Utilizing XAFS Spectroscopy in a Research Program:
Some examples in environmental geochemistry

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As with any study..... it’s necessary to decide what information you need about your system; then choose the right technique(s).

- XAFS spectroscopy has become a mainstay in environmental chemistry, especially for the study of chemical contaminants.

- Examples of inorganic contaminant species are Pb, Cd, Zn, U, Sr-90.

- Contaminants are commonly present in low concentrations and are usually associated with one or more phases.

- What questions are we trying to answer?
  - Will the contaminant bind with solid phases or is it mobile?
  - Is the species stable or labile?
  - What is the species’ toxicity? Bioavailability?
Other system parameters:
- pH, $\Sigma[M]$, T, P
- phases, surface area, etc.
\[
\text{CrO}_4^{2-}  \quad [\text{Cr(VI)}] \text{ is relatively unreactive and soluble, so it’s mobile and bioavailable. Cr(VI) is also toxic. Cr(VI) is tetrahedrally coordinated by oxygen; } <\text{Cr-O}> = 1.6 \text{ Å.}
\]

However, Cr(VI) may become reduced to Cr(III).

\[
\text{Cr(III) is insoluble in most solutions and readily precipitates, so it’s immobile and has low bioavailability. Cr(III) is non-toxic. Cr(III) is octahedrally coordinated by oxygen; } <\text{Cr-O}> = 2.0 \text{ Å.}
\]
What information do we want?

Element-specific info (concentration is often dilute)

- Oxidation state  \((\text{XANES})\)
- Identity and number of neighbors \((\text{EXAFS})\)
- Distance to neighbors \((\text{EXAFS})\)
- Coordination \((\text{XANES}^* \text{ and EXAFS}^*)\)
- Concentration
- Stability/lability
- Phase association (host, substrate, sorbent)

In some instances we need to obtain this information \textit{in situ} to avoid altering structural state. Can temp. be changed?

In other cases one or more of these parameters may change over time, so temporal constraint on data collection.
Mechanisms of Metal Interaction at the Mineral-Water Interface

Adsorption

Co-precipitation

Surface precipitation

Mineral surface layers

Outer sphere

Inner sphere

Water
Decision time…

Should I work with a model system or a real system?

A model system: Cd$^{2+}$ sorption on pure FeOOH

A real system: Cd$^{2+}$ in a soil
First example: Uranium(VI) substitution in apatite*

Apatite is a common mineral phase:

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorapatite</td>
<td>Ca$_5$(PO$_4$)$_3$(F)</td>
</tr>
<tr>
<td>Hydroxylapatite</td>
<td>Ca$_5$(PO$_4$)$_3$(OH)</td>
</tr>
<tr>
<td>Chlorapatite</td>
<td>Ca$_5$(PO$_4$)$_3$(Cl)</td>
</tr>
</tbody>
</table>

There is great interest in the use of apatite as a solid nuclear-waste form and in engineered contaminant barriers.

- High affinity for U and other radionuclides (5+ wt.%)
- Low solubility
- Low annealing temperature

Questions: How is U(VI) accommodated in the structure? Is the U-doped phase stable?

U(VI) usually occurs as the linear dioxo unit: O=U=O

• Fluorapatite synthesized at 1380 °C in air
• Starting materials: U^{IV}O_{2}, Ca_{3}(PO_{4})_{2}, and CaF_{2}
• Product: fluorapatite with 2.3 wt.% U
• U(IV) suspected of oxidizing to U(VI) during preparation
Fluorapatite
$\text{Ca}_5(\text{PO}_4)_3\text{F}$
Potential substitution sites at both Ca positions

Ca1 site

Ca2 site
Strategy for XAFS characterization:

1) Confirm oxidation state (XANES, luminescence)
2) Determine local structure (EXAFS)

• Sample preparation: grind to powder in air (sample not moisture sensitive). Seal in sample holder.

