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Isotope Fractionation by Diffusion in Liquids

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Objectives: The overall objective of the DOE-funded research by grant E-FG02-01ER15254 was document and quantify kinetic isotope fractionations during chemical and thermal (i.e., Soret) diffusion in liquids (silicate melts and water) and in the later years to include alloys and major minerals such as olivine and pyroxene. The research involved both laboratory experiments and applications to natural settings. The key idea is that major element zoning on natural geologic materials is common and can arise for either changes in melt composition during cooling and crystallization or from diffusion. The isotope effects associated with diffusion that we have documented are the key for determining whether or not the zoning observed in a natural system was the result of diffusion. Only in those cases were the zoning is demonstrably due to diffusion can use independently measured rates of diffusion to constrain the thermal evolution of the system.

Project Description: In the early stages of the research diffusion couples are used to measure both major and minor element isotopic fractionation by chemical diffusion in natural composition melts using starting materials made from Mid-Ocean Ridge Basalt juxtaposed with a natural rhyolite glass (Richter et al. 2003, 2008, 2009). Further experiments exploring the effect of melt composition on the magnitude of kinetic isotope fractionation were also run (Watkins et al., 2014). The field component of our work involved finding natural analogues of isotopic fractionations seen in the laboratory and interpreting these in terms of dominant chemical transport mechanism (molecular diffusion versus magma mixing) in the natural system. This was done in a study of basalt-granite contacts on Vinal Haven Island, Maine where isotopic fractionations very much like what was measured in our laboratory experiments were found (Chopra et al. 2012). As the project evolved laboratory experiments were used to measure isotopic effects associated with diffusion different materials including water (Richter et al., 2006) iron-nickel alloys (Watson et al, 2016), major minerals such as pyroxene (Richter et al., 2014) and olivine (Richter et. al 2016). A separate set laboratory experiments involves quantifying thermal isotope fractionations that arise when a temperature gradient is maintained across an initially homogeneous fluid for a sufficient length of time. Numerical models reproducing the kinetic elemental and isotopic fractionation of dissolved salts in water were developed to provide insight into what controls the magnitude of kinetic effects in water (Bourg et al, 2010). Yet another set of laboratory experiments involved quantifying thermal isotope fractionations that arise when a temperature gradient is maintained across an initially homogeneous fluid for a sufficient length of time (Richter et. al, 2008, 2009, 2014 and Richter 2011).

Results:

Kinetic isotope fractionation in laboratory experiments: The laboratory diffusion experiments with molten and crystalline silicates found large - many permil per atomic mass unit - isotopic fractionations of major elements including calcium, magnesium, and iron; and the trace element lithium. The lithium results are especially important becasue of its uniquely fast diffusion both in melts and in all major minerals. The most unexpected result was the very larger isotopic fractionation of major elements including silicon, oxygen, iron, and magnesium. For example magnesium in an initially homogeneous silicate melt was fractionated by almost 5 permil per atomic mass unit per 100˚ difference in temperature. Isotopic fractionation by diffusion of dissolved species in water was found to be very much less than that in that in silicate materials. For example the isotopic fractionation of magnesium diffused in water was below detection even though our precision in making magnesium isotopic measurements is of the order of 0.1 permil. We used numerical molecular calculations to show that the very significantly reduced isotopic fractionation of dissolved species in water was due to hydration spheres with typically four inner sphere water molecules surrounding the dissolved specie and the residence time of individual water molecules in the inner hydration sphere.

Kinetic isotope fractionation in natural settings: The field study of magnesium isotopic fractionations associated with chemical diffusion of magnesium between melts of different composition exposed in Vinalhaven Igneous Complex, Maine was compared to the results of laboratory diffusion couples were made using rock powers from various rock types exposed in the complex. When the results of the laboratory experiments are compared to the magnesium isotopic fractionation associated with magnesium concentration gradients in the natural system we found cases where the lab and field results are virtually identical, however along other profiles there is no measurable magnesium isotopic fractionation associated with the magnesium concentration gradient. The degree of magnesium isotopic fractionation along a concentration gradient was used to determine the relative importance of transport between melts by diffusion (which fractionates isotopes) and by mechanical mixing that does not fractionate isotopes.

Analytical developments: We completed two studies documenting the magnitude of instrumental mass fractionation (matrix effects) associated with microanalytical methods using laser ablation inductively coupled plasma mass spectrometry - LAICPMS (Janney, et al., 2010) and secondary ionization mass spectrometry - SIMS (Chaussidon et al, 2016 in press). The main focus was on silicon, magnesium and lithium isotopes and the matrix samples included a broad range of glasses with compositions ranging from rhyolite to basalt and the mineral olivine. The results showed that the instrumental mass fractionation for both methods are large and provide guidelines as to how closely one has to bracket samples with unfractionated standards in order to remove matrix effects to a given level of realistic precision.

References acknowledging DOE support.

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