FINAL REPORT

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TITLE: Experiments and Models for Chemical Diffusion
in Silicate Melts

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Objectives: To characterize and understand multi-component chemical diffusion in silicate melts using laboratory experiments on molten $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$, $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$, $\text{MgO-CaO-Al}_2\text{O}_3\text{-SiO}_2$ at 1500°C and 10 Kbar.

Project Description: Chemical diffusion can be characterized by a diffusion matrix whose elements are a set of linear coefficients relating the flux of each component to chemical gradients of all the components that make up the system. The first part of this project involved laboratory experiments from which the diffusion matrix is derived by inversion of chemical interdiffusion profiles. The chemical diffusion matrix so obtained is an empirical construct that provides a general and accurate representation of chemical fluxes, but of itself, gives no insight into the underlying reasons for the often very complicated dependence of the flux of a given component on the various chemical gradients present.

The second part of this project involved using additional experiments together with theoretical models to identify the mechanisms responsible for the complex coupling among diffusing components of a silicate melt indicated by large off-diagonal terms in the diffusion matrix. There are at least two reasons for diffusive coupling. The first follows from diffusion being driven by gradients in chemical potential, not concentration gradients, thus the more a system departs from ideality, the greater the diffusive coupling when fluxes are written in terms of concentration gradients. Thermodynamic coupling is theoretically

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straightforward, but in practice very difficult to measure in a silicate melt with high accuracy. With this in mind, an additional set of experiments was carried out to independently measure the chemical activity-composition relations in molten $\text{MgO-CaO-Al}_2\text{O}_3\text{-SiO}_2$ using a recently developed method of equilibrating the molten silicate compositions with palladium metal under suitably reducing conditions. The second source of diffusive coupling arises from a volume constraint, which involves the fact that components cannot migrate freely (without regard for the other components) because were they to do so, they would very likely result in more mass entering or leaving a fixed volume than is consistent with the molar volume of the mixture. The diffusive coupling due to the volume constraint is addressed by constructing different theoretical models for how the constraint is apportioned among the various components, and then using exiting molar volume data along with new component mobility (self diffusion) measurements to produce model predictions of the chemical diffusion matrix, which are then compared to the actual diffusion matrix. The mobility data for all elements including Al were derived from ion microprobe measurements of isotope exchange in otherwise isochemical diffusion couples.

Results: The diffusion matrix in molten $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ was determined from relatively high silica contents (25% CaO , 15% Al_2O_3 , 60% SiO_2) to low silica content (35% CaO , 25% Al_2O_3 , 45% SiO_2) by simultaneously inverting chemical diffusion profiles that intersect these composition in different directions in composition space. Multicomponent diffusion, and also double diffusive convection, in molten $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ at 1550°C and 5 Kbar was also studied using diffusion couples formed around the composition of 22.5 (wt%) MgO , 17.5% Al_2O_3 , and 60% SiO_2 . The diffusion matrix was obtained from the simultaneous least squares inversion of two stable chemical diffusion profiles, while double-diffusive fingering instabilities, very similar to those reported earlier in $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$, were documented in other directions by detailed X-ray concentration mapping of the sectioned diffusion charges. The mobility (self diffusion) of Ca, Al, Si, and O was measured at 10 compositions in molten $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$, with a precision documented by replicate runs. This data set has been used to show the general inadequacy - at least for the system studied - of the Stokes-Einstein and the Eyring relationships between mobility and viscosity. Plots of mobility vs degree of polymerization, or vs molar volume, are piecewise linear but interrupted by an abrupt change in slope that we earlier interpreted as resulting from an abrupt change in melt structure. However, NMR measurements on some of our quenched glasses showed no change in the coordination of Al across the discontinuities in slope.

The theoretical model that best accounts for the measured diffusive behavior of chemical components in molten $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ is one in which thermodynamic nonideality plays an important role (quantified by Pd based activity-composition relations) and the volume constraint is satisfied by each component in proportion to the product of its concentration times its mobility. The important conclusion that follows from this model is that the flux of a dilute component is dominated by the diagonal term of the diffusion matrix and thus the activity-composition relations for fast diffusing dilute components can be derived directly from their diffusion profiles.

Key Words:

Topical index: geochemical transport, properties and dynamics of magmas

Scientific index: chemical diffusion, self diffusion, convection, silicate melts

Publications:

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The largest item of cost under this grant was salary for Research Associate Y. Liang who has since gone on to a tenure track faculty position in the Department of Geological Sciences at Brown University. The P.I. (Frank Richter) derived a month summer salary per year. Other significant cost items were:

1. Isotopically enriched Ca, Al, Si, Ge, and O used in the determination of self-diffusion coefficients and the relative mobility of isotopes of Ca and Ge.

2. Travel and lodging costs in connection with our making extensive use of experimental facilities at Renssalaer Polytechnic Institute, Troy, New York.