

## SIGNIFICANCE OF URANIUM(V) IN MARINE SEDIMENTARY PROCESSES

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SUMMARY: Investigations of uranium(V) stability in model alkaline solutions were carried out. Uranium(V) is apparently stabilized in the solid phase due to its lower solubility in comparison with U(VI) salts. The potential significance of U(V) as a transitional oxidation state in the marine environment is emphasized.

RESUME: Le comportement d'uranium pentavalent dans les solutions alcalines modèles a été étudié. Il semble que U(V) est stabilisé dans la phase solide à cause de sa solubilité inférieure que les composés de U(VI). L'importance potentielle d'uranium(V), un état d'oxydation transitif dans le milieu marin, est soulignée.

It has been suggested(1) that the fate of uranium in some coastal waters may be influenced by alterations in speciation under reducing conditions, involving the reduction of U(VI) - present in seawater mainly as the tricarbonate complex - to lower oxidation states(2). A revised value for the redox potential of the U(VI)/U(IV) couple led some authors(3) to the rather interesting conclusion that U(IV) is less stable with respect to the oxidation states VI and V. Uranium(V), a species until recently practically ignored by geochemists, has an appreciable field of stability in reduced waters below pH 7. Part of the stability field of the  $UO_2^+$  species falls well within the Eh-pH limits of natural environments, as outlined by Baas Becking et al.(4).

Sediments abundant in organic matter represent environmental restrictions commonly involving stagnation of the depositional medium. The water column above such sediments is usually neutral, occasionally even slightly acidic and reduced, capable of accomodating uranium partially in the oxidation state V. Carbonate complexation could, however, interfere with the stability of U(V) leading to its disproportionation between the states IV and VI. The enhancement of uranium within sediments deposited in anoxic surroundings is well established

- there is however, as yet, no unequivocal evidence that the reduction of uranium in overlying waters is a contributing process. Eh's found in bottom waters of basins with impaired circulation are low enough to bring about the reduction of U(VI) and the deposition of highly insoluble U(IV) precipitates. On the other hand, sorption interactions on organic material and the formation of organic complexes also result in the enrichment of uranium in anoxic sediments. Sediments of this type can be assigned to the restricted humid (euxinic) environment of the Krumbein-Garrels classification of chemical sediments(5), deposited under conditions similar to those in which many geologically old uraniferous black shales also accumulated.

Results of our studies of uranium(V) in model alkaline solutions and its precipitation following electrochemical reduction of U(VI) in LiOH(7) solution showed that the precipitate is a hydrated lithium uranate(V) of somewhat variable composition, the  $UO_2^+$  group being preserved. ESR studies of solid U-compounds (8) showed that selective determination of U(V) is possible even in the presence of U(VI) and U(IV). We have suggested that U(V) is stabilized in the solid phase due to its lower solubility compared with U(VI) compounds.  $UO_2^+$  complexes are evidently much less stable than  $UO_2^{2+}$  and  $U^{4+}$  complexes formed with the same ligands(6).

To conclude, our results and the published data imply that U(V) is probably present as a transitional oxidation state within a limited Eh-pH realm, at the boundary of oxic and anoxic marine environments. This should particularly be true for the region below the depositional interface where U(V) would be incorporated into the solid phase of the reduced uranium minerals and organic and humate complexes within the oxygen-depleted sediment layer.

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Paper presented by G. Kniewald (Yugoslavia)

#### Discussion

- R. Bojanowski: Did you try to demonstrate the presence of U(V) compounds in the natural environment using the technique you mentioned for U-Li examination?
- G. Kniewald: Selective determination of U(V) was done using the ESR technique. However, we obtained only qualitative results with Li-uranate(V) samples. For the moment we are not certain whether we would obtain unambiguous results on natural samples where the uranium concentration levels are certainly much lower and where other components would possibly interfere with their spin spectra.
- B. Čosović: If the solid phase stabilises U(V), what is the fate of uranium in particulate matter in comparison to the fate of uranium in water?
- G. Kniewald: That would depend primarily on the nature of the particulate matter itself-whether it is of organic or inorganic composition. Nevertheless, the reduction of the adsorbed U(VI) to U(V) would be controlled by redox conditions prevailing at the deposition/adsorption interface.

