

Thermodynamic and hydrogeochemical controls of the redox speciation of uranium in the marine environment

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The chemical speciation and redox equilibria of uranium in seawater (and natural waters in general) are controlled by a suite of physico-chemical processes. Among these, of primary significance from the thermodynamic point of view are major and trace constituent interactions, redox processes and sorption phenomena. The complex redox system of uranium in natural waters, involving at least three of the five known oxidation states of this element, is highly sensitive to changes of the redox potential (Eh) of the milieu. Several hydrogeochemical equilibrium models were applied to the calculation of uranium distribution between the oxidation states VI, V and IV. Subroutines for inclusion of varying redox potentials, solubility products and stability constants were used to identify thermodynamically feasible reactions, the predominating oxidation states of uranium and the respective solubility-limiting solids. The results indicate that the redox equilibria of uranium do not necessarily follow the classic concept of soluble U(VI) vs. insoluble U(IV) species. The presence and geochemical relevance of transient redox state of uranium (V) has to be accounted for in models predicting the redox speciation of uranium and its mass transfer reactions in the marine environment. Significant environmental implications include the reaction pathways of uranium precipitation and remobilization in anoxic environments, but also coastal waters, with a possibly detrimental effect on the environmental quality of such areas.