

The pathways of uranium reduction in the marine environment

Goran KNIEWALD, Marko BRANICA

Center for Marine Research Zagreb, "Rudjer Boskovic" Institute, ZAGREB, (Croatia)
and

Institute of Applied Physical Chemistry, Research Center JUELICH, (Germany)

In the marine environment and natural waters in general, three well defined oxidation states of uranium are present and coexist under appropriate conditions of redox potential and pH. Classic geochemistry interprets the biogeochemical cycle of uranium in natural waters and sedimentary environments in terms of the rather simplified concept of "soluble uranium(VI) - insoluble uranium(IV)". This perception works comparatively well for a wide range of uranium's thermodynamic equilibria in oxygenated aqueous solutions, so that the two less stable oxidation states of uranium, III and V, were not regarded as being of significance in natural waters. Uranium(III) certainly is much too strong a reducing agent to persist in natural aquatic environments, but U(V) is a possible intermediate redox species. However, the UO_2^+ species is rather unstable in the realm of natural Eh and pH conditions and quickly disproportionates between the oxidation states VI and IV. A further handicap is the analytical difficulty of distinguishing between the U(V) entity and a mixture of the redox states of U(IV) and U(VI). The instability of this aquatic species renders solution-based analytical methods (spectrophotometry, emission and absorption spectroscopy) unsuitable for experimental identification of uranium(V) - regardless of their sensitivity or degree of instrumental sophistication.

Dissolved uranium is removed from the oceans primarily by diffusion across the sediment-water interface of organic-rich sediments (Klinkhammer and Palmer, 1991). It is thus obvious that the redox shifts of the coexisting oxidation states of uranium in seawater and sediment (particularly along the redoxcline, and as a rule after iron reduction in the diagenetic sequence) will have a significant effect on the speciation, ligand interactions and surface reactions with various sediment matrices.

The geochemical equilibrium code MINTEQA2 was used to predict the solubilities of uraninite in model groundwaters and pure water. The predicted equilibria are influenced by dissolved uranium(V) species but vary considerably with the database used. A recently reevaluated value of 0.254 V for the standard redox potential of the U(VI)/U(IV) couple was used for the construction of appropriate potential-pH diagrams. The resulting stability field of the UO_2^+ ion is considerably larger. An "intrusion" of ca. 100 mV into the uranium(IV) predominance area, in the vicinity of the lower water stability fence, brings the UO_2^+ ion well into the reducing realm of Eh values. An extrapolation of this observation into conditions of Eh and pH prevailing in natural waters provides arguments for a greater geochemical role of uranium(V).

In the marine environment, the role of biomass in the equilibrium reactions of uranium has to be considered. Recent investigations have indicated that microbial reduction and the associated enzymatic precipitation of uranium are significant reaction pathways for its removal from seawater (GORBY and LOVELY, 1992). An additional challenge which needs to be addressed in further investigations is the influence of marine colloidal matter (of both inorganic and organic origin) on the redox reactions of dissolved uranium species. The concept of a thermodynamically stable U(V) species may be used to give argument to the still existing controversy over principal reduction mechanisms for uranium in the marine and sedimentary environment.

Since the scavenging (or diffusion) of uranium from seawater into suboxic sediment accounts for ca. 3/4 of dissolved uranium removal from seawater, uranium distributions may be used to estimate sedimentation rates in hemipelagic sediments and also as an indicator of paleoredox conditions.

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