



Water distribution in the lower mantle: Implications for hydrolytic weakening

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ABSTRACT

The presence of water in lower mantle minerals is thought to have substantial effects on the rheological properties of the Earth's lower mantle in what is generally known as “hydrolytic weakening”. This weakening will have profound effects on global convection, but hydrolytic weakening in lower mantle minerals has not been observed experimentally and thus the effect of water on global dynamics remains speculative. In order to constrain the likelihood of hydrolytic weakening being important in the lower mantle, we use first principles methods to calculate the partitioning of water (strictly protons) between mineral phases of the lower mantle under lower mantle conditions. We show that throughout the lower mantle water is primarily found either in the minor Ca-perovskite phase or in bridgmanite as an $\text{Al}^{3+}-\text{H}^+$ pair. Ferropericlaase remains dry. However, neither of these methods of water absorption creates additional vacancies in bridgmanite and thus the effect of hydrolytic weakening is likely to be small. We find that water creates significant number of vacancies in bridgmanite only at the deepest part of the lower mantle and only for very high water contents (>1000 ppm). We conclude that water is thus likely to have only a limited effect on the rheological properties of the lower mantle.

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1. Introduction

A growing number of studies are finding that incorporating a water dependent rheology into global mantle convection models has a strong effect on global dynamics. For instance the feedback between water recycling and rheology can control mantle cooling history, the efficiency and timescale of water recycling, the initiation of plate tectonics, continental growth, and the formation of dense chemical anomalies (Crowley et al., 2011; Korenaga, 2011; Sandu et al., 2011; Nakagawa et al., 2015; Honing and Spohn, 2016). These results are based on the assumption that water has a strong effect on the rheological properties of mineral and rocks (hydrolytic weakening) and that this occurs throughout the connecting mantle. However, while there is an abundance of experimental evidence showing that upper mantle minerals deformed under hydrous conditions are significantly weaker than when dry (e.g. Griggs and Blacic, 1965; Karato et al., 1986; Mei and Kohlstedt, 2000a, 2000b; Karato and Jung, 2003; Faul et al., 2016), there is no such experimental evidence for lower mantle minerals.

Although the exact mechanism for hydrolytic weakening in upper mantle minerals is still in debate (Fei et al., 2013), the most likely reason is that water increases the number of vacancies avail-

able for diffusion (Kohlstedt, 2006; Faul et al., 2016). This in turn lowers the viscosity either through diffusion creep or via diffusion-controlled dislocation climb. In order to evaluate the likelihood that hydrolytic weakening also occurs in lower mantle minerals, we need to know, therefore, how water partitions between the different lower mantle phases and how water affects the concentration of deformation-controlling defects. To approach this problem we have calculated the energetics of water partitioning between various lower mantle mineral sites using Density Functional Theory (DFT) which allows us to simulate the high pressure and high temperature conditions of the lower mantle that are hard to replicate experimentally.

2. Methods

Our overall method is to use *ab initio* molecular dynamics (MD) simulations to calculate the free energy of dry and hydrous ferropericlaase, aluminous bridgmanite, calcium perovskite and $\delta\text{-AlOOH}$ and MgSiO_4H_2 at 25 and 125 GPa. Free energies were obtained as linear functions of temperature and water content, and polynomial functions of temperature. A mixture of phases representing the lower mantle was constructed, and with a fixed water content the concentrations and site locations of water were determined by solving partitioning reactions that transfer the water between various mineral sites and phases.

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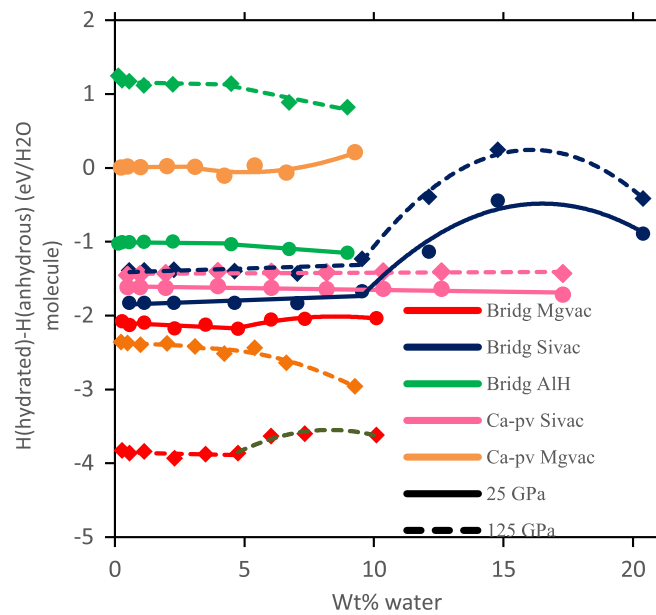


Fig. 1. Variation of the hydration enthalpy (defined as the enthalpy difference between a hydrated structure and an anhydrous structure) with increasing water concentration for different adsorption sites at 25 and 125 GPa. Lines represent 2 fits, one up to 4 wt% where enthalpy changes are essentially linear with concentration and one above 4 wt% where more complex behaviour is observed.

