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The Chemical Form and Transformation Reactions of Plutonium in Hanford Soils and Sediments

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The Chemical Form and Transformation Reactions of Plutonium

- Objectives and scope

  - This project focuses on the identification of Pu contamination issues at Hanford and, wherever possible, identification of the chemical form of the disposed Pu and the subsurface transport mechanism.

- Research Tasks
  - **Task 1**: Comprehensive and on-going assessment of Pu contamination issues at Hanford and the acquisition of site specific materials
    - Literature review and coordination with other groups at the site

  - **Task 2**: Fundamental studies to determine the chemical form and reactivity of Pu
    - Experimental task utilizing both natural and model materials
    - Focused on identification of the chemical form and principal transport vector

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- **Current Status**
  - Task 1:
    - Literature on Pu disposal issues at Hanford
      - Cantrell and Reilly (1/08) reviewed the information available on Pu disposal from activities associated with the 200-PW-1/3/6 operable units (Plutonium/Organic-Rich Process Condensate Operable Units)
      - K. Cantrell currently extending this review to include the entire Hanford site
      - Completed a literature review of past analysis of crib samples collected from the 200 West area (PFP Complex)
    - Obtaining site specific materials
      - Obtained crib samples from two disposal cribs (Z-9 and Z-12) in the PFP complex
      - Obtained 46 subsamples from a drilling project that was conducted in 2004 to 2006 beneath the Z-9 trench

Importance: Pu discharges from the PFP complex largest source of Pu contamination at Hanford

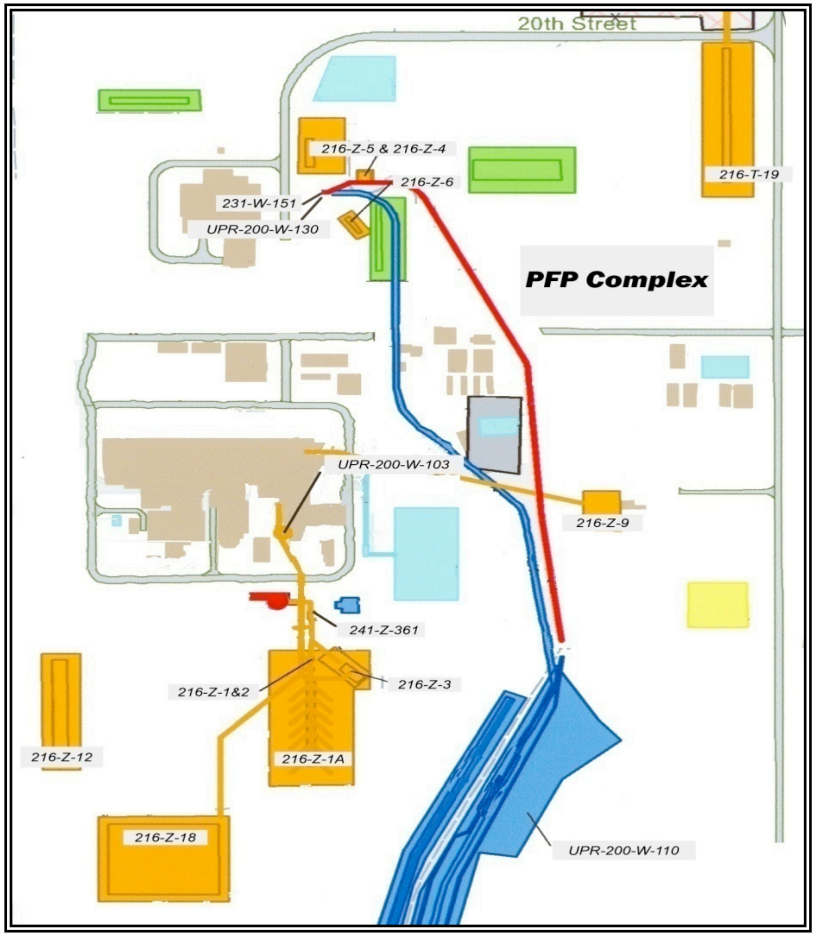

Figure 2. Waste disposal sites adjacent to the Plutonium Finishing Plant complex.

