

Mercury species and thiols from GEOTRACES cruises in the North and South Atlantic Ocean

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As part of GEOTRACES research activities, we have measured dissolved and particulate mercury (Hg) species, aerosol and rainwater total Hg and dissolved thiols from a US zonal transect in the North Atlantic Ocean as well as total Hg from a meridional transect in the South Atlantic Ocean from a Dutch/UK sponsored cruise. This is currently the largest database of its kind. Findings include: 1) total Hg profiles are nutrient-like in the upper 1000 m, but show a mixture of qualities in deep water that appeared to be controlled by water mass transport; 2) surface total Hg concentrations were strongly affected by rain inputs, productivity and the Amazon River plume; 3) dissolved elemental Hg frequently followed nitrate distributions; 4) monomethyl- and dimethyl-Hg showed distinctive peaks in the oxygen minimum zones; 5) methylated Hg concentrations showed a lower response to organic carbon remineralization rates than those recently reported for the Pacific and Indian Oceans; 6) thiols appear to be important complexing agents for Hg (and other metals) in surface waters; 7) thiol concentration distributions are similar to chlorophyll, and therefore do not predict methylated Hg concentrations well.

Transformations of aqueous U(VI) during redox cycling of Fe phases

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The activity of dissimilatory iron-reducing bacteria or the corrosion of waste containers often result in the presence of Fe^{II} and Fe^{III} species in subsurface environments. Recent work has shown that dissolved Fe^{II} exchanges atoms with Fe^{III}-containing solids in a dissolution-precipitation equilibrium, which likely proceeds via formation of minor but highly reactive Fe^{II}/Fe^{III} species at the surface. The fate of dissolved or adsorbed U^{VI} during such transformations will depend on the reactivity and transformations of both major and minor Fe phases, with possible outcomes including reduction and precipitation of U^{IV}O₂ (uraninite), reduction and incorporation of U^{IV} atoms in other phases, and non-reductive solid-phase incorporation of U^{VI}. We examined the reaction of dissolved U^{VI} with a host of Fe^{II}-containing phases, including dissolved and carboxyl-adsorbed Fe^{II}, green rusts with different interlayer anions, magnetite, and NAu-2 nontronite clay, as well as with oxidized analogues such as maghemite and pyroaurite. The goal was to establish the uptake mechanisms and to characterize the molecular structure of the solid-associated U species.

Experimental Methodology

We used x-ray absorption fine-structure spectroscopy (EXAFS and XANES) at the U L_{III}- and Fe K-edge to probe the speciation of U and Fe in the hydrated solid phases after reaction. Samples were reacted under geochemical conditions relevant to the subsurface, including the presence of carbonate and/or phosphate.

Discussion of Results

U^{VI} was reduced to U^{IV} by sulfate, chloride, and carbonate green rusts; the speciation of reduced U^{IV} varied between that in uraninite and a non-uraninite, adsorbed/incorporated U^{IV} species. Pyroaurite sequestered U^{VI} as a U^{VI}-carbonate complex, presumably by interlayer ion exchange. Magnetite reduced U^{VI} to nanoparticulate uraninite when its Fe^{II}/Fe^{III} content exceeded 0.38. Reactions with more oxidized magnetite (Fe^{II}/Fe^{III} < 0.38) resulted in oxidized U species. The latter had less uranyl character than U^{VI} adsorbed to maghemite, suggesting U uptake in a distinct phase. Reactions between U^{VI}, nontronite, and Fe^{II} also resulted in oxidized, non-uranyl U species that were distinct from nontronite-adsorbed U^{VI}. Carboxyl-adsorbed U^{VI} and Fe^{II} reacted only when Fe^{II}-OH-Fe^{II} bonds formed, resulting in a combination of uraninite and U^{IV} atoms coordinated to Fe atoms in the nucleated mineral. The presence of dissolved phosphate (U:P=1:1) in the same system inhibited uraninite formation and resulted in U^{IV} atoms in phosphate-coordinated sites. The diversity of U incorporation modes in these model systems highlights the complexity in predicting U fate in subsurface environments — non-uraninite U^{IV} and non-uranyl oxidized U were also significant species in biostimulated sediments from a contaminated field site (Oak Ridge, TN), and in naturally reduced soil from Hedrick, IA, reacted with U^{VI}.