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Title: Identification and Forensic Characterization of Nuclear Materials

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Identification and Forensic Characterization of Nuclear Materials

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Chemistry – Nuclear and Radiochemistry

15 September 2010

LANL Laboratory Directed Research and Development – Directed Research

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- Dr. David K. Shuh

Collaborators – Lomonosov Moscow State University, Moscow, Russian Federation
- Dr. Stepan Kalmykov
- Dr. Irina Vlasova

Relevance: Why a chemical approach to forensics?

An important aspect of a law enforcement framework for homeland security:

- Detection and identification of smuggled materials
- Identification of production origin and process history

Available samples may be bulk or may be small.

Conversion and weathering processes are chemical in nature

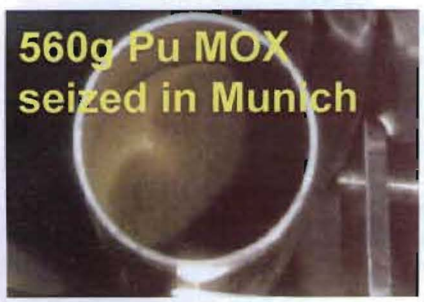
Research at Los Alamos National Laboratory is making contributions to development of new tools to correlate materials characteristics with its technical history.

A chemical approach to forensics can detail composition of the material.

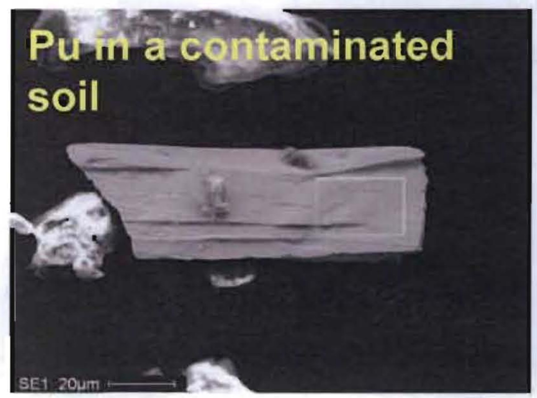
There are two issues to address:

- Bulk (average) speciation versus impurities/inhomogeneities

- Bulk (size) versus particle

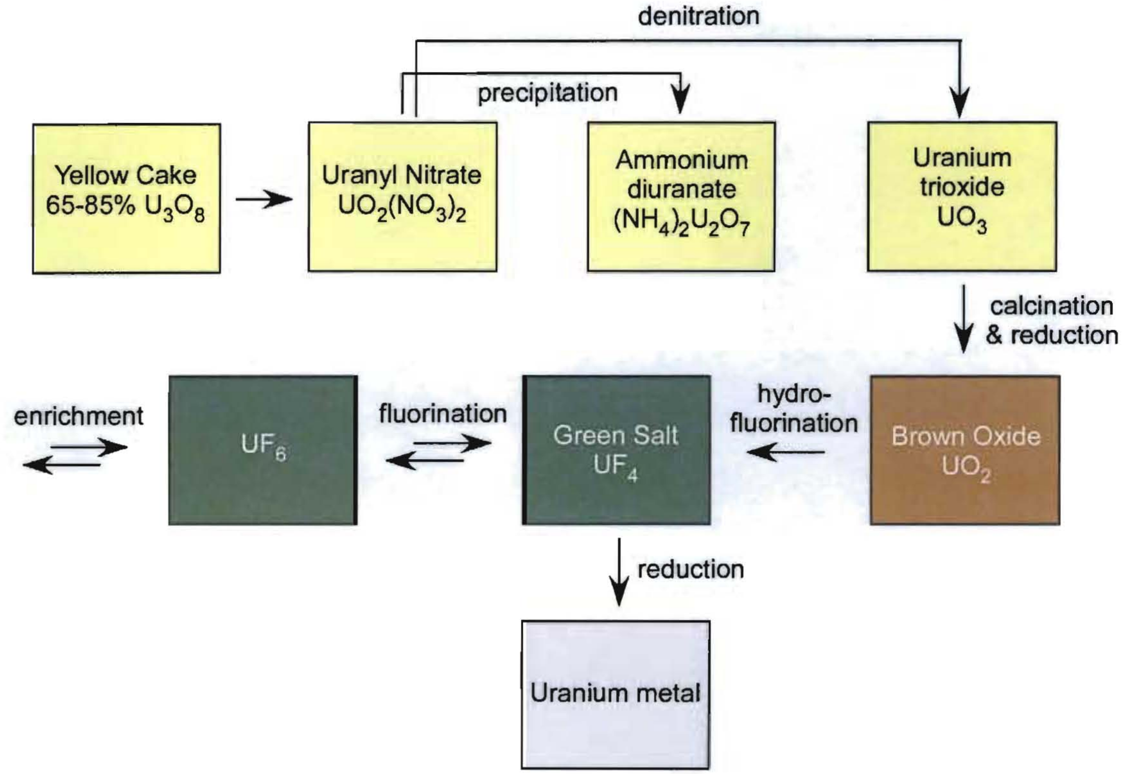


"CSI: Karlsruhe, Nuclear Forensics Sleuths Trace the Origin of Trafficked Material" *Actinide Research Quarterly 4th Quarter 2007*, pp. 1-9.



The chemical composition of actinide materials is rich in information.

- **Close to a dozen phases between UO_2 and UO_3**
- **UO_3 itself exists in seven polymorphs, in addition to hydrated forms**
- **Deceptively simple formula and cubic structure of UO_2 masks incredibly complex behavior**

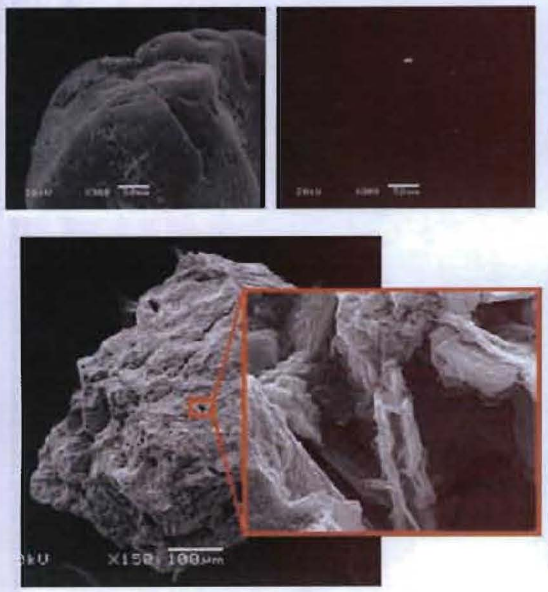


"The complexity of the U-O system is awesome."

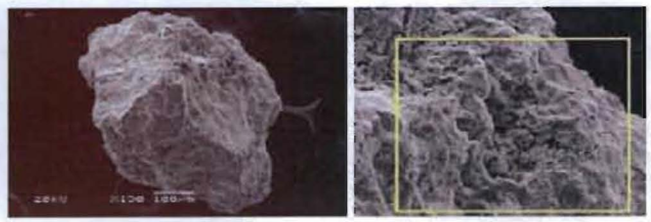
Edelstein, N. M.; Fuger, J.; Katz, J. J.; Morss, L. R. Summary and Comparison of the Actinide and Transactinide Elements. In *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Morss, L. R., Edelstein, N. M., Fuger, J., Kaptz, J. J., Eds.; Springer: Dordrecht, The Netherlands, 2006; Chapter 15, pp. 1753-1835.