Z Complex "High Risk" Liquid Waste Streams

<u>High Salt Waste</u> Disposed to Z-9 trench, Z-1-A- tile field, and Z-18 crib

From RECUPLEX process (i.e. PUREX Solvent extraction with TBP and CCl_4)

<u>Low Salt Waste</u> sent to the Z-361 Settling Tank and then to Z-1, Z-2, Z-3, and Z-12 cribs

Conversions of Pu oxide to Pu tetrafluoride, essentially a dilute HF waste stream with Pu ions

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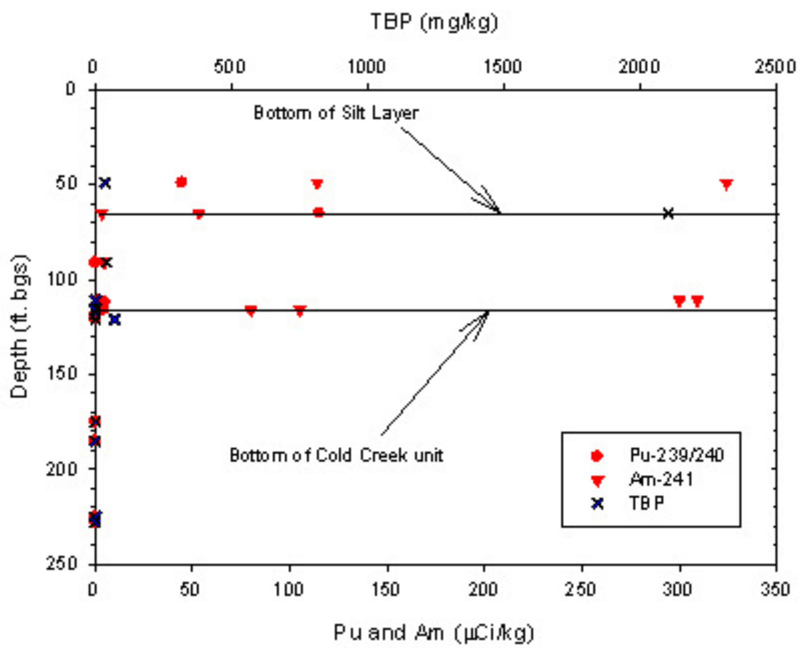
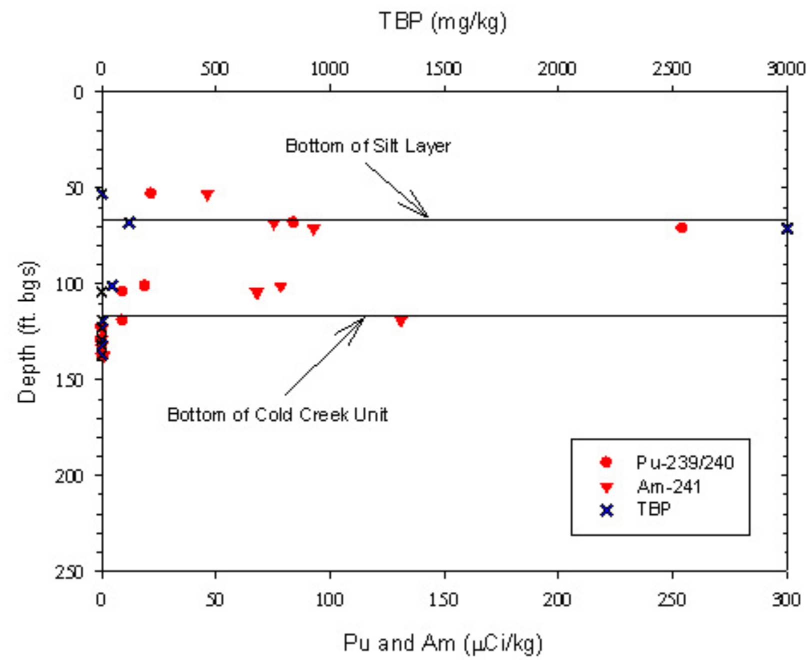
- Disposal at the PFP complex (High salt waste)
  - Large quantities of Pu disposed (max estimate168 kgs)
    - As particulate PuO_2 and as Pu(IV) species
    - Initial pH ~ 2.5; 4 million liters
  - Co-disposed chemicals
    - Tributylphosphate (TBP) and its breakdown products DBP and MBP
    - Other organics lard oil (glycerol fatty acids) – 60 tons
    - Co-solvents (CCl_4) – 300,000 liters
    - salts (nitrate, fluoride, aluminum)
- Resulted in Pu/Am migration deep into the subsurface

Vertical Distribution of Pu, Am and TBP in Boreholes 299-W15-46 and 299-W15-48 (2004-2006 Drilling)



