Chemical Geology 258 (2009) 28–37

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Structural control over equilibrium silicon and oxygen isotopic fractionation: A first-principles density-functional theory study

Merlin Méheut [a],*, Michele Lazzeri [a], Etienne Balan [a,b], Francesco Mauri [a]

[a] IMPMC, Université Paris VI et VII, CNRS, IPGP, 4 Place Jussieu, 75252, Paris cedex 05, France
[b] IRD, 213 rue La Fayette, 75480 Paris cedex 10, France

ARTICLE INFO

Article history:
Received 16 November 2007
Received in revised form 10 May 2008
Accepted 27 June 2008

Keywords:
Isotopic fractionation
First-principles calculations
Silicon
Oxygen
Silicate polymerization
Kaolinite
Lizardite
Enstatite
Forsterite
Quartz
Isotopes
DFPT
Phonons
Harmonic approximation

ABSTRACT

Isotopic fractionation factors for oxygen and silicon in selected silicates (quartz, enstatite, forsterite, lizardite, kaolinite) are calculated using first-principles methods based on density-functional theory. Good agreement between theory and experiment is found in the case of oxygen. In the case of silicon, agreement and differences with existing estimates of equilibrium fractionation factors are discussed. The relationship between silicon and oxygen fractionation factors, silicate polymerization degree and chemical composition is studied and compared with previous semi-empirical models.

1. Introduction

Silicon isotopic studies have been carried out for over half a century (Reynold and Verhoogen, 1953; Epstein and Taylor, 1970; Clayton et al., 1978; Douthitt, 1982; Ding et al., 1996; De la Rocha et al., 2000; Georg et al., 2007a,b). A large number of terrestrial and extraterrestrial samples were investigated and the general picture of silicon isotope distribution in nature was outlined (Douthitt, 1982; Ding et al., 1996). In recent years, several studies have also been devoted to surface environments and low temperature conditions, even though it is difficult to conclude about the nature (kinetic or equilibrium) of the fractionation process (De la Rocha et al., 1997; Basile-Doelsch et al., 2005).

Concerning igneous rocks, the systematic trends of δ^{30}Si led previous workers to postulate equilibrium fractionation processes (Douthitt, 1982). Nevertheless, the very small amplitude of silicon fractionation, conjugated with the limited analytical accuracy, prevented precise understanding of the systematics of silicon fractionation in igneous processes. Based on theoretical considerations, the study of Grant (1954) suggested that silicon equilibrium isotopic fractionation should depend on the degree of polymerization of the SiO_4 tetrahedra in the silicate structure. In particular, the silicon isotopic content should be heavier with higher polymerization degree, and therefore silicon content of the material. In fact, the use of stable-isotope fractionation to track natural processes depends on the determination of the controlling structural parameters. In particular, the conclusions of Grant (1954) imply that chemical differentiation associated with igneous processes should lead to an enrichment in ^{30}Si of the silica-rich phases. Such an approach is similar to the proposed empirical relationships between fractionation of oxygen and chemical composition (Garlick, 1966).

While Grant's calculation of the quartz–topaz fractionation greatly overestimates the typically observed values, his theoretical discussion provided an inspiration for subsequent studies of the geochemical fractionation of silicon isotopes. Douthitt (1982) remarks that δ^{30}Si of igneous rocks shows a positive correlation with silicon content. Ding et al. (1996) also provide several examples for which these trends are confirmed. The similarity between silicon and oxygen isotopic fractionations has been also emphasized. Douthitt (1982) remarks that silicon fractionations are roughly 1/3 the magnitude of concomitant oxygen isotopic fractionations at 1150 °C.

In this context, first-principles computational methods based on density-functional theory (DFT) can provide a precise and independent

---

* Corresponding author.
E-mail address: merlin.meheut@gmail.com (M. Méheut).