What kinds of chemical information do we want to know?

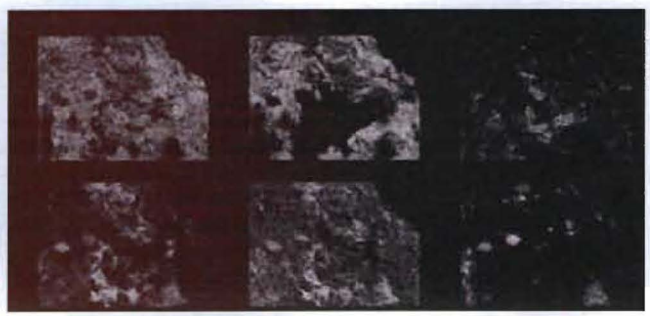
Scanning Electron Microscopy (morphology)



SEM-Energy Dispersive Spectroscopy (elemental)

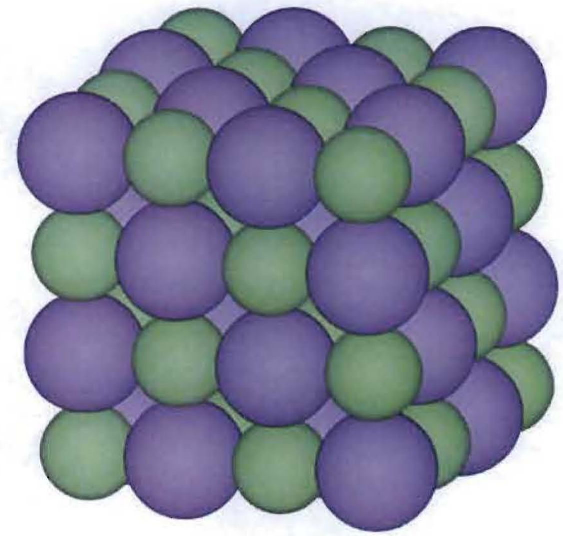


SEI Image of HP-12 (left) and area mapped by EDS (right)



Elemental maps of HP-12. Clockwise from top left: Pu, U, Ga, Si, O, Al

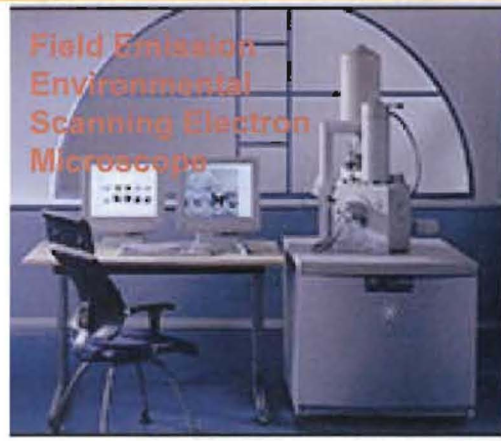
X-ray Fluorescence mapping (elemental)

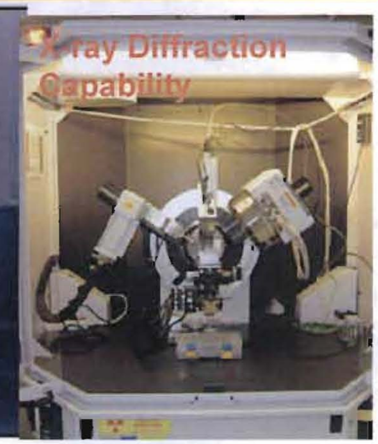


Crystal lattice

- **X-ray diffraction analysis (phase and long range order)**
- **EXANES (oxidation state and geometry)**
- **EXAFS (local order)**

What tools are available to probe this information?



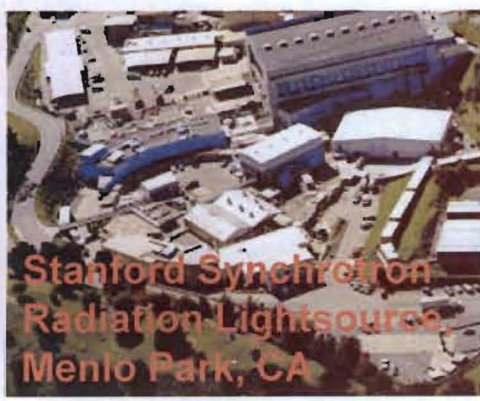


In-house methods:

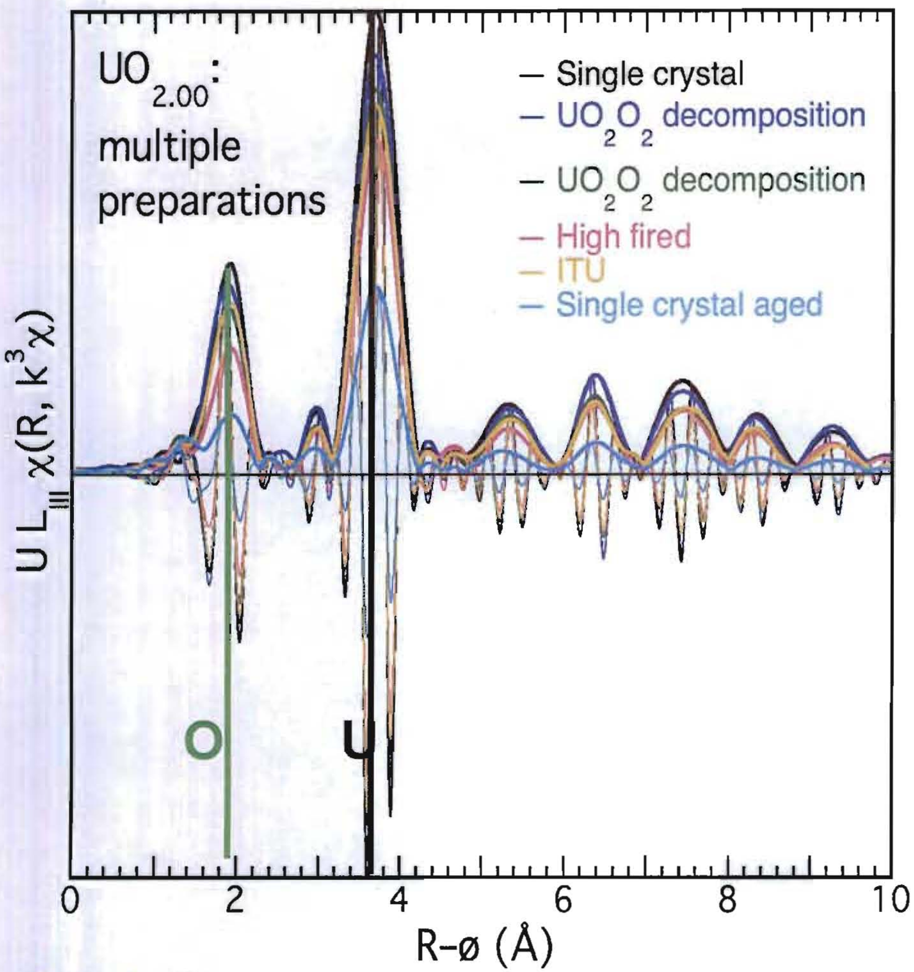
- Scanning Electron Microscopy
- X-ray Fluorescence
- Powder X-ray Diffraction Analyses
- Optical Imaging

