Summary of results of research by Frank M. Richter
## Work supported by Department of Energy Grant FG02-97ER14773

We have used a variety of different experiments to document isotopic fractionation by diffusion in liquid silicates. The initial set of experiments involved measuring the mass dependence of isotope mobility (or equivalently the self diffusion coefficient) in isothermal, isochemical diffusion couples (see Richter et al., 1999). The couples were made by juxtaposing glasses of the same chemical composition that had been doped isotopically to produce a large concentration step in the two isotopes whose mobility we wanted to compare (e.g. ^{40}Ca vs ^{48}Ca) but with the same isotopic ratio (e.g.$^{48}Ca/^{40}Ca$) in each half of the couple. The couples were heated to temperatures sufficient to melt the glasses and held at high temperature for sufficient time for diffusion on a measurable length scale to take place. Given the initial conditions, any significantly greater mobility of ^{40}Ca relative to ^{48}Ca would manifest itself as low (high) $^{48}Ca/^{40}Ca$ in that part of the couple that ^{40}Ca and ^{48}Ca diffused into (out of). As shown in Figure 2, this is exactly what we found.
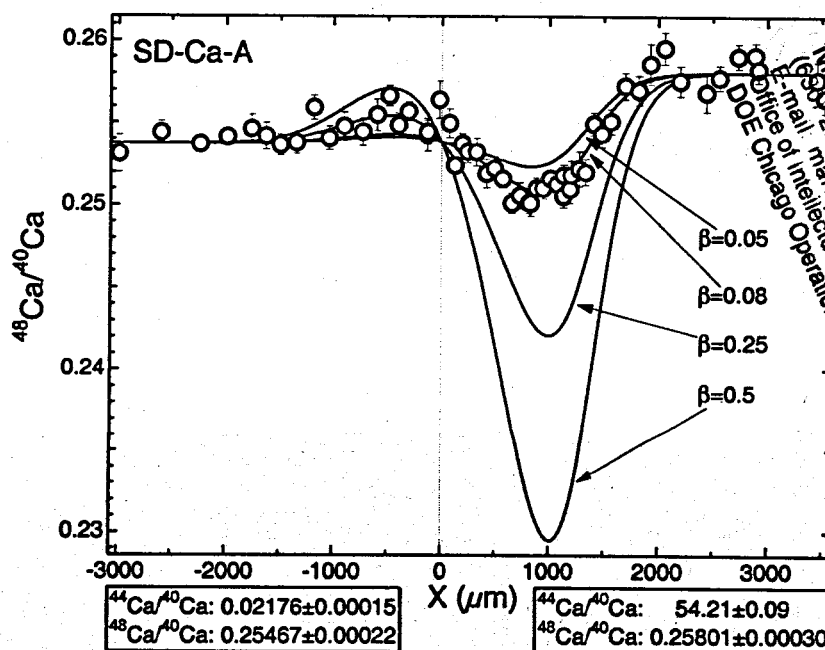
Figure 2. Ca isotope fractionation by diffusion in a $CaO-Al_2O_3-SiO_2$ glass recovered from an experiment run for 1.5 hours at 1500°C and 1.0Gpa (from Richter et al., 1999) Initial conditions were a large step in both ^{40}Ca and ^{48}Ca (high concentrations x<0) but relatively uniform $^{48}Ca/^{40}Ca$ (0.255 for x<0, 0.258 for x>0). The locally low isotopic ratios ($^{48}Ca/^{40}Ca$~0.250) centered on x=1000μm are explained by ^{40}Ca diffusing faster than ^{48}Ca by an amount $D_{40}/D_{48}=(48/40)^\beta$ with $\beta \approx 0.1$. Error bars for each data point are 1σ standard deviations based on 20 measurements of the $^{48}Ca/^{40}Ca$ ratio.

