Alteration Products of Uraninite from the Colorado Plateau

Donggao Zhao and Rodney C. Ewing

Department of Nucl. Engin. & Radiological Sci.
Department of Geological Sciences
University of Michigan

Michigan**Engineering**

Outline

- Background
- Objectives
- Radionuclides in U^{6+} phases: e.g., ^{79}Se
- Sample localities & selection
- Sample petrography
- Chemical compositions
- Trace elements
- Conclusions

Background

- Corrosion of UO_2 in spent nuclear fuel: U(IV) -> U(VI)
- Incorporation of fission products and actinides into uranyl phases
  - Theoretical consideration based on crystal chemistry
  - Studies of uraninite and alteration products for confirmation

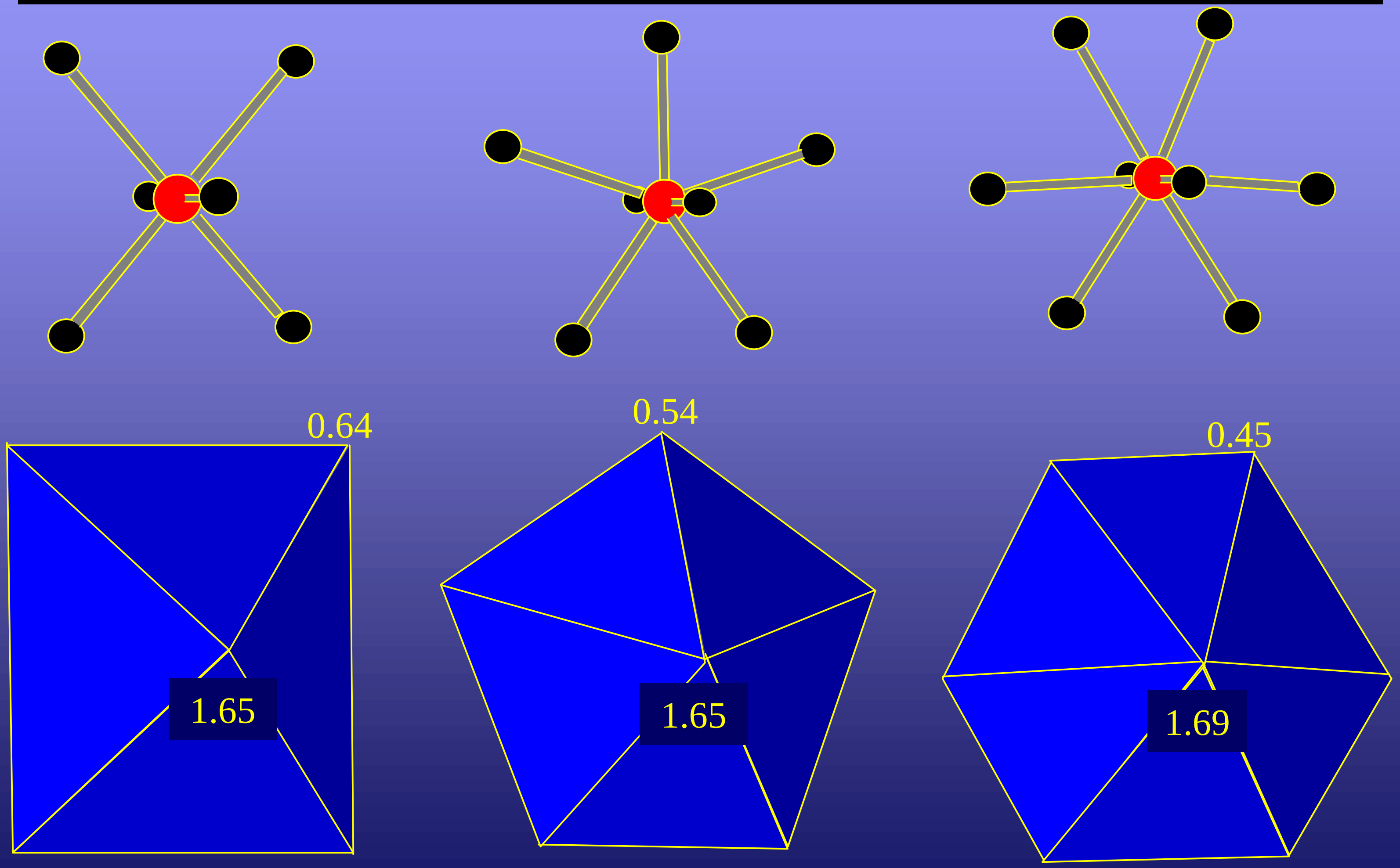
Michigan Engineering

Objectives

- Corrosion products of natural uraninite
- Trace element contents and migration
- Confirmation of incorporation mechanisms