Out-of-house

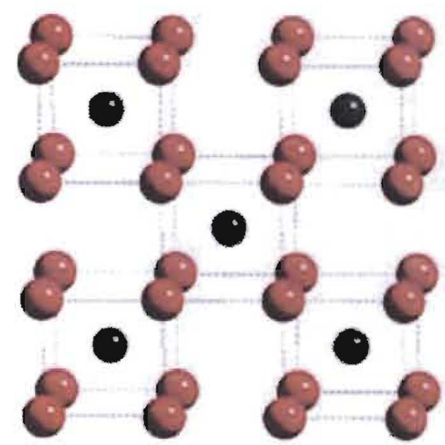
- X-ray Diffraction Analyses
- X-ray Absorption Fine Structure



Bulk analysis of uranium oxides: EXAFS measurements reveal materials sensitivity to process.



Fluorite structure, *Fm3m*



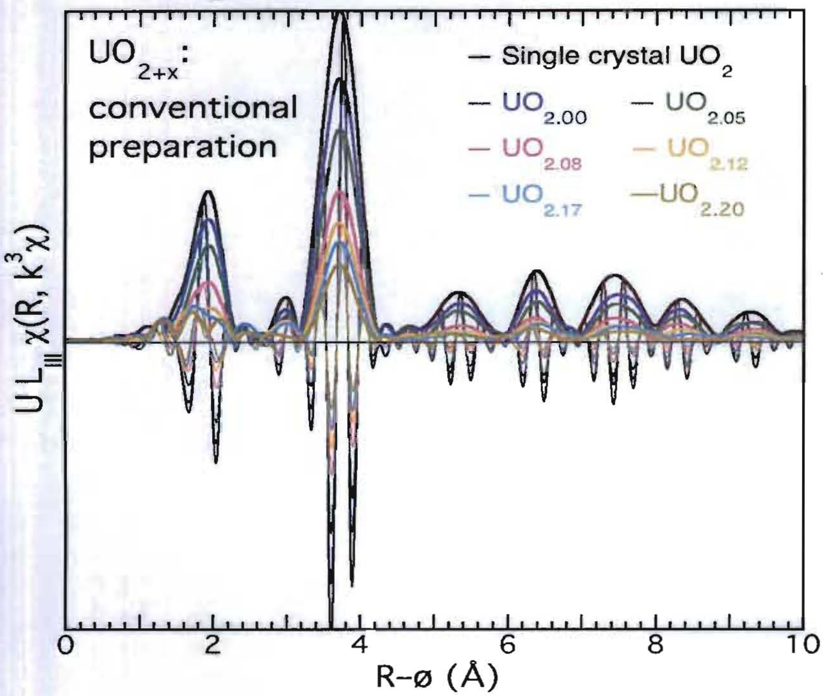
Red = Oxygen

Black = U

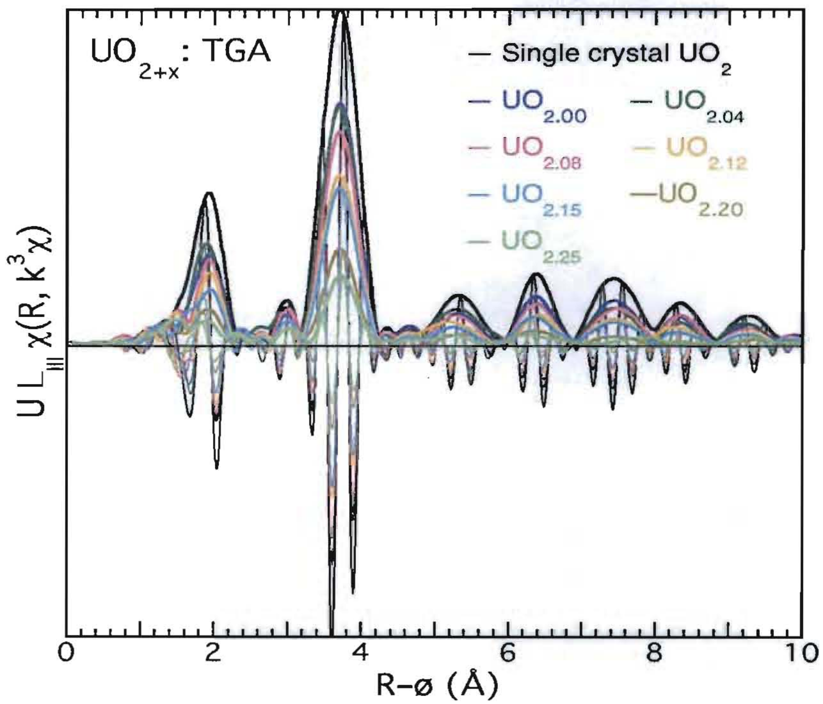
Variations in amplitudes in even "pure" UO_2 are observable in EXAFS and suggestive of preparation method

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

With H_2O, intermediate temperature



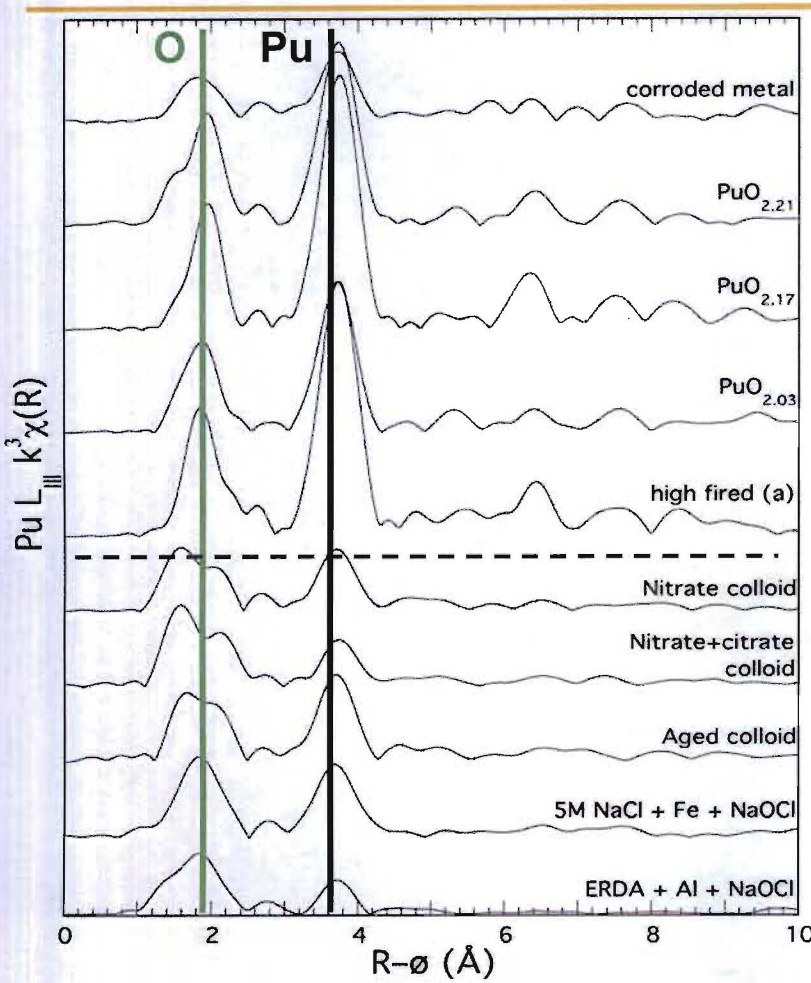
Weak $CO:CO_2$ oxidizer, high temperature



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.