Well 299-W15-46

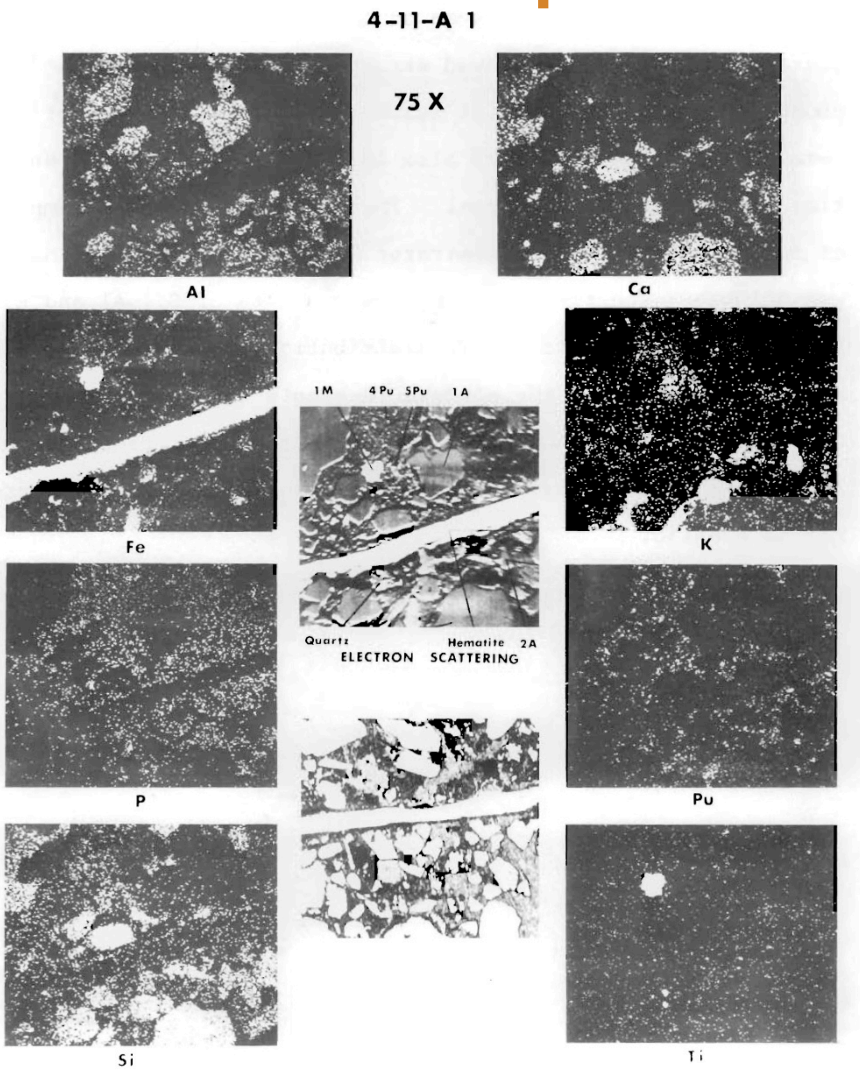


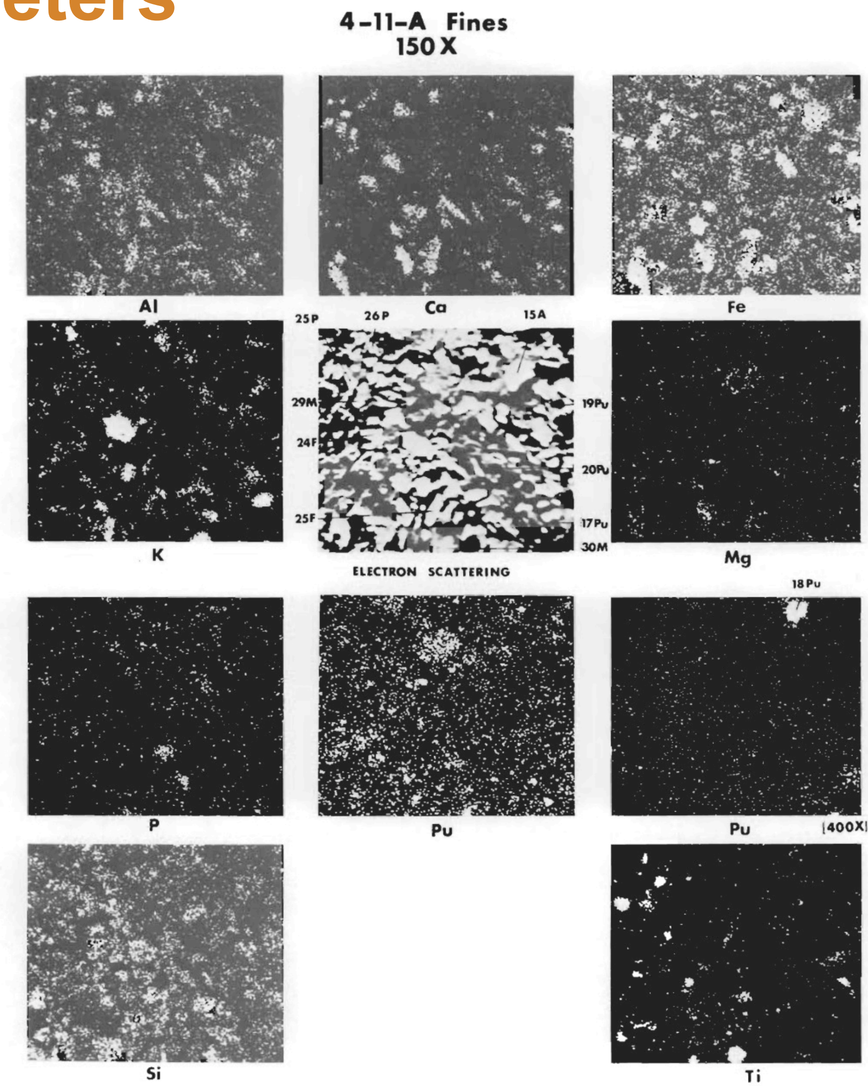
Well 299-W15-48

Analysis of Surface Sediments (Crib Samples) Top 60 Centimeters

- Samples taken from Z-9 trench in 1973 prior to a Pu mining operation conducted in 1977-78
  - Two 10.5cm cores diameter and 60 cm long
  - Cores were sub cored (2.5cm), dried, impregnated in plastic, and trimmed from the core with a diamond saw
  - Pu microprobe detection limit 0.3 wt%
- Represent the initial source term for subsequent vertical Pu transport

