

# X-ray Spectroscopic Studies of Uranium Speciation in 300 Area Samples

**Jeffrey G. Catalano**

**Department of Geological and Environmental Sciences**

**Stanford University**



# Speciation is a description of the chemical characteristics of an element

- Important speciation parameters for uranium include:
  - Oxidation state (4+ vs. 6+)
  - Physical form (solid vs. aqueous)
  - Chemical form (precipitate vs. solution complex vs. surface complex)
  - Distribution between multiple forms
- Information on the speciation of uranium will help:
  - Explain the observed behavior of uranium in the environment
  - Predict the future fate and transport of uranium at a contaminated site

# X-rays at Synchrotron Light Sources



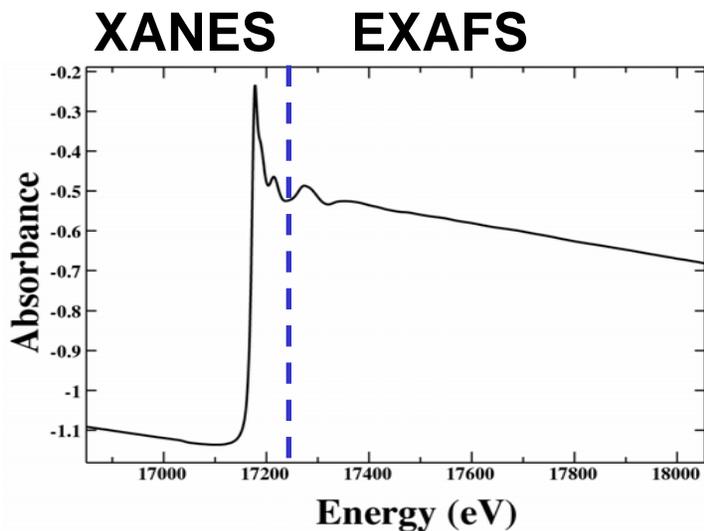
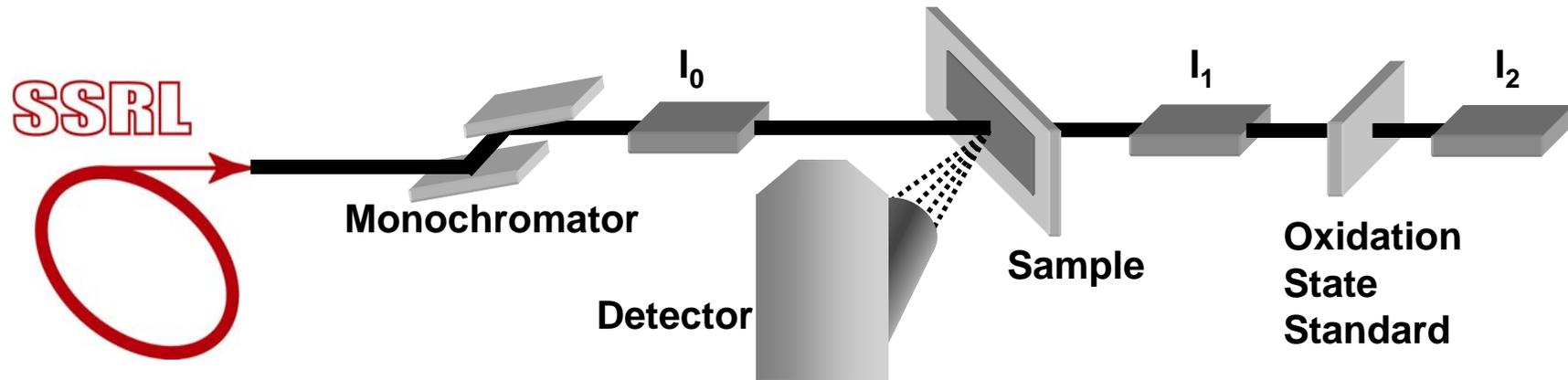
Stanford Synchrotron Radiation Lab (SSRL)