Systematic experiments on PuO_2 using EXAFS to measure sensitivity to oxidation.



Significant differences in PuO_2 XAFS: Corroded metal highly disordered

Solid *(top)*

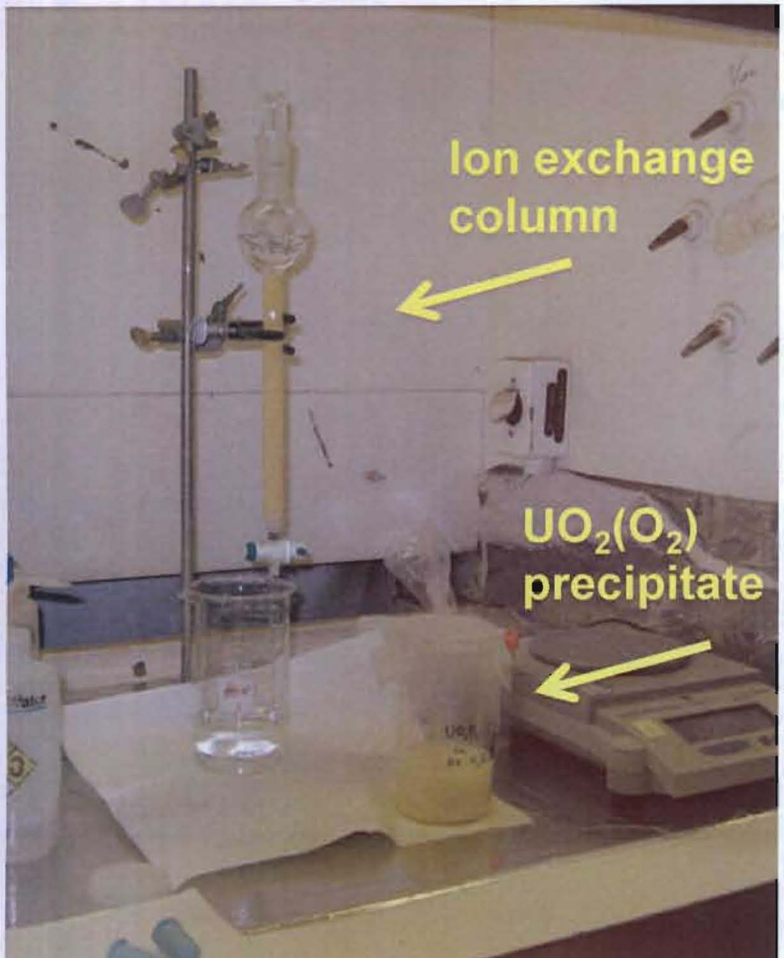
- **Pu more ordered**
- **Multisite O distribution**

Solution *(bottom)*

- **Pu more disordered**
- **Broader multisite O distribution**

Conradson, S. D.; Begg, B. D.; Clark, D. L.; den Auwer, C.; Ding, M.; Dorhout, P. K.; Espinosa-Faller, F. J.; Gordon, P. L.; Haire, R. G.; Hess, N. J.; Hess, R. F.; Keogh, D. W.; Lander, G. H.; Manara, D.; Morales, L. A.; Neu, M. P.; Paviet-Hartmann, P.; Rebizant, J.; Rondinella, V. V.; Runde, W.; Tait, C. D.; Veirs, D. K.; Villella, P. M.; Wastin, F. *J. Solid St. Chem.* 2005, 178, pp 521-535.

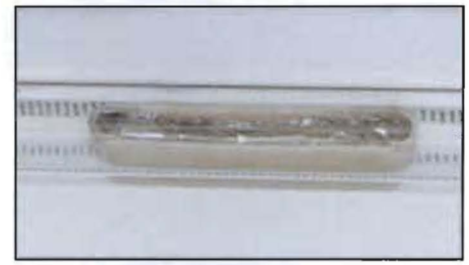
Preparation of uranium oxide materials for controlled aging experiments on bulk samples.



$$UO_2(O)_2\text{-}2H_2O \xrightarrow[\text{air}]{400^oC} A\text{-}UO_3$$

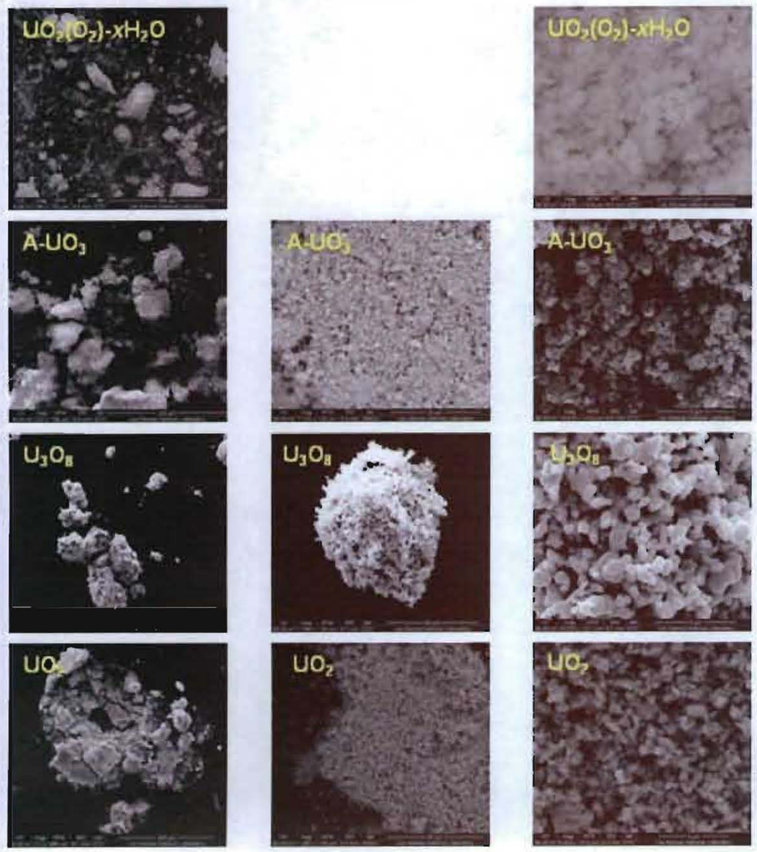
$$A\text{-}UO_3 \xrightarrow[\text{air}]{900^oC} U_3O_8$$

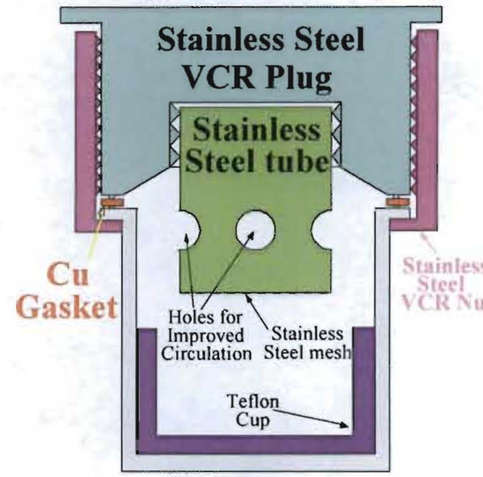
$$A\text{-}UO_3 \xrightarrow[H_2]{500^oC} UO_2$$



Preparation of uranium oxide materials for controlled aging experiments on bulk samples.