Michigan Engineering

Coordination Geometries and Bond-Valence Distribution of Uranyl Polyhedra



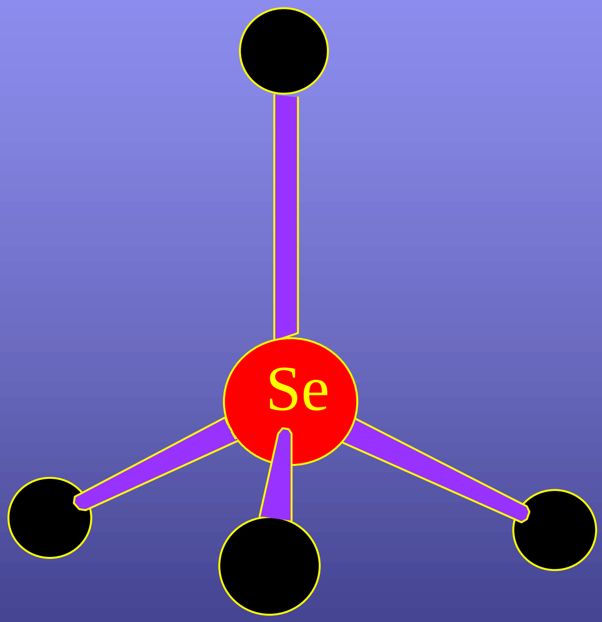
(Burns, Ewing and Hawthorne, 1997, Can. Min. 35, 1551-1570)

Immobilization of fission products by incorporation into uranyl phases

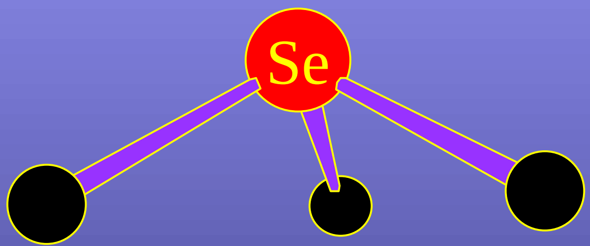
- Substitution for U^{6+}
- Substitution for cations other than U^{6+}: e.g., ^{79}Se
- Occupation of vacancies

(Burns, Ewing and Miller, 1997, J. Nucl.Mat. 245, 1-9)

Stereo-Diagram of selenite SeO_3^{2-} and selenate SeO_4^{2-} Groups in Crystal Structures



$(SeO_4)^{2-}$ tetrahedron



One-sided coordination polyhedron of $(SeO_3)^{2-}$ that contains three essentially co-planar anions

(Chen, Burns and Ewing, 1999, J. Nucl.Mat. in press)

^{79}Se: α-uranophane and rutherfordine

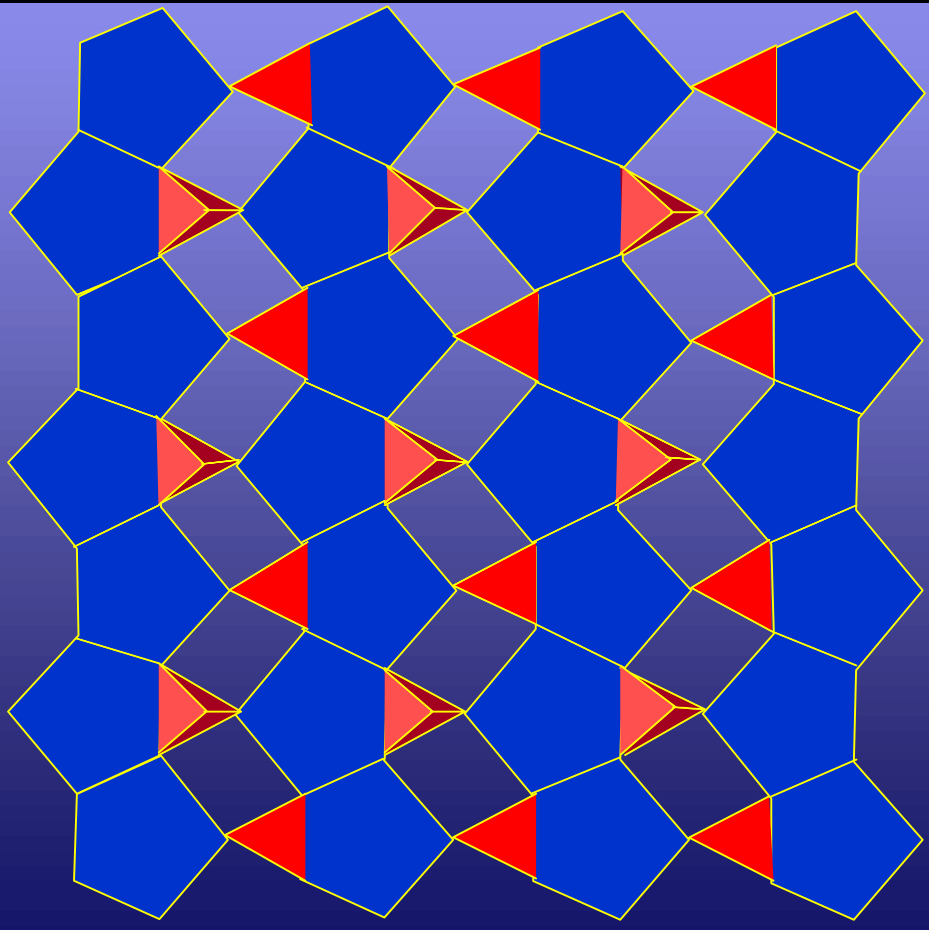
- $(SeO_3) \leftrightarrow (SiO_3OH)$ in α-uranophane $Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$ - dominant alteration product of UO_2 in Si-rich groundwater
- $(SeO_3) \leftrightarrow (CO_3)$ in rutherfordine $(UO_2)(CO_3)$

