the presence of catechol

The first-principle calculations and the experiments performed in this study verify an extreme equilibrium Si isotope fractionation in the presence of the organic ligand catechol. The 25 °C calculated equilibrium isotope fractionation factor between the aqueous Si-catecholate complex (SiCat_3^{2-}) and silicic acid (H_4SiO_4^0) is $-19.8 \pm 1.2\text{‰}$ at 25 °C while the experimental value was determined to be $-18.69 \pm 0.49\text{‰}$. This contrasts with the relatively small 25 °C equilibrium isotopic fractionation factors observed between the two major naturally forming aqueous inorganic Si species H_3SiO_4^- and H_4SiO_4^0 ; values of $\Delta_{\text{eq}}^{30}\text{Si}_{\text{H}_3\text{SiO}_4^- - \text{H}_4\text{SiO}_4^0}$ range from $-1.60 \pm 0.30\text{‰}$ to $-2.34 \pm 0.13\text{‰}$ (Dupuis et al., 2015; Stamm et al., 2019). In each case silicic acid is enriched in the heavier ^{30}Si isotope, but this fractionation is far greater in the presence of the aqueous Si-catecholate complex (SiCat_3^{2-}).

This large increase in Si equilibrium isotope fractionation is due to the increase in the aqueous Si coordination number from IV to VI, and the resulting increase of the Si-O bond length ($\sim 1.645 \text{ \AA}$ for Si(IV) versus $\sim 1.815 \text{ \AA}$ for Si(VI)) due to the addition of catechol to the aqueous solution. Note, the amount of catechol used in our experiments is far higher than that typically found in nature. Nevertheless, even a small concentration of catechol or any organic ligand forming with Si organosilicon complexes containing hexa-oxo-silicon sites can have a significant effect on the equilibrium fractionation factors between aqueous Si and co-existing solid phases. This is because the overall fractionation of an element between a fluid and an aqueous phase depends on the mole fraction weighted distributed speciation in the aqueous phase (see Eqn. (1)).

The formation of aqueous V-fold coordinated silicon species with aliphatic sugar acids or polyhydroxy alcohols has been demonstrated in previous studies (Kinrade et al., 1999, 2001a, 2001b). The equilibrium isotopic fractionation factors associated with such penta-oxo-silicon coordinations have not yet been investigated experimentally. However, the first principle calculations performed in this study suggest that the equilibrium fractionation factor between a V-fold coordinated aqueous Si complex and H_4SiO_4^0 is -9.9‰ , which is approximately half of the corresponding fractionation between VI-fold coordinated Si and H_4SiO_4^0 .

4.3. Implications for biosilicification

Silicon is an essential element in the biomineralization i.e. biosilicification processes. When dissolved Si is absorbed into organisms, the proteinaceous matrices within these organisms can facilitate the precipitation of Si and thus the mineral growth (Perry, 2003). Enzymes and proteins play an important role in the se-

molecules containing at least four adjacent hydroxyl groups. *S. enterobacti*, a complex of the siderophore enterobactin, where Si is hexacoordinated, has been isolated from an endophytic *Streptomyces* sp. occurring in *Piper guinensis* (Kenla et al., 2013). The results presented in this study suggest that the presence of even a small concentration of hypercoordinated organosilicon complexes would lead to a strong negative fractionation between the fluid phase and Si incorporated in the plant structure.

As aqueous Si complexation alters the fractionation of this metal into solids, and as aqueous ligands are abundant in various organisms, it seems reasonable to conclude that insight into the biosilicification process would be gained from the Si isotopic compositions of biomaterials. The results in this study show that both rigorous experiments and detailed first-principle calculations can aid in this effort.