~200 X Magnification | ~1,240 X Magnification | ~10,000 X Magnification





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**

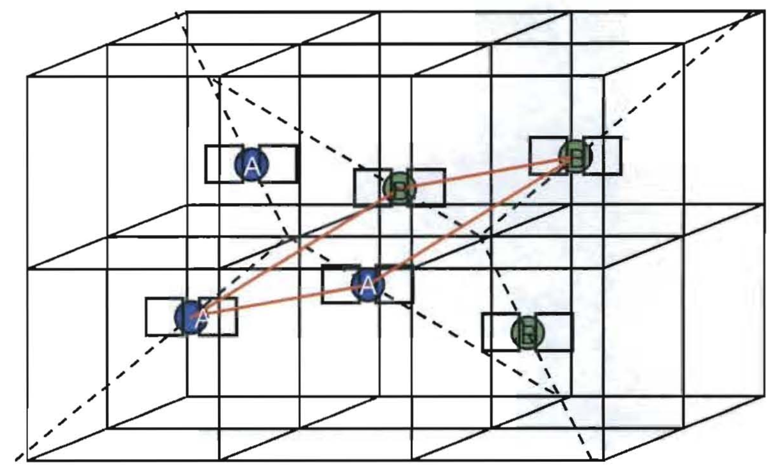
How can perturbations on the composition of ulkb uranium oxide materials be predicted?

Key issues:

- **Where are the excess oxygen ions located?**
- **How are the properties of UO_{2+x} different from PuO_{2+x}?**
- **What is the influence of particle sizes on the reactivity, e.g., to what extent do surfaces and other inhomogeneities exhibit unique characteristics?**

DFT allows self-consistent investigations of the structure and dynamics of UO_{2+x} and other actinide oxide compounds.

Split quad-interstitial



Two split di-interstitials (blue and green) make up a stable cluster in AnO_{2+x}.

Andersson, D. A.; Lezama, J.; Uberuaga, B. P.; Deo, C.; Conradson, S. D. *Phys. Rev. B 2009, 79, 042110.*

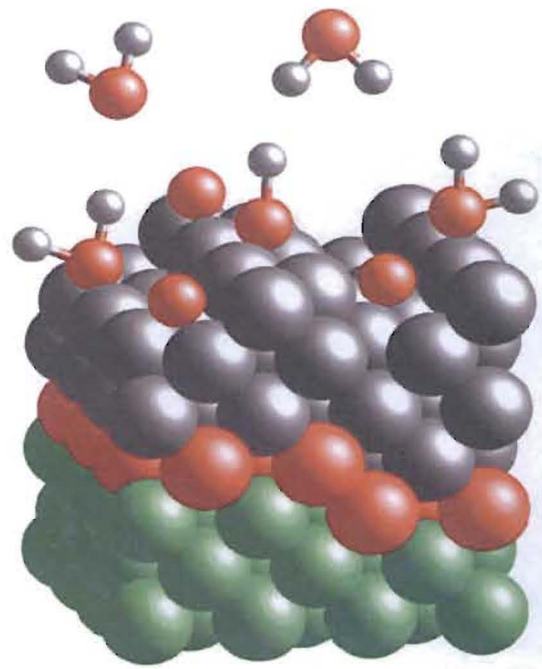
Preparation of oxidized plutonium materials for controlled aging experiments presents challenges.

Plutonium metal coupon

24 Hours | 500 Hours | 1100 Hours

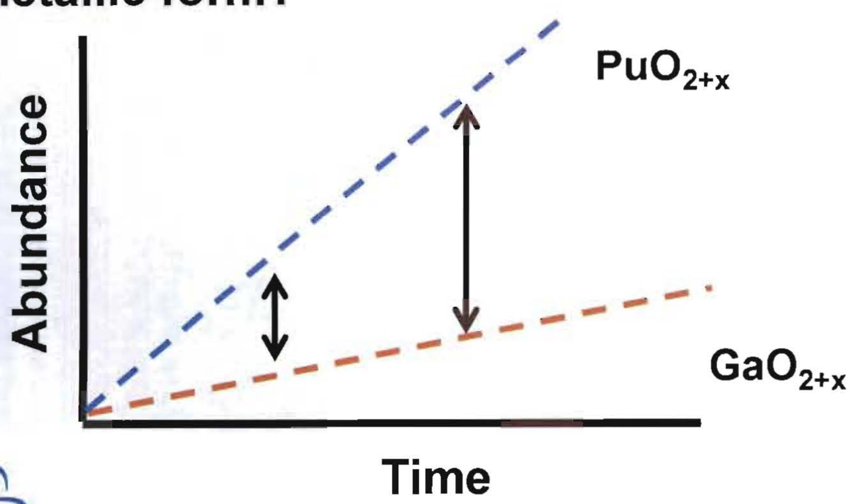
Traditional views of Pu corrosion:

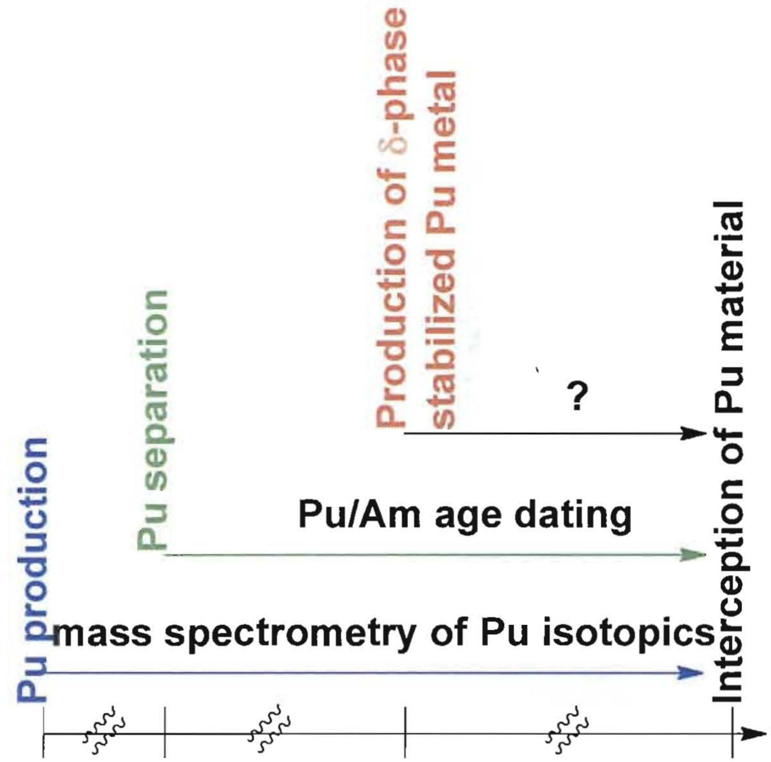
- $Pu + 2H_2O \rightarrow PuO_{2+x} + 2H_2$
- Occurs within weeks/months on contact with H_2O via a Pu_2O_3 layer



Can the rate of Pu oxidation tell anything about the technical history of the material?

