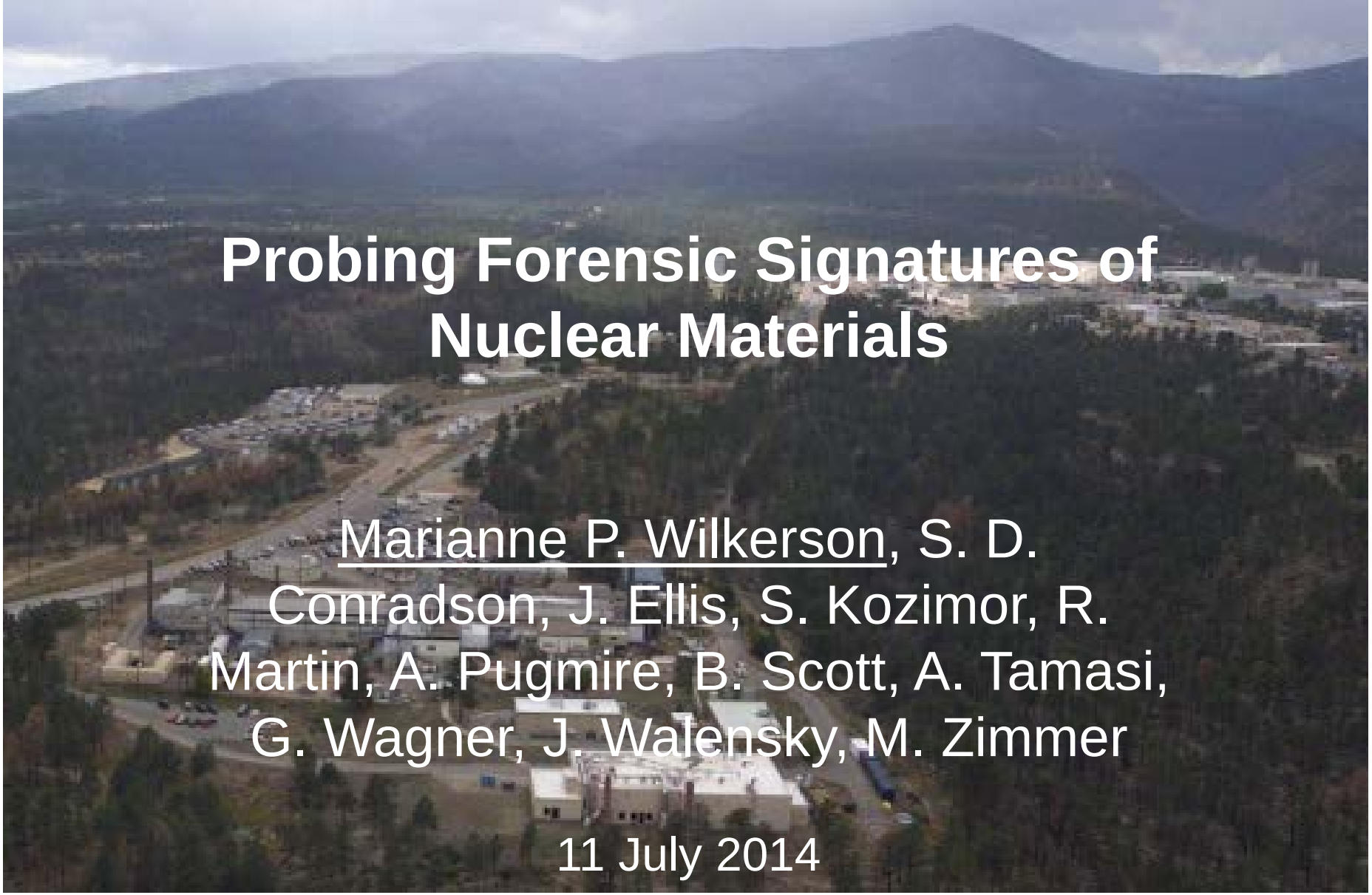

Probing Forensic Signatures of Nuclear Materials

Marianne P. Wilkerson, S. D. Conradson, J. Ellis, S. Kozimor, R. Martin, A. Pugmire, B. Scott, A. Tamasi, G. Wagner, J. Walensky, M. Zimmer

11 July 2014

Transformational and Applied Research Directorate, National Technical Nuclear Forensics Center
U.S. Department of Homeland Security

Los Alamos NATIONAL LABORATORY EST.1943
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LA-UR 14-24839

NNSA

What is the problem that a *Molecular and Chemical Forensic approach* is addressing?

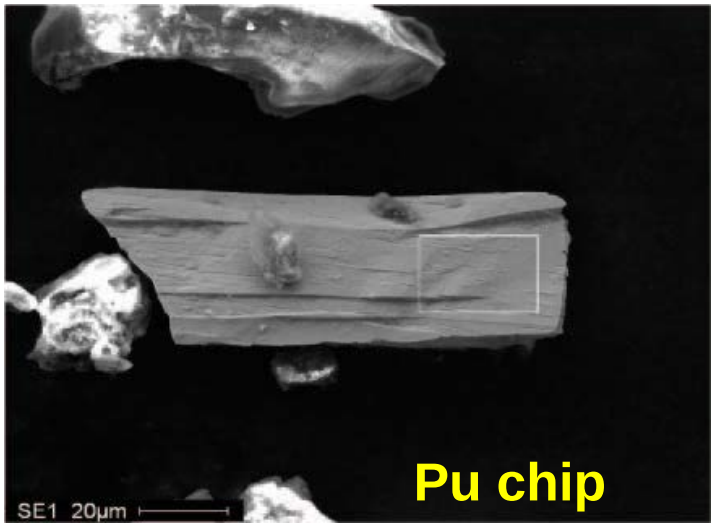
• Increasingly varied and asymmetric threats are expanding the scope of nuclear forensics

• Signatures are varied and can evolve, while any given sample may include multiple signatures

• The scale of a signature may be tiny or LARGE

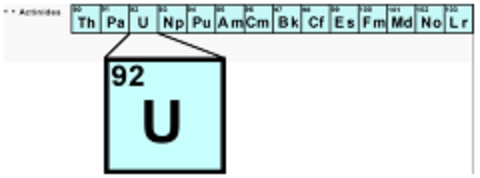
• Accurate, effective technical analysis depends on
  - identifying new signatures
  - understanding measurement limitations
  - evaluating complementary nature between traditional and new measurements
  - assessing the value of the information

• Production, conversion and aging of actinide materials are chemical in nature



What do we mean by chemical speciation?

Levels of "Chemical Analysis"



Physical (or Phase) Speciation

- Refers indirectly to the phase association: dissolved, or associated with various mineral or colloidal phases

Chemical Speciation

- Refers to the chemical form and generally includes a knowledge of phase

- Depending on the type of information, various levels exist
  - Identity of the element
  - Physical state

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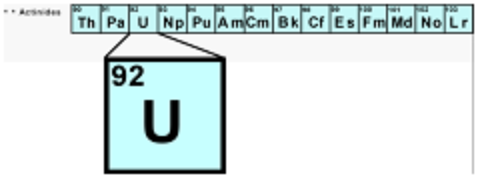
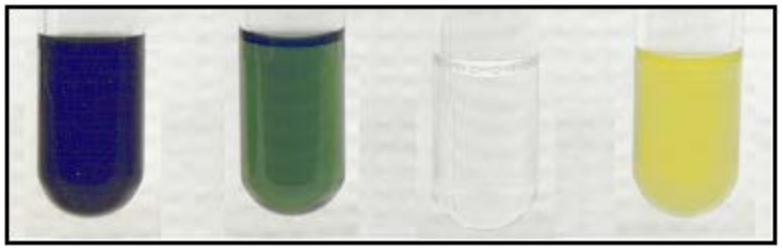
  - Oxidation state



U(III) U(IV) U(V) U(VI)



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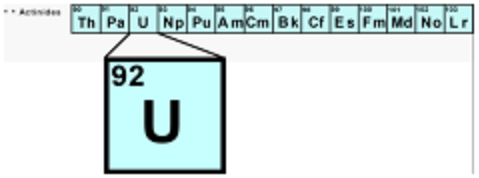
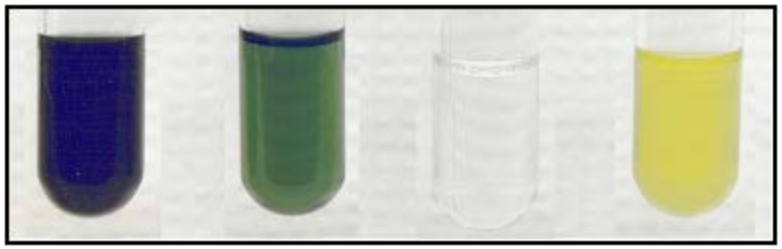
  - Oxidation state
  - Empirical formula



U(III) U(IV) U(V) U(VI)



$UO_2(OH)^+$

What do we mean by chemical speciation?

Levels of "Chemical Analysis"

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Chemical Speciation

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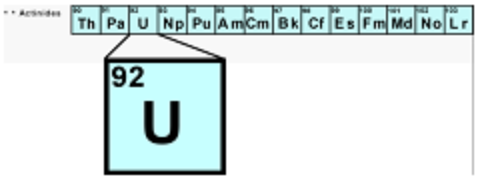
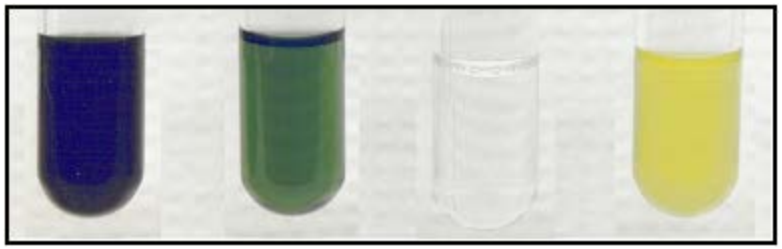
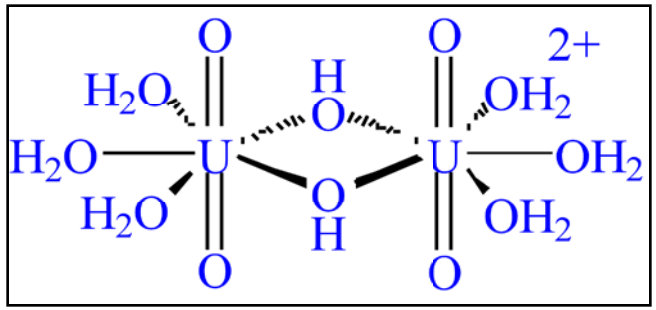
- Depending on the type of information, various levels exist
  - Identity of the element
  - Physical state
  - Oxidation state
  - Empirical formula
  - Molecular formula
  - Molecular structure

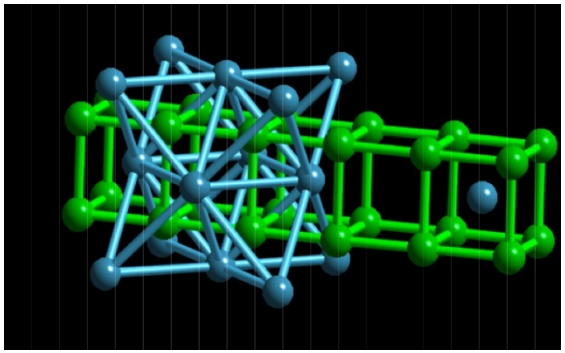


U(III) U(IV) U(V) U(VI)



