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Nature of hydrogen defects in clinopyroxenes from room temperature up to 1000 °C: Implication for the preservation of hydrogen in the upper mantle and impact on electrical conductivity

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Abstract

Water incorporated as hydrogenated defects in mantle minerals can influence physical properties of the mantle. Knowledge of hydrogen defects at high temperatures (*T*) is fundamental to understand and quantify their influence on mantle physical properties. Clinopyroxene contributes significantly to the upper mantle water budget. Here, we investigate the behavior of hydrogen defects in 10 natural clinopyroxene crystals at temperatures up to 1000 °C using in situ and quenched experiments. The in situ high-*T* Fourier transform infrared (FTIR) spectra indicate no proton transfer between point defects, but the local environments of hydrogen defects vary. Dehydration rates at 1000 °C of the six samples with different chemical compositions are calculated based on the quenched experiments. These rates are not only slightly site-specific but also increase with Fe and tetrahedrally coordinated Al contents. Indeed, the near-FTIR spectra suggest that the dehydration of the samples in this study involves oxidation of Fe^{2+}. For two diopsides with a mantle affinity, the diffusivity is about 10^{-12} m^2/s at 1000 °C. The results mainly have the following implications: (1) the different local environments of hydrogen defects between high *T* and low *T* may be responsible for the different mechanism of water impact on electrical conductivity between high and low *T* experiments; and (2) since the hydrogen diffusivities are positively related to Fe and ^{IV}Al contents, more care is required for interpretation of measured water concentrations for clinopyroxene samples with high Fe and ^{IV}Al contents. Among the hydrogen diffusivities of olivine, orthopyroxene, and clinopyroxene in mantle peridotite, clinopyroxene should be the most reliable recorder of water from a given depth.

Keywords: Hydrogen defect, clinopyroxene, high temperature, diffusivity, in situ FTIR, electrical conductivity, effect mechanism