- Pu metal rapidly oxidizes to PuO_{2+x}
- Ga metal slowly oxidizes to Ga_2O_3 (years)
- Could the Ga chemistry within Pu particle provide a chronometer to determine how long ago the Pu was in metallic form?





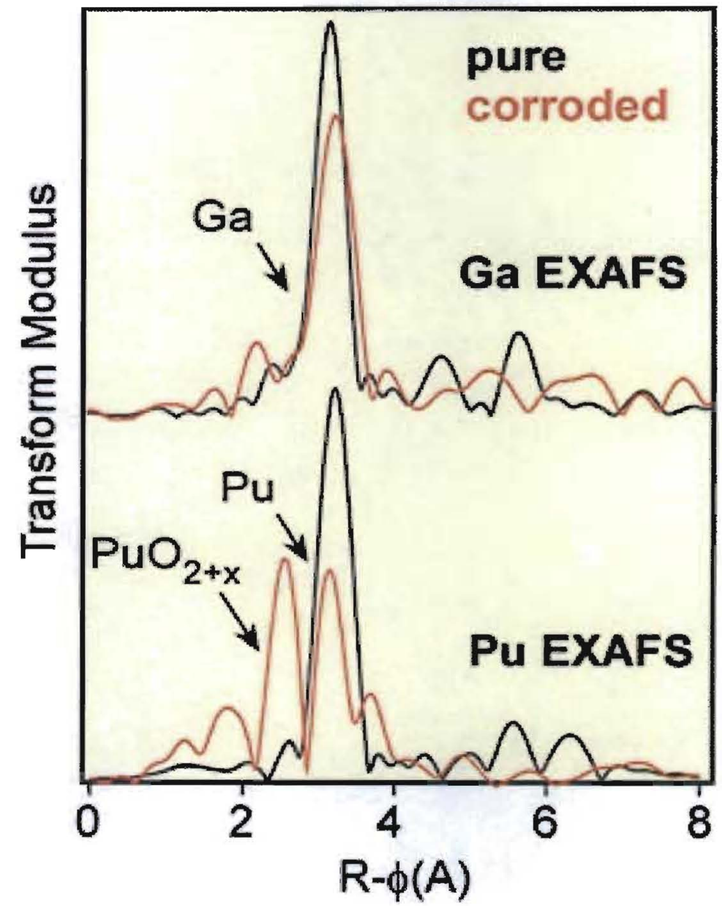
Can the rate of Pu versus Ga oxidation tell anything about the technical history of the material?

Results from EXAFS measurements on δ-phase stabilized Pu following slow exposure to water

- **Corrosion of bulk Pu to PuO_{2+x}**
- **Ga spectra show only metallic Pu as nearest neighbors**

  (Does Ga inhibit Pu oxidation? Does Pu compete more effectively for oxygen?)

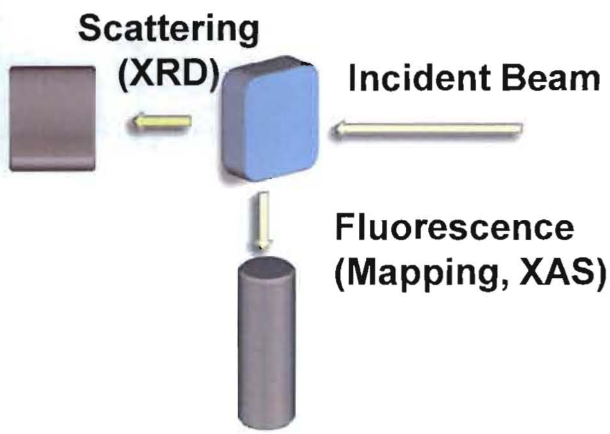
Suggests a heterogeneous, more complex oxidation process



Can we use chemical measurements to determine technological history of particles?

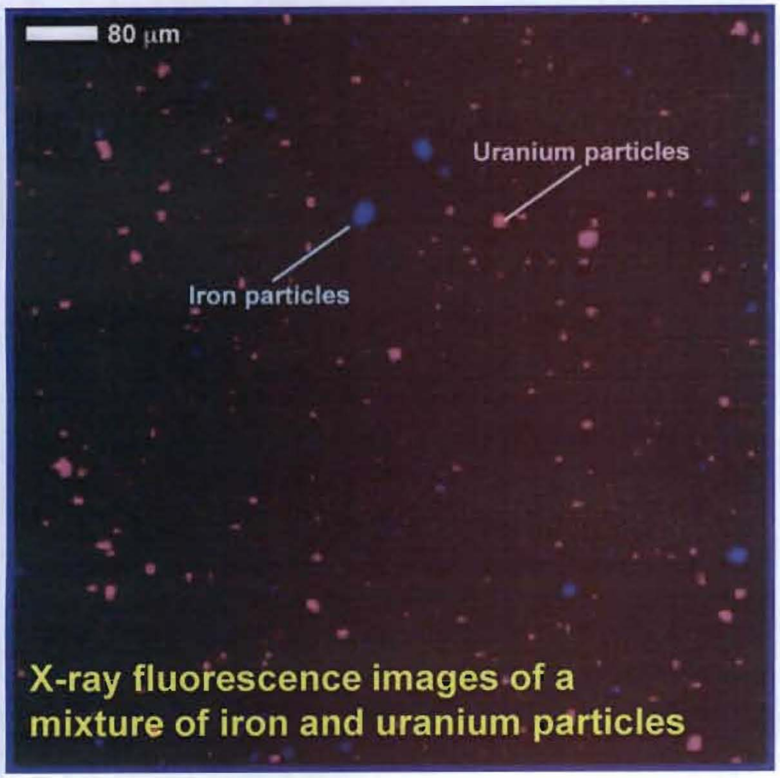
Microprobe spectroscopy on "Stardust"

