

# **Radionuclide Immobilization in the Phases Formed by Corrosion of Spent Nuclear Fuel: The Long-Term Assessment**

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## Rationale for Research Program

- One of the unique and scientifically most difficult aspects of nuclear waste management is the extrapolation of short-term laboratory data to the long time ( $10^3$ - $10^5$  years) required by the performance objectives as set by regulations, i.e., 10CFR60.
- The direct verification of these extrapolations or interpolations is not possible, but methods must be developed to demonstrate compliance with government regulations and to satisfy the public that there is a demonstrable and reasonable basis for accepting the long-term extrapolations of waste form behavior.
- Previous investigations have established that natural uraninite,  $\text{UO}_{2+x}$  with its impurities can be used as a good structural and chemical analogue for the analysis of the long-term behavior of the  $\text{UO}_2$  in spent nuclear fuel.
- This program is based on the study of uraninite and naturally occurring alteration products of  $\text{UO}_{2+x}$  under oxidizing conditions.

## Significance of Research Program to the EMSP

- This program provides the basis for establishing the extent to which models of the alteration and corrosion processes of  $\text{UO}_2$  in spent fuel, which are used in the performance assessments, are useful or valid.
- The successful performance of the waste form or subsequent incorporation of radionuclides into alteration products will result in near-field containment.
- Studies on naturally occurring  $\text{UO}_2$  and its alteration products holds great potential for the confirmation of performance assessments of near-field behavior.

## First Year Accomplishments

- Developed theoretical models to predict  $\Delta G_f^\circ$  and  $\Delta H_f^\circ$  and estimated the structural contributions to the third-law entropies for uranyl phases.
- Initiated systematic structural analysis of the capacity of uranyl phases to incorporate radionuclides (e.g.  $^{79}\text{Se}$  and  $^{99}\text{Tc}$ ).
- This presentation includes two subtitles: “Prediction of the stability of uranyl phases” and “Incorporation of radionuclides into uranyl phases”.

## Collaborators

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**Subtitle:**

Prediction of the Stability of  
Uranyl Phases

## Introduction

- Under oxidizing conditions, both the solution concentration of uranium and the secondary phase immobilization of radionuclides depend largely on the stability of the secondary uranyl phases formed. However, the thermodynamic data base for these uranyl phases is limited and in some cases contradictory.
- The true third-law entropies of solid phases may be quite different from the widely adopted entropy values obtained based on calorimetric measurements due to residual or unextracted contributions resulting from site-mixing, substitutions, vacancies and disorder in the structures. This discrepancy affects significantly the interpolation and extrapolation of experimentally determined thermodynamic data and the stability relations of the phases.
- We have developed an empirical method for predicting the Gibbs free energies and enthalpies of uranyl phases which is based on the sum of the polyhedral contributions; calculated the chemical site-configurational contributions; and examined the probable importance of other contributions to the third-law entropies of uranyl phases.

## Basic Model for the Estimation of $\Delta G_f^0$ and $\Delta H_f^0$

$$\Delta G_f^0 = \sum n_i g_i$$

$$\Delta H_f^0 = \sum n_i h_i$$

$n_i$ : Number of moles of constituent polyhedron  $i$ ;

$g_i$  and  $h_i$ : Contributions of polyhedron  $i$  to the  $\Delta G_f^0$  and  $\Delta H_f^0$  of uranyl phases, respectively

- $g_i$  and  $h_i$  are determined by regression analysis using all the thermodynamic data of uranyl phases with known structures.
- The constituent polyhedra for 110 uranyl phases have been compiled in this study.



## Advantages of the Estimation Method over Previous Efforts

### 1- Estimation of $\Delta G_f^\circ$ of Uranyl phases -- previous studies

- Van Genderen and Van Der Weijden (1984): for phases of the same structure.
- Finch (1997) and Clark et al. (1998): Oxide-summation technique.

### 2- The advantage of this study:

- provides improved accuracy over the oxide-summation technique because the coordination of the cations is considered;
- the  $\Delta G_f^\circ$  and  $\Delta H_f^\circ$  may be estimated even though the data for representative phases in the similar class are not available.
- Small errors in individual data of the reference phases can be reduced through the average provided by the multiple regression analysis.

## The Model for Site-Configurational Contributions to Third-Law Entropy

$$S_{\text{conf}} = R \sum_j (Y_j / Z) \sum_i X_{i,j} \cdot \ln X_{i,j}$$

$S_{\text{conf}}$ : ideal site-configurational entropy for the adopted formula;

R: gas constant

$Y_j$ : crystallographic multiplicity of site j (as determined by the symmetry elements of space group).

Z: number of formula units per cell;

$X_{i,j}$ : molar fraction of component i randomly distributed on a crystallographic site j.

