LA-UR- 11-00203

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Title: Molecular Forensic Science of Nuclear Materials

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Intended for: LDRD-DR Program Review
13 January 2011
Los Alamos, NM USA

Los Alamos NATIONAL LABORATORY
EST.1943

Molecular Forensic Science of Nuclear Materials
20100048DR

Marianne P. Wilkerson

13 January 2011

Laboratory Directed Research and Development – Directed Research

Los Alamos National Laboratory

Charge and Review Criteria for 12-15 month projects

Assessment: Strengths and weakness of the project with respect to the standard OMB criteria for Federally supported R&D:

Quality: Are the science and technology results of high quality compared to national and international peers?
Performance (Project Execution): Is the project making good progress against its milestones? Is it well-conceived and executed?
Leadership: Are the results of the project defining R&D directions for the broader community?
Relevance: Is the project continuing to support the strategic directions of the Laboratory?

Advice: Given the finite time remaining to the project, how might the project maximize its impact (both to its field and to the Los Alamos mission) at the end of 3 years? How should the project approach its transition to non-LDRD funding?

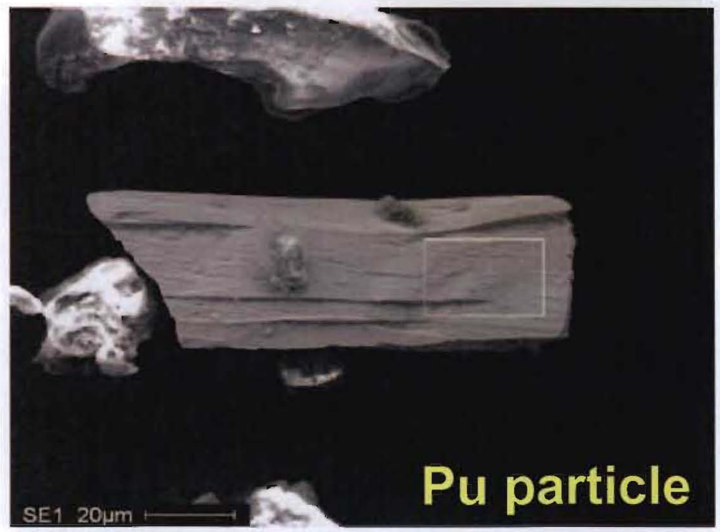
What is the problem that *Molecular Forensic Science of Nuclear Materials* is addressing?

- 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 sample 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, but chemical signatures are not exploited



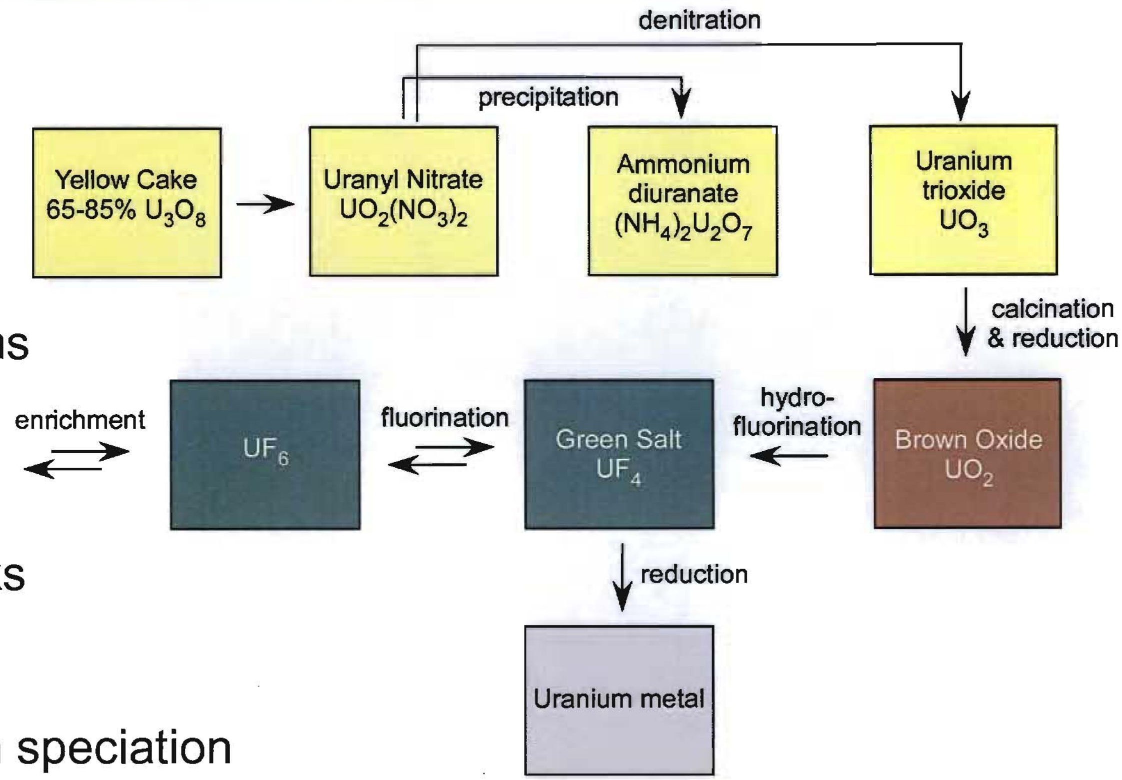
Uranium material science is rich in information !

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

- > 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 initiates changes in speciation



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

Edelstein, N. M. et al, Summary and Comparison of the Actinide and Transactinide Elements. In *The Chemistry of the Actinide and Transactinide Elements*, 2006; Chapter 15, pp. 1753-1835.

What do we mean by chemical speciation?

Levels of Chemical Speciation

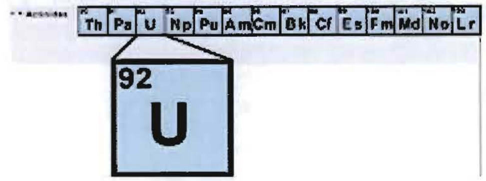
Physical (or Phase) Speciation

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

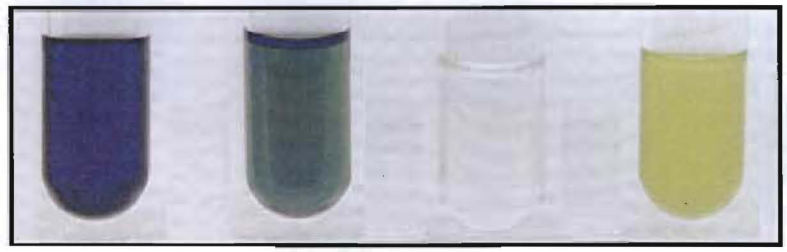
Chemical Speciation

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

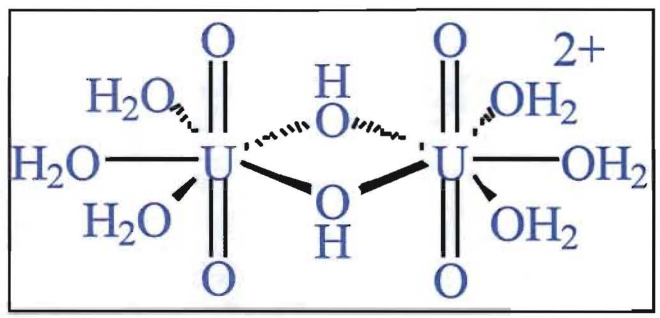
- Depending on the type of information, various levels exist
  - Identity of the element
  - Physical state
  - Oxidation state
  - Molecular formula
  - Molecular structure



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



$UO_2(OH)^+$



Plutonium oxidation is more complex than originally suggested.