Advanced Photon Source (APS)

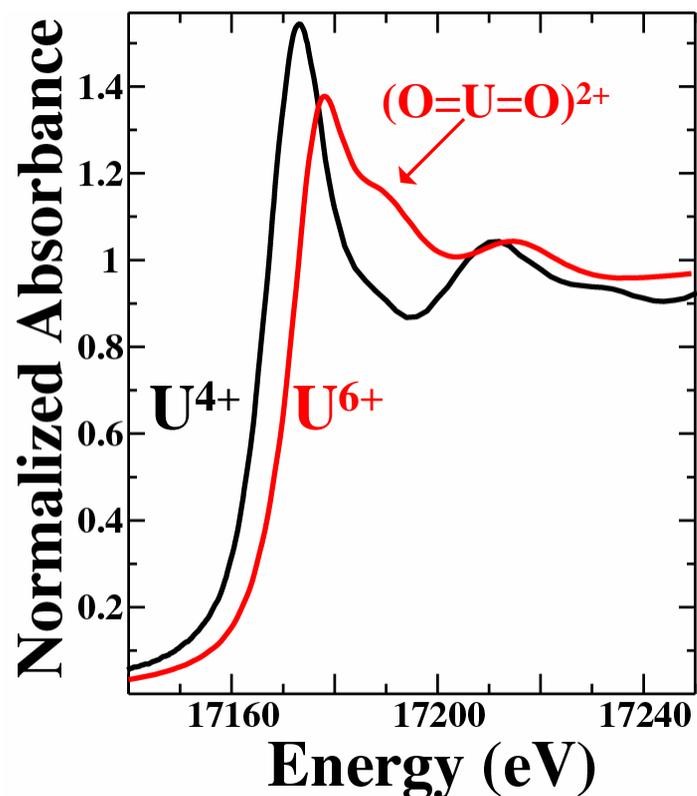
- Source of intense X-ray radiation
- $10^9$  to  $10^{12}$  more flux (more X-ray photons) than from a conventional lab source
- Wavelength/energy tunable

# X-ray Absorption Spectroscopy (XAS)



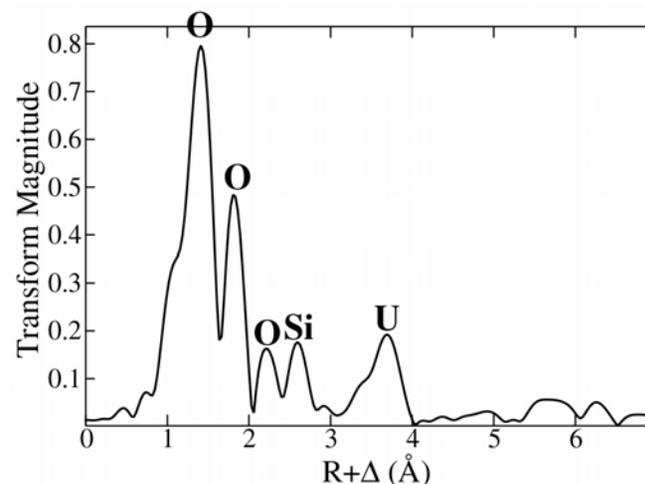
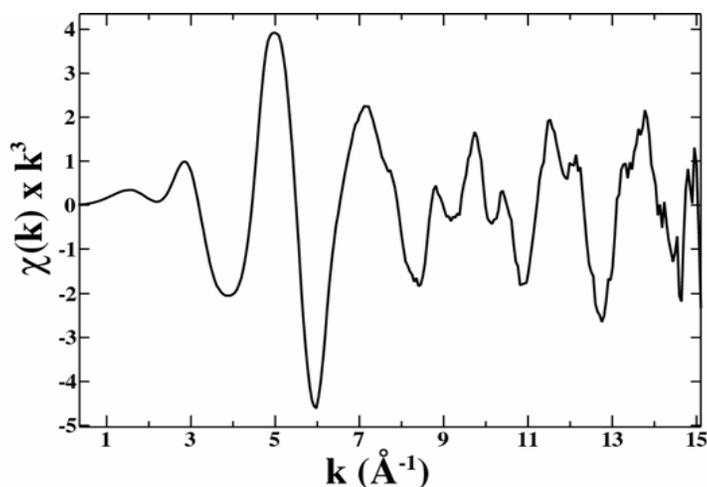
- Provides element-specific speciation information
- High-intensity synchrotron sources allow for analysis of relatively low concentration samples
  - >10 ppm U for XANES
  - >100 ppm U for EXAFS
- Minimal sample preparation
- Analyses performed under ambient conditions

