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Redox Distribution of Uranium Species in Suboxic Marine Environments

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Uranium is a member of the 5f (actinide) series of elements, all of which have a pronounced inherent sensitivity to the redox state of the environment. There are six well defined oxidation states of uranium which occur in nature. In the marine environment, including the complete vertical water column from the surface layer of the ocean down to the bottom sediments, three oxidation states of uranium - U(IV), U(V) and U(VI) - can coexist. In oxygenated seawater uranium is associated with the carbonate ion forming the very stable $UO_2(CO_3)_3^{4-}$ complex. This results in the rather high dissolved uranium concentration in the ocean, the average values being 3.3 ug L^{-1} (Chen et al., 1986). In the euphotic zone of the ocean, mixed complexes between uranium, carbonate and peroxide may be significant (Djogić and Branica, 1990).

In sedimentary processes the uranyl species are reduced to lower oxidation states and are incorporated into insoluble uranium minerals or bound to particulate organic matter. The problem of the solid(s) limiting the solubility of uranium in seawater, and thus also its concentration, remains unsolved and minerals such as uraninite, schoepite, haiweeite and others have been deemed responsible as the solubility controling solids. Under all circumstances, the oxidation state of uranium depends on the stability of reduced uranium species, which involves complex redox equilibria and processes sensitive to system parameters such as Eh-pe, pH, concentration of dissolved and particulate organic matter, free radical activity and degree of anoxia.

In the transitional suboxic/anoxic layers of the water column, particularly if the oxygen/hydrogen sulfide interface is involved, uranium(V), i.e. UO_2^+ species are thermodynamically stable (Langmuir, 1978; Kniewald and Branica, 1988). However, at the pH of seawater, the disproportionation reaction of U(V) into the (IV) and (VI) oxidation states is a feedback process resulting in a "dynamic disequilibrium" between dissolved U(VI) and U(V) species and U(V) precipitation.

The geochemical equilibrium computer code MINTEQ (Felmy et al., 1984) was used to evaluate the thermodynamic likelyhood of various uranium redox reactions under conditions of low Eh prevailing in reducing marine environments. The two probable mechanisms of reduction are:

a) reduction of dissolved UO_2^{2+} to dissolved UO_2^+ involving a kinetic equilibrium between the disproportionation reaction and the precipitation of insoluble U(V) and U(IV).

   Preliminary investigations of UO_2^+ formation in seawater, using visible and ultraviolet spectrophotometry yielded encouraging results and provide evidence that even dissolved U(V) species (the UO_2^+ cationic complex) is a probable redox species to be encountered in suboxic marine milieus, because the reduction from UO_2^{2+} to UO_2^+ involves no structural changes of the UO_2^{n+} (n = 1 or 2) ion.

b) binding of U(VI) to particulate/suspended organic matter (such as humic material) and its subsequent reduction to the less soluble redox species of U(V) and U(IV) during early diagenetic stages. This reduction process may take place at the solid/liquid interface, either in suspension or in the sediment proper.

Nonetheless, a combination of these mechanisms is also possible and will obviously depend on the prevailing redox potential of the environment, supply of DOM and POM, structure and texture of the sediment, dynamics of water exchange as well as the activity of anaerobic microorganisms.

Literature:

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