# Hydrogen in enstatite: A density functional theory study

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Water (or more precisely, hydrogen) has a profound influence on the physical properties of mantle such as viscosity, melting temperature, transmission of seismic waves, and electrical conductivity (e.g. Hirschmann and David Kohlstedt, 2012). The hosts for water would be nominally anhydrous minerals (NAMs) such as olivine, pyroxene, and garnets, which are major minerals in mantle.. In order to understand the effect of water on the physical properties of these NAMs, we have to investigate how hydrogen is incorporated in these NAMs. First-principles electronic state calculations based on density functional theory (DFT) have an advantage for understanding the positions of hydrogen in minerals. Recent first-principle study has revealed the configuration of H substitution for Mg and Si ions in forsterite (Fo; $Mg_2SiO_4$) (Umemoto et al., 2011). The lowest-energy structure involved four hydrogen atoms in a tetrahedral site by substituting for silicon. The calculated O-H stretching frequencies for the structure were in good agreement with experimental IR absorption spectra of Fo.

In this study, we focused on the water in orthopyroxene (Opx; $(Mg,Fe)_{2-x}Al_{2x}Si_{2-x}O_6$). The water solubility in Opx increased linearly with increasing $Al_2O_3$ content (Rauch and Keppler, 2002). Why does the water content of Opx increase with increasing $Al_2O_3$ content? The aim of this study is to understand the mechanism of hydrogen substitution in Opx.

We have calculated the electronic state in Enstatite (En; $MgSiO_3$) which is an end member of Opx using the DFT. Calculations were performed using the generalized gradient approximation (GGA-PBE) (Perdew et al., 1996). The pseudepotential method was employed. The optimized lattice constants of En without vacancies are $a$ = 18.4556 A, $b$ = 8.92120 A, and $c$ = 5.24794 A (for the *Pbca* symmetry). The 1∗2∗4 k-point mesh was used for this supercell. Dynamical matrices for hydrogen atoms were computed using density functional perturbation theory (Giannozzi et al., 1991). We substituted hydrogen and/or $Al^{3+}$ for $Si^{4+}$ in the *T2* site and $Mg^{2+}$ in the *M1* site. Four types of the substitution $(4H)_{Si}$, $(2H)_{Mg}$, $(Al+H)_{Si}$ and $(4H)_{Si}+(Al+H)_{Si}$ were considered. Here the ions in parenthesis refer to added ions, the subscript ions refer to removed ions. Highly reactive site in En was evaluated from the lowest unoccupied molecular orbital (LUMO) distribution around various atoms. Stable positions of hydrogen in En were estimated from the direct comparison of the vibrational frequencies obtained by experimental FT-IR method and by the first-principles methods.

The calculated O-H stretching frequencies distributed from 3800 to 3000 $cm^{-1}$ depending on the substitution types. The frequencies for the structures of $(4H)_{Si}$, whose frequencies were dominant at high frequencies, can explain the high-intensity experimental IR absorption spectra of En. The calculated O-H stretching frequencies for the structures of $(4H)_{Si}+(Al+H)_{Si}$ were in good agreement with the experimental band which appeared only for $Al_2O_3$-bearing En. In En with $(Al+H)_{Si}$ substitution, there was a remarkable change for the LUMO distribution around a Si ion in *T2* site compared to the Si ion in En without the substitution. This change of the LUMO distribution implied that the Al incorporation enhances the instability of Si ions in close *T2* site. This would be explain why the Al incorporation in En enhances its the water solubility.

Keywords: orthopyroxene, hydrogen position, frequency calculation, IR, density functional theory