

Spectroscopic and Microscopic Characterization of Contaminant Uptake and Retention by Carbonates in the Soil and Vadose Zone

DOE Environmental Management Science Program

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Relevance to DOE-EMSP Mission

Calcium carbonate occurs as a locally important mineral in soils and the vadose zone at the Hanford Site and at other sites in the DOE complex. What role does CaCO_3 play in the uptake and sequestration of toxic metals and radionuclides?

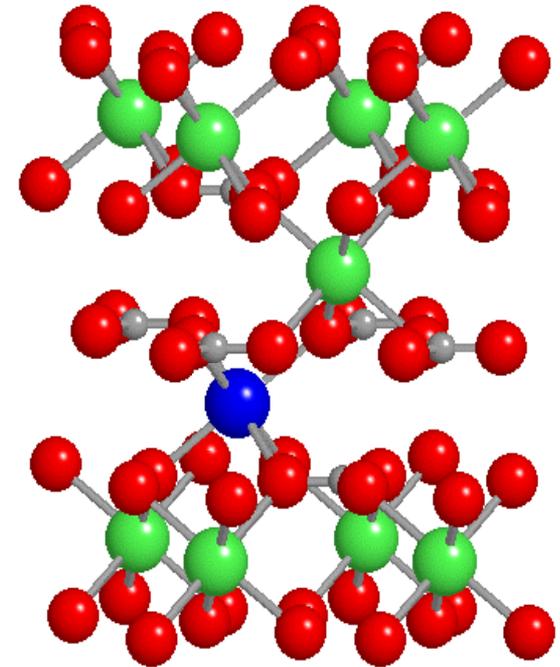
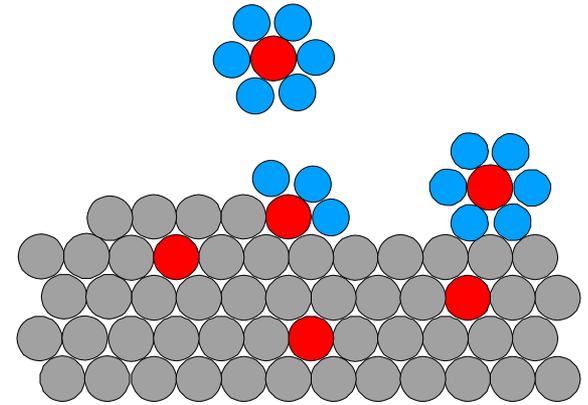
Distribution and occurrence of CaCO_3 (Hanford)

- Primarily calcite; pedogenic origin
- Surface coatings on clastic grains
- Caliche, calcrete (hardpan)
- Disseminated particles, nodules

Coatings and high surface-area components may exert much greater influence on uptake than reflected by volume

Uptake and Sequestration by Calcite

- Common constituent in soils, sediments
- Moderate solubility (pH, P_{CO_2} , solid solution)
- Highly reactive; rapid growth/dissolution kinetics
- Rapid surface recrystallization and/or exchange
- Coprecipitation, adsorption, surface precipitation all important (continuum of states?)
- Extensive impurity substitution in bulk
- Rapid crystallization increases K_d (co-ppt.) for incompatible species (e.g., Sr, Cs, U, Cr)
- Strong surface control on uptake/incorporation



Methodology

Uptake/release are molecular processes

Contaminant “speciation”

- XAFS, XANES, luminescence, optical spectroscopies (NSLS, APS)

Micro-spatial distribution

- μ -XAS/XRF (NSLS, APS, ALS)

Batch experiments

- Adsorption (radiotracers)
- Coprecipitation

Materials

- Model systems
- Natural samples

Research completed:

- UO_2^{2+} coprecipitation with calcite [f (pH)]
Systematics; rate effect; micro-distribution
Speciation, surface site preferences
- REE^{3+} coprecipitation with calcite
Analog for An^{3+} radionuclides
- Sr^{2+} and Pb^{2+} uptake on natural caliche
Micro-distribution, heterogeneous
- Cu^{2+} and Zn^{2+} adsorption on calcite
Speciation, surface site preferences

Research underway:

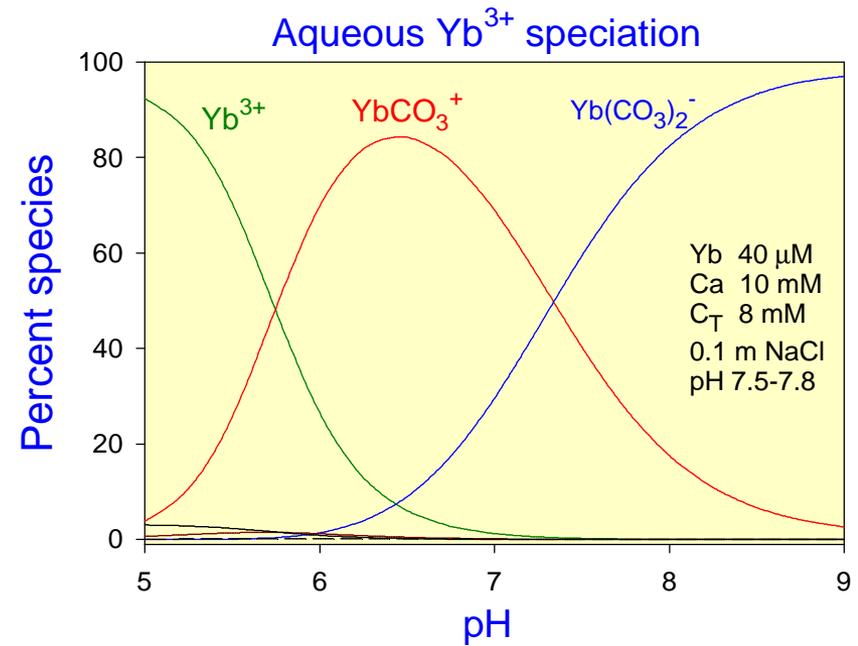
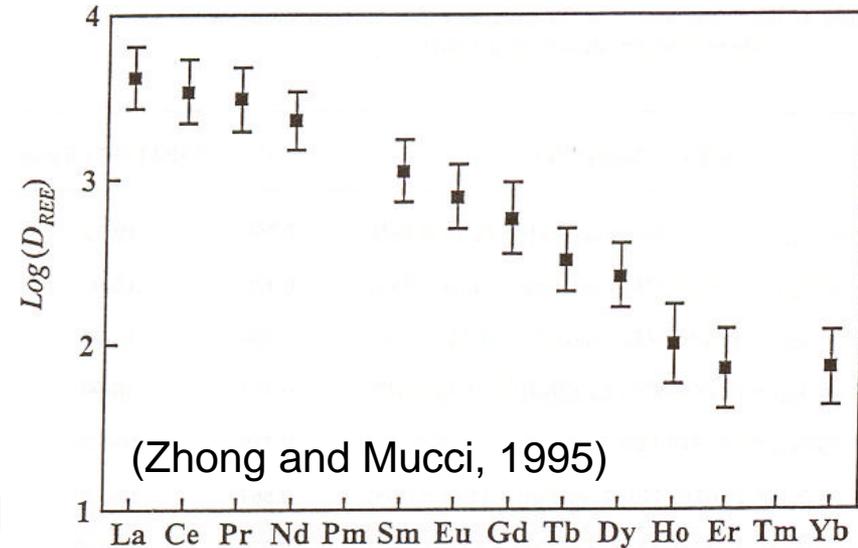
- UO_2^{2+} adsorption on calcite [f (loading)]
Surface speciation (XAFS)
- REE^{3+} adsorption on calcite
Speciation, kinetics
- Cs^+ and Pb^{2+} sorp/desorp on calcite [f (pH, I)]
Systematics, radiotracers, speciation (XAFS)
- CrO_4^{2-} coprecipitation with calcite
Micro-distribution, coordination, redox

