

# 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  $\text{CaCO}_3$  play in the uptake and sequestration of toxic metals and radionuclides?

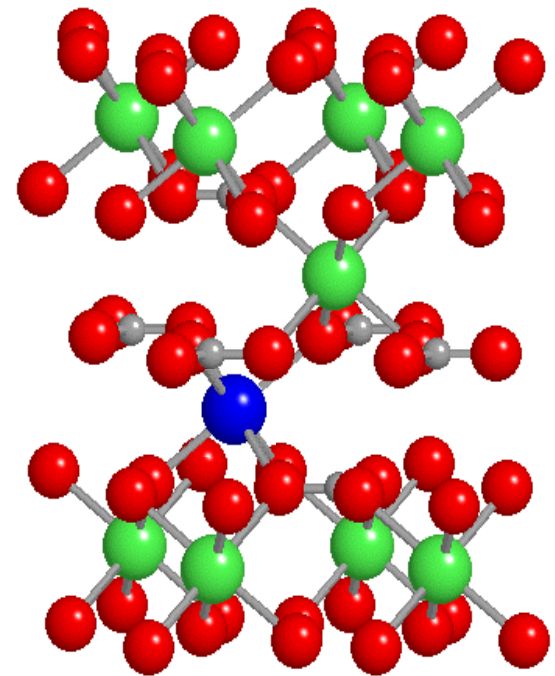
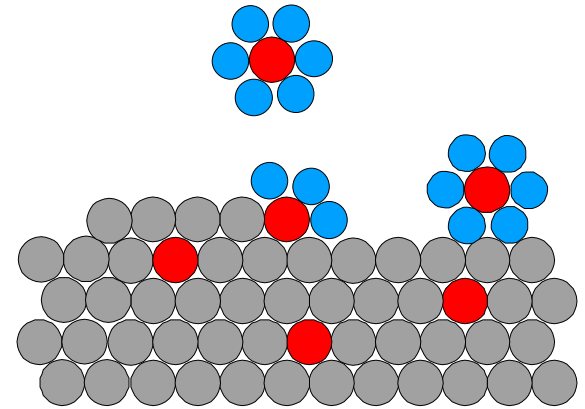
### Distribution and occurrence of $\text{CaCO}_3$ (Hanford)

- 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,  $P_{\text{CO}_2}$ , 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

- $\mu$ -XAS/XRF (NSLS, APS, ALS)

## Batch experiments

- Adsorption (radiotracers)
- Coprecipitation

## Materials

- Model systems
- Natural samples

## Research completed:

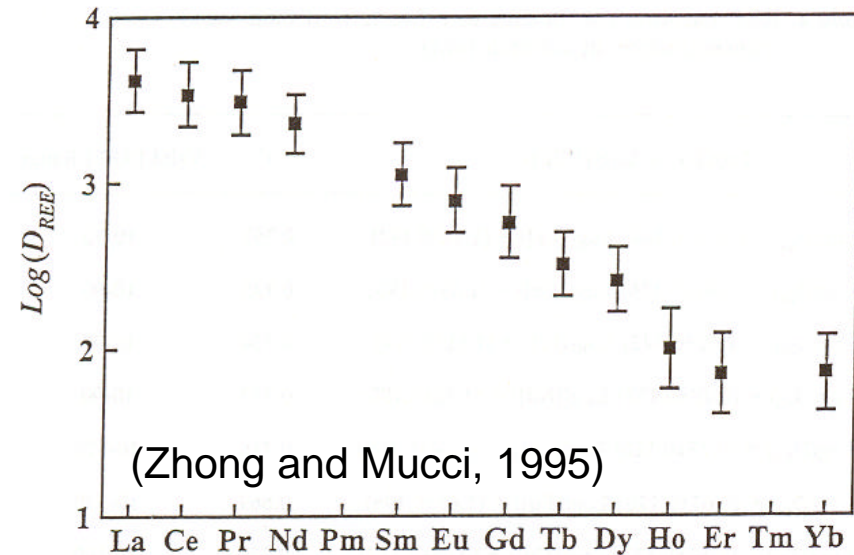
- $\text{UO}_2^{2+}$  coprecipitation with calcite [ $f$  (pH)]  
Systematics; rate effect; micro-distribution  
Speciation, surface site preferences
- $\text{REE}^{3+}$  coprecipitation with calcite  
Analog for  $\text{An}^{3+}$  radionuclides
- $\text{Sr}^{2+}$  and  $\text{Pb}^{2+}$  uptake on natural caliche  
Micro-distribution, heterogeneous
- $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  adsorption on calcite  
Speciation, surface site preferences

