



# Fractionation of silicon isotopes in liquids: The importance of configurational disorder

Romain Dupuis<sup>a,b,\*</sup>, Magali Benoit<sup>b</sup>, Elise Nardin<sup>a</sup>, Merlin Méheut<sup>a</sup>

<sup>a</sup> GET, CNRS UMR 5563, IRD UR 154, Université Paul-Sabatier, Observatoire Midi-Pyrénées, 14 avenue Edouard Belin, 31400 Toulouse, France

<sup>b</sup> CEMES CNRS UPR8011, 29 rue Jeanne Marvig, 31055 Toulouse Cedex, France

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## ABSTRACT

Silicon isotopes are a promising tool to assess low-temperature geochemical processes such as weathering or chert precipitation. However, their use is hampered by an insufficient understanding of the fractionation associated with elementary processes such as precipitation or dissolution. In particular, the respective contributions of kinetic and equilibrium processes remain to be determined. In this work, equilibrium fractionation factors for silicon isotopes have been calculated using first-principles methods for quartz, kaolinite, and dissolved silicic acid ( $\text{H}_4\text{SiO}_4$  and  $\text{H}_3\text{SiO}_4^-$ ) at 300 K.

The two liquid systems are treated both as realistically as possible, and as consistently with the solids as possible. They are first simulated by *ab initio* molecular dynamics, then individual snapshots are extracted from the trajectories and relaxed, giving inherent structures (IS). The fractionation properties of these IS are then calculated. A significant variability of the fractionation properties ( $\sigma = 0.4\%$ ) is observed between the independent snapshots, emphasizing the importance of configurational disorder on the fractionation properties of solutions. Furthermore, a correlation is observed between the fractionation properties of these snapshots and the mean Si–O distances, consistent with calculations on minerals. This correlation is used to identify other parameters influencing the fractionation, such as the solvation layer. It is also used to reduce the number of configurations to be computed, and therefore the computational cost.

At 300 K, we find a fractionation factor of  $+2.1 \pm 0.2\%$  between quartz and  $\text{H}_4\text{SiO}_4$ ,  $+0.4 \pm 0.2\%$  between kaolinite and  $\text{H}_4\text{SiO}_4$ , and  $-1.6 \pm 0.3\%$  between  $\text{H}_3\text{SiO}_4^-$  and  $\text{H}_4\text{SiO}_4$ . These calculated solid–solution fractionations show important disagreement with natural observations in low-temperature systems, arguing against isotopic equilibration during silicon precipitation in these environments. On the other hand, the large fractionation associated with the de-protonation of silicic acid suggests the importance of speciation, and in particular pH, for the fractionation of silicon isotopes at low temperature.

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## 1. Introduction

Due to analytical progress, silicon isotopes have recently emerged as a promising tool for estimating the impact of alteration on the long-term  $\text{CO}_2$  budget (Opfergelt and Delmelle, 2012, and references therein), understanding soil formation (Ziegler et al., 2005), or constraining oceanic productivity (De La Rocha et al., 1998). Although numerous studies have measured silicon isotope compositions in natural samples, very few document quantitatively the fractionation related to elementary processes. A quantitative understanding of the basic mechanisms causing isotopic fractionation is nevertheless essential to realize the full potential of this isotopic system, and can be attained through careful theoretical studies and laboratory experiments. Such experiments are difficult to realize, due in particular to the slow speed of Si precipitation, and to the complexity of alteration processes. So far, the identified causes for isotopic variability in these surface

environments are inorganic precipitation of clays or silica (Li et al., 1995; Basile-Doelsch, et al., 2005; Georg et al., 2007; Geilert et al., 2014), organic precipitation of silica (de la Rocha et al., 1997; Hendry and Robinson, 2012), dissolution of silica (Demarest et al., 2009), or adsorption of silica onto oxides (Delstanche, et al., 2009). In all these situations, the fractionation occurs between a solid and a liquid phase.

