Electron and X-ray Microscopy of Process Pond and Vadose Zone Sediments

James McKinley

Pacific Northwest National Laboratory

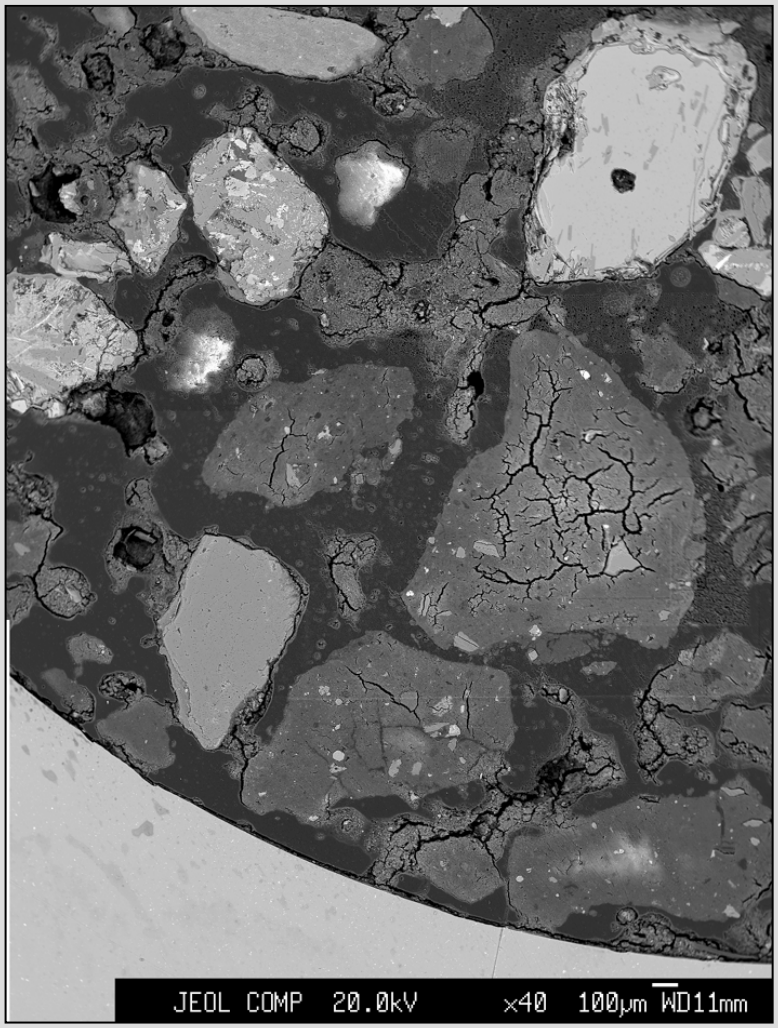
Microscopic Examination of Contaminated Sediments

- Process pond history makes the prediction of solid-phase chemistry and the impact of waste on contaminated sediments difficult
  - Uranium disposed in acidic and alkaline solutions/suspensions
  - Aluminate sludge disposed at high pH
  - NaOH added to limit Cu mobility
  - Fly ash dumped along with many other chemical wastes
- Detailed examination of impacted sediment may determine
  - Uranium phase distribution
  - Relation of U phases to waste-induced alteration/mineralization
  - Variation of U occurrence with depth
  - Source term for future uranium release and migration

Experimental Methods

- Sediments
  - Process Pond Sediment, e.g., NP4 depth 1'
    - Green staining, U: 3000 mg/kg (13 mmol/kg)
  - Contaminated Vadose Zone Sediment, e.g., NPP Pit 2 depth 0.5'
    - U: 12 - 238 mg/kg (0.05 - 1 mmol/kg)
- Preparation
  - Sediments imbedded and sectioned
  - Sediments as received
- Instrumentation
  - X-Ray Microprobe: detection limit 1 mg/kg, optical resolution 5,000 - 10,000 nm, (EXAFS capability)
  - Electron Microprobe: detection limit 50 - 100 mg/kg, optical resolution 6 nm
  - Scanning electron microscope: detection limit 1000 - 5000 mg/kg, optical resolution 1.2 nm