5. Conclusions

The results of this study demonstrate that the formation of organosilicon complexes containing aqueous pentaoxo- and hexaoxo- silicon species rather than the IV-coordinated Si centres typical of most aqueous silica species can have a large influence on the equilibrium Si isotope fractionation between fluids and Si-bearing solids. Indeed, the study has shown that the isotopic composition of the aqueous hexaoxo-SiCat₂²⁻ complex is about 19‰ lighter than that of aqueous silicic acid at ambient temperature. This value, which is far larger than ever previously measured for Si fractionation between a natural solid and its coexisting aqueous fluid is in close agreement with the results of the first-principle calculations performed in this study demonstrating the robustness of both type of Si isotope quantifications. Note that the Si isotope composition of organosilicon complexes containing pentaoxo-silicon is calculated for the Si-diolate, Si-glyconate and Si-methylactate systems to be about 10 ‰ lighter than that of silicic acid. Such results demonstrate that the presence of aqueous organic ligands in natural systems can play an important role on the Si isotopes fractionation and thus might explain the strong negative fractionation found in numerous biological systems.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was funded by ISONOSE a People Programme (Marie Curie Actions) of the European Unions' Seventh Framework Programme FP7/2017-2013/ under REA grant agreement n° [608069]. This work was performed using HPC resources from CALIMP (Calcul eb Midi-Pyrénées; Grant 2017-P1037). The authors acknowledge Gwénaëlle Guittier from the Laboratoire de Génie Chimique (INP-ENSIACET) for TGA measurements, Philippe De Parseval, and Teresa Hungria from the Centre de MicroCaractérisation Raimond Castaing for SEM and TEM measurements, and Marc Vedrenne from the Institut de Chimie de Toulouse (ICT) for NMR measurements. Furthermore, the authors thank Alain Castillo, Carole Causserand, and Manuel Henry from the Géosciences Environnement Toulouse for their assistance in the laboratories. Kate Hendry from the University of Bristol is acknowledged for her input on biosilicification. François-Xavier d'Abzac, Anna Harrison, Chiara Marieni, Moritz Lissner, Giuseppe Saldi, and Martin Voigt are acknowledged for constructive discussions, and contributions to this work. This work has benefited from the insightful comments of two anonymous reviewers.

Appendix A. Supplementary material

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.epsl.2020.116287>.