Given results such as those shown in Figure 2 it became quite clear that chemical diffusion can indeed fractionate isotopes of elements such as Ca by measurable amounts We also carried out experiments using germanium isotopes in molten GeO_2 (a lower

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.

melting point analogue for SiO_2) and found no measurable isotope fractionation. Our experimental results for both Ca and Ge isotopes are in good agreement with molecular dynamics calculations carried out by Zhou (1997) as part of her Ph.D. dissertation at the University of Chicago. Tsuchiyama et al. (1994) carried out MD simulations for the mobility of Mg isotopes in molten MgO and their results are very similar to what we found for Ca. Figure 3 summarizes the degree of isotopic fractionations expected in natural systems based on the mobility relations found by Richter et al. (1999).
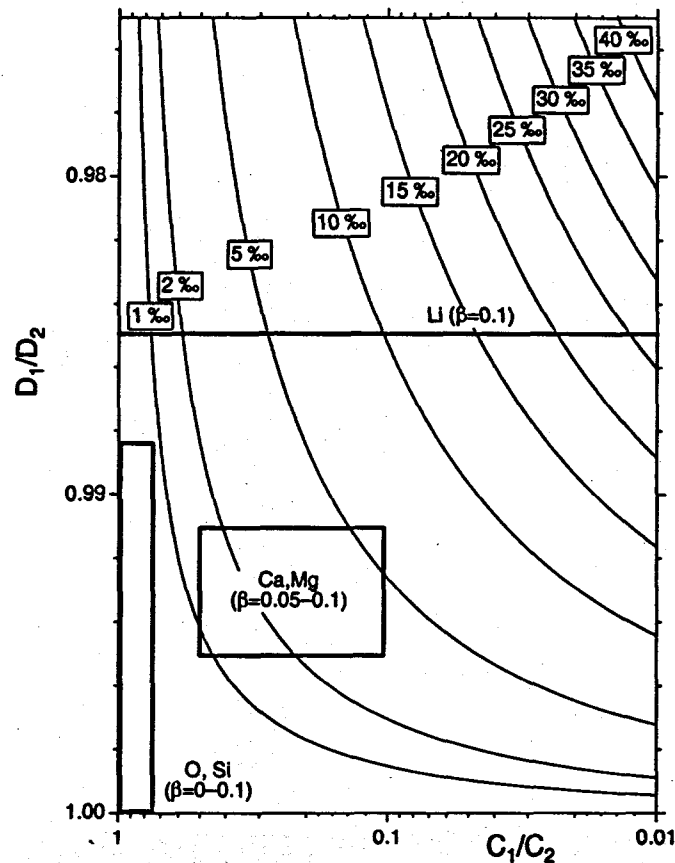

Figure 3. Contours of isotopic fractionation by diffusion as a function of the ratio of the diffusivity of the isotopes and the concentration difference driving diffusion. Also shown are expected ranges of isotopic fractionation in natural silicate melts of $^{18}O/^{16}O$, $^{30}Si/^{28}Si$, $^{44}Ca/^{40}Ca$, $^{26}Mg/^{24}Mg$, and $^7Li/^6Li$, based on measured or calculated values of the fractionation exponent β used in $D_i/D_j=(m_j/m_i)^\beta$ (D_i is the diffusivity of the isotope of mass m_i, similarly for j). Oxygen and silicon are not expected to show much diffusive isotopic fractionation in molten silicate systems because the contrast in O and Si concentration between natural melts is too small. Ca, Mg, and Li, however, are good candidates for significant isotopic fractionation by diffusion in natural silicate systems.

Our early laboratory experiments showed that diffusion in liquids can fractionate isotopes in isochemical, isothermal, isotopically-doped diffusion couples. The critical next step was to show that measurable isotopic fractionations would also occur when isotopically-normal natural composition melts are juxtaposed. We were well aware that if isotope fractionation by diffusion can only be detected in isotopically doped systems, the results would be of very limited practical importance with regard to natural systems. With this in mind we have been using diffusion couples made from natural rhyolite and MORB

basalt to tested the predictions made in Figure 3 for the fractionation of Ca and Li isotopes between melts of initially equal isotopic composition.