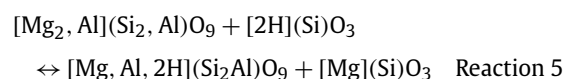
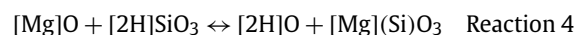
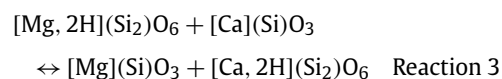
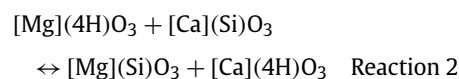
All simulations were carried out with the DFT code VASP (Kresse and Furthmüller, 1996) using the projector-augmented-wave (PAW) method (Kresse and Joubert, 1999) and the PBE formulation of GGA (Perdew et al., 2008) with the standard PAW-PBE VASP pseudopotentials used (Mg_pv, Ca_sv, H, Si and O). As our cells had unpaired H atoms we tested long range dispersion using the DFT-D3 method of Grimme (Grimme et al., 2010) and the DFT-TS method of Tkatchenko–Scheffler (Tkatchenko and Scheffler, 2009) at static conditions and found no difference in optimised geometry or enthalpy than with non-D methods. Static calculations (to determine static enthalpy differences of reactions) were run with an energy cutoff of 850 eV, ($6 \times 6 \times 6$) k points and self-consistent runs that were relaxed to within 10^{-6} eV. MD simulations (to determine thermal effects on energy differences) were run to obtain properties at high T using an NVT ensemble with the Nosé thermostat (Nosé, 1984) and with Nosé frequencies of ~ 20 THz. MD calculations were run at the gamma point with a cutoff of 600 eV, relaxation to within 10^{-4} eV and were run for at least 30 ps though all measured properties were fully relaxed by 12 ps. For Mg atoms the semicore 2p states were treated as valence and for Ca the semicore 3s and 3p states were treated as valence. All static and molecular dynamics runs were spin-polarised.

Water is treated as a replacement of protons for cations in each mineral structure, with each proton forming an OH pair. Water was simulated in Ca/Mg/Si vacancies in bridgmanite, ferropericlase, calcium perovskite and in Al–H pairs in bridgmanite by removing the cation and replacing it with 2 (Ca/Mg) or 4 (Si) H atoms and in δ -AlOOH and MgSiO_4H_2 phases where the H is bound in the structure. Both tetragonal and cubic CaSiO_3 were simulated, with the lowest energy phase (which depends upon P , T and water concentration) used. Conditions at the top (25 GPa 1000/2000 K) and near the bottom of the lower mantle (125 GPa 1000/2000/3000 K) were simulated. Below 125 GPa the post-perovskite phase may become stable, but that has not been considered here. Static cutoffs were 850 eV with ($6 \times 6 \times 6$) k -points, and dynamics cutoffs were 600 eV with the gamma point. Unit cell sizes were 80 atoms for the pv phases and 64 for fp and H-phases. δ -AlOOH and MgSiO_4H_2 crystal structures were built with a space group of P21nm and

a Pnnm respectively. Energies were determined with 1 Si or Mg (Ca) vacancy filled with 2 H (for Mg vacancies) or 4 H (for Si vacancies). This is a concentration of 1.1 (1.0) wt% water in the Mg (Ca) vacancy and 2.3 (2.0 in Ca-pv) in the Si vacancy. To simulate Al–pv we replaced an Mg–Si pair in the 80 atom unit cell of pv with an Al–Al pair ($\text{AlMg}_{15}\text{AlSi}_{15}\text{O}_{48}$) which equates to an Al_2O_3 concentration of wt% of 6.3. The enthalpy of Al substitution was found to be linear with Al concentration (as outlined in the supplementary materials) and so the energy was then scaled from 6.3 wt% to 5 wt% Al_2O_3 . To simulate the introduction of Al–H, either 1 or 2 Si atoms were replaced by an Al–H pair in the 80 atom unit cell (no difference was found between these systems).

To test the effect of water concentration we removed between 1 and 8 Mg/Ca/Si from the 80 atom unit cell and replaced them with H atoms. Due to computational constraints, this was only done at 0 K. To test lower water concentrations, we placed one hydrous vacancy in a larger 160 and 320 atom unit cell. This covers a concentration of 0.3 to 10% wt% water in Mg/Ca vacancies and 0.6 to 20 wt% in Si vacancies. For $\text{MgSi}_{1-x}(\text{AlH})_x\text{O}_3$ we tested all values of x in an 80 atom unit cell and with 1 AlH pair in a 160 and 320 atom unit cell, which gives a water concentration of 0.1 to 9 wt%. The results of this are given in Fig. 1 and show that the enthalpy change of incorporating 1 molecule of water is relatively independent of water concentration up until very large concentrations of water (~ 4 wt%).

To determine the partitioning of water we used the following reactions:



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