## Research underway:

- $\text{UO}_2^{2+}$  adsorption on calcite [ $f$  (loading)]  
Surface speciation (XAFS)
- $\text{REE}^{3+}$  adsorption on calcite  
Speciation, kinetics
- $\text{Cs}^+$  and  $\text{Pb}^{2+}$  sorp/desorp on calcite [ $f$  (pH, I)]  
Systematics, radiotracers, speciation (XAFS)
- $\text{CrO}_4^{2-}$  coprecipitation with calcite  
Micro-distribution, coordination, redox

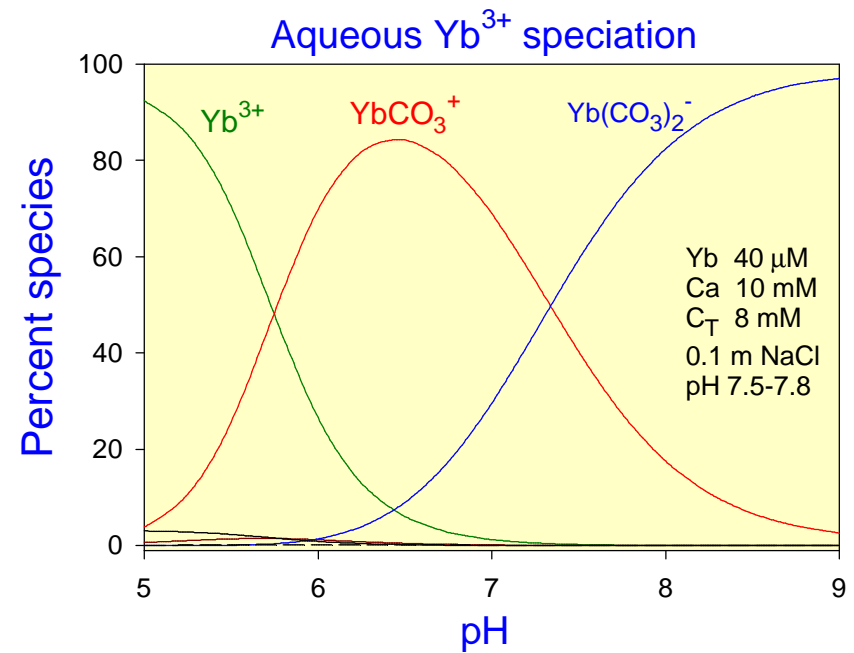
# REE<sup>3+</sup> Uptake by Calcite

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



## Questions:

- Mode of REE<sup>3+</sup> incorporation
- Local structure of heterovalent impurity
- Mechanism of charge compensation
- Role of adsorption, surface speciation