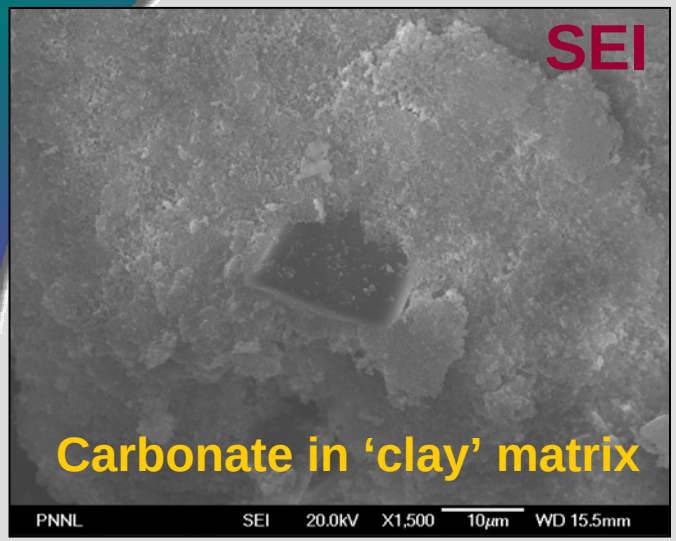
Backscattered Electron Image of Sectioned Process Pond Sediment

