

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, 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 UO_2 in spent nuclear fuel.
- This program is based on the study of uraninite and naturally occurring alteration products of 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 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 UO_2 and its alteration products holds great potential for the confirmation of performance assessments of near-field behavior.



Second Year Accomplishments

- Estimated the structural contributions to the third-law entropies and their influences on the calculated solubility of uranyl phases based on calorimetric data.
- Initiated systematic compositional analysis of uraninite (with impurities) and its natural occurring alteration phases as natural analogues of UO_{2+x} corrosion in spent fuel.
- This presentation includes two subtitles: “Structural contributions to the third-law entropy of uranyl phases” and “Immobilization of radionuclides by uranyl phases--Natural analogue studies”.



Collaborators

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Aarhus University, Denmark



Sbutitle:

Structural contributions to the third-law entropy of uranyl phases

Introduction

- Uranyl phases may become the long-term source term of radionuclides in an oxidizing repository. Thus, the thermodynamic stability of these phases is of importance in the safety assessment of spent nuclear fuel under oxidizing conditions.
- The reliability of calculated solubility based on calorimetric data and the extrapolation of experimentally determined thermodynamic data largely depend on a knowledge of the third-law entropy of the relevant phases.
- Because the contribution of residual entropies cannot be extracted by calorimetric measurements, the true third-law entropies for many uranyl phases may be quite different from those values derived from calorimetric measurements.
- We present the sources of residual entropies for uranyl phases and their influences on the calculated solubilities.



Possible Sources of Residual Entropies

- The residual entropies are related to site-mixing, disorder of polar molecules and hydrogen bonds, and the lack of significant magnetic ordering at those temperatures reached by heat capacity measurements.
- There is no significant magnetic spin-configurational contribution to the third-law entropies of most uranyl phases (e.g., uranyl phases that are expected to occur as important alteration phases of spent fuel).
- Site-mixing due to substitution and vacancies may occur in the structure of uranyl phases, especially on the inter-structural unit sites (most uranyl phases with sheet or chain structures).
- The interstitial H_2O group is essential in uranyl phases, and the hydrogen bonds associated with the interstitial H_2O molecules contribute significantly to the connection of the structural units. Thus, disorder in the orientation of the polar H_2O molecules and the associated hydrogen bonds may occur in these phases.



Ideal site-configurational entropies of selected uranyl phases

Mineral	Formula	Space Group	z	S _{conf}	S _{cal} [*]
	NaUO ₄	<i>Fmmm</i>	4	97.8	166.0
	Na(UO _{1.5})O ₂	<i>R$\bar{3}m$</i>	3	69.6	138.0
	KUO _{3.5}	<i>R$\bar{3}m$</i>	3	60.1	148.5
compreignacite	K ₂ [(UO ₂)O ₂ (OH) ₃] ₂ (H ₂ O) ₇	<i>Pnmm</i>	2	46.1	
curite	Pb ₃ [(UO ₂) ₈ O ₈ (OH) ₆](H ₂ O) ₃	<i>Pnam</i>	2	15.2	
	Pb ₃ U ₈ O ₂₇ (H ₂ O) ₅	<i>Pnam</i>	2	18.7	
weeksite	(K _{0.62} Na _{0.38})(UO ₂) ₂ (Si ₅ O ₁₃)(H ₂ O) ₃	<i>Cmmm</i>	2	91.7	
boltwoodite	(K _{0.56} Na _{0.42})[(UO ₂)(SiO ₃ OH)](H ₂ O) _{1.5}	<i>P2₁/m</i>	2	38.1	
meta-autunite	Ca[(UO ₂) ₂ (PO ₄) ₂](H ₂ O) ₆	<i>P4/nmm</i>	1	48.9	
dewindtite	Pb ₃ [H(UO ₂) ₃ O(PO ₄) ₂] ₂ (H ₂ O) ₁₂	<i>Bmmb</i>	4	92.2	
phospuranylite	KCa(H ₃ O)(UO ₂)[(UO ₂) ₃ O ₂ (PO ₄) ₂] ₂ (H ₂ O) ₈	<i>Cmcm</i>	4	23.1	
bayleyite	Mg ₂ [(UO ₂)(CO ₃) ₃](H ₂ O) ₁₈	<i>P2₁/a</i>	4	46.1	
	K ₆ [(UO ₂)(B ₁₆ O ₂₄ (OH) ₈)](H ₂ O) ₁₂	<i>P2₁/n</i>	4	67.2	

S_{cal} calorimetric entropy



Model for the Residual Entropies from Structural Disorder

$$S_{dis} = R/N_0 \ln p^n$$

S_{dis} : the residual entropy caused by structural disorder.

R and N_0 are the gas constant and Avogadro's numbers, respectively.

P : the number of possible structural states (configurations).

n : the number of different structural components (molecules, atoms or micro-domains) affected by the disorder.