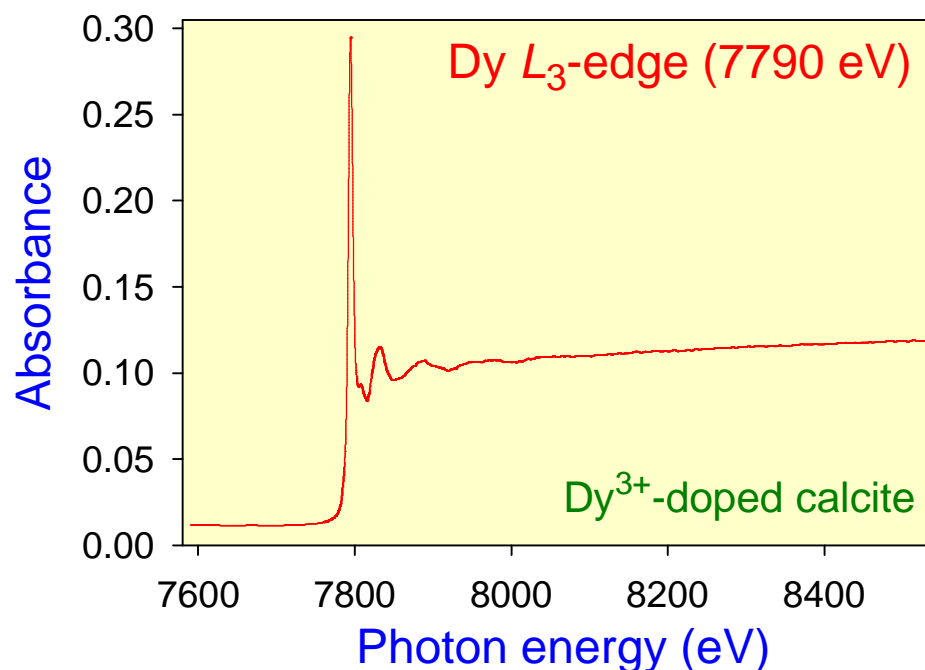
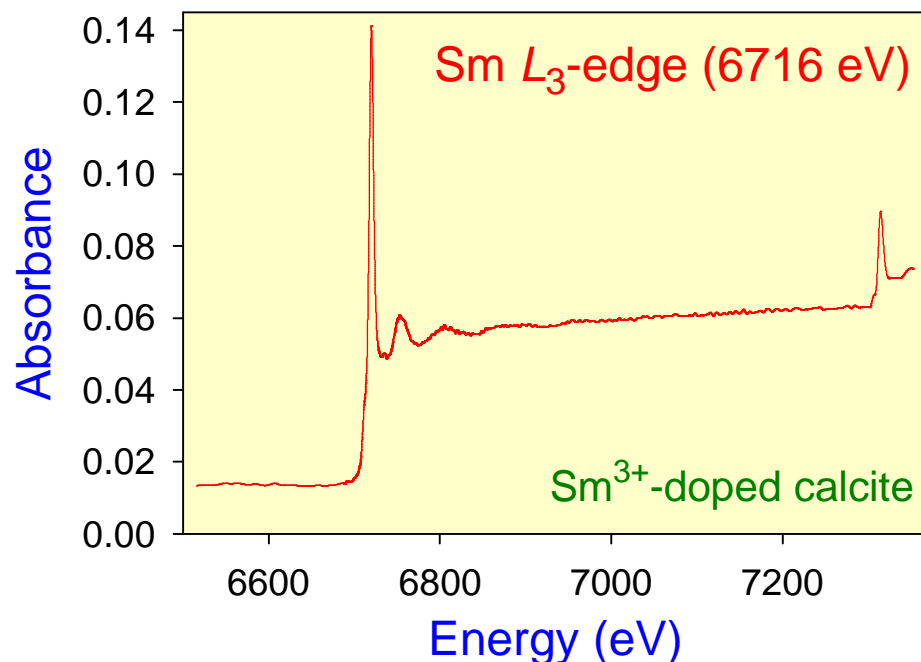


## Approach:

- Coprecipitation of individual REE<sup>3+</sup> with calcite with controlled solution chemistry
- Characterize local structure (EXAFS)
- Characterize REE site symmetries using optical and IR spectroscopy

