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# 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 $H_2O$ 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 ($Ca^{2+} \rightarrow 2H^+$) and octahedral ($Si^{4+} \rightarrow 4H^+$) 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 $H_2O$ storage in the lower mantle.

**Keywords:** $CaSiO_3$ perovskite, water, mantle, first-principles calculation