LA-UR- 10-08174

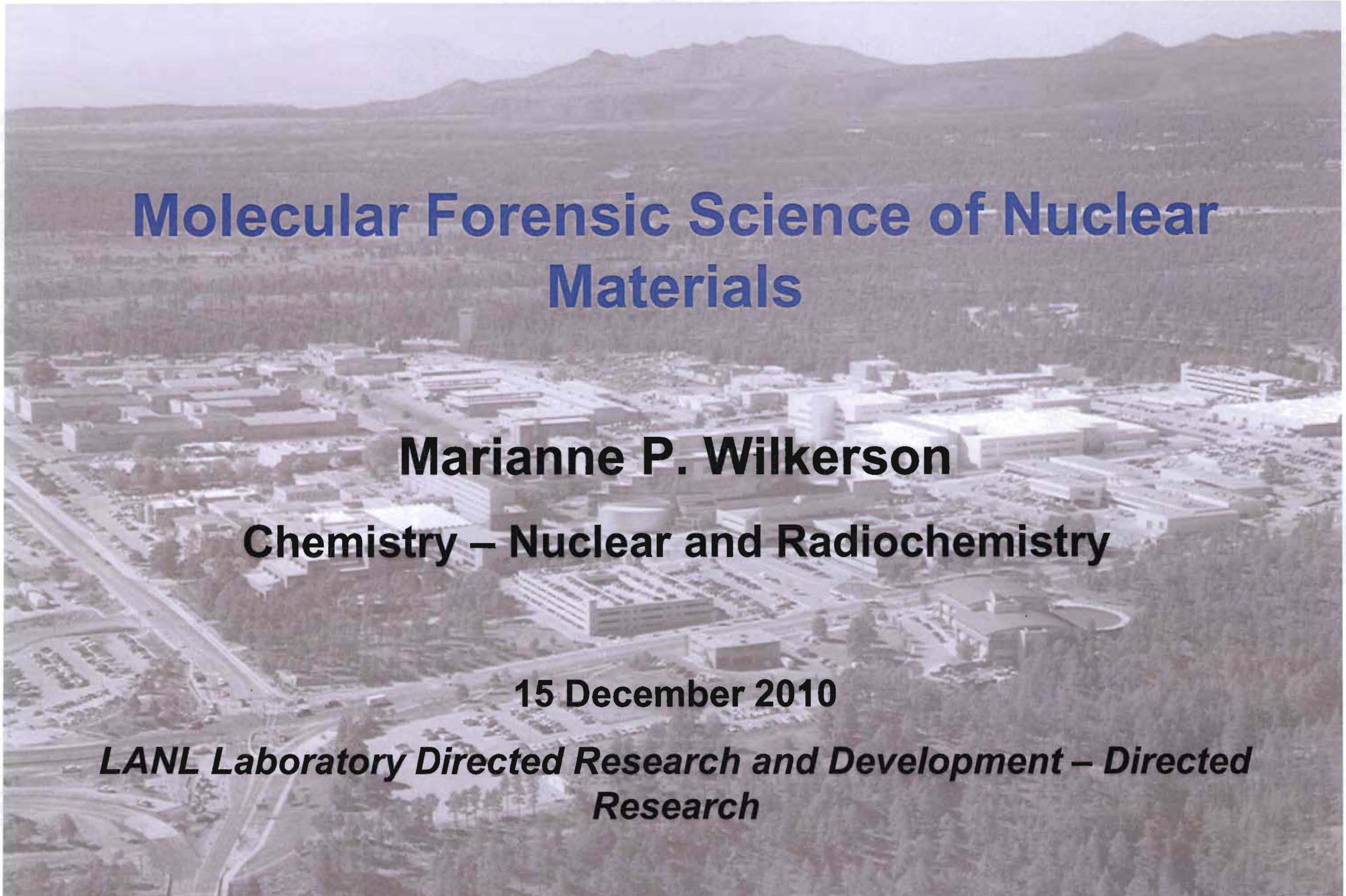
Approved for public release; distribution is unlimited.

Title: Molecular Forensic Science of Nuclear Materials

Author(s): Marianne P. Wilkerson, C-NR

Intended for: Pacifichem 2010
Honolulu, Hawaii
15-20 December 2010

Los Alamos
NATIONAL LABORATORY
EST.1943



Molecular Forensic Science of Nuclear Materials

Marianne P. Wilkerson

Chemistry – Nuclear and Radiochemistry

15 December 2010

LANL Laboratory Directed Research and Development – Directed Research

Acknowledgments

Sample Preparation

- Mr. Frank Archuleta, C-PCS
- Mr. Kevin S. Boland, C-IIAC
- Dr. Carol J. Burns, C-NR
- Dr. David E. Hobart, C-AAC
- Dr. Scott A. Kinkead, WX-3
- Dr. Stosh A. Kozimor, C-IIAC
- Dr. Patrick E. Martinez, C-AAC
- Dr. Jeremy Mitchell, MST-16
- Mr. Gregory L. Wagner, C-PCS

Chemical Characterization – X-ray Absorption and X-ray Fluorescence Measurements

- Dr. Olga Batuk, MST-8
- Dr. David L. Clark, The LANL Institutes Office
- Dr. Steven D. Conradson, MST-8
- Dr. Alison L. Costello, C-IIAC
- Mr. Patrick Kennedy, MST-6
- Mr. Dallas Reilly, University of Nevada – Las Vegas
- Dr. Hugh Selby, C-NR

Morphology and Isotopic Measurements

- Dr. William S. Kinman, C-NR
- Ms. Sharon M. Baldwin, C-NR
- Mr. James Bowen, University of Cincinnati
- Dr. David Podlesak, C-NR
- Dr. Lee R. Riciputi, C-NR

Theory and Modelling

- Dr. Anders D. Andersson, MST-8

Chemical Characterization – X-ray Diffraction, Imaging and Optical Spectroscopy

- Dr. John M. Berg, PMT-2
- Dr. Kirk D. Rector, C-PCS
- Dr. Brian L. Scott, MPA-MC

Advanced Lightsource – Lawrence Berkeley National Laboratory

- Dr. David K. Shuh

Lomonosov Moscow State University, Moscow, Russian Federation

- Dr. Stepan Kalmykov
- Dr. Irina Vlasov

Pacific Northwest National Laboratory

- Dr. Andrew Felmy

Stanford Synchrotron Radiation Lightsource

- Dr. Sam Webb

University of Cincinnati

- Dr. Sam Glover

University of Nevada – Las Vegas

- Dr. Ken Czerwinski
- Dr. Richard Gostick

Relevance: What does materials science contribute to nuclear forensics?

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

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

Traditional methods in forensics focus on isotopic and bulk analysis

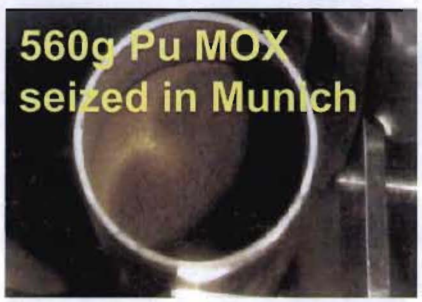
Research at Los Alamos National Laboratory is contributing to the development of new tools to correlate materials characteristics with its technical history.

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

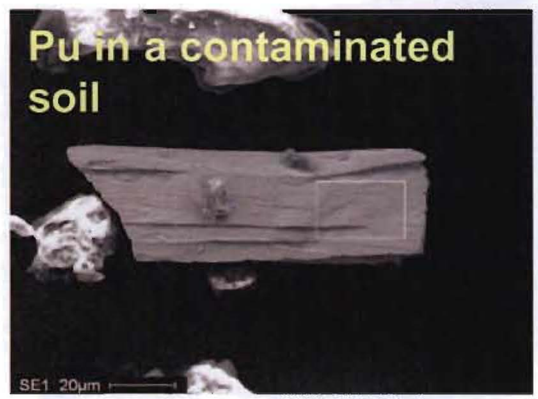
There are two issues to address:

- Bulk (average) speciation versus impurities/inhomogeneities

- Bulk (size) versus particle

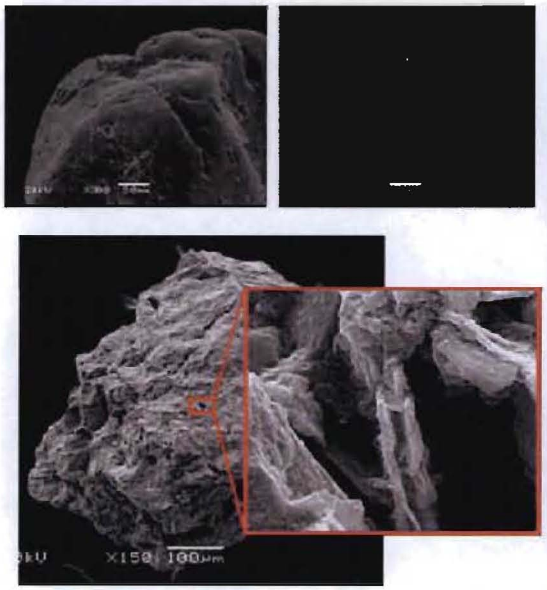


"CSI: Karlsruhe, Nuclear Forensics Sleuths Trace the Origin of Trafficked Material" *Actinide Research Quarterly 4th Quarter 2007*, pp. 1-9.



