Fe-Mg isotope fractionation in silicate melt by thermal diffusion

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Recent work indicates a significant mass dependence of thermal diffusion in silicate melts [1-3]. Both Soret and thermal migration experiments produce large co-variations in Fe-Mg isotope ratios along a temperature gradient [2, 3]. Because the isotopic fractionation by thermal diffusion appears to be much larger than that produced by equilibrium phase partitioning, thermal diffusion may provide a more plausible explanation for $\delta^{26}Mg$ and $\delta^{56}Fe$ variations in high temperature materials.

We measured Fe-Mg isotope ratios across Soret experiment ZM71 from [4] to assess the Fe-Mg isotope variation in andesitic melt from Mt. Hood with large ΔT (260°C). The hot end is depleted in heavy isotopes ($\delta^{56}Fe_{IRMM-14}$ = -3.0‰; $\delta^{26}Mg_{DSM-3}$ = -10.0‰) while the cold end is enriched (3.1‰ and 6.7‰, respectively). The magnitude of these isotope fractionations is similar to that found by [1] for oxygen for the same bulk composition subject to a ΔT of 200°C (cold end $\delta^{18}O$ 9.0‰; hot end $\delta^{18}O$ 2.2‰).

The thermal diffusion sensitivity (Ω, defined as the isotopic fractionation per temperature offset in units of ‰/°C/amu) describes the magnitude of stable isotope fractionation along a temperature gradient [2]. For Mt. Hood andesite melt, Ω_{Fe}, Ω_{Mg}, and Ω_O are 0.012‰/°C/amu, 0.032‰/°C/amu, and 0.017‰/°C/amu, respectively. These sensitivity factors are generally consistent with the values observed in a long duration thermal migration experiment of [3] with ΔT = 126 °C and thermal diffusion experiments on basaltic melt (ΔT= 100 - 110°C) [2]. While the maximum isotopic offset appears to be proportional to the temperature offset in near steady-state, melt-present systems, the magnitude of the sensitivity factor is not simply related to mass or atomic number as expected from kinetic theory. The role of melt structure on thermal diffusion isotopic fractionation in silicate melts is being assessed.

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Kinetics of microbial arsenate reduction in the presence of different iron and aluminium hydroxides

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The interaction of arsenic with mineral surfaces strongly influences its mobility in soil-water systems. Mircobial reduction of arsenate (As(V)) to arsenite (As(III)) may not only increase the mobility but also the toxicity of arsenic in the environment [1]. While previous studies indicated that As uptake by mineral surfaces may slow down microbial As(V) reduction [2], detailed data on this effect is still lacking. Therefore, we investigated the influence of As(V) adsorption to ferrihydrite, goethite and boehmite on the kinetics of As(V) reduction by *Shewanella putrefaciens* CN-32 in incubation experiments. The experiments were carried out at environmentally realistic total concentrations of 10 μM As(V) and 25 μM lactate at pH 7.0 (10 mM PIPES) in the absence and presence of mineral.

In mineral-free solution, the rate of As(V) reduction by *Shewanella putrefaciens* CN-32 (5×10^9 cells mL^{-1}) did not vary greatly with initial As(V) concentration and followed pseudo-first order kinetics with a half-life of ~2.6 hours. Increasing amounts of ferrihydrite, goethite, or boehmite in suspension (0.2, 2.0, and 20 g L^{-1}) substantially decreased As(V) reduction rates. This effect increased from goethite to boehmite to ferrihydrite, in parallel with the specific surface area (600, 250, and 18 m^2 g^{-1}, respectively) and the As(V) adsorption affinity of the minerals. Since desorption of As(V) from all minerals was fast (equilibration ~30 min), our data suggest that the rate of As(V) reduction in the presence of mineral surfaces was mainly limited by the reduced soluble As(V) concentrations rather than by desorption kinetics. The data further suggest that As(V) reduction by *Shewanella putrefaciens* proceeds predominantly via As(V) desorption and subsequent reduction and that reduction of adsorbed As(V) is less important.

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