# X-ray Absorption Near Edge Structure (XANES)



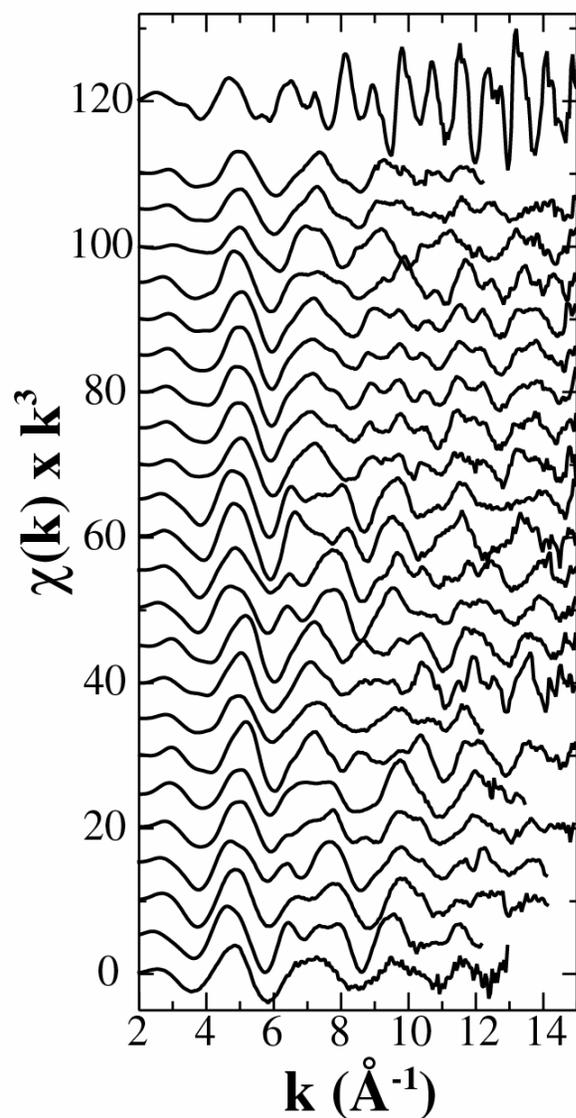
- Position of absorption edge is dependent on oxidation state
  - U(IV) and U(VI) edges separated by ~4 eV
  - Average oxidation state of U in unknown samples can be determined to  $\pm 10\text{-}25\%$
- XANES features may indicate specific structural information

# Extended X-ray Absorption Fine Structure (EXAFS)



- EXAFS is sensitive to the local atomic environment of the element of interest (within 4-5  $\text{\AA}$ )
  - Fourier Transform of the EXAFS yields a radial distribution function
- Can be used as a phase fingerprint
  - Actually a “local atomic environment” fingerprint

