U(IV)-mineral complexation may explain U speciation in reduced sediments

MAXIM I. BOYANOV[1,2], DREW E. LATTA[2,3], MICHELLE SCHERER[3], BHOOPESH MISHRA[2,4], CAROLYN I. PEARCE[5], KEVIN M. ROSSO[5], EDWARD J. O'LOUGHLIN[2], KENNETH M. KEMNER[2]*

[1]Bulgarian Academy of Sciences, Sofia 1113, Bulgaria (mboyanov@ice.bas.bg)
[2]Argonne National Laboratory, Argonne, IL 60439, USA (oloughlin@anl.gov)
(*correspondence: kemner@anl.gov)
[3]The University of Iowa, Iowa City, IA 52242, USA (drew-latta@uiowa.edu, schererm@engineering.uiowa.edu)
[4]University of Leeds, Leeds LS2 9JT, UK (B.Mishra@leeds.ac.uk)
[5]Pacific Northwest National Laboratory, Richland, WA 99352, USA (carolyn.pearce@pnnl.gov, kevin.rosso@pnnl.gov)

Uranium (U) poses a significant contamination hazard to soils, sediments, and groundwater due to its extensive use in energy production. Development of improved reactive transport modeling codes is paramount to understanding the risks associated with potential U dispersal. Current models assume the reduction of U(VI) to U(IV) results in the precipitation of the insoluble uraninite mineral. However, we have demonstrated previously the formation of both nanocrystalline uraninite and monomeric U(IV) as a result of biotic or abiotic electron transfer to U(VI). To further investigate the controls on the mineralization products resulting from reduction of U(VI), we studied the role of mineral surface area:U ratios and mineral chemistry on the formation of nanocrystalline uraninite versus monomeric U(IV). We exposed U(VI) solutions to model minerals (rutile, magnetite, titanomagnetite, clays) under reducing conditions with different U:mineral surface area ratios and different concentrations of Ti within titanomagnetite. Results from U L_{III}-edge XANES and EXAFS and electron imaging analysis indicate that at low surface loading, U(IV) forms monomeric inner-spere complexes with rutile and magnetite (at <1.3 U nm^{-2} and 0.037 U nm^{-2}, respectively). Similarly, monomeric U(IV) species were identified upon reduction of U(VI) in the presence of titanomagentite. XAFS results also indicate the formation of nanocrystalline uraninite for high surface loadings in the rutile and magnetite systems. These results and their relevance to understanding both near- and far-field contaminant fate and transport will be presented.