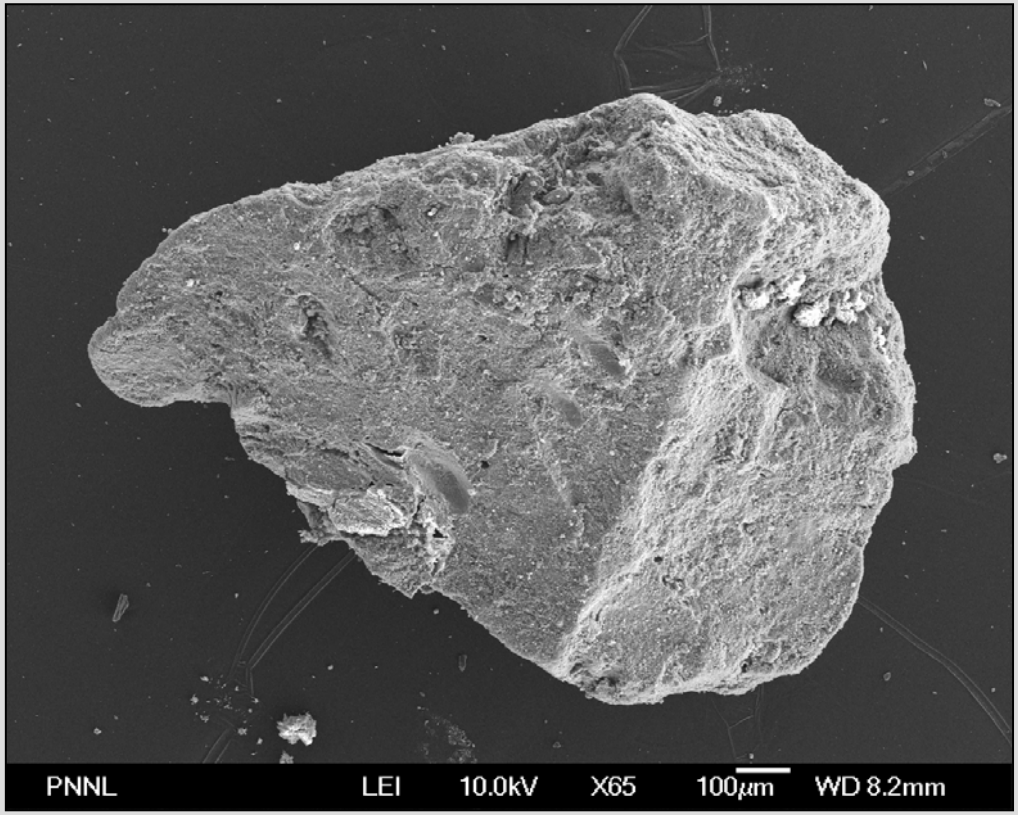


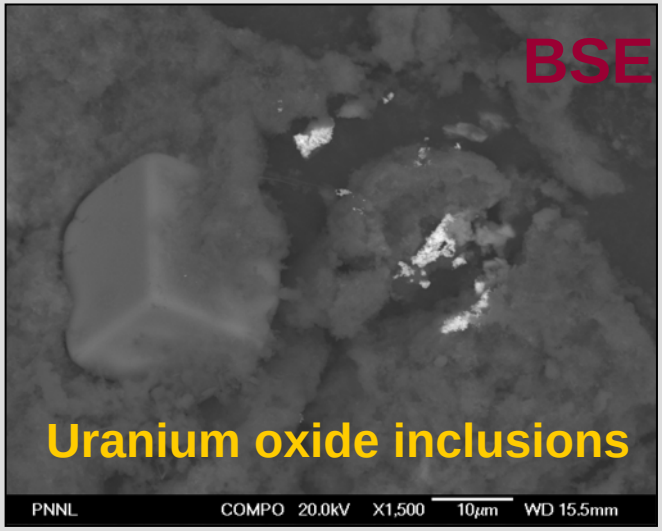
- Abundant clasts of secondarily precipitated material
- Compositionally heterogeneous clast-to-clast
- Heterogeneous assemblages of material representing multiple precipitation events
- 'Smectite' composition: Si, Al, O, with other components, Cu, Fe,...
- Dessicated internally
- Sediments tinted green