(Chen, Burns and Ewing, 1999, J. Nucl.Mat. in press)

MichiganEngineering

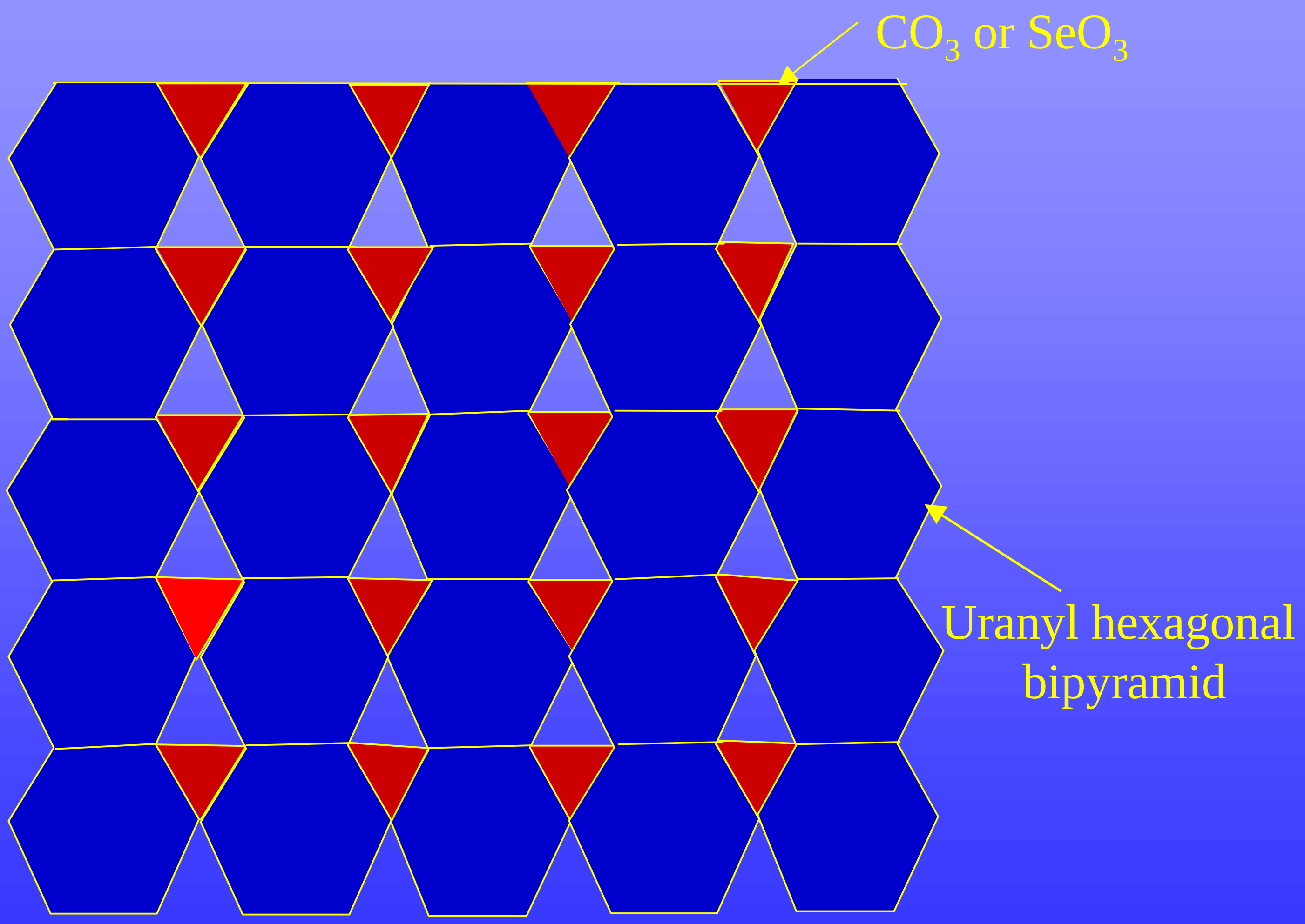
Sheets of uranyl silicates in structures of α-uranophane

