Hydrogen mobility in transition zone silicates

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Hydrogen defects in mantle silicates adopt a variety of charge-balanced defects, including  $V_{Mg}$ ' '+2(H\*),  $V_{Si}$ '''+4(H\*), and  $V_{Si}$ '+(Mg+2H\*). Constraining the defect mechanism experimentally can be quite difficult, as it relies almost entirely on vibrational spectroscopy whose interpretation can often be controversial. Here we use a computational alternative: we study the above-mentioned defect mechanisms using molecular dynamics simulations based on the density-functional theory, in the VASP implementation. We perform isokinetical NVT simulations at 2000 and 2500 K using supercells containing 16 equivalent formula units of  $Mg_2SiO_4$ .

Our results show that temperature has a tremendous effect on mobility. H is significantly more mobile when incorporated as  $V_{Mg}^{\prime\prime}+2H^*$  defects than as hydrogarnet defects and that  $V_{Mg}^{\prime\prime}+2H^*$  defects are more mobile in wadsleyite than ringwoodite. This result is the opposite from the proton conductivity inferences of Yoshino et al. [2008] and Huang et al [2006], as well as the observed increase in electrical conductivity with depth through the transition zone [e.g. Kuvshinov et al, 2005; Olsen 1998].

Over the simulation time of several tens of picoseconds the H travel over several lattice sites. However, during its path it spends a considerable amount of time pinned in the defect sites. The lowest mobility is for the  $V_{\text{Si}}^{\prime\prime\prime\prime}+4(\text{H*})$  defect, where the H atoms remain inside the octahedron from which they replaced the Si.

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