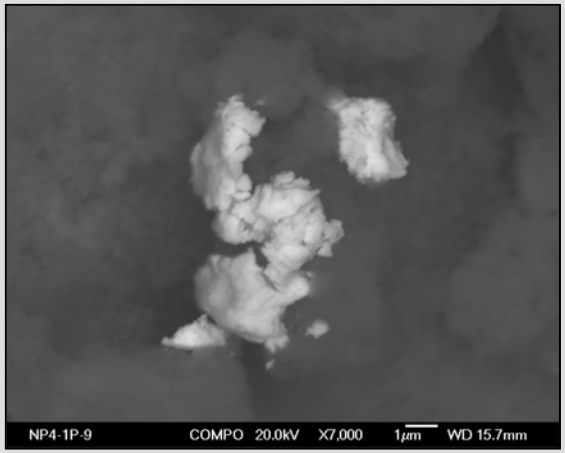
NP4-1

Particles Isolated from North Process Pond Sediment









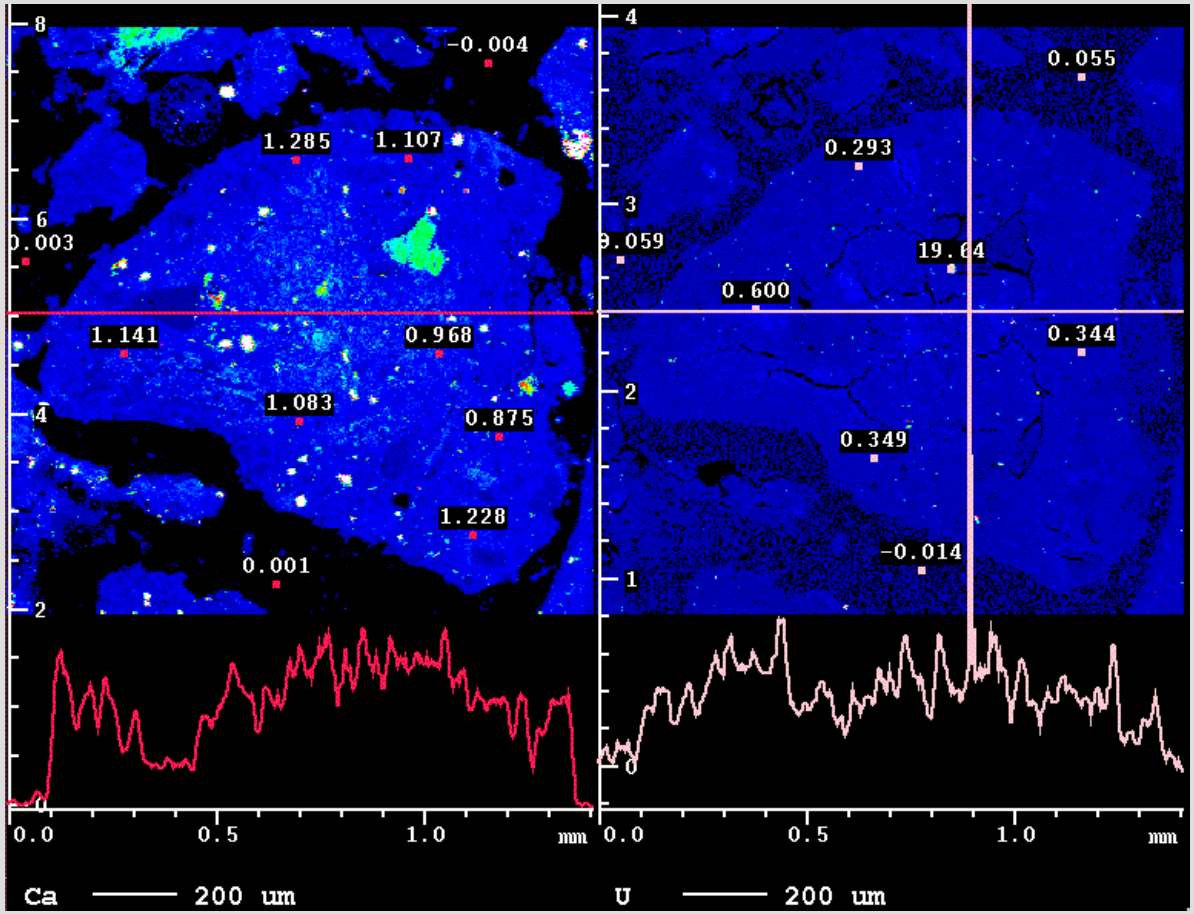
NP4-1

Clasts:

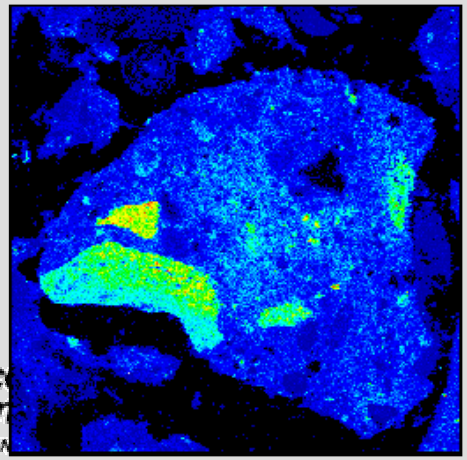
- Indurated (calcite)
- Secondary clay min.
- U oxide inclusions

Electron Microprobe Elemental Distribution Maps for North Process Pond Sediment in Thin Section

- Ca and U distributed throughout grain
  (Ca: Calcium Carbonate)
- U-rich inclusions
- Majority of U is in low concentration
- U and Cu are not correlated (not in single phase)



