

## Water in the crystal structure of CaSiO<sub>3</sub> 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<sub>3</sub> perovskite, which is the third most abundant mineral in the lower mantle, reported possible storage of H<sub>2</sub>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<sup>2+</sup> → 2H<sup>+</sup>) and octahedral (Si<sup>4+</sup> → 4H<sup>+</sup>) substitution configurations for a tetragonal perovskite lattice have very small energy differences, suggesting the coexistence of multiples of H configurations in CaSiO<sub>3</sub> perovskite at mantle pressures and temperatures. The dodecahedral substitutions decrease the bulk modulus, resulting in a smaller unit-cell volume of hydrous CaSiO<sub>3</sub> 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<sub>6</sub> octahedra. Such distortion may be responsible for the non-cubic peak splittings observed in experiments on hydrous CaSiO<sub>3</sub> perovskite. Our calculated infrared spectra suggest that the observed broad OH modes in CaSiO<sub>3</sub> 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<sub>3</sub> can be an important mineral phase to consider for the H<sub>2</sub>O storage in the lower mantle.

**Keywords:** CaSiO<sub>3</sub> perovskite, water, mantle, first-principles calculation