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Proton conduction and hydrogen diffusion in olivine: Reconciling laboratory and field observations and implications for the role of grain boundary diffusion in enhanced conductivity

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Proton conduction is directly related to the diffusion of hydrogen through the Nernst-Einstein equation, but prior attempts to use this relationship have always invoked additional terms to try to reconcile proton conduction and hydrogen diffusion data. However, experimental data on hydrogen diffusion through the mineral lattice only constrain the rate of proton migration coupled with defects (such as vacancies) or coupled to polarons (electron holes mostly associated to ferric iron) and not the diffusion of uncoupled free protons. New diffusion experiments on olivine demonstrate that lattice diffusion associated to vacancies is indeed highly dependent on the defect site where hydrogen is bonded, but in any case is not fast enough to explain the observed laboratory proton conduction experiments. Hydrogen diffusion associated to polarons (redox-exchange) is significantly faster but still cannot explain the low activation energy typical of electrical conductivity measurements. A process of bulk diffusion, which combines lattice diffusion (either associated to redox-exchange or vacancies) with the far faster grain boundary diffusion, explains both the laboratory results and also field observations, and infers an average grain size of 0.5-2 cm at 100 km below the Jagersfontein kimberlite field on the Kaapvaal craton, which is consistent with petrological observations on xenolith material. Beneath the Gibeon kimberlite field on the nearby Rehoboth terrane, the higher conductivity observed cannot solely be explained by elevated temperature; either there is more water in the lithosphere (approx. double), or the average grain size is smaller (approx. half), or a combination of the two.