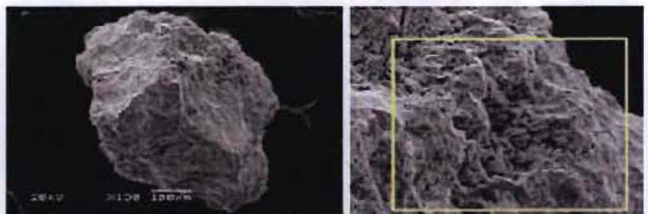
What kinds of material information do we need to know?

Morphology



- **Scanning Electron Microscopy**

Elemental

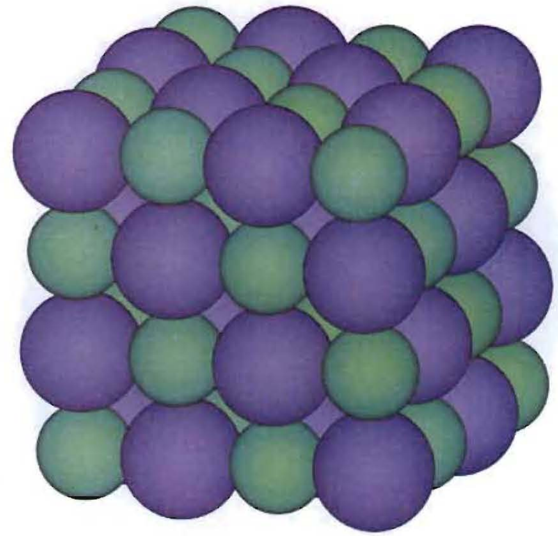


SEM (left) and SEM-EDS (right)

Clockwise from top left: Pu, U, Ga, Si, O, Al

- **SEM-Energy Dispersive Spectroscopy**
- **X-ray Fluorescence**

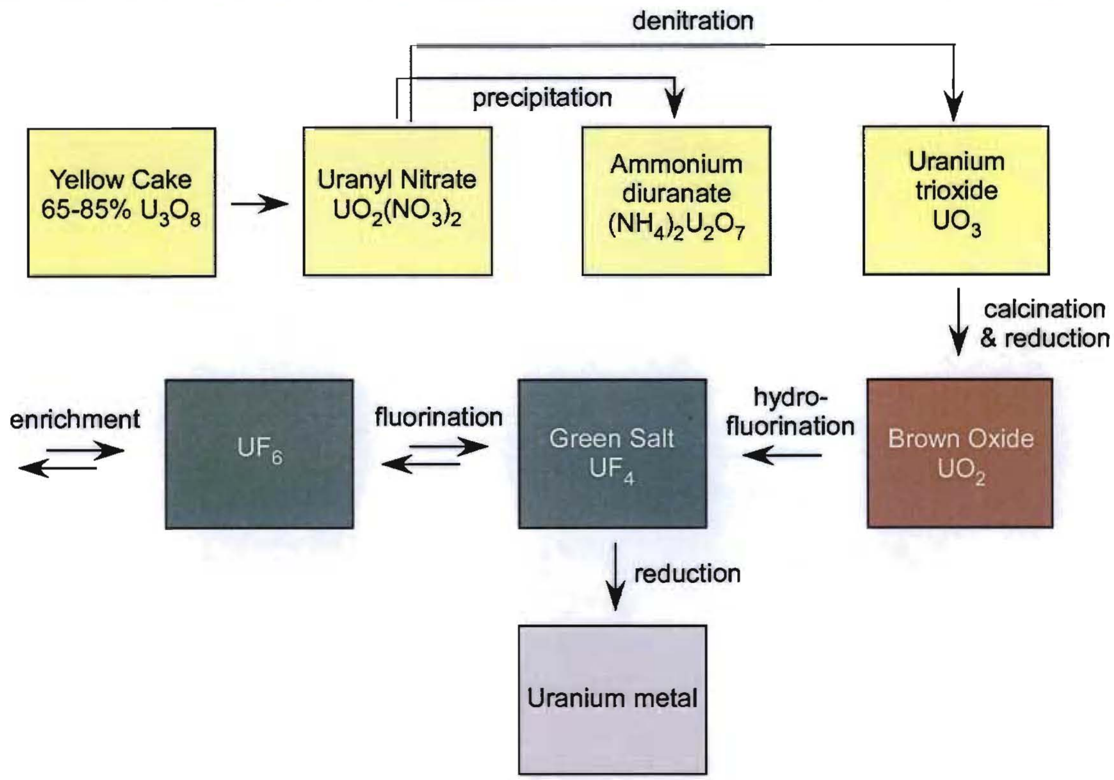
Structural (lattice)



- **X-ray diffraction analysis**
- **EXANES**
- **EXAFS**

Actinide materials science is rich in information.

- **Uranium pitchblend ores must be separated from as many as 40 elements**
- **More than 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**



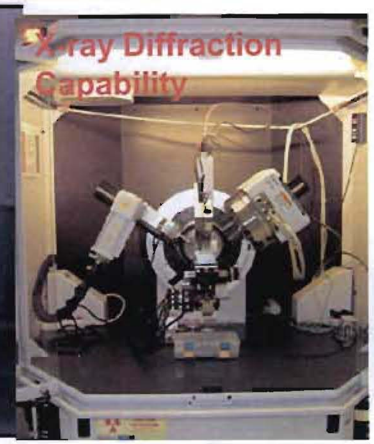
"The complexity of the U-O system is awesome."

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., Katz, J. J., Eds.; Springer: Dordrecht, The Netherlands, 2006; Chapter 15, pp. 1753-1835.

What tools are available to probe the technological history of materials?

In-house methods:

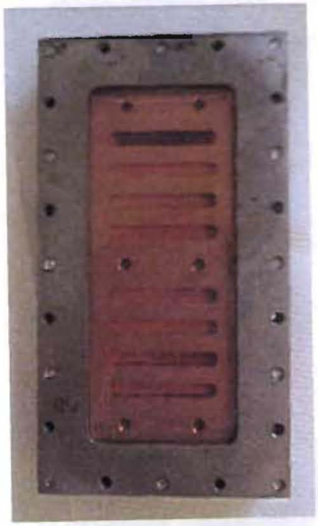
- Scanning Electron Microscopy
- X-ray Fluorescence
- Powder X-ray Diffraction Analyses
- Optical Imaging

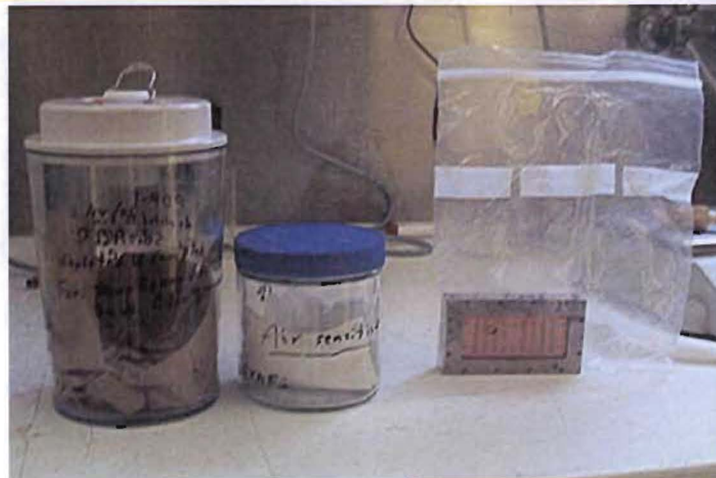


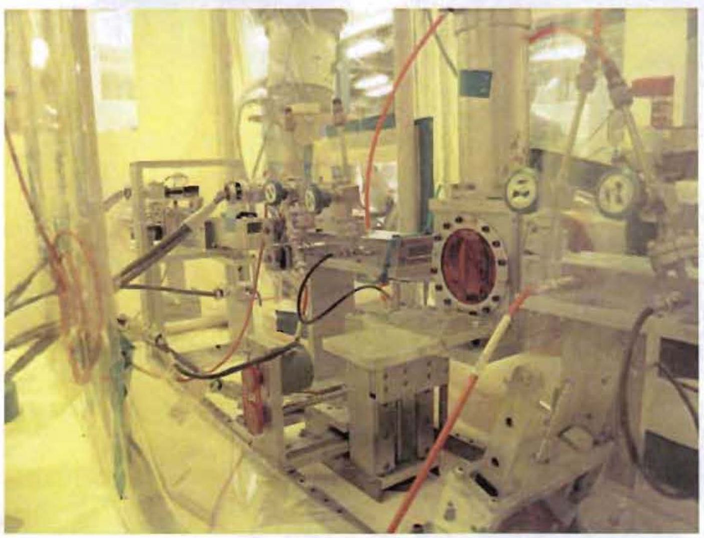
Out-of-house

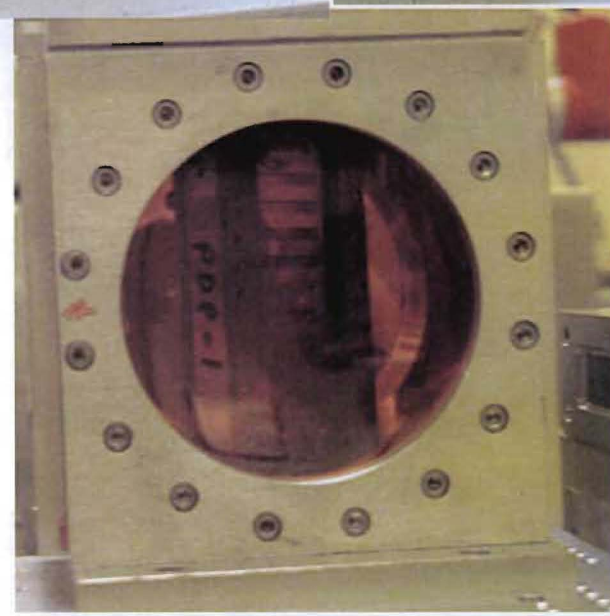
- X-ray Diffraction Analyses
- X-ray Absorption Fine Structure