Cu



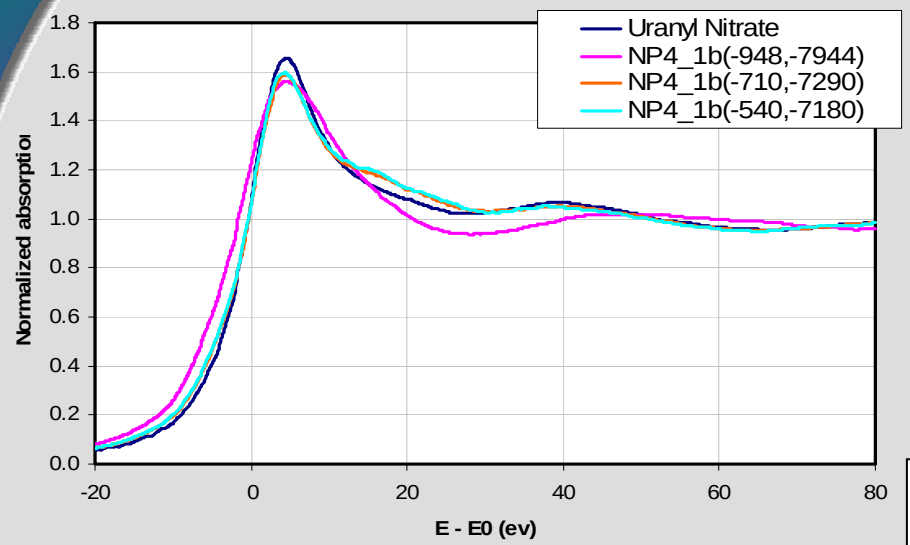
Calcium

Uranium

--- 3000 mg/kg ---

NP4 - 1

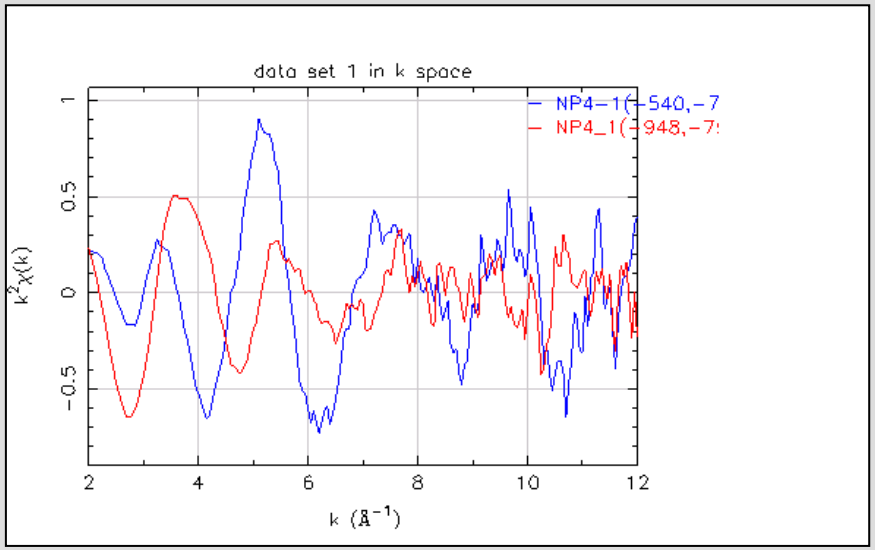
X-Ray Microprobe Spot Measurements on North Process Pond Sediment Thin Section