Ca isotope frationation: Figure 4 on page 7 shows selected elemental profiles from a typical rhyolite/basalt diffusion experiment. Aluminum exhibits some uphill diffusion, but otherwise the profiles are typical of multicomponent chemical diffusion (see Liang et al. 1996b, 1997). The CaO panel includes both concentration and isotopic measurements showing that $^{44}Ca/^{40}Ca$ has become fractionated by diffusion by about 5‰ in $\delta^{44}Ca$. This fractionation is in excellent agreement with the expectation based on Figure 3 for a concentration difference of a factor of 20. The $^{44}Ca/^{40}Ca$ was measured by thermal ionization mass spectrometry at the Berkeley Center for Isotope Geochemistry using methods developed by Russell et al. (1978). We are in the process of remeasuring the Ca fractionation in a second diffusion couple and will also measure isotopic fractionation of other elements such as Mg, possibly Fe; but certain conclusions can already be drawn: Chemical diffusion between natural composition melts does fractionate isotopes based on their relative mobility, and at least in the case of $\delta^{44}Ca$, the magnitude of the fractionations are large compared to both analytical precision (~0.2‰) and the previously measured natural variability of $\delta^{44}Ca$ (~0.2‰) among the major igneous rock types (Russell et al.,1978; Marshall and DePaolo, 1989). We now have the "fingerprint" for the diffusive transport of Ca in silicate melts, and we can start thinking about applications to natural settings where this fingerprint provides the only quantitative evidence that diffusive transport has taken place. In a later section we discuss some of the applications that we have so far identified as most promising.

Li isotope fractionation: Figure 5 on page 8 shows diffusion profiles from an experiment using the same rhyolite and basalt end-members as Figure 4 but now run at T=1350°C (rather than 1450°C) for only 6 minutes (rather than 15.7 hours). The basalt end-member was doped with a small amount of spodumene $(LiAlSi_2O_6)$ to produce a reasonably large contrast in Li content between the basalt and the rhyolite. Because of the short duration of this experiment, all elements other than lithium have hardly diffused. Indeed the most striking and unexpected feature is that Li diffuses so much faster than anything else in the system. This result is contrary to the prevailing view that Li diffuses more or less like Na (see data and discussion in Hoffman (1980) based on Li tracer diffusion data in obsidian glass. Jambon and Semet (1978) reported Li diffusion being virtually indistinguishable in both frequency factor and activation energy from that reported by Sipple (1963) for Na. Our results are clearly very different in that Li is orders of magnitudes faster diffusing than anything else including Na. It should be noted that in our experiments Li is sufficiently low in concentration that we are effectively measuring tracer diffusivity while the Na content is in the 3-5% range and thus it might be somewhat slowed by off-diagonal terms in the full diffusion matrix. However, our experimental and theoretical understanding of chemical diffusion matrices in other molten silicate systems (Liang et al.1996a, 1996b, 1977; Richter et. al, 1998) suggest that Na might be slowed relative to its tracer diffusivity by a small numerical factor but not by anything approaching the difference we found between Na and Li. More to the point perhaps is the fact that in most natural silicate systems lithium is a trace constituent, and thus there is no reason to doubt that it will diffuse orders of magnitude faster than all other major components and