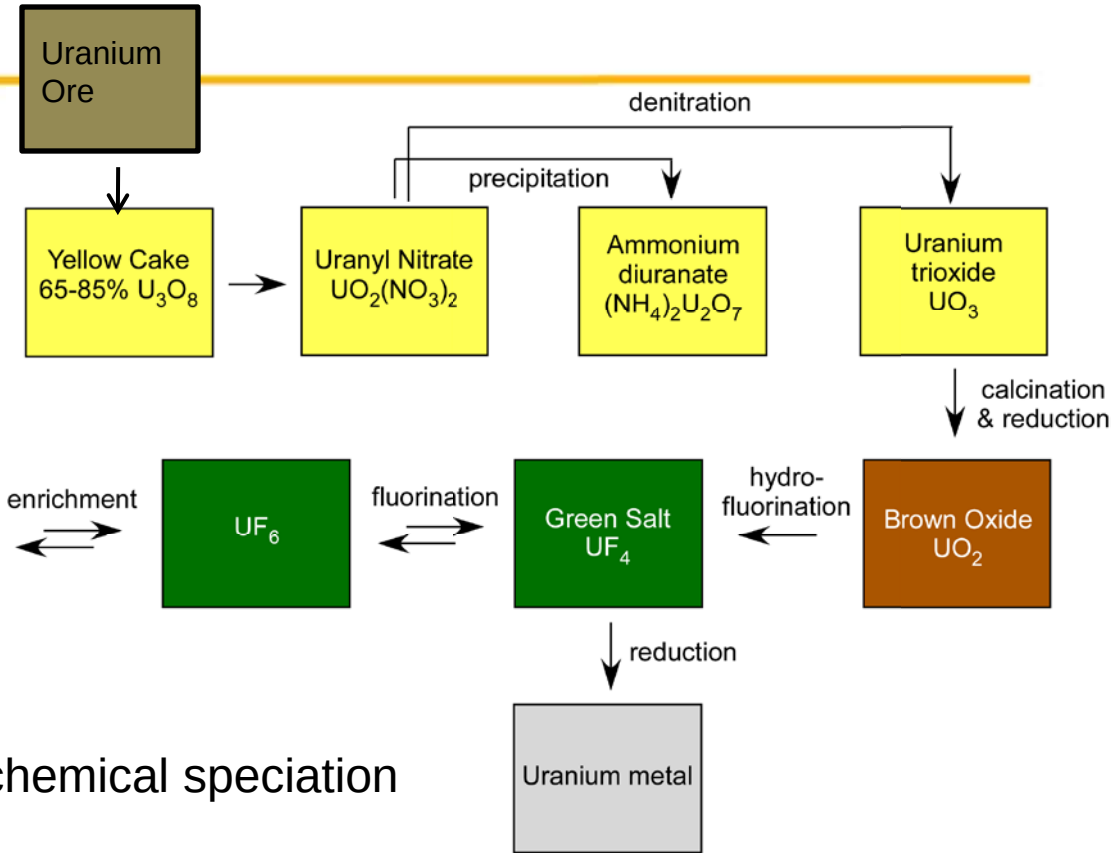
$UO_2(OH)^+$





Actinide processing is rich in chemical information

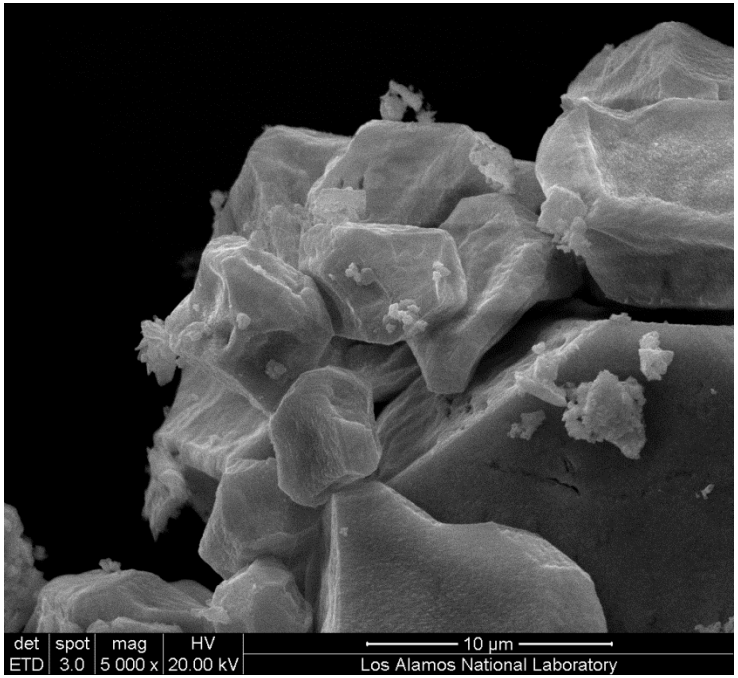
- > 10 phases between UO_2 and UO_3, in addition to hydrated forms of UO_3
- Deceptively simple formula and cubic structure of UO_2 masks incredibly complex speciation
- Weathering under environmental conditions may effect changes in morphology, chemical speciation



- *Can chemical speciation of major and minor constituents be measured?*
- *Do signatures of chemical speciation change over time?*
- *How can we ground these measurements with standards?*

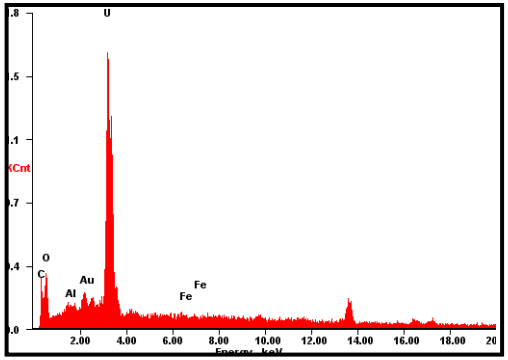
What tools provide access to chemical speciation?

Morphology

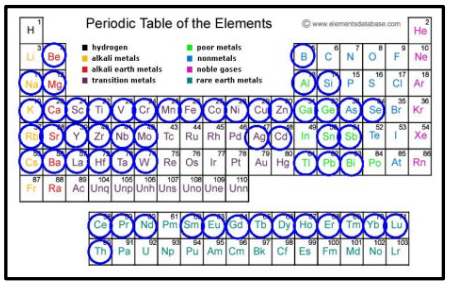


- Scanning Electron Microscopy

Elemental



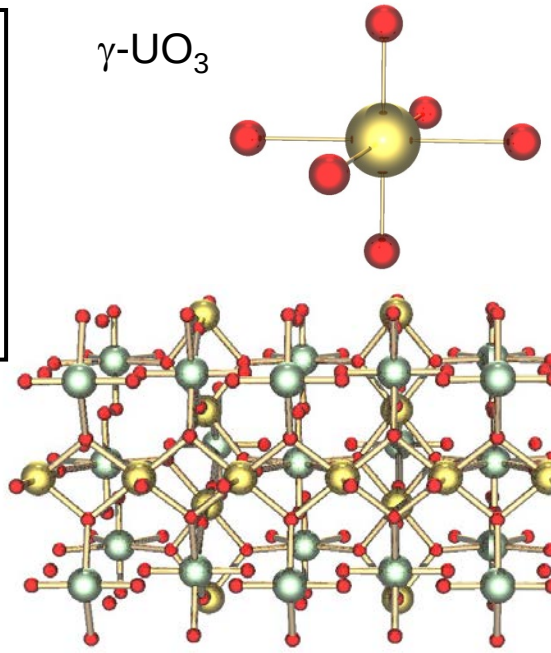
- SEM-Energy Dispersive Spectroscopy



- Inductively Coupled Plasma – Mass Spectrometry

Structural (lattice)

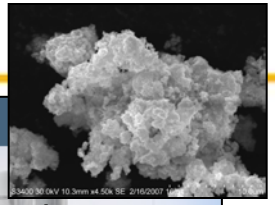
γ-UO_3

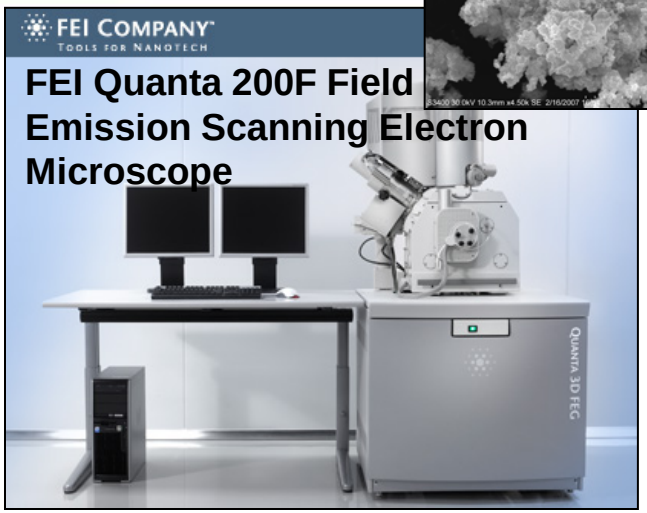


- X-ray diffraction analysis
- X-ray Absorption Spectroscopy

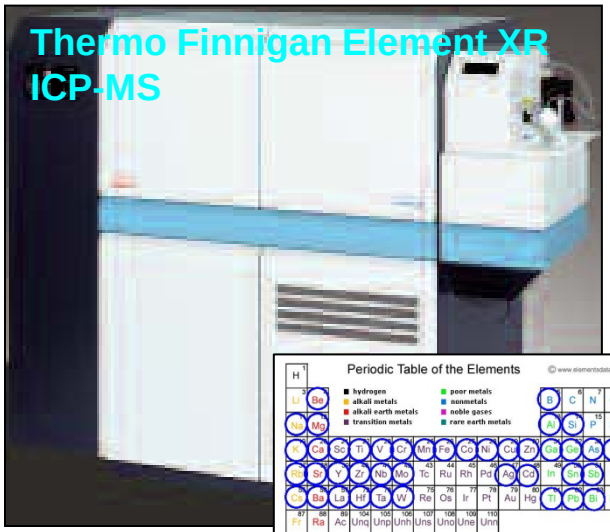
Measurement Capabilities

Morphology

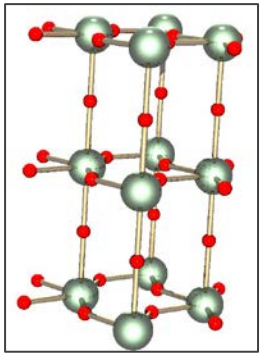




Elemental/isotopic Analysis

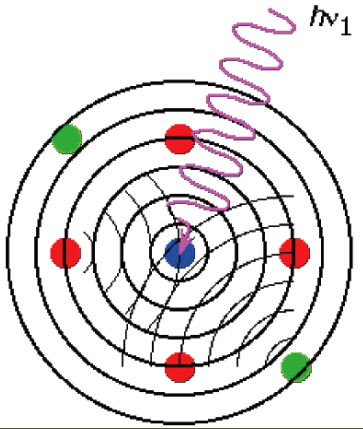


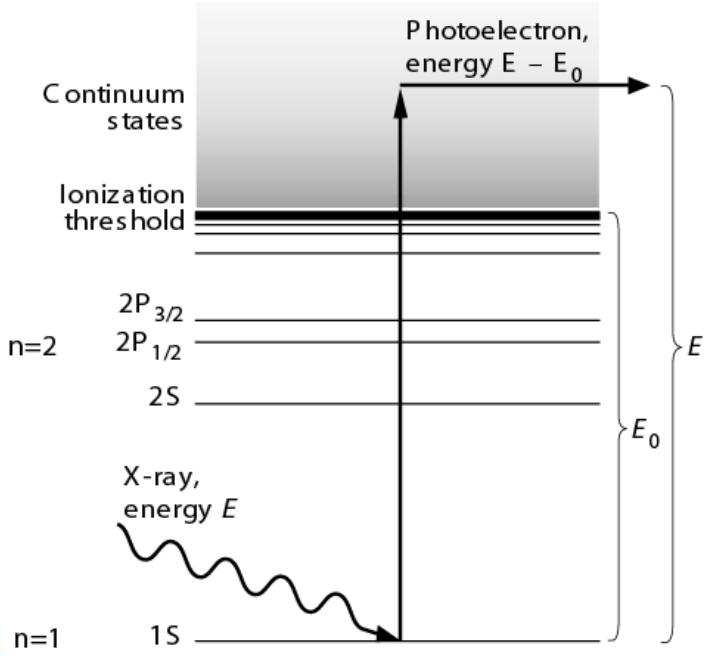
Chemical Speciation

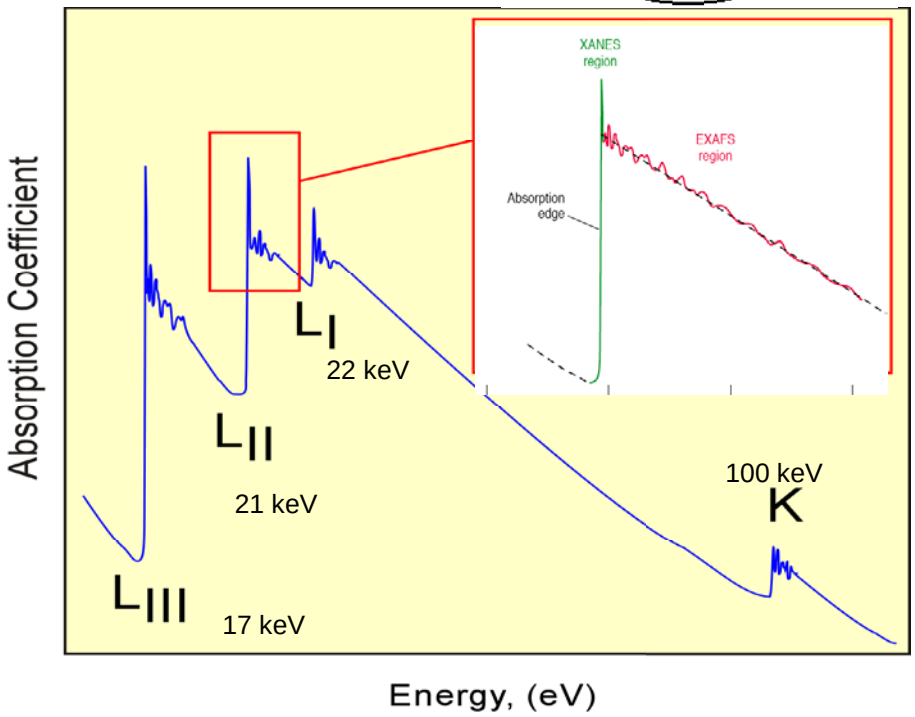


How is local structure through XAFS determined?

