Pore-scale Process Coupling and Apparent Surface Reaction Rates

CHONGXUAN LIU[1]*, CHANGYONG ZHANG[1], ZHI SHI[1], JIANYING SHANG[1], SEBASTIEN KERISIT[1], AND JOHN ZACHARA[1]

[1]Pacific Northwest National Laboratory, Fundamental and Computational Directorate, Chemistry and Material Sciences Division, Richland, WA 99354, USA.
chongxuan.liu@pnnl.gov

Introduction

Surface reactions such as metal oxide dissolution, reduction, and surface complexation occur in coupling with transport processes at the pore scale in subsurface sediments. The transport processes provide reactants and remove reaction products for continuous reactions, while reactions change concentration gradients and porous media properties that affect subsequent transport processes. This presentation discusses how the pore-scale process coupling affects the manifestation of surface reaction rates at the grain and Darcy scales. Uranium silicate dissolution, uranyl surface complexation, and hematite reductive dissolution by quinone-type reductants will be used as examples to demonstrate the coupled effects of reactions with transport processes on the apparent reaction rates.

Results and Discussion

Microscopic characterization revealed that geochemical reactions of interest often occur in intragranular domains in subsurface sediments such as in intragranular fractures, pores, or grain coating porous regions where reaction rates are affected by intragranular diffusion and intergranular diffusion and advection. Uranium silicate dissolution and uranyl surface complexation are two examples of such reactions that have been found to control contaminant release and transport in US Department of Energy (DOE) Hanford site [1, 2]. Experimental and modelling results at various scales consistently showed that the apparent rates of both uranium silicate dissolution and uranyl surface complexation reactions decreased with increasing scale from a single phase, to the grain scale, and to the Darcy scale. Pore-scale simulations in intragranular and flow domains revealed that the scale-dependence of the apparent reaction rates can be explained from the pore-scale coupling of the reactions with transport processes. A micromodel with complex pore-networks with pore surfaces coated with hematite are used to rigorously investigate the pore-scale coupling of reactions, diffusion, and advection and its effects on the apparent reaction rates. The surface-coated hematite in the micromodel was reduced by quinone-type reductants to mimic microbial reduction of iron oxides in the intragranular domains through a biogenic electron shuttling process. Local scale measurements within the micromodel and effluent monitoring, as well as pore-scale simulations, are collectively used to explore the coupling effect of reactions with the transport processes. The presentation will also discuss challenges to scale reaction rates at different scales and discuss effective approaches to the scale the reaction rates that can be used in reactive transport modelling at the continuum scale.

[1] Liu et al. (2004), *Geochim. Cosmochim. Acta*, 68, 4519-4537.
[2] MicKinley et al. (2007), Geochim. Cosmochim. Acta, 71, 305-325.

Age structure of lithospheric mantle beneath southeastern (SE) China

CHUAN-ZHOU LIU[1,*], FU-YUAN WU[1], JING SUN[1]

[1]Institute of Geology and Geophysics, Chinese Academy of Sciences, chzliu@mail.iggcas.ac.cn (* Presenting author)

Cenozoic basalts are widespread in southeastern China and commonly contain abundant deep-seated mantle xenoliths. In this study, we report the Re-Os isotope compositions of Cenozoic mantle xenoliths from two localities (Xinchang and Mingxi) to reveal the age structure of the lithospehric mantle beneath SE China. Twelve Xinchang mantle xenoliths have been analyzed, including two spinel lherzolites, seven spinel harzburgites and three garnet lherzolites. The relatively refractory spinel harzburgites contain 0.95-1.73% Al_2O_3, and 0.65-1.49% CaO. They have $^{187}Re/^{188}Os$ ratios ranging from 0.01 to 0.06 and $^{187}Os/^{188}Os$ ratios varying from 0.11999 to 0.12258, giving rehenium depletion ages (T_{RD}), relative to the primitive upper mantle, of 0.99-1.35 Ga and model ages (T_{MA}) of 1.09-1.48 Ga. In contrast, the fertile spinel- and garnet-lherzolites have higher Al_2O_3 contents (2.4-5.43%) and more radiogenic $^{187}Os/^{188}Os$ (0.12424-0.12801), which yield T_{RD} of 0.22-0.75 Ga.

The studied twenty-six Mingxi mantle xenoliths include eight spinel lherzolites, eight spinel harzburgites, nine garnet lherzolites and one garnet harzburgite. The spinel lherzolites have Al_2O_3 contents of 1.89-4.46%, whereas spinel harzburgites have lower Al_2O_3 contents (0.83-1.41%). The garnet lherzolites have Al_2O_3 contents of 1.41-3.59%, whereas the only garnet harzburgite contains 0.83% Al_2O_3. The spinel harzburgites display $^{187}Os/^{188}Os$ ratios ranging from 0.11685 to 0.12197, giving T_{RD} ages of 1.08-1.97 Ga. The $^{187}Os/^{188}Os$ ratios of the spinel lherzolites (0.11889-.13037) are more radiogenic than the spinel harzburgites, which yield T_{RD} ages ranging from 1.51 Ga to modern age. The garnet lherzolites have $^{187}Os/^{188}Os$ ratios of 0.12313-0.12733 and T_{RD} ages of 0.33-0.96 Ga. In contrast, the garnet harzburgite has a depleted $^{187}Os/^{188}Os$ ratio of 0.11737 and an old T_{RD} age of 1.72 Ga.

Our results show that spinel harzburgites from both localities have Proterozoic T_{RD} ages, which supports the existence of the Proterozoic mantle relics in the shallow depths beneath SE China. The garnet harzburgites and some garnet lherzolites from Mingxi also have unradiogenic $^{187}Os/^{188}Os$ ratios and ancient T_{RD} ages. This suggests that the ancient lithospheric mantle relic beenath Mingxi is thicker than that beneath Xinchang. In contrast, most spinel- and garnet-lherzolites from both localities have Os isotope compositions indistinguishable from the modern convecting upper mantle [1], representing the juvenile accretion of asthenospheric mantle in SE China. The juvenile mantle accretion in SE China could be accompanied with the lithospehric extension in this region since the Mesozoic [2].

[1] Liu *et al.* (2008) *Nature* **452**, 311-316; [2] Liu *et al.* (2012) *Chem. Geol.* **291**, 186-198.