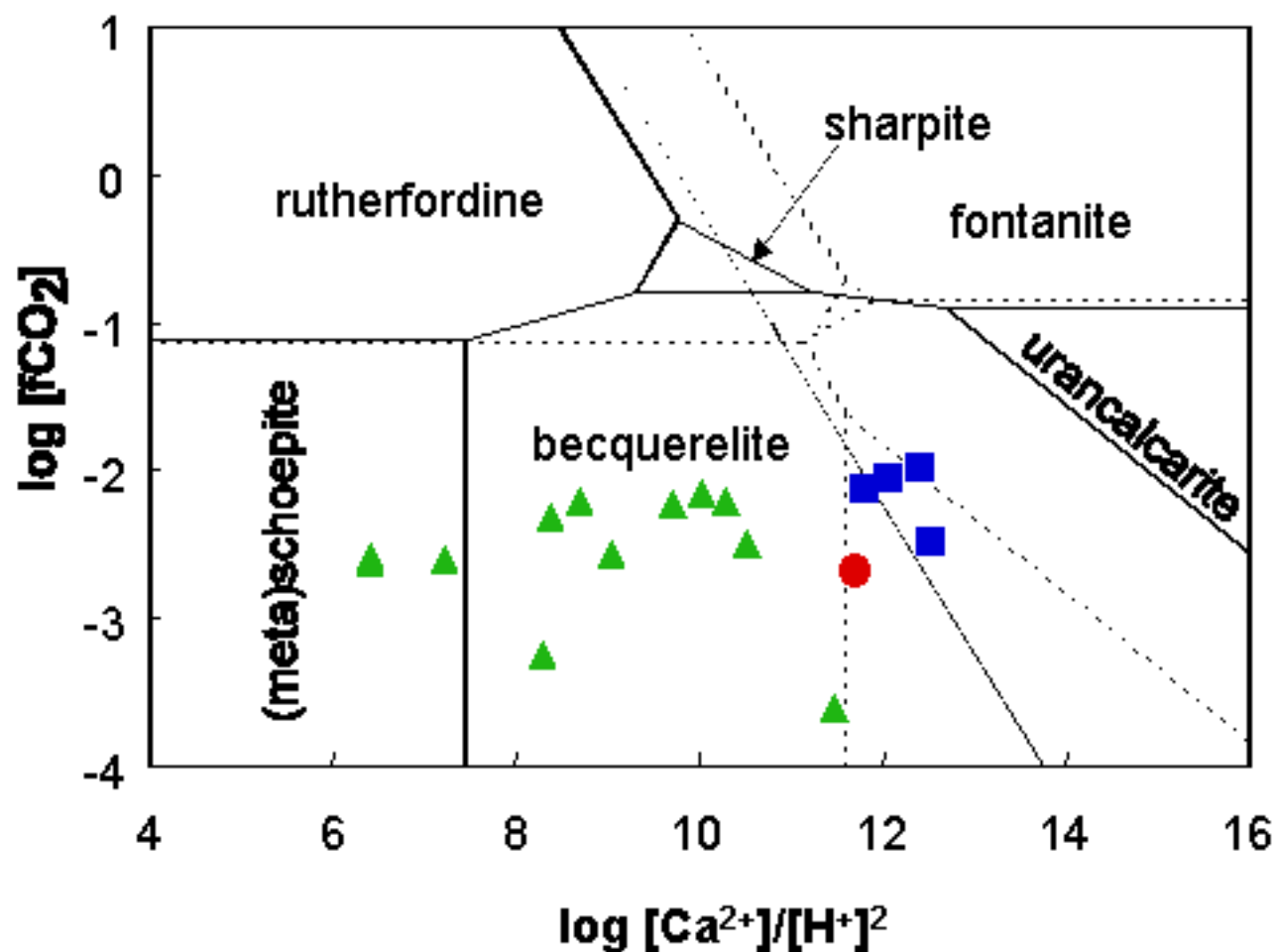
# Measured and Predicted $\Delta G_f^0$ (kJmol<sup>-1</sup>) Values for the Phases Used in the Model and the Associated Errors

U(VI) phases	measured	predicted	Absolute residuals	Relative residuals
$[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}] \cdot 10\text{H}_2\text{O}$	-13092.0±6.8	-13122.9	30.9	0.24
$\beta\text{-UO}_2(\text{OH})_2$	-1398.7±1.8	-1399.3	-0.6	0.04
$\text{UO}_3 \cdot 0.9\text{H}_2\text{O}$	-1374.6±2.5	-1375.6	1.0	0.07
$\text{Na}_2\text{U}_2\text{O}_7$	-3011.5±4.0	-3013.0	1.5	0.05
$\text{Na}_4\text{UO}_2(\text{CO}_3)_3$	-3737.8±2.3	-3739.8	2.0	0.05
$\text{UO}_2\text{CO}_3$	-1563.0±1.8	-1562.3	-0.67	0.04
$\text{BaUO}_4$	-1883.8±3.4	-1886.6	2.8	0.15
$\text{BaU}_2\text{O}_7$	-3052.1±6.7	-3048.8	-3.3	0.11
$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	-2584.2±1.6	-2583.8	-0.4	0.01
$\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	-1864.7±2.0	-1862.9	-1.8	0.09
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	-1620.5±2.0	-1622.6	2.1	0.13
$\text{UO}_2\text{SO}_4 \cdot 3.5\text{H}_2\text{O}$	-2535.6±1.8	-2537.1	1.5	0.06
$\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$	-2416.6±1.8	-2416.9	0.3	0.01
$\text{UO}_2\text{SO}_4 \cdot 2.5\text{H}_2\text{O}$	-2298.5±1.8	-2296.8	-1.7	0.08
$(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$	-3655.7±7.6	-3651.8	-3.9	0.11
$\text{Na}(\text{UO}_2)(\text{SiO}_3\text{OH}) \cdot 1.5\text{H}_2\text{O}$	-2844.8±3.9	-2838.8	-6.0	0.21
$\text{Na}_2(\text{UO}_2)_2(\text{Si}_5\text{O}_{13}) \cdot 3\text{H}_2\text{O}$	-7993.9±9.6	-8000.5	6.6	0.08
$\text{Ba}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 4\text{H}_2\text{O}$	-9387.0±17.1	-9370.0	-17.0	0.18
<b>Average</b>				<b>0.095</b>

# Chemical site-configuration Contributions ( $S_{conf}$ ) to the Third-Law Entropies of Uranyl Phases ( $\text{J mol}^{-1} \cdot \text{K}^{-1}$ )