• Edge: $L_3$ (17166 eV) ($K$-edge not accessible: 115 keV)

• Uranium concentration 2.3 wt.%. Slightly low for transmission measurement ($\Delta \mu X = 0.4$), but well suited for fluorescence. Either PIPS or Stern-Heald type detector (filter Sr-3)

For EXAFS: Perform multiple scans out to about 16k
For XANES: Scan edges of apatite:U and U(IV) (or U(VI)) standard simultaneously

Reference samples: $U^{IV}O_2$ and $U^{VI}O_2(NO_3)_2\cdot6H_2O$
XANES spectra of apatite:U and U(IV) and U(VI) standards

Edge position coincides with U(VI) standard but does not show typical uranyl near-edge structure.
U L$_3$-edge EXAFS of apatite:U

Raw absorption spectrum (average of 15 scans)
EXAFS fitting approach:

• We assumed that the U could occupy either or both Ca sites.
• Fitting used theoretical phases and amplitudes calculated from FEFF7.
• Structure model for FEFF calculations: fluorapatite structure with the Ca1 (or Ca2) replaced by U.
• Compare fits.
No axial O atoms at short distance. U(VI) is not in dioxo configuration.

Single oxygen shell with small D-W suggests regular octahedral coord.

No apparent contribution from three O3 atoms.
So, what’s it all mean?

- XANES indicates uranium is in 6+ oxidation state but not as uranyl.

- U has six oxygen neighbors at a distance of 2.06 Å. This U-O distance is similar to that found in uranates (2.02-2.12 Å), which have octahedral coordination.

- Luminescence spectroscopy confirms 6+ oxidation state and gives spectrum the same as known uranates.

- XANES simulation (FEFF8) for octahedral coordination reproduces the edge structure. The local coordination is octahedral or close to it.
• We can conclude that U(VI) substitutes in the Ca1 site of fluorapatite, but with some or all of the O3 atoms probably missing (bond valence calculations support this). This would require slight rotations of the O1 and/or O2 atoms.

Unanswered question: What is the stability of the U-substituted apatite?
Example 2: Zn(II) sorption mechanism at the calcite-water interface*

- Zn is an essential nutrient in low concentrations, but may be toxic at high concentrations.
- Zn interacts strongly with calcite (CaCO₃), but shows anomalous adsorption behavior (Zachara et al., 1991).
- Calcite exhibits rapid precipitation/dissolution kinetics, and Zn also exhibits high affinity for co-precipitation with calcite.

Questions:
- How does Zn bind with calcite in aquatic systems?
- Can we distinguish between adsorption and co-precipitation?
- Can we explain the anomalous sorption behavior of Zn?

Needed info: local structure and coordination of Zn, including nearest metal neighbors

(* Elzinga and Reeder (2002) GCA, 66, 3943-3954)
Special considerations:

Information needed for spatially restricted portions of system

Adsorption Co-precipitation Both

Designing the experiment to obtain the desired info:

• If the target species is sorbed at the solid-water interface, it’s desirable to investigate the local structure and coordination in situ. Sample should not be allowed to dry.

• If the sample remains wet, then any target species dissolved in the water will contribute to the EXAFS spectrum.
How to look “only” at species sorbed at the solid-water interface

• Filter (or centrifuge) sorption suspension to recover solids, but not to dryness. “Wet paste” consistency is preferred. This retains normal hydration environment at solid-water interface.

• How much of the target metal remains dissolved in residual solution? If it’s less than 2-3% of the total, it can usually be ignored.

• How would you determine if this is the case? Determine partitioning behavior from batch sorption experiments.

• For Zn sorption on calcite, we have <1% total Zn\(^{2+}\) in the solution.

• We have a sample that has >99% of the target element sorbed at the solid-water interface, and it retains the chemistry and structure as in the bulk suspension.
Designing the experiment to obtain the desired info (cont’d):

• Sorption processes are dynamic. If the structure and coordination of the surface species change over time, then the data must be collected over a short enough time frame to avoid mixing structural information.
  -- Collect scans for samples equilibrated for different durations.