XANES ANALYSES

- **Multivalent, U(IV) and U(VI)**

NP4 - 1

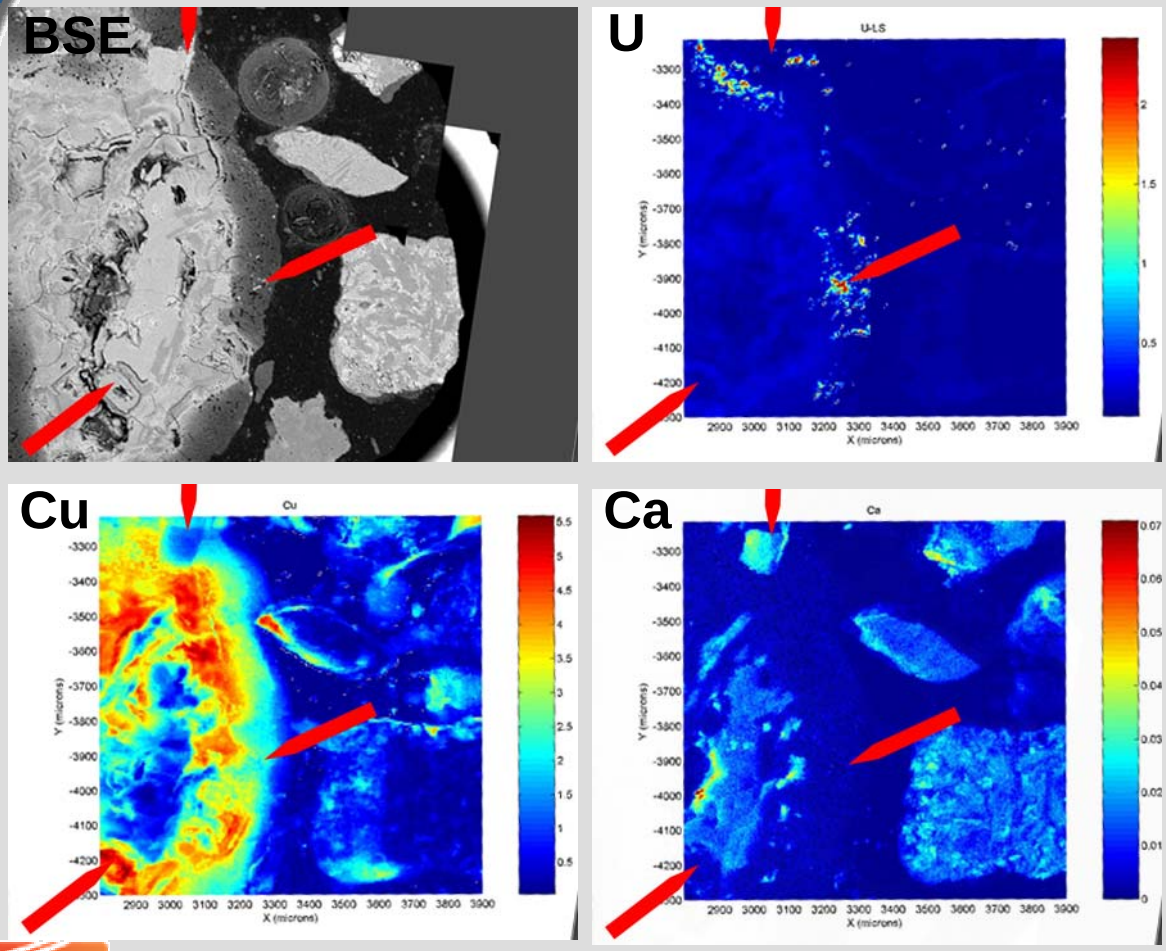


EXAFS ANALYSES

- **U(IV) phase 8 O at 2.25 A**
- **(UO_2 has 8O at 2.37 A)**
- **U(VI) phase 2 short, 6 long bonds with O**

Upper Vadose Zone Sediment (0.5’ bgs)

--- 238 mg/kg U ---

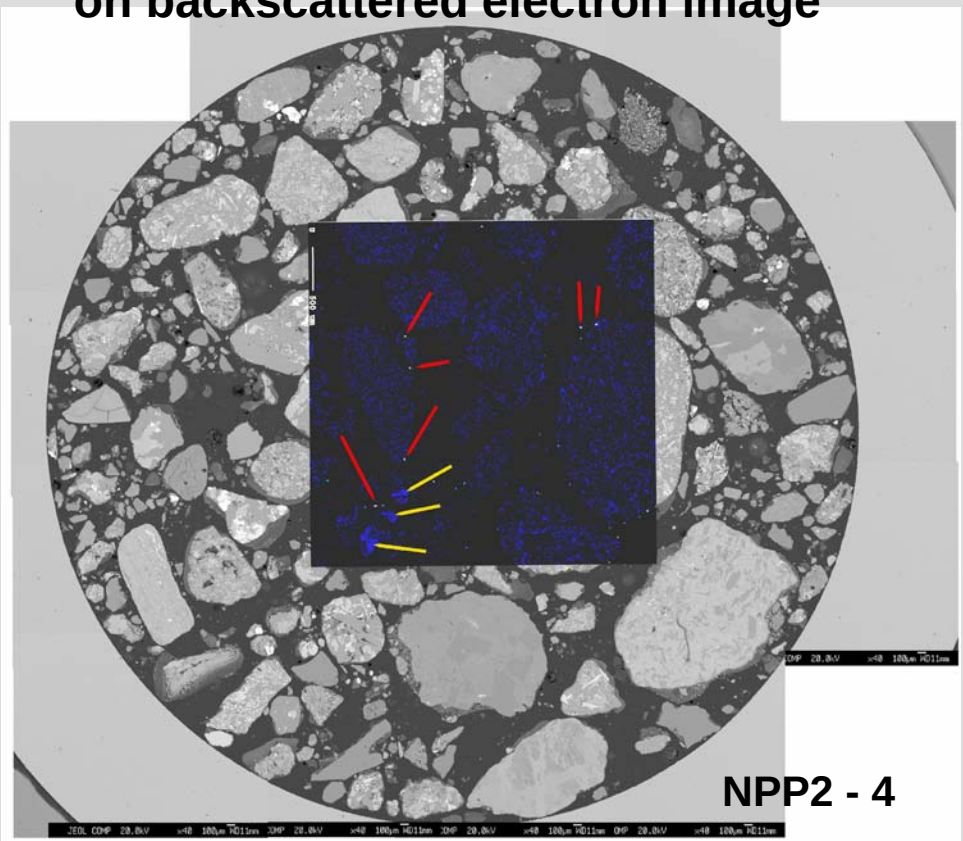


NPP2 - 0.5’

- Secondary precipitates less common
- Core includes Cu, Fe (base treatment to limit Cu mobility)
- U inclusions in aluminosilicate ‘rind’ on precipitate clast
- Multiple or varying precipitation environment
- U, Cu, and Ca do not correlate, but
- Low U associated with low Ca

