



First-principles investigation of equilibrium isotopic fractionation of O- and Si-isotopes between refractory solids and gases in the solar nebula

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ABSTRACT

First-principles methods based on density functional theory (DFT) allow the calculation of isotopic partition functions of small gaseous molecules and crystalline compounds with comparable levels of accuracy. We applied these methods to a few species of interest in cosmochemical problems, with a special emphasis on molecules up to now rather neglected in isotopic cosmochemistry: silicon monoxide and silicon monosulfide. These species are likely to play an important role in future cosmochemical studies and already appear in studies such as those related to mass independent fractionation (MIF) generation. We explore the equilibrium mass dependent fractionation (MDF) of these molecules with major gaseous solar species (CO, H₂O) and some key meteorite minerals: examples of results are given for the role of SiO on silica enrichment of magnesian chondrules and for the isotopic composition of SiO and SiS during the genesis of silicon solid-solutions in chondritic Fe-Ni metal, a possible starting product for planetary cores. It is shown that the oxygen isotopic composition of early solar silicon monoxide likely lays at the intersection ($\delta^{18}\text{O} = 2.12 \pm 0.4\%$, $\delta^{17}\text{O} = 1.1 \pm 0.2\%$) of the Young Russell line with the MDF lines corresponding to the main inner solar system bodies. This can be related to solar water abundance in the frame of self-shielding models. At the time of E chondrites' formation the $\delta^{30}\text{Si}$ of the nebular gas, dominated by SiS, was $\sim -6\%$.

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1. Introduction

The dominant forms of silicon in a gas of standard solar composition at high temperature are silicon monoxide SiO and silicon monosulfide SiS. Classical descriptions (e.g., Wasson, 1985) of a standard solar nebula at 1500 K and 10^{-4} bars give for SiO and SiS pressures of $6.4 \cdot 10^{-9}$ and $2.7 \cdot 10^{-9}$ bars, respectively, that is, together, the whole silicon content of the nebula. For a P-T range of 10^{-4} –10 bars and 1200–1800 K, the SiO/SiS ratio is little variable for normal solar compositions. Strongly oxidizing conditions related to dust concentration and subsequent total volatilization (Ebel and Grossman, 2000) greatly increase the oxygen fugacity (f_{O_2}) but not very much the SiO/SiS ratio. On the contrary, the combined very low f_{O_2} and very high f_{S_2} recorded by the enstatite chondrites (e.g., Fogel et al., 1989), lower significantly this ratio according to reaction of SiO with S₂ or H₂S. Under the conditions of E chondrites' formation (low f_{O_2} 's, high f_{S_2} 's), the SiO/SiS ratio becomes very low at medium temperatures ($\sim 10^{-4}$ at 1000 K) and increases gradually with temperature ($\sim 2 \cdot 10^{-3}$ at 1500 K) (Fogel et al., 1989; Javoy et al., 2010).

Silicon monoxide is quoted for its postulated role in silica enrichment of chondritic components (e.g., Chaussidon et al., 2008; Javoy,

2005; Javoy et al., 2010; Libourel et al., 2006; Tissandier et al., 2002). This has been substantiated by reproducing observed chondritic mineral parageneses in laboratory experiments (e.g., Tissandier et al., 2002). SiO₂ precipitation occurs either directly by:



or by disproportionation of silicon monoxide according to:



The latter is favored by the very low value (from $\sim 10^{-6}$ at 1000 K to $\sim 10^{-3}$ at 2000 K) of the activity coefficient of silicon γ_{Si} in Fe solid or liquid solutions. This is observed in the strongly reduced E chondrites (e.g., Fogel et al., 1989, and references therein; Javoy et al., 2010). SiO is also quoted as a key molecule for generating mass-independent isotopic fractionation (MIF) (Thiemens, 2006; Young et al., 2008, and references herein). Last, both SiO and SiS may play a major role as silicon reservoirs in the increasingly studied problem of planetary cores' formation, and its tracing by silicon isotopes' fractionation (e.g., Armytage et al., 2011; Chakrabarti and Jacobsen, 2010; Fitoussi et al., 2009; Georg et al., 2007a,b; Shahar et al., 2009; Ziegler et al., 2010).

