

SOME ASPECTS OF THE REDOX BEHAVIOUR OF URANIUM IN SEDIMENTARY  
PROFILES OF MARINE AND TERRESTRIAL ORIGIN

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Summary. This work presents a theoretical assessment of the redox state of uranium in sedimentary cycles within marine and terrestrial surroundings. It is based on investigations concerning the behaviour of uranium in model solutions of alkaline hydroxides as well as calculations of the stability of various redox species of uranium derived from thermodynamic data. Certain redox-dependent aspects of uranium fixation and mobilization are discussed.

Résumé. Ce travail présente une considération théorique sur l'état d'oxydation de l'uranium dans les cycles sédimentaires de l'environnement marin et terrestre. Il est basé sur les recherches du comportement de l'uranium dans les solutions alcalines modèles et sur les calculs de la stabilité des espèces redox d'uranium dérivé des données thermodynamiques. Certains aspects de fixation et mobilisation de l'uranium sont discutés.

The geochemical behaviour of uranium in aqueous solutions, including natural waters, concerning the influence of the redox potential and pH with regard to its fixation and mobilization within the sedimentary environment is fairly well defined. Nevertheless, very little is known about the processes involved during diagenesis (particularly its early stages) of uraniferous organogenic components of ancient and contemporary sediments. The mobile forms of uranium (i.e. particles smaller than 0.45  $\mu\text{m}$  which may be regarded as "dissolved") include ionic species, molecular solutes and colloidal-size particles associated with suspended matter. Apart from uranium bound to suspended particles of organic origin, uranium is mobilized primarily as U(VI). Presenting a kind of "geochemical trap", organic matter - humic acids in particular - efficiently scavenge uranium from natural waters, reducing it to the oxidation state (IV). However, under anoxic conditions which are encountered within oxygen depleted sediment layers (and occasionally within the overlying watercolumn) U(V) may form as an intermediate in the process of reduction of U(VI). This is particularly true for solid phases such as reduced uranium minerals, where uranium seems to be stabilized in its oxidation state (V). The Eh-pH diagram of Fig. 1

based on thermodynamic data of Langmuir (1) shows the realm within which U(V) species are stable. This corresponds to euxinic sediment types found in connection with slightly acidic waters (2).

A survey of selected literature (3) resulted in the observation of a very interesting phenomenon. A comparison of the uranium content and

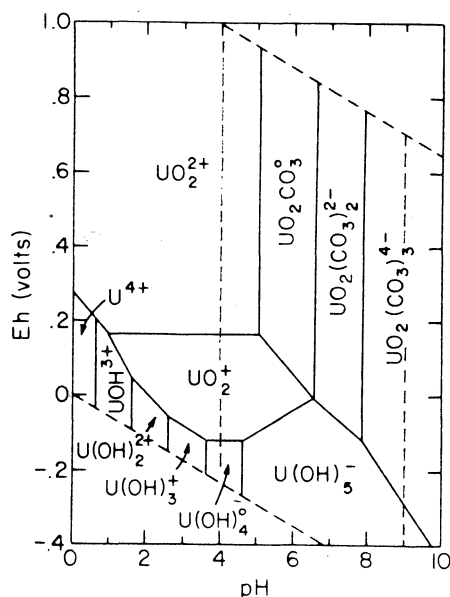


Fig.1. Relative importance of +4, +5 and +6 valent uranium species in aqueous solution at 298 K.

$$U_{\text{total}} = 10^{-6} \text{ mole l}^{-1}$$

CO<sub>2</sub> pressure is 32.05 Pa (1)

the kind of chemical binding of uranium showed that in low grade ore samples and sediments (less than 0.1% U), the U is bound to organic substance. Within sediments with higher U concentrations, inorganic chemical binding is the dominating mode, although a statistical correlation between organic matter and uranium content is still present. Circumstances where the sedimentary environment presents rather few reducing facies and complexing phases, show that an elevated sorbent availability (i.e. ferric oxy-hydroxide) such as in ferrolitic soils or stream sediments of the tropics, could be the main cause of uranium fixation. The lateritic environment is geochemically characterized, among other parameters, by strong oxidation and intense leaching. Under these conditions, uranium is oxidized to its highest oxidation state (VI) and is highly mobile. This would normally result in a hydrogenic dispersion process, although it has been noted (4) that lateritisation can, under specific circumstances, lead to absolute concentration of uranium.

#### References:

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