Ab initio study of water speciation in forsterite

Authors: Tian Qin[1], Renata Wentzcovitch[2,3], Koichiro Umemoto[4], Marc Hirschmann[1], and David Kohlstedt[1]

1. Department of Earth Sciences, University of Minnesota, 310 Pillsbury Drive SE, Minneapolis, Minnesota 55455, USA
2. Department of Applied Physics and Applied Mathematics, 500 W. 120th Street, New York, NY 10027
3. Lamont-Doherty Earth Observatory, 61 Route 9w, Palisades, NY 10964
4. Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1-IE-12 Ookayama, Meguro-ku, Tokyo,152-8550, Japan.

In this *ab initio* study, we expand previous investigations of charge-balanced hydrous Mg and Si defects, $(2\mathrm{H}^{\cdot})_{\mathrm{Mg}}^{\mathrm{x}}$ and $(4\mathrm{H}^{\cdot})_{\mathrm{Si}}^{\mathrm{x}}$, to address the relative stability of these two defects. First, we have identified new configurations for the $(2\mathrm{H}^{\cdot})_{\mathrm{Mg}}^{\mathrm{x}}$ defect; second, we have included the contribution of vibrational energy and defect configurational entropy in the calculation of formation energies of both defects; third, we have addressed the effect of pressure and temperature simultaneously on their relative stability. Based on these considerations, we demonstrate that hydrous Mg defects ($(2\mathrm{H}^{\cdot})_{\mathrm{Mg}}^{\mathrm{x}}$) can be stabilized with respect to hydrous Si defects ($(4\mathrm{H}^{\cdot})_{\mathrm{Si}}^{\mathrm{x}}$) at relevant mantle conditions and that configurational entropy and vibrational free energy play key roles in this stabilization.