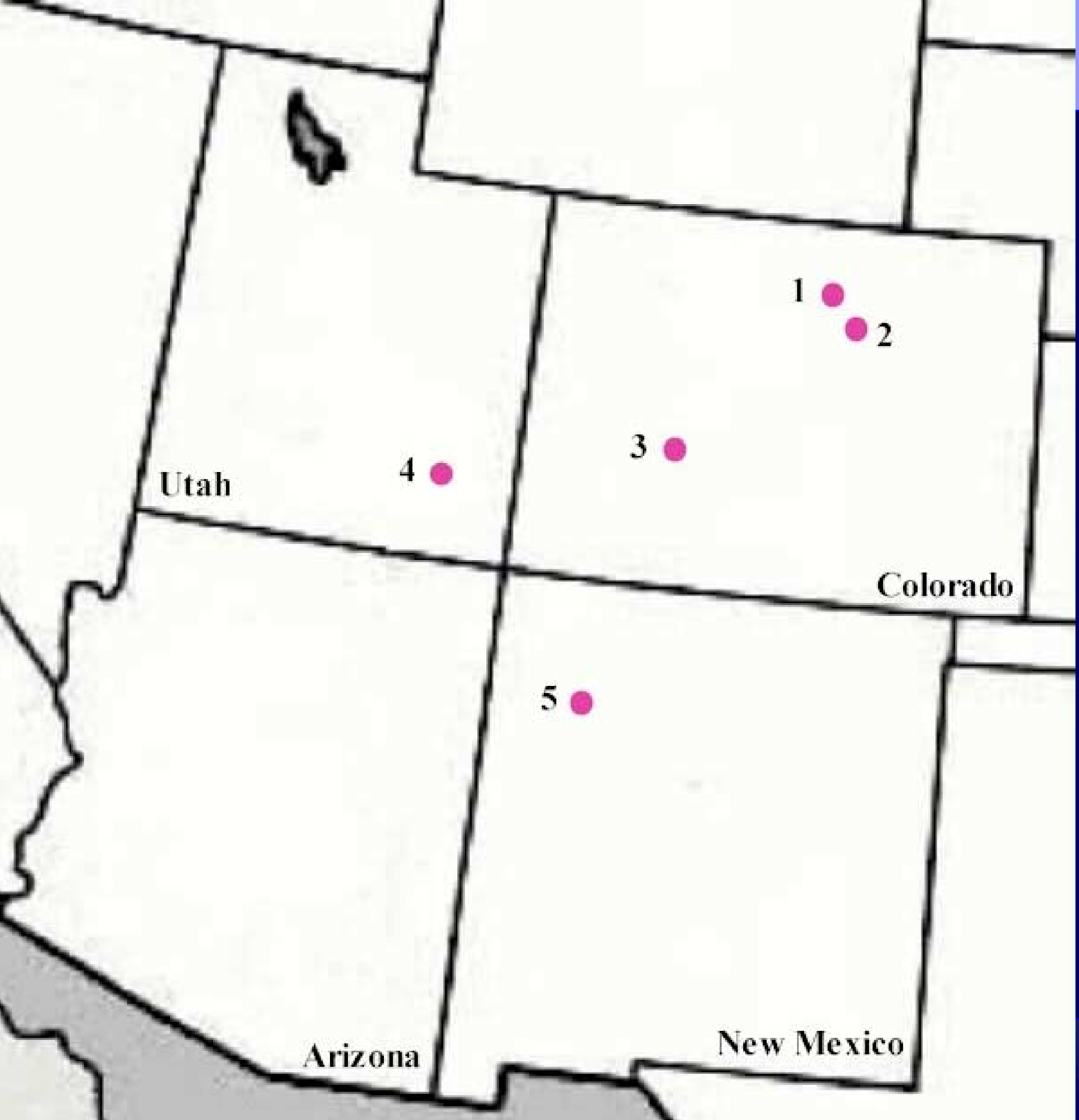
(Chen, Burns and Ewing, 1999, J. Nucl.Mat. in press)



Sheets in $(UO_2)(SeO_3)$ and rutherfordine $(UO_2)(CO_3)$

(Chen, Burns and Ewing, 1999, J. Nucl.Mat. in press)