other trace constituents, and therefore it can provide unique information on short time scales.
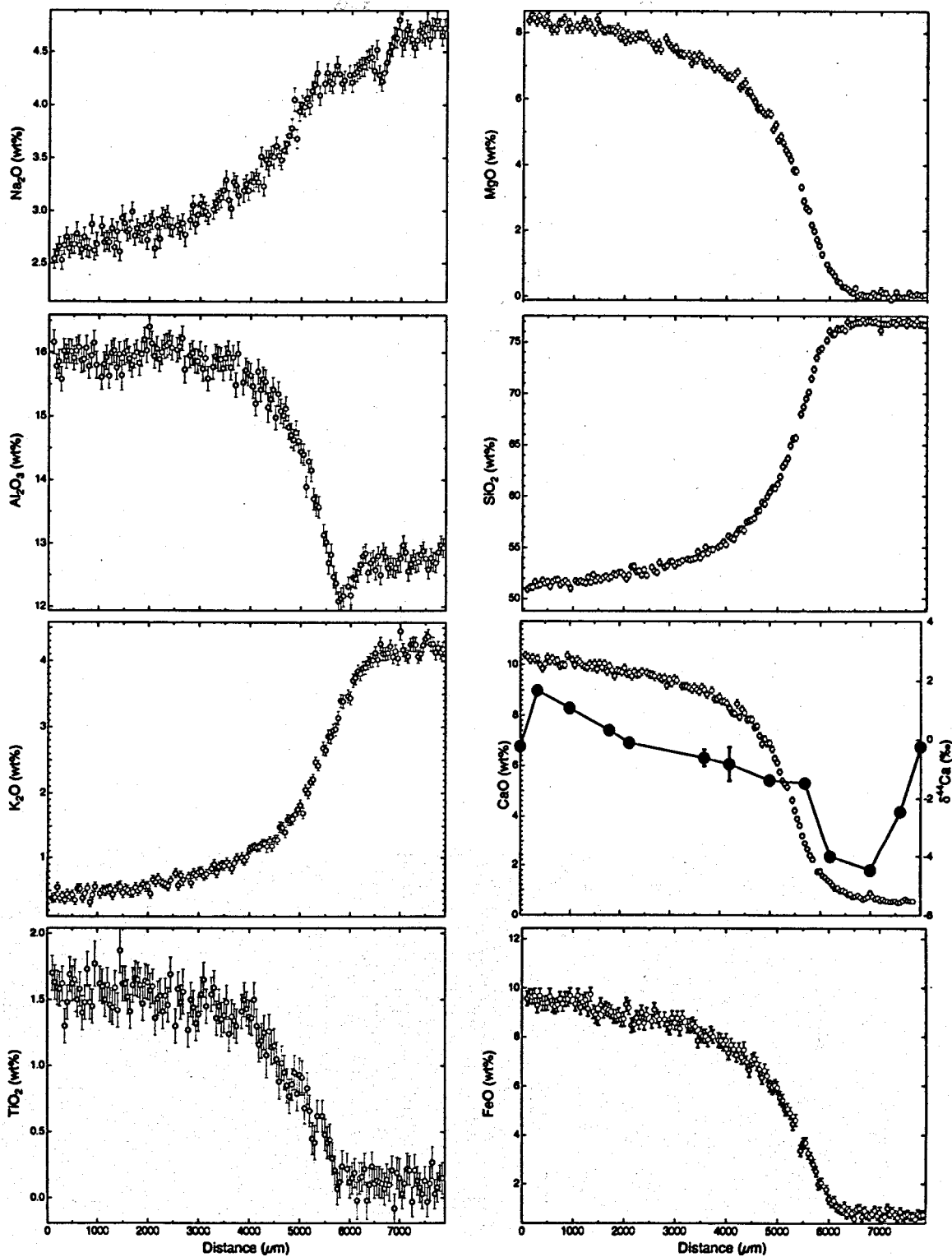
Figure 4. Diffusion profiles of major components in wt% (small unfilled circles) and Ca isotopic measurements (larger filled circles) in ‰ $\delta^{44}Ca$ from a rhyolite/basalt diffusion couple run for 15.7 hours at 1450°C and 0.5 GPa.
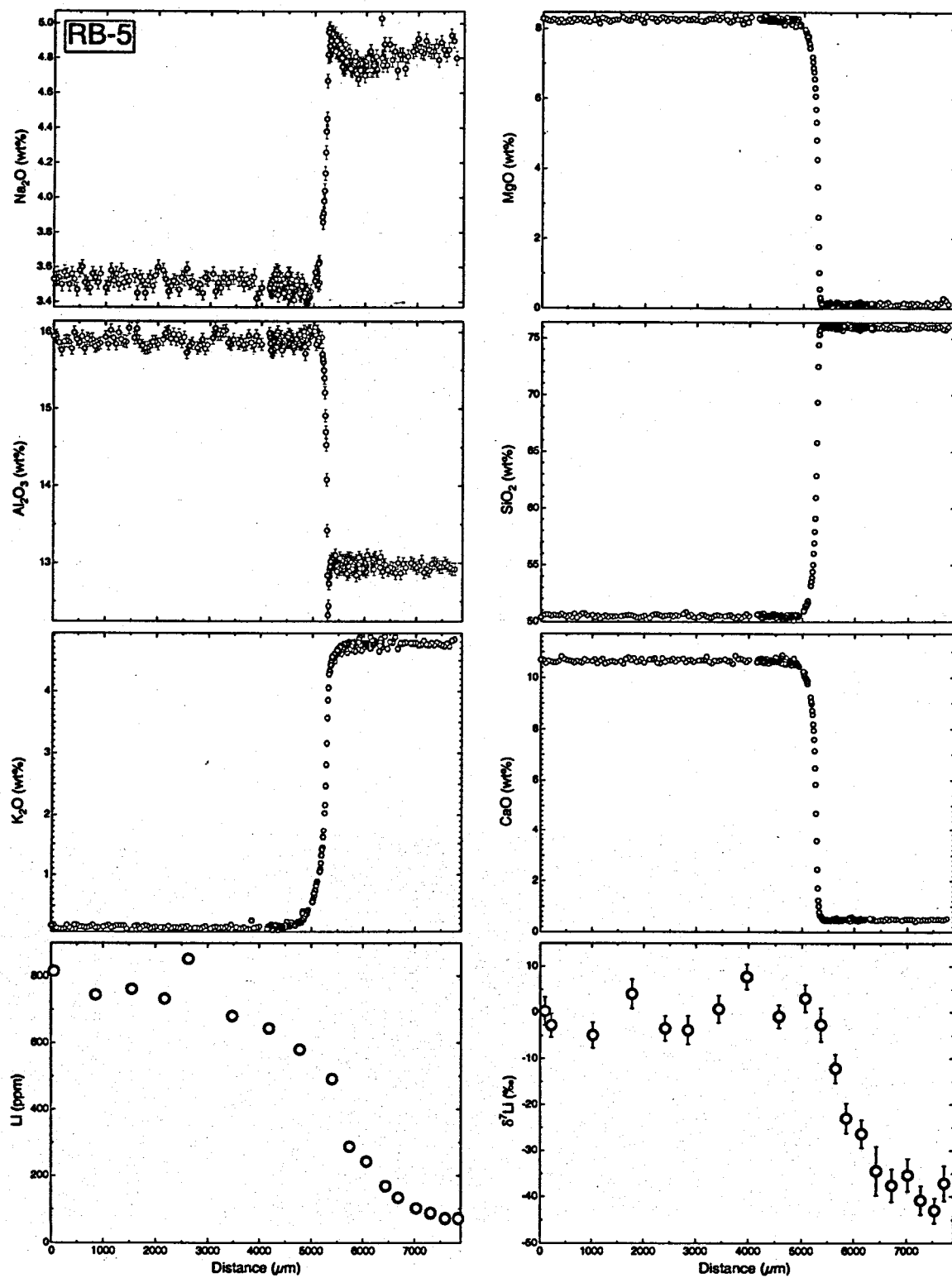
Figure 5. Diffusion profiles of major components in wt%, Li in part per million, and $\delta^7 Li$ in ‰ from a rhyolite/basalt diffusion couple run for 6 minutes at 1350°C and 0.5 GPa. The lithium content in the basalt end-member was achieved by adding about 1% spodumene. Diffusion profiles for a large number of trace elements were measured but are not shown in this figure. The abundance and isotopic composition of Li as well as the concentration of trace elements were measured using a modified AEI IM-20 ion microprobe at the University of Chicago.