Phases	$S_{conf}$	Phases	$S_{conf}$
$\text{Ca}[(\text{UO}_2)_2(\text{PO}_4)_2](\text{H}_2\text{O})_6$ (meta-autunite)	48.9	$\text{U}_3\text{Mo}_{20}\text{O}_{64}$	48.9
$\text{Pb}_3[\text{H}(\text{UO}_2)_3\text{O}(\text{PO}_4)_2]_2(\text{H}_2\text{O})_{12}$ (dewindtite)	92.2	$(\text{UO}_2)(\text{MoO}_4)(\text{H}_2\text{O})_2$	5.8
$\text{KCa}(\text{H}_3\text{O})(\text{UO}_2)[(\text{UO}_2)_3\text{O}_2(\text{PO}_4)_2]_2$ $(\text{H}_2\text{O})_8$ (phosphur anylite)	23.1	$\text{Sr}(\text{UO}_2)_6(\text{MoO}_4)_7(\text{H}_2\text{O})_{19}$	11.5
$\text{Ca}(\text{UO}_2)[(\text{UO}_2)_3(\text{OH})_2(\text{PO}_4)_2]_2$ $(\text{H}_2\text{O})_{12}$ (phosphur anylite)	115.3	$\text{Pb}_3\text{U}_8\text{O}_{27}(\text{H}_2\text{O})_5$	18.7
$\text{Cu}[(\text{UO}_2)_2(\text{PO}_4)_2](\text{H}_2\text{O})_8$ (meta-torbernite)	11.5	$\text{Pb}_3[(\text{UO}_2)_8\text{O}_8(\text{OH})_6](\text{H}_2\text{O})_3$ (curite)	23.5
$\text{Na}_{5.5}(\text{UO}_2)_3(\text{H}_{0.5}\text{PO}_4)(\text{PO}_4)_3$	11.5	$\text{K}_6[(\text{UO}_2)(\text{B}_{16}\text{O}_{24}(\text{OH})_8)](\text{H}_2\text{O})_{12}$	67.2
$\text{Nd}_4(\text{UO}_2)(\text{PO}_4)(\text{D}_2\text{O})_3$	60.5	$\text{CaB}_2\text{U}_2\text{O}_{10}$	11.5
$\text{K}(\text{UO}_2)(\text{PO}_4)(\text{D}_2\text{O})_3$	37.4	$\text{NaUO}_4$	97.9
$(\text{K}_{0.56}\text{Na}_{0.42})[(\text{UO}_2)(\text{SiO}_3\text{OH})](\text{H}_2\text{O})_{1.5}$ (boltwoodite)	31.7	$\text{NaUO}_{3.5}$ (Gasperin, 1986)	73.5
$(\text{K}_{0.62}\text{Na}_{0.38})(\text{UO}_2)_2(\text{Si}_5\text{O}_{13})(\text{H}_2\text{O})_3$ (weeksite)	114.8	$\text{NaUO}_{3.5}$ (Kovba, et al., 1958)	9.4
$\text{Mg}_2[(\text{UO}_2)(\text{CO}_3)_3](\text{H}_2\text{O})_{18}$ (bayleyite)	46.1	$\text{K}_2[(\text{UO}_2)\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_7$ (compreignacite)	46.1
$\text{K}(\text{UO}_2)_2(\text{SO}_4)(\text{OH})_3(\text{H}_2\text{O})$	11.5	$\text{KUO}_{3.5}$ (Jove et al., 1988)	60.1
		$\text{KUO}_{3.5}$ (Kovba et al., 1958)	11.5
		$\alpha\text{-Cs}_2\text{U}_2\text{O}_7$	11.5
		$\text{Cs}_2\text{U}_{15}\text{O}_{46}$	31.7
		$\text{Cs}_2\text{U}_4\text{O}_{13}$	42.8
		$\text{Cs}_2\text{U}_5\text{O}_{16}$	17.3
		$(\text{Ca}_{0.5}\text{Sr}_{0.5})\text{UO}_4$	5.8
		$\text{Ca}(\text{K}_6\text{Ba}_2)\text{U}_6\text{O}_{24}$	8.9

