

Sorption of uranium on synthetic porous phases as a model for understanding grain-scale diffusion kinetics in contaminated sediments

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Uranium mobility in contaminated aquifers, particularly in the oxidized U (VI) form, is largely controlled by sorption to mineral surfaces. Laboratory experiments with sediments from the Rifle, CO and Naturita, CO mill-tailing sites and from the Hanford 300 Area have demonstrated that desorption of the adsorbed U pool is slow, with batch-scale desorption requiring hundreds to thousands of hours to reach equilibrium. This kinetic limitation is believed to result primarily from intragranular/intra-aggregate diffusion; diffusion of U within grain fractures, clay aggregates, and clay coatings on sediment grain surfaces. A complete understanding of this process is complicated by multiple factors that are each poorly understood, including the complex aqueous and surface speciation of U, the precise nature of the diffusion process (whether it occurs predominantly in the aqueous-phase or along surfaces), anion exclusion effects, and the heterogeneous nature of the intragranular/intra-aggregate pore network.

The objective of our work is to independently address the effects of chemical speciation/retardation, physical diffusion, and diffusion domain heterogeneity in order to obtain a better overall understanding of the intragranular diffusion process. To this end, U adsorption/desorption experiments are being performed using model sorbents, including highly porous silica gel and activated aluminum oxide substrates (~6 nm internal pore diameter). Adsorption experiments with these materials yield predictable kinetic trends with varying chemical conditions and solid:solution ratio. Desorption experiments to test the effects of contact time and time-varying solution conditions are currently underway. We are also using non-reactive tracer diffusion experiments with tritium and bromide and high-resolution microscopy to independently characterize the physical diffusion regime, in order to construct a sorptive diffusion model consistent with the physical domain and to resolve the diffusion mechanism (aqueous-phase vs. interfacial diffusion). A better understanding of U (VI) diffusion in these simpler model systems will aid in the quantitative description of this process in more complex, heterogeneous natural sediments.

Trace element partitioning in the Fe-S-C±P system

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Element partitioning in metal-light element systems is important to our understanding of planetary differentiation processes. There have been numerous studies of partitioning in solid-metal/liquid-metal systems, but none have explored the simultaneous influence of S and C. Here we study the influence of both elements on trace element partitioning in the graphite-saturated Fe-S-C±P system.

Fe-S±P powders were doped with a powder mix of Ag, As, Au, Co, Cr, Cu, Ge, Ir, Ni, Os, Pd, Pt, Mo, Mn, Re, Ru, Se and W such that the concentration of each element was several hundred ppm. The Fe-S±P powders were packed into a graphite capsule, placed in a silica glass tube, and sealed under vacuum to buffer the fO_2 at C-CO-CO₂. The capsules were held in a 1-atm furnace at temperatures between 975–1350°C for a period of 4–600 hrs and then quenched in cold water. Trace element analyses were done by LA-ICPMS and major element analyses were done by electron microprobe.

Solid-metal/liquid-metal partition coefficients (1025–1125°C in Fe-S-C) show only small changes with temperature that correspond to a small change in S in the liquid. They are generally consistent with solid/liquid partition coefficients predicted by the pure Fe-S system [1], which is likely due to the nearly equal distribution of C between the solid and liquid.

Above 1125°C the solid γ -Fe metal is replaced by a C-rich, S-bearing liquid. The presence of C keeps the S content of the sulfide liquid high, and thus partition coefficients for the highly siderophile elements (HSE) remain high up to 1350°C, 10–100x higher than in pure Fe-S [1]. The immiscible liquids in the Fe-S-C system are therefore capable of producing strong HSE fractionations at much higher temperatures than pure Fe-S. If the metallic core of planetary bodies generated immiscible liquids at certain stages of their evolution [2], such coexisting liquids could have very different trace element compositions. We also present preliminary results on the Fe-S-C-P system.

[1] Chabot and Jones (2003) *Met. Planet. Sci.* **38**, 1425–1436

[2] Ulff-Moller (1997) *Met. Planet. Sci.* **33**, 207–220.