Water in the crystal structure of CaSiO$_3$ perovskite

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**ABSTRACT**

While the water storage capacities of the upper 700 km depths of the mantle have been constrained by high-pressure experiments and diamond inclusion studies, the storage capacity of the lower mantle remains controversial. A recent high-pressure experimental study on CaSiO$_3$ perovskite, which is the third most abundant mineral in the lower mantle, reported possible storage of H$_2$O up to a few weight percent. However, the substitution mechanism for H in this phase remains unknown. We have conducted a series of density functional theory calculations under static-lattice conditions and high pressures to elucidate hydration mechanisms at the atomic scale. All of the possible dodecahedral (Ca$^{2+}$ → 2H$^+$) and octahedral (Si$^{4+}$ → 4H$^+$) substitution configurations for a tetragonal perovskite lattice have very small energy differences, suggesting the coexistence of multiples of H configurations in CaSiO$_3$ perovskite at mantle pressures and temperatures. The dodecahedral substitutions decrease the bulk modulus, resulting in a smaller unit-cell volume of hydrous CaSiO$_3$ perovskite under pressure, consistent with the experimental observations. Although the octahedral substitutions also decrease the bulk modulus, they increase the unit-cell volume at 1 bar. The H atoms substituted in the dodecahedral sites develop much less hydrogen bonding with O atoms, leading to a large distortion in the neighboring SiO$_6$ octahedra. Such distortion may be responsible for the non-cubic peak splittings observed in experiments on hydrous CaSiO$_3$ perovskite. Our calculated infrared spectra suggest that the observed broad OH modes in CaSiO$_3$ perovskite can result from the existence of multiples of H configurations in the phase. Combined with the recent experimental results, our study suggests that CaSiO$_3$ can be an important mineral phase to consider for the H$_2$O storage in the lower mantle.

**Keywords:** CaSiO$_3$ perovskite, water, mantle, first-principles calculation

**INTRODUCTION**

Global cycles involving volatile elements, such as hydrogen, are important for a range of processes in Earth and planetary systems, including interior-atmosphere interaction, mantle mixing and convection, and surface tectonics (Bolfan-Casanova 2005; Hirschmann 2006; Ohtani et al. 2016). Laboratory studies have shown that some nominally anhydrous minerals (NAMs) in the mantle transition zone can contain a large amount of H$_2$O in the crystal structure (Kohlstedt et al. 1996; Smyth 1994; Bell and Rossman 1992), which has been recently supported by diamond inclusion studies (Pearson et al. 2014).

However, the H$_2$O storage capacities of the major nominally anhydrous mineral phases in the lower mantle have been controversial. Earlier studies proposed a possible large storage for bridgmanite (Murakami et al. 2002; Litasov et al. 2003). Later, it was suggested that the existence of small hydrous inclusions can bias the earlier results and that the H$_2$O storage capacity of bridgmanite is very low compared with the nominally anhydrous mineral phases in the mantle transition zone (Bolfan-Casanova 2005; Panero et al. 2015). However, a more recent study reported a large amount of H$_2$O stored in bridgmanite crystallized from melt (Fu et al. 2019). Therefore, the H$_2$O storage capacity of bridgmanite remains uncertain. It appears that ferropericlase can contain only a very small amount of H$_2$O (Bolfan-Casanova et al. 2003).

CaSiO$_3$ perovskite is the third most abundant phase in the pyrolytic lower mantle composition (Kesson et al. 1998; Lee et al. 2004). It is one of the main mineral phases in subducting oceanic crust materials (Hirose et al. 2005; Ricolleau et al. 2010; Grocholski et al. 2012). Inclusions in diamond crystals from the deep mantle support the existence of CaSiO$_3$ perovskite in the lower mantle (Smith et al. 2018; Nestola et al. 2018). The importance of the crystal structure and elastic properties of CaSiO$_3$ perovskite has also been highlighted for the topmost lower mantle and the core-mantle boundary region in some recent studies (Thomson et al. 2019; Gréaux et al. 2019). Astrophysical studies have shown that some stars may produce a larger amount of Ca (Hinkel and Unterborn 2018). Earth-like exoplanets around those stars may therefore contain a larger amount of CaSiO$_3$ perovskite in their lower mantle. Accordingly, it is important to measure possible storage of H$_2$O and its impact on the equation of state for understanding the geophysics and geochemistry of those planets. Although some studies have suggested possible H$_2$O storage in this mineral phase (Murakami et al. 2002; Németh et al. 2017; Chen et al. 2020), it has been difficult to characterize the amount