0009-2541/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemgeo.2008.06.051

determination of the equilibrium fractionation properties of silicates (Méheut et al., 2007). In this work, we use the same first-principles approach as in Méheut et al. (2007) to determine the stable isotopic fractionation of oxygen and silicon for several minerals displaying various degrees of polymerization of silicate units. We study quartz (Q^4), lizardite (Q^3), kaolinite (Q^3), enstatite (Q^2), and forsterite (Q^0), where Q^n denotes the degree of polymerization, n being the number of bridging oxygens for one SiO_4 unit. Despite the fact that these minerals do not always coexist in nature or occur in high-temperature environments, they were chosen for their structural and chemical diversity, as well as for their small unit-cell size. Therefore, this study should be mostly considered as a thought experiment in which the effect of polymerization on silicon isotopic fractionation is investigated. However, some comparisons with experimental measurements on natural systems are tentatively proposed in the second part of the paper.

2. Methods

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 fractionation factor $\alpha(a,b,Y)$ relative to an atom Y, between two phases a and b can be written as the ratio of the β-factors relative to this atom and to each phase separately (Richet et al., 1977).

If a is a crystalline solid, $\beta(a,Y)$ can be computed from the harmonic vibrational properties of a using

$$\beta(a,Y) = \left[\frac{Q(AY_N^*)}{Q(AY_N)}\right]^{1/N} \left[\frac{m_Y}{m_{Y*}}\right]^{3/2} \tag{1}$$

where $Q(AY_N^*)$ is the partition function of the system having all the Y atoms substituted by Y^*. As discussed in Méheut et al. (2007), Eq. (1) is precise when Y has a mass larger than hydrogen. The harmonic partition function of a crystalline solid is:

$$Q = \left[\prod_{i-1}^{3N^{\mathrm{at}}} \prod_{\{\boldsymbol{q}\}}^{*} \frac{e^{-h\nu_{\boldsymbol{q},i}/(2kT)}}{1-e^{-h\nu_{\boldsymbol{q},i}/(kT)}}\right]^{1/(N_q)} \tag{2}$$

where $\nu_{\mathbf{q},i}$ are the frequencies of the phonon with wavevector $\boldsymbol{q}$ and branch index $i=1,3N^{\mathrm{at}}$. N^{at} is the number of atoms in the unit cell, N is the number of sites for the Y atom in the unit cell, T is the temperature, k is the Boltzmann constant and h is Plank's constant. The product is performed on a sufficiently large grid of N_q $\boldsymbol{q}$-vectors in the Brillouin zone. The * symbol above the product of Eq. (2) indicates that the three translational modes with $\nu_{\mathbf{0},i}=0$ are not considered.

2.2. Vibrational analysis

We now discuss an alternative formulation for the β factors. This formulation will be used to determine the contribution of the different vibrational modes ($\boldsymbol{q}$,i) to the total fractionation.

Let us call $\nu^*_{\mathbf{q},i}$ *and* $\nu_{\mathbf{q},i}$ *the frequencies of the same vibrational mode in two isotopically different materials. The isotopic fractionation is due to the quantum-mechanical nature of the vibrations. As a consequence, for temperatures higher than the Debye temperature, i.e. when the system behaves classically, the isotopic fractionation is zero and* $\beta=1$. *By imposing* $\lim_{T\to\infty}\beta=1$ *in Eqs. (2) and (1), we have*

$$\left[\frac{m}{m^*}\right]^{3/2} = \left[\prod_{i-1}^{3N^{at}} \prod_{\{\boldsymbol{q}\}}^{*} \frac{\nu^*_{\boldsymbol{q},i}}{\nu_{\boldsymbol{q},i}}\right]^{1/(N_q N)}, \tag{3}$$

Eq. (3) is the well-known “rule of the high-temperature product”, also called Teller–Redlich rule (Urey, 1947; Bigeleisen and Mayer, 1947) for molecular systems.