REE³⁺ Uptake by Calcite

- Analogs for trivalent actinides (Am³⁺, Cm³⁺)
- REE³⁺ strongly partitioned into calcite
 K_d (co-ppt) = 10^2 – $10^{3.5}$
- Heterovalent substitution. Charge compensation mechanism via Na⁺ co-substitution (Zhong and Mucci 1995)
- Fm. of Nd-Ca carbonate phase (Carroll 1993)
- Highly particle reactive: K_d (ads) > 10^3
- Aqueous speciation – carbonate complexes

Questions:

- Mode of REE³⁺ incorporation
- Local structure of heterovalent impurity
- Mechanism of charge compensation
- Role of adsorption, surface speciation

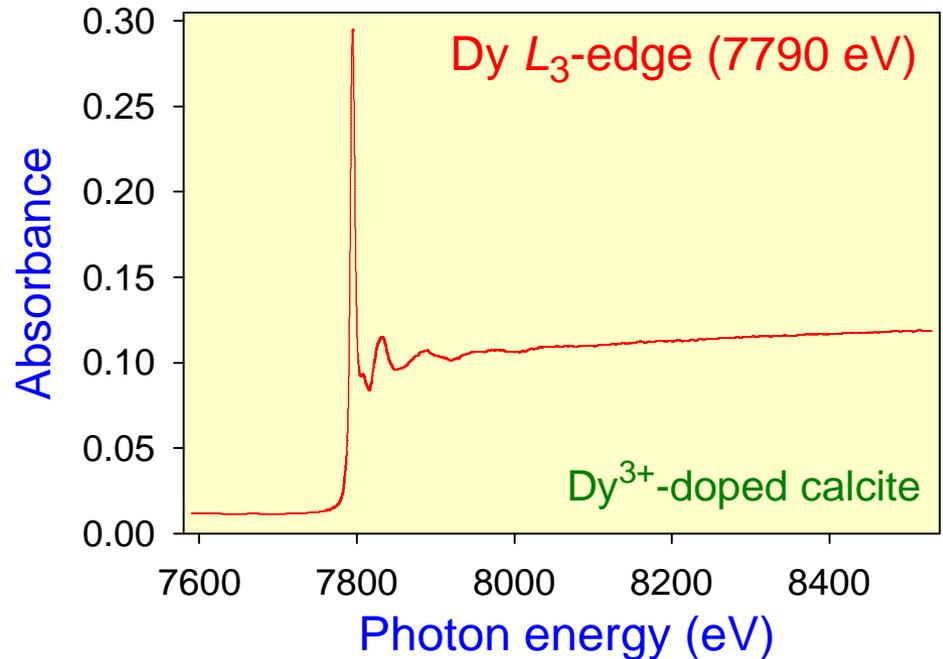
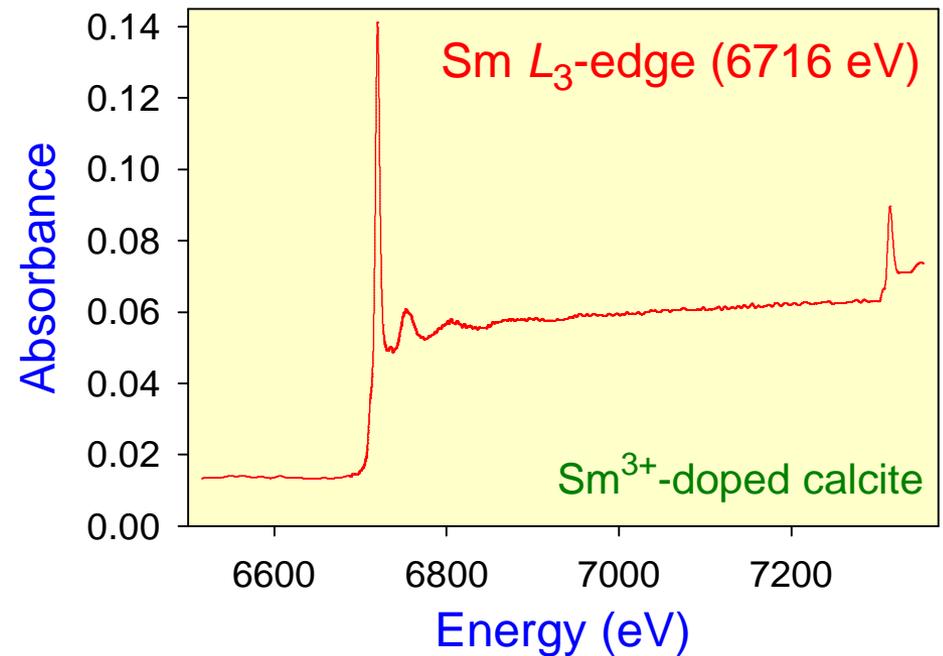


Approach:

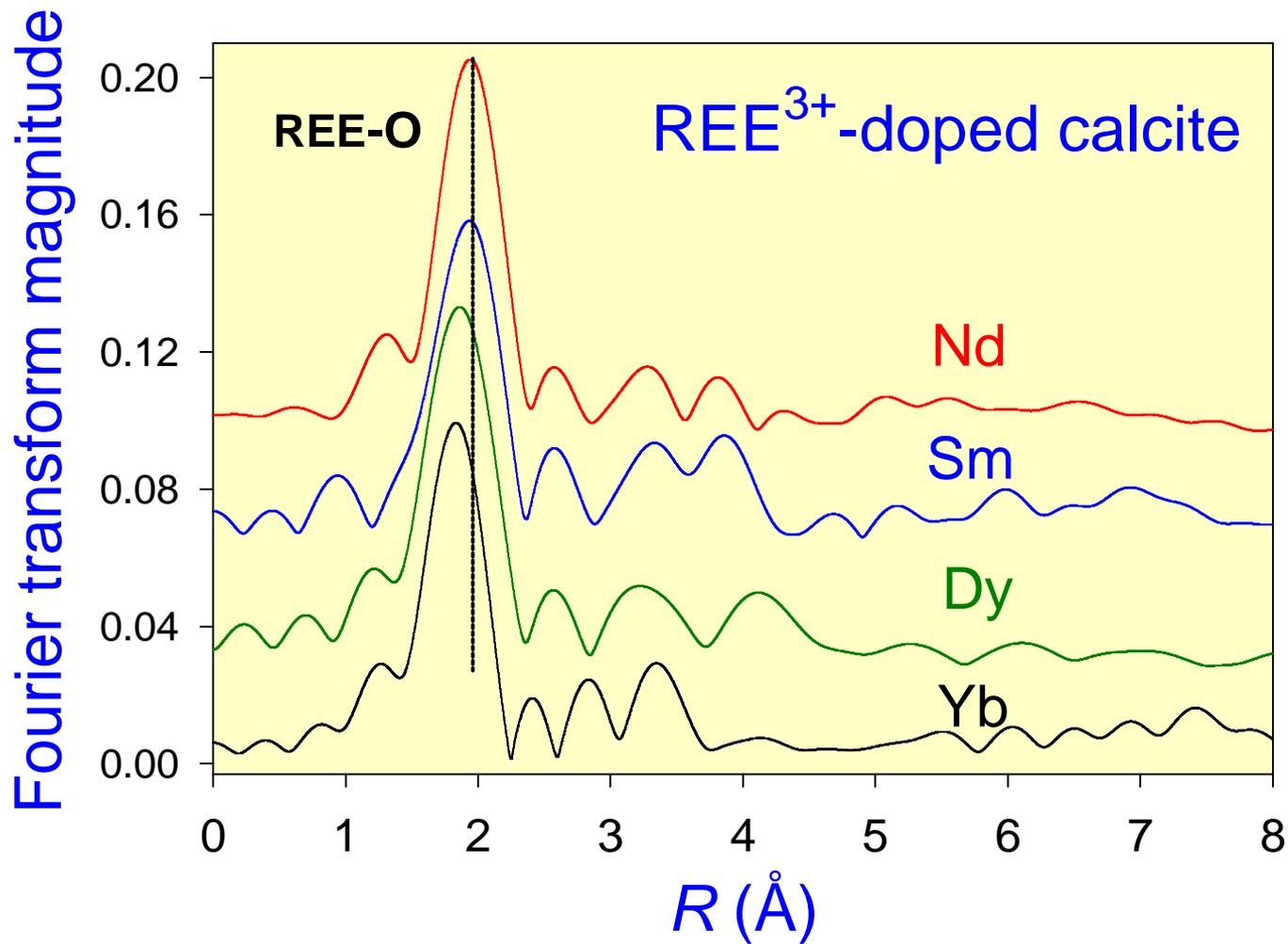
- Coprecipitation of individual REE³⁺ with calcite with controlled solution chemistry
- Characterize local structure (EXAFS)
- Characterize REE site symmetries using optical and IR spectroscopy

EXAFS Spectroscopy

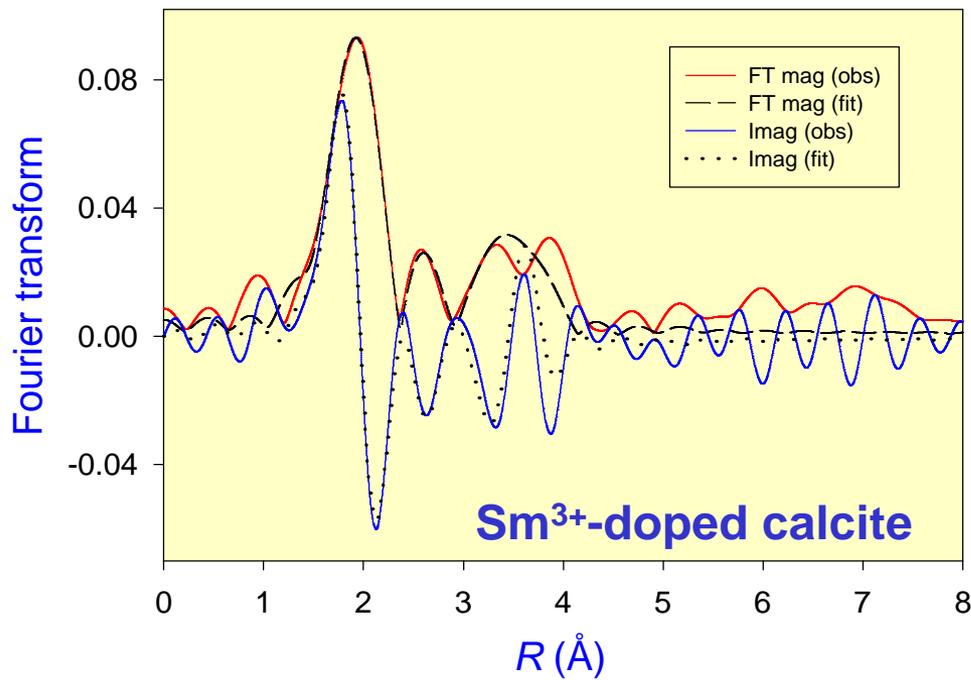
- X11A, X18B (NSLS)
- Fluorescence detection (13 element Ge detector)
- L₃-edges
 - Limited *k* range (LREE)
 - Multielectron excitations?



