Thorium complexation by humic acid: Results from ligand competition experiments

JENNIFER C. STERN[1,3], JEROEN E. SONKE[2] AND VINCENT J.M. SALTERS[3]

[1]NASA GSFC, Greenbelt, MD 20771 (Jennifer.Stern@nasa.gov)
[2]LMTG, CNRS IRD, Toulouse, France (sonke@lmtg.obs-mip.fr)
[3]NHMFL and FSU, Tallahassee, FL 32310 (salters@magnet.fsu.edu)

The mobility of metals in soils and subsurface aquifers is strongly affected by sorption and complexation with dissolved and colloidal organic matter, oxyhydroxides, clay minerals, and inorganic ligands. Humic substances (HS) are ubiquitous organic macromolecules made up of functional groups that have a strong affinity for binding metals. The effects of HS on mobilization dynamics of actinides are of particular interest in risk assessment of nuclear waste repositories. To model actinide speciation and to determine radionuclide mobility, it is important to evaluate the binding strengths of metal-humic complexes. Thorium is often studied as an analog for tetravalent actinides, and has been shown to have a strong association with colloidal HS in natural waters. The presence of HS has also been shown to enhance sorption of Thorium to inorganic particles.

Here we present conditional binding constants ($K_{c,ThHA}$) of Thorium, Hafnium, and Zirconium-humic acid complexes from ligand competition experiments using capillary electrophoresis coupled with ICP-MS (CE-ICP-MS), a rapid and sensitive method to separate and detect metal species at trace-element compositions. Equilibrium dialysis ligand exchange (EDLE) experiments using size exclusion via a 1000 Da membrane were performed to validate CE-ICP-MS experiments. Experiments were performed at pH 3.5-7 with solution compositions of 10-100 nmol L^{-1} Th, Hf, and Zr, 10-40 mg L^{-1} Elliot Soil Humic Acid (EHA) and Pahokee Peat Humic Acid (PHA), and 0.1 mol L^{-1} $NaNO_3$. EDTA was used as the competing ligand at concentrations of 0.1-10 µmol L^{-1}. We find that tetravalent metals form strong complexes with humic acids, with $K_{c,ThHA}$ several orders of magnitude above REE-humic complexes. Our results suggest that tetravalent actinide-humic acid complexes could be important over a wider range of pH than previously thought, and that these complexes should be included in predictive speciation models.

Variation of Hg isotope ratios between cinnabar and its resulting calcines by multicollector ICP-MS with standard sample bracket correction

SARAH STETSON[1,2]*, JOHN GRAY[2], W. IAN RIDLEY[2], RICHARD B. WANTY[2], MICHAEL PRIBIL[2], RUTH E. WOLF[2] AND DONALD L. MACALADY[1]

[1]Colorado School of Mines, Department of Chemistry and Geochemistry, 1500 Illinois St, Golden, CO 80401 (*correspondence: sstetson@mines.edu)
[2]US Geological Survey, Denver Federal Center, Denver, CO 80225

The development of methods for precise measurement of mercury (Hg) stable isotopes using multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) allows the determination of small differences in isotopic composition of Hg. Methods for analysis of Hg stable isotopes vary and require validation. We report on a method for the analysis of Hg isotopes that uses cold vapor generation with 5% stannous chloride reduction. Mass bias is corrected using NIST standard reference material (SRM) 3133 and the standard-sample bracketing method, which makes no assumptions regarding the nature of the mass bias. The precision for this method was ±0.10‰(2δ) based on twenty-five measurements of the UM-Almadén Hg standard [1] over a 5-month period.

A suite of cinnabar and calcine samples (retorted cinnabar ore) collected from waste piles at the McDermitt, Nevada mine were analyzed using this method. The δ202Hg for the cinnabar samples ranged from -0.43‰ to -0.72‰ relative to NIST SRM 3133. δ202Hg of the calcine samples ranged from -1.48‰ to +0.29‰. The calcines with the highest Hg concentrations showed minimal isotopic shift with respect to the cinnabar samples. Other calcines samples were significantly heavier isotopically than the original cinnabar, indicating that mass fractionation occurred during the retorting process.

[1] Blum, J.D. & Bergquist, B.A. (2007) *Anal. Bioanal. Chem.* **388,** 353-359.