In order to interpret these observations, and in particular to understand the relative contribution of kinetic and equilibrium processes, it is of primary importance to document fractionations related to the equilibria between minerals and liquids, and between different dissolved species. The most common species of Si in solution at ambient conditions are silicic acid  $\text{H}_4\text{SiO}_4(\text{aq})$  (denoted hereafter H4), and its associated base  $\text{H}_3\text{SiO}_4^-$  (aq) (denoted hereafter H3). In this work, we will focus on the isotopic fractionation between these two species and between  $\text{H}_4\text{SiO}_4$  and two minerals, quartz and kaolinite. The calculated quartz/solution fractionation can be compared with the existing estimates of fractionation during precipitation of amorphous silica, whereas the kaolinite/solution fractionation is more relevant to the behavior of Si isotopes during clay precipitation.

\* Corresponding author.

E-mail address: [rdupuisbelin@gmail.com](mailto:rdupuisbelin@gmail.com) (R. Dupuis).

Theoretical methods based on first-principles approaches have proved their ability to predict the fractionation at equilibrium among solids or gaseous phases for many isotopic systems including silicon (e.g. Schauble, et al., 2006; Méheut et al., 2009; Huang et al., 2013). For these phases, fractionation factors are satisfactorily computed using the harmonic approximation. The success of this approximation relies on the fact that, in gases or solids, atoms move around their equilibrium positions with small amplitudes.

For liquids, in particular aqueous solutions, however, the correct treatment to compute fractionation properties under thermodynamical equilibrium remains an open question. Most studies are based on the cluster approach (Yamaji et al., 2001; Domagal-Goldman and Kubicki, 2008; Hill and Schauble, 2008; Zeebe, 2009, 2010; Hill et al., 2010; Rustad et al., 2010a,b), in which the dissolved species of interest ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{H}_3\text{BO}_3$ ) is surrounded by water molecules (the hydration shell). This water cluster is then treated as an isolated molecule, and its fractionation properties are computed within the harmonic approximation. These approaches are hindered by several difficulties, such as the number of water molecules to be included, the symmetry of the cluster, how to be consistent between several species, or whether we have to consider implicit solvation models or other empirical schemes (see e.g. Zeebe, 2009; Rustad and Dixon, 2009).

A difficulty with the computation of the fractionation properties of liquids is the dynamical aspects of solutions. In particular, the arrangement of water molecules around the species of interest is constantly evolving in a solution. Rustad et al. (2008, 2010a, 2010b) used molecular dynamics to generate several water clusters in order to study the conformational variability of fractionation properties. For dissolved  $\text{Mg}^{2+}$ , for example, they found a variability of 1‰ for the  $\beta$ -factor. In the case of dissolved Si, such a variability would be very significant, compared to the limited fractionations of this element.

More recently, Schauble (2011) proposed to take hydrate minerals as analogs for dissolved species. A major advantage of this approach is that solids and solutions are treated in a fully consistent manner, using lattice dynamics to compute the vibrational properties of both phases. To our knowledge, this approach is not applicable to the case of silicic acid due to the non-existence of hydrate compounds containing  $\text{H}_4\text{SiO}_4$  or  $\text{H}_3\text{SiO}_4^-$  species.

A way to take into account the dynamical aspects of solution, and treat solution and solid in a consistent manner at the same time, relies on molecular dynamics (MD) simulations. A molecular dynamics trajectory is realized with the species of interest. Then, individual configurations are quenched, giving the so-called “inherent structures” (IS), and the IS harmonic vibrational properties are computed within lattice dynamics, consistent with an “ice-like” model (by opposition to a “molecular-like” water cluster). The idea of using the inherent structures for computing thermodynamic properties was introduced by Stillinger and Weber (1983), and was first applied to the computation of fractionation properties by Rustad and Bylaska (2007) who considered boron isotope fractionation between  $\text{B}(\text{OH})_3(\text{aq})$  and  $\text{B}(\text{OH})_4^-(\text{aq})$ .

