



## **Point defects and diffusion in the upper mantle minerals – Experimental and theoretical insights**

Ralf Dohmen

Dept. Earth Sciences, University of Bristol, UK (r.dohmen@bristol.ac.uk)

Solid-state diffusion controls a variety of dynamic processes within the Earth, e.g., the rheological behavior of rocks as well as the element and isotopic exchange on different spatial scales. Modeling these processes requires well-defined diffusion coefficients along with appropriate physical models. In the last decade a significant increase in number and improvement of quality of diffusion data for the major mantle minerals olivine, clinopyroxene, and orthopyroxene have been achieved mainly due to improved experimental and analytical techniques. A reliable application of these data to various conditions within the Earth is ultimately linked to a basic and quantitative understanding of the diffusion mechanisms and the parameters affecting the concentration of the relevant point defects. These have to be identified by a combination of experimental studies and point defect thermodynamic models. The availability of a large body of systematic diffusion data makes olivine the mineral of choice to explore this avenue. Diffusion coefficients for monovalent (Li, H), divalent (Fe, Mg, Mn, Ni, Co, Ca, Sr), trivalent (REE, Cr) and tetravalent (Si, Hf) cations as well as O are known typically as a function of temperature, and often as a function of other variables such as pressure, oxygen fugacity or water fugacity. The large amount of experimental data can be reproduced using a quantitative point defect model, which explicitly considers the various minor and trace elements in olivine (Dohmen and Chakraborty, 2007). This method was further developed to consider also H related defects and this provides now a parameterized equation to predict Fe-Mg diffusion (and potentially also Ca, Mn, Ni, etc.) in olivine over the whole range of conditions in the Earth's upper mantle. The approach is perfectly general and can be extended to any other mineral provided enough data are available. Much less is known about diffusion mechanisms and point defects in other major mantle minerals like orthopyroxene or clinopyroxene (diopside). There is also an increasing data set available for these minerals, but the role of thermodynamic parameters other than temperature (like pressure, oxygen fugacity and water fugacity) are almost unknown. Olivine will serve here as a reference case to discuss and evaluate these effects. However, a significant difference compared to olivine is the ability of the pyroxene structure to accommodate higher concentrations of heterovalent ions (e.g., Fe<sup>3+</sup>, Al<sup>3+</sup>, Cr<sup>3+</sup>, H<sup>+</sup>...). Thus, heterovalent cations may or may not increase the concentrations of the relevant point defects e.g. vacancies on the metal sites of pyroxenes, depending on the charge balancing mechanism. Despite the larger concentrations of impurities in pyroxenes, the new data sets for Fe-Mg diffusion in clinopyroxene and orthopyroxene (Chakraborty et al. 2008, ter Heege et al. 2006) show that diffusivities are significantly slower. The effect of oxygen fugacity is also smaller than in olivine, suggesting, in combination, that the concentration of vacancies on the metal site is lower. It could be concluded that vacancy formation in pyroxenes is energetically much less favorable than in olivine. Detailed experimental and also computational studies should help to quantify these effects to provide a full description of diffusion in the earth's upper mantle.

ter Heege et al. (2006) EOS Trans. AGU 87(52) MR21A-0004. Dohmen and Chakraborty (2007) Phys. Chem. Minerals, 34, 409. Chakraborty et al. (2008) EOS Trans. AGU 89(53) MR21C-0004.