The lower right hand panel of Figure 5 shows that $^6 Li$ and $^7 Li$ have been fractionated by $\delta^7 Li \sim 45$‰, which is somewhat larger than predicted by Figure 3. This suggests that for Li the exponent β might be closer to 0.2 than 0.1 as assumed when Figure 3 was originally drawn. The important point is that given a sufficiently large contrast in Li concentration, chemical diffusion will produce fractionations of the Li isotopes that are large compared to analytical precision.

D/H fractionation: Diffusion of water in silicate melts can be extremely important because of its effect on key melt properties such as viscosity, bulk density, volatile exsolution and liquidus temperature. D/H fractionation during the diffusion of water in a silicate melt is particularly interesting because there is more than one way by which D/H can be fractionated. In common with the two cases discussed above, D/H fractionation can arise from the greater mobility of H_2O compared to the heavier HDO. Both OH and OD are generally considered to be immobile compared to molecular HDO and H_2O (for a detailed account, see the recent review of water diffusion in melts by Zhang, 1999). A second kinetic process for fractionating D/H ratios along a diffusion profile arises from possible equilibrium D/H fractionation between the mobile molecular water species and the immobile hydroxyl species. Newman et al. (1988) argued on the basis of δD-H_2O variations in obsidians from Mono Craters that $(D/H)_{dissolved-H_2O}/(D/H)_{dissolved-hydroxyl}=1.052$. This is a very large fractionation of D/H between the mobile and the immobile species and it will have the effect that the diffusing water will be heavy rather than light. Thus the effect of mass on mobility will produce a negative δD anomaly in regions into which water diffuses while the fractionation of D/H between molecular water and hydroxyl will produce positive values. These opposing effects are illustrated by the model results shown in Figure 6.
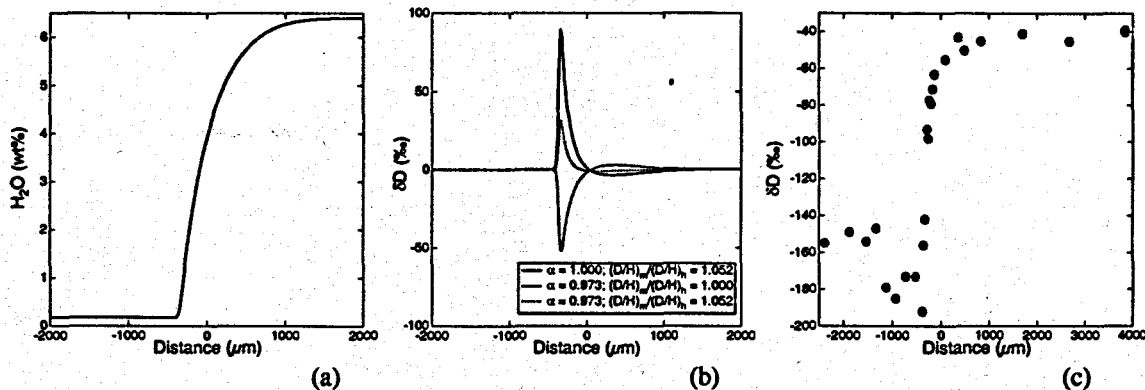