# EXAFS as a Phase Fingerprint



Name	Chemical Formula
Uraninite	UO <sub>2+x</sub>
Schoepite, syn	(UO <sub>2</sub> ) <sub>8</sub> O <sub>2</sub> (OH) <sub>12</sub> ·12H <sub>2</sub> O
Compreignacite	K <sub>2</sub> (UO <sub>2</sub> ) <sub>6</sub> O <sub>4</sub> (OH)·7H <sub>2</sub> O
Clarkeite, syn	Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub> ·xH <sub>2</sub> O
Soddyite, syn	(UO <sub>2</sub> ) <sub>2</sub> SiO <sub>4</sub> ·2H <sub>2</sub> O
Uranophane	Ca(UO <sub>2</sub> ) <sub>2</sub> (SiO <sub>3</sub> OH) <sub>2</sub> ·5H <sub>2</sub> O
Boltwoodite, syn	KUO <sub>2</sub> SiO <sub>3</sub> OH·1.5H <sub>2</sub> O
Sklodowskite	Mg(UO <sub>2</sub> ) <sub>2</sub> (SiO <sub>3</sub> OH) <sub>2</sub> ·5H <sub>2</sub> O
Cuprosklodowskite	Cu(UO <sub>2</sub> ) <sub>2</sub> (SiO <sub>3</sub> OH) <sub>2</sub> ·6H <sub>2</sub> O
Kasolite	PbUO <sub>2</sub> SiO <sub>4</sub> ·H <sub>2</sub> O
Liebigite	Ca <sub>2</sub> UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> ·11H <sub>2</sub> O
Sodium uranyl carbonate	Na <sub>4</sub> UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> ·xH <sub>2</sub> O
Rutherfordine	UO <sub>2</sub> CO <sub>3</sub>
Zellerite	CaUO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> ·5H <sub>2</sub> O
Salecite	Mg(UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O
Metaautunite	Ca(UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O
Phosphuranylite	KCa(H <sub>3</sub> O) <sub>3</sub> (UO <sub>2</sub> ) <sub>7</sub> (PO <sub>4</sub> ) <sub>4</sub> O <sub>4</sub> ·8H <sub>2</sub> O
Metatorbernite	Cu(UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O
Uranyl hydrogenphosphate	UO <sub>2</sub> HPO <sub>4</sub> ·2H <sub>2</sub> O
Uranyl orthophosphate	(UO <sub>2</sub> ) <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O
Uranyl nitrate	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O
Uranyl, aqueous	UO <sub>2</sub> <sup>2+</sup> <sub>(aq)</sub>
Uranyl-carbonato, aqueous	UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>4-</sup> <sub>(aq)</sub>
Uranyl adsorbed on smectite	S-UO <sub>2</sub> <sup>2+</sup> (Fe-UO <sub>2</sub> CO <sub>3</sub> ?)