XAFS- X-ray Absorption Fine Structure
high energy X-rays allow for excitation of core electrons to bound states
XANES- X-ray Absorption Near Edge Structure
arises from differences in oxidation state, local structure
EXAFS- Extended X-ray Absorption Fine Structure
distribution of interatomic distances around atoms

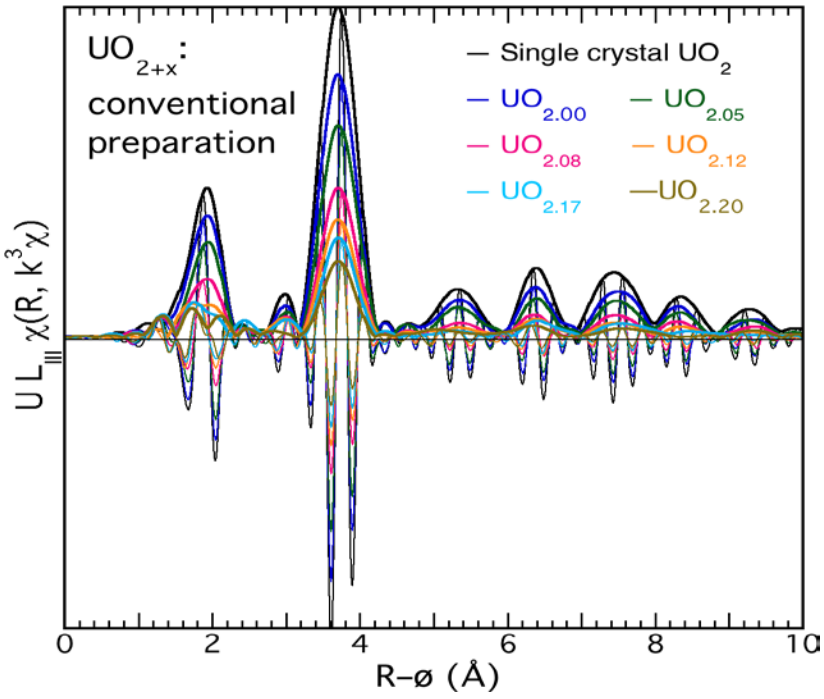




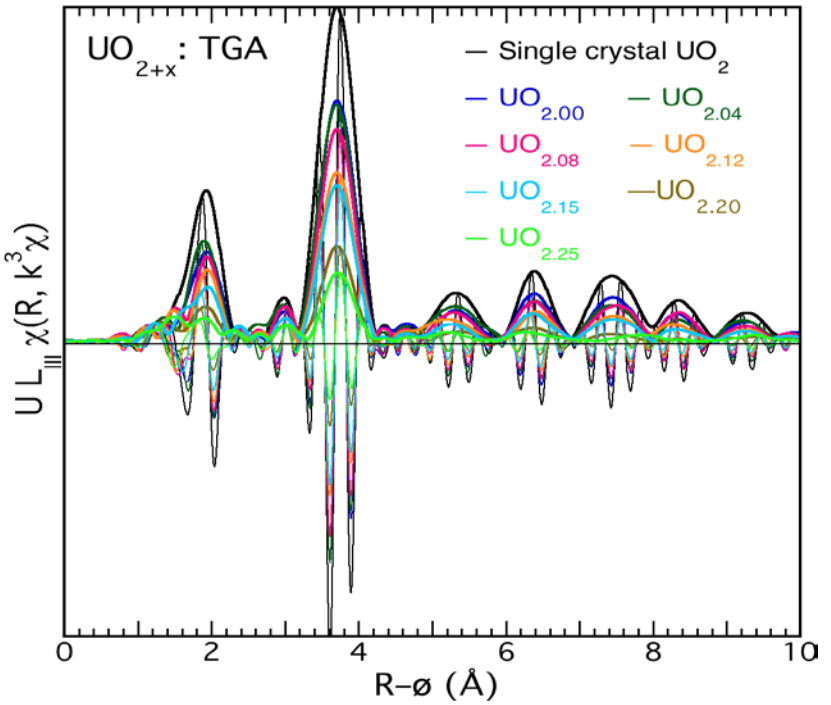


Systematic experiments on UO_2 using EXAFS to measure sensitivity to oxidation.

With H_2O, intermediate temperature



Weak CO:CO_2 oxidizer, high temperature



Increased oxidation yields monotonic changes.

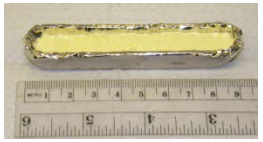
Conradson, S. D.; Manara, D.; Wastin, F.; Clark, D. L.; Lander, G. H.; Morales, L. A.; Rebizant, J.; Rondinella, V. V. . *Inorg. Chem.* 2004, *43(22)*, pp 6922-6935.

Reference information is derived from high-purity uranium oxide bulk materials

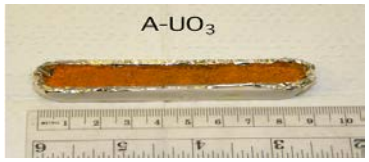
$U^o \longrightarrow UO_2^{2+}$

NIST SRM U960
NBL A112A

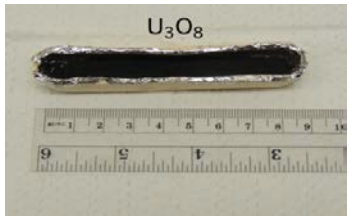
$UO_2^{2+} + H_2O_2 \xrightarrow[\text{air}]{\text{pH 3}} UO_2(O_2)\cdot xH_2O$



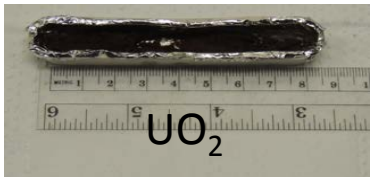
$UO_2(O_2)\cdot 2H_2O \xrightarrow[\text{air}]{400^oC} A\text{-}UO_3$

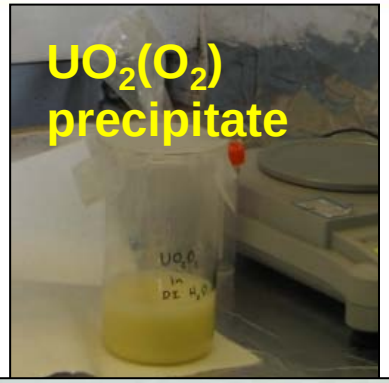


$A\text{-}UO_3 \xrightarrow[\text{air}]{900^oC} U_3O_8$



$A\text{-}UO_3 \xrightarrow[H_2]{500^oC} UO_2$



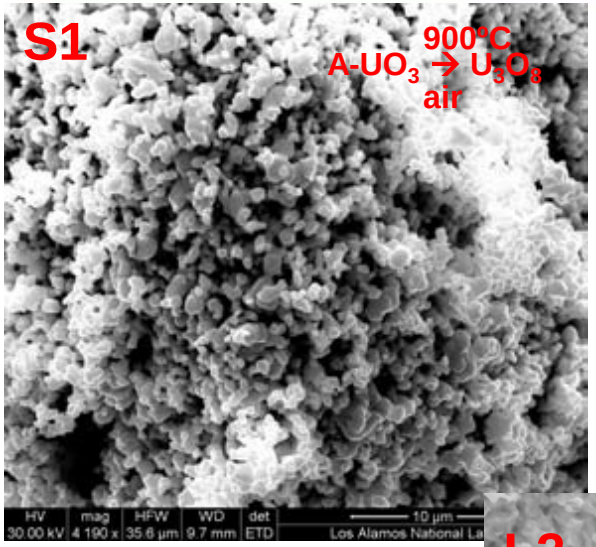


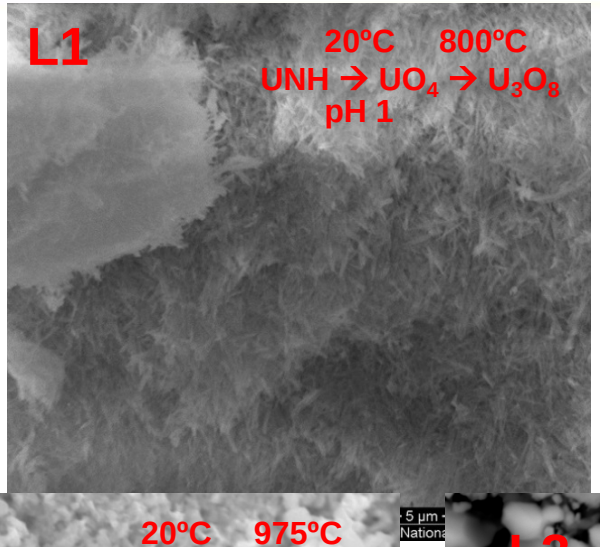
Can trace chemical species be measured from legacy samples of U_3O_8

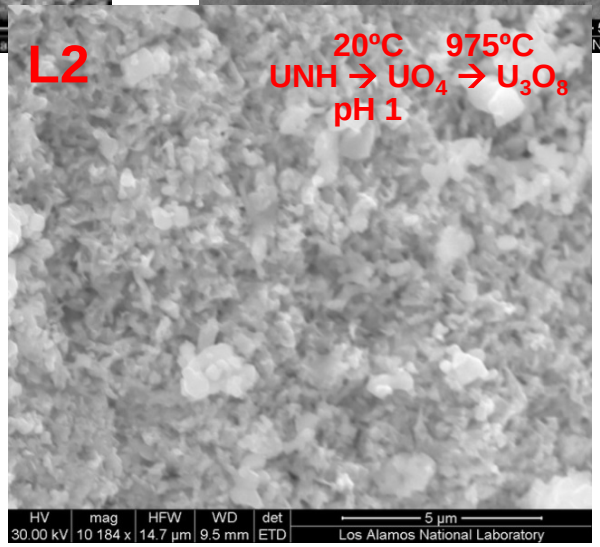
Precipitate Source		Precipitate		Sample Product
UNH	pH 1, 20ºC →	UO4	800ºC →	U3O8
UNH	pH 1, 20ºC →	UO4	975ºC →	U3O8
UO2F2	pH 8.4, 20ºC →	ADU	800ºC →	U3O8

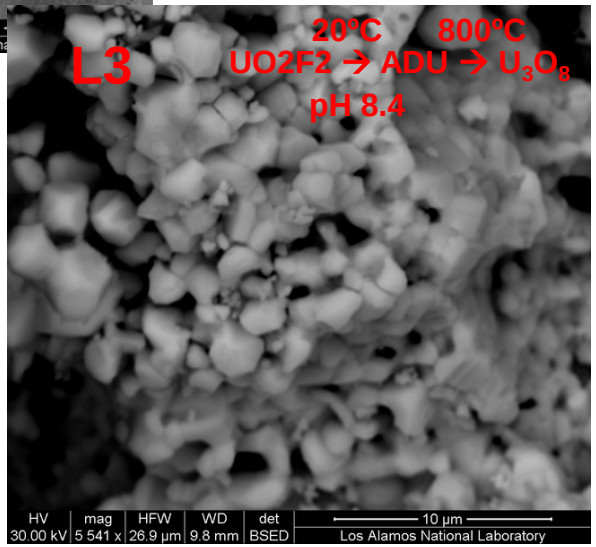
Age of samples: ~2-3 years
Common source of starting material
Preparation scale: 10 g

Comparison of SEM images of U_3O_8 materials at time 0

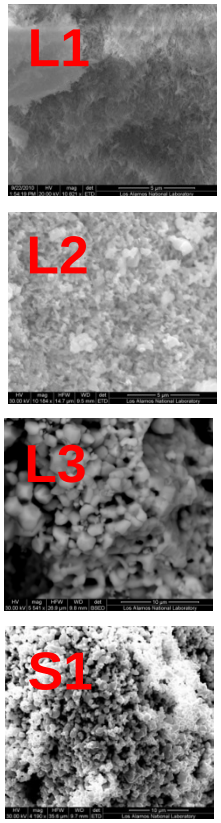


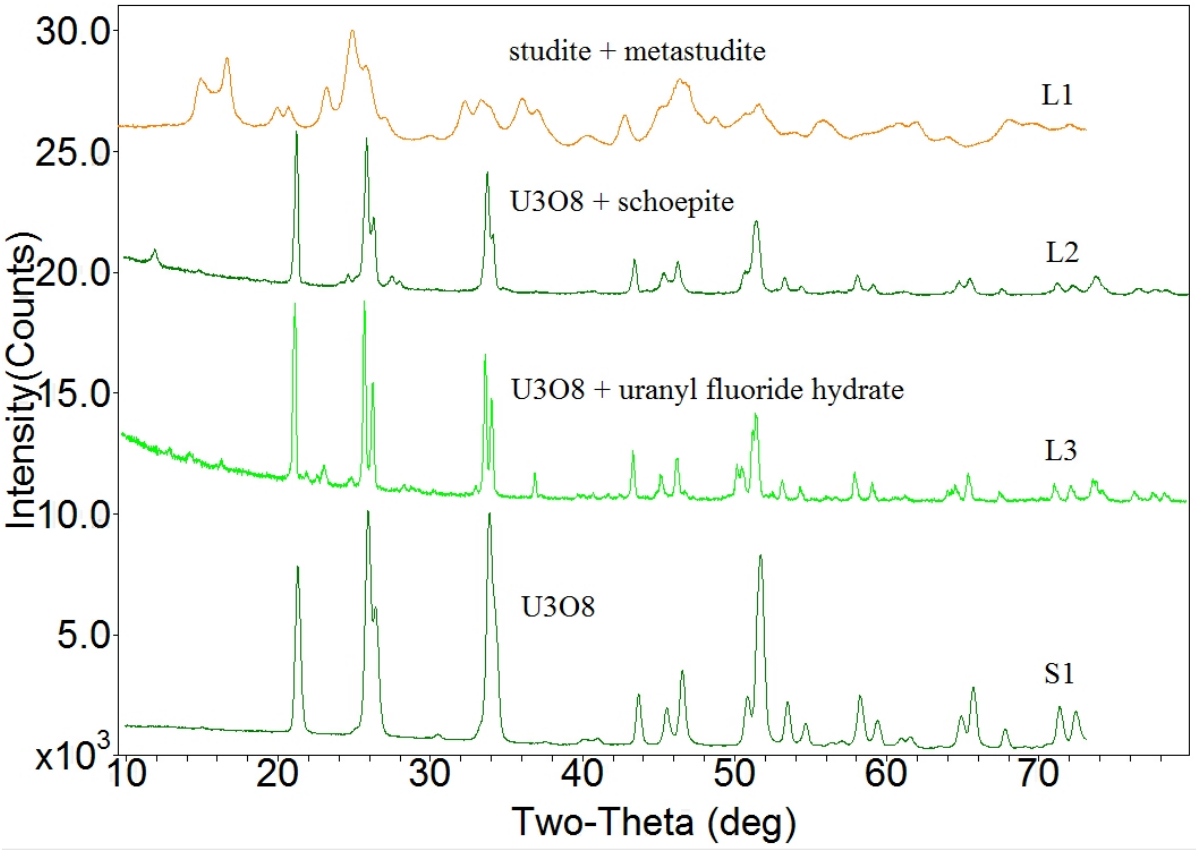






Comparison of reference lines with pXRD patterns of U_3O_8 materials identifies speciation