# Predicted Phase Stability Relations in the System $\text{SiO}_2\text{-CaO-UO}_3\text{-H}_2\text{O}$



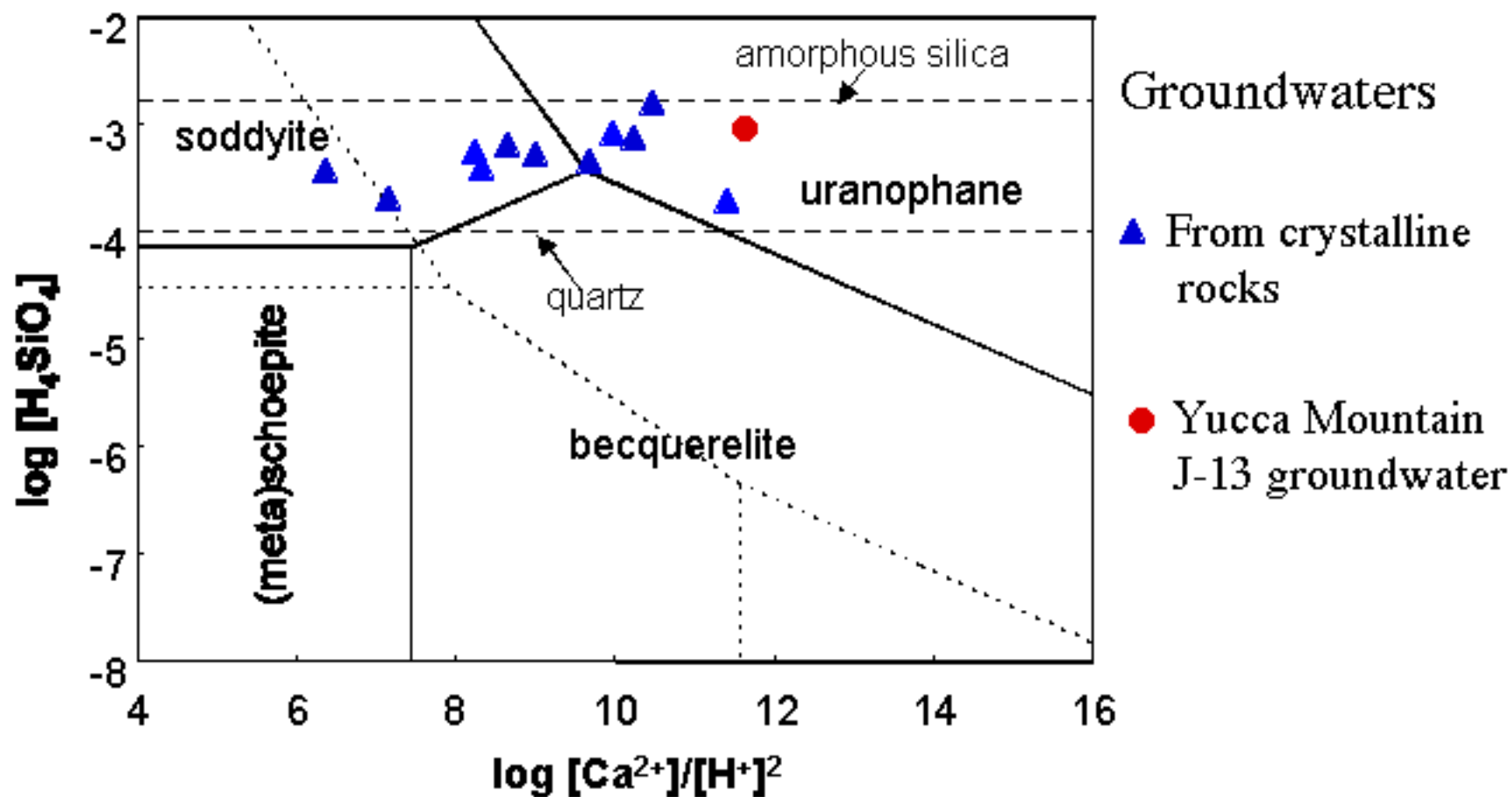
Groundwaters

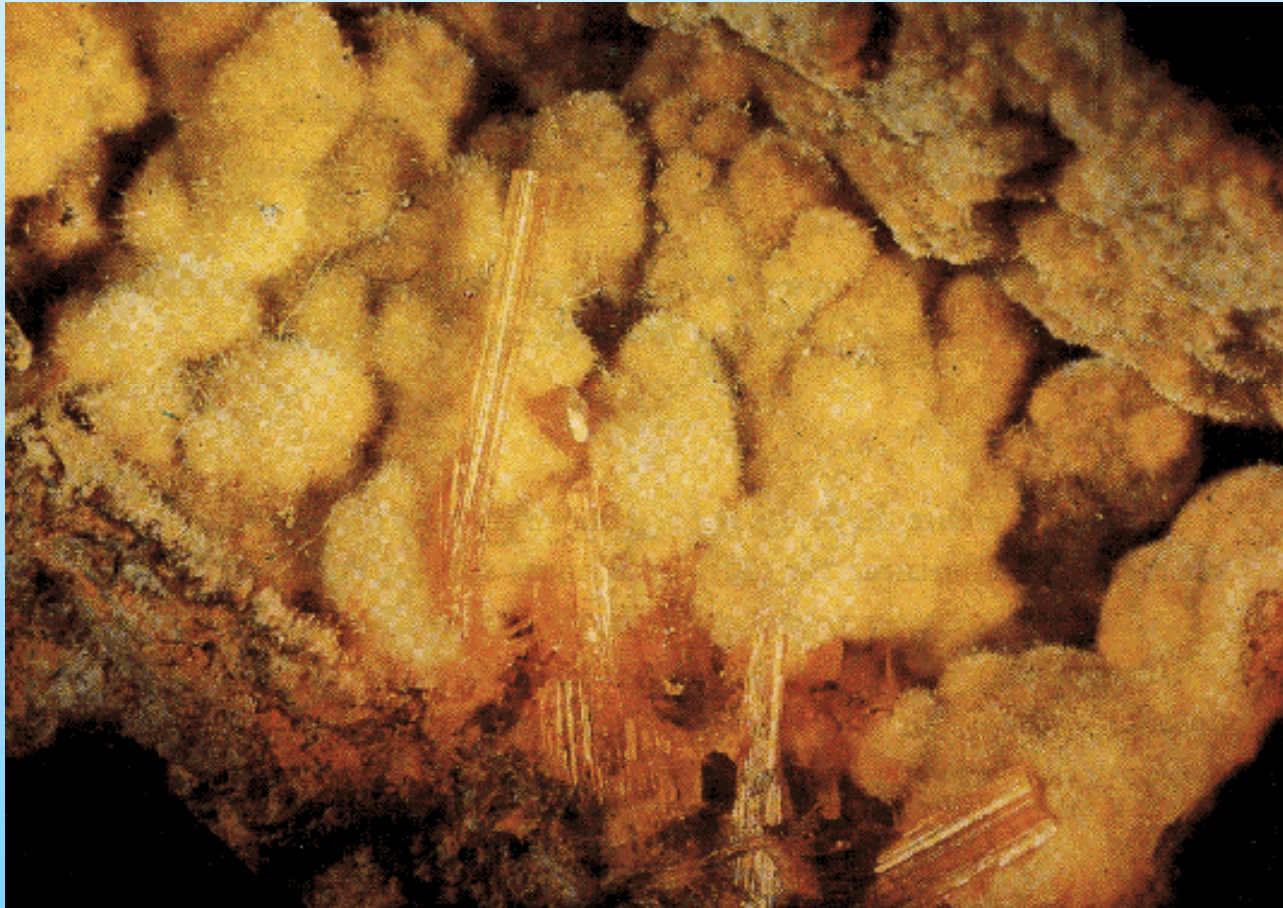
▲ From carbonate terrains

■ From crystalline rocks

● Yucca Mountain J-13 Groundwater

# Predicted Phase Stability Relations in the System $\text{SiO}_2\text{-CaO-UO}_3\text{-H}_2\text{O}$





Fabric uranophane forms nodules infilling a crack, which is followed by the crystallization of becquerelite prism.

**Locality:** Shinkolobwe, Shaba, Zaire

**Source:** M. Deliens, P. Piret and G. Comblain (1981)



## Conclusions

- **There is good agreement:** (1) between the estimated and measured thermodynamic values for the phases used in the model; (2) between the predicted mineral stability relations and field occurrences in the  $\text{SiO}_2\text{-CaO-UO}_3\text{-H}_2\text{O}$  and  $\text{CO}_2\text{-CaO-UO}_3\text{-H}_2\text{O}$  systems.
- **Application:** The model can be used to estimate the thermodynamic data and solubility products of phases for which experimental data are not yet available or for which suitable samples are not available for experimental determinations.
- **Implication:** Derivations, interpolations and extrapolations of thermodynamic data using third-law entropies should be corrected by taking into account the structural contributions; samples with known structures should be used in calorimetric measurements.