• If the sorption density is inherently low, then final sample may be very dilute (e.g., 50-5000 ppm).
  -- Take multiple scans (5-50)
  -- Maximize loading on surface

Problems?

• For dilute systems, fluorescence detection is usually preferred.
  (Multi-element solid-state detector, or a Stern-Heald type detector.)
How can we determine if surface precipitation has occurred?

Controlling factor is saturation state.

-- Increase solution concentration of adsorbate until ppt does occur.

-- Or decrease solution concentration to see if any change is evident in the EXAFS.

-- Compare with spectra of reference samples for potential precipitates

\[ \text{ZnCO}_3 \]
\[ \text{Calcite}:\text{Zn}^{2+} \]
\[ \text{Hydrozincite} \]
\[ \text{ZnO} \]
\[ \text{Aqueous Zn}^{2+} \]
XANES spectra of Zn\(^{2+}\) samples

- ZnCO\(_3\): octahedral
- Calcite:Zn\(^{2+}\): octahedral
- Zn\(^{2+}\) sorbed calcite: ?
- Hemimorphite: tetrahedral
- ZnO: tetrahedral

Normalized Absorbance vs. E-E\(_0\) (keV)
Zn K-edge EXAFS and Fits

$R + \Delta R$ (Å)

$K^2\chi^2(k)$

Calcite:Zn$^{2+}$

ZnCO$_3$

ZnO

Adsorption

$[\text{Zn}] = 1 \, \mu\text{M}$

$[\text{Zn}] = 5 \, \mu\text{M}$

$[\text{Zn}] = 10 \, \mu\text{M}$
Calcite: Zn\(^{2+}\) dilute solid solution

<table>
<thead>
<tr>
<th>Shell</th>
<th>N</th>
<th>R (Å)</th>
<th>(\sigma^2) (Å(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-O</td>
<td>7.1</td>
<td>2.12</td>
<td>0.008</td>
</tr>
<tr>
<td>Zn-C</td>
<td>6*</td>
<td>3.13</td>
<td>0.005</td>
</tr>
<tr>
<td>Zn-O</td>
<td>6*</td>
<td>3.36</td>
<td>0.006</td>
</tr>
<tr>
<td>Zn-Ca</td>
<td>6*</td>
<td>3.95</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Zn\(^{2+}\) sorption on calcite (5 \(\mu\)M)

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<th>R (Å)</th>
<th>(\sigma^2) (Å(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-O</td>
<td>4.3</td>
<td>1.96</td>
<td>0.007</td>
</tr>
<tr>
<td>Zn-C</td>
<td>4.1</td>
<td>2.87</td>
<td>0.01*</td>
</tr>
<tr>
<td>Zn-O</td>
<td>3.4</td>
<td>3.07</td>
<td>0.01*</td>
</tr>
<tr>
<td>Zn-Ca</td>
<td>1.0</td>
<td>3.35</td>
<td>0.01*</td>
</tr>
</tbody>
</table>
Adsorption in kink/step sites on (10\(\bar{1}4\))

Zn\(^{2+}\) (obs) = 3.35 Å
Zn-Ca (pred) = 3.45 Å

Cu\(^{2+}\) (obs) = 3.90 Å
Cu-Ca (pred) = 3.8–3.9 Å
Metal adsorption on (10\overline{1}4) terraces less favored.

“Underbonded” oxygens

10\overline{1}4 slice

Polyhedral edge length
\[ \text{ZnO}_4 \sim 3.1 \, \text{Å} \]

Monodentate adsorption or exchange in Ca position is more likely on (10\overline{1}4) terrace.
Caveats

• Rarely does XAFS (alone) provide all the answers.

• When more than one species is present, XAFS may have limited value or not be suitable.

• Use complementary techniques whenever possible.