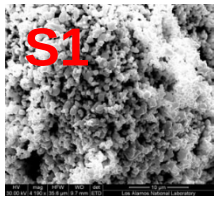
20ºC 800ºC
UNH → UO_4 → U_3O_8
pH 1

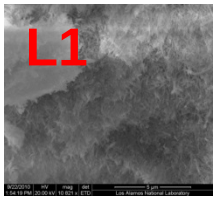
20ºC 975ºC
UNH → UO_4 → U_3O_8
pH 1

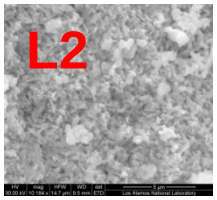
20ºC 800ºC
UO2F2 → ADU → U_3O_8
pH 8.4

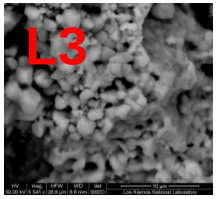
900ºC
A-UO_3 → U_3O_8
air

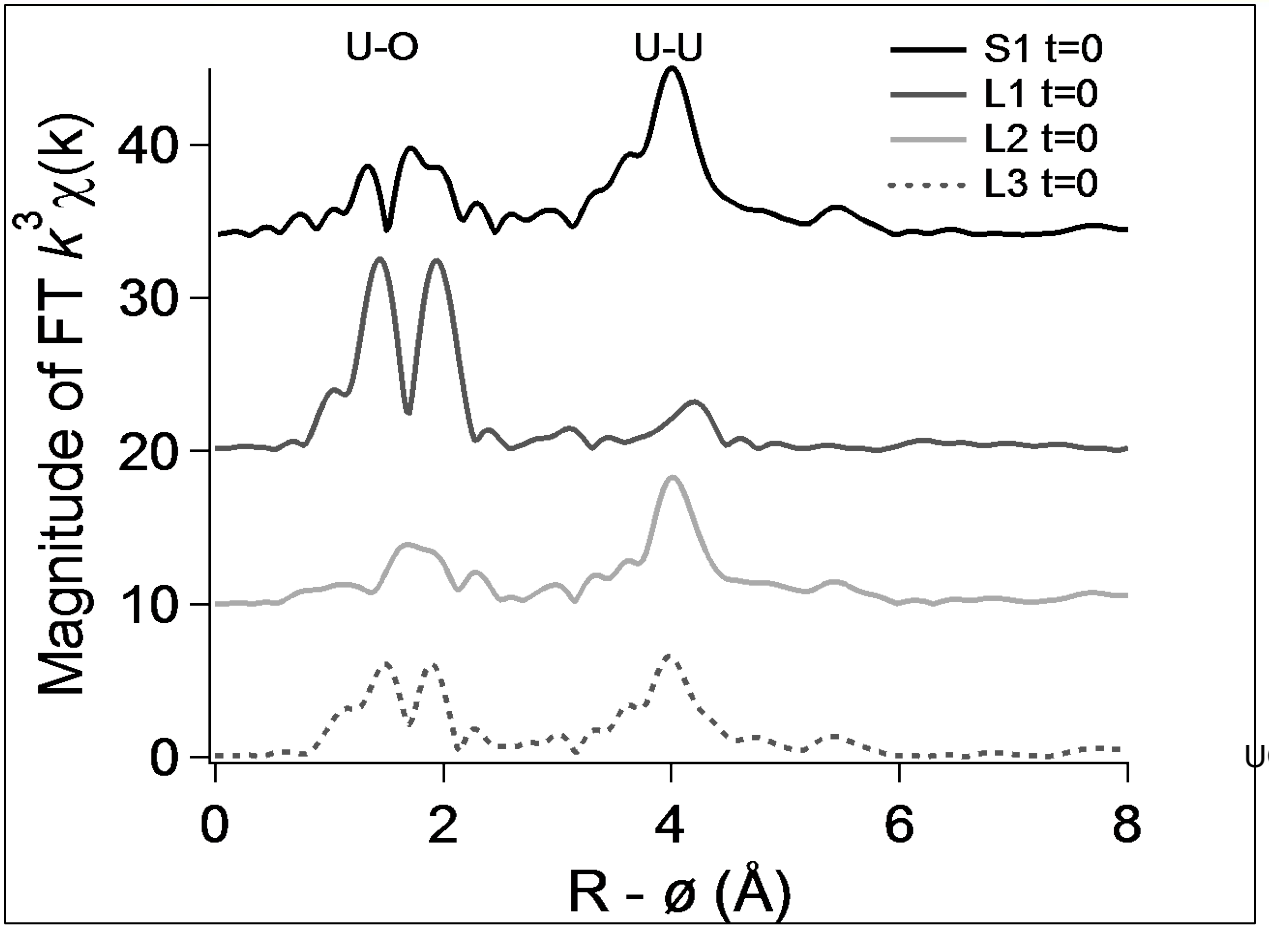
EXAFS of U_3O_8 materials reveals disorder











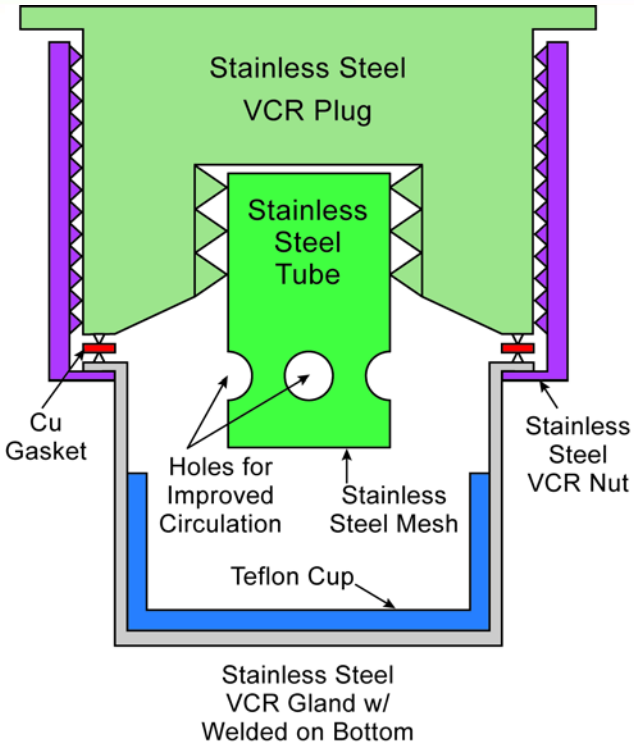
900ºC
A-UO_3 → U_3O_8
air

20ºC 800ºC
UNH → UO_4 → U_3O_8
pH 1
($UO_2(O_2)\cdot xH_2O$)

20ºC 975ºC
UNH → UO_4 → U_3O_8
pH 1
(U_3O_8 + $UO_3\cdot xH_2O$)

20ºC 800ºC
UO2F2 → ADU → U_3O_8
pH 8.4
(U_3O_8 + $UO_2F_2\cdot xH_2O$)

Aging Vessels and Circulating Bath



Anovitz, L. M.; Riciputi, L. R.; Cole, D. R.; Gruszkiewicz, M. S.; Elam, J. M. **J. Non-Cryst. Solids** 2006, *352*, 5652.

Do these chemical signatures change over time?

Constant relative humidity (+/- 2%) is produced by an excess of a water soluble salt in contact with its saturated solution.

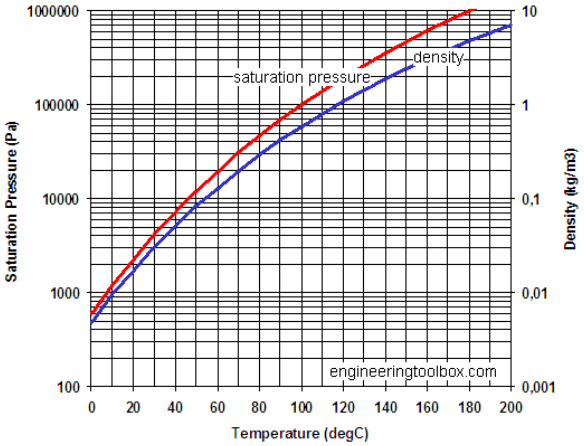
- ASTM International, Designation: E104-02, *Standard Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions*

- CRC Manual, *Constant Humidity Solutions*

RH = A*exp(B/T)

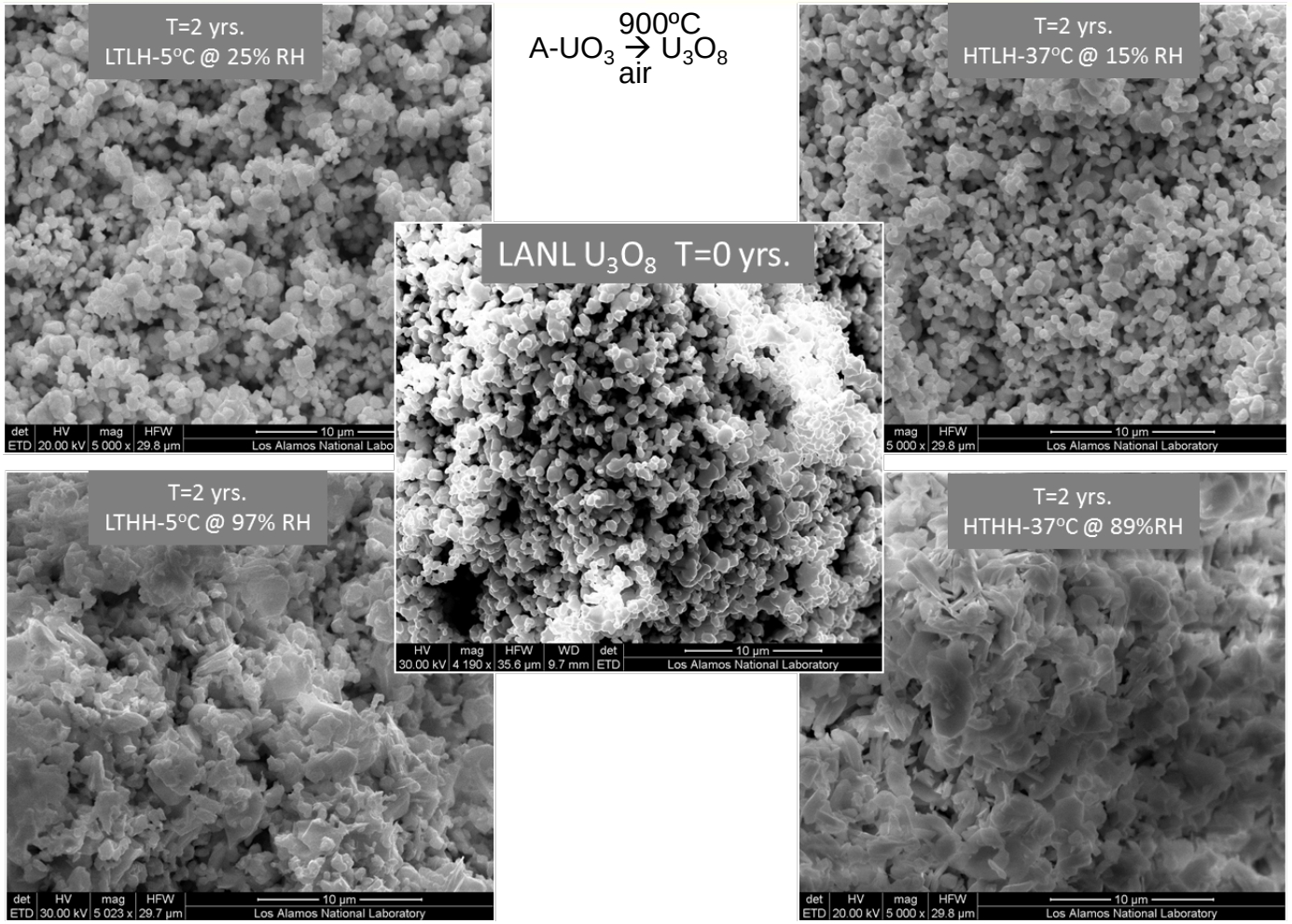
Lithium Iodide: 25% RH at 278.15 K
15% RH at 310.15 K
Potassium Nitrate: 97% RH at 278.15 K
89% RH at 310.15 K