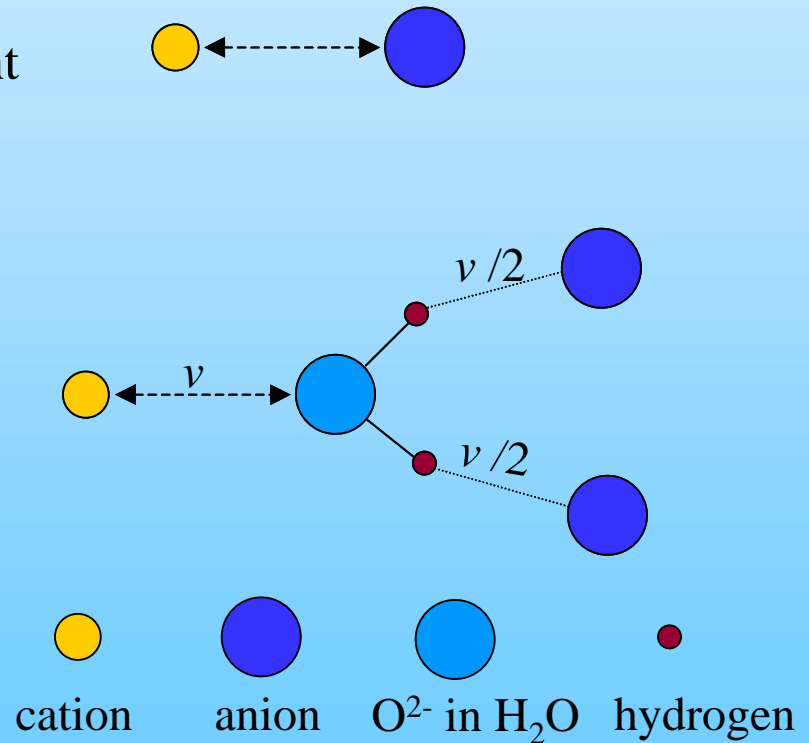
Types of H₂O Groups in Crystal Structures

- As a component of a structural unit: The amount of OH⁻ and H₂O that are components of structural units is stoichiometrically fixed by the topology of the bond connectivity of the structural unit, and each of the atomic species occupies a well defined site in the structural unit.
- An interstitial (H₂O)⁰ group bonded to interstitial cations;
- An interstitial (H₂O)⁰ group not bonded to interstitial cations;
- An occluded (H₂O)⁰ group that occurs in a cage or cavity, only interacting with surrounding structures via Van der Waals forces. This kind of (H₂O)⁰ groups is not expected to occur in most uranyl phases.



Function of Interstitial H₂O Groups Bonded to Interstitial Cations

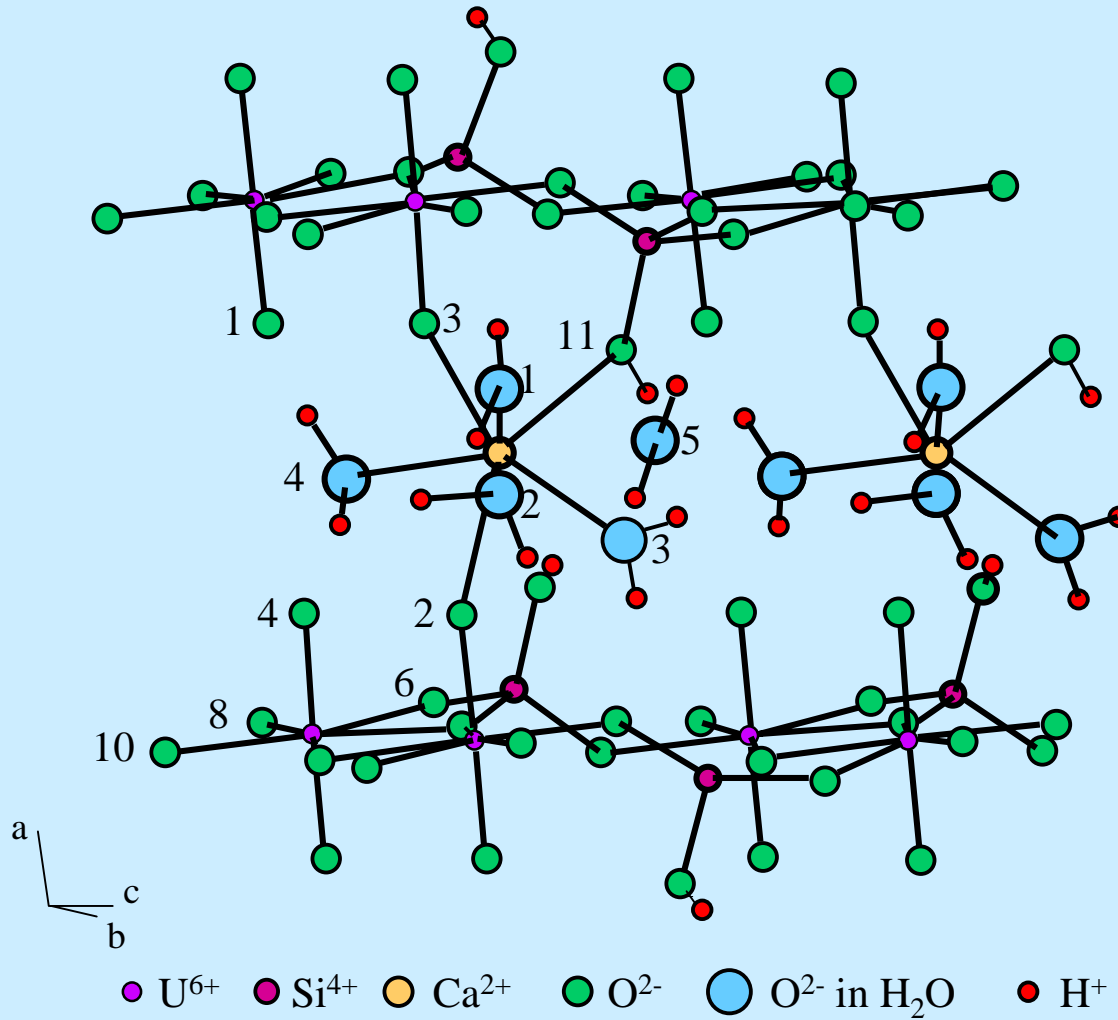
- to satisfy the bond-valence requirement of the cation and transform the strong bond valence to two weaker hydrogen-bonds.
- to satisfy the coordination requirement of the cation and allow the bond-valence to satisfy the bond requirements of distant anions.