(a)   (b)   (c)

Figure 6. The panel on the left shows a calculated profile of total water in a rhyolite diffusion couple with 6.4% water juxtaposed with 0.18% water after annealing at T=1205°C, P=500MPa for 1060 seconds. The middle panel shows calculated D/H profiles assuming (i) Only equilibrium fractionation of D/H by a factor of 1.052 between the mobile dissolved water and the immobile hydroxyl. (ii) Only a mass dependent

mobility difference such that $D_{HDO}/D_{H2O}=\alpha$. (iii) Combined effects of (i) and (ii). The panel on the right shows measured D/H ratios along the water diffusion profile.

Our very preliminary data for the fractionation of D/H during diffusion of water in a silicate melt (Figure 6c) is somewhat difficult to interpret given the large contrast in D/H ratio between the end-members. The sample we analyzed was provided by Youxue Zhang (University of Michigan), and consisted of a low water content Mono Crater rhyolite (similar to that previously analyzed by Newman et al.,1988) juxtaposed with the same rhyolite that had been rehydrated in the laboratory. Zhang provided us with water content and speciation profiles measured by infrared spectroscopy for a sample that he had annealed at T=1205°C, P=500MPa for 1060 seconds. The sample was then sent to Erik Hauri (Department of Terrestrial Magnetism, Carnegie Institution of Washington) for ion microprobe measurements of the D/H ratio along the water diffusion profile. The results to date are shown in Figure 6c. It was only after analysis that we realized that there are a number of problems with this particular sample. To begin with, the end-member glasses are very different in their D/H ratio ($\delta D \sim -45\%o$ vs. $\delta D \sim -150\%o$) and therefore the mass dependent fractionation we are trying to document will be superimposed on a large diffusive gradient. The data suggest that δD is anomalously low in the direction that water has diffused, which is what we would expect when the kinetic fractionations due to mobility dominate over the effect of partitioning D/H between mobile molecular water and immobile hydroxyl species. There is a problem, however, in that the lowest δD values ($\delta D < -160\%o$) extend to about $1000\mu m$ beyond the original interface whereas very little water has reached beyond about $x=500\mu m$. We see no evidence for any significant equilibrium fractionation of $(D/H)_{dissolvedH_2O}$ relative to $(D/H)_{dissolved-hydroxyl}$, but even this has to be regarded as tentative given that there are first order features of the data that we do not yet understand. We will continue to pursue these studies partly because of the general importance of water in silicates melts, and also because water represents the simplest case we can study where speciation might produce kinetic isotope fractionation. Kinetic isotope fractionations associated with speciation may well be important in a number of other systems (e.g. dissolved silica in aqueous solution), but it will easiest to study in the case of water because the speciation is both well understood and directly measurable if necessary.

In summary, we have investigated a number of different diffusive systems, and except for Ge in molten GeO_2 found large (relative to analytical precision) mass-dependent kinetic isotopic fractionations. It appears that kinetic isotope fractionations are a pervasive fingerprint of transport by diffusion in all but the most polymerized of systems.