Pore-scale process coupling and its effect on the apparent rates of uranyl surface complexation

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Surface complexation is a major process that affects uranyl [U (VI)] fate and reactive transport in subsurface sediments. Surface complexation reactions occur at the pore-scale in coupling with other processes including aqueous speciation reactions, diffusion, and advection. Extensive characterization of U (VI)-contaminated sediments collected from US DOE Hanford site has revealed that U (VI) preferentially associates with certain types of porous domains including intragranular fractures, grain-coating regions, and grain-aggregates. This presentation discusses the nature and complexity of process coupling at the scales of single pore, intragranular domain, and pore-network in flow media that fundamentally control the apparent rates of U (VI) surface complexation reactions and reactive transport in subsurface porous media. Experiments and modeling studies at various scales revealed that the molecular rate of U (VI) surface complexation reactions in a single pore domain was fast with a first-order rate constant of 10^2 - 10^4 s^{-1}. The apparent rate of U (VI) surface complexation, however, decreased to 10^{-3} s^{-1} at the grain scale as a result of coupling of intragranular diffusion and reactions, and further decreased to 10^{-5} - 10^{-6} s^{-1} in flow domains where complex pore-scale coupling of flow, diffusion and reactions occurred in both inter-granular and intragranular domains in field-textured sediments. The scale-dependent reaction rates present a significant challenge to apply laboratory-determined reactions and parameters to predict field-scale reactive transport, and indicate that conceptual and numerical upscaling approaches to scale reaction rates are critically needed. This presentation will also discuss pore-network-based upscaling concepts and theories to scale reactions from the intragranular pore-network to the grain-scale, and from the grain-scale to the flow media. These upscaling approaches explicitly considered pore size and connectivity variability in porous media that affect pore-scale flow and diffusion, and their coupling with intrinsic reactions.

Fragments of hot and metasomatized mantle lithosphere sampled by mid-Miocene ultrapotassic lavas, Southern Tibet

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The first suite of mantle peridotite xenoliths have been discovered in mid-Miocene (~ 17 Ma) ultrapotassic lavas from Salipu, southern Tibet [1]. The Sailipu mantle xenoliths are very tiny with diameters of less than 1 cm, and characterized by presence of abundant phlogopite. Olivines of Salipu xenoliths have Fo [100×Mg/ (Mg+Fe)] content of 83~89, lower than typical upper mantle olivines. Both orthopyroxene and clinopyroxene in Salipu xenoliths also became iron-rich with Mg# [Mg/(Mg+Fe)] values of 0.83~0.91 and 0.84~0.89, respectively. Equilibrium temperatures of 1050~1250 ºC have been obtained for the Salipu mantle xenoliths by two-pyroxene geothermometer gives. Spinels reacted with phlogopites became Al-rich with a Cr# [Al/(Cr+Al)] of 0.1~0.2, whereas spinels that are not surrounded by phlogopites have higher Cr# values (0.32 vs. 0.36, respectively). Phlogopites in Salipu xenoliths with Mg# values of 0.82~0.94 are F-rich (2.64~8.1 %), Ti-rich (0.92~4.48 %) and contain variable contents of H_2O (0.5-5 %). Clinopyroxenes in Salipu xenoliths display convex upward rare earth element (REE) patterns, with enrichment of light rare earth elements (LREE) over heavy rare earth elements (HREE). They also mimic some trace element characteristics shown by ultrapotassic lavas in southern Tibet, especially the negative Sr, Nb, Ta, Zr, Hf and Ti anomalies. These features suggest that the metasomatic melts should be subduction-related rather than asthenosphere-derived.

Results of the Sailipu mantle xenoliths indicate the existence of hot, highly metasomatized lithospheric mantle beneath southern Tibet during the mid-Miocene, and thus support the idea that convective thinning of the lithosphere was responsible for the uplift of the plateau. The relict mantle was later removed or squeezed northward by the underthrusting Indian continental lithosphere, which terminated magmatism in southern Tibet and played a role in creating the entire plateau.

[1] Zhao, ZD. *et al.* (2008) *Acta Petrologica Sinica* **24**, 193–202.