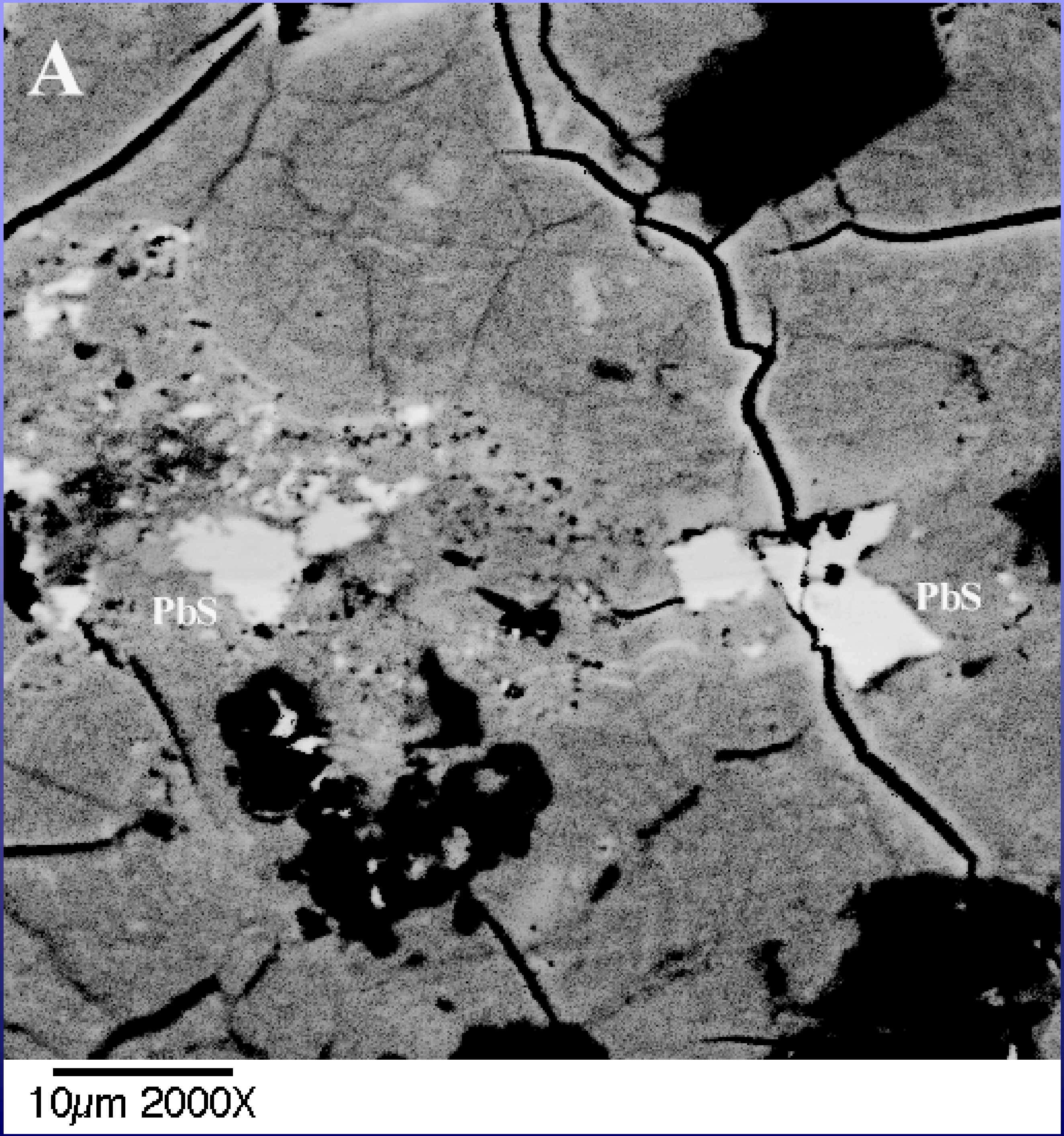


Four Corners area:

1. Caribou Mine, Boulder, CO;
2. Jefferson, CO;
3. Marshall Pass, Saguache, CO;
4. Happy Jack, White Canyon, Blanding, UT;
5. Grants, NM.