Radioactive Sample Containment and Bulk Measurements at SSRL







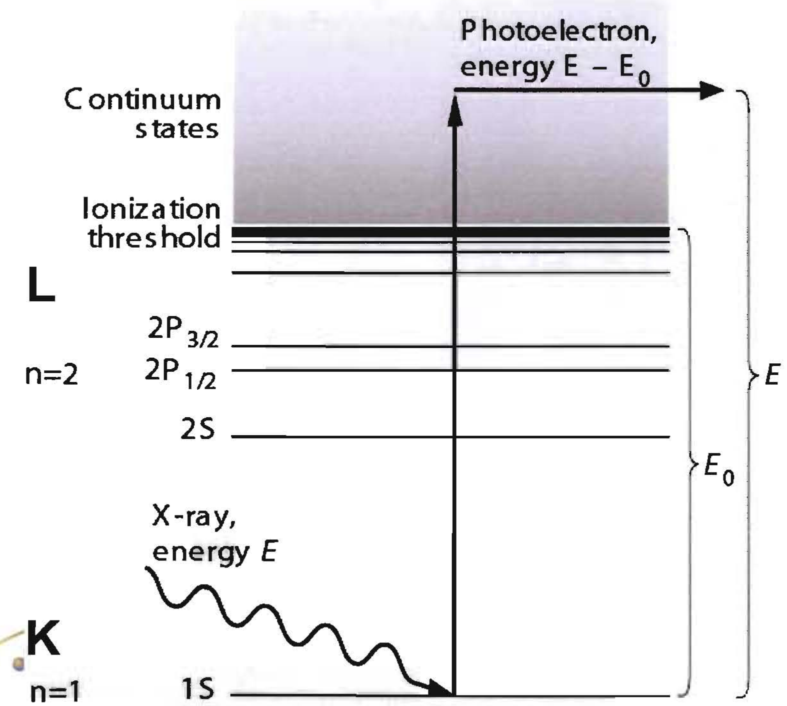


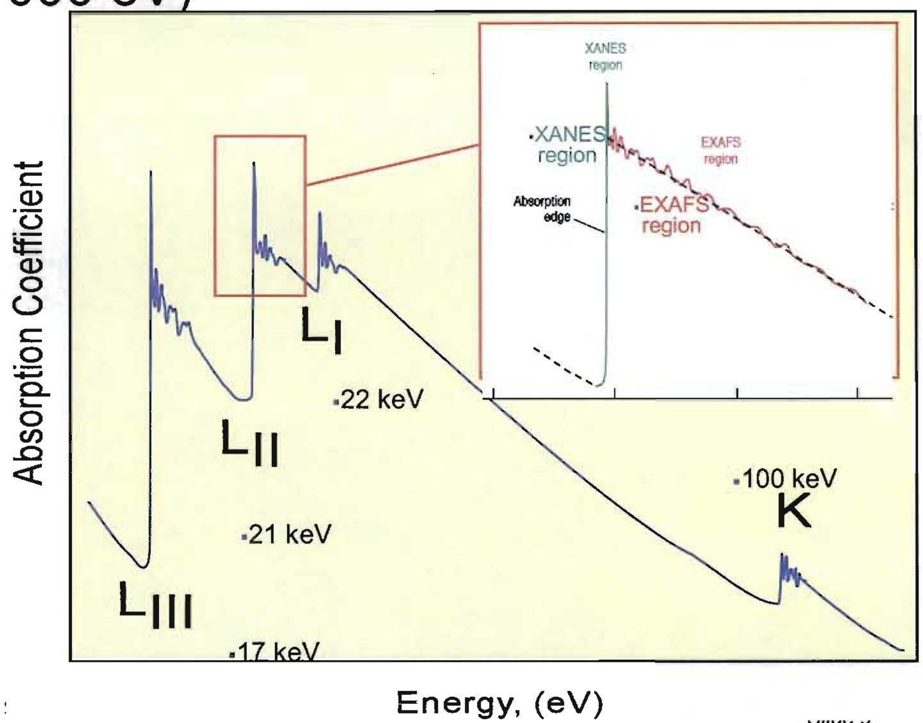
Research Design and Local Structure through XAFS

XAFS- X-ray Absorption Fine Structure- high energy X-rays allow for excitation of core electrons to bound states or a continuum

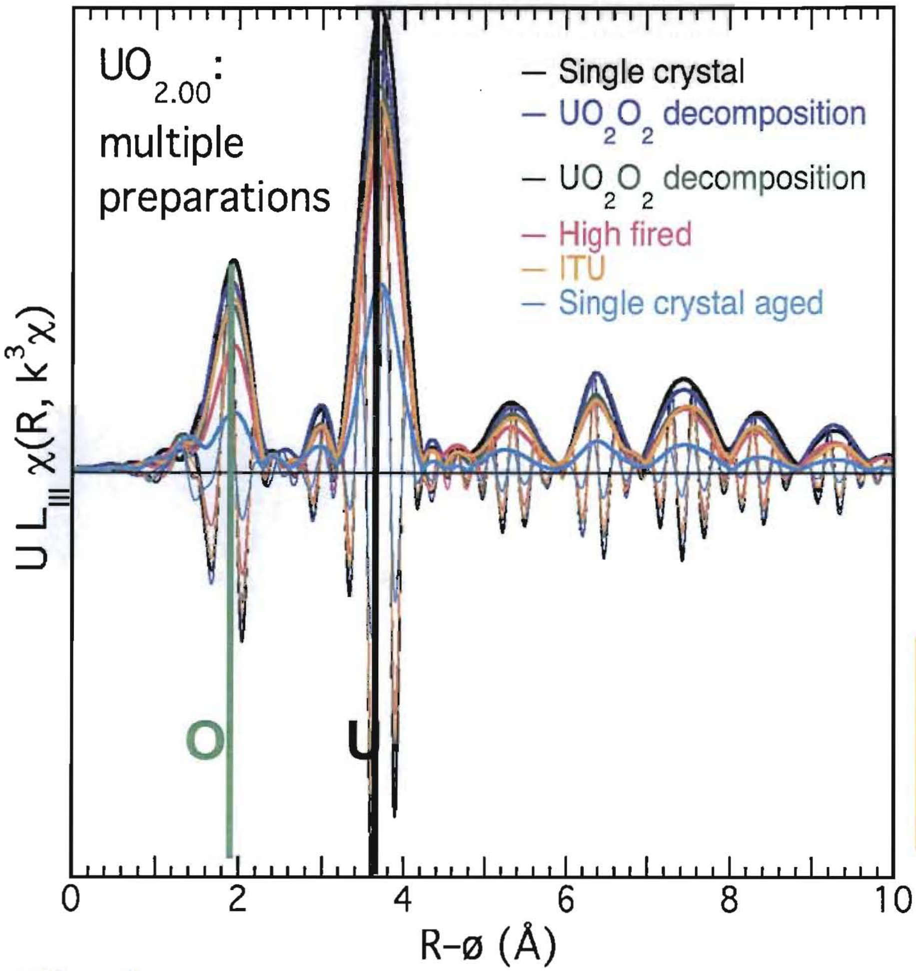
XANES- X-ray Absorption Near Edge Structure- arises from differences in effective charge (oxidation state) and local structure (20-30 eV)

EXAFS- Extended X-ray Absorption Fine Structure- gives distribution of interatomic distances around atoms (~1000 eV)

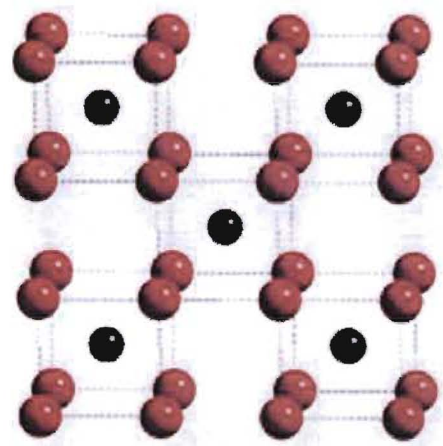




Bulk analysis of uranium oxides: EXAFS measurements reveal materials sensitivity to process.