U(VI)-hydroxides

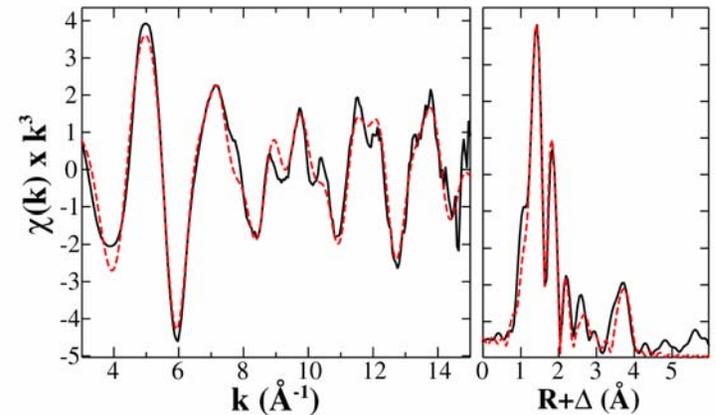
U(VI)-silicates

U(VI)-carbonates

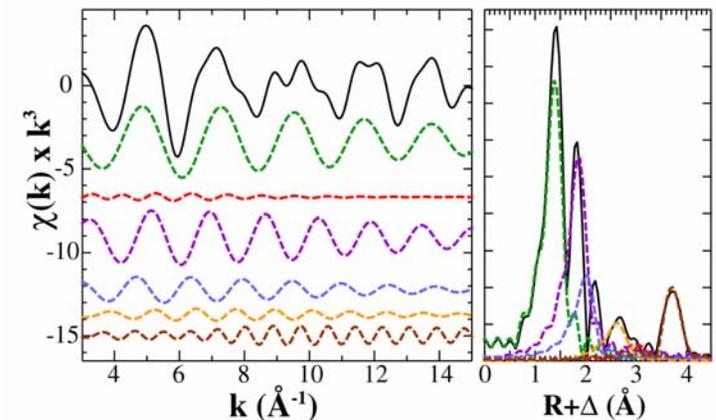
U(VI)-phosphates

# Obtaining structural information from EXAFS

- Can fit “atomic shells” to the EXAFS spectra
- Sensitive to:
  - Coordination number,  $N$
  - Distance (bond length),  $R$
  - Disorder,  $\sigma^2$
  - Element,  $Z$
- Requires the use of experimental or theoretical functions that describe the scattering for each atom type
  - e.g., for U-O, U-Si, U-U, etc.
  - Can be calculated using the *ab initio* code FEFF



Fit to the EXAFS of boltwoodite

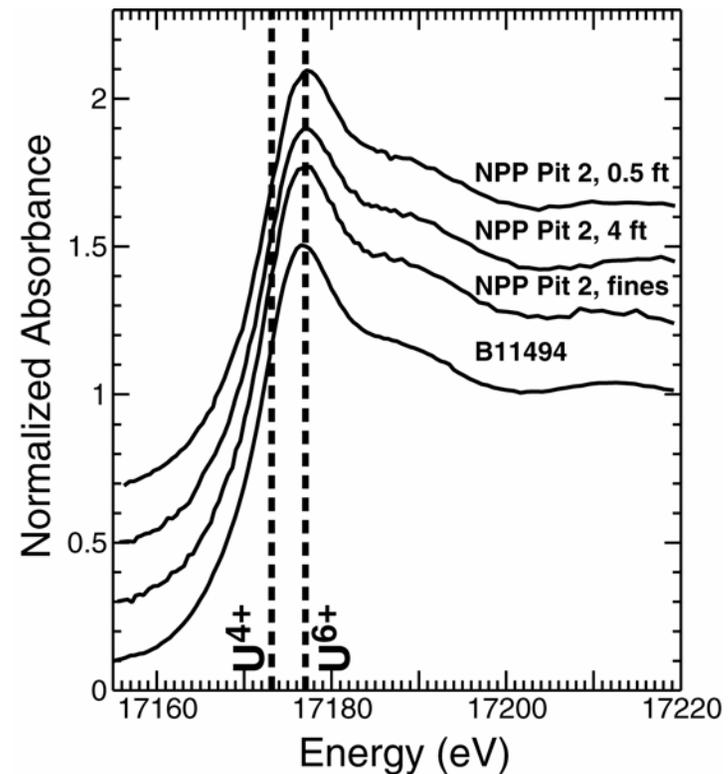
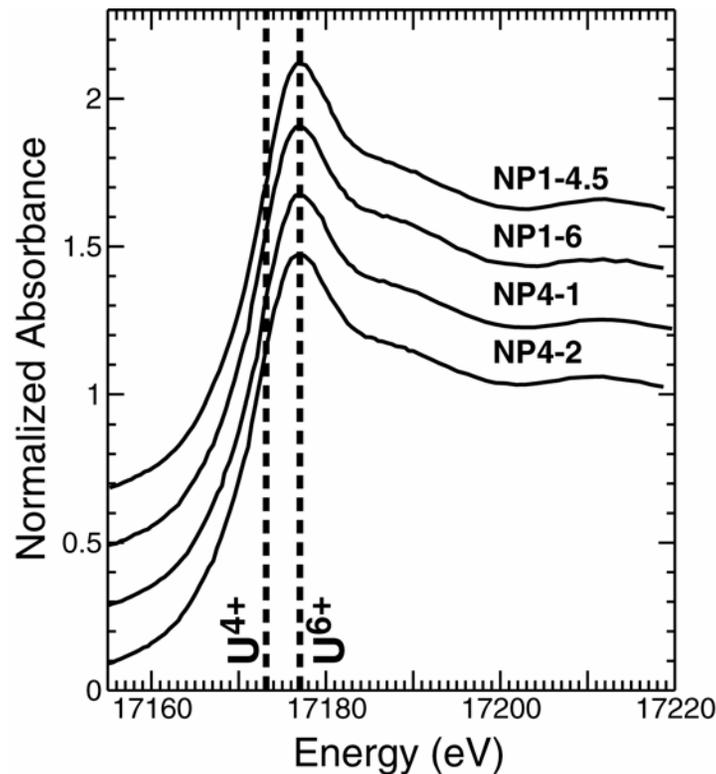