(Hawthorne, 1992)

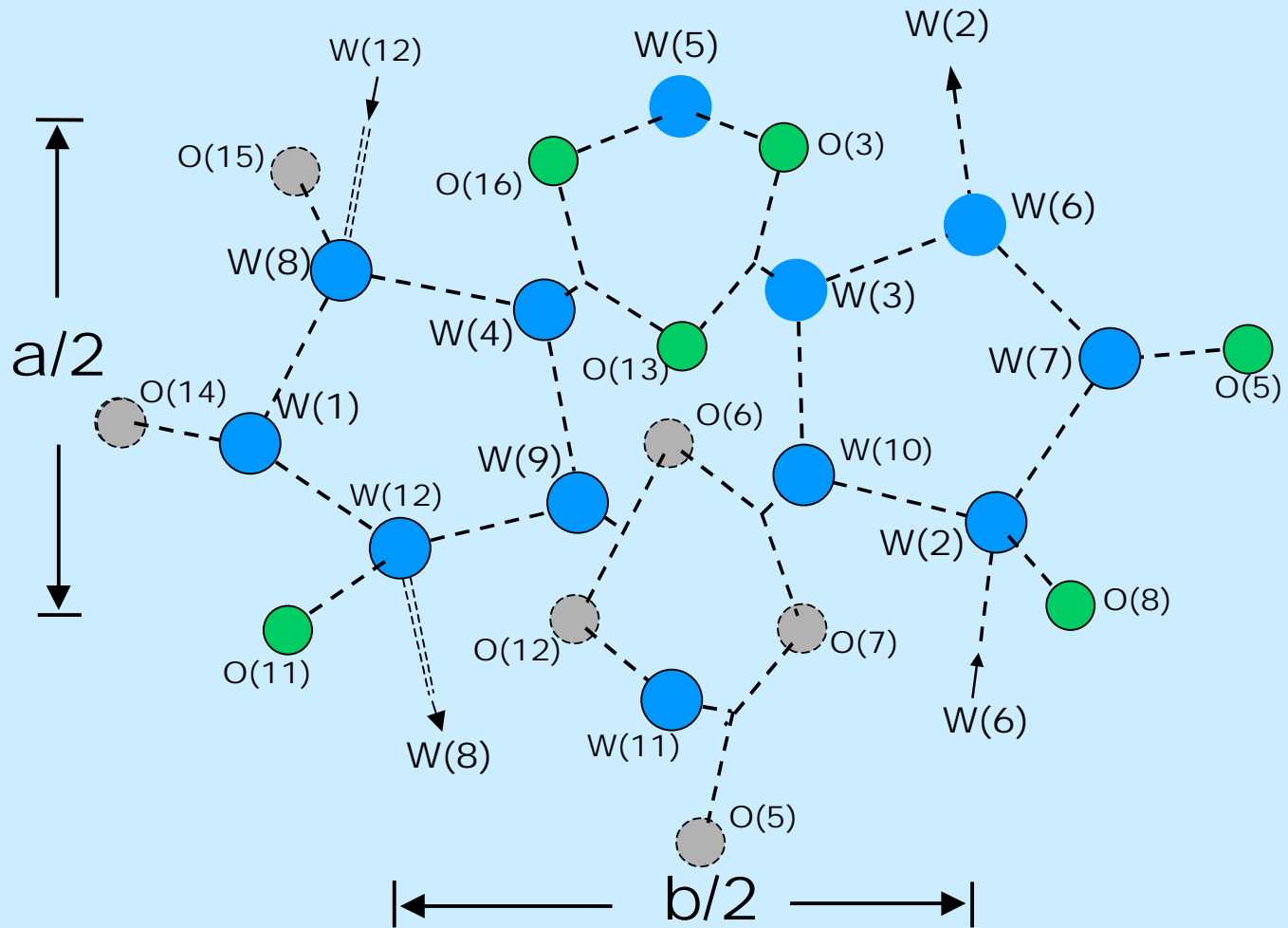


Water Groups in α -Uranophane



(Ginderow, 1988)