Fluorite structure, *Fm3m*



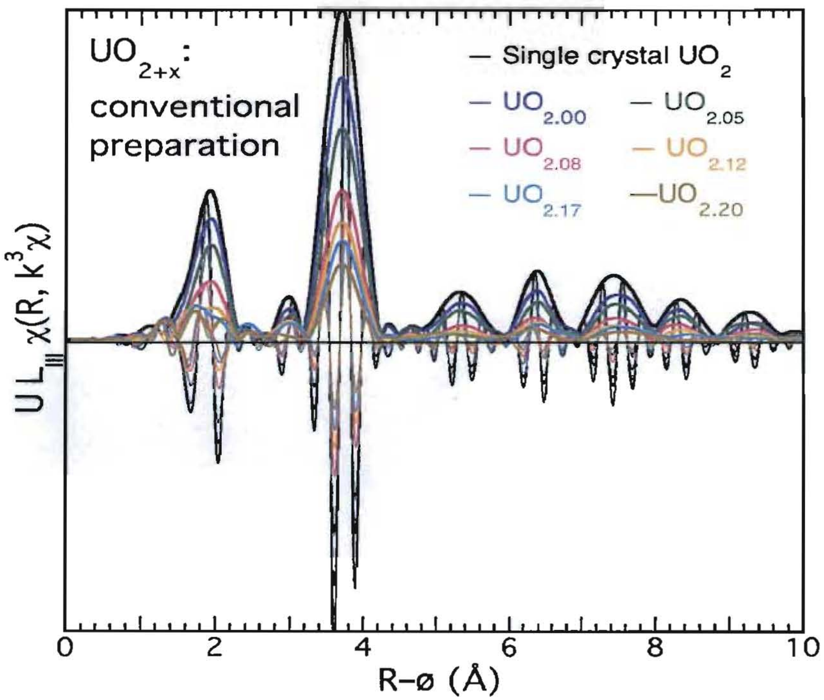
Red = Oxygen

Black = U

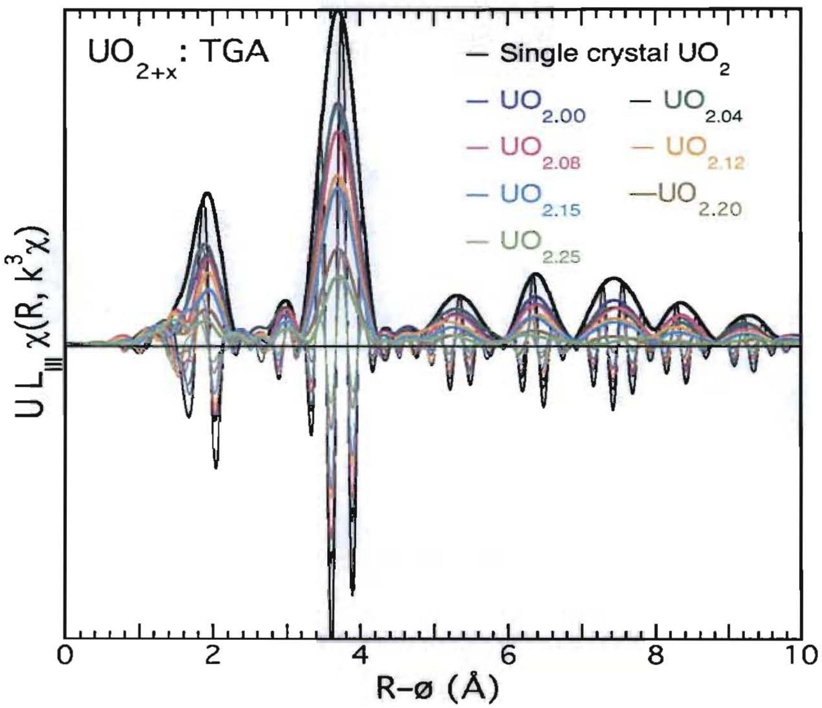
Variations in amplitudes in even "pure" UO_2 are observable in EXAFS and suggestive of preparation history.

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

With H_2O, intermediate temperature



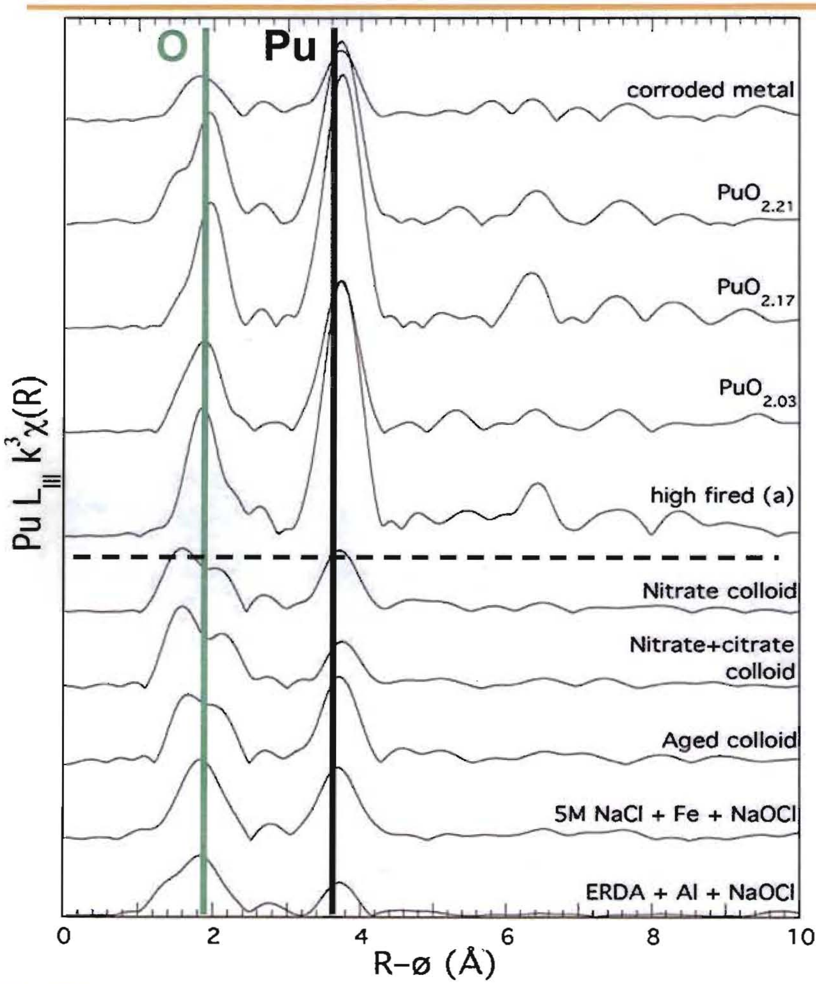
Weak CO:CO_2 oxidizer, high temperature



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 EXAFS: 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.

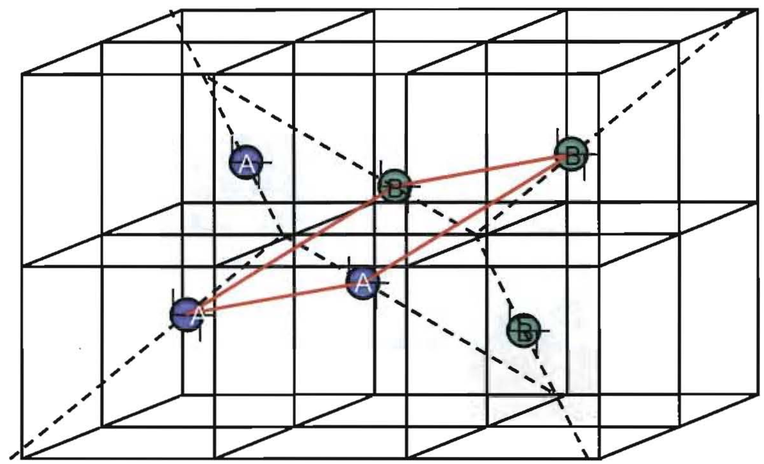
How can perturbations on the composition of bulk uranium oxide materials be predicted?

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 and other actinide oxide compounds.

Split quad-interstitial

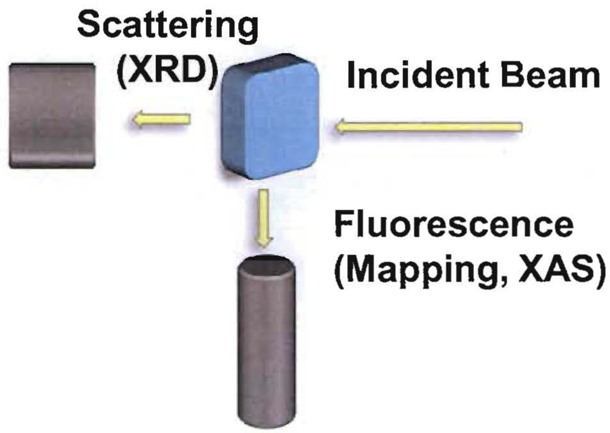


Two split di-interstitials (blue and green) make up a stable cluster in AnO_{2+x}.