Intermediate-Depth Vadose Sediment (4' bgs)
--- 139 mg/kg U ---

Electron microprobe U abundance map on backscattered electron image

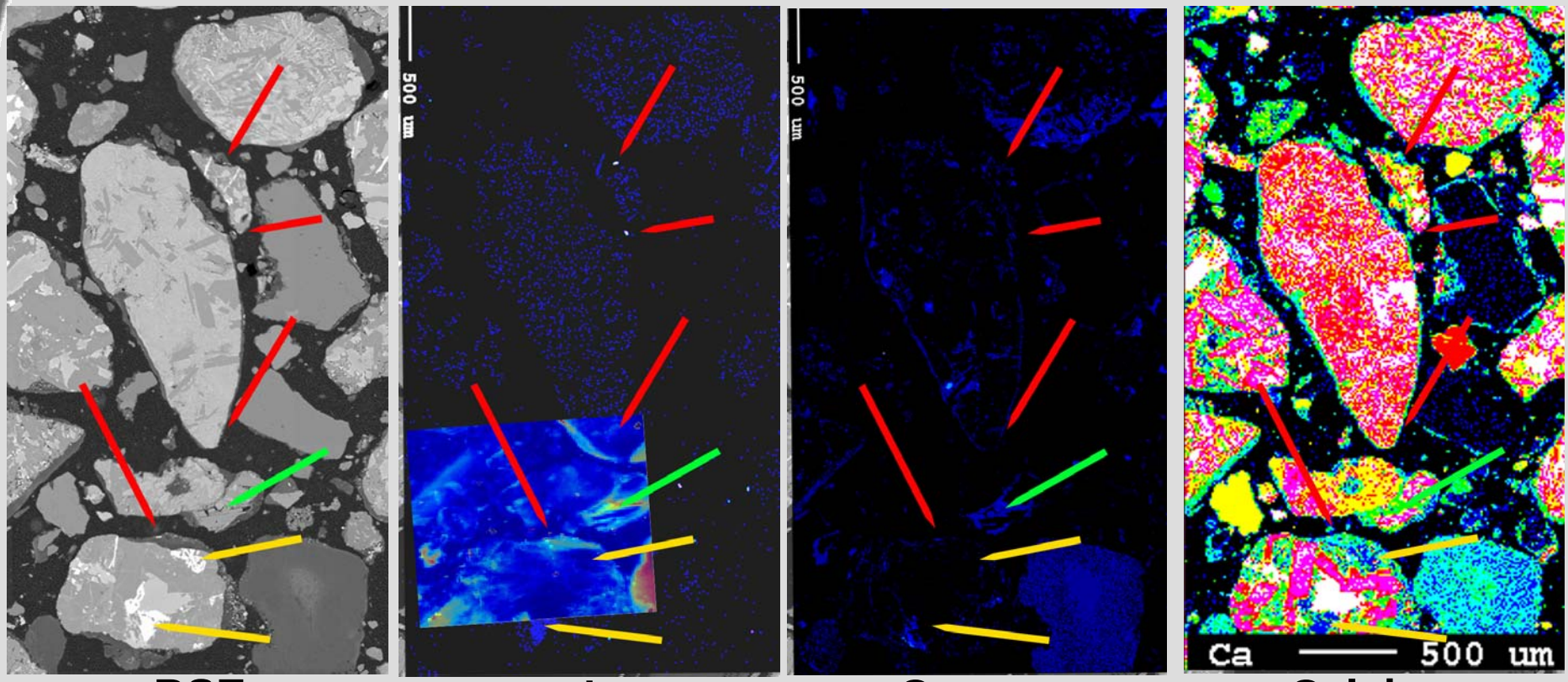


- **Secondary precipitate clasts uncommon**
- **Primary clasts coated with secondary aluminosilicate rind**
- **Uranium precipitates imbedded in secondary mineralization**

Elemental Abundances in Intermediate Depth Vadose Zone Sediment (4' bgs)

- U(VI) discrete microscopic inclusions in aluminosilicate rinds (Red Arrows)
- Low-level U(VI) present in aluminosilicate rinds (Green Arrow)
- Cu associated with low-level uranium in aluminosilicate rinds
- Low-level U associated with (Ca: calcium carbonate)