Hydrogen-Bonding Network associated with the Interlayer H₂O Groups in Schoepite



(Finch *et al.*, 1996)

Influence of residual entropy on the solubility calculated based on calorimetric data

$$\log[UO_2^{2+}] = \{\log[UO_2^{2+}]\}_{cal} - S_{res} / (2.303\Psi R)$$

$\{\log[UO_2^{2+}]\}_{cal}$: solubility limited UO_2^{2+} activity calculated based on calorimetric data

S_{res} : residual entropy

Ψ : moles of uranyl ion, UO_2^{2+} , in the adopted formula of a uranyl phase.



Influence of site-configurational entropy (S_{conf}) on ΔG_f^0 and solubility of selected uranyl phases

Mineral	Formula	ΔG_f^0 ^a (kJ/mol)	$-TS_{\text{conf}}$ (kJ/mol)	$-TS_{\text{conf}}/\Delta G_f^0$	U_{res} ^b
compreignacite	$\text{K}_2[(\text{UO}_2)\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_7$	-5361.1	-13.7	0.25	-1.2
weeksite	$(\text{K}_{0.62}\text{Na}_{0.38})(\text{UO}_2)_2(\text{Si}_5\text{O}_{13})(\text{H}_2\text{O})_3$	-7643.2	-27.3	0.36	-2.4
boltwoodite	$(\text{K}_{0.56}\text{Na}_{0.42})[(\text{UO}_2)(\text{SiO}_3\text{OH})](\text{H}_2\text{O})_{1.5}$	-2818.3	-11.4	0.40	-2.0
meta-autunite	$\text{Ca}[(\text{UO}_2)_2(\text{PO}_4)_2](\text{H}_2\text{O})_6$	-6122.7	-14.6	0.24	-1.3
phospuranylite	$\text{Ca}(\text{UO}_2)[(\text{UO}_2)_3(\text{OH})_2(\text{PO}_4)_2]_2(\text{H}_2\text{O})_{12}$	-15488.7	-34.4	0.22	-1.5
bayleyite	$\text{Mg}_2[(\text{UO}_2)(\text{CO}_3)_3](\text{H}_2\text{O})_{18}$	-9164.2	-13.7	0.15	-2.4

U_{res} : change of the solubility-limited UO_2^{2+} activity in log units.



Conclusions

- No paramagnetic ionic species is expected to be present in the bulk composition of uranyl phases. As such, residual entropy associated with magnetic spin disorder in uranyl phases is negligible.
- The calculated ideal site-mixing configurational entropies for some uranyl phases based on their structural information indicate that site-mixing configurational entropy may contribute significantly to the third-law entropy of uranyl phases.
- The residual entropy associated with the disorder of the orientation of the polar H₂O groups is not considered significant in most uranyl phases. However, considerable residual entropy may be arisen from the disorder of hydrogen bonds associated with the interstitial H₂O groups. Also, disorder of micro-domains that results from randomly stacking, shift and rotation of the structural units may make considerable contributions to the third-law entropy of uranyl phases.



Sbutitle:

