Silicon isotope fractionation in silicate minerals: Insights from first-principles models of phyllosilicates, albite and pyrope

Merlin Méheut [a,*], Edwin A. Schauble [b]

[a] GET, Université Paul-Sabatier, CNRS UMR 5563, IRD UR 154, Observatoire Midi-Pyrénées, 14 Avenue Edouard Belin, 31400 Toulouse, France
[b] Department of Earth and Space Sciences, University of California, Los Angeles, Box 951567, Los Angeles, CA 90095-1567, USA

Abstract

Isotopic fractionation factors for oxygen and silicon in phyllosilicates (pyrophyllite, talc), albite and pyrope have been calculated using first-principles methods based on density functional theory. Based on exhaustive analysis of numerical convergence, we also update our previous calculations on enstatite and forsterite silicon fractionation properties. Calculated oxygen isotope fractionations agree well with existing estimates for talc and albite. In the case of silicon, qualitative agreement is found with natural data. For phyllosilicates (kaolinite, lizardite, pyrophyllite, talc), Si isotope fractionation properties appear to be correlated with stoichiometry:

$$1000 \ln \alpha^{30}\text{Si}_{\text{phyllosilicate–quartz}} = \frac{a_{\text{Mg}}(T) \cdot \text{Mg}^{\text{eq.}} + a_{\text{Al}}(T) \cdot \text{Al}^{\text{eq.}}}{\text{Si}^{\text{eq.}}}, \tag{1}$$

where $\text{Si}^{\text{eq.}} = \#\text{Si}$, $\text{Al}^{\text{eq.}} = \frac{3}{4}\#\text{Al}$ and $\text{Mg}^{\text{eq.}} = \frac{1}{2}\#\text{Mg}$ (cation equivalents) are the charge-weighed stoichiometric coefficients of each cation, normalized to the charge of the silicon atom, and $a_{\text{X}}(T)$ are proportionality coefficients depending on temperature. It is suggested that the effect of cation X on Si isotope fractionation (i.e. $a_{\text{X}}(T)$) will increase with decreasing electronegativity of X. Si isotope fractionation is further correlated with Si–O distances, suggesting a crystal chemical explanation for relation (1) in terms of electron donation effects. This relationship appears valid for quartz, pyrope and enstatite ($R^2 = 0.99$, $n = 7$), but forsterite is strongly anomalous (error of 0.7‰ at 600 °C). These models indicate that attention should be given to chemical compositions in Si isotope studies. Relation (1) would explain the enrichment in heavy silicon isotopes accompanying magmatic differentiation.

1. INTRODUCTION

Due to its ubiquitous character in Earth and planetary environments, silicon is a major potential source of information in geochemistry. Despite the early start to silicon isotopic measurements half a century ago (Reynold and Verhoogen, 1953), it is during the last decade that improvements in mass-spectrometry permitted sufficiently accurate measurements of silicon isotopic compositions to consider both high and low-temperature geochemical applications. Following these analytical advances, Si isotopes have recently drawn important attention, for example to unravel the mechanisms of planetary core formation (Georg et al., 2007; Fitoussi et al., 2009; Shahar et al., 2009, 2011; Ziegler

* Corresponding author. Tel.: +33 561332617; fax: +33 561332560.
 E-mail address: merlin.meheut@get.obs-mip.fr (M. Méheut).

et al., 2010; Chakrabarti and Jacobsen, 2010; Armytage et al., 2011; Javoy et al., 2012; Fitoussi and Bourdon, 2012; Kempl et al., 2013; Pringle et al., 2013; Zambardi et al., 2013), and for estimating the impact of alteration processes on the long-term CO_2 budget (e.g., Opfergelt and Delmelle, 2012, and references therein). In order to realize the full potential of these new measurements, it is important to understand the basic mechanisms causing the isotopic fractionation of silicon.

Starting from the works of Allenby (1954), several studies have emphasized an increase of the $\delta^{30}Si$ signatures of magmatic rocks with their degree of differentiation (Douthitt, 1982; Savage et al., 2010, 2011). An example of this trend was recently illustrated for a particular magmatic suite by Savage et al. (2011). Fig. 5 of Savage et al. (2011) shows a fairly robust linear correlation between the silicon isotopic signature of rocks form the Hekla suite, and proxies for magmatic differentiation such as the rock SiO_2 content. Since the sequence of minerals precipitating during magmatic differentiation is well established, this trend represents a good starting point for the assessment of the parameters influencing silicon fractionation in silicate minerals.