L_3 -edge EXAFS – Fourier Transforms

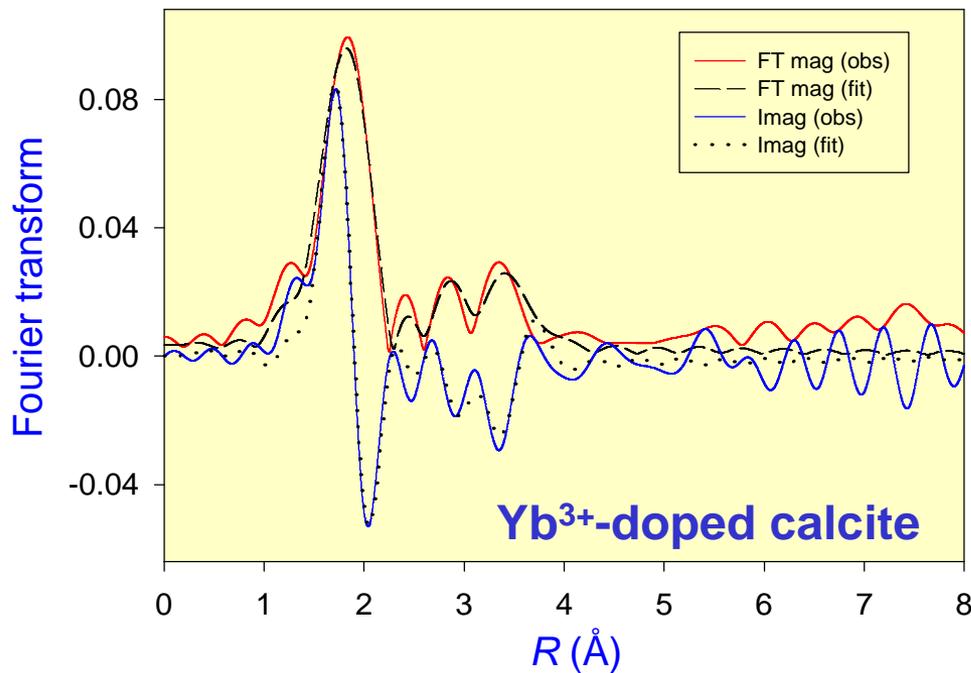


Selected XAFS Fit Results



Calcite:Sm³⁺

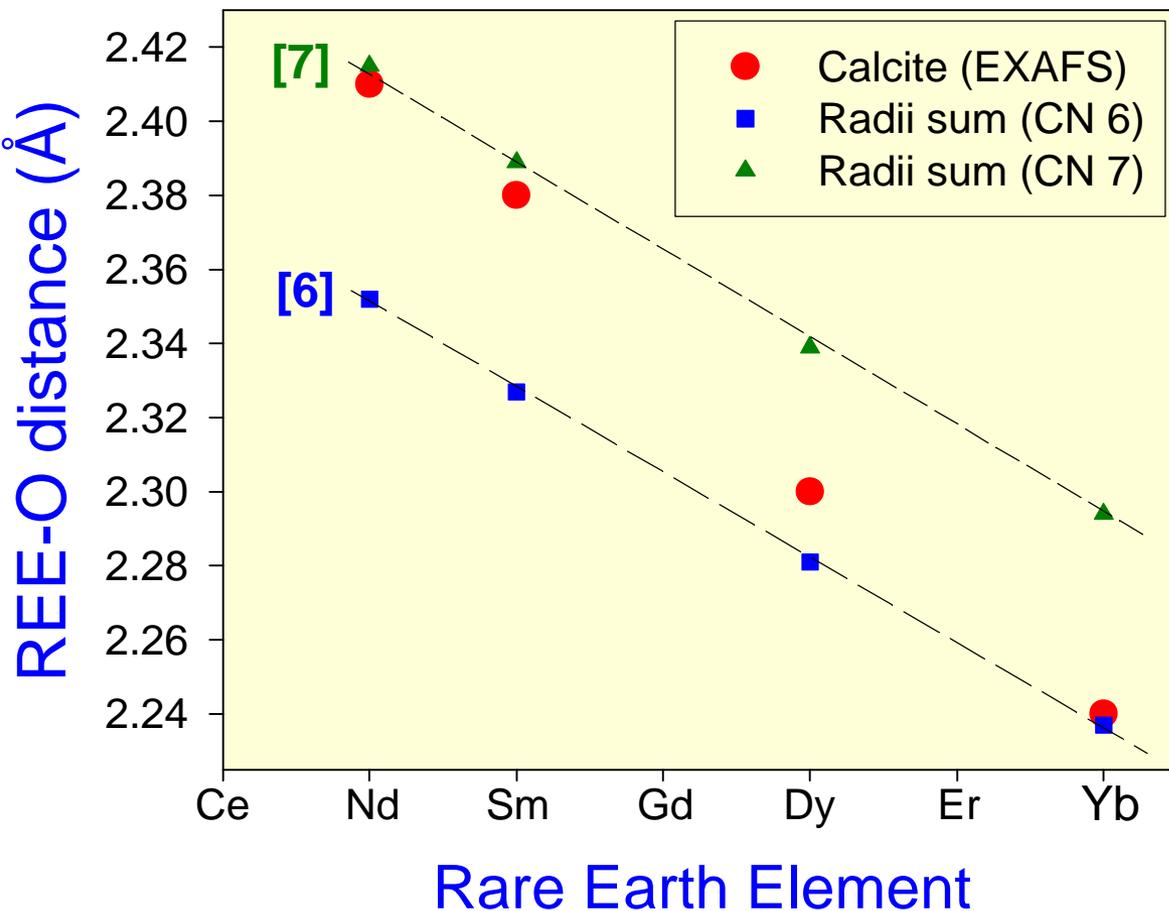
	R	CN	σ^2
Sm-O	2.38	8.3	0.009
Sm-C	3.24	6*	0.008
Sm-O	3.48	6*	0.012
Sm-Ca	4.09	6*	0.012



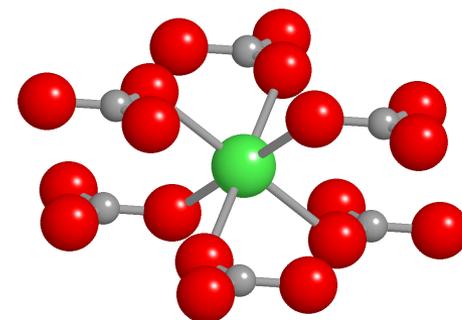
Calcite:Yb³⁺

	R	CN	σ^2
Yb-O	2.24	7.5	0.008
Yb-C	3.14	6*	0.010
Yb-O	3.27	6*	0.011
Yb-Ca	4.04	6*	0.015

First shell REE-O distances in calcite (EXAFS)