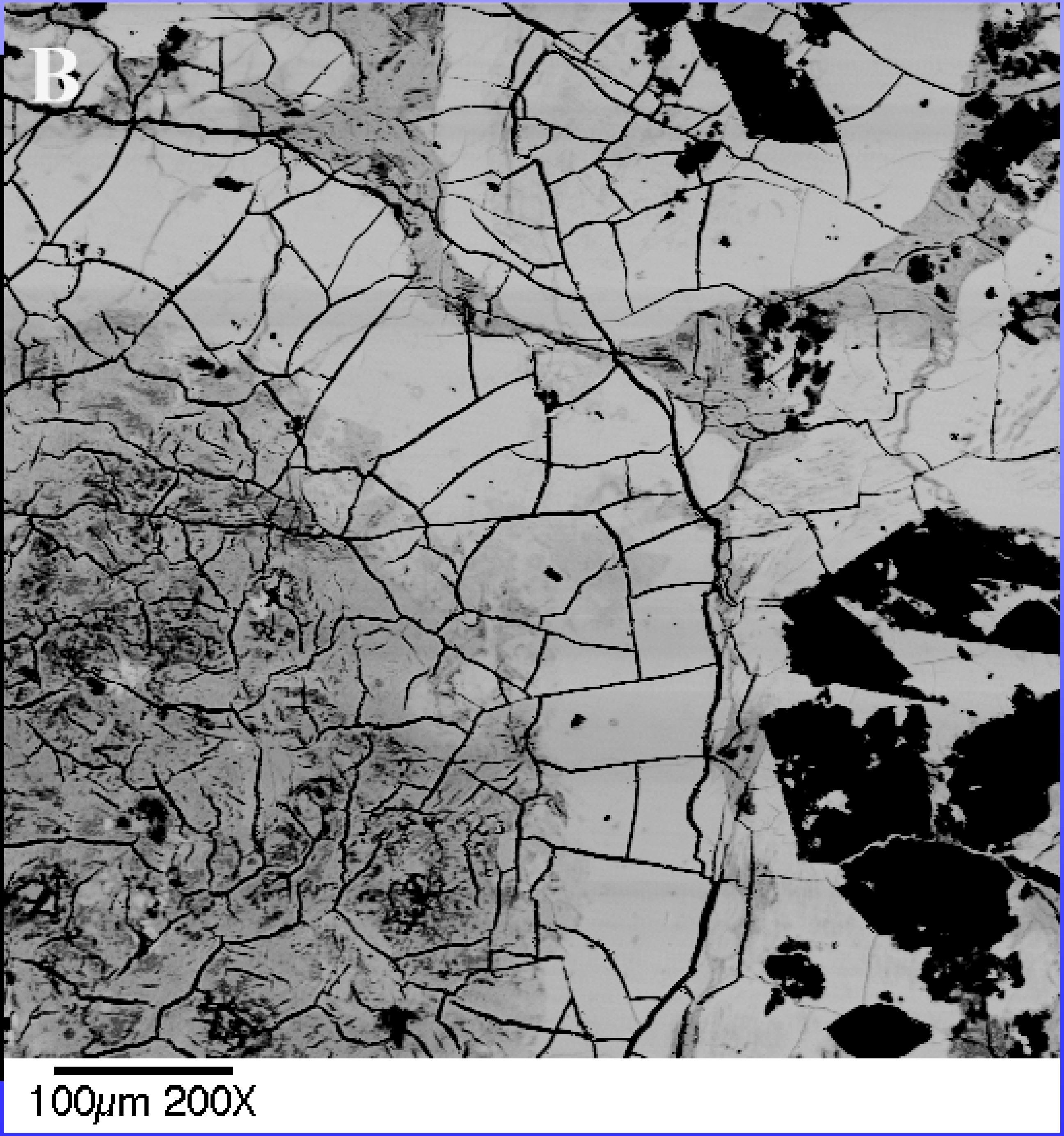
Samples from the Colorado Plateau

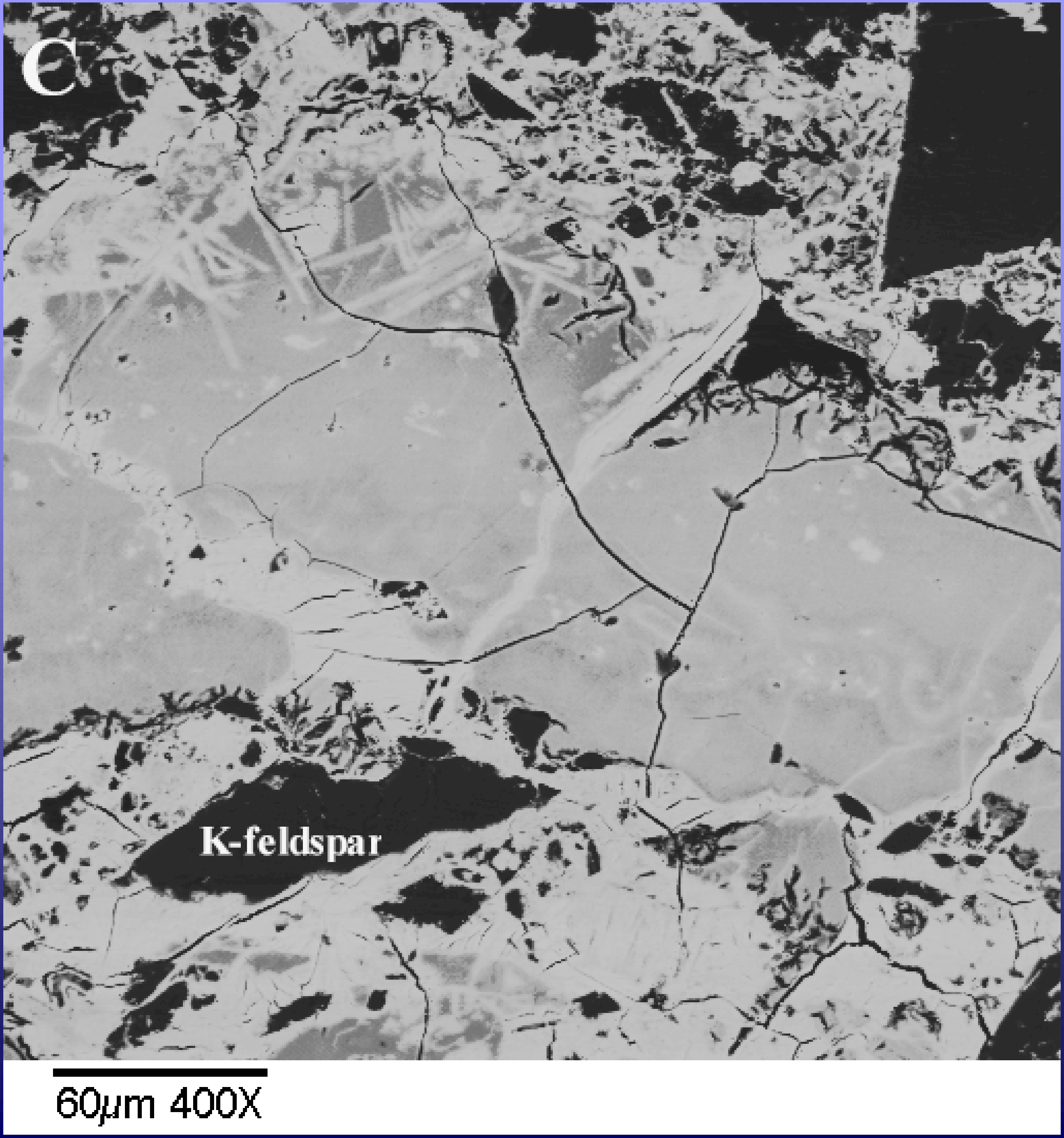
- Uranium mineralization is young: 73 to 2 Ma (Late Cretaceous to Late Tertiary)
- Both uraninite and uranyl phases identified
- In common with Yucca Mountain, i.e., relatively arid environment
- Sedimentary or hydrothermal or both in sandstone or as vein deposits