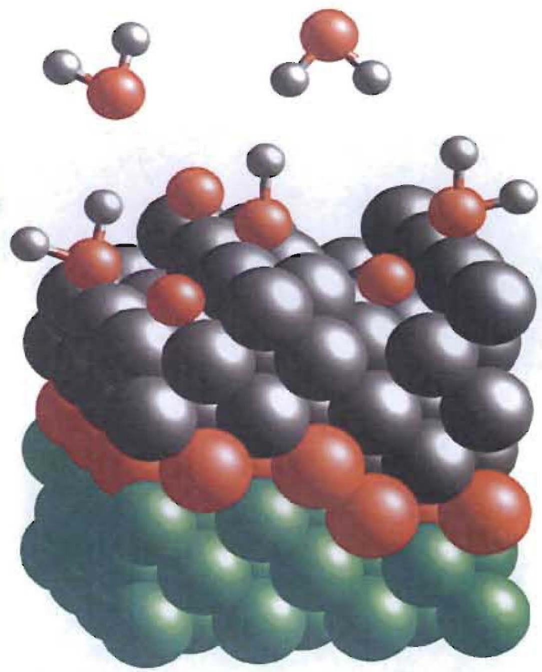
Plutonium metal coupon (1 g)

60% RH 20% RH

Traditional views of Pu corrosion:

$$Pu + 2H_2O \rightarrow PuO_{2+x} + 2H_2$$

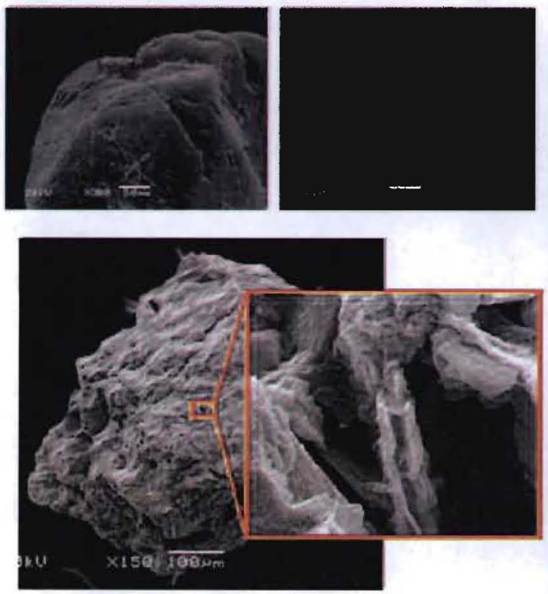
versus a new understanding of surface phase relationships



Clark, D. L.; Hecker, S. S.; Jarvinen, G. D.; Neu, M. P. Plutonium. 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.

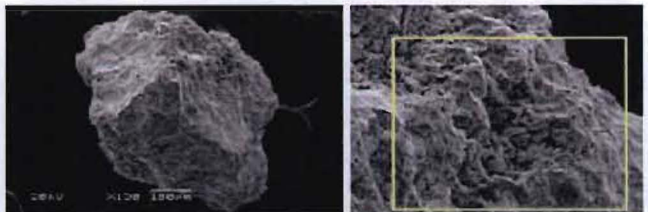
But isn't chemical speciation already applied to forensic analyses? Where is the innovation here?

Morphology



- Scanning Electron Microscopy

Elemental/isotopic

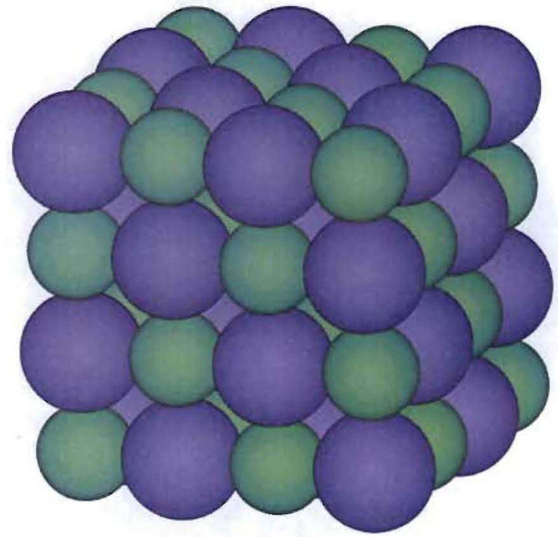


SEM (left) and SEM-EDS (right)

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

- SEM-EDX
- XRF
- TIMS/SIMS

Structural (lattice)

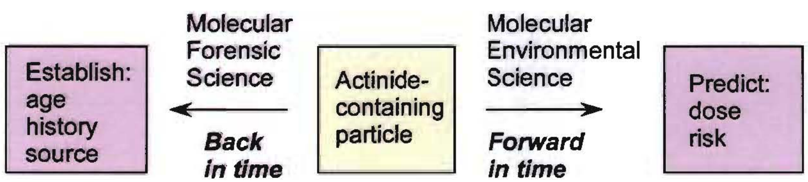


- X-ray diffraction analysis
- XANES
- EXAFS

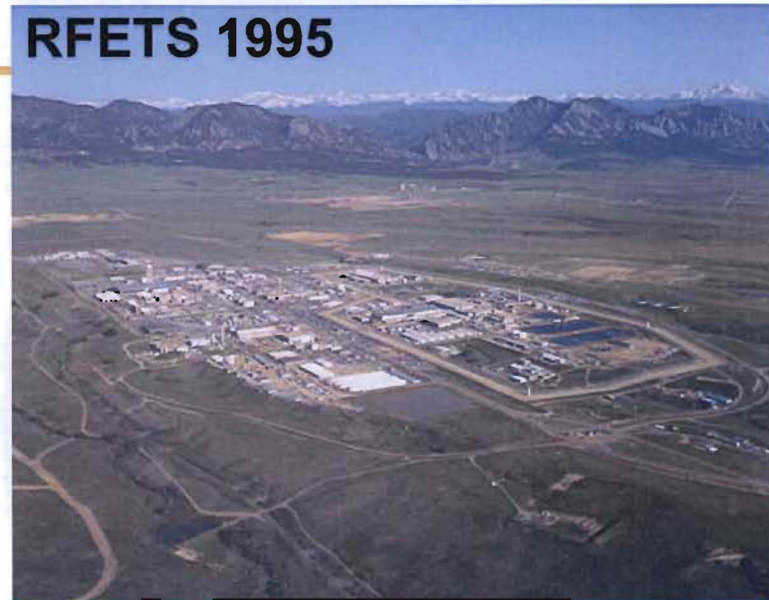
Molecular Environmental Science → Molecular Forensic Science

- Molecular level information **revolutionized** environmental science because speciation was a better determinant of future risk
  Clark, D. L.; Janecky, D. R.; Lane, L. J. "Science-based cleanup of Rocky Flats" *Physics Today*, **2006**, *59(9)*, 34-40.

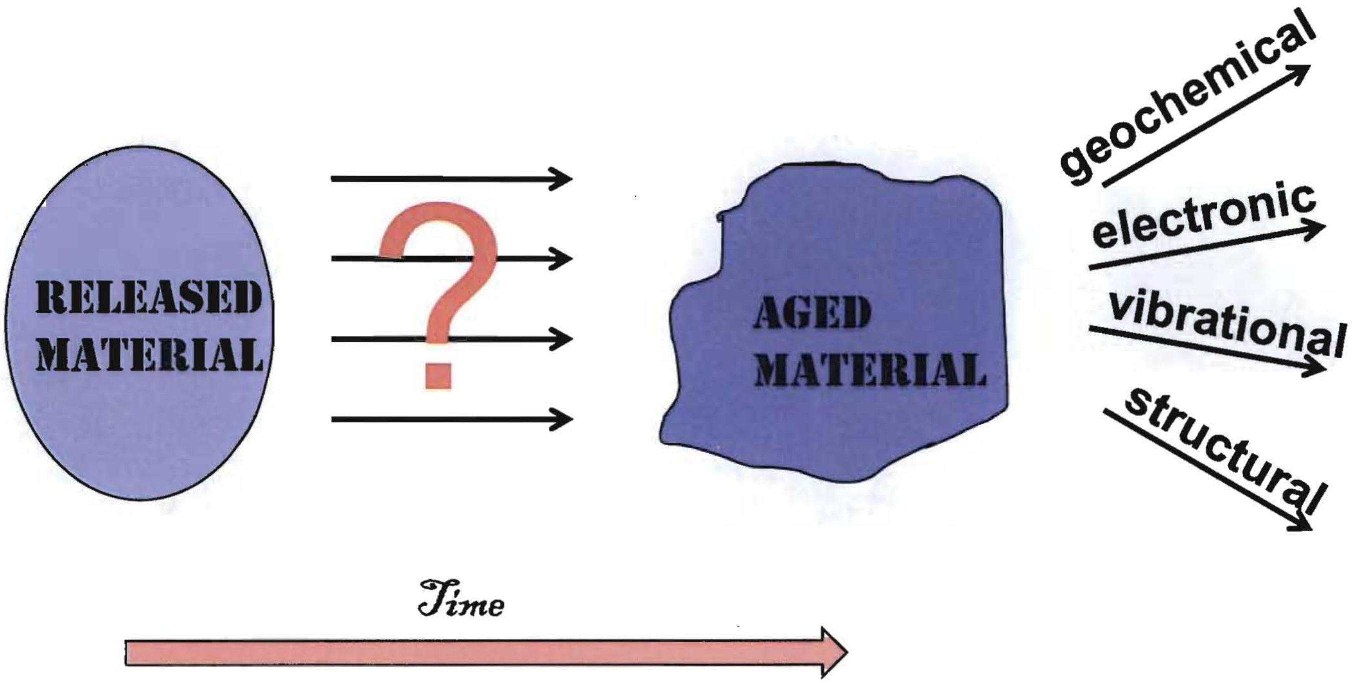
- Developed a more defined scope with clear endpoint



- We propose that ***chemical speciation*** can provide molecular level information on source, production mode, age, intended use, and history



What are the tools used to determine chemical speciation in *Molecular Environmental Science*?



