

Effect of aluminum on changing hydrous mechanism of enstatite: Estimated by FT-IR spectra

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Most nominally anhydrous minerals (NAMs) in the Earth's upper mantle can contain small amounts of hydrogen (i.e. "water"), structurally bond as hydroxyl. Structurally bounded water causes important influences on many physical properties of mantle rocks. The influence seems to be different from hydrogen atoms positions in crystal structure. Infrared (IR) spectroscopy has information to speculate the local structure around the OH⁻ in NAMs. In addition, the IR absorption bands of water in minerals can be also obtained from the electron state (DFT) calculations. In this study, we focused on the water in enstatite (En, MgSiO₃). The water solubility in Opx increased linearly with increasing Al₂O₃ content[1]. The aim of this study is to understand the water incorporation mechanism change between pure and Al-bearing En. We have calculated the electronic state in pure-En and Al-bearing En using the DFT and obtained vibrational frequencies and their intensity ratio. We substituted hydrogen and/or Al³⁺ for Si⁴⁺ in the T2 site and Mg²⁺ in the M site and consider five types of the substitution (4H)_{Si}, (2H)_{Mg}, (Al+H)_{Si}, (Al+H)_{2Mg} and (4H)_{Si}+(Al+H)_{Si}. Stable positions of hydrogen were estimated from the direct comparison of the vibrational frequencies and intensity ratio obtained by experimental FT-IR method and the first-principles methods. In pure En, principle water incorporation mechanisms are the substitution (4H)_{Si} and (2H)_{Mg}. In Al-bearing En, main water incorporation mechanisms change to the substitution (Al+H)_{2Mg} and (4H)_{Si}+(Al+H)_{Si}. This results indicate hydrogen prefer to incorporate along with Al³⁺. This would be a reason why the Al incorporation in En enhances the water solubility in En

[1] Rauch and Keppler (2002) *Contrib. Mineral. Petrol.***143**, 525–536.