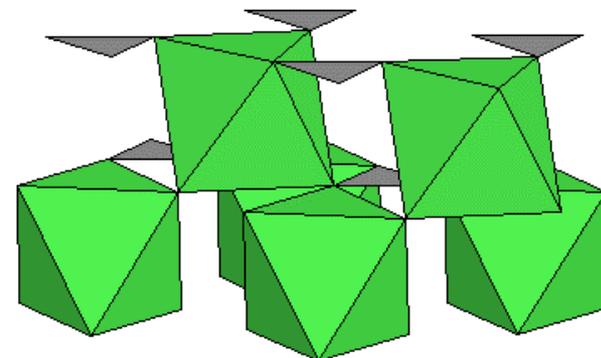


Ca octahedron
in calcite

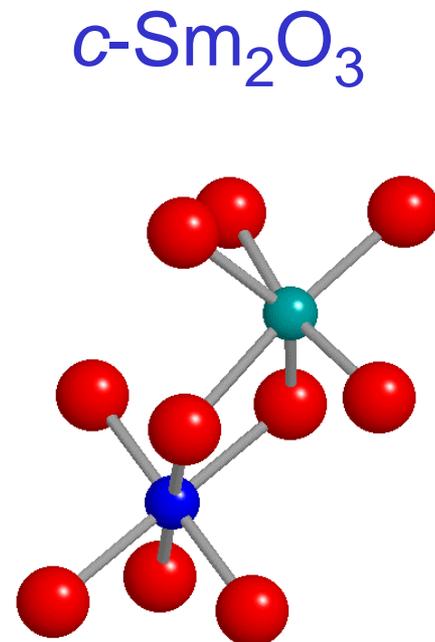
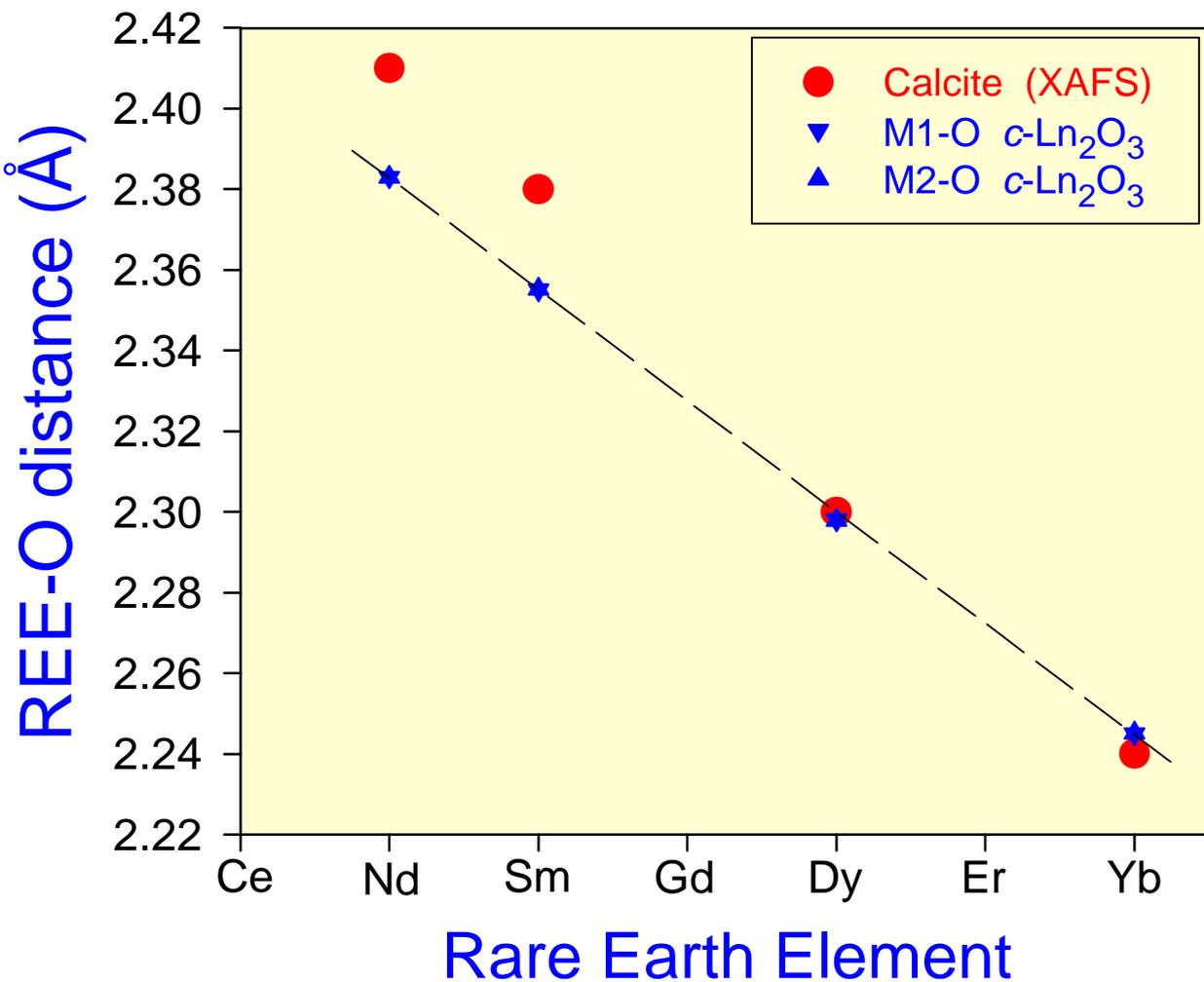


- Nd-O and Sm-O distances suggest 7-fold coord.
- Dy-O and Yb-O distances consistent with 6-fold
- Coord. differences supported by bond-valence sums

