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Ab initio study of water speciation in forsterite: Importance of the entropic effect

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ABSTRACT

In this ab initio study, we expand previous investigations of charge-balanced hydrous Mg ($(2H)^{X}_{Mg}$) and Si ($(4H)^{X}_{Si}$) defects in forsterite, the Mg end-member of olivine, to address the relative stability of these two defects. First, we systematically search for $(2H)^{X}_{Mg}$ configurations to find possible defect states; second, we include the contribution of vibrational energy and defect configurational entropy in the calculation of formation energies of both defects; third, we address the effect of pressure and temperature simultaneously on their relative stability. Based on these considerations, we demonstrate that hydrous Mg defects ($(2H)^{X}_{Mg}$) can be stabilized with respect to hydrous Si defects ($(4H)^{X}_{Si}$) at relevant mantle conditions and that configurational entropy and vibrational free energy play key roles in this stabilization. Our results reveal that water speciation in olivine is influenced by temperature and pressure. As mantle physical and chemical properties may be affected by the speciation of water in olivine, application of experimental results to the mantle should account for the temperature- and pressure-dependent changes in water speciation.

Keywords: Hydrous defects, olivine, nominally anhydrous minerals, ab initio calculations, thermodynamics; Water in Nominally Hydrous and Anhydrous Minerals