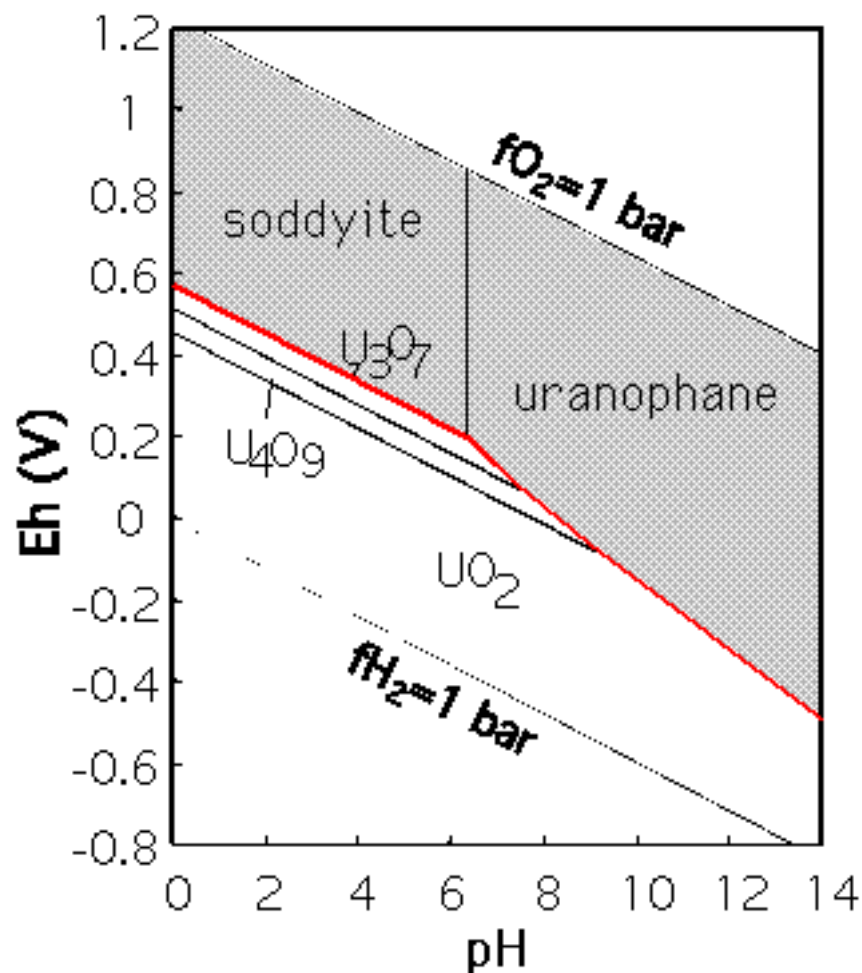
**Subtitle:**

**Incorporation of Radionuclides  
into Uranyl Phases**

# Introduction

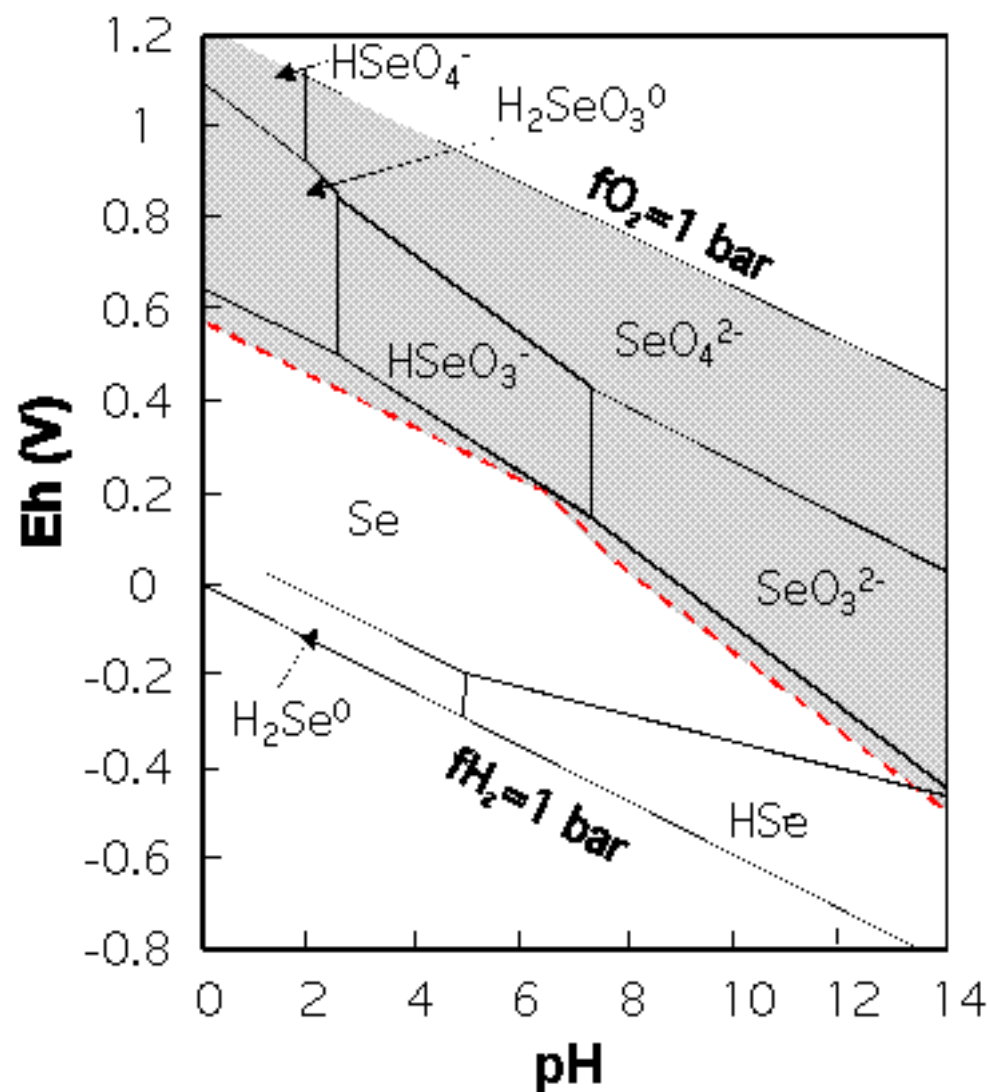
- The retardation and fate of the long-lived radionuclides are of great environmental concern for the safe disposal of nuclear waste.
- Some of the long-lived radionuclides (such as  $^{99}\text{Tc}$ ,  $^{79}\text{Se}$ ,  $^{129}\text{I}$ ) are highly mobile during the oxidative alteration of spent nuclear fuel.
- Incorporation of radionuclides into the crystal structures of secondary uranyl phases may reduce their mobility in the near-field.
- We present the incorporation mechanisms of  $^{79}\text{Se}$  into uranyl phases based on systematic structural analysis.