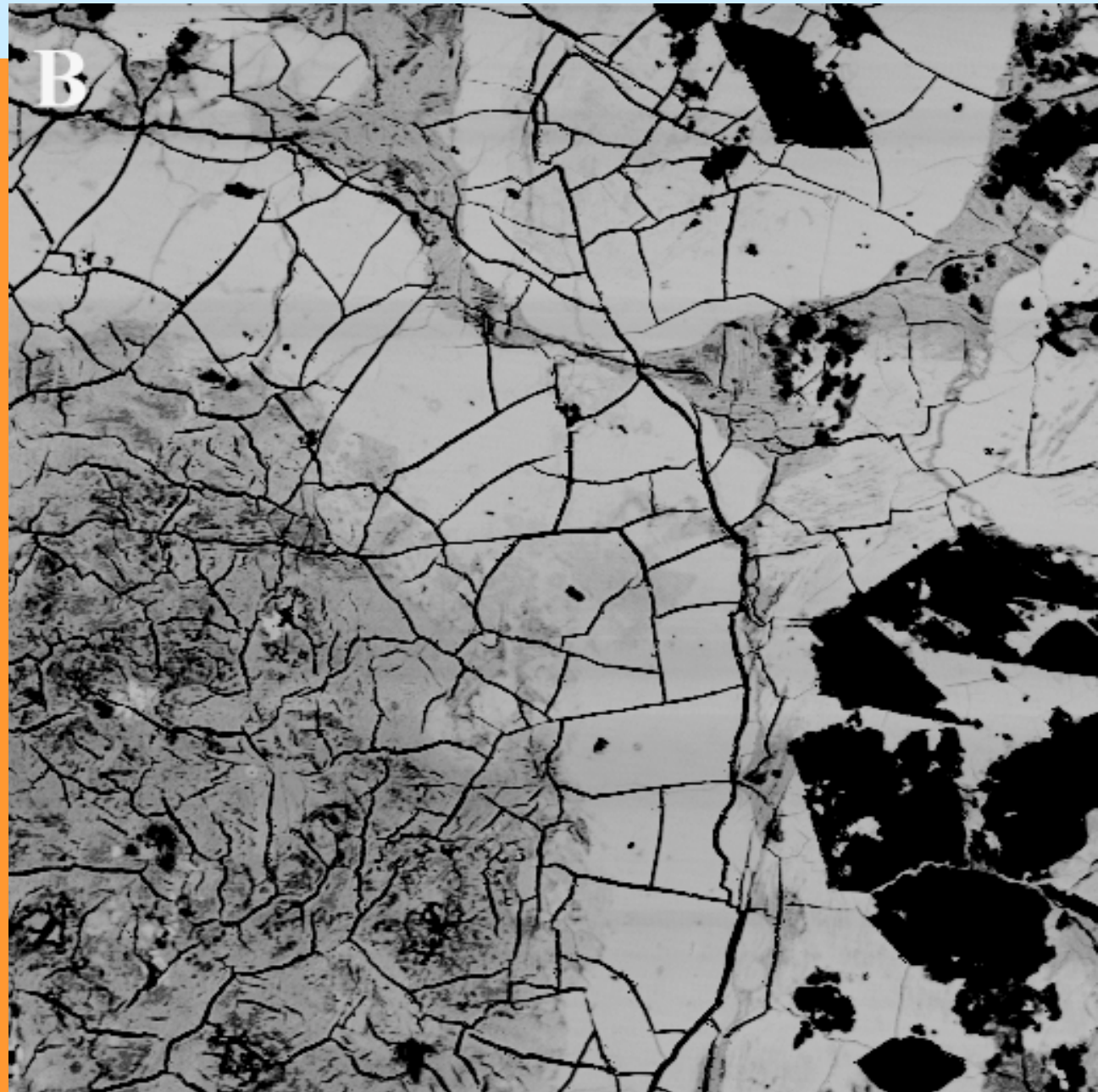
Immobilization of radionuclides by uranyl
phases--Natural analogue studies

Introduction

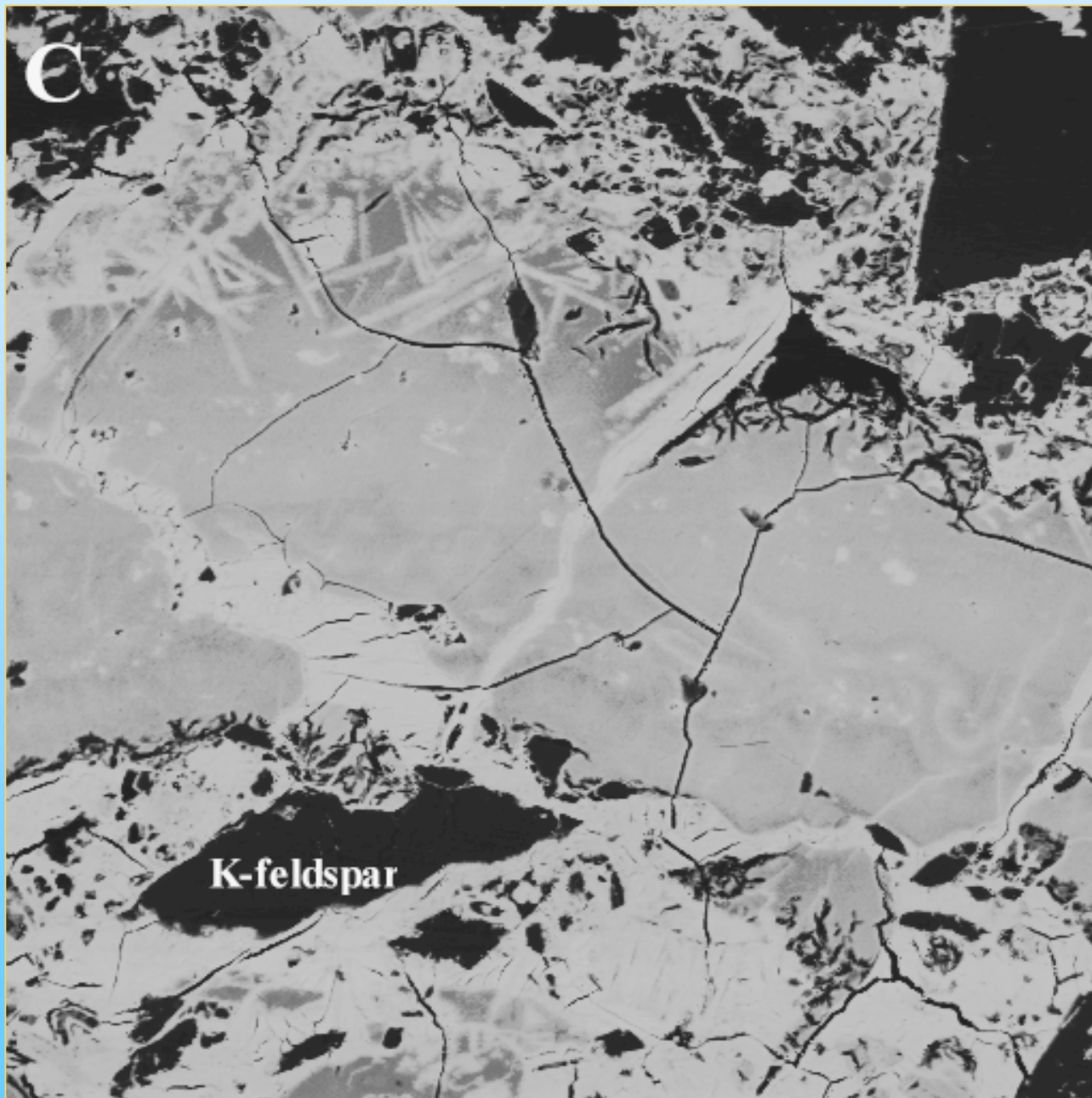
- Incorporation of radionuclides into secondary uranyl phases will result in near-field containment and reduce radionuclide mobility.
- Uraninite and uranyl phases from the Colorado plateau are identified. The bulk and trace element contents are analyzed as natural analogues of the corrosion of spent nuclear fuel.
- The uranium mineralization in Colorado plateau is young (73 to 2 Ma). Both Colorado plateau and Yucca Mountain test site are in relatively arid environment.



