The pathways of uranium reduction in the marine environment

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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, lll and V, were not regarded as being of significance in natural waters. Uranium(lll) certainly is much to 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 Vl 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 MINTEQ.A2 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(lV) 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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Metal speciation by selective adsorption

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Adsorptive stripping voltammetry of surface active complexes of metal ions and inorganic ligands can be utilized for the direct metal speciation if combined with the anodic stripping voltammetry.

A tendency in electrochemical speciation of metals is to actually measure the concentration of the particular ionic species, rather than calculating the distribution from thermodynamic data, as well as to measure it in the concentration range as close to its level in natural waters as possible (1). A progress in these efforts was achieved with inert metal complexes (2), and here a possibility of a direct quantitative measurement of a surface-active, labile inorganic metal complex is demonstrated.

Adsorption phenomena may influence voltammetric measurements significantly. Complex species of metal ions and surface active ligands can be adsorbed to the working electrode surface (3-5). For a certain metal and a certain inorganic ligand, only one complex adsorbs, usually the neutral, or negatively charged one (4). Generally, the phenomenon can be utilized for the adsorptive accumulation of surface active substances (3,5). In combination with stripping techiques especially sensitive to adsorbates, such as the square-wave voltammetry and the pulse polarography, this method enables the determination of reactants in concentrations as low as 10^{-9} M (5). In the case of metal complexation with inorganic ligands, the adsorptive preconcentration is selective since only one complex species is surface active. It will be shown that the combination of the adsorptive stripping and the anodic stripping voltammetric techniques can be used for the direct metal speciation. The anodic stripping voltammetry is used for the determination of total metal concentration. The amount of metal ions bound to the surface active complex can be determined by the independent adsorptive stripping voltammetric measurements. The character of this complex can be estimated by comparing to the theoretical ionic species distribution graph (4). Besides, an influence of electroinactive, competitive, surface-active substance, such as T-X-100, is demonstrated. Possible application to the speciation of Bi (III) in seawater is discussed.

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