Components of the fit and their FTs

## 300 Area Samples Examined

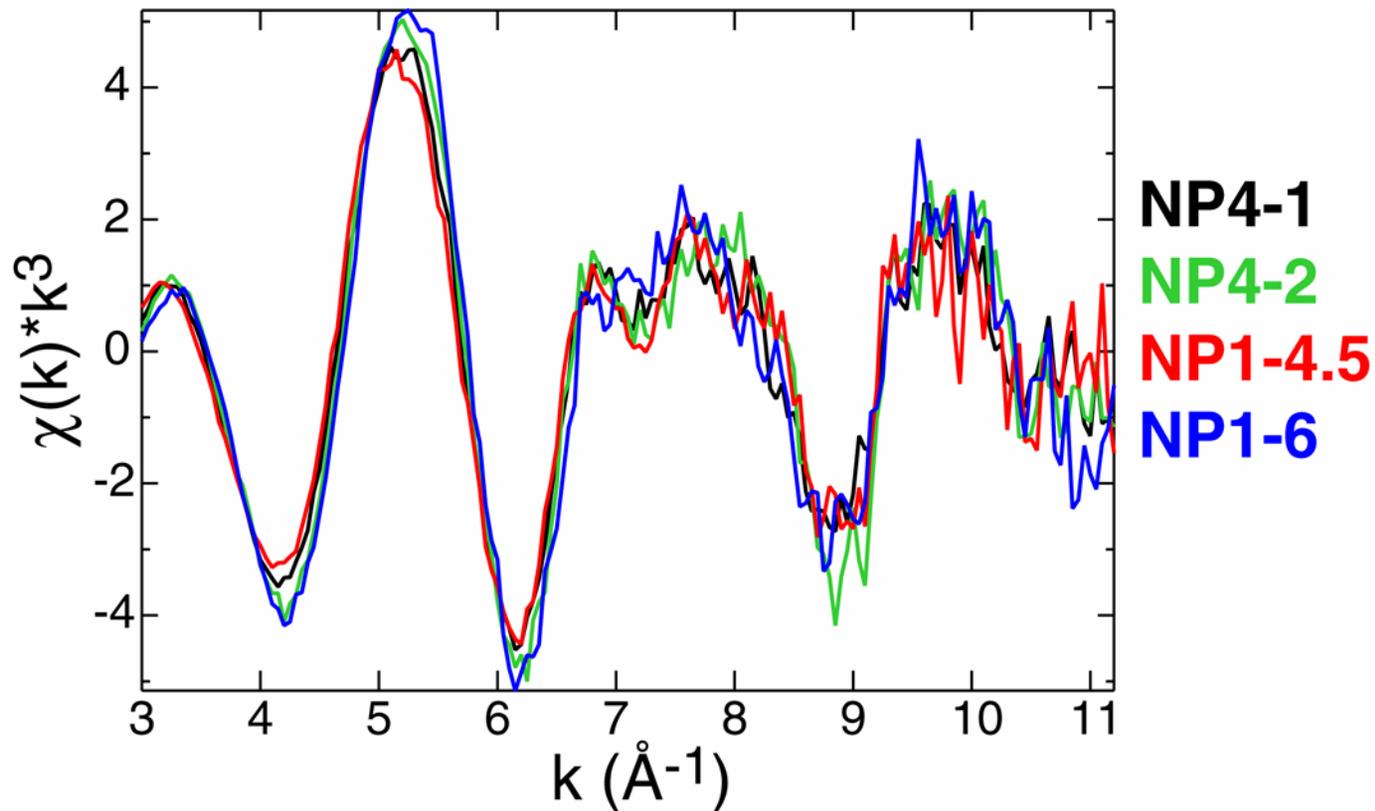
NP1-4.5	1600 ppm U
NP1-6	400 ppm U
NP4-1	3000 ppm U
NP4-2	2400 ppm U
NPP Pit 2, 0.5 ft bgs	238 ppm U
NPP Pit 2, 2 ft bgs	139 ppm U
NPP Pit 2, GW fines	200 ppm U
B11494	540 ppm U