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

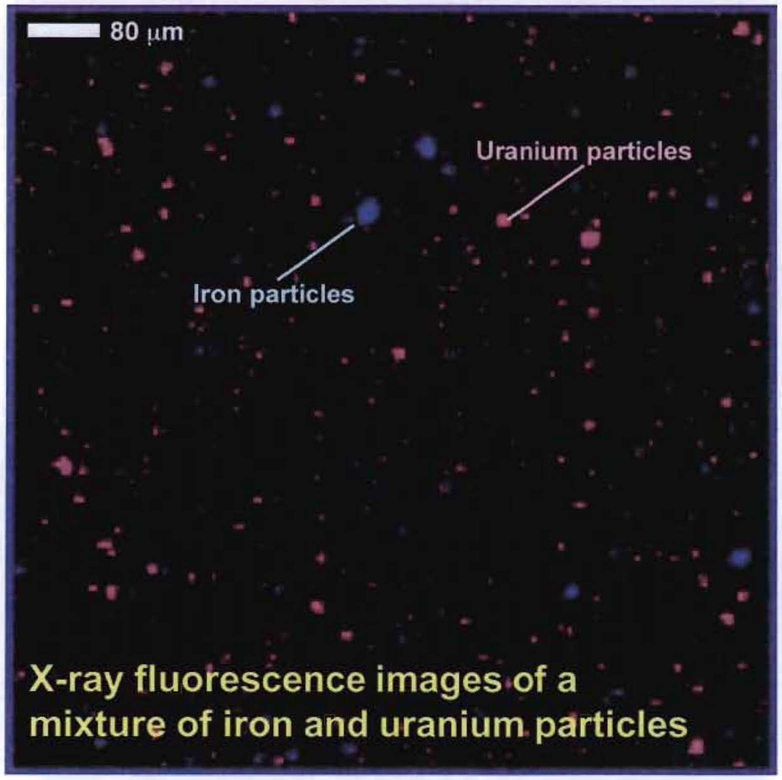
Can we use these methods to determine technological history of particles?

Microprobe spectroscopy on "Stardust"

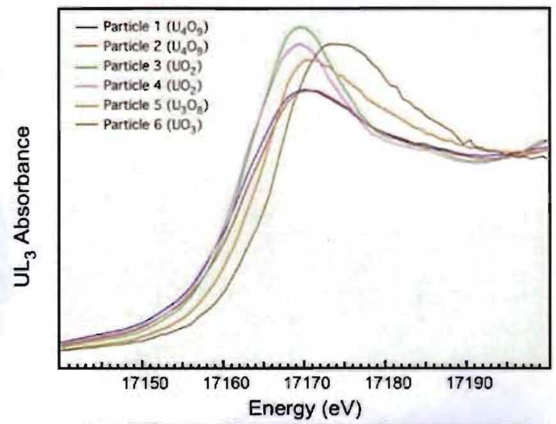


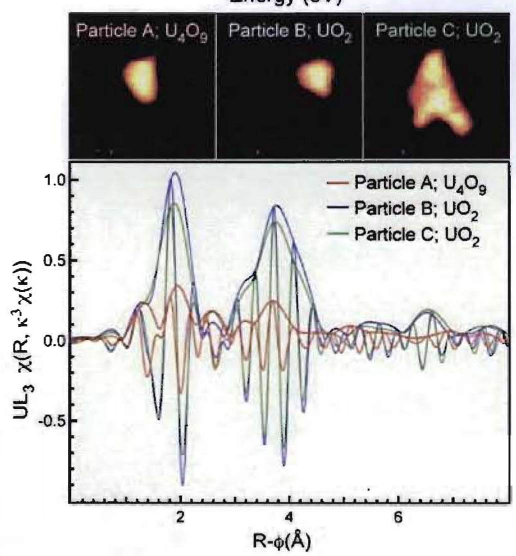
- **Raster a defocused X-ray beam over sample**
- **Map intensity of X-ray fluorescence at several energies to collect "XANES-image" of particles**
- ***Chemical speciation* of interesting spots using μ-XRD, μ-EXAFS**

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



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





XANES data

- Energy of the edge shifts
- Intensities of white lines

EXAFS data

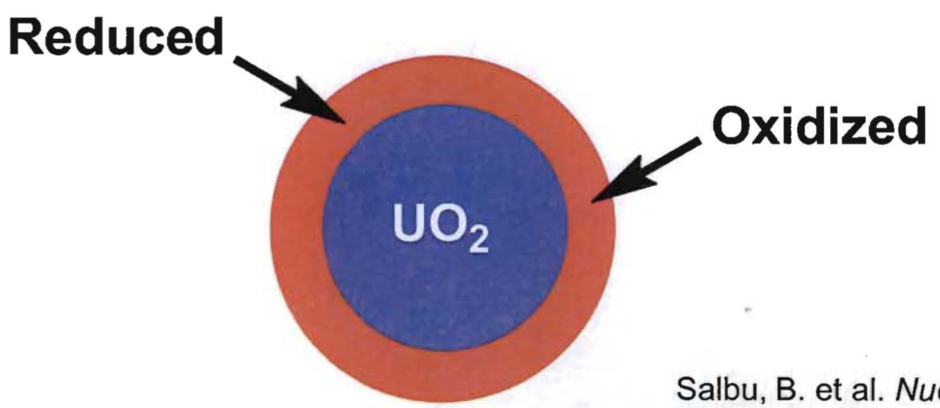
- U = oxo 1.9 Å
- U - oxo 2.33 Å
- U - U 4.5 Å

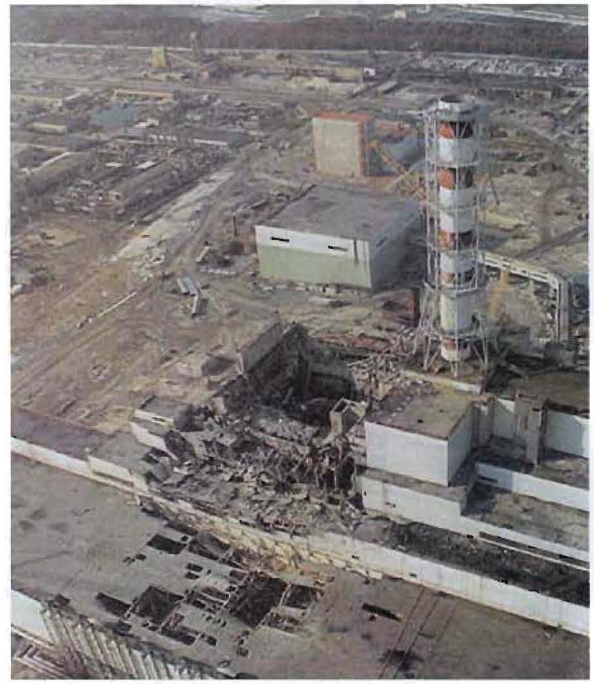
Actual Samples Released from Chernobyl Scenario

- **26^{th} April 2086 night, power generating unit Number 4 erupted following a power excursion**

- **Emission of radioactive gases, dust and aerosols**

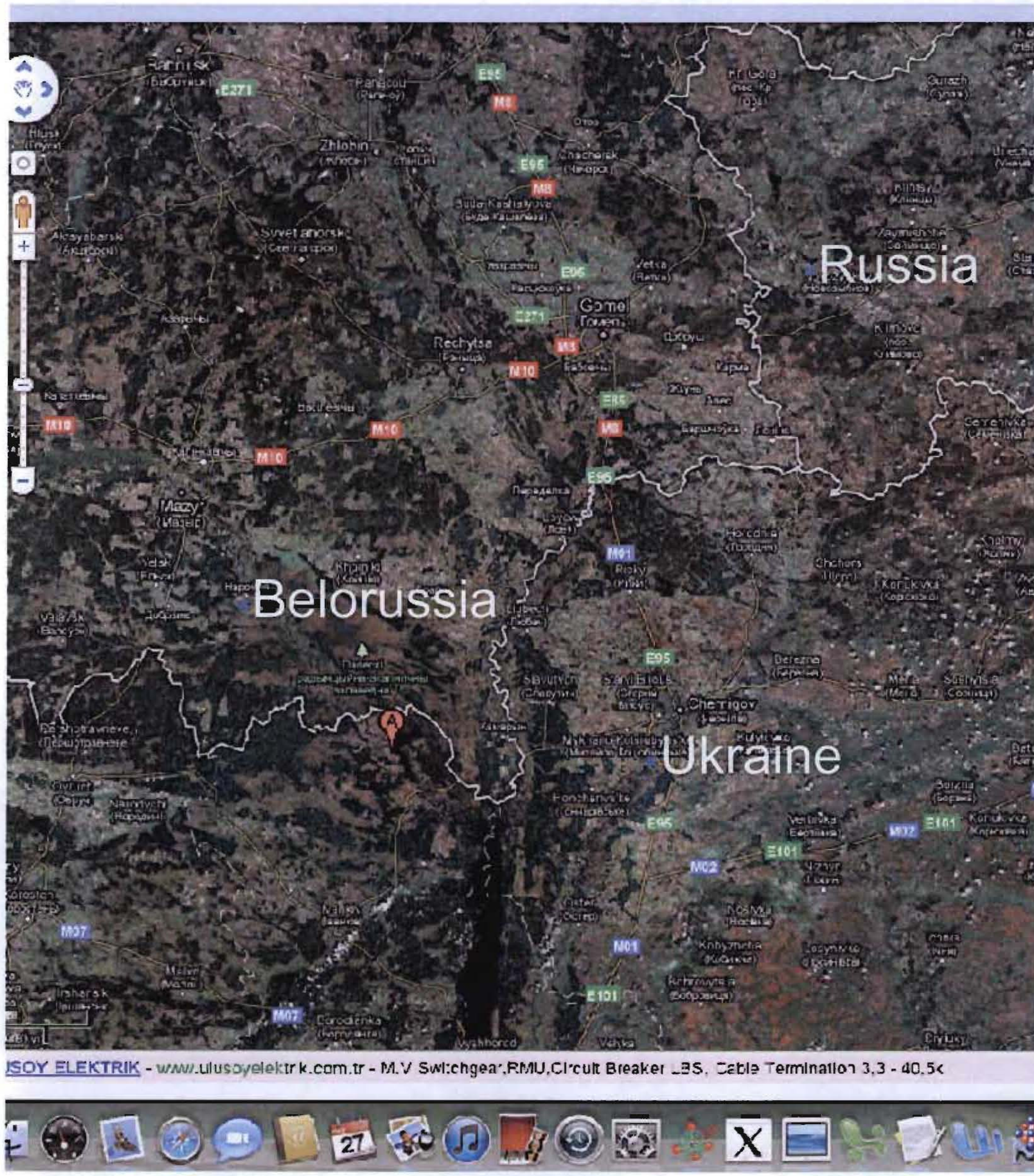
- **μ-EXAFS was carried out on five particles from Sample 10**