Our research plan defines goals to underpin a *Molecular* approach to nuclear forensics

Goal 1: Identify and prepare/receive forensic-relevant materials

- Environmental samples from nuclear production sites
- Accidents involving nuclear materials
- Controlled oxidization of Pu alloys
- Controlled hydrolysis UF_6
- Laboratory prepared, high-purity actinide oxides

Goal 2: Engage and exploit crucial, state-of-the-art capabilities to test and understand measurements on samples of known history

- Particle manipulation
- Synchrotron-based μ-probe spectroscopy
- Hyperspectral optical imagery
- Secondary Ionization Mass Spectrometry
- Modelling of surface phase relationships

Goal 3: Develop an integrated approach to measurements and analysis

- Engage collaboration between scientific disciplines
- Develop sample containment/holder to be able to exchange a sample between analyses
- Provide direct comparison of measurements on specific samples
- Evaluate the complementary nature of the tools
- Determine a logical sequence of measurements

Goal 4: Assess the value of the integrated approach

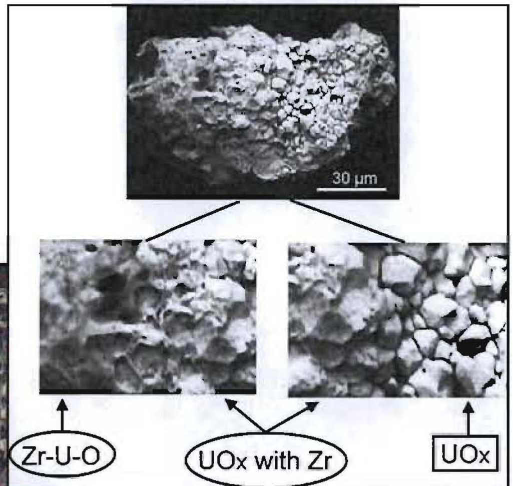
Can we make the measurements? Are they diagnostically useful?
Is the sum is greater than the parts?

Progress under Goal 1: Receive environmental samples

Samples collected following the Chernobyl Accident (1986)

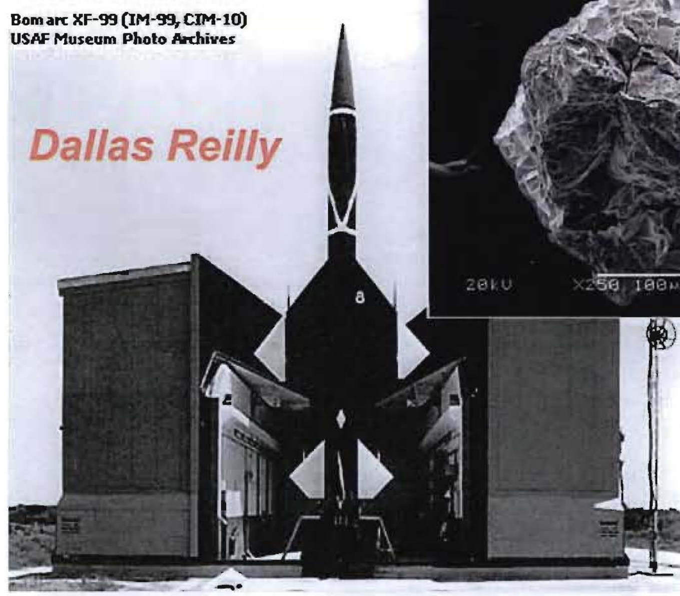
Olga Batuk

Mixed hot particles - Burakov

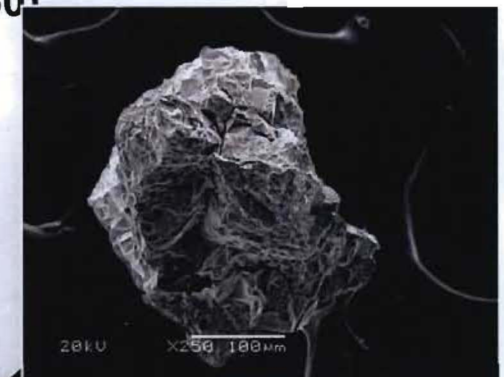


Chernobyl Nuclear Power Plant

Samples collected following U.S. BOMARC Fire (1960)

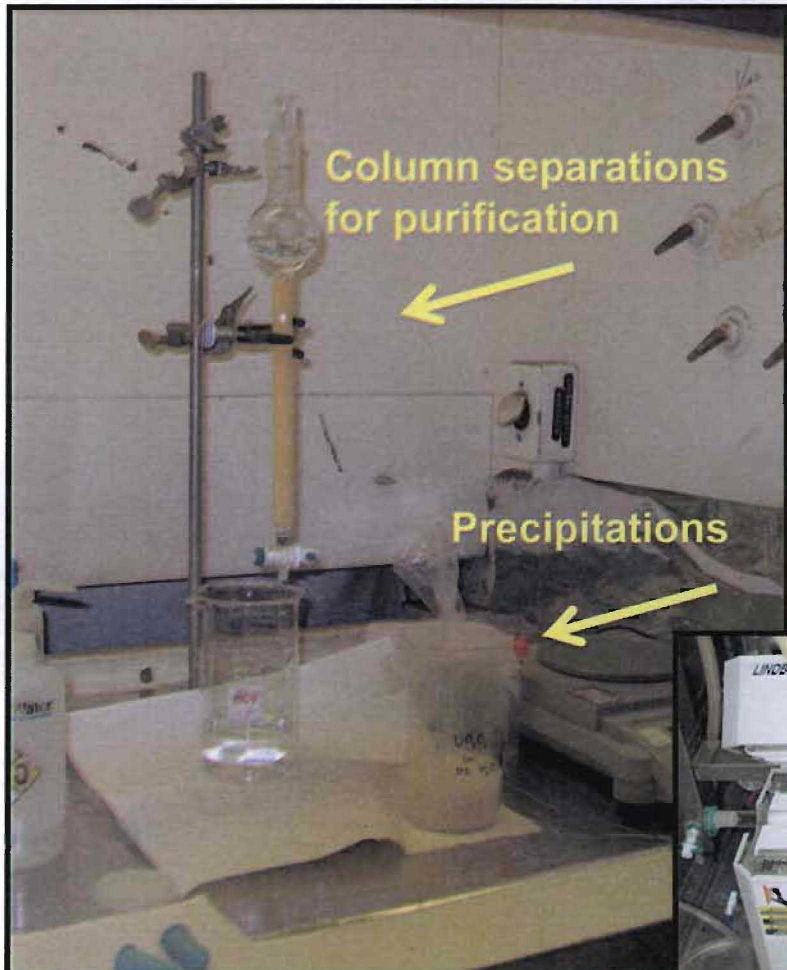


Dallas Reilly



Also,
- **Hanford Site** *Steve Conradson*
- **Rocky Flats Environmental Technology Site**
- **Mayak Nuclear Complex**
- **Australian Nuclear Science and Technology Organisation**

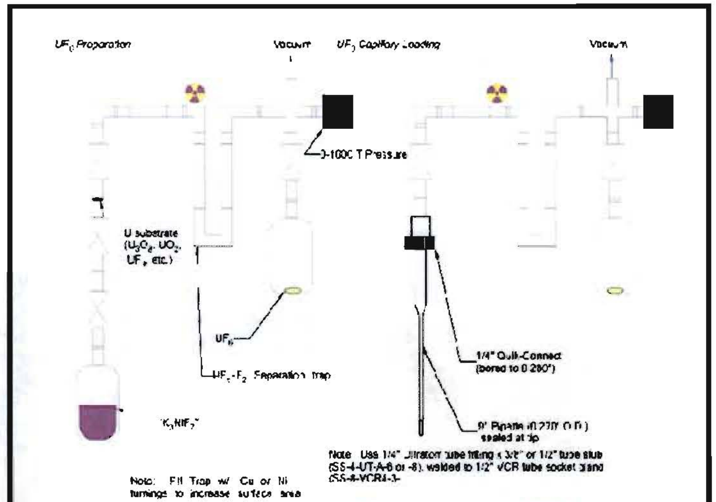
Progress under Goal 1: Prepare actinide materials (liquid/solid/gas)