# U Oxidation State in 300 Area Samples



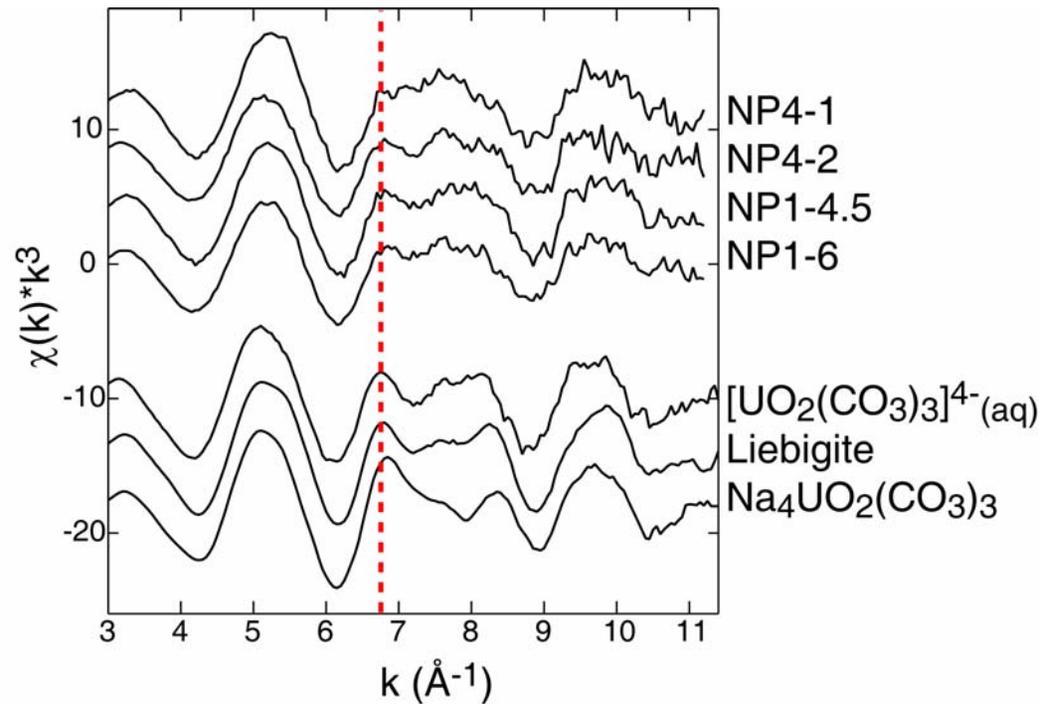
- All samples contain U in predominantly the 6+ oxidation state (>85-90 %)

