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Absolute Diffusion Rates in Minerals from First Principles

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Absolute diffusion rates in minerals depend on vacancy concentrations, the enthalpies and entropies of migration, and the ionic jump attempt frequencies. It is now possible to use ab initio (or first principles) methods to calculate all these parts, and therefore, predict diffusion rates accurately for minerals under conditions which are difficult to obtain experimentally. Techniques such as the Climbing-Image Nudged-Elastic-Band, make it straightforward to find transition states (i.e., the saddle point over which the migrating ion passes). The use of harmonic theories, such as that of Vineyard, allow us to calculate pre-factors (attempt frequencies and migration entropies). And computers are now capable of handling sufficiently large systems (i.e., several hundred atoms) that all parts can be calculated from first principles.

We have used these methods to calculate absolute diffusion rates of all three major cation species, Mg, Si, and O, in perovskite, post-perovskite and periclase. Comparison of our results with experimental results (where they exist), show excellent agreement. The largest uncertainty is the vacancy concentration. When vacancy concentrations are constrained extrinsically in the experiments and, therefore, can be accurately determined, our results agree particularly well with the experiments. Results on post-perovskite (where there is no experimental data) show that Si and Mg diffusion is highly anisotropic. Although we may expect slow diffusion across the (010) layers, the surprising results is that the anisotropy is mostly caused by extremely fast diffusion in the [100] direction, which is four orders of magnitude faster than Mg and Si diffusion in perovskite. This means that post-perovskite deforming under dislocation creep could be up to four orders of magnitude weaker than perovskite. This will have a number of important consequences for the dynamics and behaviour of the lower-most mantle.

We have also calculated Fe diffusion in these phases. In both periclase and perovskite we find that the diffusion of Fe depends strongly on spin state, with low spin Fe diffusing significantly slower than high spin Fe. Although this will strongly affect the rheology of Fe-bearing periclase, its affect on the mantle will depend on whether periclase is interconnected or not.

Results from these studies, together with on-going calculations on the diffusion of hydrogen in perovskite, will be presented.