## pH-Eh Conditions for the Oxidative Alteration of Spent $\text{UO}_2$ Fuel



- The pH-Eh conditions for the oxidative alteration of spent  $\text{UO}_2$  fuel are in the shaded area.

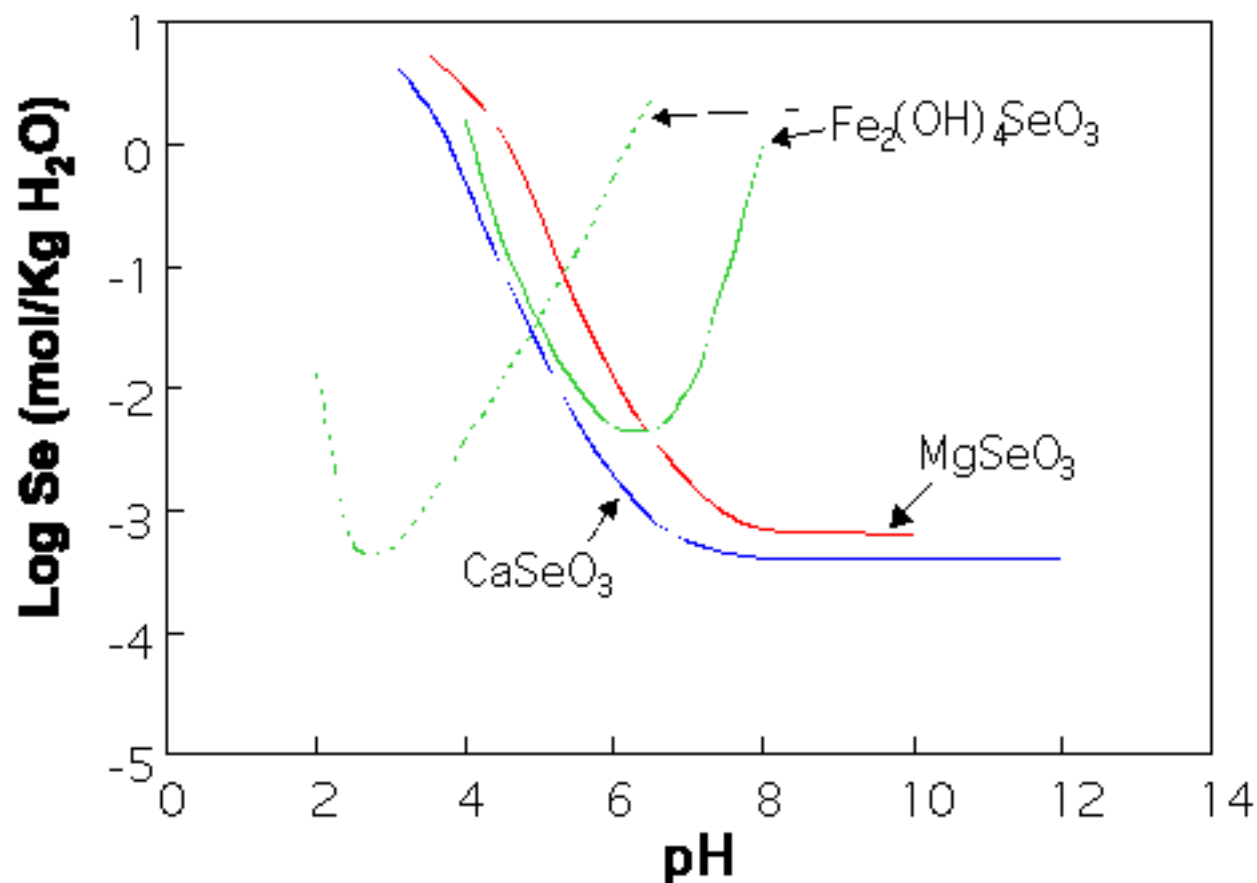
# Speciation of Selenium



- selenite ( $Se^{4+}$ ) or selenate ( $Se^{6+}$ ) are the dominant species of dissolved selenium during the oxidative corrosion of spent  $UO_2$  fuel.