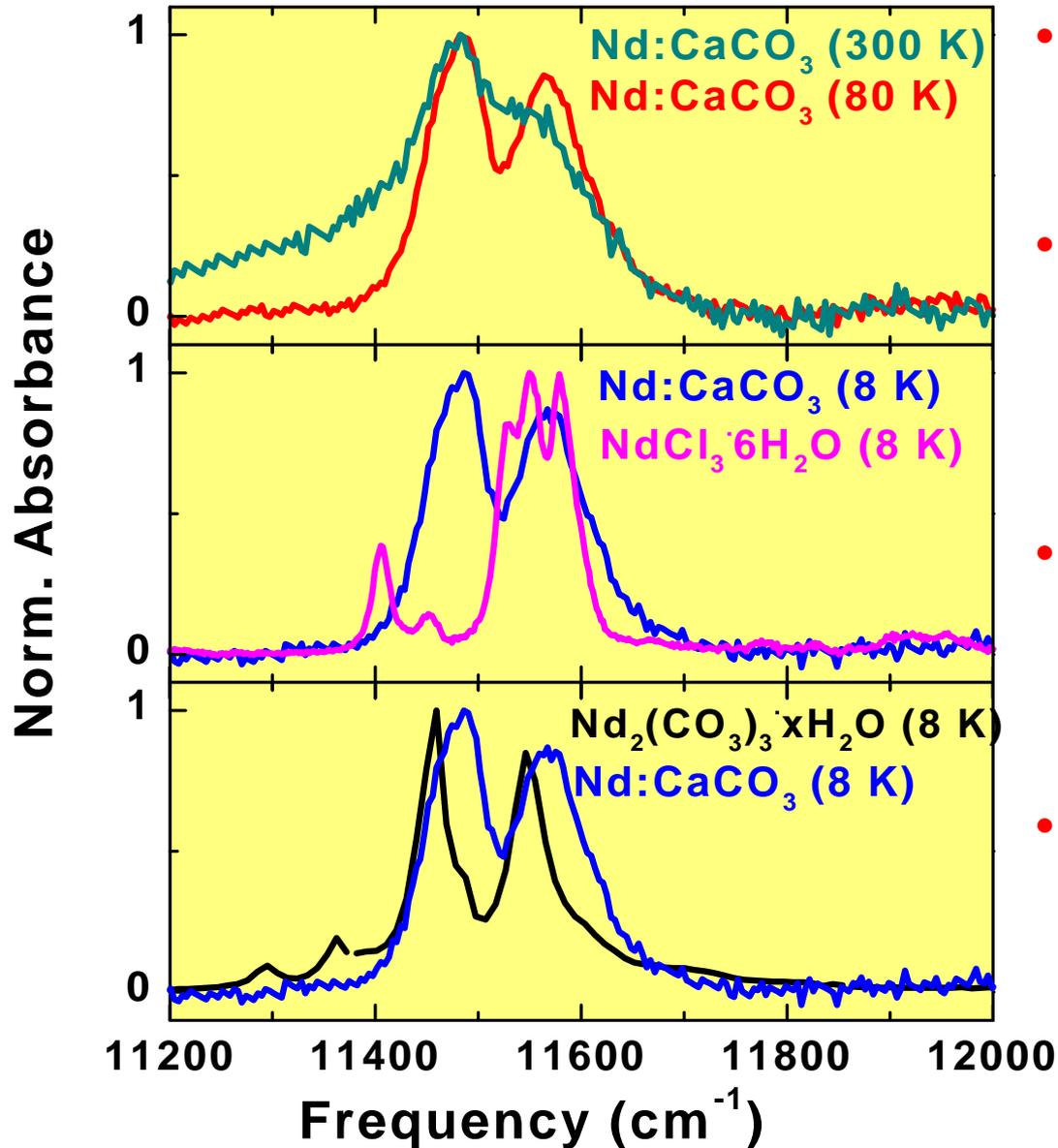
Corner-sharing
topology
in calcite



Comparison with REE-O in lanthanide sesquioxides



Optical Spectroscopy – Nd³⁺ in Calcite



- Optical spectroscopy can distinguish different Nd³⁺ crystal field environments
- Neodymium chloride and Neodymium carbonate phases are absent in Nd:CaCO₃ samples grown from solution
- Nd:CaCO₃ shows high degree of inhomogeneous broadening and no line sharpening below 80 K
- There is a broad, continuous distribution of crystal field environments for Nd³⁺ in calcite.

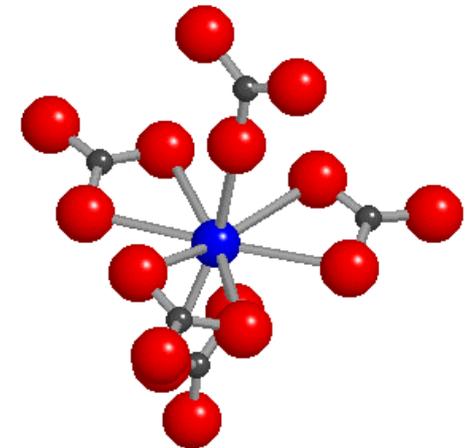
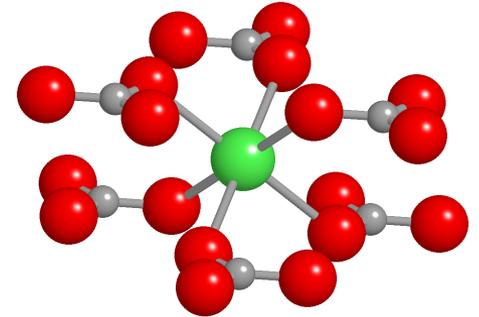
Conclusions:

- LREE coordinated to 7 oxygens in Ca* site
 - Bidentate CO₃ ligation
 - Extra OH or OH₂ ligand
- HREE coordinated to 6 oxygens in Ca site
- Some disruption of structure in higher shells
- Multiple crystal-field environments (Nd)

Implications:

