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Diffusive isotope fractionation in silicate liquids: Dependence on liquid composition, cation bonding, and isotopic exchange

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Diffusive isotope fractionation in silicate liquids: Dependence on liquid composition, cation bonding, and isotopic exchange

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Molecular diffusion in natural volcanic liquids discriminates between isotopes of major elements. Although isotope separation by diffusion is expected on theoretical grounds, the dependence on mass is highly variable for different elements and in different media. We have been using diffusion couple experiments to measure the relative diffusivities of Ca and Mg isotopes in both natural and synthetic silicate liquids of varying composition. Our recent experimental results, in combination with earlier results from natural volcanic liquids, show clearly that the efficiency of diffusive separation of Ca isotopes varies considerably with liquid composition, yet is systematically related to the normalized diffusivity - the ratio of the mobility of the cation (D_{Ca}) to the mobility of the liquid matrix (D_{Si}). The results on Ca isotopes are consistent with available data on Fe, Li, and Mg isotopes in silicate liquids, when considered in terms of the parameter D_{cation}/D_{Si}.

Large D_{cation}/D_{Si} corresponds to a greater efficiency of isotope separation during diffusion; in this regime, we infer that the cation is loosely bound to larger aluminosilicate structures in the liquid. As D_{cation}/D_{Si} approaches unity, the efficiency of isotope separation is reduced, presumably because the cation is more strongly bound to the silicate liquid matrix. Our experiments on natural volcanic liquids demonstrate that diffusive coupling between Ca and Al (or Si) can lead to large d^{44}Ca variations, even where there are small gradients in Ca concentration. These effects combined with theoretical models of diffusion allow us to move closer to a general model of isotopic fractionation during diffusion in silicate liquids, and to shed light on the bonding of cations within the liquids and the structure of the liquids themselves.

All of the experiments done thus far show diffusive isotope effects that depart from those predicted by an effective binary diffusion model, where each isotope diffuses in response to its own chemical gradient. Experiments with large D_{cation}/D_{Si} show only slight misfits, which can be explained by isotopic exchange superimposed on chemical diffusion. We propose a new model that accounts for this effect, in which the diffusivity describing the rate of isotope redistribution (Ds) is greater than that describing chemical diffusion (Dc) by a factor of 2 to 6. The new model provides a simple explanation for what has been described as chemical and isotopic "decoupling" during diffusion in silicate liquids. In natural liquids where D_{cation}/D_{Si} is close to unity; much larger deviations from simple diffusion models are observed. We are exploring alternative models of diffusion and the role that non-ideal mixing may play in generating these unexpected isotopic effects.

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