References

- Balan, E., Noireaux, J., Mavromatis, V., Saldi, G.D., Montouillout, V., Blanchard, M., Pietrucci, F., Gervais, C., Rustad, J.R., Schott, J., Gaillardet, J., 2018. Theoretical isotopic fractionation between structural boron in carbonates and aqueous boric acid and borate ion. *Geochim. Cosmochim. Acta* 222, 117–129. <https://doi.org/10.1016/j.gca.2017.10.017>.
- Baldereschi, A., 1973. Mean-value point in the Brillouin zone. *Phys. Rev. B* 7, 5212–5215. <https://doi.org/10.1103/PhysRevB.7.5212>.
- Barnum, D.W., 1972. Reaction of catechol with colloidal silica and silicic acid in aqueous ammonia. *Inorg. Chem.* 11, 1424–1429. <https://doi.org/10.1021/ic50112a052>.
- Barnum, D.W., 1970. Catechol complexes with silicon. *Inorg. Chem.* 9, 1942–1943. <https://doi.org/10.1021/ic50090a038>.
- Baroni, S., de Gironcoli, S., Dal Corso, A., Giannozzi, P., 2001. Phonons and related crystal properties from density-functional perturbation theory. *Rev. Mod. Phys.* 73, 515–562. <https://doi.org/10.1103/RevModPhys.73.515>.
- Benner, K., Klüfers, P., Schuhmacher, J., 1999. Diolato-silicat- und -germanat-Ionen aus wäßrig-alkalischer Lösung. *Z. Anorg. Allg. Chem.* 625, 541–543. [https://doi.org/10.1002/\(SICI\)1521-3749\(199904\)625:4<541::AID-ZAAC541>3.0.CO;2-A](https://doi.org/10.1002/(SICI)1521-3749(199904)625:4<541::AID-ZAAC541>3.0.CO;2-A).
- Benner, K., Klüfers, P., Vogt, M., 2003. Hydrogen-bonded sugar-alcohol trimers as hexadentate silicon chelators in aqueous solution. *Angew. Chem. Int. Ed. Engl.* 42, 1058–1062. <https://doi.org/10.1002/anie.200390274>.
- Bigeleisen, J., Mayer, M.G., 1947. Calculation of equilibrium constants for isotopic exchange reactions. *J. Chem. Phys.* 15, 261–267. <https://doi.org/10.1063/1.1746492>.
- Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* 60, 309–319. <https://doi.org/10.1021/ja01269a023>.
- Cassarino, L., Coath, C.D., Xavier, J.R., Hendry, K.R., 2018. Silicon isotopes of deep sea sponges: new insights into biomineralisation and skeletal structure. *Biogeosciences* 15, 6959–6977. <https://doi.org/10.5194/bg-15-6959-2018>.
- Cella, J.A., Cargioli, J.D., Williams, E.A., 1980. ²⁹Si NMR of five- and six-coordinate organosilicon complexes. *J. Organomet. Chem.* 186, 13–17. [https://doi.org/10.1016/S0022-328X\(00\)93813-0](https://doi.org/10.1016/S0022-328X(00)93813-0).
- Cornu, S., Lucas, Y., Lebon, E., Ambrosi, J.P., Luizão, F., Rouiller, J., Bonnay, M., Neal, C., 1999. Evidence of titanium mobility in soil profiles, Manaus, central Amazonia. *Geoderma* 91, 281–295. [https://doi.org/10.1016/S0016-7061\(99\)00007-5](https://doi.org/10.1016/S0016-7061(99)00007-5).
- Dal Corso, A., 2014. Pseudopotentials periodic table: from H to Pu. *Comput. Mater. Sci.* 95, 337–350. <https://doi.org/10.1016/j.commatsci.2014.07.043>.
- Donhär, W., Elhofer, I., Wiede, P., Schubert, U., 1998. Elemental silicon and solid SiO give the same products as SiO₂ upon reaction with alkali-metal glycolates. *J. Chem. Soc., Dalton Trans.*, 2445–2446. <https://doi.org/10.1039/A803672A>.
- Dupuis, R., Benoit, M., Nardin, E., Méheut, M., 2015. Fractionation of silicon isotopes in liquids: the importance of configurational disorder. *Chem. Geol.* 396, 239–254. <https://doi.org/10.1016/j.chemgeo.2014.12.027>.
- Frings, P.J., Clymans, W., Fontorbe, G., De La Rocha, C.L., Conley, D.J., 2016. The continental Si cycle and its impact on the ocean Si isotope budget. *Chem. Geol.* 425, 12–36. <https://doi.org/10.1016/j.chemgeo.2016.01.020>.
- Füger, A., Méheut, M., Mavromatis, V., Leis, A., Dietzel, M., 2018. Oxygen isotope fractionation during smithsonite formation from aqueous solutions. *Chem. Geol.* 495, 76–89. <https://doi.org/10.1016/j.chemgeo.2018.08.005>.
- Georg, R.B., Reynolds, B.C., Frank, M., Halliday, A.N., 2006. New sample preparation techniques for the determination of Si isotopic compositions using MC-ICPMS. *Chem. Geol.* 235, 95–104. <https://doi.org/10.1016/j.chemgeo.2006.06.006>.
- Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., Ceresoli, D., Chiarotti, G.L., Cococcioni, M., Dabo, I., Dal Corso, A., de Gironcoli, S., Fabris, S., Fratesi, G., Gebauer, R., Gerstmann, U., Gougousis, C., Kokalj, A., Lazzeri, M., Martin-Samos, L., Marzari, N., Mauri, F., Mazzarello, R., Paolini, S., Pasquarello, A., Paulatto, L., Sbraccia, C., Scandolo, S., Sclauzero, G., Seitsonen, A.P., Smogunov, A., Umari, P., Wentzcovitch, R.M., 2009. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J. Phys. Condens. Matter* 21, 395502. <https://doi.org/10.1088/0953-8984/21/39/395502>.
- Hahn, F.E., Keck, M., Raymond, K.N., 1995. Catecholate complexes of silicon: synthesis and molecular and crystal structures of [Si(cat)₂].cntdot. 2THF and Li₂[Si(cat)₃].cntdot.3.5dme (cat = catecholate dianion). *Inorg. Chem.* 34, 1402–1407. <https://doi.org/10.1021/ic00110a018>.
- Hendry, K.R., Robinson, L.F., 2012. The relationship between silicon isotope fractionation in sponges and silicic acid concentration: modern and core-top studies of biogenic opal. *Geochim. Cosmochim. Acta* 81, 1–12. <https://doi.org/10.1016/j.gca.2011.12.010>.
- Hohenberg, P., Kohn, W., 1964. Inhomogeneous electron gas. *Phys. Rev.* 136, B864–B871. <https://doi.org/10.1103/PhysRev.136.B864>.
- Huang, F., Wu, Z., Huang, S., Wu, F., 2014. First-principles calculations of equilibrium silicon isotope fractionation among mantle minerals. *Geochim. Cosmochim. Acta* 140, 509–520. <https://doi.org/10.1016/j.gca.2014.05.035>.