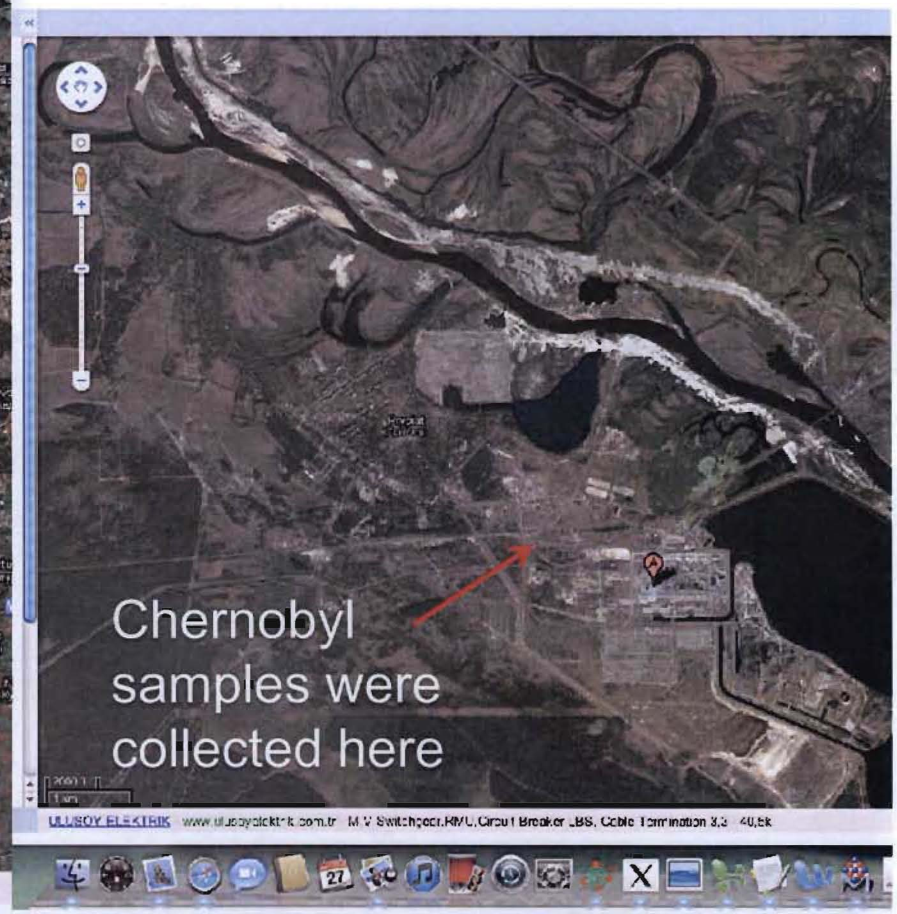




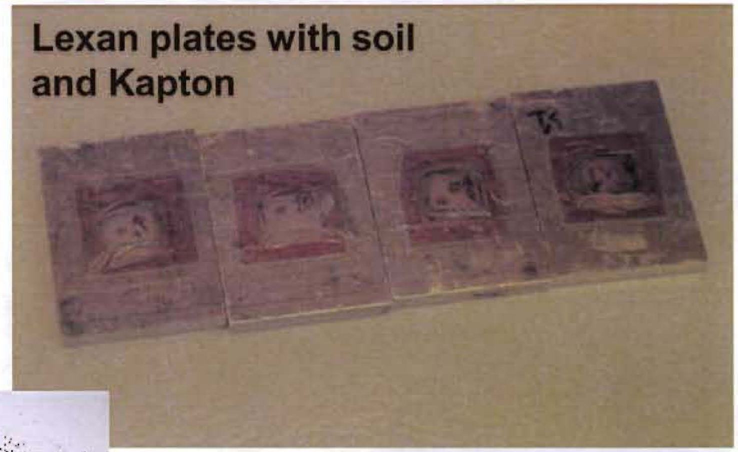
Salbu, B. et al. *Nucl. Instrum. Methods Phys, Res., Sect. A* **2001**, *467-468*, 1249-1252.

Where was the accident? Where are the samples from?





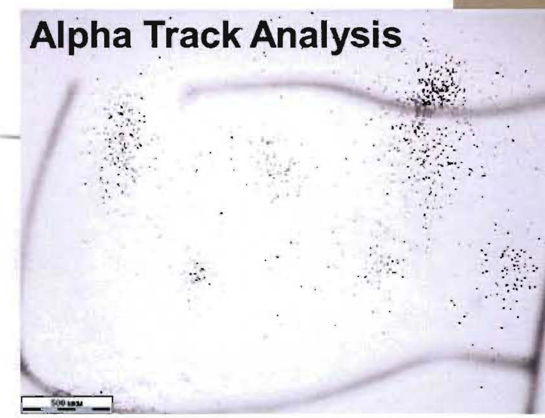
Czernobyl soils provide a test case for particle analysis.