Kevin Boland

Solid state chemistry

UF_6 preparation and hydrolysis

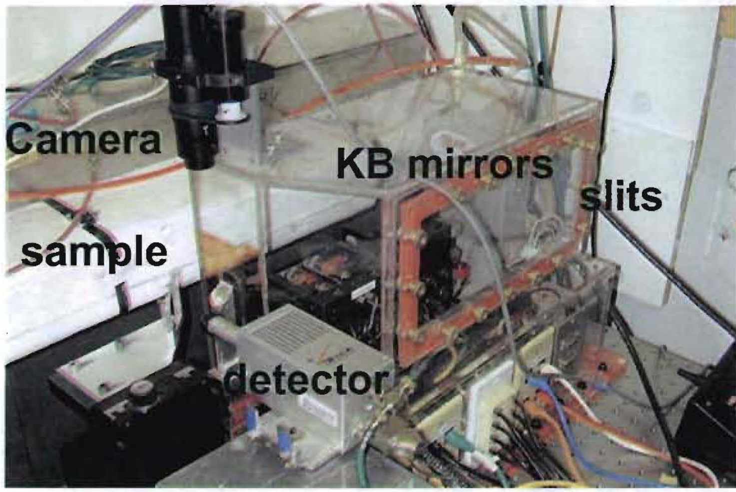


Scott Kinkead, Gregory Wagner

Hydrolysis of Pu/Ga alloy

24 hours 500 hours 1100 hours

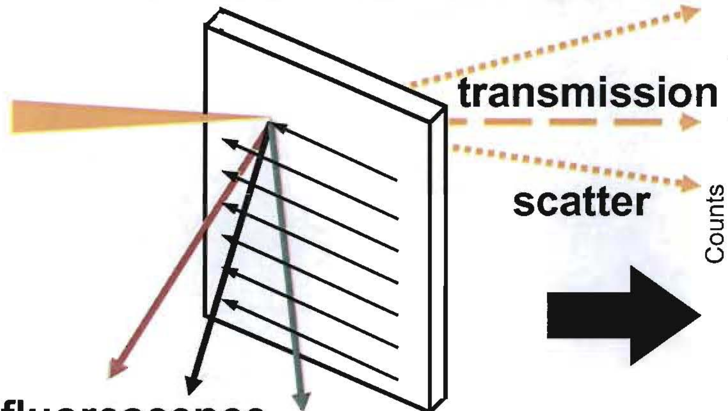
Jeremy Mitchell, David Hobart

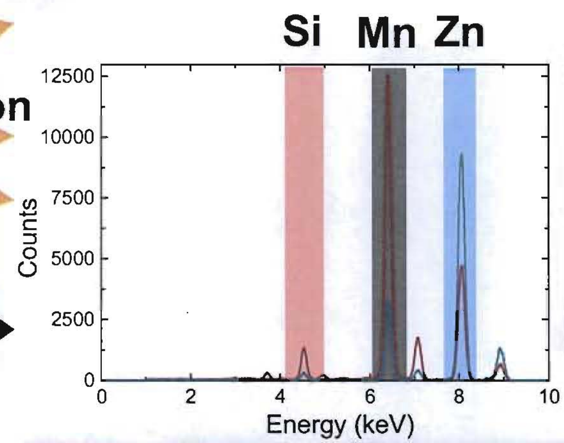


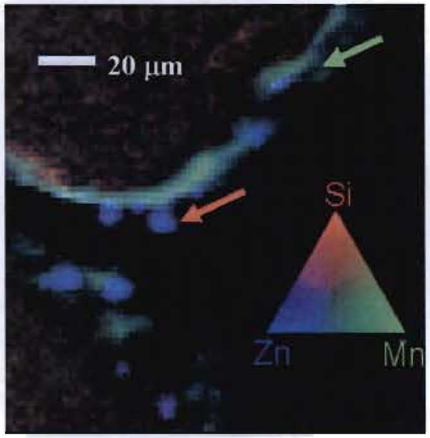
Progress under Goal 2: SSRL & microprobe spectroscopy

SSRL: Steven Conradson, Olga Batuk, Alison Costello, Dallas Reilly

ALS: Stosh Kozimor





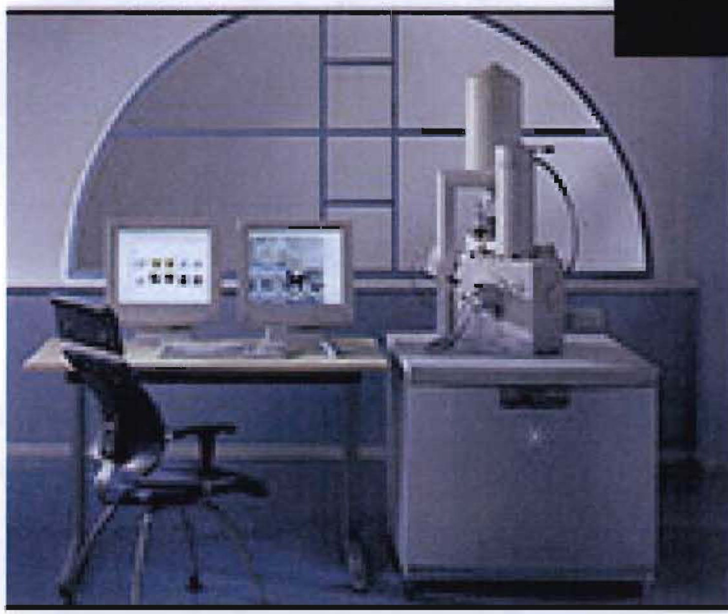


hours

Progress under Goal 2: Particle Manipulation (Capital Purchase FY10)

Field Emission Environmental Scanning Electron Microscope

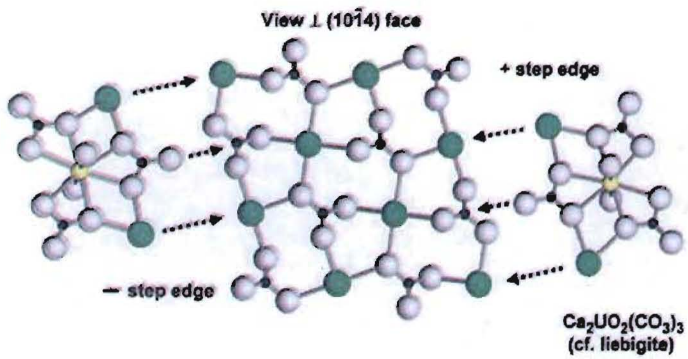
With DCG Systems Micro/nanomanipulator
- Interfaced with SEM
- Capability will be installed and developed by J. Bowen in FY2011

