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CHEMISTRY AND MINERALOGY OF EARTH'S MANTLE

Calculation of the energetics of water incorporation in majorite garnet†

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Abstract

Interpretation of lateral variations in upper mantle seismic wave speeds requires constraints on the relationship between elasticity and water concentration at high pressure for all major mantle minerals, including the garnet component. We have calculated the structure and energetics of charge-balanced hydrogen substitution into tetragonal $MgSiO_3$ majorite up to $P = 25$ GPa using both classical atomistic simulations and complementary first-principles calculations. At the pressure conditions of Earth's transition zone, hydroxyl groups are predicted to be bound to Si vacancies (□) as the hydrogarnet defect, $[\square_{Si}+4OH_O]^X$, at the Si2 tetrahedral site or as the $[\square_{Mg}+2OH_O]^X$ defect at the octahedral Mg3 site. The hydrogarnet defect is more favorable than the $[\square_{Mg}+2OH_O]^X$ defect by 0.8–1.4 eV/H at 20 GPa. The presence of 0.4 wt% Al_2O_3 substituted into the octahedral sites further increases the likelihood of the hydrogarnet defect by 2.2–2.4 eV/H relative to the $[\square_{Mg}+2OH_O]^X$ defect at the Mg3 site. OH defects affect the seismic ratio, $R = d\ln v_s/d\ln v_p$, in $MgSiO_3$ majorite (ΔR = 0.9–1.2 at 20 GPa for 1400 ppm wt H_2O) differently than ringwoodite at high pressure, yet may be indistinguishable from the thermal $d\ln v_s/d\ln v_p$ for ringwoodite. The incorporation of 3.2 wt% Al_2O_3 also decreases $R(H_2O)$ by ~0.2–0.4. Therefore, to accurately estimate transition zone compositional and thermal anomalies, hydrous majorite needs to be considered when interpreting seismic body wave anomalies in the transition zone.

Keywords: Hydrous majorite, defect mechanisms, force field, computer simulation, density functional theory