S. Brennan, et al. *Science*, 2006

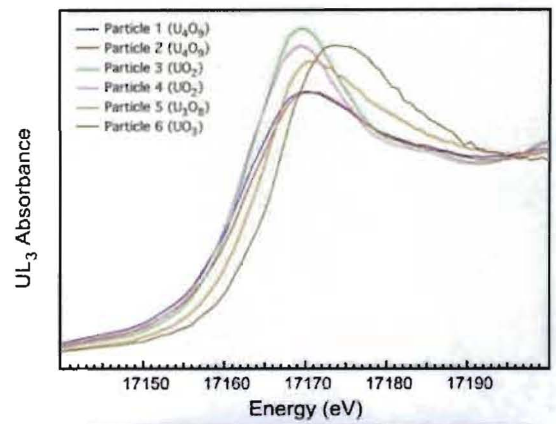


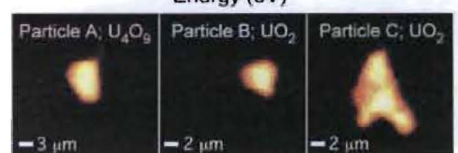
- Raster a focused high intensity x-ray beam over sample
- Map intensity of x-ray fluorescence over various parts of sample at several energies through an edge to collect "XANES-image" of particles
- *Chemical speciation* of interesting spots using μ-XAS or μ-XRD

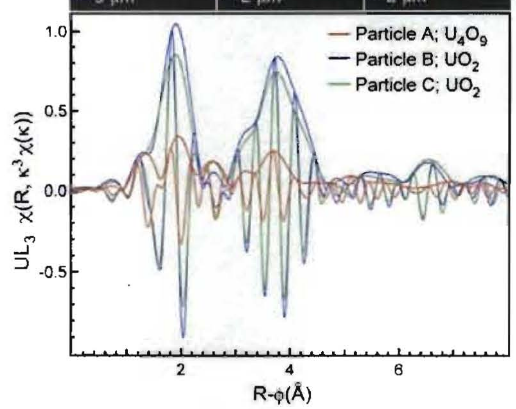
Can we use chemical measurements to determine technological history of particles? Proof-of-concept.



X-ray fluorescence images of a mixture of iron and uranium particles







XANES data

Energy of the edge shifts

Intensities of white lines

EXAFS data

- U - oxo 1.9Å
- U - O 2.33 Å
- U - U 4.5 Å

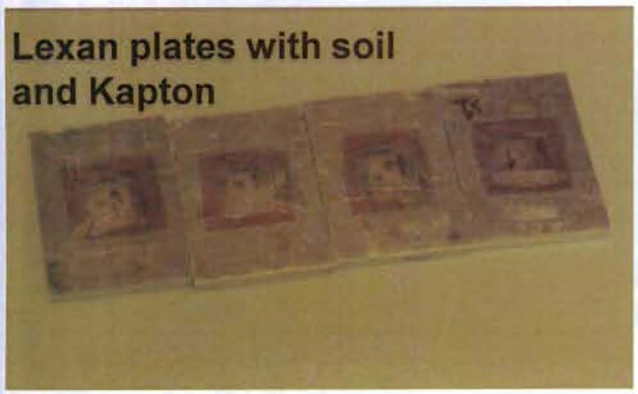
In collaboration with Dr. Sam Webb, Beamline 2-3, SSRL

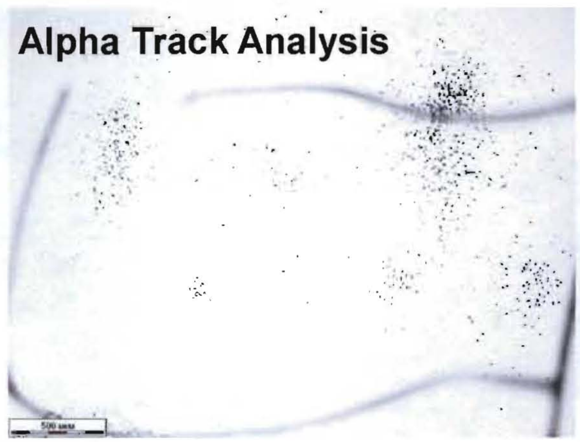
Czernobyl soils provide a test case for particle analysis.

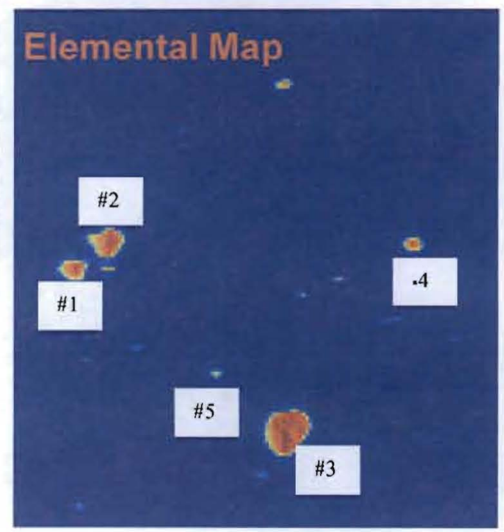
Optical microscope image

Four sets of Chernobyl soils

- **Collected July 1986**
- **1.5 km north-north-west away from village of Pripyat**

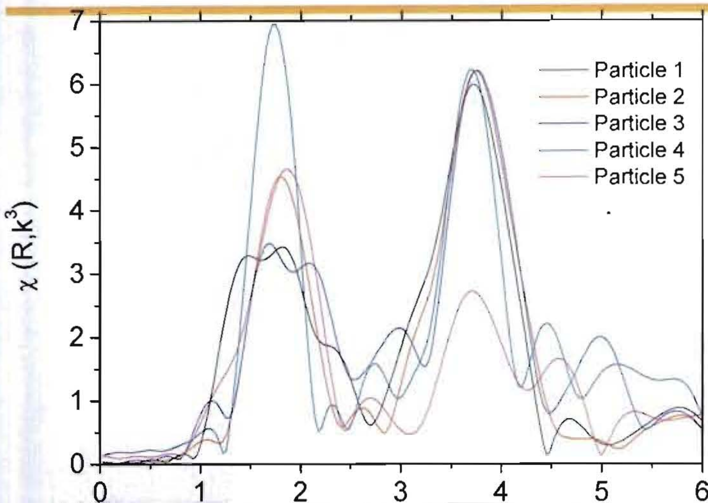


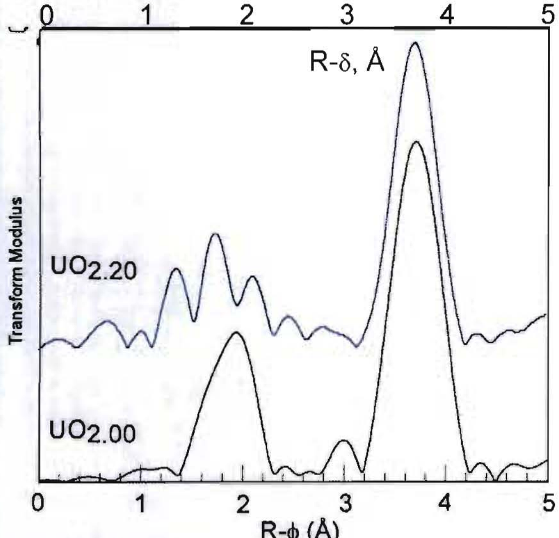




In collaboration with Dr. Stepan Kalmykov and Dr. Irina Vlasova at Lomonosov Moscow State University, Moscow, Russian Federation

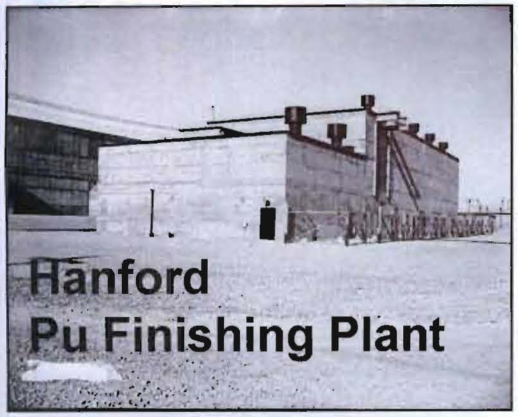
Chemical speciation is consistent with source.