Relative Humidity = Actual Vapor Density / Saturation Vapor Density

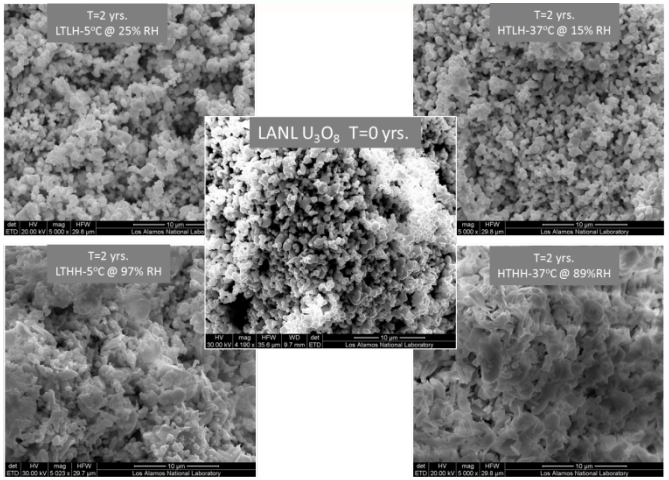


Conditions	Water vapor density
LTLH	1.7e-06 g/cm^3
HTLH	6.6e-06 g/cm^3
LTHH	6.7e-06 g/cm^3
HTHH	39e-06 g/cm^3
Liquid water	~1 g/cm^3

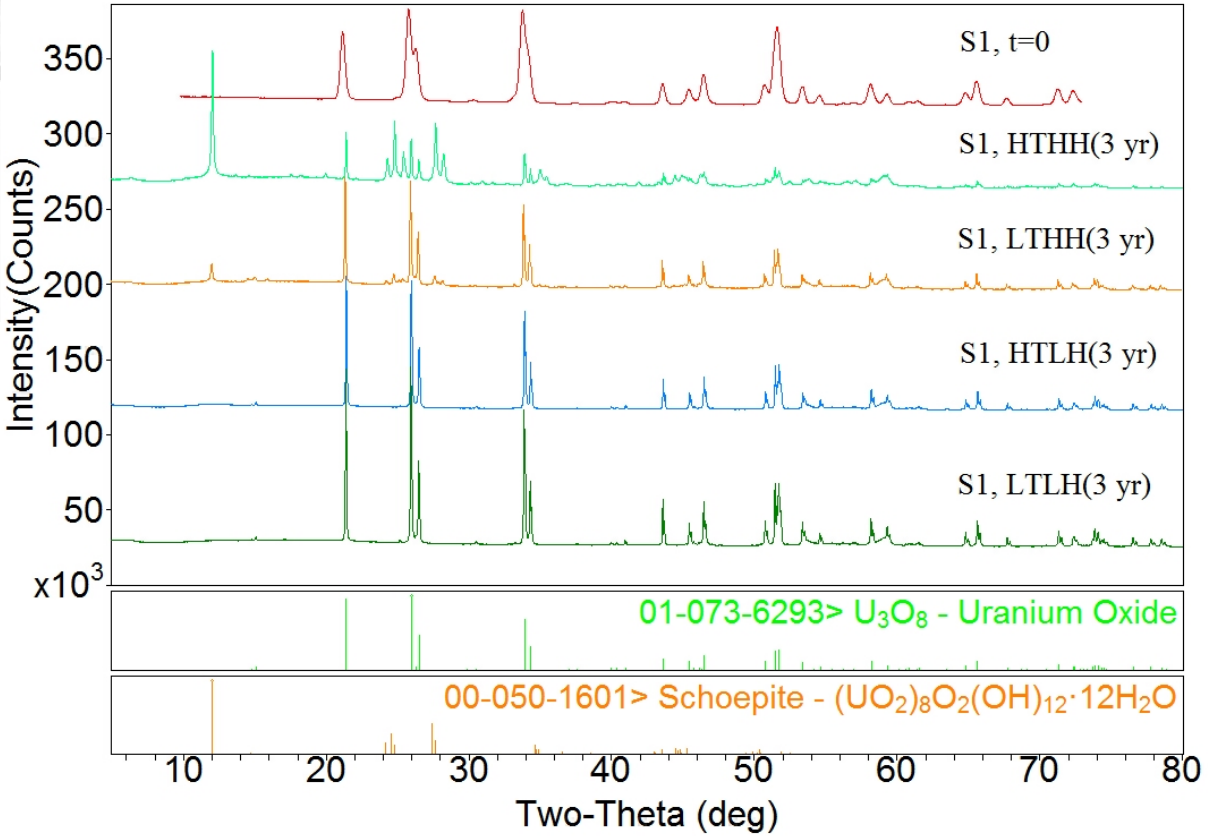
Morphology of S1 at all conditions after 0 and 2 years



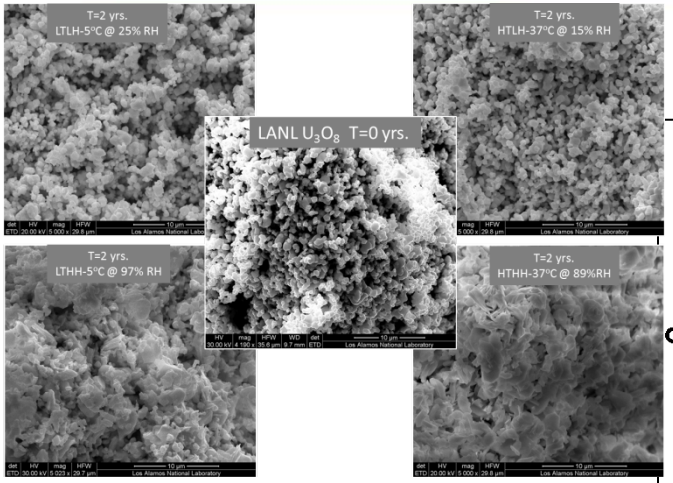
pXRD patterns of S1 at all conditions after 3 years reveals speciation



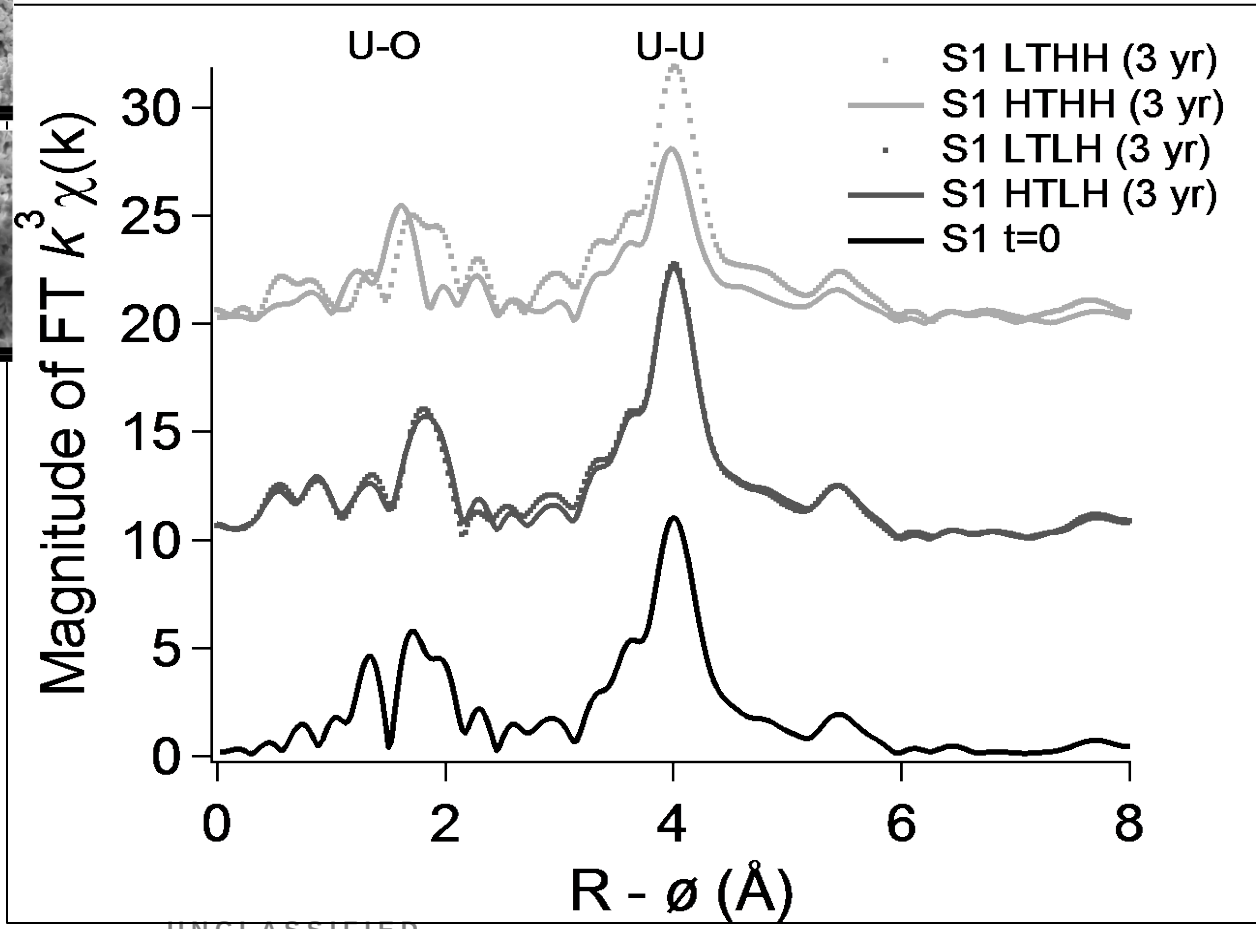
$$A\text{-}UO_3 \xrightarrow[air]{900^oC} U_3O_8$$



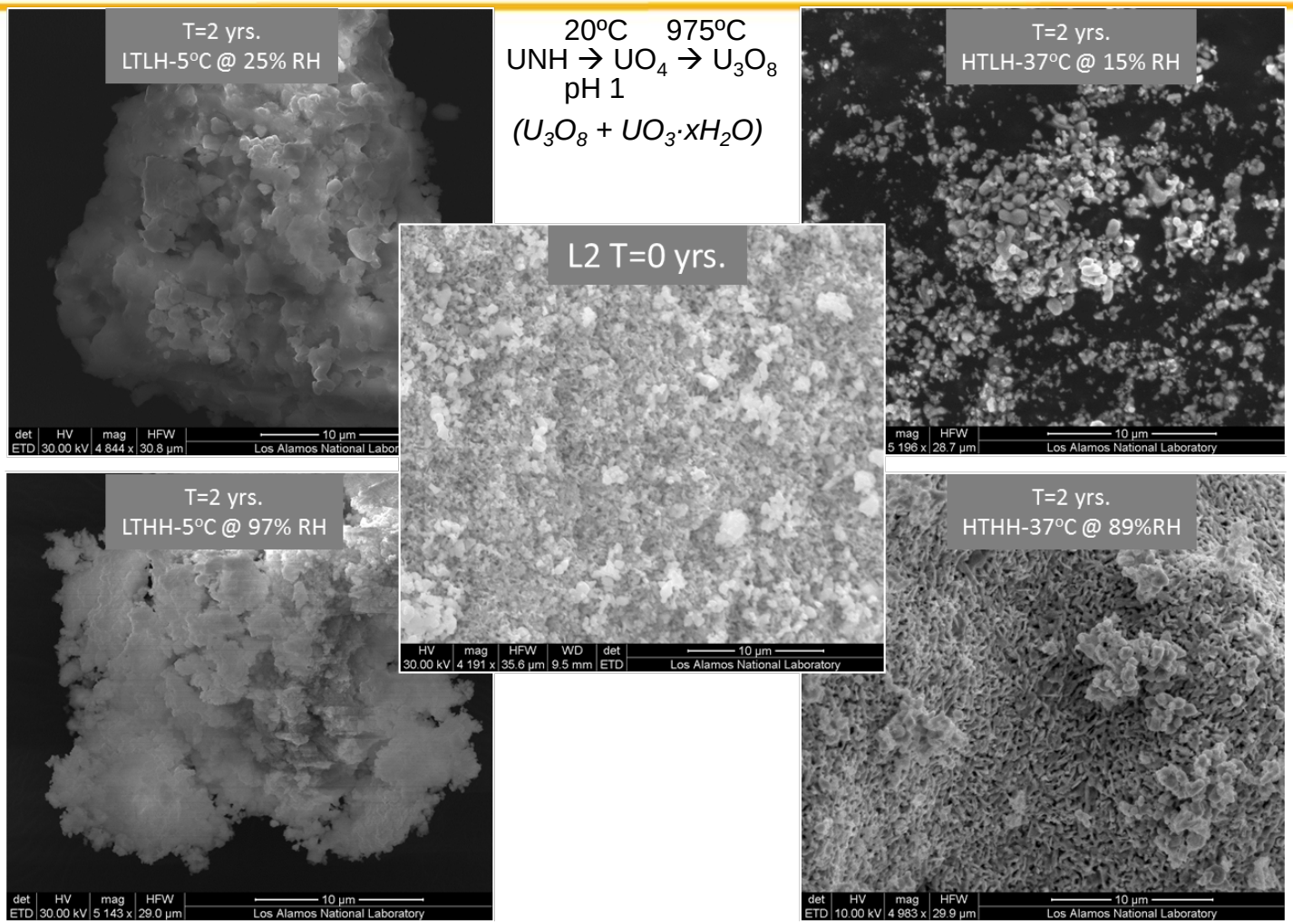
EXAFS of S1 at all conditions after 0 and 3 years