Despite this, little attention has been given to their isotopic fractionation properties. Hence, it is timely to produce a coherent set of

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equilibrium isotopic fractionation factors linking these main silicon molecules to selected gas (CO, H₂O) and solid phases (e.g., forsterite, enstatite, silica) present in the solar nebula. These fractionation factors are obtained from a theoretical modeling based on first-principles quantum mechanical calculations. The explicit treatment of the electronic nature of the chemical bond, and the absence of parameters fitted on experimental data, lead to reliable and predictive isotopic fractionation factors, as attested by recent theoretical studies (e.g., Blanchard et al., 2009; Méheut et al., 2007, 2009, 2010; Rustad and Dixon, 2009; Schauble et al., 2006). Significantly, the use of density functional perturbation theory (DFPT; Baroni et al., 2001) makes it possible to treat molecules in the gas phase and crystalline solids at the same level of approximations. In this study, we calculate equilibrium fractionation factors for temperatures ranging between 500 and 2400 K, compare them to existing data and expose the ways under which they could be translated to the study of natural systems.

2. Theoretical model of equilibrium isotopic fractionation coefficients

The isotopic fractionation coefficient of an element *Y* between two phases *a* and *b*, referred to as $\alpha(a,b,Y)$ can be related to the reduced partition function ratios (also called β -factors) of the two phases by:

$$10^3 \ln \alpha(a, b, Y) = 10^3 \ln \beta(a, Y) - 10^3 \ln \beta(b, Y) \quad (3)$$

in which the reduced partition function ratio $\beta(a,Y)$ corresponds to the isotope fractionation coefficient between the phase *a* and a perfect gas of *Y* atoms (Richet et al., 1977). Assuming that rotational contributions to the partition function can be treated as classical and using the Teller–Redlich rule, the harmonic β -factors of a diatomic molecule are given by:

$$\beta(a, Y) = \frac{\nu^* e^{-h\nu^*/(2kT)} 1 - e^{-h\nu/(kT)}}{\nu 1 - e^{-h\nu^*/(kT)} e^{-h\nu/(2kT)}} \quad (4)$$

where ν and ν^* are the harmonic stretching frequencies of the isotopically different molecules, *h* the Planck constant, *k* the Boltzmann constant and *T* the temperature (Bigeleisen and Mayer, 1947).

For a crystal, harmonic β -factors can be calculated in a similar way using the following expression:

$$\beta(a, Y) = \left[\prod_{i=1}^{3N_{at}} \prod_{\{q\}} \frac{\nu_{q,i}^* e^{-h\nu_{q,i}^*/(2kT)} 1 - e^{-h\nu_{q,i}/(kT)}}{\nu_{q,i} 1 - e^{-h\nu_{q,i}^*/(kT)} e^{-h\nu_{q,i}/(2kT)}} \right]^{1/(N_q N)} \quad (5)$$

where $\nu_{q,i}$ are the frequencies of the phonon with wave-vector *q* and branch index *i* = 1, $3N_{at}$ is the number of atoms in the unit cell, $\nu_{q,i}$ and $\nu_{q,i}^*$ are the vibrational frequencies in two isotopically different materials, *N* is the number of sites for the *Y* atom in the unit cell, N_q is the number of *q*-points used to sample the Brillouin zone (Méheut et al., 2007). The * symbol above the product of Eq. (5) indicates that the three translational modes with zero frequency at the center of the Brillouin zone are not considered. The β -factors were obtained from Eqs. (4) and (5) using the phonon frequencies calculated from first-principles. These theoretical phonon frequencies were obtained within the density functional theory (DFT) framework, using the generalized gradient approximation (GGA) to the exchange–correlation functional as proposed by Perdew, Burke and Ernzerh of (Perdew et al., 1996) and a plane-wave/pseudo-potential scheme, as implemented in the PWscf and PHonon codes from the Quantum ESPRESSO package (Giannozzi et al., 2009; <http://www.quantum-espresso.org>) (see Electronic Supplementary Materials for computational details). The GGA approximation usually leads to a systematic underestimation of vibrational frequencies that can reach ~5% in silicates, translating to a relative underestimation of ~10% on the logarithmic expression of β -factors (Méheut et al., 2009). This