By inserting Eqs. (3) and (2) into Eq. (1), it easily follows

$$\beta(a,Y) = \prod_{\boldsymbol{q},i}^{*} \left[\frac{f\left(\nu^*_{\boldsymbol{q},i}\right)}{f\left(\nu_{\boldsymbol{q},i}\right)}\right]^{1/N_q N} \tag{4}$$

where

$$f(\nu) = \nu \frac{e^{-\frac{h\nu}{2kT}}}{1-e^{-\frac{h\nu}{kT}}}.$$

Eq. (4) expresses the β-factor as a product of the contributions from each vibrational mode. We now consider $\nu^*_{\mathbf{q},i}$ *and* $\nu_{\mathbf{q},i}$ *as two values of the function* $\nu^{\mu}_{\mathbf{q},i}$, *where* $\mu=\frac{1}{\sqrt{m}}$. *Here,* $\nu^{\mu}_{\mathbf{q},i}$ *is the* ($\boldsymbol{q}$,i) *frequency in a system in which the mass of the Y atom has the arbitrary value m and all the other masses are fixed at their usual value. Using this notation, from Eq. (4) it follows*

$$\ln\beta(a,Y) \approx \frac{1}{N_q N}\sum_{q,i} \left.\frac{\partial \ln\left(f\left(\nu^{\mu}_{q,i}\right)\right)}{\partial\mu}\right|_{\mu=\bar{\mu}} \Delta\mu, \tag{5}$$

where $\bar{\mu}=(\mu_{Y*}+\mu_Y)/2$ and $\Delta\mu=\mu_{Y*}-\mu_Y$. We then define

$$F(\nu) = \frac{1}{N_q N}\sum_{\boldsymbol{q},i} \left.\frac{\partial \ln\left(f\left(\nu^{\mu}_{\boldsymbol{q},i}\right)\right)}{\partial\mu}\right|_{\mu=\bar{\mu}} \Delta\mu\,\Theta\left(\nu - l\nu^{\bar{\mu}}_{\boldsymbol{q},i}\right) \tag{6}$$

where $\Theta(t)$ is the Heaviside function ($\Theta=0$ for $t<0$ and $\Theta=1$ for $t>0$). In actual calculations, the derivative in Eq. (6) is obtained by finite differences.

By comparing Eqs. (5) and (6), $F(\nu)$ represents the integration of the contributions of all the modes with $\nu^{\bar{\mu}}_{\mathbf{q},i} \le \nu$. In the paper, $F(\nu)$ will be used to determine the contribution of the different vibrational modes to the total fractionation.

2.3. Density-functional theory calculations

The β-factors and the F function are obtained from Eqs. (1), (2), and (6) using the phonon frequencies $\nu_{\mathbf{q},i}$ computed from first-principles within density-functional theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965).

We use the generalized-gradient approximation to the exchange-correlation functional of Perdew, Burke and Ernzerhof (PBE) (Perdew et al., 1996). The PBE approximation was already used in Méheut et al. (2007), since it is known to provide a good description of silicates, including the hydrous ones. The ionic cores are described by norm-conserving pseudopotentials (Troullier and Martins, 1991) in the Kleinman–Bylander form (Kleinman and Bylander, 1982). For the Mg pseudopotential we used the $2s^2$,$2p^6$,$3d^0$ configuration, with core radius 1.65, 1.1, 1.3 a.u., respectively. The other pseudopotentials are described in the electronic annexes of Méheut et al. (2007). Computational details for quartz and kaolinite are the same as in Méheut et al. (2007). For lizardite, forsterite and clinoenstatite, the electronic wave-functions are expanded in plane-waves up to an energy cut-off $\varepsilon_{\mathrm{cut}}=150$ Ry (such a high cut-off is necessary because of semi-core states considered in the Mg pseudopotential). Electronic integration is done by sampling the Brillouin zone with a $2\times2\times2$ k-point grid for lizardite and forsterite (Monkhorst and Pack, 1976). For clinoenstatite, the sampling can be restricted to the Baldereschi point (1/4, 1/2, 1/4) (Baldereschi, 1973), because of the larger size of the unit cell.

Phonon frequencies are computed using linear response (Baroni et al., 2001), with the PWSCF package (Baroni et al., http://www.pwscf.org), using the standard procedure (Méheut et al., 2007). First, the interatomic force constants are obtained from the dynamical matrices computed exactly (within DFT) on a $n\times n\times n$ grid of $\boldsymbol{q}$-vectors ($n=2$ for lizardite, $n=1$ for clinoenstatite). Long-range effects are taken into account by computing Born effective-charges and static dielectric constant (Baroni et al., 2001). Dynamical matrices and thus phonon