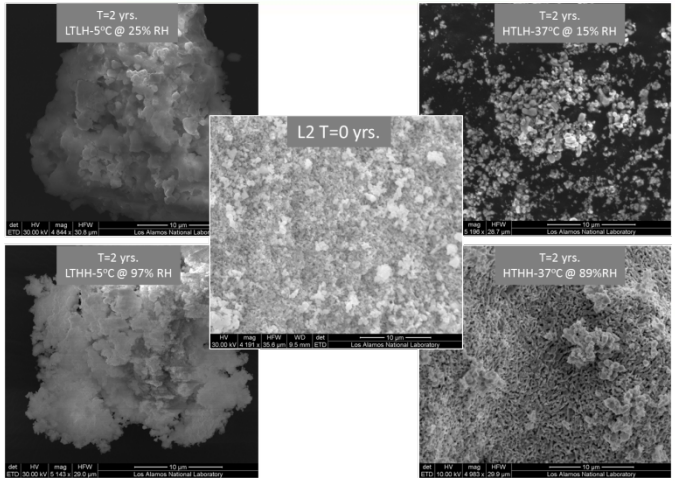
$$A\text{-}UO_3 \xrightarrow[air]{900^oC} U_3O_8$$



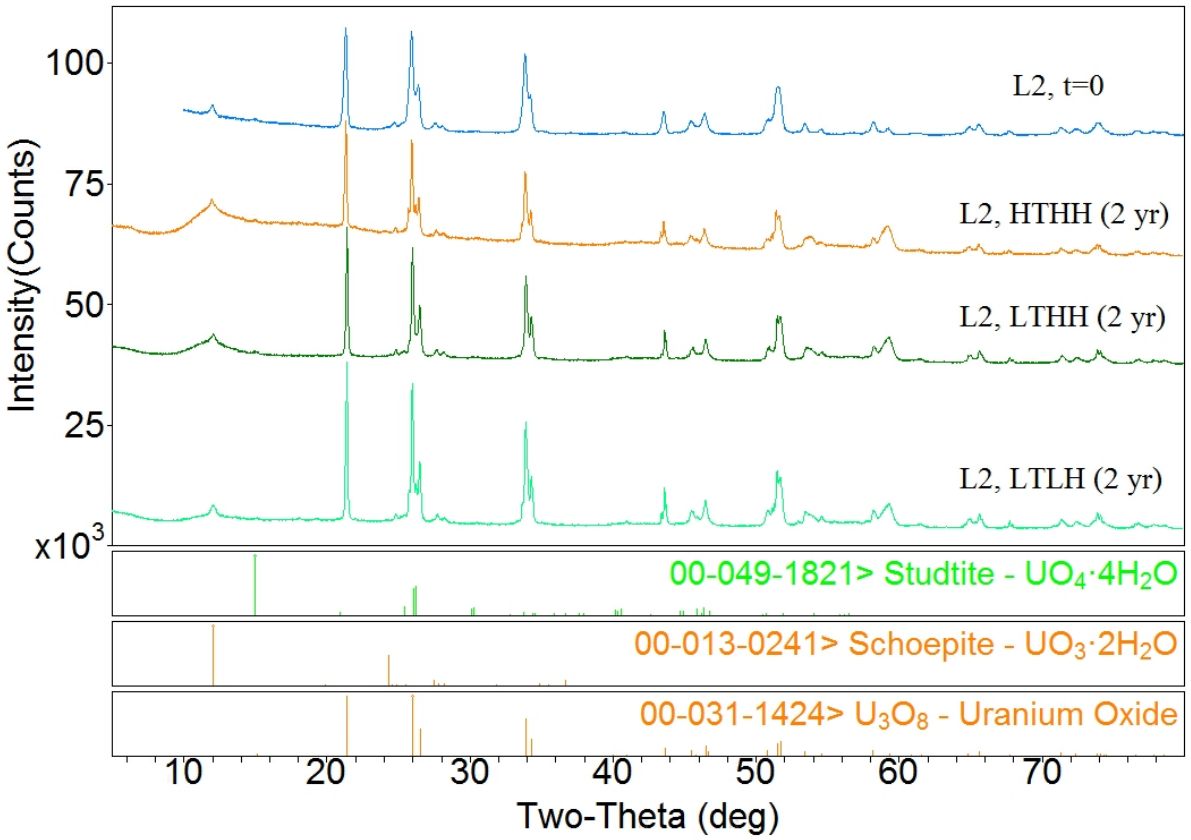
Morphology of L2 U_3O_8 at all conditions after 0 and 2 years



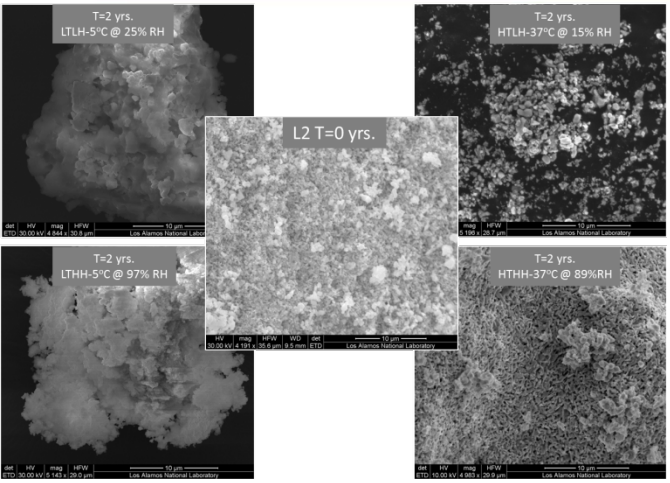
pXRD patterns of L2 U_3O_8 at all conditions after 2 years reveals speciation



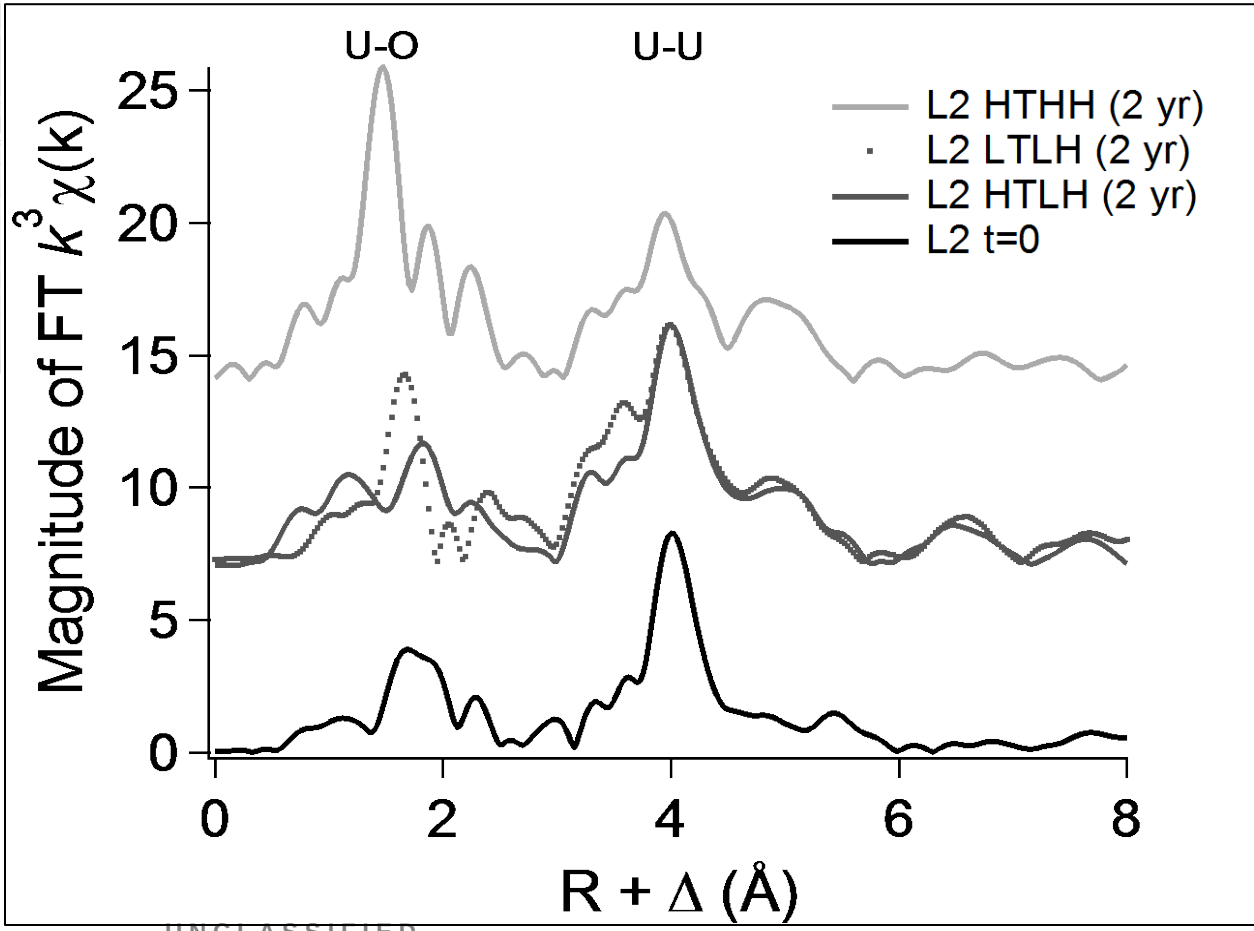
20ºC 975ºC
UNH → UO_4 → U_3O_8 *(U_3O_8 + $UO_3 \cdot xH_2O$)*
pH 1



EXAFS of L2 U_3O_8 at all conditions after 0 and 2 years

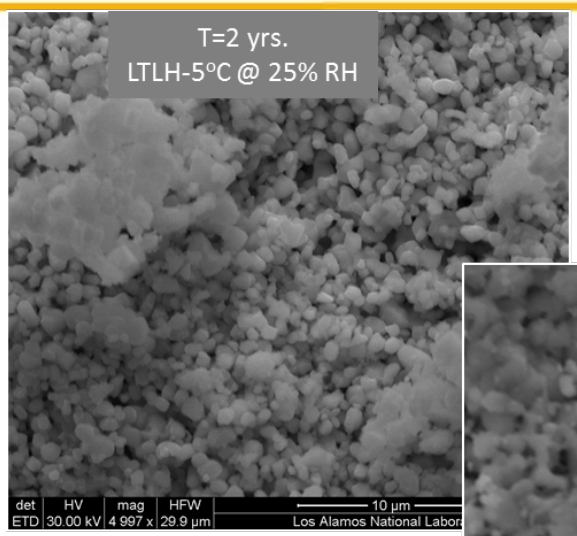


20ºC 975ºC
UNH → UO_4 → U_3O_8 *(U_3O_8 + $UO_3 \cdot xH_2O$)*
pH 1



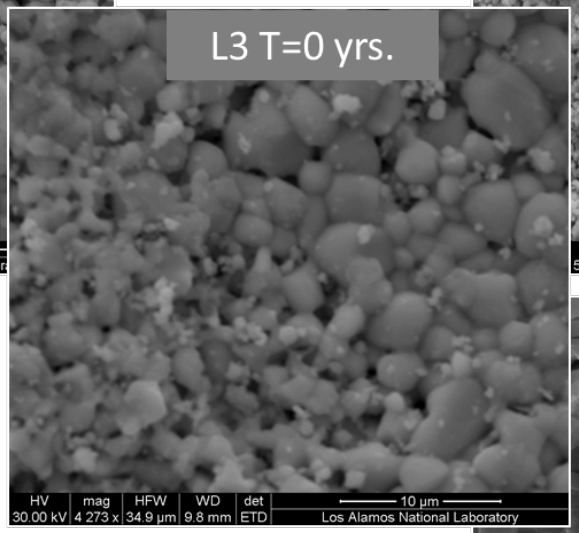
LA-UR 14-24839

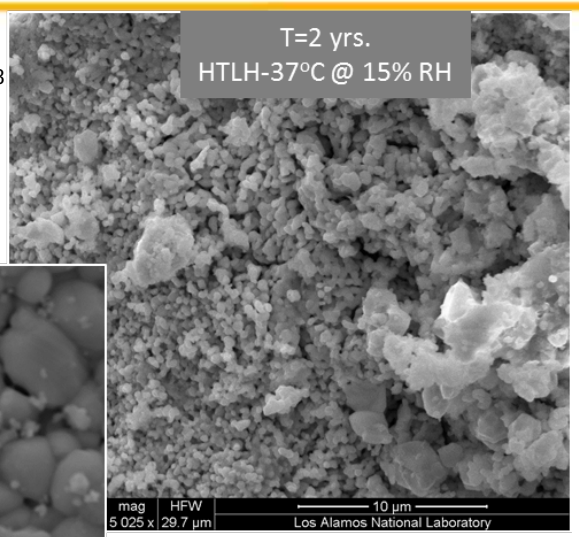
Morphology of L3 U_3O_8 at all conditions after 0 and 2 years