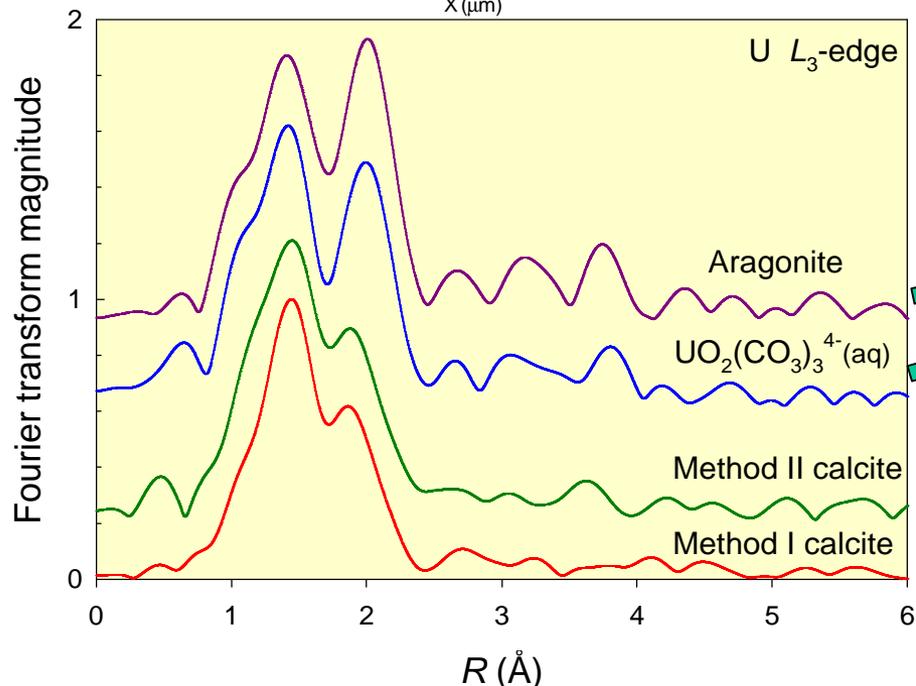
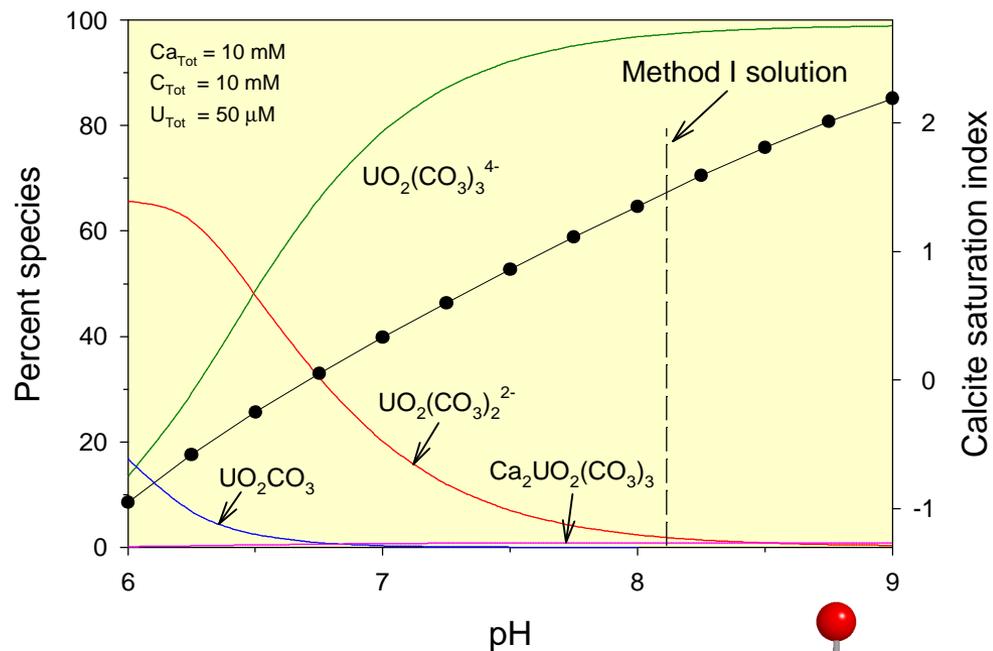
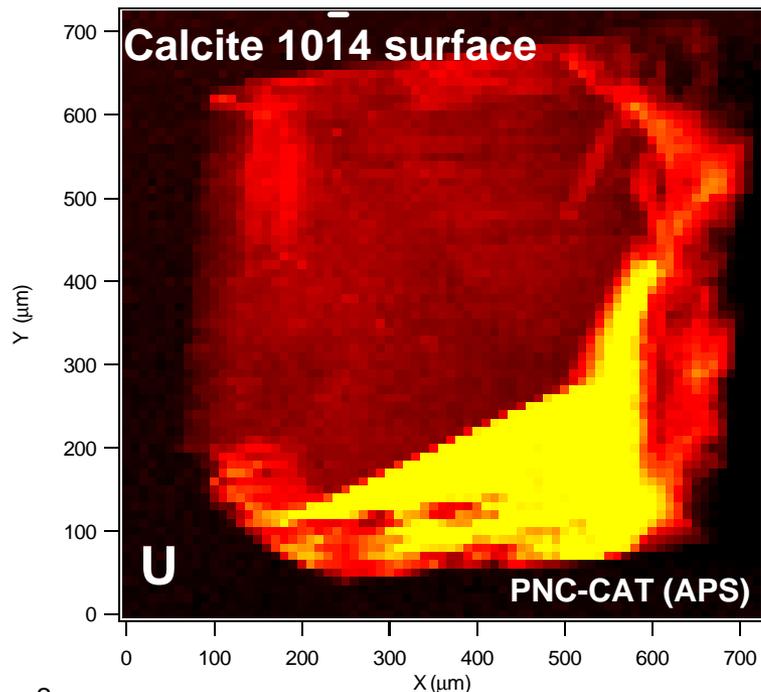
- REE³⁺ strongly taken up by calcite (An³⁺ ?)
- Local defect structure(s) for Nd, Sm (An³⁺ ?)
- Increased energetics, solubility (?)
- Difference in charge compensation mechanism for L/H REE (?)
- Effect on K_d and long-term retention (?)

Octahedral coord.
in calcite

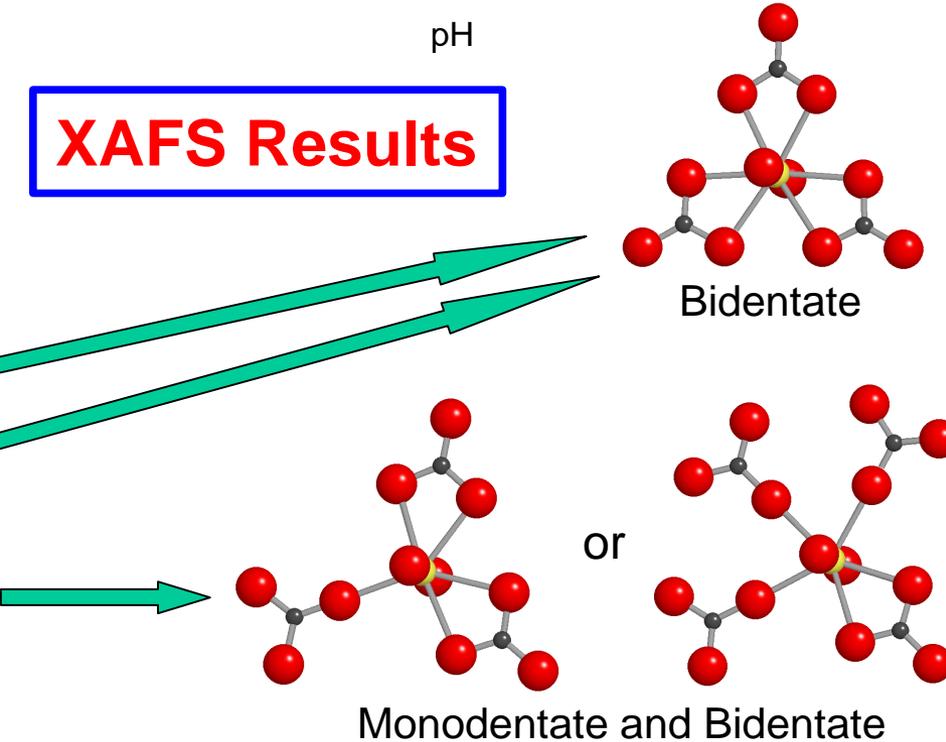


Bi- and monodentate CO₃
ligation in [Nd₂(CO₃)₈]
anion (Bond et al., 2000)

