

Insights into oxygen fugacity and charge effects on diffusion from thermal diffusion experiments

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Applications of thermal diffusion, mass diffusion driven by a temperature gradient, range from basic understanding of materials such as melt structure to possible roles in element and isotopic fractionations during rock forming processes. Here we use new temperature gradient piston cylinder (PC) experiments (T gradients determined by the spinel growth method) along with previous experiments^[1] to not only examine elemental and isotopic fractionation but also characterize valence state changes of redox active elements like Fe and V.

We performed thermal diffusion experiments from 1 hr to 100 hr in PC at 1.5 GPa and hot spot temperature from 1650 °C to 1560 °C with about 200 °C drop over ~4 mm capsule. For these, we used a basalt doped with either ~1wt.% Cr or V oxides. XANES spectroscopy at APS determined the valence state of V and Fe along the length of the capsules. The valence states of Fe and V are predominantly +2 and +3 for basaltic thermal diffusion experiments near the CCO buffer along the temperature gradient (Pt+graphite configuration). Notably, thermal diffusion in rhyolite liquid shows the existence of Fe³⁺ which is most likely due to the composition effect on Fe reduction potential. This provides a constraint for redox reaction thermodynamic datasets in the silicate melts at high temperature ^[2,3].

We also used 193nm laser ablation ICP-MS to determine major and trace element abundances in these experiments for rhyolitic to basaltic composition. Soret coefficients, which describes the overall separation by temperature gradient, of rare earth elements produce a negative Eu anomaly relative to its neighboring elements in the basaltic melts. This is attributed to the presence of Eu²⁺, and thus Soret behavior between 2+ cation and other REE³⁺. The valence state dependence of Soret coefficient of trace elements in basaltic melts is observed and can be potentially applied to the determination of the valence state of multi-valent elements.

[1] Lesher and Walker 1986, 1991. [2] Kavner et al., 2007.

[3] Toplis et al., 2002.