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}''+2H* defects than as hydrogarnet defects and that V_{Mg}''+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_{Si}''''+4(H*) defect, where the H atoms remain inside the octahedron from which they replaced the Si.

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