# U Chemical Form in 300 Area Samples



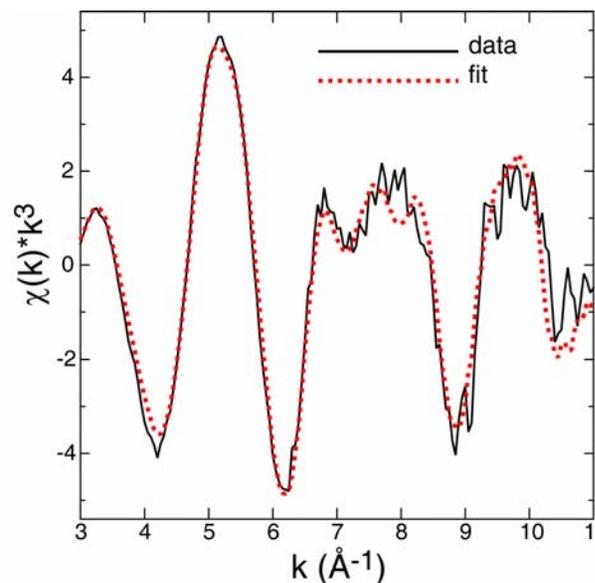
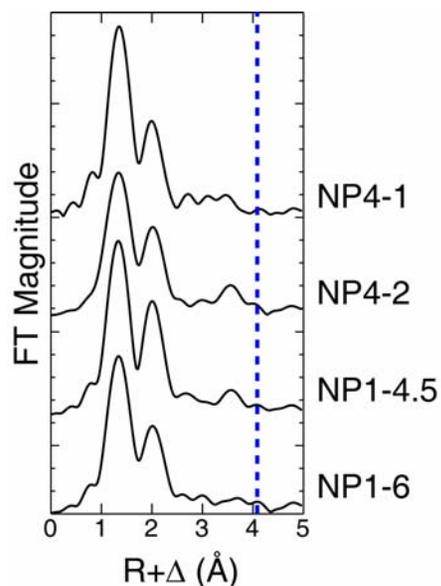
- Little to no variability in chemical form among NP samples

# U Chemical Form in 300 Area Samples



- Uranium EXAFS spectra of NP samples are similar to spectra of uranyl tricarbonate phases
  - Spectra indicate uranium is at least partially coordinated by carbonate

# U Chemical Form in 300 Area Samples



**NP4-2**  
**67% Liebigite**  
**33% Schoepite**

- Small feature in FT suggests a separate uranium precipitate is also present, possibly a hydroxide
- A mixture of uranyl carbonate and hydroxide spectra reproduced the data well
  - NP samples contained 42-67% uranyl carbonate and 33-58% uranyl hydroxide
  - Two other samples examined contained 20-49% uranyl carbonate and 51-80% uranyl hydroxide

## Similarity to Uranyl-Sorbed $\text{CaCO}_3$

- EXAFS spectra closely match those of uranyl-sorbed  $\text{CaCO}_3$  studied by Rich Reeder et al.
  - Spectra of U sorbed to aragonite similar to those of uranyl tricarbonates phases
  - Spectra of U sorbed to calcite are varied, some similar to uranyl tricarbonates phase, others difficult to identify
  - 300 Area sample spectra look most similar to those of U sorbed to calcite
- Problem: It is not clear from previous studies what form(s) of U are present when it sorbs to calcite

# Conclusions

- Uranium occurs primarily in the 6+ oxidation state
- There is little variability in the chemical form of uranium among the samples studied
- The speciation of uranium is complex in the NP samples:
  - Uranium is (partially) bound to carbonate anions
  - Data are best fit as a mixture of uranyl carbonate and hydroxide
  - Spectra also look like published spectra of U sorbed to calcite
- EXAFS data suggests U occurs as multiple phases, likely schoepite and either a uranyl tricarbonate phase or U sorbed to  $\text{CaCO}_3$
- Need to integrate XAS data with that of other spectroscopic and microscopic measurements to obtain a consistent picture of U speciation in these samples

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