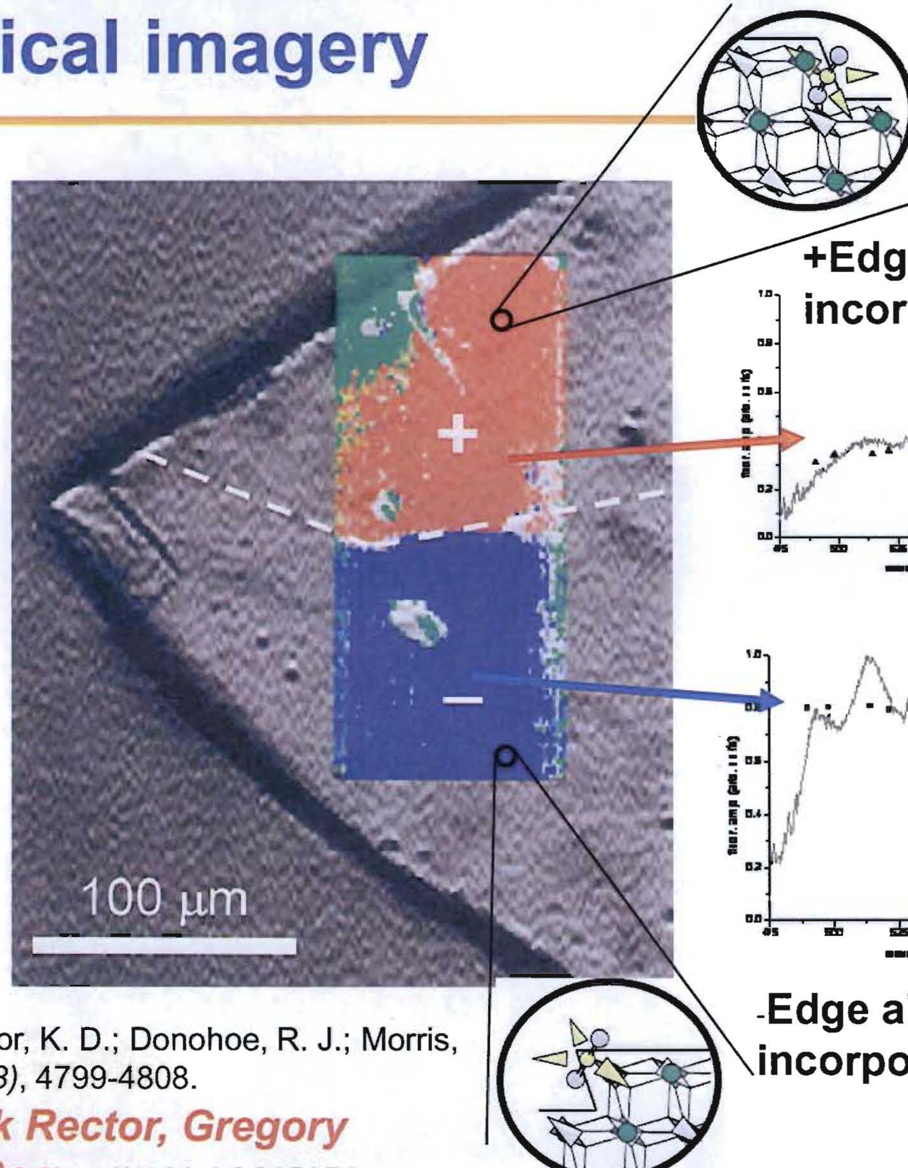


James Bowen and William Kinman

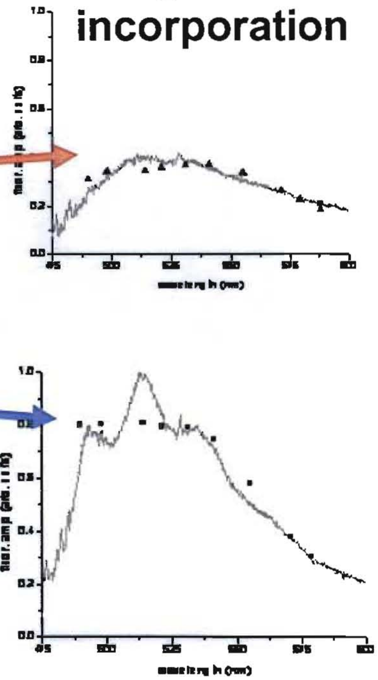
Progress under Goal 2: Capital Purchase FY10
Hyperspectral optical imagery

+/- step edge growth of $CaUO_2(CO_3)_3$





+Edge hinders UO_2 incorporation



-Edge allows easy incorporation

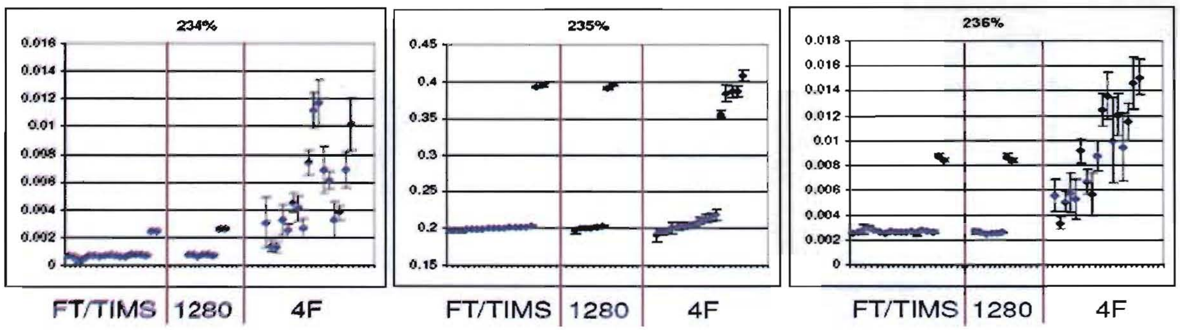
Manmade calcite crystal at step edge

Reeder, R. J.; Elzinga, E. J.; Tait, C. D.; Rector, K. D.; Donohoe, R. J.; Morris, D. E. *Geochim.Cosmochim. Acta* **2004**, *68(23)*, 4799-4808.

Heming He, Kirk Rector, Gregory Wagner, John Berg

Progress under Goal 2: 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



Lee Riciputi and Mindy Zimmer

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).**

Progress under Goal 2: Modelling and Theory

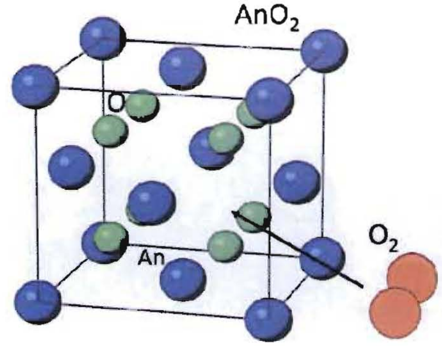
David Andersson

- Apply modeling to develop predictive capabilities to complement experimental efforts.

- Remaining questions regarding the structure of actinide oxides and the relation between various phases.

- Previous theoretical work (LDRD funded) investigated the static aspects of O clustering in UO_{2+x} for x<0.25. Here, expand to higher x (including U_3O_7, U_3O_8 and UO_3) and include finite temperature dynamics as well the effect of inhomogeneities such as surfaces present in particles.

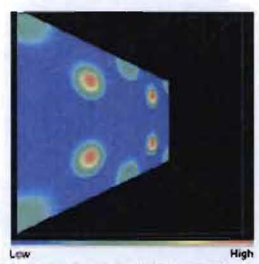
Problem to solve:

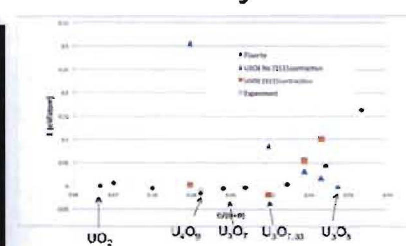


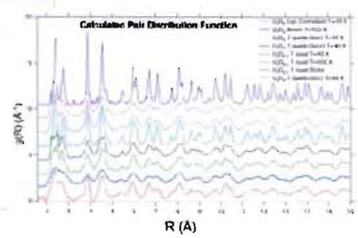
Supercomputer (maximum control of chemistry and extreme spatial and temporal resolution)

Predicted properties compared to experimental observables:

Electronic | Thermodynamic | Dynamics

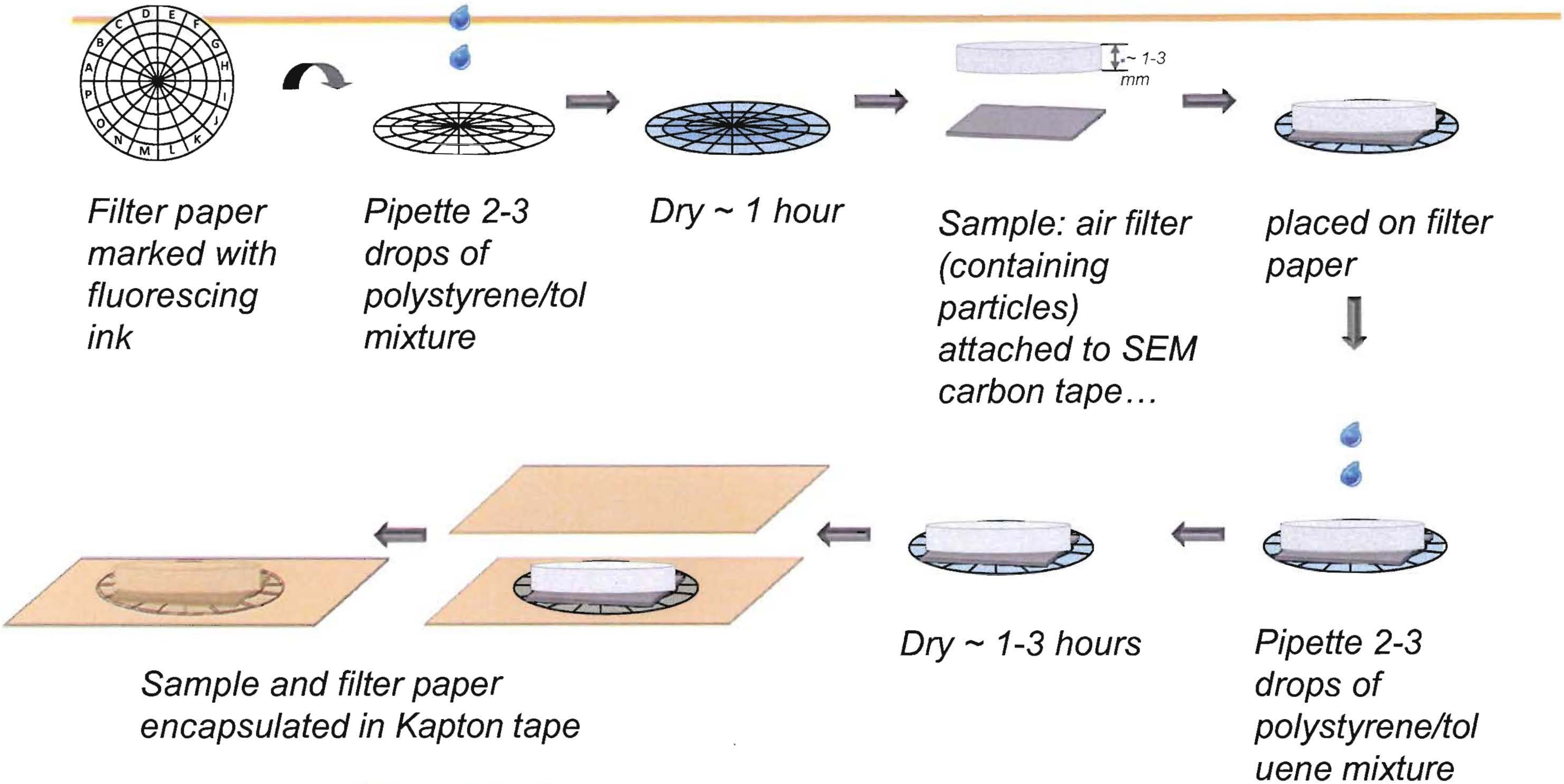






UNCLASSIFIED

Progress under Goal 3: Particle Registration and Containment



Alison Costello and Gregory Wagner

Progress under Goal 3: Complementary nature of measurements

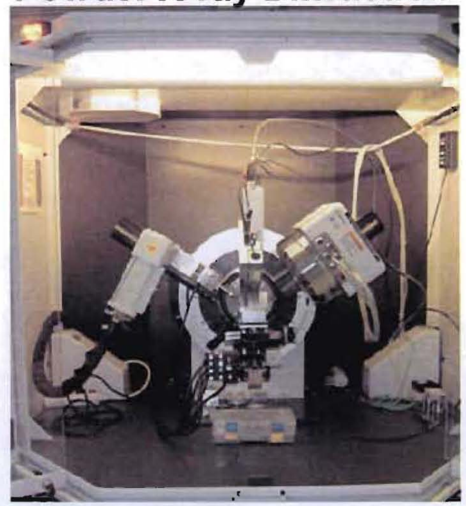
Is the value of one analytical measurement complementary another. Do different techniques that measure a given physical phenomenon yield the same information?

- **XRF versus XAS**
  - different sensitivities to different elements
  - pre-screening?

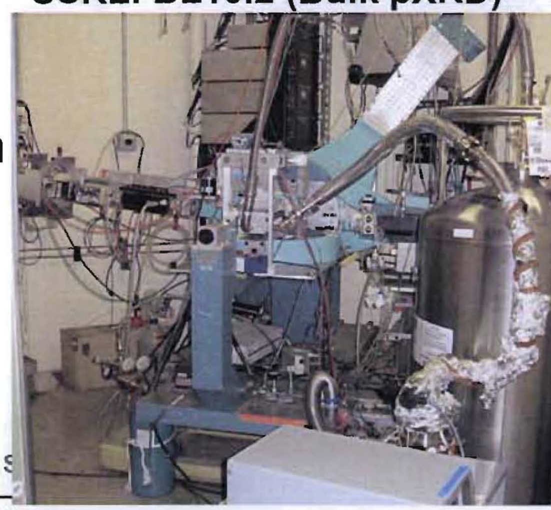
- **powder X-ray diffraction versus μ-XRD/μ-XANES/ μ-EXAFS**
  - ordered lattice versus local structure in disordered fraction
  - long range order versus short range order
  - error in analyses?

Are techniques complementary?

Powder X-ray Diffraction

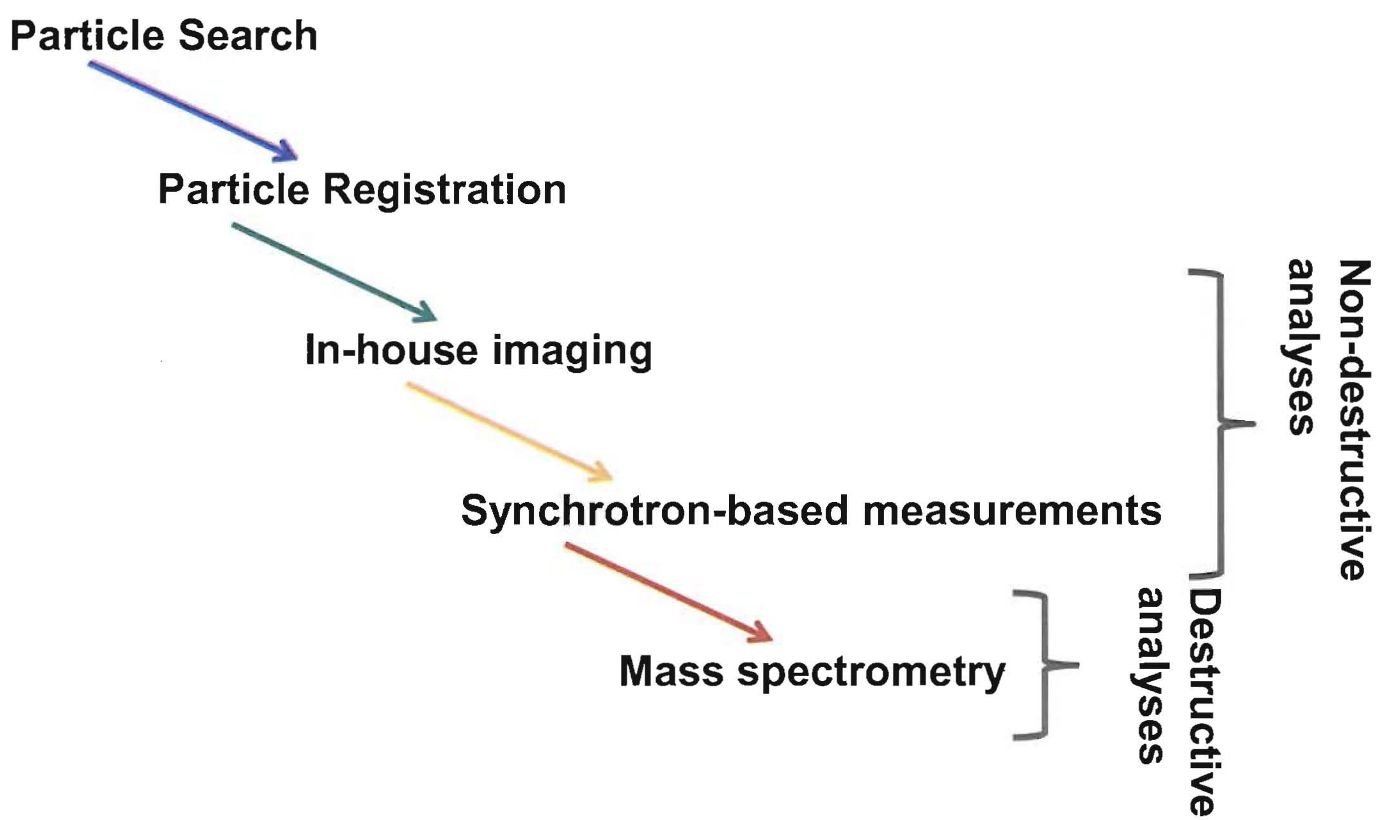


SSRL: BL10.2 (Bulk pXRD)



BL2.3 (particle XRD)

Progress under Goal 4: Complementary nature of between measurements, measurements/models



Why is it important to study *Molecular Forensic Science of Nuclear Materials* at LANL?

- LANL's three missions:
  - Ensure the safety, security and reliability of the U.S. nuclear deterrent
  - **Reduce global threats**
  - **Solve emerging national security challenges**

- LANL is poised to address complex R&D challenges in forensic science
  - History in U.S. Weapon's Complex
  - Pu Science and Research Strategy
  - Nuclear nonproliferation and related areas
  - Actinide process engineering and material science
  - Radioanalytical chemistry
  - Heavy Element Chemistry
  - Theory and Modelling
  - Environmental science and analyses

What makes *Molecular Forensic Science of Nuclear Materials* appropriate for LDRD funding?

- "LDRD at Los Alamos is the basis for science and technology excellence for the laboratory, and builds capabilities for future mission challenges." *LDRD Strategic Investment Plan*

- **Fundamental forensic science** crosscuts LANL's eight Grand Challenges

- "Need for new technology" to "maximize the potential impact of nuclear forensics"...