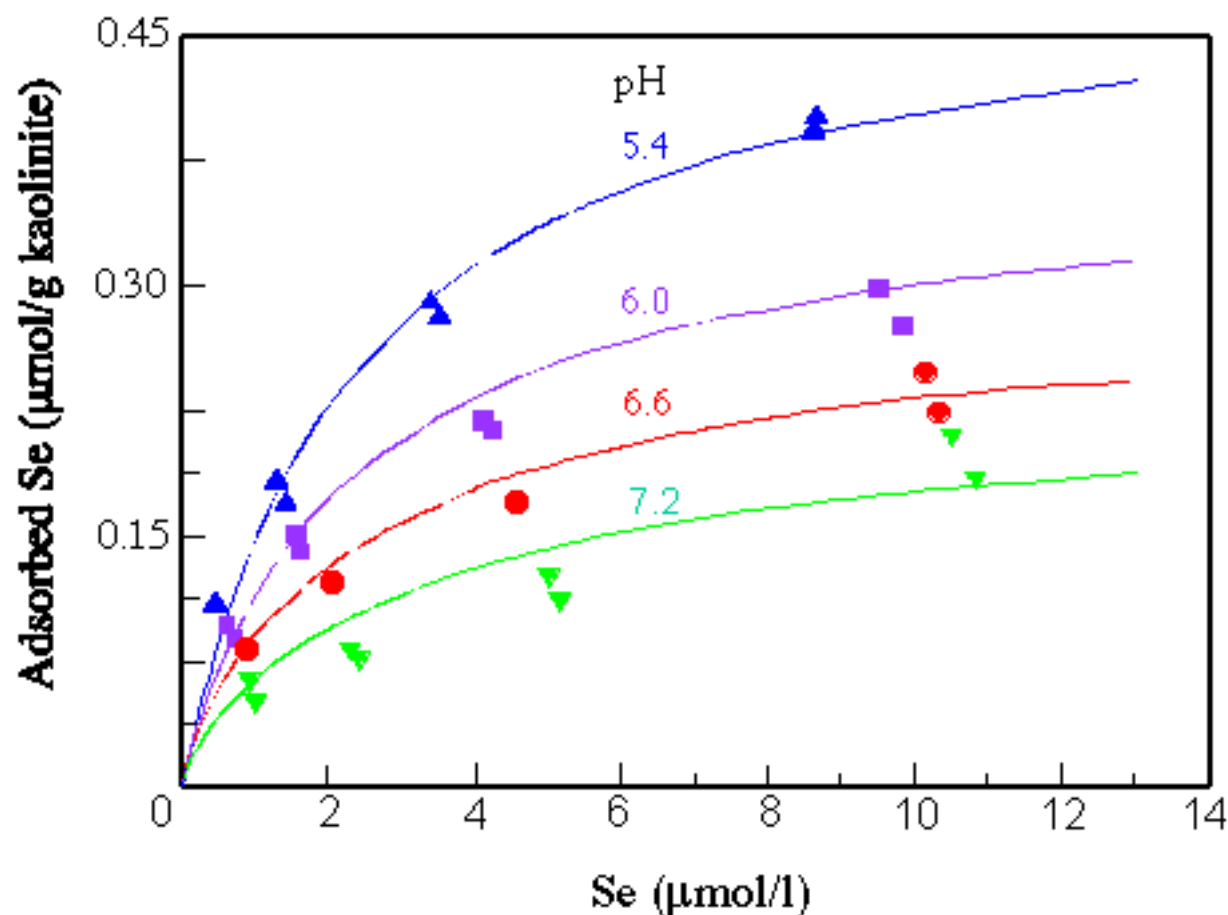
(based on the data from Wagman et al., 1982)

## Solubility-Limited Concentration of Selenium as a Function of pH



\* The dashed line is calculated assuming the  $\text{Fe}^{3+}$  concentration in solution is controlled by the solubility of amorphous  $\text{Fe}(\text{OH})_3$ ; other lines are calculated assuming the concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Fe}^{3+}$  are the same as those in J-13 groundwater, respectively.

## Sorption Isotherms of Selenite ( $\text{Se}^{4+}$ ) by Kaolinite at the indicated pH Values



(After Bar-Yosef and Meek, 1987)

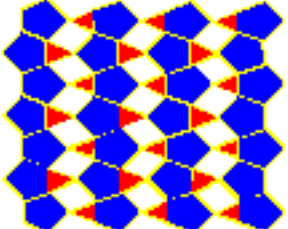
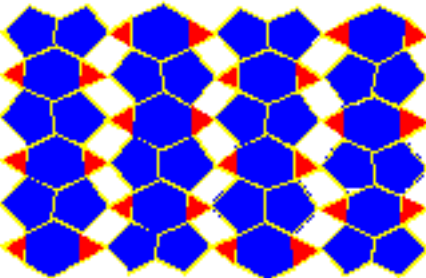
## Crystal Chemistry of $\text{Se}^{4+}$ , $\text{Se}^{6+}$ , $\text{Si}^{4+}$ and $\text{P}^{5+}$ in Uranyl Phases

	$\text{Se}^{4+}$	$\text{Se}^{6+}$	$\text{Si}^{4+}$	$\text{P}^{5+}$
electronegativity	2.4	2.4	2.0	1.8
X-O bond-length	1.69	1.64	1.62	1.52
polyhedra types*	$\text{Se}^{4+}\text{O}_3\text{E}^\dagger$	$\text{Se}^{6+}\text{O}_4$	$\text{Si}^{4+}\text{O}_4$	$\text{P}^{5+}\text{O}_4$

\* for sites within the sheets or chains.

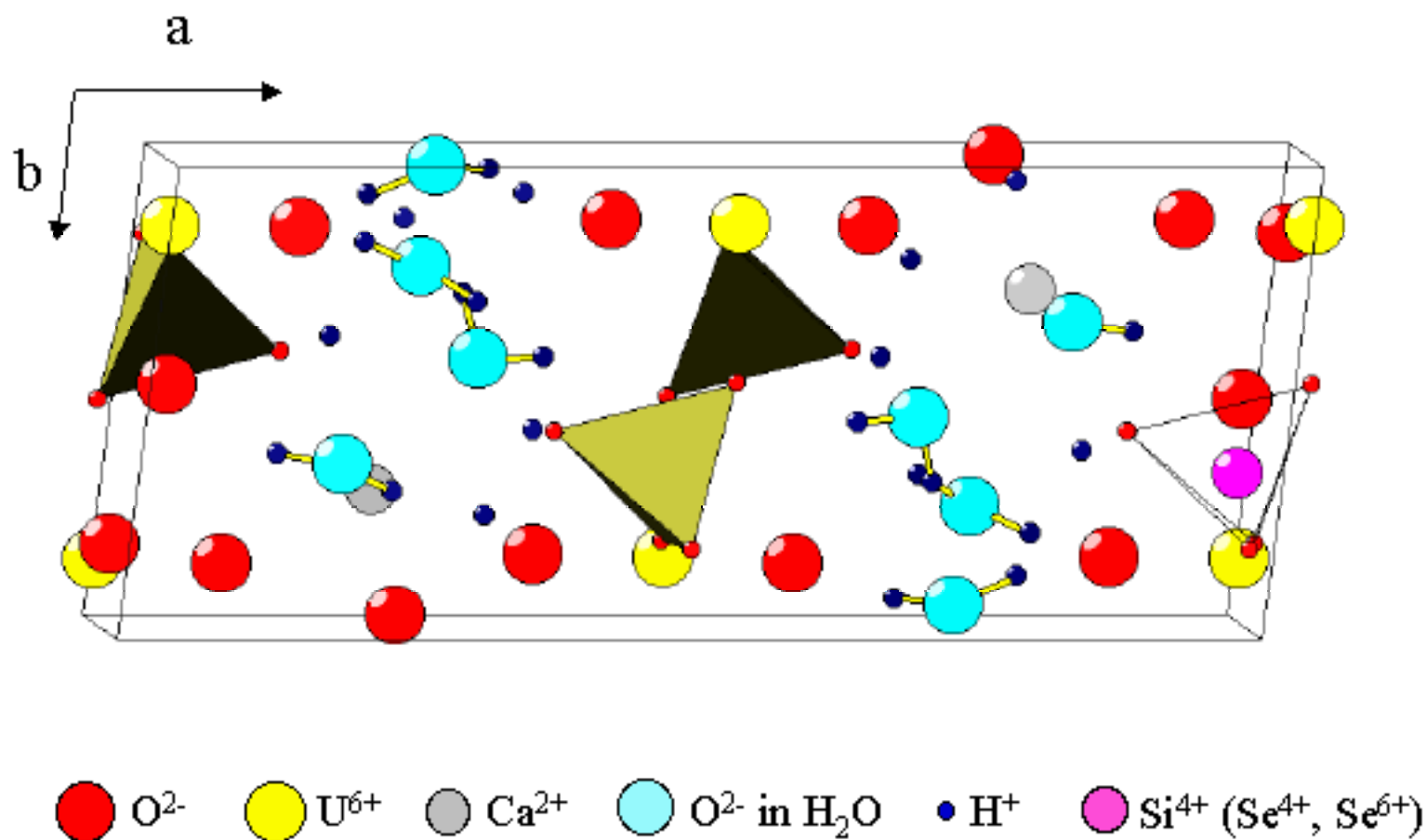
†E: the lone-pair electron in  $\text{Se}^{4+}$ .

