Crystal structure of uranyl oxalates

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Uranyl-organic complexation in geologic fluids can have a profound impact upon uranium solubility and transport. Studies of uranyl organic crystal structures provide a basis for understanding complexation in solution.

Novel uranyl oxalates

The crystal structures of six novel uranyl oxalates have been determined. The compounds were synthesized by mild hydrothermal methods and their structures determined by single crystal X-ray diffraction. Three of these compounds form a compositional series:

 $\begin{array}{l} K(UO_2)_2(C_2O_4)_2OH(H_2O)_2\,(KUrOx),\\ Rb(UO_2)_2(C_2O_4)_2OH(H_2O)_{1.7}\,(RbUrOx), \text{ and} \end{array}$

 $Cs(UO_2)_2(C_2O_4)_2OH(H_2O)$ (CsUrOx).

The other three compounds differ only in structure and hydration state:

 $\begin{array}{l} (UO_2)_2C_2O_4(OH)_2(H_2O)_2\text{-}\alpha \ (UrOx2A), \\ (UO_2)_2C_2O_4(OH)_2(H_2O)_2\text{-}\beta \ (UrOx2B), \ \text{and} \\ (UO_2)_2C_2O_4(OH)_2(H_2O)_3 \ (UrOx3). \end{array}$

These structures demonstrate new features not previously known in this chemical system, in particular polymerization into infinite sheets and direct linkage of uranyl polyhedra. Further work on this chemical system seems likely to turn up further insights.

Structural classification scheme for uranyl oxalates

Although a hierarchical scheme exists for classifying inorganic uranyl compounds (Burns et al. 1996), no similar work has been done for organic compounds. Such a hierarchy would have practical benefits, in particular making structural information more accessible and understandable to workers studying related problems such as the environmental transport of hexavalent uranium as dissolved organic complexes. We offer a simple scheme that classifies uranyl oxalate structures by analyzing the long-range structural features and the coordination environments of uranyl ions, which leads to a structural symbol that can be used to easily identify uranyl oxalates with common structural features.

Reference

Burns, P. C., Miller, M. L., and Ewing, R. C. (1996). U6+ minerals and inorganic phases: A comparison and hierarchy of crystal structures. *The Canadian Mineralogist*, 34:845–880.

Comparative migration behaviour of ¹³⁷Cs, ⁹⁰Sr, ²⁴¹Am and ²³⁹⁺²⁴⁰Pu in soils: Examples of forest soil of Vosges and wetland of Mercantour areas (France)

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The aim of the present work is to compare the behaviour of RNs (¹³⁷Cs, ⁹⁰Sr, ²⁴¹Am and ²³⁹⁺²⁴⁰Pu) in two soils (acidic forest soil in Vosges and organic wetland of Mercantour Mountains). The inventories, vertical distribution of the RNs and their ratios were calculated for each soil. A compartment model has been developed in order to estimate the migration rate of the RNs in the horizons.

The results show that the inventory of ²⁴¹Am and ²³⁹⁺²⁴⁰Pu is 2-3 times higher in soil of Vosges (74±3.5 Bq.m⁻² and 207 ± 7.6 Bq.m⁻²) than in soil of Mercantour (25 ± 1.1 Bq.m⁻² and 86±3.0 Bq.m⁻² respectively); it is lower for ⁹⁰Sr in Vosges soil (530±130 Bq.m⁻²) compared to Mercantour soil (2300±60 Bq.m⁻²) and similar for ¹³⁷Cs (16500±2000 Bq.m⁻² and 11400±650 Bq.m⁻² respectively). In the first 10 cm, the retention of ²⁴¹Am was more important in wetland of Mercantour (93 % of the inventory) than in forest soil of Vosges (only 68 %). For ²³⁹⁺²⁴⁰Pu, retention in surface layer was less important in Mercantour soil (65 %) with respect to Vosges soil (75 %) whereas comparable values were observed for Cs (80 %) and Sr (60 -65 %). The migration rate of ²³⁹⁺²⁴⁰Pu in Mercantour wetland, calculated with the compartment model, was more important compared to ²⁴¹Am while it was less important in mineral forest soil of Vosges. In both studied cases estimated migration rates of RNs could explain the different evolution of ²⁴¹Am/²³⁹⁺²⁴⁰Pu ratio with the depth. The results are discussed in term of the different affinity of the components of two types of soils to the RNs. Further geochemical modelling is planed to understand the interactions occurring between RNs and solid/liquid phases in both studied soils.