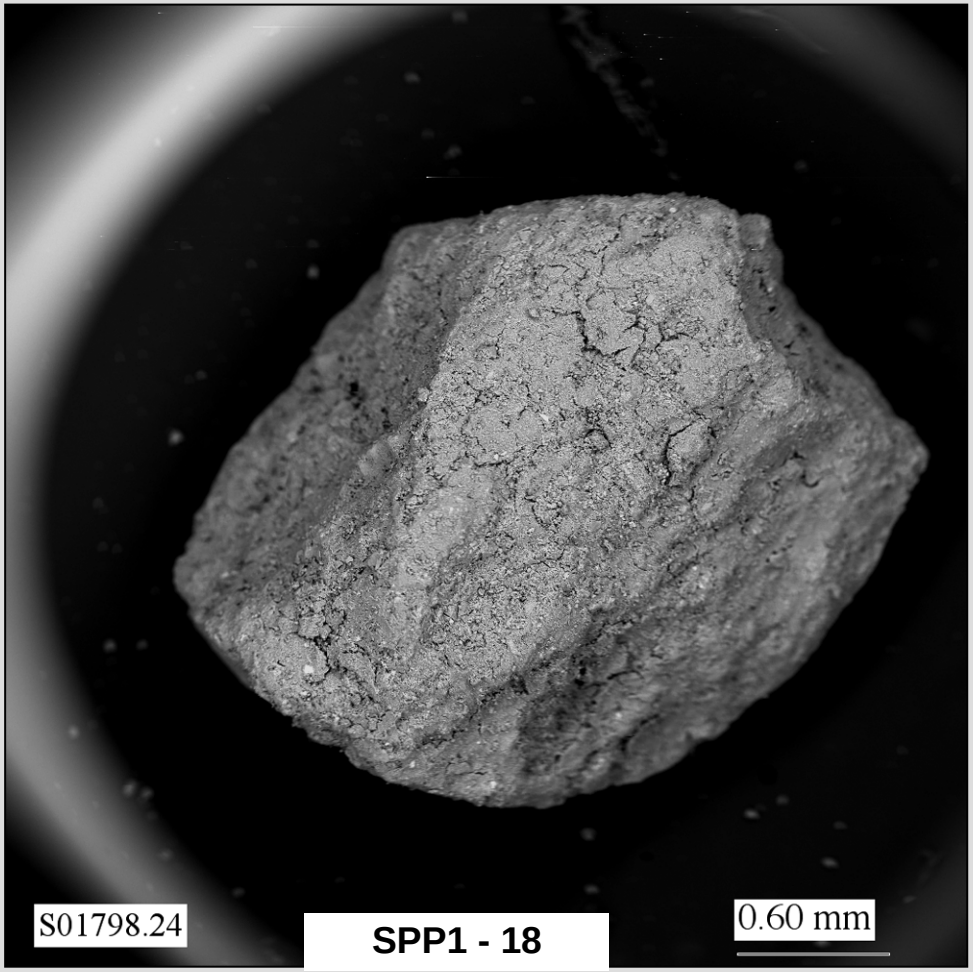
NPP2 - 4



BSE | Uranium | Copper | Calcium

--- 139 mg/kg ---

Deep Vadose Zone Sediment (18' bgs)
--- 12 mg/kg U ---



SPP1 - 18

- Secondary surface precipitates even at this depth
- No uranium observed, yet

Summary

- Process Pond Sediments
  - Most U associated with (calcium carbonate) and aluminosilicate mineralization at very low concentration
  - Discrete reduced phase (UO_2) imbedded in precipitates
- Upper Vadose Sediment
  - Similar to NP; low-level U with (calcium carbonate)
  - Discrete U(VI) oxides segregated in aluminosilicate rind
- Intermediate Vadose Sediment
  - Secondary mineral clasts rare
  - U(VI) as discrete precipitates imbedded in aluminosilicate rind
  - Low-level U associated with (calcium carbonate) phase
- Deep Vadose Sediment
  - Surface secondary mineralization penetrates to groundwater

Summary, cont'd

- Implications for Plume Behavior
  - Mixed phases may impose complicated dissolution behavior on U leaching
  - Association of U with aluminosilicate coatings may inhibit leaching

Microscopic examination complimentary to spectroscopic techniques (calcium carbonate?)

Continuing Work

- Variation in clast morphology and composition; potential impacts on U leachability
- Mineralogy of individual U-bearing clasts
- U mineralogy and valence