Core 4-11 - Top 5 Centimeters

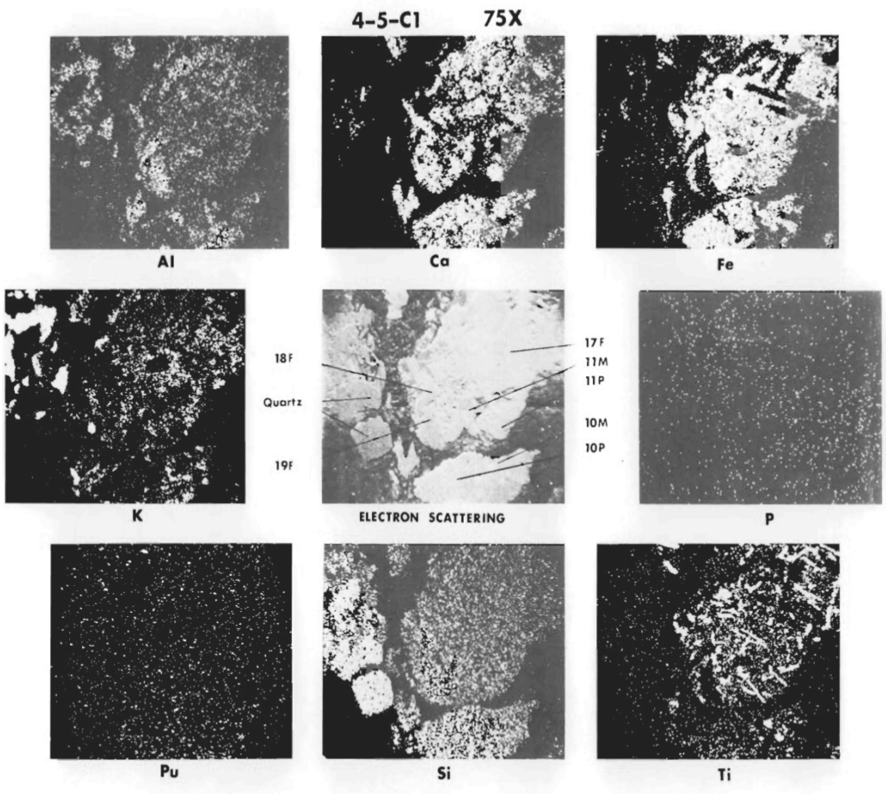




Pu content high – no association with hematite layer

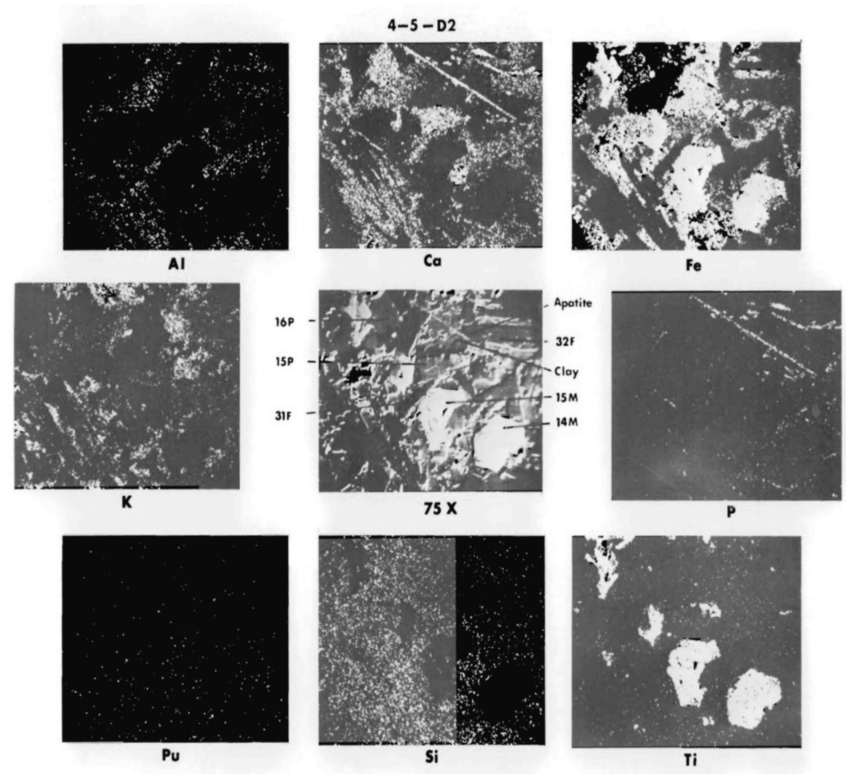
Pu occurs in two forms: large particles and smaller sized “precipitates’