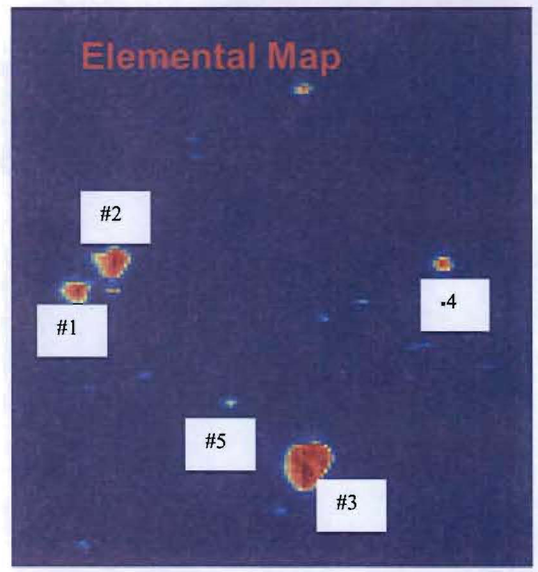


Four sets of Chernobyl soils

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

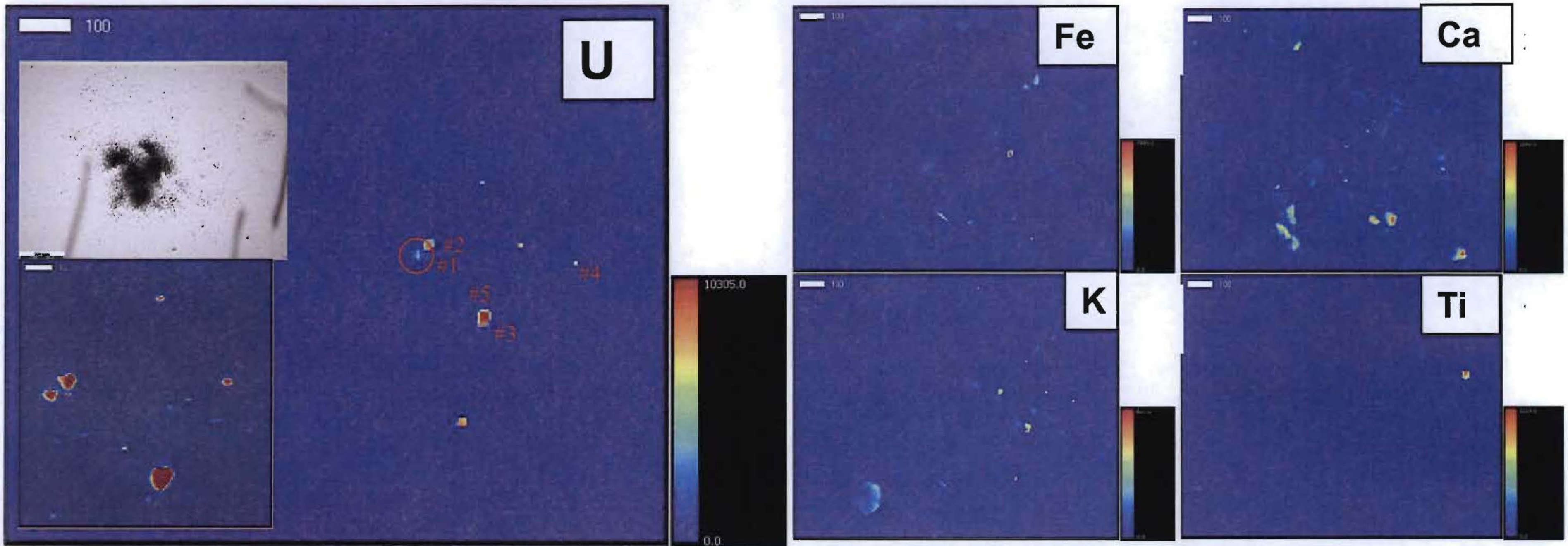
Optical microscope image

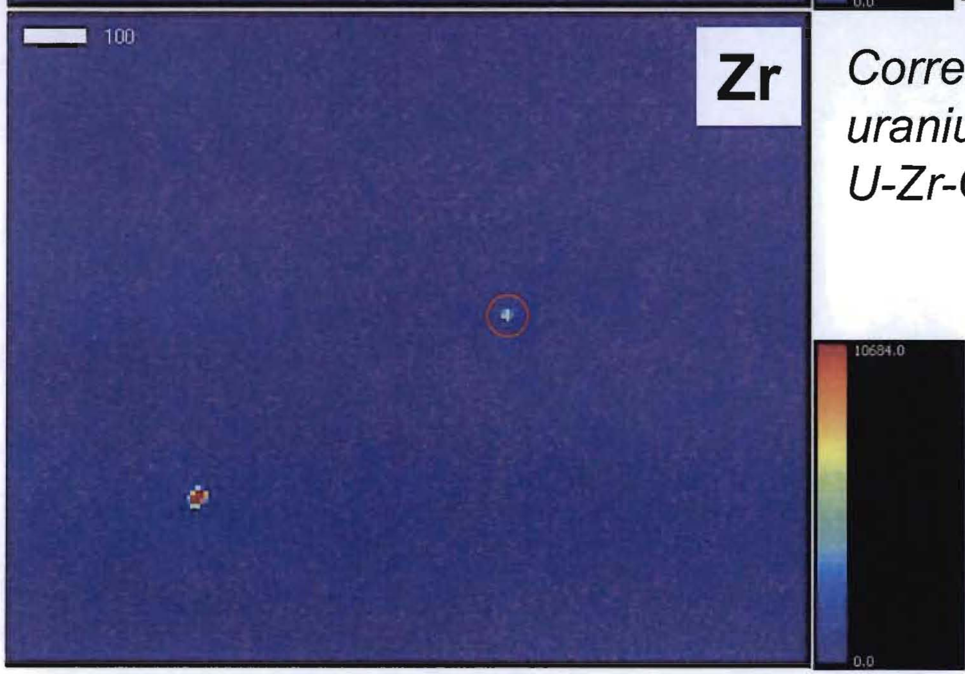




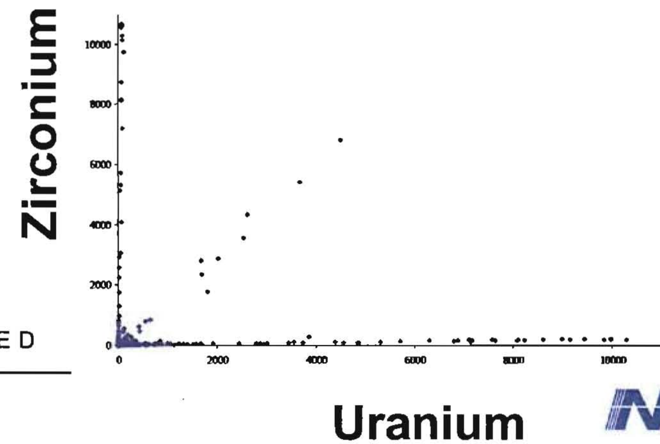
In collaboration with Dr. Stepan Kalmykov and Dr. Irina Vlasova at Lomonosov Moscow State University, Moscow, Russian Federation

X-Ray Fluorescence maps of Chernobyl samples

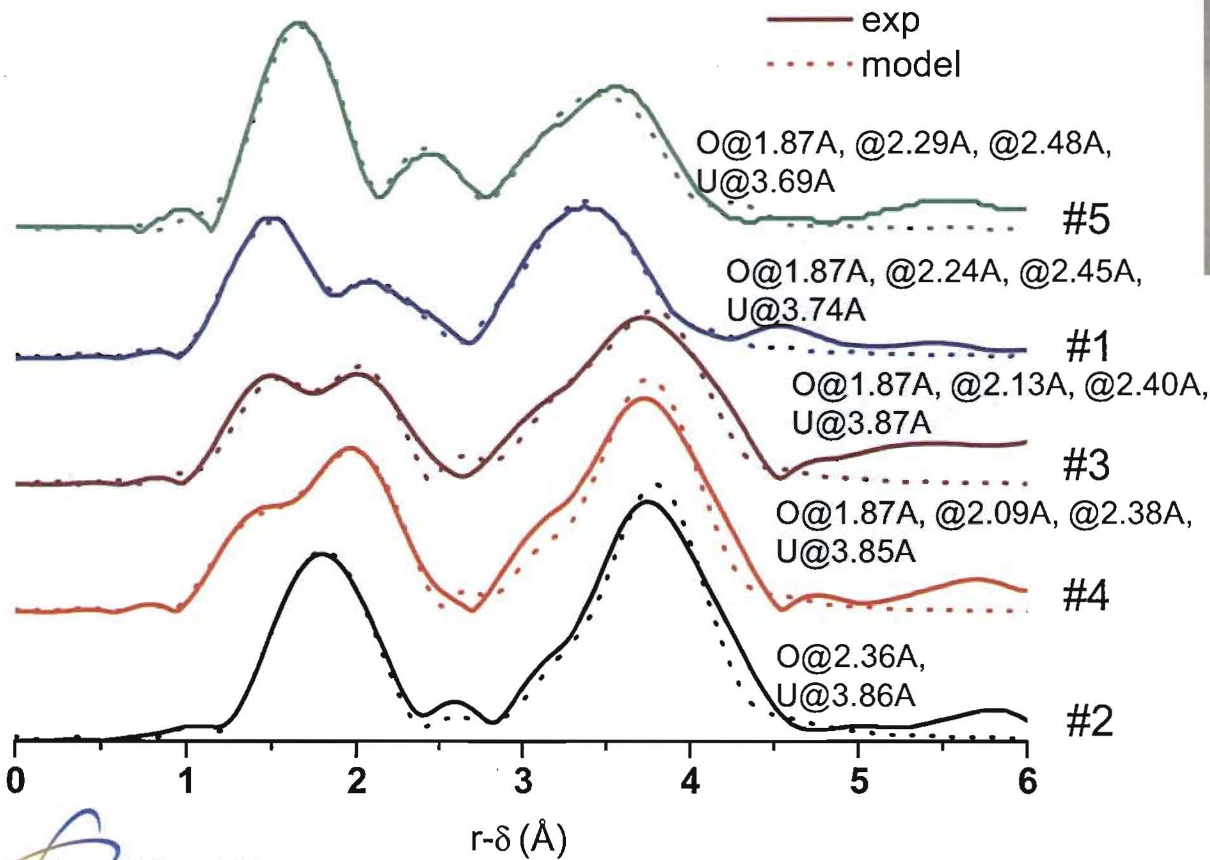




Correlation plot reveals presence of pure uranium oxide, pure zirconium oxide and mixed U-Zr-O particles

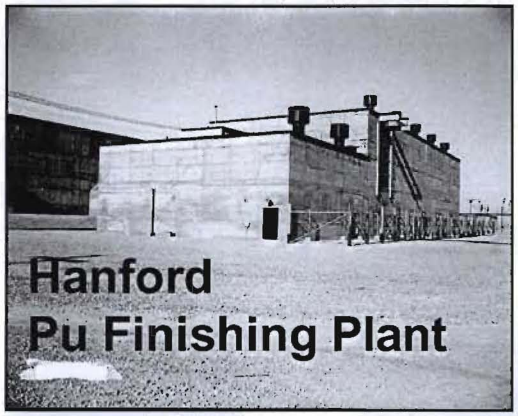


Results of EXAFS analysis on Chernobyl samples

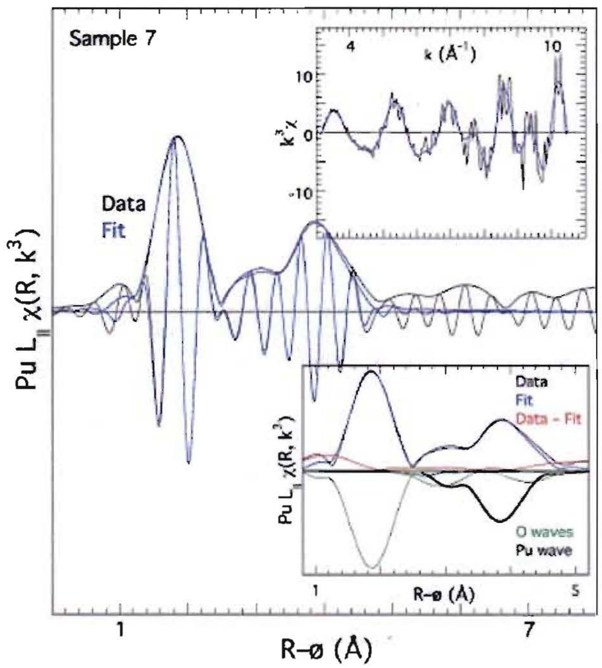


- **Hot particles correspond to UO2+x, 0 ≤x<0.25**
- **No correlation of U redox state in the particles with their size and other factors**

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.



