Hydrogen diffusion in olivine: challenges and opportunities

Michael Jollands
(jollands@ldeo.columbia.edu)

Understanding rates and mechanisms of diffusion in geologically relevant materials is important when considering, for example, electrical conductivity, rheology and, of course, diffusion chronometry. Olivine has received much attention in this regard – not only is it important in upper mantle and many volcanic settings, but its wide range of stability in pressure-temperature-chemical activity space makes it extremely amenable to experimental petrology. Furthermore, olivine is simple enough to study systematically, but contains different crystallographic sites, diffusion pathways and is anisotropic, thus has sufficient complexity to remain interesting. Like many common rock-forming minerals, olivine is nominally anhydrous, but normally contains trace amounts of hydrogen. This is generally bonded to structural oxygen, forming hydroxyl groups. These can be easily imaged by infrared spectroscopy, which simultaneously elucidates both their concentration and associated point defect chemistry.

The combination of a mineral that is quite straightforward to study experimentally, and the ability to distinguish between different H substitution mechanisms, a major strength of infrared spectroscopy, has proved to be hugely useful. However, the more we know, the more complex the system seems to become. For example, firstly, small changes in the major element composition of olivine were shown to have considerable effects on H diffusion. Secondly, close inspection of infrared spectra from experiments and natural samples revealed the presence of point defects that, according to the generally invoked theory, should not be there. Thirdly, small variations in experimental design between different studies apparently led to major discrepancies in results, even if the experiments were designed to measure ostensibly the same process. Fourthly, apparent diffusivities extracted from well-constrained natural samples showed results in complete disagreement with experiments in the same system.

On the one hand, these complexities have the potential to severely limit the accuracy of diffusion chronometry using H diffusion. On the other hand, complexity is opportunity. Given the wealth of published studies, both experimental and natural, and given that H-bearing point defects in olivine can be easily distinguished, we are presented with a unique possibility to truly unravel the diffusive behaviour of H in olivine. Recently developed theories suggest that treating H mobility as diffusion alone is insufficient (even if multiple diffusion mechanisms are invoked), and instead it is necessary to consider the way in which different H-bearing point defects interact within the crystal. A model describing this process in both pure and trace element-doped forsterite will be presented, which reconciles, to some extent, these previous discrepancies. The model suggests that the true mobility of H is one to two orders of magnitude higher than that which has been
directly measured when assuming simple diffusion. Work is in progress to expand the model towards crystals with chemistries relevant for nature. If a similar model can be invoked for natural olivine, then this will require that models of processes invoking H diffusion (e.g. rheology, diffusion chronometry, electrical conductivity) will need to be reevaluated.