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Using X-Ray Spectroscopy to Define the Interplay Between Fe, S, and U Dynamics in Batch Reactors and Flow-Through Columns

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Successful modelling of elemental cycling and contaminant transport in natural environments requires detailed knowledge on the transformations of the major, minor, and contaminant elements. Information such as the reactive species, the products, and the kinetics of transformation is needed for the definition of reactions in Reactive Transport Models (RTMs). While mechanistic information is available for some reactions, others are included empirically and may not reflect the actual mechanism. The disadvantage of not including a reaction or using an incorrect reaction is that the model predictions may become inaccurate outside the conditions where the model was validated.

The Argonne Subsurface SFA is continuing to provide the mechanistic understanding of processes needed for the improvement of RTMs. We have studied the transformations of U in the presence of reduced subsurface components (Fe-containing clays and green rusts, GRs). We used carbonate extractions and XAFS spectroscopy to investigate the identity and stability of the phases resulting from U^{VI} reduction by biogenic and abiotic GRs. The results show that the initial products in the abiotic GR system were U^{IV}-carbonate complexes, which transformed to uraninite over several days. The proportion of extractable U concurrently decreased from ~95% to ~10%. In contrast, the solid-phase U^{IV} atoms in the biogenic GR system remained as non-uraninite U^{IV} species that were labile (~80% extractable).

The role of clays as adsorbents and redox buffers in subsurface environments is recognized but remains poorly understood. Using XAFS spectroscopy we studied the reducibility of Fe^{III} in SWy-2 and NAu-1 clays by sulfide or AH₂QDS. The addition of 0.2 – 10 mM sulfide leads to increasing extents of Fe^{III} reduction in 2g/L SWy-2 clay, without ferrous sulfide formation. The same limiting extent and EXAFS spectrum were observed with 2mM AH₂QDS as the reductant, also indicating lack of ferrous sulfide formation. The role of clays in controlling U speciation was also explored. We find that low loadings of reduced clay minerals reduce U^{VI} to a mixed-valence U^V-U^{VI} oxide, whereas higher loadings result in the formation of uraninite and adsorbed U^{IV} species. By varying the amounts of reductant and surface in the system we find that the stabilization of the U^V or U^{IV} state is controlled by the reducing capacity, whereas the distribution between uraninite and adsorbed U^{IV} is controlled by surface site availability. These reaction pathways are currently not included in transport models, but may be important in governing U transport in sediments with fluctuating reducing conditions.