A. Concentric structure (BSE). Galena associated with a uranyl silicate. Quartz, dolomite and calcite. Gneiss host rock (# 603, Caribou Mine, Boulder, CO)

B. 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)

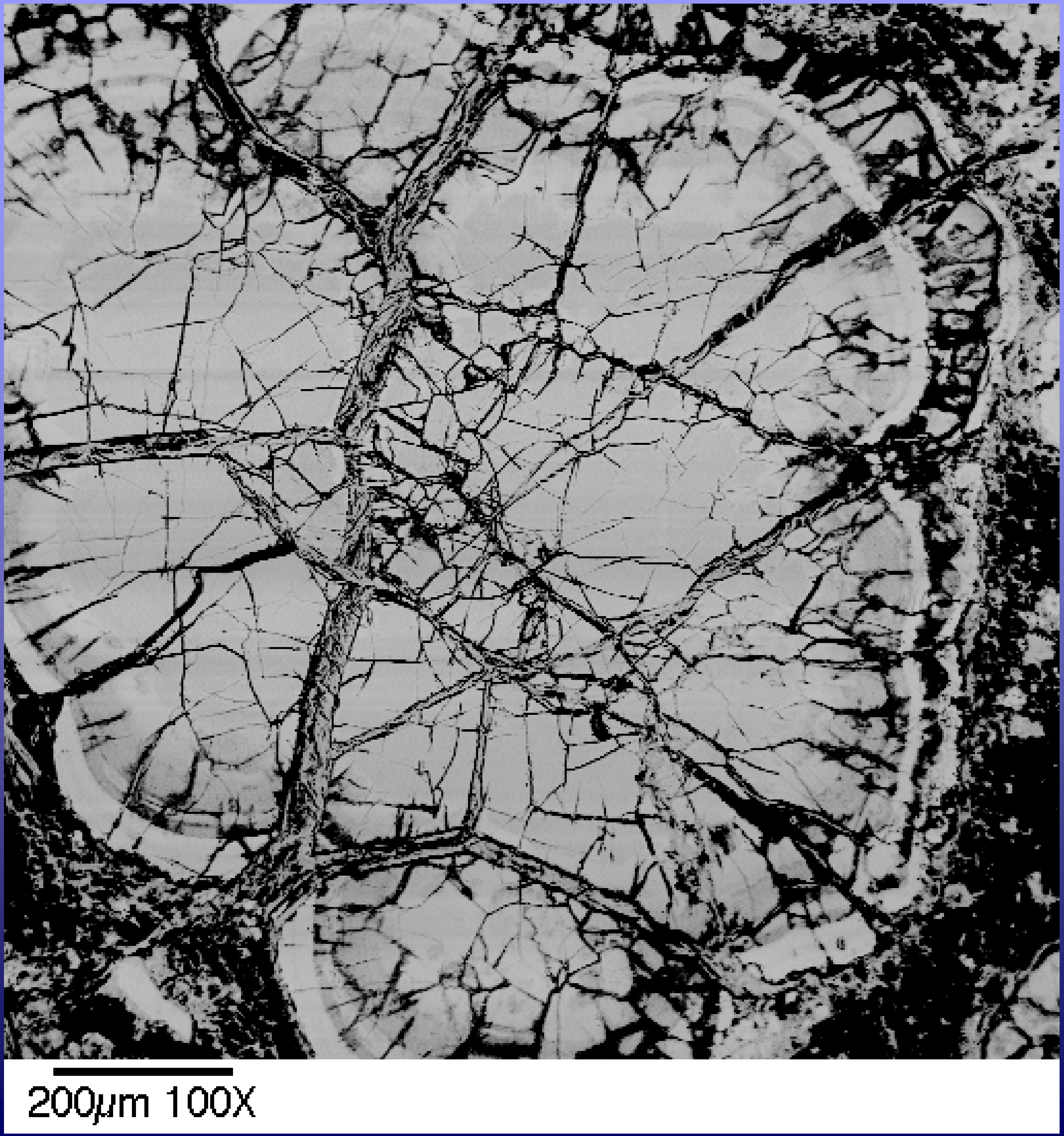




C. Coexisting uranophane (bright) and Fe-rich uranyl phase (grey). Metasedimentary host rock (# 637, Jefferson, CO)

D. Concentric structure of uraninite (bright) and schoepite (grey). Limestone host rock (# 530, Marshall Pass, Saguache, CO)

D2. 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)



EMPA conditions

- Cameca CAMEBAX EMP (WDS)
- Voltage: 20 kV
- Beam: 80 nA for Pb, U, Th; 20 nA for other elements; size: 3x3 μm^2
- Peak count time: 30 seconds
- Cameca PAP (modified ZAF)

Structural Formula

- $[U^{4+}_{1-x-y-z-u}\,U^{6+}_{x}(Th^{4+})_{u}REE^{3+}_{y}M^{2+}_{z}]O_{2+x-(0.5)y-z}$
- PbO to UO_2
- U^{4+} to U^{6+}, adding oxygen
- All U^{4+} converted to U^{6+}:
  - – total > 100 wt %, both U^{4+} and U^{6+} exist
  - – total < 100, H_2O and/or CO_2 may exist

MichiganEngineering

Uraninite UO_{2+x}

Locality	*Marshall Pass District, CO*	*Happy Jack Mine, UT*
U^{6+}	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_2O_3 0.09 to 0.14 wt %	ThO_2 b.d.l.; Y_2O_3 0.28; Nd_2O_3 0.12 wt %
Origin	similar to secondary uraninite or U_3O_8	close to unaltered uraninite

Other phases

Uranium phase	*Locality*	*Features*	*Host rock*
schoepite $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$	Marshall Pass, CO (# 530)	associated with uraninite	limestone
schoepite $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$	Jefferson, CO (#637)	dehydrated	metasedimentary rock