Depth 30 – 32 cm



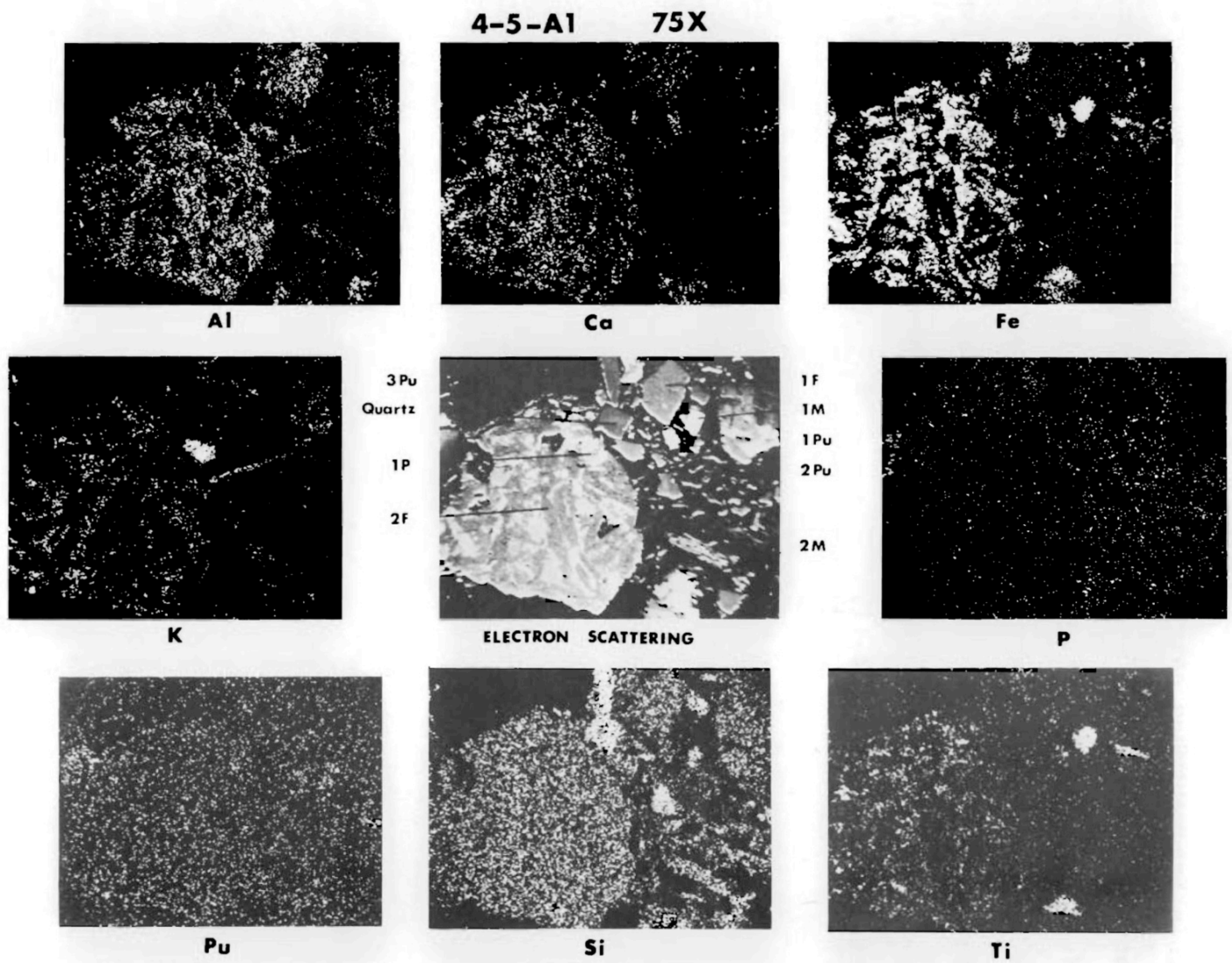
Pu lower - most correlated with P

Depth 48-50 cm



Pu content much lower, no association with the apatite layer

Core 4-5 Top 5 cm – P Concentrated in Plastic



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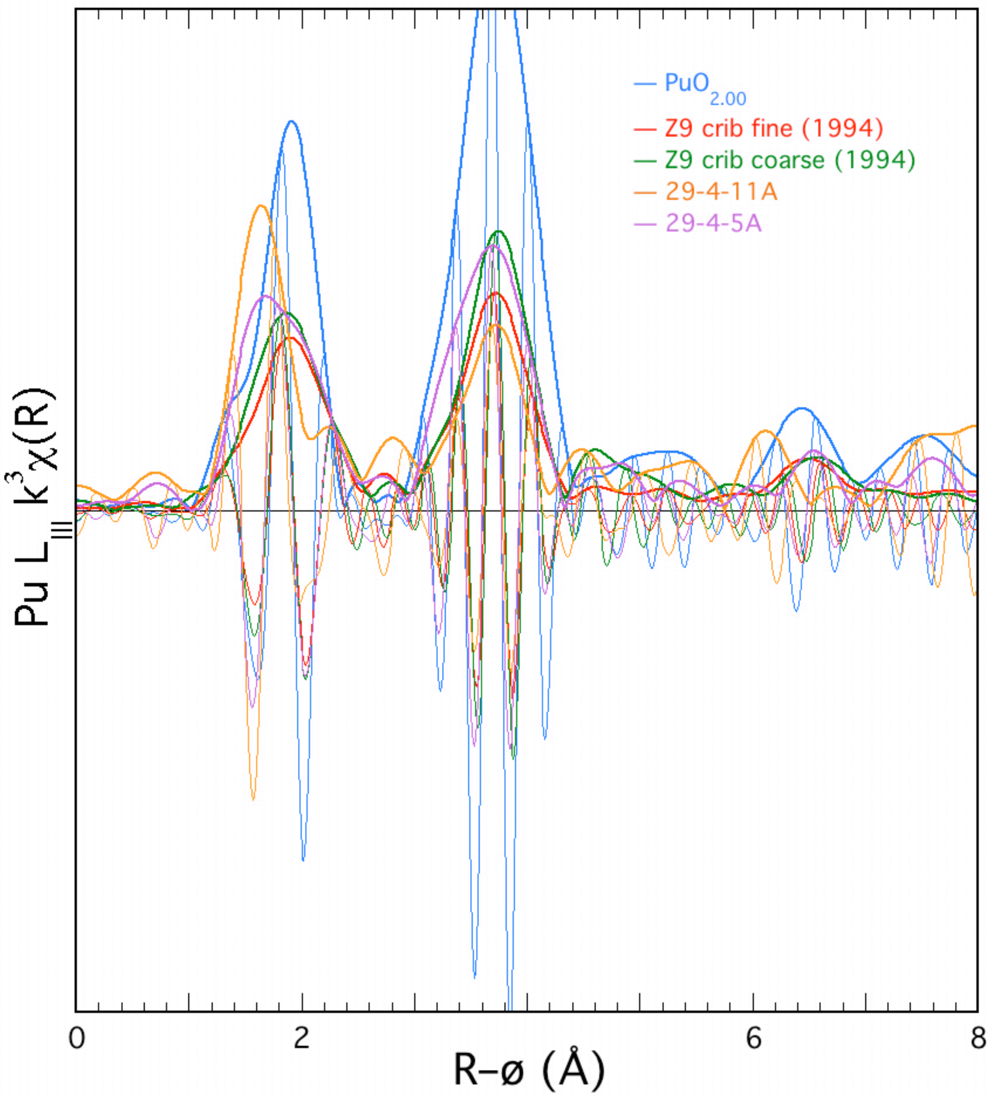
- X-Ray Absorption Spectroscopy (Steve Conradson)
- Six samples analyzed last week
  - 2 samples from the top 5cm of the Z-9 trench
  - 1 sample from the top of the Z-12 crib
  - 3 samples from core W15-48 (slant borehole)
    - Depth intervals (67-69’, 70-72’, 117-120’)
- Only initial analysis of data performed