Coprecipitation of uranyl with calcite – Coordination and surface controls on K_d



XAFS Results



Uranyl Sorption on Calcite

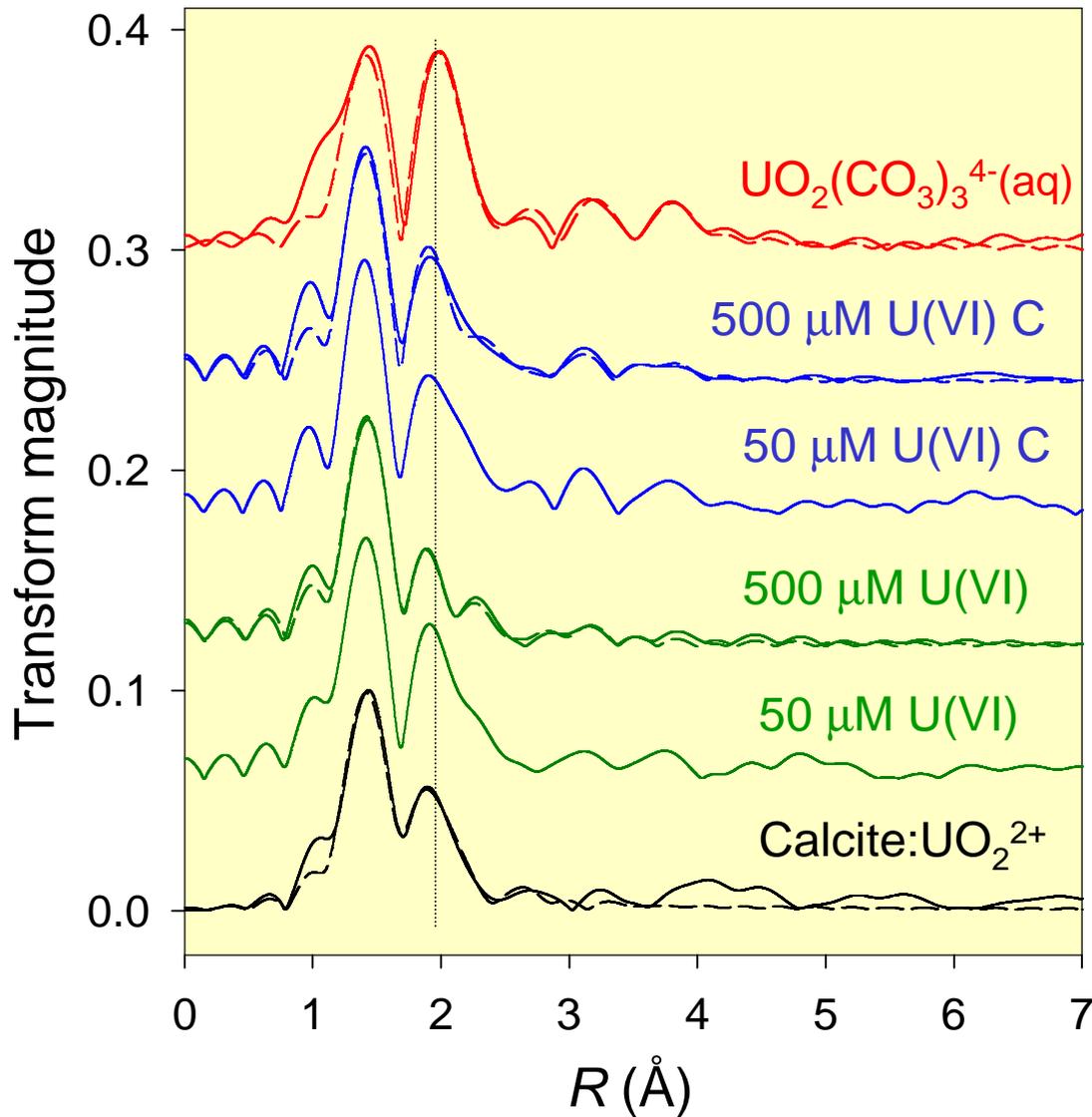
- Complex sorption/desorption behavior shown: initial uptake followed by desorption (Morse et al., 1984); possible scavenging of CO_3^{2-} (?)
- Uranyl uptake by adsorption at low $[\text{U(VI)}]$; surface precipitation occurs at higher $[\text{U(VI)}]$ and high pH (Carroll and others, 1991, 1992)
- Adsorption studies on silicates show surface complex varies with solution pH: inner-sphere at near-neutral pH and outer-sphere at low pH

Present work: evaluate sorption complexes at calcite surface [f (loading, pH)]

Method:

- Calcite suspension equilibrated at $\log P(\text{CO}_2) = -3.5$ (eq. pH = 8.28)
- U(VI) concentrations: 50 and 500 μM (undersat. w.r.t. rutherfordine, schoepite)
- U(VI) added w/ and w/o additional CO_3^{2-} (pH constant)
- Wet pastes extracted for EXAFS (APS-BESSRC)
- EXAFS analysis in progress

Uranyl adsorption complexes - EXAFS



- Sorption complex similar to triscarbonate species but with shorter U-O_{eq} dist. and possible disorder and/or weak splitting in equatorial shell.
 - No obvious U-Ca back-scattering; expected at 3.5 Å; MS contribution at 3.6 Å
 - Pronounced splitting in eq. shell only in 500 μM (no CO_3); ppt?
 - U-O_{eq} slightly longer in sorbed species than in co-ppt.
- Adsorbed uranyl shows weak interaction at calcite surface.

Implications for Understanding Attenuation and Remediation

- Potential for uptake of UO_2^{2+} by calcite via coprecipitation, adsorption, and possibly surface precipitation. Significant Ln^{3+} uptake.
- Adsorbed UO_2^{2+} complex shows only slight or no splitting of eq. shell. Possible inner-sphere complex, but stability unclear as yet.
- Contaminant uptake on carbonates is very heterogeneous. Surface characteristics are important on several length scales.
- Retention of co-ppt contaminants dependent on stability of (dilute) solid solutions.
- Retention of adsorbed contaminants dependent on stability of surface complex (and solution composition).

Work planned for the final year:

- Complete work on uranyl adsorption
- REE adsorption on calcite
- Influence of surface loading; transition b/t adsorption and surface (co-)precipitation
- CrO_4^{2-} , Sr^{2+} coprecipitation with calcite
- Predictive capability and applications