

Isotope fractionation by diffusion of multi-atom chemical species in silicate liquids

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Chemical speciation in molten silicates is of broad interest for understanding thermodynamic and transport properties. However, it is difficult to elicit the nature of dissolved species in silicate liquids or their role in the diffusion process.

Diffusion of calcium (Ca) between natural mafic and felsic liquids in diffusion-couple experiments produces ⁴⁴Ca/⁴⁰Ca variations of ca. 5‰ due to the mass dependence of Ca diffusion coefficients. For Ca diffusion between molten rhyolite and various mafic compositions (two tholeiitic basalts and a ugandite) the mass dependence of Ca isotope-specific diffusion coefficients varies with bulk liquid composition and correlates with the magnitude and direction of aluminum (Al) gradients. Some Ca isotopic fractionations arise solely from gradients in Al. These observations suggest that isotopic discrimination by diffusion reflects the mass difference between isotopically-distinct molecular species, and there is evidence for at least one Ca-bearing and one Ca-Al-bearing diffusing species.

We have modeled our results using a multicomponent diffusion model that accounts for Ca-Al diffusive coupling. In the deduced chemical diffusion matrix, off-diagonal terms (Ca-Al coupling) are comparable in magnitude to diagonal terms, and isotopic discrimination is greater for the off-diagonal (Ca-Al species) term. The masses we calculate for Ca-bearing species are consistent with molecules such as (Mg,Fe)CaSi₂O₆ and CaAl₂O₄. Experiments on simple systems are underway to further explore the nature of multi-atom species.

We propose that the effective mass of a diffusing species is given by the relative contribution of site hopping versus translation of larger structural units to the overall diffusion behavior of the cation. This is quantified as the ratio of cation diffusivity to the Eyring diffusivity (a proxy for melt matrix mobility). Combining our Ca results with Ca, Mg, and Li data from previous studies, we show that this simple description can explain most of the cation- and composition-dependence of diffusive isotopic fractionations observed thus far. However, all experiments exhibit isotopic features that are not yet fully explained; some of these may relate to small temperature gradients in the capsules, competing chemical versus isotopic diffusion, or to more complex coupling effects that are not captured in simplified diffusion models.

Organic geochemistry of the crater-fill sediments from Boltys impact crater, Ukraine

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The Boltys impact crater, is a complex structure formed on the basement rocks of the Ukrainian shield which has been dated at 65.17±0.64 Ma [1]. The Boltys crater has been known for several decades and was originally drilled in the 1960s - 1980s in a study of economic oil shale deposits. Unfortunately, the cores were not curated and have been lost. However we have recently re-drilled the impact crater and have recovered a near continuous record of ~400 m of organic rich sediments deposited in a deep isolated lake which overlies the basement rocks spanning a period ~10 Ma.

At 24km diameter, Boltys will not have contributed substantially to the worldwide devastation at the end of the Cretaceous. However, the precise age of the Boltys impact relative to the Chicxulub impact and its location on a stable low lying coastal plain which allowed formation of the post-impact crater lake make it a particularly important locality. After the impact, the crater quickly filled with water in a short marine phase but returned to fresh water which persisted for >10Ma [2]. These strata contain a valuable record of Paleogene environmental change in central Europe, and one of very few terrestrial records of the KT event. This pre-eminent record of the Paleogene can help us to answer several related scientific questions including the relative age of Boltys compared with Chicxulub, recovery from the impact, and later climate signals.

The organic geochemistry and palynology indicate main inputs to be algal and higher plant within most of the core although there are some marked changes in inputs in some sections. A number of carbon isotope excursions are also present within the core which are currently being further investigated.

[1] Gurov *et al.* (2006) In: Cockell, C. *et al.* (Eds) *Biological Processes Associated with Impact Events*, Springer-Verlag, Berlin pp. 335-358. [2] Kelley & Gurov (2002) *Meteorit. Planet. Sci.* **37**, 1031-1043.