EXAFS: Fourier Transform Representation



- The EXAFS clearly resembles PuO_{2+x} in being dominated by the nearest neighbor (nn) O (R~1.8 Å) and Pu (R~3.7 Å) peaks

- The Pu environment is disordered; no longer range structure (just noise) and reduced amplitudes for the Pu peaks

- The nn O distribution is complicated, being shifted to significantly lower R and asymmetric with multiple features

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- Potential Transport Mechanisms
  - Aqueous Complexation
    - Complexants present (DBP, MBP, F, acidic solutions) – no thermodynamic data for Pu(IV)-DBP or MBP
  - Colloid/nanoparticle transport – aqueous phase
    - Composition of PuO_2 particles and their surface charge unknown
  - Organic phase transport
    - Pu(IV) extracts by complexation with TBP, DBP, MBP, highly pH dependent – all data at high acidity
    - PuO_2 particles can adsorb DBP and MBP, form a hydrophobic surface coating and extract into organic phase

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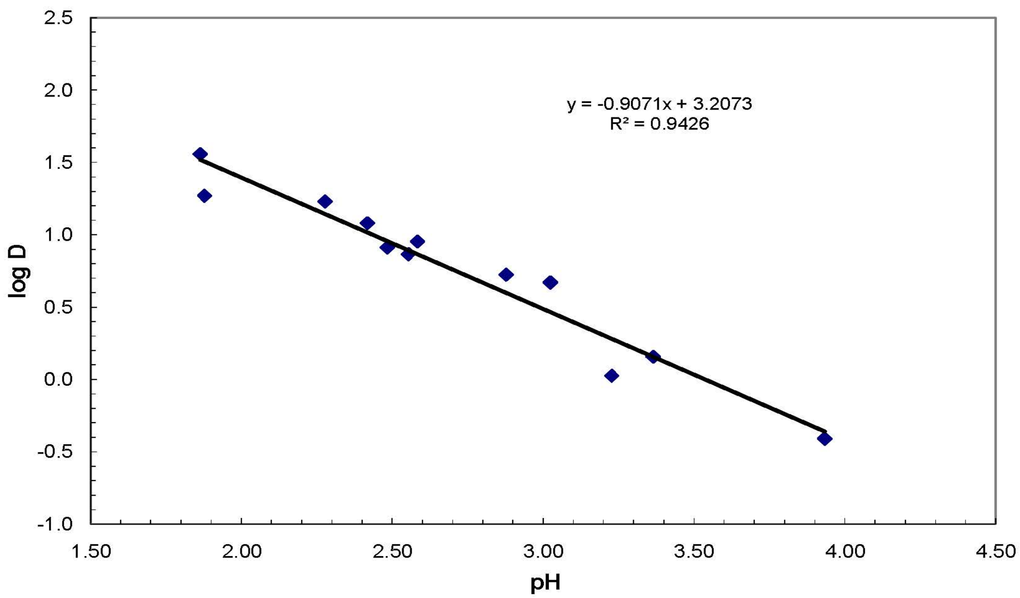
- Task 2: Mechanistic studies
  - Task 2a: Determine partitioning of soluble Pu(IV) between organic phase (CCl_4) and aqueous solution
    - Evaluate changes in DBP, MBP, and F concentrations as a function of pH



Initial indication DBP will favor aqueous phase complexation over organic phase above pH 3

Loss of total Pu at higher pH. – precipitate formation

Extraction of Pu(IV) by 0.001 M DBP in CCl_4 as a function of pH at I = 1.0 M of $NaNO_3$ and at room temperature. The distribution coefficient, D, equals the ratio of the concentration of Pu in the organic phase divided by the concentration in the aqueous phase. Negative log D values indicate the majority of the Pu is in the aqueous phase

