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The incorporation of water into lower-mantle perovskites: A first-principles study

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ABSTRACT

We have used first principles methods to calculate the partitioning of water between perovskite and ringwoodite under lower mantle and Fe-free conditions. We find that incorporation of water into ringwoodite is more favourable than into perovskite by about 0.25 eV per formula unit, or about 24 kJ/mol. This translates to a ringwoodite to perovskite partition coefficient of between 10 and 13, depending on temperature. These values are in good agreement with the partitioning experiments of Inoue et al. (2010) on Fe-bearing samples, where they find a partition coefficient of about 15. We also find that water incorporates into perovskite more readily than into periclase (also under Fe-free conditions), and we predict a perovskite to periclase partition coefficient of 90 at 24 GPa and 1500 K. We conclude, therefore, that the lower-mantle is able to contain substantial amounts of water, perhaps as much as 1000 ppm.

1. Introduction

It has long been known that the nominally anhydrous transition zone minerals, wadsleyite and ringwoodite, can incorporate substantial amounts of water into their structure (Bell and Rossman, 1992; Smyth, 1994; Kohlstedt et al., 1996; Bolfan-Casanova, 2005). This has led to various models for how the dynamics and behaviour of upper mantle and transition zone may be affected by water, particularly through hydrolytic weakening and lowering of melting temperatures. Although the ability of the upper mantle and transition zone to incorporate large amounts of water is well accepted, the actual amount of water that the lower mantle is able to contain is still a matter of some debate. Some experimental studies conclude that perovskite can accommodate almost no water into its structure (Bolfan-Casanova et al., 2000, 2002), or perhaps a maximum of 100 ppm (Litasov et al., 2003), while others (Murakami et al., 2002; Inoue et al., 2010) have reported larger water uptake, ranging between 0.1 and 0.2 wt% (1000–2000 ppm).

It is currently not clear which results are correct. The apparent discrepancies between the available experimental reports can perhaps be explained in terms of the differing compositions employed in each study. Although all the experiments analysed pressure and temperature quenched samples far from their thermodynamic stability field, the earlier experiments of Bolfan-Casanova et al. (2000) used infra-red (IR) spectroscopy to analyse for water content, while Inoue et al. (2010) used secondary ion mass spectroscopy (SIMS). It is possible that the samples lost their bound OH during quench, which would reduce the IR signal, but it is also possible that the SIMS analysis includes a contribution from micro-fluid inclusions. Whatever the reason, it is important to understand which is correct and to quantify H_2O solubility in perovskite.

We have, therefore, used first principles methods to calculate water partitioning between pure Mg-endmember perovskite and ringwoodite under mantle conditions. We find a partition coefficient of 13 at 1500 K and 10 at 2000 K. These are slightly lower, but still very similar to those found by Inoue et al. (2010). We also found that water strongly prefers perovskite over periclase (again under Fe-free conditions). We suggest, therefore, that the solubility of water in perovskite may indeed be as high as 1000 ppm. This figure results if we accept the partition coefficients between olivine, wadsleyite, ringwoodite and perovskite to be 6:30:15:1 (Inoue et al., 2010; Chen et al., 2002) and assume a maximum water storage capacity of 3.3 wt%, as determined by Inoue et al. (1995).

Because of its important geophysical implications, the incorporation of hydrogen into mantle minerals has been addressed employing computer simulations by several authors. Wright and Catlow (1994) studied the structure and energetics of OH defects in olivine using empirical potentials; Haiber et al. (1997) used first-principles molecular dynamics to study the dynamics of interstitial protons in the α, β and γ polymorphs of Mg_2SiO_4. Brodholt and Refson (2000)

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used density functional theory to study hydrogen as an interstitial impurity and in interaction with cation vacancies in forsterite; they showed that the presence of hydrogen could promote the formation of cation vacancies, and this in turn could result in hydrolytic weakening. Braithwaite et al. (2003) used empirical potentials, quantum-mechanics/molecular-mechanics embedding methods and periodic electronic structure calculations to study the structure, energetics and vibrational frequencies of hydroxyl defects in forsterite. They found that hydroxyl ions were most likely to bind to cation vacancies forming neutral defects. Walker et al. (2006) later extended that study to cover also the cases of wadsleyite and ringwoodite. A review of the simulation work on hydrogen in mantle-forming minerals can be found in Wright (2006). More recent studies include those of Verma and Karki (2009), Panero (2010), and Umemoto et al. (2011). Verma and Karki (2009) have reported an extensive first principles study of both native and protonated defects in Mg_2SiO_4 polymorphs up to pressures of 30 GPa. Using the same methodology, Panero (2010) concluded that hydrogen would be most likely found in ringwoodite bound to cation vacancies; in particular, this study reported that the most abundant hydrogen-containing defect should be the Mg vacancy saturated by two protons, followed by the Si vacancy, containing four protons, and, less abundant, a substitutional Mg cation at a Si vacancy, saturated by two protons. Recently Li et al. (2011) calculated the elastic constants of H bearing olivine, wadsleyite and ringwoodite. They found that the bulk modulus of ringwoodite was unusually sensitive to water content, and suggested that $d\ln V_s/d\ln V_p$ could be used as a discriminator for water content in the transition zone.

