Diffusion of trivalent cations in MgO: Implications for diffusion in Earth's lower mantle

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Diffusion in periclase, the second most abundant mineral in Earth's lower mantle, is key to understanding chemical exchange mechanisms and diffusive length scales at the core-mantle boundary. Diffusion of trivalent cations is a complex process in which the impurity cations tend to bind to oppositely charged cation vacancies to form pairs, which are extremely mobile; the continual presence of a vacancy adjacent to the trivalent impurity allows it to move through the lattice much more rapidly than it would in the absence of binding. Experiments were performed on Ga, Sc, and Cr in periclase to determine rates of diffusion and the energy of binding between the trivalent cation and vacancy, at 1 atm and 2 GPa and temperatures between 1468K and 2273K. Theoretical diffusion profiles were calculated numerically, and were fit to the experimental profiles through chi-square minimization, in order to extract the binding energy and impurity-vacancy pair diffusivity. Although there is no clear trend linking diffusivity to ionic radius, Cr diffuses much more slowly than Ga (Fig. 1) despite its nearly identical ionic radius. This may be accounted for by the crystal field effect, which is controlled by d-orbital electron configuration.

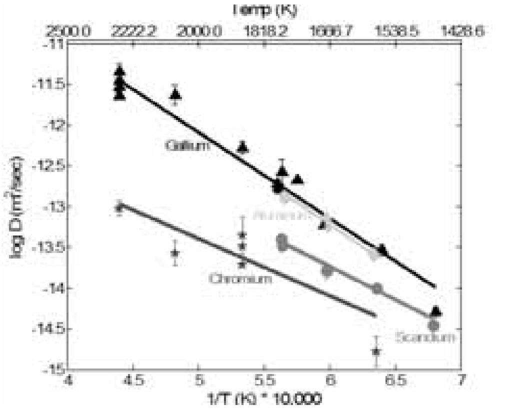

Figure 1: Arrhenius plot of diffusivity versus reciprocal temperature at a trivalent concentration of 4000 ppm. Aluminum data[1] are included here for comparison.

[1] Van Orman J.A., Chen, L., Crispin, K.L. (accepted) *Phys. Earth Planet. Interiors.*

Mixing dynamics at Mt. Etna (Italy) from textural and compositional features of phenocrysts

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Small-scale oscillatory zoning has been ascribed to local changes in kinetics at the crystal-melt interface, without necessarily implying significant variations of physic-chemical conditions of magmatic systems. At Mt. Etna, such a process can be viewed as the main among those ruling the phenocrysts evolution in lavas emitted from conduits linked to summit craters. Here, magma differentiation is chiefly driven by polybaric crystallization within the steady degassing open-conduit, where fractionation effects are continuously compensated by magma inputs from depth. Petrochemical features of phenocrysts in products emitted from lateral eruptions, not related to the open-conduit, highlight that plagioclase and clinopyroxene differing in their major and trace element zoning patterns generally coexist in the same sample. Equilibrium between crystals rim and hosting lava was tested on the least differentiated and porphyritic products, for getting information on conditions as close as possible to thermodynamic equilibrium. In spite of the spread of ${}^{Ca/Na}D_{plg/melt}$, ${}^{Fe/Mg}D_{cpx/melt}$ values, results show that the phenocrysts rim is far away from equilibrium with the hosting lava. This occurs especially when compositions abruptly change towards high An% for plagioclase and Mg# for clinopyroxene. At most two large changes were recorded along phenocryst profiles. The same crystal envelopes are characterized by low REE abundances in plagioclase and clinopyroxene as well as high Sr/Ba ratio in plagioclase. Although equilibrium cannot be verified, this might be evidence that evolving magmas repeatedly mixed with less differentiated ones during their stagnation. Assuming widths (~50 μm) of plagioclase envelopes with reverse zoning as representative of growing time under changed equilibrium conditions due to mixing, we may assess the length of destabilization events. A wide range of plagioclase growth rates in basaltic systems has been taken into account. If a minimum rate of 10^{-8} cm/s is assumed, a 50 μm-thick envelope grows within ~2 months, whereas ~12 hours are needed at the highest rate (10^{-6} cm/s), implying fast kinetics for mixing dynamics. Further developments will be aimed at establishing possible links between recharging phases, residence time of crystals within the chamber and eruption triggering.