uranophane $Ca(UO_2)_2Si_2O_7 \cdot 6H_2O$	Jefferson, CO (#637)	fill fractures; rich in Si and Ca	metasedimentary rock
fourmarierite $PbU_4O_{13} \cdot 6H_2O$	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 $(UO_2)_2SiO_4 \cdot 2H_2O$ nor uranophane $Ca(UO_2)_2Si_2O_7 \cdot 6H_2O$ (not enough Ca)	Caribou, CO (# 603)	U:Si atomic ratio of 1:1; Y_2O_3 0.9 wt %	gneiss
calciouranoite $(Ca,Ba,Pb)U_2O_7 \cdot 5H_2O$	Grants, NM (# 369)	rich in Ca	limestone

MichiganEngineering

Highest average trace element contents

	uraninite	*alteration product*
ThO_2	0.17 wt %	0.21
Y_2O_3	0.28	0.88
La_2O_3	0.03	0.05
Ce_2O_3	0.10	0.15
Pr_2O_3	0.02	0.05
Nd_2O_3	0.14	0.18

	uraninite	*alteration product*
Sm_2O_3	0.12 wt %	0.14
Eu_2O_3	0.04	0.11
Gd_2O_3	0.08	0.08
Al_2O_3	0.13	1.25
ZrO_2	0.93	2.11
TiO_2	0.54	2.74

Trace element contents of coexisting uraninite and schoepite

Sample # 531	***uraninite***	***schoepite***
ZrO_2	0.37-0.53 wt %	2.00 wt %
TiO_2	0.20-0.29	0.42
Y_2O_3	0.11-0.14	0.15
Ce_2O_3	0.05-0.10	0.15
Nd_2O_3	0.06-0.14	0.18
Sm_2O_3	0.07-0.12	0.14
Eu_2O_3	0.01	0.14

Conclusions

- Trace element contents of uraninite are generally lower, as compared with those in secondary uranyl phases. Therefore, trace elements preferentially enter secondary phases.
- Concentric structures and micro-fractures may represent physical structure after spent fuel alteration.

Conclusions

- Two types of uraninite:
  - – high U^{6+} (0.587 to 0.808 apfu), similar to secondary uraninite;
  - – low U^{6+} (0.212 to 0.489 apfu), close to primary uraninite
- Two types of schoepite:
  - – associated with uraninite;
  - – different degrees of dehydration