The structure of this paper is as follows: in Section 2 we review our computational procedure, and derive an approximate expression for the partition coefficient. In Section 3 we present our results, starting with an evaluation of the ringwoodite to perovskite plus periclase phase boundary; this is a necessary prerequisite to evaluate the hydrogen partition coefficient at the relevant coexistence conditions. We then discuss the structures of various relevant cation vacancy-hydrogen complexes, and present our estimation of the hydrogen partition coefficient. Finally, our conclusions and discussion are presented in Section 4.

2. Computational details

2.1. First principles calculations

Our calculations have been carried out using the VASP program (Kresse and Furthmüller, 1996), an efficient code that implements density functional theory using a plane-wave basis set, with a convenient charge-density extrapolation technique (Alfè, 1999) which speeds up the simulations by roughly a factor of two. The valence electron–ion interaction has been treated employing the Projector Augmented Wave (PAW) method of Blöchl (1994) as implemented in VASP (Kresse and Joubert, 1999). We retained the $3s^2$ electrons of Mg, the $3s^2 3p^2$ electrons of Si and $2s^2 2p^4$ electrons of O, as well as the $1s^1$ electron of H (when appropriate), in the valence. A plane-wave kinetic energy cutoff of 500 eV was employed in all calculations, and the exchange–correlation energy was accounted for with the Perdew–Wang GGA functional (Perdew and Wang, 1992).

In order to determine the ringwoodite to perovskite and periclase phase boundary at finite temperatures we have used the quasi-harmonic approximation to obtain the Helmholtz free energy of each phase at constant volume. This was done by determining the phonon density of states of each phase at a series of volumes. The phonon band structure and density of states were obtained using the program PHON (Alfè, 2009) in conjunction with VASP. From the phonon densities of states two different approximations can be obtained to the free energy, namely a quantum approximation, which results from considering the lattice vibrations as an ensemble of quantum harmonic oscillators, or a classical one. These approximations are equivalent at high temperatures, but can differ slightly in the limit of low temperature.

Protonated cation vacancies in ringwoodite were modelled in the conventional cubic unit cell, which contains 56 atoms (16 Mg, 8 Si, 32 O). Since we anticipated that in both ringwoodite and the perovskite structures protons would preferentially substitute at Mg vacancies (see e.g. Panero, 2010), we performed our calculations in a $2\times2\times1$ supercell of perovskite (a total of 80 atoms), thus containing the same number of Mg ions as the ringwoodite cell. Convergence tests indicated that a $3\times3\times4$ Monkhorst–Pack (1976) grid gave sufficiently converged values of total energy and pressure in the case of the perovskite structure, while for ringwoodite a $4\times4\times4$ grid was employed. Structural optimisations were carried out with a convergence criterium requiring the absolute value of the force components to be smaller than 0.03 eV/Å.

2.2. Partition coefficient

The main objective of the present study is to provide an estimate of the partition coefficient of protons between the ringwoodite and perovskite phases at pressure conditions relevant to their coexistence in the Earth's mantle. Let us denote by n_r and n_p the number of proton-containing cation vacancies, $V_X(H_n)$, in ringwoodite and the perovskite phases, respectively, where X=Mg or Si and $n=2$ (if X=Mg) or $n=4$ (if X=Si). The total number of $V_X(H_n)$ complexes, n_v, is fixed, which implies the constraint $n_r+n_p=n_v$. We will further impose the condition of thermodynamic equilibrium between ringwoodite and the perovskite and periclase phases; this being the case, we can assume that there will be the same number of ringwoodite unit cells as of perovskite, denoted by N. However, because of the stoichiometry difference between these materials, there will be twice as many Mg sites in the former as there are in the latter. With the further assumption that the number of vacancy–proton complexes is small compared to N, i.e. $n_v \ll N$, we can construct a simple statistical model to estimate the partition coefficient, n_p/n_r, as follows: let us denote by $G_P(n_P)$ the Gibbs free energy of the perovskite phase containing n_p $V_X(H_n)$ complexes. With the above assumptions, this free energy can be written as

$$G_p(n_p)=G_p^0(n_p)-TS_p^{Conf}(n_p), \tag{1}$$

where $G_p^0(n_p)$ is the Gibbs free energy of N unit cells of perovskite containing n_p isolated (i.e. not clustering) $V_X(H_n)$ complexes, and $S_p^{Conf}(n_p)$ is the configurational entropy associated with the different ways in which n_p $V_X(H_n)$ can be distributed among N lattice sites. This configurational entropy has the form

$$S_p^{Conf}(n_p)=k_B\ln\frac{N_X!}{(N_X-n_p)!n_p!}, \tag{2}$$

where N_X is the number of X cation sites in the crystal (which in the cases considered is equal to N except in the case of Mg sites in ringwoodite, where $N_X=2N$; see below), and k_B is Boltzmann's constant. The first term in Eq. (1) can be written as

$$G_p^0(n_p)=(N-n_p)F_p^0+n_pF_p^f(V_X(H_n))+n_pP\Delta V_p, \tag{3}$$

where it is assumed that $V_X(H_n)$ complexes remain sufficiently far apart from each other that their mutual interaction can be ignored. In Eq. (3) F_p^0 is the Helmholtz free energy per unit cell for the perfect perovskite phase, $F_p^f(V_X(H_n))$ is the free energy of formation of a single $V_X(H_n)$ complex, P is the external pressure,