# Favorable Structures for Incorporating $\text{Se}^{4+}$ and $\text{Se}^{6+}$

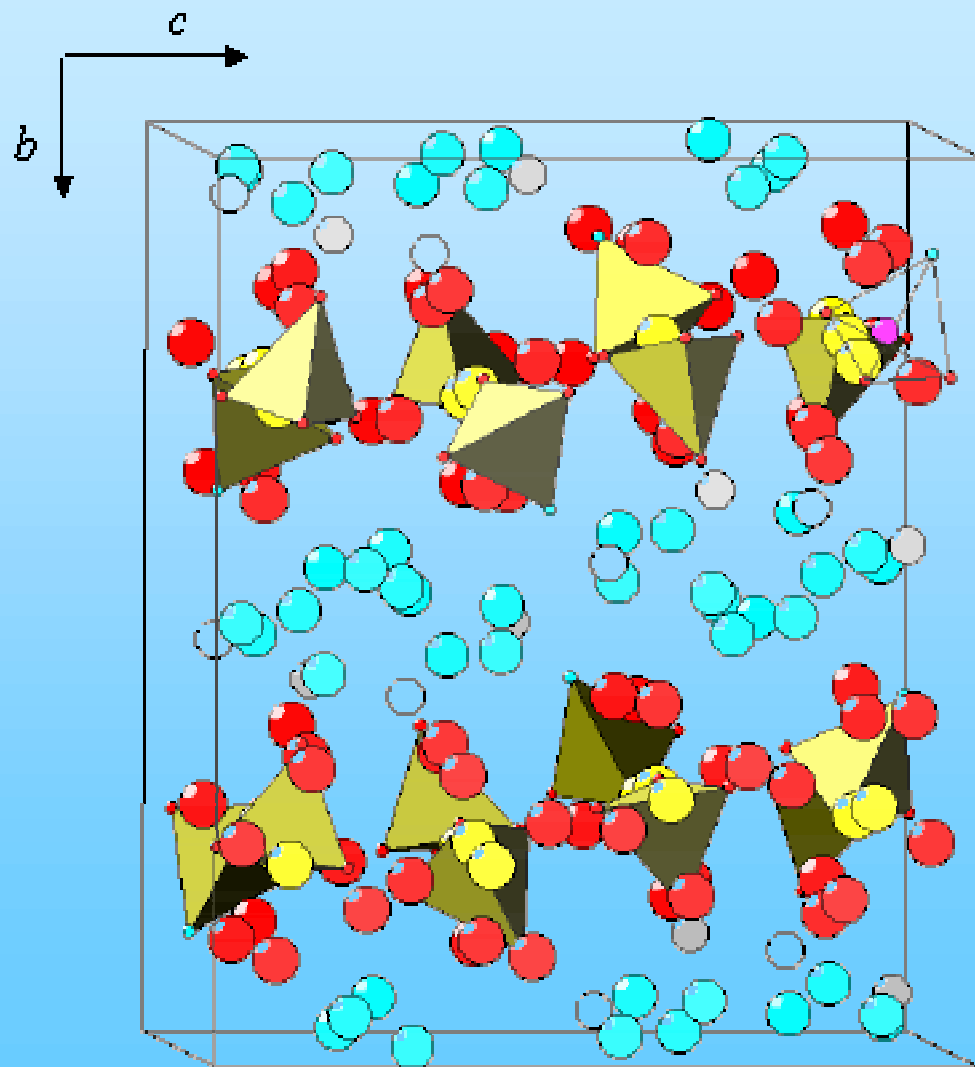
Mineral Group	Type of anion-topology	Example minerals
uranyl silicate	uranophane 	$\alpha$ -uranophane, boltwoodite sklodowskite, kasolite
uranyl phosphate	phosphuranylite 	phosphuranylite, phurcalite, phuraluminite, dumontite








# Schematic Structure of $\alpha$ -Uranophane



# Schematic Structure of Phurcalite



-   $O^{2-}$
-   $Ca^{2+}$
-   $O^{2-}$  in  $H_2O$
-   $U^{6+}$
-   $P^{5+}$  or  $Se^{4+}$

## Conclusions

- Under the Eh-pH conditions typical for the oxidative alteration of spent nuclear fuel, selenite or selenate are the dominant species of aqueous selenium.
- Selenite and selenate may be highly mobile in the near-field of a nuclear waste repository.
- $\text{Se}^{4+}$  and  $\text{Se}^{6+}$  are likely to substitute for  $\text{S}^{4+}$  in structures with the uranophane anion-topology (uranophane, sklodowskite, boltwoodite and kasolite);  $\text{Se}^{4+}$  can readily substitute for  $\text{P}^{5+}$  in uranyl phosphates with the phosphuranylite anion-topology.