Concentric structure and micro-fractures (BSE), possible pattern of spent fuel corrosion. Strongly dehydrated (bright) and weakly dehydrated (grey inner part) schoepite. Metasedimentary host rock (# 637, Jefferson, CO)



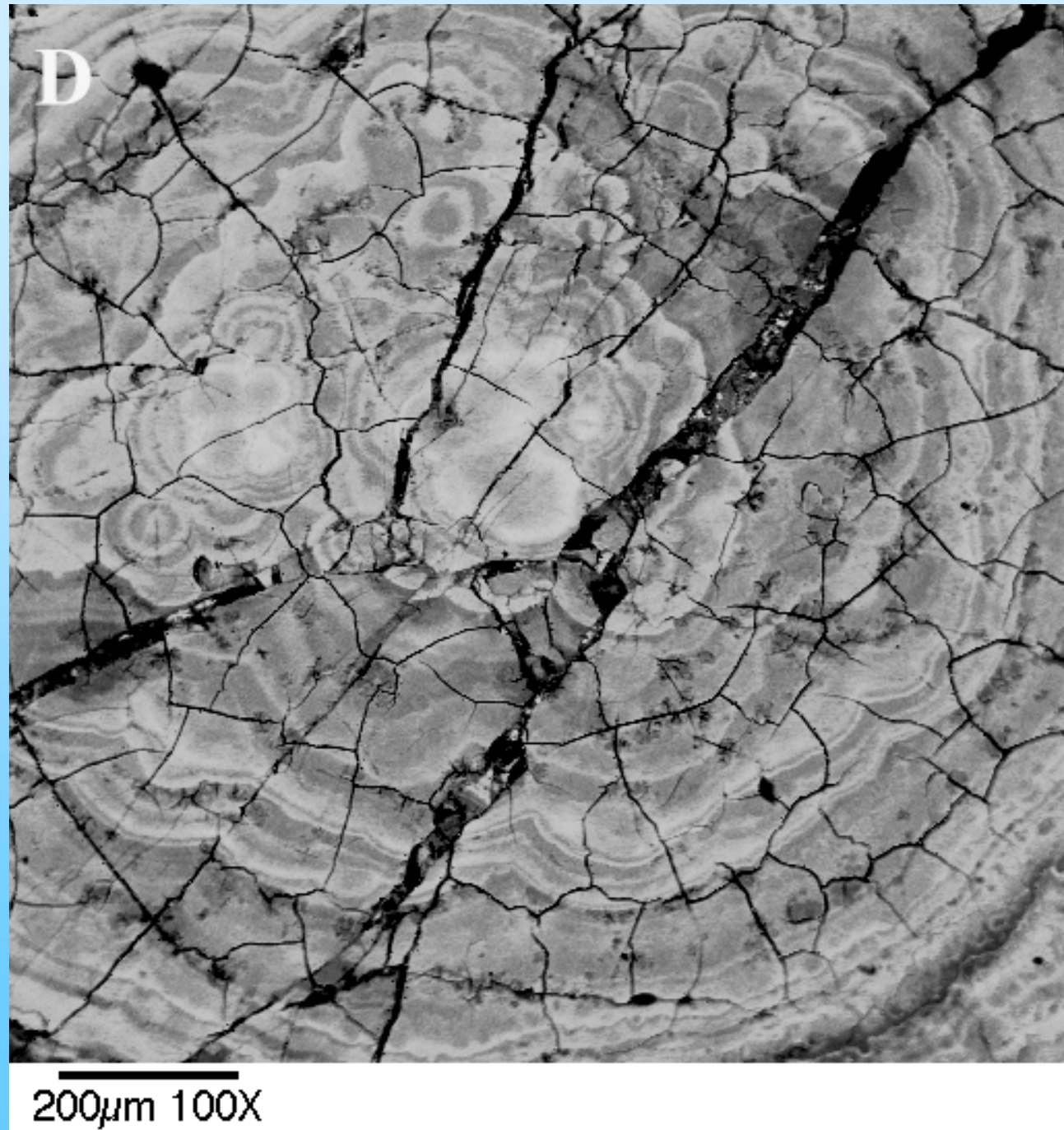
100 μ m 200X



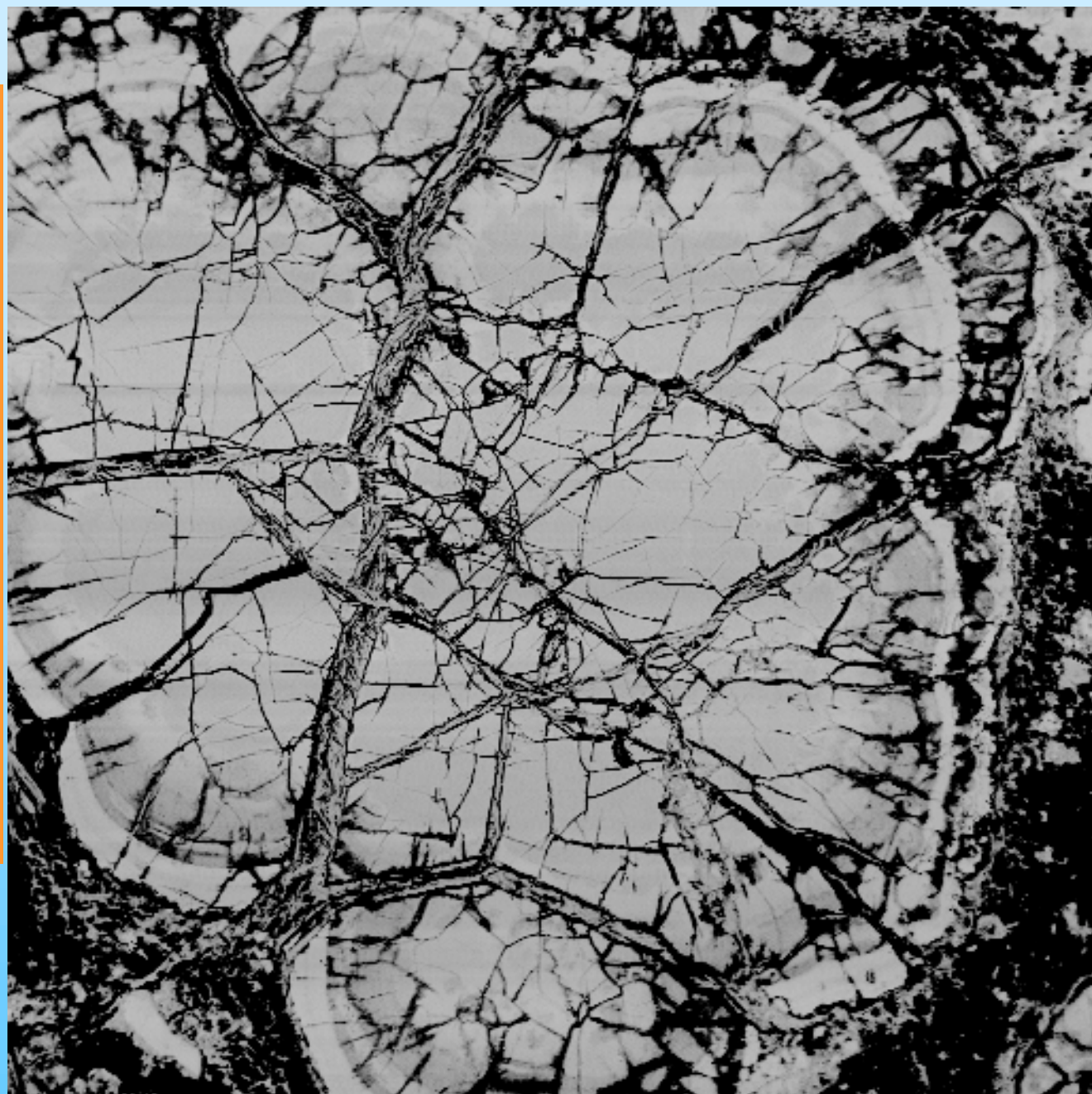
Coexisting
uranophane
(bright) and Fe-
rich uranyl phase
(grey).
Metasedimentary
host rock (# 637,
Jefferson, CO)