bias can be partly corrected by scaling the theoretical frequencies on a finite sets of experimental frequencies (e.g., Blanchard et al., 2009; Schauble et al., 2006). However, such scaling procedure introduces additional uncontrolled uncertainties and limits the generality of the theoretical approach (Méheut et al., 2007). In the present study, such scaling procedure was not used.

3. Results

3.1. Theoretical structural and vibrational properties of molecules and crystals

The theoretical vibrational stretching frequencies of the SiO, SiS and CO molecules (Table EA1) underestimate their experimental counterpart by 3 to 5%, whereas bond lengths are slightly overestimated. Similar small discrepancies between theory and experiment are commonly observed in GGA calculations on oxide and silicate minerals (e.g., Balan et al., 2007; Méheut et al., 2007). On the other hand, the frequency shifts related to isotopic substitution are in very good agreement with experimental values.

The theoretical equilibrium unit-cell parameter of MgO (4.207 Å) is in very good agreement with the experimental value (4.21 Å) and slightly smaller than that obtained in previous theoretical studies at the GGA level (4.234 Å, Alfè, 2005; 4.25 Å, Oganov et al., 2003). The vibrational frequencies of MgO (Table EA2) are consistent with those previously computed by Karki et al. (2000) and Schütt et al. (1994) at the local density approximation (LDA) level and with their experimental counterparts (Sangster et al., 1970). For example, the theoretical transverse optical frequency at the center of the Brillouin zone (383 cm⁻¹) underestimates the experimental frequency (408 cm⁻¹) by 5.4%.

The theoretical equilibrium unit-cell parameter of b.c.c. iron is 2.85 Å, in good agreement with the experimental value (2.87 Å) (Ridley and Stuart, 1968) and that obtained in a previous theoretical study at the σ -GGA level (2.86 Å) (Dal Corso and de Gironcoli, 2000). The theoretical magnetic moment per iron atom (2.40 μ_B) is in good agreement with the experimental (2.22 μ_B) and previous theoretical values (2.38 μ_B). The phonon dispersion pattern (Fig. EA1) also displays an overall good agreement with experimental values (Brockhouse et al., 1967) and the theoretical results of Dal Corso and de Gironcoli (2000). As in this previous study, the phonon frequencies of two branches are overestimated around the point N with coordinates (π/a , π/a , 0) in the Brillouin zone; whereas other branches are correctly reproduced. A single Si atom was substituted for an Fe atom in a $2 \times 2 \times 2$ cubic super-cell containing 16 atoms, providing a close chemical approximation of FeSi alloys found in E chondrites (e.g., Javoy et al., 2010). The cell parameter was fixed at the equilibrium value of pure b.c.c. iron. The incorporation of the Si atom leads to almost no structural relaxation, which is consistent with the similarity of atomic radius of Si (1.32 Å) and Fe (1.26 Å).

3.2. Theoretical reduced partition function ratios and isotopic fractionation coefficients

The theoretical reduced partition function ratios (β -factors) have been calculated for oxygen and silicon. For the diatomic molecules, the relative values of β -factors are fully determined by the stretching frequencies. This leads to a higher oxygen β -factor for CO than for SiO (Fig. 1). In contrast the relative values of β -factors observed between molecules and solids are not simply determined by the highest vibrational frequencies but also by contributions related to other vibrational modes. The oxygen β -factor of SiO is very close to that of enstatite and forsterite. This means that a compensation occurs between the higher stretching frequency of SiO (~1200 cm⁻¹ vs. ~900–1000 cm⁻¹ for the silicates), which tends to increase the β -factor, and the lack of softer vibrational modes in the SiO molecule.

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