  Nuclear Forensics Role, State of the Art and Program Needs, Joint Working Group of the APS and AAAS

- **Detection and analysis** is key Objective in the ***Plutonium Science and Research Strategy***

  - *Signature definition, analysis & interpretation*
  - *Detection in challenging situations*

Major accomlishments in Year 1 !

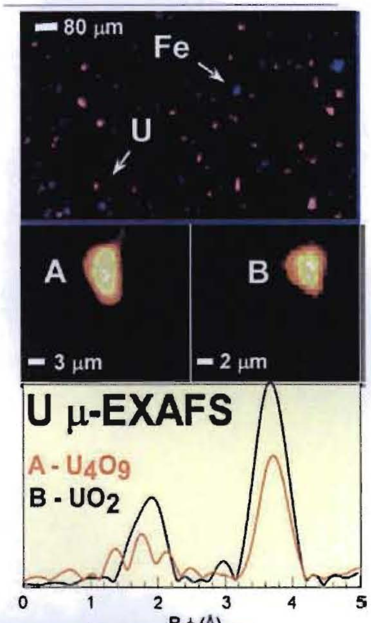
Science

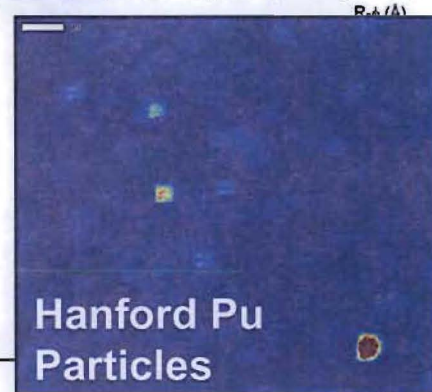
- **Proof-of-concept μ-spectroscopy**
  - high-purity particles
  - Environmental samples

(Chernobyl accident, Hanford waste, BOMARC fire)

- **Significant observations**
  - **Chernobyl**: structural relationships between Zr/U may reveal temporal evolution of reactor conditions
  - **Oxidation of Pu/Ga alloy**: Lattice parameters sensitive to oxidation
  - **Hanford Site**: Additional chemical species imaged, likely resulting from process chemistry

Uranium oxide particles





Major accomlishments in Year, cont.

Personnel
- Olga Batuk (MST-8)
- Alison Costello (MST-16)
- Heming He (C-PCS)
- Mindy Zimmer (C-NR)
- Dallas Reilly (UNLV)
- James Bowen (U. Cincinnati)

Collaborations
- Stepan Kalmykov, Irina Vlasov from Moscow State University
- Britt Salbu, Norwegian University of Life Sciences
- Lou Vance, Australian Nuclear Science and Technology Organisation
- Kenneth Czerwinski, University of Nevada – Las Vegas
- Samuel Glover, University of Cincinnati
- Andrew Felmy, PNNL
- Ruth Kips, Lawrence Livermore National Laboratory
- David Shuh, Advanced Lightsource-Lawrence Berkeley National Laboratory
- Sam Webb, Stanford Synchrotron Radiation Lightsource

Publications and Conference Proceedings

Andersson, A. D.; Espinosa-Faller, F. J.; Uberuaga, B. P.; Conradson, S. D. "Configuational stability and migration of large oxygen clusters in UO_{2+x}: Density functional theory calculations" *Manuscript in preparation.*

Batuk, O. N.; Vlasova, I. E.; Costello, A. L.; Kalmykov, S. N.; Conradson, S. D.; Wilkerson, M. P.; Clark, D. L. "Characterization of U and Pu oxide particles formed during the accident at the Chernobyl NPP by various spectroscopic and microscopic techniques" 2010 In *Plutonium Futures – The Science 2010.* (Keystone, Colorado, 19-23 September 2010). p. 89. LaGrange Park, Illinois: American Nuclear Society.

Bowen, J. M.; Kinman, W.; Selby, H. D.; Glover, S.; Spitz, H. "Characterization of residual plutonium particles extracted from soil contaminated by the 1960 BOMARC incident" *Manuscript in preparation.*

Bowen, J. M.; Kinman, W.; Smith, M.; Glover, S.; Spitz, H. "Method for identifying and isolating residual particles of plutonium in soil" *Manuscript in preparation.*

Conradson, S. D.; Costello, A. L.; Espinoa-Faller, F. J.; Hobart, D. E.; Mitchell, J. N.; Martinez, P. T. "Atomic scale mechanism of plutonium corrosion" 2010 in *Plutonium Futures – The Science 2010.* (Keystone, Colorado, 19-23 September 2010). p. 232. LaGrange Park, Illinois: American Nuclear Society.

Conradson, S. D.; Costello, A. L.; Hobart, D. E.; Martinez, P. T.; Mitchell, J.; Espinosa-Faller, F. "Atomic scale mechanism of corrosion of metallic Pu from X-ray absorption fine structure (XAFS) and synchrotron X-ray diffraction (XRD) measurements" *Manuscript in preparation.*

Daly, S. R.; Boland, K. S.; Kozimor, S. A.; Minassian, S. G.; Shuh, D. K.; Tyliszczak, T.; Wagner, G. L.; Wilkerson, M. P. "F K-edge X-ray absorption spectroscopy in nuclear forensics" *Manuscript in preparation.*

Felmy, A. R.; Cantrell, K. J.; Conradson, S. D. "Plutonium contamination issues in Hanford soils and sediments: discharges from the Z-Plant (PFP) complex. 2010 *Physics and Chemistry of the Earth.* **35** (6-8): 292.

Hobart, D. E.; Peterson, D. S.; Kozimor, S. A.; Boland, K. S.; Wilkerson, M. P.; Mitchell, J. N. "Diffuse reflectance spectroscopy of plutonium metal, alloys, and compounds". 2010. In *Plutonium Futures – The Science 2010* (Keystone, Colorado, 19-23 September 2010). p. 61. LaGrange Park, Illinois: American Nuclear Society.

Publications and Conference Proceedings

Reilly, D.; Batuk, O. N.; Costello, A. L.; Gostic, R.; Wilkerson, M. P.; Conradson, S. D.; Czerwinski, K. "Analysis of BOMARC plutonium hot particles with synchrotron techniques" *Manuscript in preparation.*

Reilly, D.; Boland, K. S.; Kozimor, S. A.; Wagner, G. L.; Wilkerson, M. P. "Na-22 generation from actinide fluorides" *Manuscript in preparation.*

Wilkerson, M. P.; Andersson, A. D.; Berg, J. M.; Boland, K. S.; Burns, C. J.; Clark, D. L.; Conradson, S. D.; Costello, A. L.; Hobart, D. E.; Kennedy, P. K.; Kozimor, S. A.; Martinez, P. T.; Mitchell, J.; Rector, K. D.; Reilly, D.; Riciputi, L. R.; Tandon, L.; Wagner, G. L. "Application of chemical structure and bonding of actinide oxide materials for forensic Science" *Institute of Nuclear Materials Management 51st Annual Meeting*. (Baltimore, Maryland, 11-15 July 2010).

Comparison to forensic work done by the international scientific community

Institute for Transuranium Chemistry – Karlsruhe

Norwegian University of Life Sciences

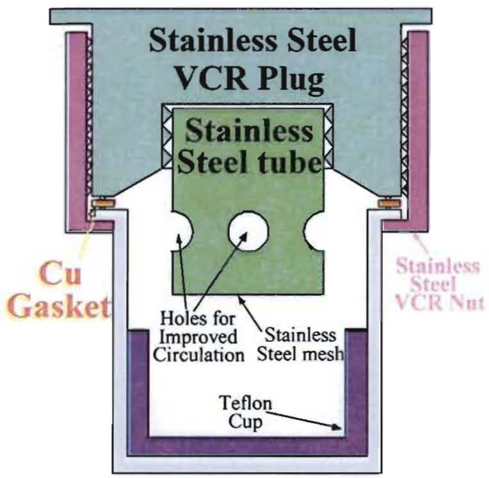
Lawrence Livermore National Laboratory

Beamlines at other facilities

Is, is it likely to influence or be taken over by programmatic efforts at some future time?

YES!!!