Pu L_{II} EXAFS

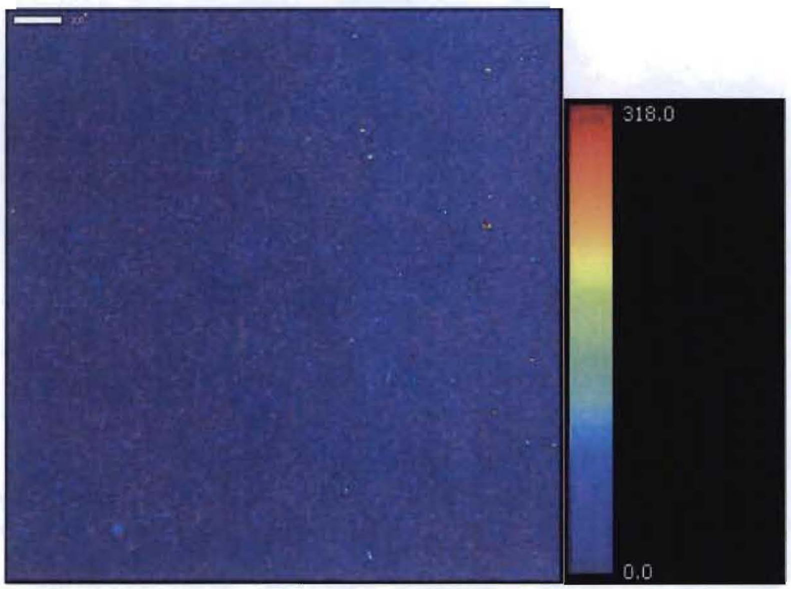
Pu-oxo	2.32(1) Å
Pu-Pu	3.84(1) Å
Pu-oxo	4.62(2) Å

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

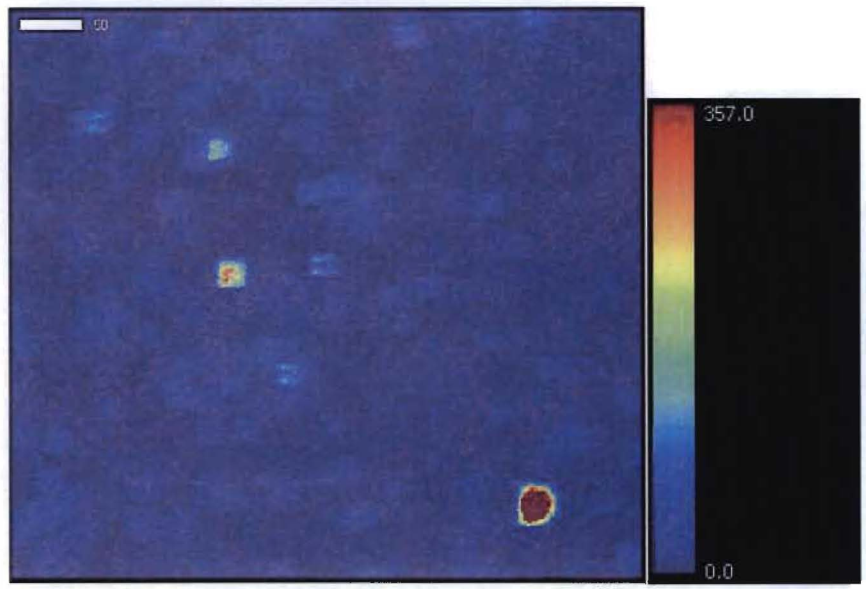
What can be measured via μ-EXAFS?

- μ-EXAFS analyses reveal two types of particles from the surface

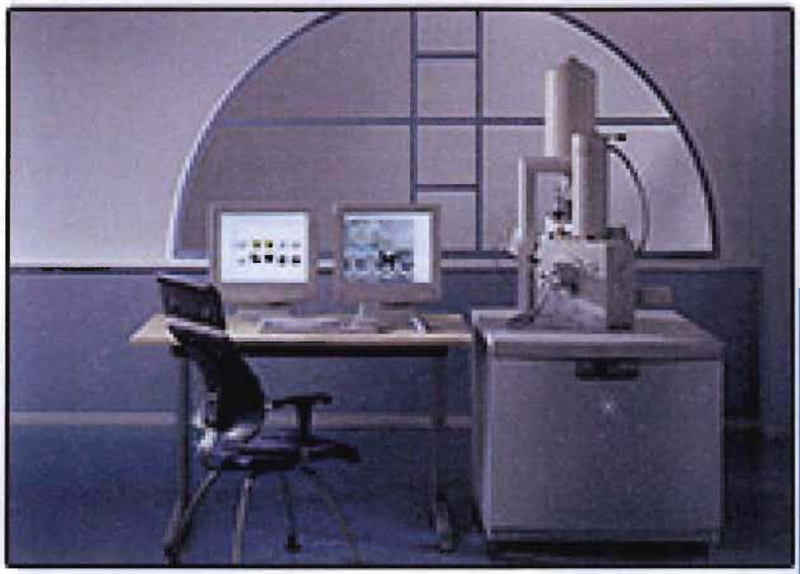
random shapes



material correlates with blocks containing low Z elements

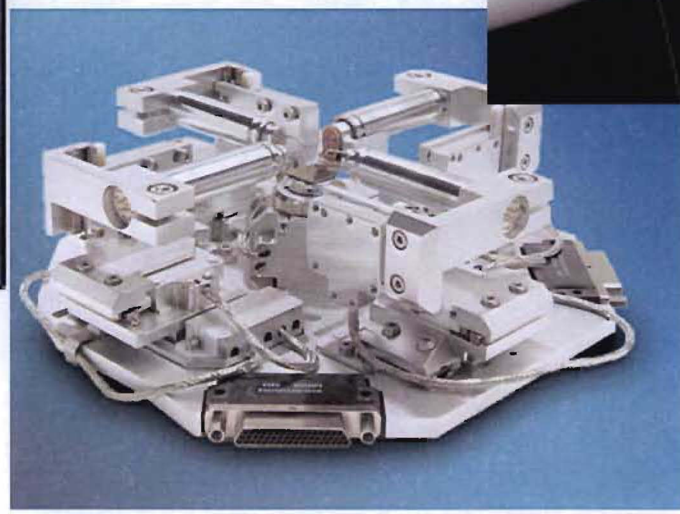


Single Particles – Manipulation is Key to Transfer of Particle of Interest Between Capabilities



Field Emission Environmental Scanning Electron Microscope

- Morphology
- Major, minor elementals with WDS, EDS

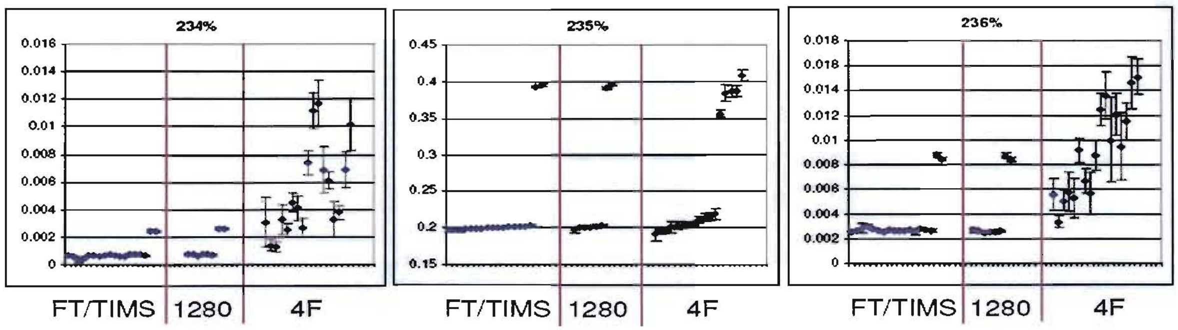


DCG Systems Micro/nanomanipulator

- 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).**

Summary

Validation of diagnostic value of approach

Spatially resolved speciation of *small samples*

- μ-XANES, μ-EXAFS, μ-Raman

New approaches to locate and study *single particles*

- Secondary Ionization Mass Spectrometry (SIMS) and X-ray microprobe

Methodology to move samples between techniques

Test capability with archived soils from various sites

New chemical chronometers based on molecular speciation and chemical alteration in environment

- Chemical aging studies