In this work, we applied the approach of Rustad and Bylaska (2007) to the  $\text{H}_4\text{SiO}_4$  and  $\text{H}_3\text{SiO}_4^-$  species. We computed several configurations for both systems, aiming at a clear understanding of the effects of configurational disorder in these systems. We consider solutions as statistical ensembles. Therefore, their fractionation properties are computed by averaging over several configurations extracted from the trajectory. The major drawback of this approach is its numerical cost. To be realistic, the present molecular dynamics simulation contains hundreds of independent atoms. The cost for computing complete vibrational properties on several configurations along the trajectory is far greater than computations on most solids. To remedy to this, Kowalski and Jahn (2011) proposed computing partial vibrational properties, by considering the displacement of a limited number of atoms (in their case, only the Li atom). More precisely, they used a high-temperature approximation allowing the use of local force constants instead of the vibrational frequencies. Not only does this reduce computational costs

significantly, but it also permits the dynamical aspects of solutions to be considered as realistically as possible, since it requires only local relaxation. We attempted similar approaches in our study (see Section 3.3) but this proved disappointing in our case. Instead, we carefully analyze the relationships between fractionation properties and liquid structure, so as to rationalize the configurational disorder. This permits an approach to be proposed that reduces the number of configurations to be computed, and therefore the computational cost.

The paper is organized as follows. In the first section, the methodology used to compute the isotopic fractionation factor from first-principles calculations in the harmonic approximation is briefly detailed and the calculation of the fractionation factor in  $\alpha$ -quartz, which will be used as a reference, is presented. The approximations used to compute the fractionation factor in liquids are then described. In the second section, the main results are given for the two species in solution, H4 and H3. First, the structural properties of the simulated liquids are presented, and then the correlations between these properties and the calculated fractionation values are analyzed. The importance of the configurational disorder on the calculation of fractionation properties in liquids is subsequently investigated. Finally, the implications for geochemical processes are discussed.

## 2. Methods

### 2.1. Calculation of the isotopic fractionation factor

A theoretical isotopic fractionation factor  $\beta^{30}\text{Si}_A$  for a rare isotope  $^{30}\text{Si}$  and the most abundant form  $^{28}\text{Si}$  of an element Si, can be calculated between a phase A and a perfect gas of Si atoms, having the natural mean isotopic concentration:

$$\beta^{30}\text{Si}_A = \frac{(n_{30}/n_{28})_A}{(n_{30}/n_{28})_{\text{gas}}} \quad (1)$$

where  $n_{30}$  refers to the quantity of the heavy isotope  $^{30}\text{Si}$  and  $n_{28}$  corresponds to the quantity of the light element  $^{28}\text{Si}$ . The isotopic fractionation factor at equilibrium  $\alpha^{30}\text{Si}_{A-B}$  associated with the element Si, which can be measured experimentally, corresponds to the ratio of two  $\beta^{30}\text{Si}_A$  and  $\beta^{30}\text{Si}_B$  factors calculated in two phases A and B:

$$\alpha^{30}\text{Si}_{A-B} = \frac{\beta^{30}\text{Si}_A}{\beta^{30}\text{Si}_B} \quad (2)$$

thus, the  $\beta^{30}\text{Si}_A$  and  $\beta^{30}\text{Si}_B$  factors correspond to the respective contributions of phases A and B to the isotopic fractionation  $\alpha^{30}\text{Si}_{A-B}$  and the two systems A and B can be treated separately (Richet et al., 1977). The common formula (Richet et al., 1977) used for the calculation of  $\beta^{30}\text{Si}_A$  is:

$$\beta^{30}\text{Si}_A = \left[ \frac{Q(^{30}\text{Si}_N)_A}{Q(^{28}\text{Si}_N)_A} \right]^{1/N} \left[ \frac{m_{28}}{m_{30}} \right]^{3/2} \quad (3)$$

where  $Q(^{30}\text{Si}_N)_A$  denotes the partition function of the system of  $N$  Si atoms, with all Si isotopes substituted with  $^{30}\text{Si}$  and  $Q(^{28}\text{Si}_N)_A$  the one with  $^{28}\text{Si}$ .

In order to estimate  $\beta^{30}\text{Si}_A$ , one then needs to calculate the partition function ratio for the system having all heavy atoms and for the same system having all light atoms. For crystalline solids, this can be done in the harmonic approximation using the phonon modes frequencies:

$$Q = \left\{ \prod_{i=1}^{3 \times N_{\text{at}}} \prod_{q=1}^{N_q} \frac{e^{-\frac{h\nu_{q,i}}{2k_B T}}}{1 - e^{-\frac{h\nu_{q,i}}{2k_B T}}} \right\}^{\frac{1}{N_q}} \quad (4)$$

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