- Jugdaohsingh, R., Pedro, L.D., Watson, A., Powell, J.J., 2015. Silicon and boron differ in their localization and loading in bone. *Bone Rep.* 1, 9–15. <https://doi.org/10.1016/j.bonr.2014.10.002>.
- Kenla, T.J.N., Tatong, M.D.K., Talontsi, F.M., Dittrich, B., Frauendorf, H., Laatsch, H., 2013. Si-enterobactin from the endophytic streptomyces sp. KT-S1-B5 – a potential silicon transporter in nature?. *Chem. Commun.* 49, 7641. <https://doi.org/10.1039/c3cc44437f>.
- Kinrade, S.D., Del Nin, J.W., Schach, A.S., Sloan, T.A., Wilson, K.L., Knight, C.T.G., 1999. Stable five- and six-coordinated silicate anions in aqueous solution. *Science* 285, 1542–1545. <https://doi.org/10.1126/science.285.5433.1542>.
- Kinrade, S.D., Gillson, A.-M.E., Knight, C.T.G., 2002. Silicon-29 NMR evidence of a transient hexavalent silicon complex in the diatom *Navicula pelliculosa*. *J. Chem. Soc., Dalton Trans.*, 307–309. <https://doi.org/10.1039/b105379p>.
- Kinrade, S.D., Schach, A.S., Hamilton, R.J., Knight, C.T.G., 2001a. NMR evidence of penta-oxo organosilicon complexes in dilute neutral aqueous silicate solutions. *Chem. Commun.*, 1564–1565. <https://doi.org/10.1039/b104713m>.
- Kinrade, S.D., Hamilton, R.J., Schach, A.S., Knight, C.T.G., 2001b. Aqueous hypervalent silicon complexes with aliphatic sugar acids. *J. Chem. Soc., Dalton Trans.*, 961–963. <https://doi.org/10.1039/b010111g>.
- Kohn, W., Sham, L.J., 1965. Self-consistent equations including exchange and correlation effects. *Phys. Rev.* 140, A1133–A1138. <https://doi.org/10.1103/PhysRev.140.A1133>.
- Kubicki, J.D., Heaney, P.J., 2003. Molecular orbital modeling of aqueous organosilicon complexes: implications for silica biomineralization. *Geochim. Cosmochim. Acta* 67, 4113–4121. [https://doi.org/10.1016/S0016-7037\(03\)00093-0](https://doi.org/10.1016/S0016-7037(03)00093-0).
- Lee, K., Murray, É.D., Kong, L., Lundqvist, B.I., Langreth, D.C., 2010. Higher-accuracy van der Waals density functional. *Phys. Rev. B* 82, 081101(R). <https://doi.org/10.1103/PhysRevB.82.081101>.
- Marron, A., Cassarino, L., Hatton, J., Curnow, P., Hendry, K.R., 2019. The silicon isotopic composition of choanoflagellates: implications for a mechanistic understanding of isotopic fractionation during biosilicification. *Biogeosciences* 16, 4805–4813. <https://doi.org/10.5194/bg-2019-181>.
- Matsuhiya, Y., Goldsmith, J.R., Clayton, R.N., 1978. Mechanisms of hydrothermal crystallization of quartz at 250 °C and 15 kbar. *Geochim. Cosmochim. Acta* 42, 173–182. [https://doi.org/10.1016/0016-7037\(78\)90130-8](https://doi.org/10.1016/0016-7037(78)90130-8).
- Matthews, A., Goldsmith, J.R., Clayton, R.N., 1983. On the mechanisms and kinetics of oxygen isotope exchange in quartz and feldspars at elevated temperatures and pressures. *Geol. Soc. Am. Bull.* 94, 396. [https://doi.org/10.1130/0016-7606\(1983\)94<396:OTMAKO>2.0.CO;2](https://doi.org/10.1130/0016-7606(1983)94<396:OTMAKO>2.0.CO;2).
- Méheut, M., Lazzari, M., Balan, E., Mauri, F., 2009. Structural control over equilibrium silicon and oxygen isotopic fractionation: a first-principles density-functional theory study. In: *Applications of Non-traditional Stable Isotopes in High-Temperature Geochemistry*. *Chem. Geol.* 258, 28–37. <https://doi.org/10.1016/j.chemgeo.2008.06.051>.