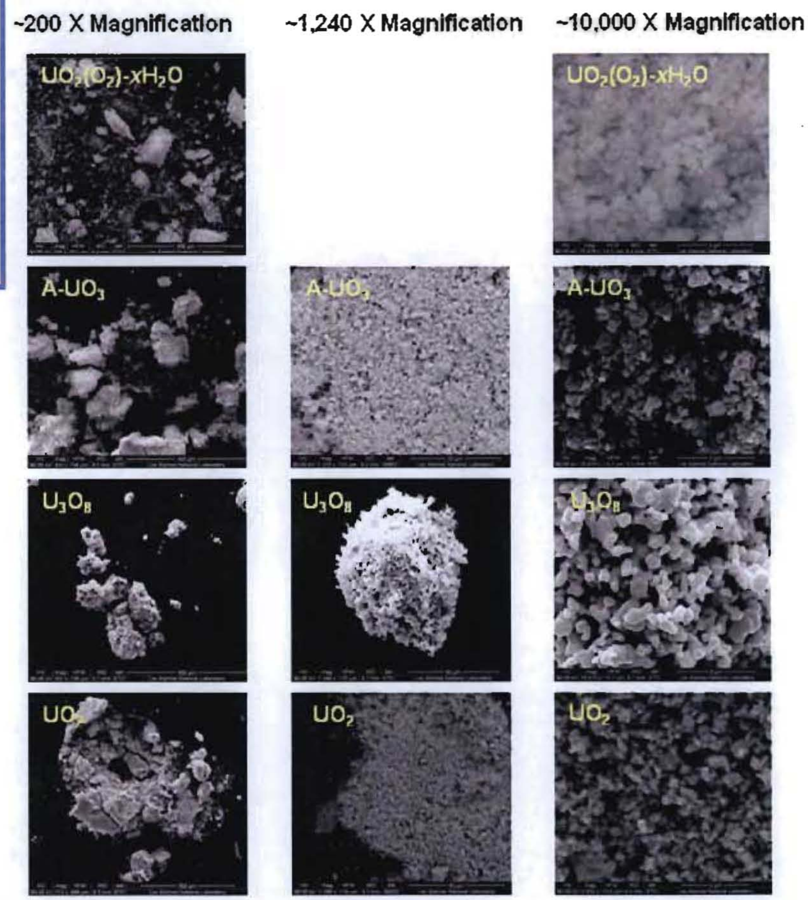
- Domestic Nuclear Detection Office/Department of Homeland Security
- ....
- ....



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

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

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



European Materials Research Society 2010 Annual Meeting in Warsaw, Poland

Research Plan and Deliverables through the end of the project

- Publish key papers in this field

- Develop capabilities to manipulate particles (J. Bowen and W. Kinman) and transfer between measurements (G. Wagner et. Al.)

- Hydrolysis of UF_6 (also in collaboration with R. Kips at LLNL)

- Hyperspectral imaging (Heming He)

- SIMS (Mindy Zimmer and Lee Riciputi)

- Extend measurements to Mayak samples, Rocky Flats Environmental Techology Site (already have bulk measurements), additional BOMARC samples, additional Czernobyl samples

Project cost

Actual, *projected*

	FY2010	FY2011	FY2012
Original Request	**$1,650k**	**$1,650k**	**$1,650k**
Budget	**$1,216.5k**	**$1,670k**	
Cost	**$1,181k**		
Staff Labor	$550k	$550k	*$550k*
PD, Students	$50k	$500k	*$500k*
Travel – conferences	$40k	*$95k*	*$100k*
Travel – experimental	$100k	*$300k*	*$300k*
Capital	$325k	*$75k*	*$50k*
M&S	$100k	*$150k*	*$150k*

Integration, Education and Training

Co Investigators
David Andersson, MST-8
John M. Berg, MET-1
Steven D. Conradson, MST-8
David E. Hobart, C-AAC
Scott A. Kinkead, WX-6
William Kinman, C-NR
Stosh A. Kozimor, C-IIAC
Patrick T. Martinez, C-AAC
Jeremy Mitchell, MST-16
Mark T. Paffett, MST-6
David Podlesak, C-NR
Kirk D. Rector, C-PCS
Lee R. Riciputi, C-NR
Brian L. Scott, MPA-MC

Students, Post Docs
Olga Batuk, MST-8
James Bowen, University of Cincinnati, C-NR
Alison L. Costello, MST-16 (converted to staff)
Heming He, C-PCS
Dallas Reilly, UNLV, C-NR
Mindy Zimmer, C-NR

Technologists
Kevin S. Boland, C-IIAC
Patrick Kennedy, MST-6
Gregory L. Wagner, C-PCS

Collaborators
Kenneth Czerwinski, UNLV
Andrew Felmy, PNNL
Richard Gostick, LLNL
Stepan Kaplmykov, Lomonosov Moscow State University, Moscow, Russian Federation
Robert C. Roback, EES-14
Brit Salbu, Norwegian University of Life Sciences
Hugh Selby, C-NR
David Shoesmith, University of Western Ontario
David K. Shuh, ALS-LBL
Mark Smith, C-NR
Lou Vance – ANSTO
Irinia Vlasova, Lomonosov Moscow State University, Moscow, Russian Federation
Sam Webb, SSRL

Programmatic Mentorship
David L. Clark, Director Seaborg Institute, Plutonium Strategy Leader
George A. Erickson, Program Director for GS-IA

Final Agenda for LDRD DR Review

Date: Thursday, 13 January 2011
Location: TA-3, Building 1415, Room 141

8:30 – 8:35 "Welcome and Introduction to the LANL LDRD Program" William Priedhorsky, Program Director of the LANL LDRD Office

8:35 – 9:05 "Project overview of *Molecular Forensic Science of Nuclear Materials*" Marianne P. Wilkerson (C-NR)

9:05 – 9:25 "Speciation, local structure and reactivity of actinide oxide materials" Steven D. Conradson (MST-8)

9:25 – 9:45 "Oxidation of UO_2 from density functional theory calculations: Evolution of U_4O_9, U_3O_7 and U_3O_8" David Andersson (MST-8) and Steven D. Conradson (MST-8)

9:45 – 10:05 "Particle Analysis using synchrotron microprobe techniques: m-XRD, m-XAFS and m-XRD" Alison L. Costello (MST-16), Olga Batuk (MST-8), David L. Clark (INST-OFF), Steven D. Conradson (MST-8), Stosh A. Kozimor (C-IIAC), Dallas Reilly (C-NR), and Marianne P. Wilkerson (C-NR)

10:05 – 10:20 Break

10:20 – 10:40 "Chemistry of Uranium Oxides: Fundamentals and Forensics Applications" Steven D. Conradson (MST-8), Olga Batuk (MST-8), and Alison L. Costello (MST-16)

10:40 – 11:00 "Chemistry of Plutonium Oxides: Fundamentals and Forensics Applications" Steven D. Conradson (MST-8), Alison L. Costello (MST-16), Jeremy Mitchell (MST-16), and Dallas Reilly (C-NR)

Final Agenda for LDRD DR Review, cont.

11:00 – 11:30 "Analysis of BOMARC Hot Particles" Dallas Reilly (UNLV, C-NR), Steven D. Conradson (MST-8), Richard Gostic (UNLV, LLNL), Alison L. Costello, (MST-16), Olga Batuk (MST-8), Marianne P. Wilkerson (C-NR), and Kenneth Czerwinski (UNLV)

11:30 – 11:40 "Collaborative Plans and Future Directions" Marianne P. Wilkerson (C-NR)

11:40 – 12:30 Poster Session and Lunch

"Planned Applications of Secondary Ionization Mass Spectrometry for *In-Situ* Isotopic/Chemical Characterization" Lee. R. Riciputi (C-NR) and Mindy Zimmer (C-NR)

"Controlled Hydrolysis of UF_6 for Forensic Analyses" Scott A. Kinkead (WX-6), Gregory L. Wagner (C-PCS), Stosh A. Kozimor (C-IIAC), Mark T. Paffett (MST-6), and Marianne P. Wilkerson (C-NR)

"Developing Light Atom XAS for Molecular Forensic Analyses" Stosh A. Kozimor (C-IIAC), Kevin S. Boland (C-IIAC), Scott R. Daly (C-IIAC), Stefan G. Minasian (C-IIAC, Advanced Light Source/Lawrence Berkeley National Laboratory), David K. Shuh (ALS/LBL), Tolek Tyliszczak (ALS/LBL), Gregory L. Wagner (C-PCS), and Marianne P. Wilkerson (C-NR)

"Hyperspectral fluorescence and Raman spectroscopy of forensic signatures in uranium oxides" Kirk D. Rector (C-PCS), Heming He (C-PCS), and Gregory L. Wagner (C-PCS)

"The Influence of Hyper-Stoichiometry and Defect Structure on Local Reactivity of UO_2" Heming He (C-PCS), and David W. Shoesmith (University of Western Ontario)

Final Agenda for LDRD DR Review, cont.

11:40 – 12:30	Poster Session and Lunch, cont.
	"Isolation of individual particles for analysis – Development of an electron microscopy nanomanipulation capability" James Bowen (University of Cincinnati, C-NR), William Kinman (C-NR), and Marianne P. Wilkerson (C-NR)
12:30 – 1:30	Review Committee Caucus and Out-brief
1:30	Adjourn