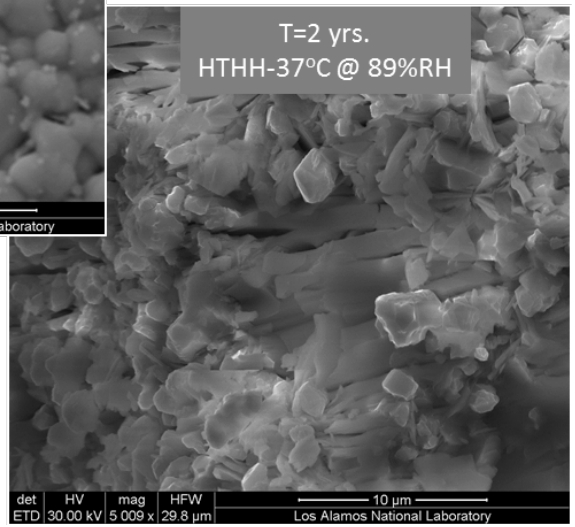


20°C 800°C
UO2F2 → ADU → U_3O_8
pH 8.4

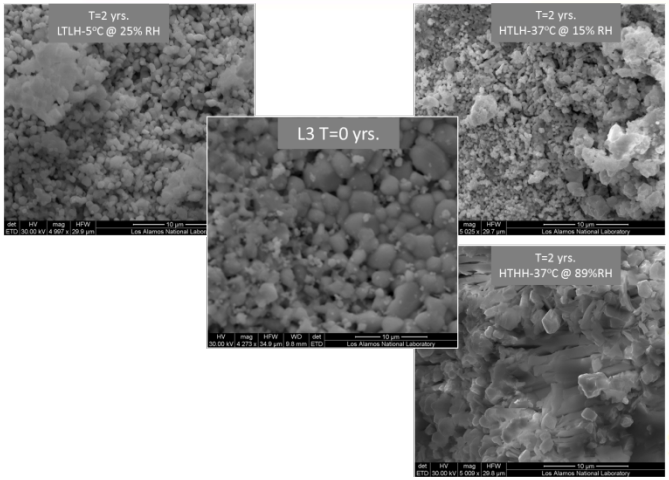
(U_3O_8 + $UO_2F_2 \cdot xH_2O$)



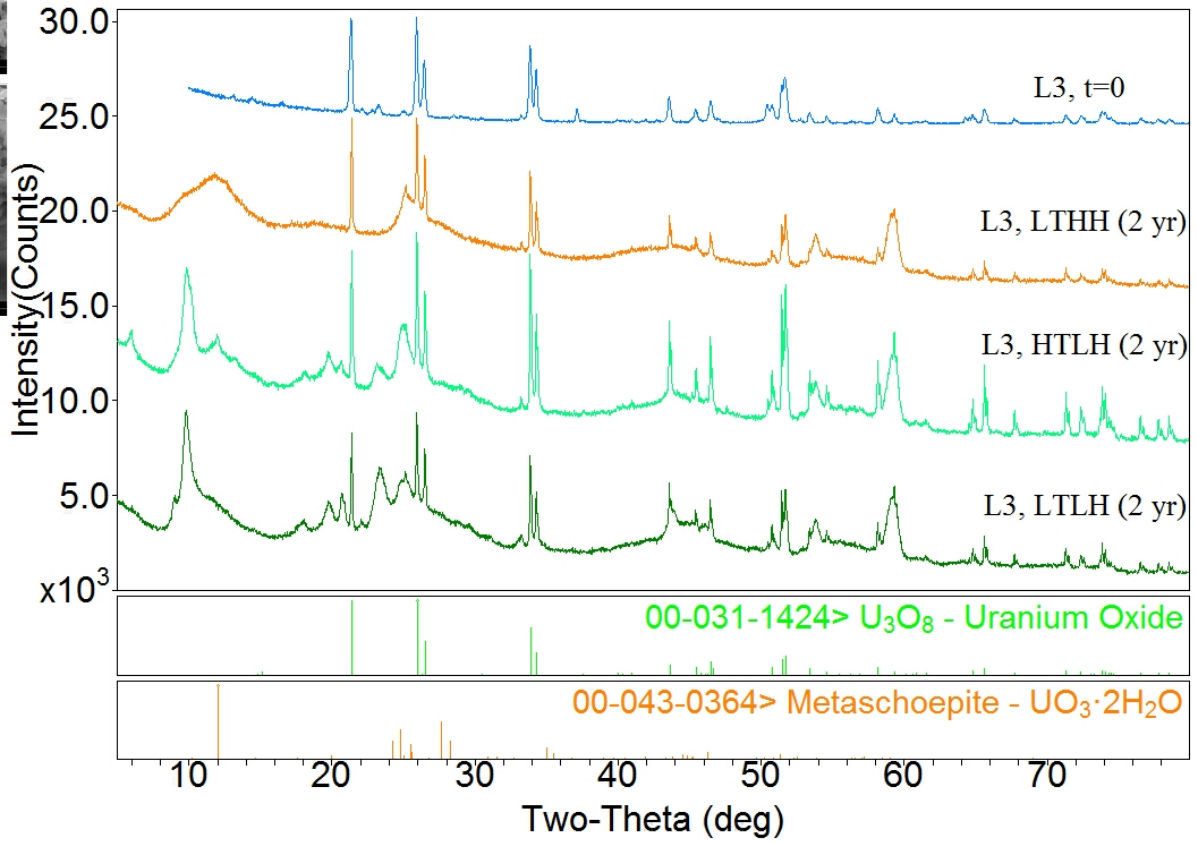




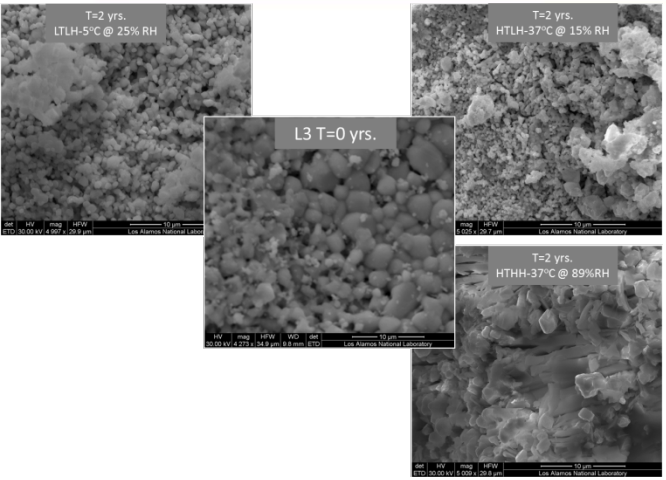
pXRD patterns of L3 U_3O_8 at all conditions after 2 years reveals oxidation



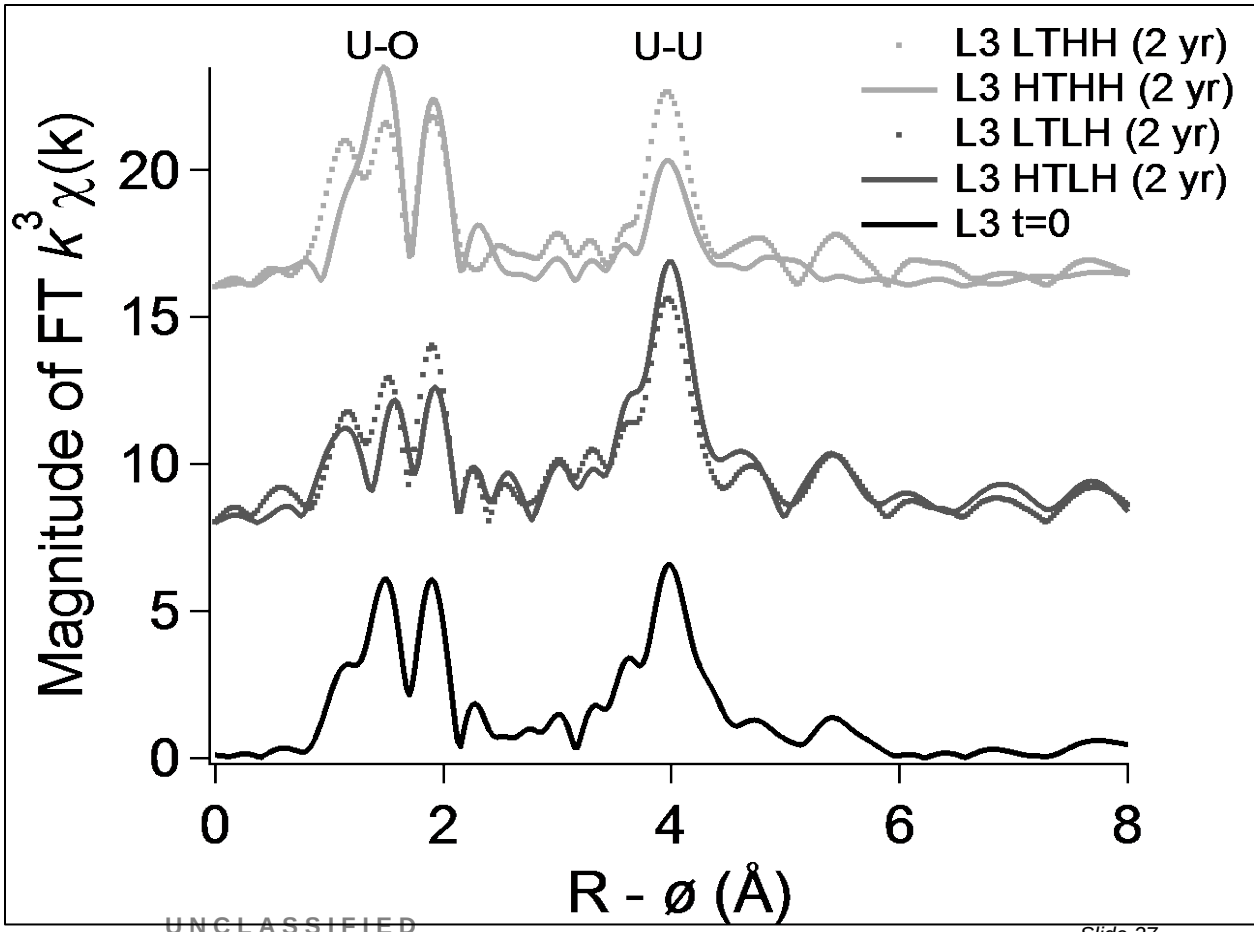
20ºC 800ºC
UO2F2 → ADU → U_3O_8 *(U_3O_8 + $UO_2F_2 \cdot xH_2O$)*
pH 8.4



EXAFS of L3 U_3O_8 at all conditions after 0 and 2 years

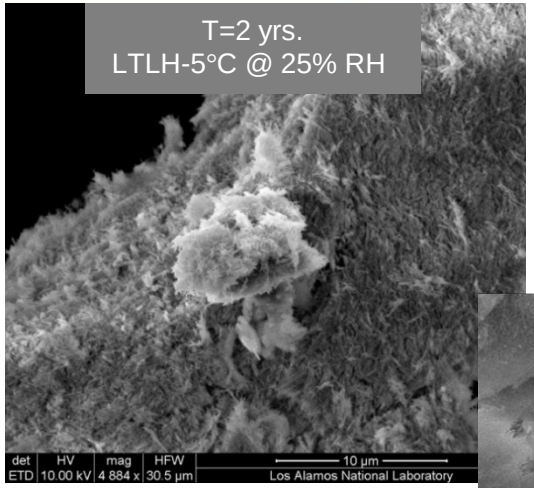


20ºC 800ºC
UO2F2 → ADU → U_3O_8 $(U_3O_8 + UO_2F_2 \cdot xH_2O)$
pH 8.4



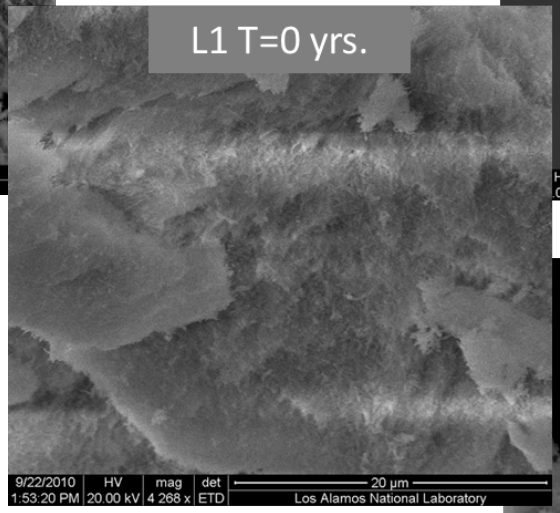
LA-UR 14-24839

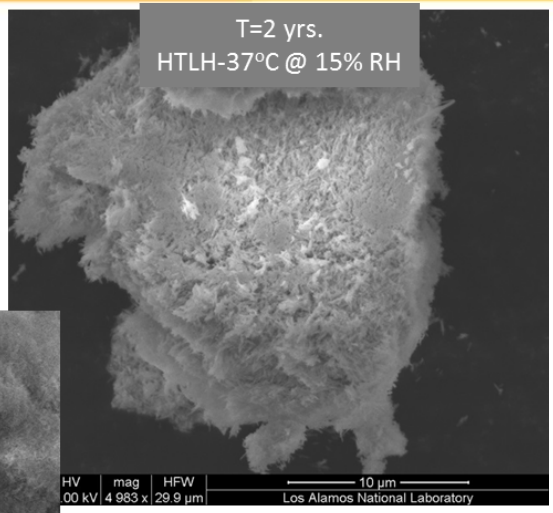
Morphology of L1 at all conditions after 0 and 2 years