- Méheut, M., Lazzari, M., Balan, E., Mauri, F., 2007. Equilibrium isotopic fractionation in the kaolinite, quartz, water system: prediction from first-principles density-functional theory. *Geochim. Cosmochim. Acta* 71, 3170–3181. <https://doi.org/10.1016/j.gca.2007.04.012>.
- Méheut, M., Schauble, E.A., 2014. Silicon isotope fractionation in silicate minerals: insights from first-principles models of phyllosilicates, albite and pyrope. *Geochim. Cosmochim. Acta* 134, 137–154. <https://doi.org/10.1016/j.gca.2014.02.014>.
- Milligan, A.J., Varela, D.E., Brzezinski, M.A., Morel, F.M.M., 2004. Dynamics of silicon metabolism and silicon isotopic discrimination in a marine diatom as a function of pCO₂. *Limnol. Oceanogr.* 49, 322–329. <https://doi.org/10.4319/lo.2004.49.2.0322>.
- Opfergelt, S., Cardinal, D., Henriot, C., André, L., Delvaux, B., 2006. Silicon isotope fractionation between plant parts in banana: in situ vs. in vitro. *J. Geochem. Explor.* 88, 224–227. <https://doi.org/10.1016/j.gexplo.2005.08.044>.
- Otzen, D., 2012. The role of proteins in biosilicification. *Scientifica* 2012, 1–22. <https://doi.org/10.6064/2012/867562>.
- Parkhurst, D.L., Appelo, C.A.J., 2013. *Description of Input and Examples for PHREEQC Version 3—a Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations*. U.S. Geological Survey Techniques and Methods, vol. 6, p. 497. chap. A43.
- Perdew, J.P., Burke, K., Ernzerhof, M., 1996. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 77, 3865–3868. <https://doi.org/10.1103/PhysRevLett.77.3865>.
- Perdew, J.P., Zunger, A., 1981. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B* 23, 5048–5079. <https://doi.org/10.1103/PhysRevB.23.5048>.
- Perry, C.C., 2003. Silicification: the processes by which organisms capture and mineralize silica. *Rev. Mineral. Geochem.* 54, 291–327. <https://doi.org/10.2113/0540291>.
- Poitrasson, F., 2017. Silicon isotope geochemistry. *Rev. Mineral. Geochem.* 82, 289–344. <https://doi.org/10.2138/rmg.2017.82.8>.
- Pokrovski, G.S., Schott, J., 1998. Experimental study of the complexation of silicon and germanium with aqueous organic species: implications for germanium and silicon transport and Ge/Si ratio in natural waters. *Geochim. Cosmochim. Acta* 62, 3413–3428. [https://doi.org/10.1016/S0016-7037\(98\)00249-X](https://doi.org/10.1016/S0016-7037(98)00249-X).
- Russell, W.A., Papanastassiou, D.A., Tombrello, T.A., 1978. Ca isotope fractionation on the Earth and other solar system materials. *Geochim. Cosmochim. Acta* 42, 1075–1090. [https://doi.org/10.1016/0016-7037\(78\)90105-9](https://doi.org/10.1016/0016-7037(78)90105-9).
- Savage, P.S., Armytage, R.M.G., Georg, R.B., Halliday, A.N., 2014. High temperature silicon isotope geochemistry. *Lithos* 190–191, 500–519. <https://doi.org/10.1016/j.lithos.2014.01.003>.
- Schauble, E.A., 2004. Applying stable isotope fractionation theory to new systems. *Rev. Mineral. Geochem.* 55, 65–111. <https://doi.org/10.2138/gsrmg.55.1.65>.
- Schindelin, J., Arganda-Carreras, I., Frise, E., Kaynig, V., Longair, M., Pietzsch, T., Preibisch, S., Rueden, C., Saalfeld, S., Schmid, B., Tinevez, J.-Y., White, D.J., Hartenstein, V., Eliceiri, K., Tomancak, P., Cardona, A., 2012. Fiji: an open-source platform for biological-image analysis. *Nat. Methods* 9, 676–682. <https://doi.org/10.1038/nmeth.2019>.
