Uranium(IV) mobility in a mining-impacted wetland

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Uranium is known to accumulate in wetlands through its association with organic-rich soils. The precipitation of relatively insoluble U(IV) minerals under reducing conditions is considered as a means to immobilize U in constructed wetland systems [1]. A wetland in the Limousin region in France, located adjacent to a former U mine was impacted by mining activity for several decades and contains U hotspots (~4,000 ppm) [2]. The concentration of U steadily increases as a function of distance in a stream flowing through the wetland, suggesting U release from the wetland into the stream. We collected soil and porewater samples under anoxic conditions from two selected U hotspots in the wetland as a function of depth and season to assess the geochemical conditions leading to this release. High porewater Fe(II) concentrations suggest that metal-reducing conditions prevail in the wetland soil. Using laser fluorescence spectroscopy (LFS) and X-ray absorption spectroscopy (XAS), we concluded that the predominant U redox state in both porewater and soil was tetravalent. A near constant U(IV) concentration is observed throughout the porewater profile while soil U(IV) is restricted to the top 30 cm. Evidence for U association with colloidal $Fe(OH)_2$-organic matter assemblages provided a ready explanation for the mobility of porewater U. Furthermore, U in the soil occurs primarily as a non-crystalline U(IV) species corresponding to U(IV) adsorbed onto amorphous Fe-Al-P-Si aggregates. Hence, U(IV) species in the porewater are distinct from those present in the soil. These results show that the form of U(IV) in soil is labile and releases U(IV) to form mobile colloids that ultimately result in the release of U into the stream. The surprising mobility of U(IV) in this system brings into question the often assumed immobilization of U through reduction, particulary in high organic matter environments such as wetlands.

[1] Owen *et al.* (1995) *Ecol. Eng.* **5**, 77-93. [2] Moulin (2008) PhD thesis, Ecole Centrale de Paris.

Nano pore evolutions of shale and coal during petroleum generation process using SANS and pyrolysis

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This study aims to examine the changes of nano- to microscaled pores of shale (marine and lacustrine) and coal with petroleum generation, retaining and cracking. Pyrolysis was used to define oil and gas window, as well as study the compositions of expulsed and retained oil while small-angle neutron scattering (SANS) was used to characterize nano- to microscaled pores of residual source rocks. Oil windows are defined as 0.6-1.3%Ro for shale and 0.5-1.2%Ro for coal; wet gas window are 0.9-3.0% Ro for shale and 0.8-3.0% Ro for coal; dry gas windows are 1.3-3.6%Ro for both shale and coal. In oil window, marine shale oil shows mainly saturated and aromatic fractions, resins and less asphaltene. In gas window, higher saturated fractions is due to its higher stability. Coal oil shows dominant asphaltene fraction with higher aromatic HC, resin, asphaltene and rare saturated HC.

Pore features corresponding to oil and gas windows by SANS show that shale and coal have unique pore features at the scale between 1 to 100 nm. Results also show that pore features change more significantly in coal relative to shale rock during hydrocarbon generation and expulsion from source rocks, presumably due to the much higher organic carbon content of the coal and unique HC fractional compositions (Fig. 1).

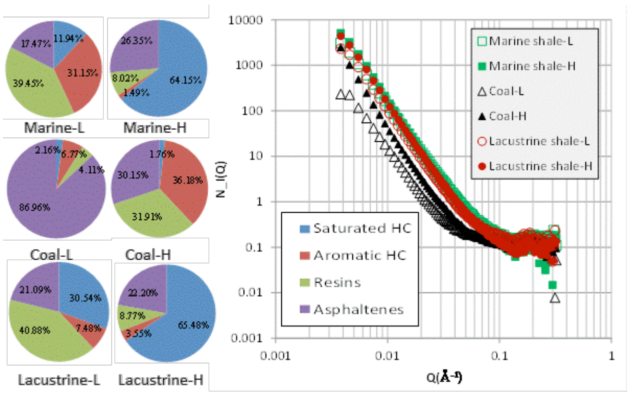

Figure 1 SANS plot of shale and coal in early oil window(L, 0.4%Ro) and post gas window(H,3.8%Ro) as well as the corresponding hydrocarbon(HC) fractional compositions

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