Based on theoretical considerations, the study of Grant (1954) suggested that equilibrium silicon isotopic fractionation should depend on the degree of polymerization of the SiO_4^{4-} tetrahedra in the silicate structure. More precisely, minerals with a higher degree of polymerization should be isotopically heavier than less polymerized ones. Since mineral polymerization increases with the degree of magmatic differentiation of the rock, this would explain the above-mentioned trend. However, our previous study (Méheut et al., 2009), based on calculations involving silicates with various degrees of polymerization (quartz, lizardite/kaolinite, enstatite and forsterite) showed a more complex relationship to mineral structure. In particular, we emphasized the large difference between kaolinite and lizardite isotopic properties, even though both minerals have very similar structures and the same degree of polymerization. A more comprehensive study of phyllosilicate structures (to which kaolinite and lizardite belong) so as to understand the structural parameters influencing silicon isotopic fractionation properties was needed. Another reason supporting the study of phyllosilicates is the great variety of their structures (various stackings of the silicate layers) and cationic compositions (Al^{3+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Li^+, Ni^{2+}), as illustrated in Fig. 1.

In this study, we have computed the silicon isotope fractionation properties of two additional phyllosilicate structures, talc and pyrophyllite (which makes four with kaolinite and lizardite, see Fig. 1), as well as albite and pyrope. We focus on the four phyllosilicate minerals to better understand the parameters governing silicon isotopic fractionation at equilibrium, and discuss the extension of the obtained laws to the other calculated minerals (quartz, enstatite, forsterite, albite and pyrope).

These fractionation factors are obtained from theoretical modeling based on first-principles quantum mechanical calculations. The explicit treatment of the electronic nature of chemical bonds, and the absence of parameters fitted to experimental data, lead to reliable predictions of isotopic

fractionation factors, as attested by recent theoretical studies (e.g., Schauble et al., 2006; Méheut et al., 2007; Méheut et al., 2009; Blanchard et al., 2009; Rustad and Dixon, 2009; Méheut et al., 2010; Schauble, 2011; Huang et al., 2013).

2. METHODS

Theoretical calculations of equilibrium isotopic fractionation based on statistical physics require the knowledge of the complete vibrational properties of minerals with different isotopic compositions (see Section 3.1). This information is difficult to obtain from experiment, and calculations based on experimental data have been limited to simple, or particularly well known systems. For molecules (e.g., Richet et al., 1977), the method could be applied to simple systems, and to isotopic systems for which isotopic substitution induces a sufficiently large change in vibrational frequencies. For minerals, additional approximations are required (Kieffer, 1982), because common spectroscopic techniques (Raman or IR spectroscopy) only give partial information on vibrational properties. For solids, such calculations based on experiment have mostly been limited to the calculation of carbon and oxygen fractionations (Bottinga, 1968; Kawabe, 1978; Kieffer, 1982).

Our calculations are based on first-principles methods using density functional theory (DFT). First-principles techniques rely on the resolution of the equations of quantum mechanics to compute the electronic structure of a material, i.e. its electronic energy and wavefunction. Because of this fundamental basis, first-principles approaches can be used to quantitatively predict, without any input from experiment, material properties deriving from the electronic structure, in particular complete vibrational properties. Except in simple cases, however, electronic structure cannot be resolved exactly, and requires approximations. Density functional theory is a theoretical scheme to solve these equations in an efficient and usefully accurate way (Kurth et al., 2005). The critical ingredient required for the resolution of electronic structure in the scheme of DFT is the "exchange and correlation functional of density". It describes the mathematical link between the electronic energy and electronic density. LDA (for local density approximation), PBE (for Perdew, Burke and Ernzerhof, used in this study) and PW91 (for Perdew and Wang, 1991) are examples of approximated forms of this functional. In practice, the numerical resolution of these equations in minerals and complex molecules requires additional ingredients in order to be computationally efficient. The plane-wave pseudopotential (PW-PP) technique has become widely recognized as the method of choice for computational studies of solid-state materials (Milman et al., 2000). The plane-waves denote the basis of functions on which the electronic densities and wavefunctions are described, whereas the pseudopotentials describe a way to approximate the effect of core electrons.

2.1. The isotopic fractionation factor α

$\beta(a, Y)$ is the isotopic fractionation factor of the element Y between the phase a and a perfect gas of Y atoms, having the natural mean isotopic concentration. The isotopic