- Schröder, H.C., Wang, X., Tremel, W., Ushijima, H., Müller, W.E.G., 2008. Biofabrication of biosilica-glass by living organisms. *Natl. Prod. Rep.* 25, 455. <https://doi.org/10.1039/b612515h>.
- Sillen, L.G., Martell, A.E., 1971. *Stability Constants of Metal-Ion Complexes*. Suppl. Chemical Society.
- Sjöberg, S., Ingri, N., Nenner, A.-M., Öhman, L.-O., 1985. Equilibrium and structural studies of silicon(IV) and aluminium(III) in aqueous solution. 12. A potentiometric and ²⁹Si-NMR study of silicon tropolones. *J. Inorg. Biochem.* 24, 267–277. [https://doi.org/10.1016/0162-0134\(85\)85055-8](https://doi.org/10.1016/0162-0134(85)85055-8).
- Stamm, F.M., Zambardi, T., Chmieleff, J., Schott, J., von Blanckenburg, F., Oelkers, E.H., 2019. The experimental determination of equilibrium Si isotope fractionation factors among H₄SiO₄, H₃SiO₄[−] and amorphous silica (SiO₂·0.32 H₂O) at 25 and 75 °C using the three-isotope method. *Geochim. Cosmochim. Acta* 255, 49–68. <https://doi.org/10.1016/j.gca.2019.03.035>.
- Tacke, R., Pfrommer, B., Pülm, M., Bertermann, R., 1999. New chiral zwitterionic λ 5Si-silicates with an SiO₅ or SiO₄C framework: syntheses, crystal structures, and properties. *Eur. J. Inorg. Chem.* 1999, 807–816. [https://doi.org/10.1002/\(SICI\)1099-0682\(199905\)1999:5<807::AID-EJIC807>3.0.CO;2-Y](https://doi.org/10.1002/(SICI)1099-0682(199905)1999:5<807::AID-EJIC807>3.0.CO;2-Y).
- Tesson, B., Lerch, S.J.L., Hildebrand, M., 2017. Characterization of a new protein family associated with the silica deposition vesicle membrane enables genetic manipulation of diatom silica. *Sci. Rep.* 7, 13457. <https://doi.org/10.1038/s41598-017-13613-8>.
- Truesdale, V.W., LeCorre, P., 1975. *Manuel d'analyse des sels nutritifs dans l'eau de mer: Utilisation de L'autoanalyser II technique (r)*. Université de Bretagne Occidentale, France.
- Wang, W., Wei, H.-Z., Jiang, S.-Y., Liu, X., Lei, F., Lin, Y.-B., Zhao, Y., 2019. Silicon isotope geochemistry: fractionation linked to silicon complexations and its geological applications. *Molecules* 24, 1415. <https://doi.org/10.3390/molecules24071415>.
- Wille, M., Sutton, J., Ellwood, M.J., Sambridge, M., Maher, W., Eggins, S., Kelly, M., 2010. Silicon isotopic fractionation in marine sponges: a new model for understanding silicon isotopic variations in sponges. *Earth Planet. Sci. Lett.* 292, 281–289. <https://doi.org/10.1016/j.epsl.2010.01.036>.
- Zambardi, T., Poitrasson, F., 2011. Precise determination of silicon isotopes in silicate rock reference materials by MC-ICP-MS. *Geostand. Geoanal. Res.* 35, 89–99. <https://doi.org/10.1111/j.1751-908X.2010.00067.x>.
- Zhang, J., Quay, P.D., Wilbur, D.O., 1995. Carbon isotope fractionation during gas-water exchange and dissolution of CO₂. *Geochim. Cosmochim. Acta* 59, 107–114. [https://doi.org/10.1016/0016-7037\(95\)91550-D](https://doi.org/10.1016/0016-7037(95)91550-D).
- Zhou, Y., Shimizu, K., Cha, J.N., Stucky, G.D., Morse, D.E., 1999. Efficient catalysis of polysiloxane synthesis by silicatein α requires specific hydroxy and imidazole functionalities. *Angew. Chem., Int. Ed. Engl.* 38, 779–782. [https://doi.org/10.1002/\(SICI\)1521-3773\(19990315\)38:6<779::AID-ANGE779>3.0.CO;2-#](https://doi.org/10.1002/(SICI)1521-3773(19990315)38:6<779::AID-ANGE779>3.0.CO;2-#).