60 μ m 400X

Concentric structure of uraninite and schoepite. The alternating bright and gray bands correspond to uraninite and schoepite, respectively. Limestone host rock (sample # 530, Marshall Pass District, Saguache County, Colorado)



Concentric structure of uraninite and schoepite. A thin schoepite rim (about 10 μm) is located between a massive uraninite core and a late stage uraninite crust. Limestone host rock (# 531, Marshall Pass, Saguache, CO)



200 μm 100X

EMPA conditions

- Cameca CAMEBAX EMP (WDS)
- Voltage: 20 kV
- Beam: 80 nA for Pb, U, Th; 20 nA for other elements; size: $3 \times 3 \mu\text{m}^2$
- Peak count time: 30 seconds
- Cameca PAP (modified ZAF)



Uraninite UO_{2+x}

Locality	<i>Marshall Pass District, CO</i>	<i>Happy Jack Mine, UT</i>
U⁶⁺	high (0.587 to 0.808 apfu)	low (0.212 to 0.489 apfu)
O	high (2.480 to 2.727 apfu)	low (2.107 to 2.354 apfu)
Minor	Ca, Zr, Ti, Fe, Si and P	Ca, Zr, Ti, Fe, Si and P
Trace (Th & REE)	ThO ₂ 0.04 to 0.17; Y ₂ O ₃ 0.09 to 0.14 wt %	ThO ₂ b.d.l.; Y ₂ O ₃ 0.28; Nd ₂ O ₃ 0.12 wt %
Origin	similar to secondary uraninite or U ₃ O ₈	close to unaltered uraninite



Other phases

<i>Uranium phase</i>	<i>Locality</i>	<i>Features</i>	<i>Host rock</i>
schoepite [(UO ₂) ₈ O ₂ (OH) ₁₂](H ₂ O) ₁₂	Marshall Pass, CO (# 530)	associated with uraninite	limestone
schoepite [(UO ₂) ₈ O ₂ (OH) ₁₂](H ₂ O) ₁₂	Jefferson, CO (#637)	dehydrated	metasedimentary rock
uranophane Ca(UO ₂) ₂ Si ₂ O ₇ ·6H ₂ O	Jefferson, CO (#637)	fill fractures; rich in Si and Ca	metasedimentary rock
fourmarierite PbU ₄ O ₁₃ ·6H ₂ O	Jefferson, CO (#637)	damaged by electron beam; high ZrO ₂ (1.25 wt %) and TiO ₂ (0.89 wt %)	metasedimentary rock
Fe-dominated uranyl phase	Jefferson, CO (#637)	UO ₂ 29.27 wt %; FeO 41.16 wt %; Zr, Ti, Si, Al and Ca	metasedimentary rock
unknown uranyl silicate (neither soddyite (UO ₂) ₂ SiO ₄ ·2H ₂ O nor uranophane Ca(UO ₂) ₂ Si ₂ O ₇ ·6H ₂ O (not enough Ca)	Caribou, CO (# 603)	U:Si atomic ratio of 1:1; Y ₂ O ₃ 0.9 wt %	gneiss
calciouranoite (Ca,Ba,Pb)U ₂ O ₇ ·5H ₂ O	Grants, NM (# 369)	rich in Ca	limestone



Highest average trace element contents

	<i>uraninite</i>	<i>alteration product</i>		<i>uraninite</i>	<i>alteration product</i>
ThO₂	0.17 wt %	0.21	Sm₂O₃	0.12 wt %	0.14
Y₂O₃	0.28	0.88	Eu₂O₃	0.04	0.11
La₂O₃	0.03	0.05	Gd₂O₃	0.08	0.08
Ce₂O₃	0.10	0.15	Al₂O₃	0.13	1.25
Pr₂O₃	0.02	0.05	ZrO₂	0.93	2.11
Nd₂O₃	0.14	0.18	TiO₂	0.54	2.74



Trace element contents of coexisting uraninite and schoepite

<i>Sample # 531</i>	<i>uraninite</i>	<i>schoepite</i>
ZrO₂	0.37-0.53 wt %	2.00 wt %
TiO₂	0.20-0.29	0.42
Y₂O₃	0.11-0.14	0.15
Ce₂O₃	0.05-0.10	0.15
Nd₂O₃	0.06-0.14	0.18
Sm₂O₃	0.07-0.12	0.14
Eu₂O₃	0.01	0.14



Conclusions

- Concentric structures and micro-fractures may represent physical structure after spent fuel alteration.
- Trace element contents in secondary uranyl phases are generally higher, as compared with those in uraninite. Thus, trace elements preferentially enter secondary phases.
- The high incorporation capacity of trace elements into secondary uranyl phases may significantly reduce the mobility of radionuclides in the near-field