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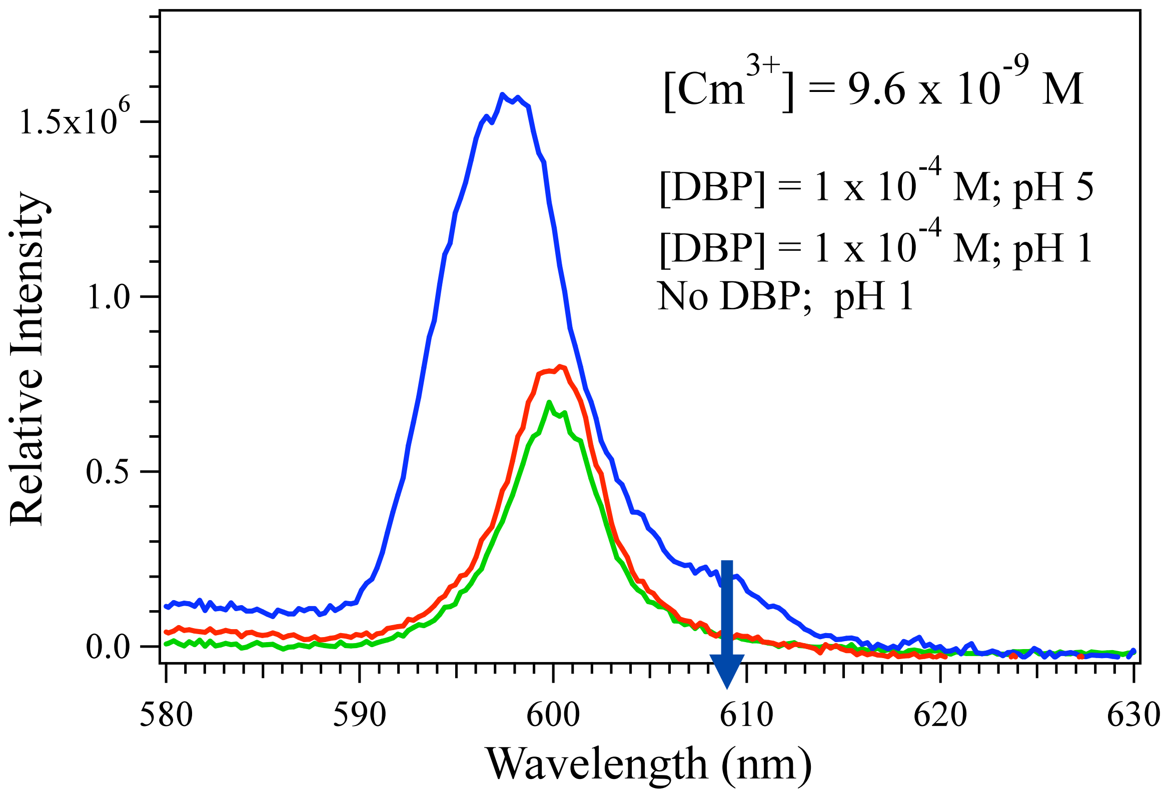
- Pu(III) or Am(III) transport?
  - Aqueous complexation by DBP or MBP?



Cm(III) Fluorescence spectra With and Without DBP, 10^0K

In the presence of DBP at pH 5, the spectra were more intense and a weaker peak at 609 nm appears

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- Current studies
  - Continuing literature review of Pu contamination – K. Cantrell
  - Working with Jim McKinley to prepare core and crib samples for microprobe and autoradiography analysis
  - Working with Herman Cho to conduct ^{31}P NMR studies of core samples
  - Fluorescence studies of Cm(III) – DBP, MBP
  - Uptake of TBP and MBP on ThO_2 (then PuO_2) and the impact on partitioning into the organic phase
- Synergies with other activities
  - Possible Transuranic Scientific Focus area

Milestones and Deliverables

- Presentation at MIGRATION 2009 on Pu migration issues.
  - Paper in Radiochimica Acta as part of the conference
  - Special session on Hanford subsurface issues
- Characterization paper on Z-9 crib samples
  - XAS and other characterization data
- Submit a paper on the co-association of organics with the surface of ThO_2 and PuO_2
  - Impact on surface charge, partitioning between solvents, and surface-organic coordination
- Submit a paper on Pu(IV) partitioning between aqueous and organic phases
- Cm(III) – DBP/MBP Complexation?

Questions?

Water Extract Data (Core W15-48) Anions and Totals

Depth (BGS)	pH	NO_3 (mg/l)	P (mg/l)	SO_4(mg/l)	Alkalinity mg/l $CaCO_3$	Organic C (total ug/g)	Inorganic C (ug/g)
57-59’	7.7-7.9	<100	9.2	323	82	600	<200
59-61’	7.3-7.9	<100	30	238	129	2,500	<200
85-87’	4.6-5.4	5,380	<7	160	<24	500	<200
101-102’	8.0-8.1	566	<7	<150	119	500	550
104-106’	8.1-8.1	746	<7	157	125	<200	2,900
Groundwater	8.04	9	0	71	187		

Water Extract Data (Core W15-48)
Cations

Depth (BGS)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Mn (mg/l)	Pu (uCi/kg)	Am (uCi/kg)
57-59’	101	21	50	<15	1.1	92 (1,750)	<2000
59-61’	120	21	77	<15	0.9	231 (1,003)	<2000
85-87’	449	220	1,000	90	40	<38 (47)	<2000
101-102’	165	20	104	<15	<0.1	<42 (<40)	<2000
104-106’	132	16	241	30	<0.1	<40 (<40)	<2000
Groundwater	60	22	24	8			