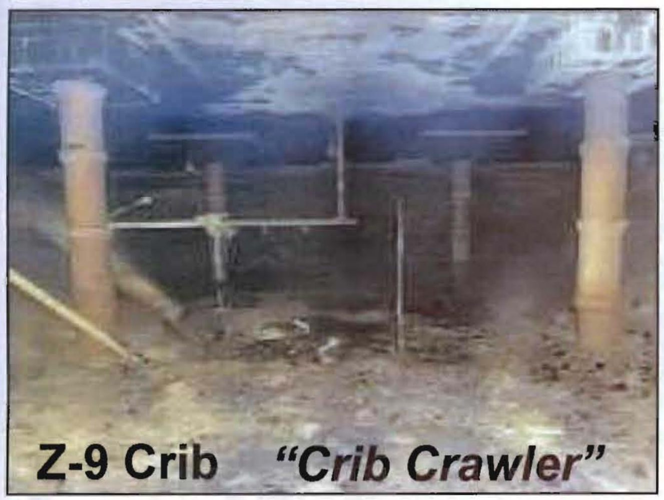




- μ-EXAFS was carried out on five particles from Sample 10.
- Uranium does not correlate with the Zr cladding
- Comparison of the measurements from the Chernobyl soils with LANL "standards" reveals the presence of UO_2 (Particles 2, 4, 5) and U_4O_9 (Particles 1, 3).

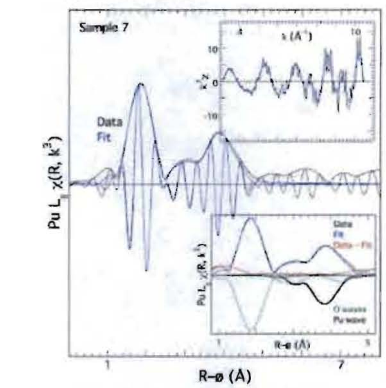
Can we use chemical measurements to determine technological history of Pu particles? Hanford soils.





Hanford Site: aqueous solutions of Pu were poured into outdoor cribs.

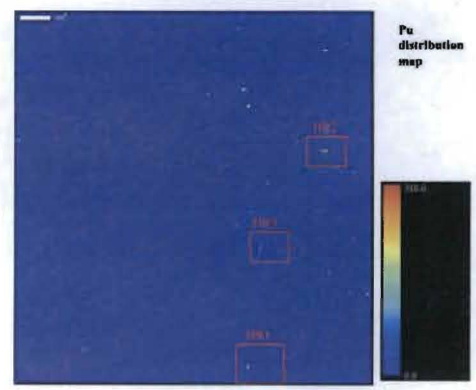
- **EXAFS of soils from within the cribs is definitive for PuO_{2+x}**



Pu L_{II} EXAFS

Pu-O	2.32(1) Å
Pu-Pu	3.84(1) Å
Pu-O	4.62(2) Å

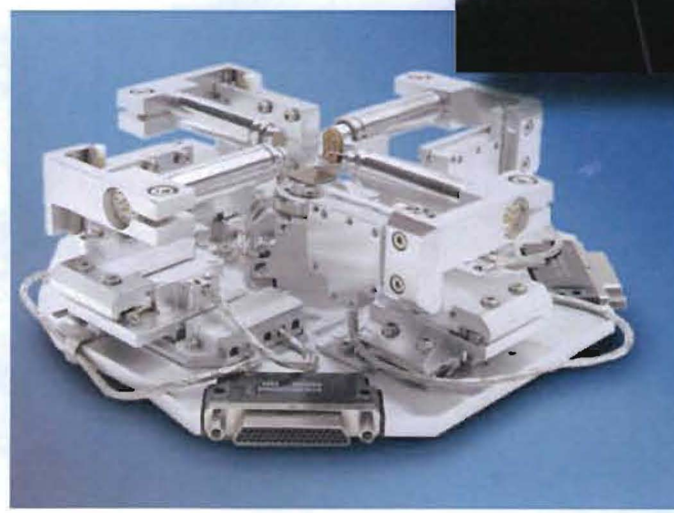
- **What will EXAFS data measured from soils collected from above the cribs reveal?**



Single Particles – Manipulation is Key to Transfer of Particle of Interest Between Capabilities

Field Emission Environmental Scanning Electron Microscope

- Morphology
- Major, minor elementals with WDS, EDS

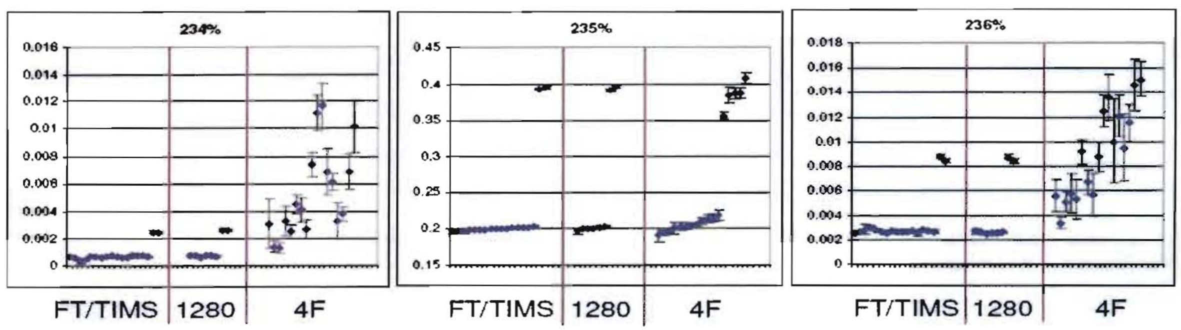


DCG Systems Micro/nanomanipulator

- Interfaces with SEM
- Position particle samples

Single Particles - a major improvement via Secondary Ionization Mass Spectrometry

- **Precise and accurate measurements of both major and minor isotopes of interest.**
- **Ability to search through *millions of particles* to find the particles of interest**



Comparing FT/TIMS, UHS-SIMS (Cameca 1280) and normal SIMS (Cameca 4F). The sample has a high Gd background and is an example where it is very difficult to analyze the minor isotopes with a normal SIMS. **(3.5h was spent analyzing this sample on the 1280).**

Conclusions

- New approaches to locate and study *single particles*
  - Secondary Ionization Mass Spectrometry (SIMS) and x-ray microprobe
- Molecular-level speciation of *single particles*
  - µ-XANES, µ-EXAFS, µ-Raman, µ-LIF
- Methodology to move samples between techniques
- New chemical chronometers based on molecular speciation and chemical alteration in environment
  - Chemical aging studies
- Integrate molecular-level information into existing forensics efforts
  - Better decision making
- Test capability with archived soils from nuclear weapon's production, test sites, and reactor sites