Glenn T. Seaborg Center Seminar

The Consequences of Iron Complexation by Organic Molecules for Carbon and Iron Cycling

Benjamin Gilbert

Energy Geoscience Division
Lawrence Berkeley National Laboratory

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4:00 pm – 5:00 pm
Bldg. 70A, Room 3377

In terrestrial and subsurface environments, the binding of metals by natural organic matter (OM) critically influences the cycling of carbon and metal nutrients and contaminants. In particular, the biogeochemical cycles of iron and OM are closely linked because of the high affinity of the metal in both common oxidation states to many classes of organic compounds.

Numerous groups have examined iron(III) complexation by soil OM because this can strongly increase the mobility of this insoluble cation in aerobic environments. In anaerobic environments, soluble iron(II) cations are also readily complexed by OM but this interaction is poorly characterized. Several studies have also reported iron(II) species to be preserved in aerobic systems by a mechanism speculated to be due to organic complexation. We used Fe K-edge EXAFS to study the complexation of iron(II) by reference organic ligands and by reduced OM, finding a variable abundances of functional groups associated with iron in all samples studied, and studied the consequences for iron(II) oxidation by dioxygen.

In surface waters, photochemical oxidation of carbon can play a major role in degrading organic molecules to CO_2. Binding of organic acids to iron(III) can dramatically increase photodegradation rates because the resulting complexes absorb in the visible spectrum causing ligand-to-metal charge-transfer processes that form iron(II) and unstable organic radicals. We used ultrafast infrared spectroscopy to determine the photolysis pathway of ferrioxalate, a model compound for natural iron–organic complexes.

We are also studying trace element biogeochemistry. Molybdenum is an essential nutrient for diazotrophic bacteria that use nitrogenase I to fix atmospheric nitrogen in soils into bioavailable forms such as ammonia. The molybdate ion, MoO_4^{2-}. is readily bound by *ortho* dihydroxybenzene molecules such as catechol and catecholate groups in siderophores. We are studying the interactions of molybdate with Suwannee river HA using ultraviolet-visible (UV-vis) absorption spectroscopy and isothermal titration calorimetry (ITC) ITC data revealed that binding enthalpies and kinetics were strongly influence by ionic strength, suggesting a role for macromolecular reorganization driven by metalloid addition.

Host: Rebecca Abergel (510) 486-5249 RJAbergel@lbl.gov | Admin. Asst: Catherine Mendez (510) 486-5587
Ernest Orlando Lawrence Berkeley National Laboratory One Cyclotron Road, Berkeley, California 94720