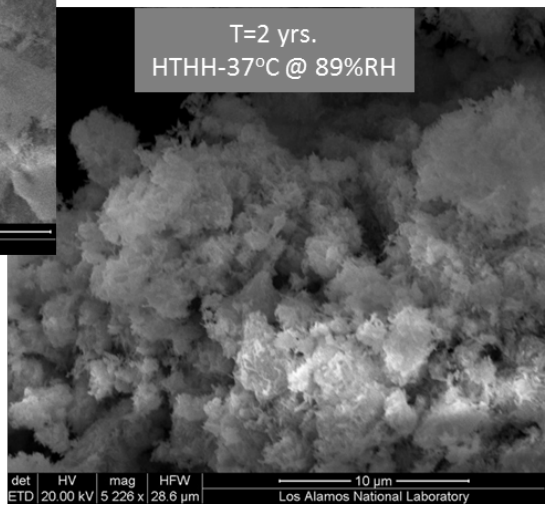


20ºC 800ºC
UNH → UO_4 → U_3O_8
pH 1

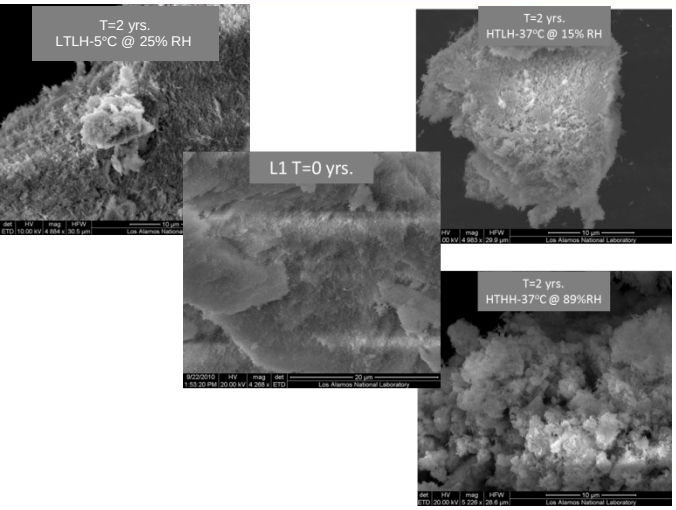
$(UO_2(O_2)\cdot xH_2O)$



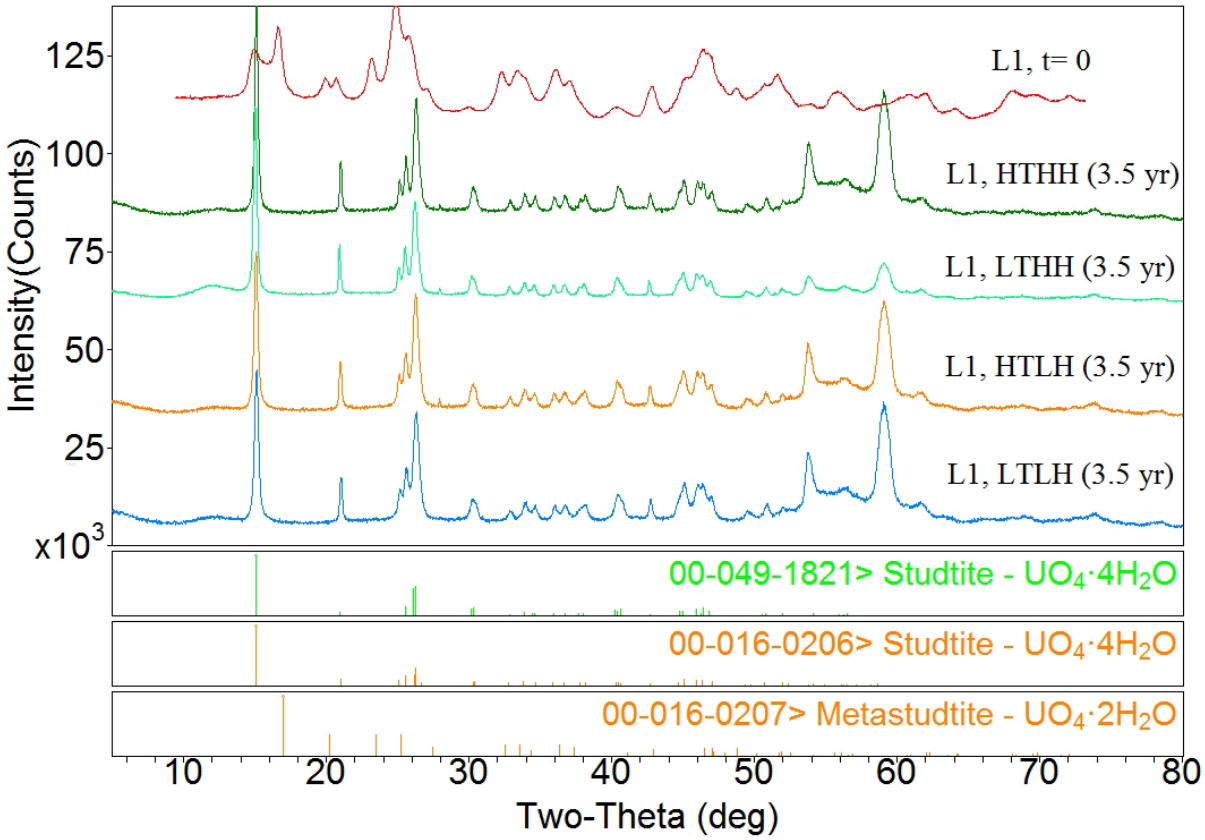




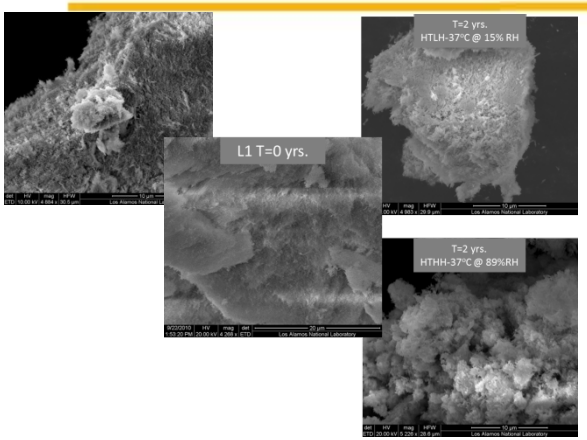
pXRD patterns of L1 U_3O_8 at all conditions after 3 years reveals hydration



20ºC
UNH → UO_4 → U_3O_8 *($UO_2(O_2)\cdot xH_2O$)*
pH 1

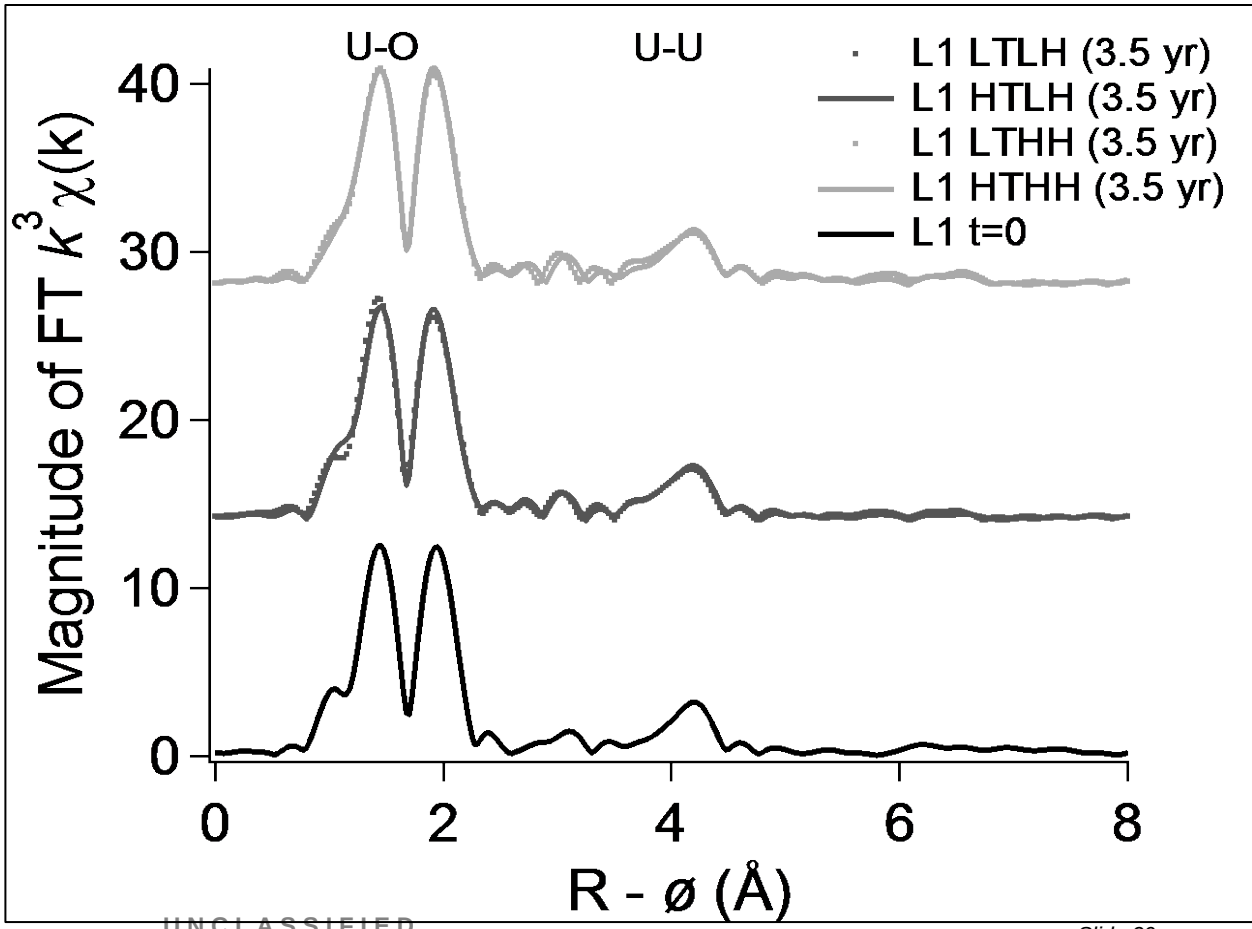


EXAFS of L1 U_3O_8 at all conditions after 0 and 3.5 years



20ºC
UNH → UO_4 → U_3O_8
pH 1

($UO_2(O_2)\cdot xH_2O$)



LA-UR 14-24839

Conclusions

- Processing of uranium oxides is chemical in nature, providing opportunities for measurements of chemical signatures
- Results from an integrated approach rely upon synthesis, spectroscopy and morphologic characterization of a variety of materials
- Chemical speciation following aging under environmental conditions is providing insights into chemical transformations
- Speciation can be characterized, not only by μ-XRD and μ-XANES spectroscopy, but also via μ-EXAFS measurements, an incisive technique for determining chemical speciation and changes in local structure

Acknowledgements

Synthesis
Dallas D. Reilly, Univ. Nevada-Las Vegas
Alison L. Tamasi, Univ. Missouri-Columbia (NTNFC Graduate Fellow)

Morphology
Beau J. Barker, LANL Seaborg Institute Postdoc Fellow
Gregory L. Wagner, Technologist 2
Sandra A. Zerkle, UCSD undergraduate
Mindy M. Zimmer, Postdoc

Powder X-ray Diffraction Analysis
Brian L. Scott

X-ray Absorption Spectroscopy
Steven D. Conradson
Stosh A. Kozimor
Alison L. Pugmire (LANL LDRD Early Career Award)

Isotopic Analysis
William S. Kinman

Computational Analysis
Tyler Mullen, High School Co-Op
Reid B. Porter
Christy E. Ruggiero
Lav Tandon

Theory
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Richard L. Martin

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Susan D. Hanson
Justin Holland, Y-12 NSC
Andrew Sutton
Larry E. Ussery
Gregory J. Van Tuyle
Justin R. Walensky, Univ. Missouri
Sam Webb, SSRL

This work has been supported by the U.S. Department of Homeland Security, Domestic Nuclear Detection Office, under competitively awarded IAA HSHQDC-08-X-00805. This support does not constitute an express or implied endorsement on the part of the Government.