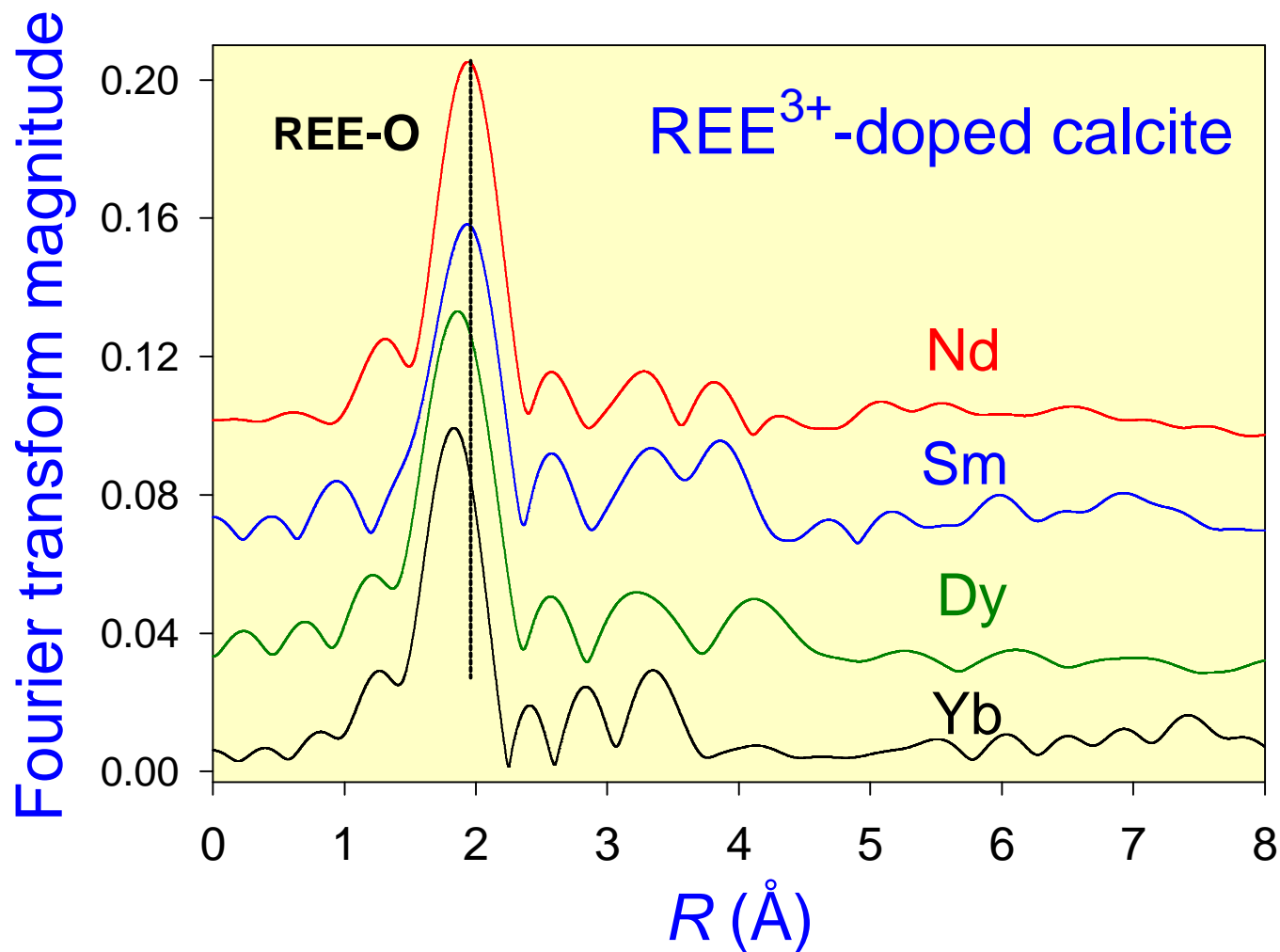
## EXAFS Spectroscopy

- X11A, X18B (NSLS)
- Fluorescence detection (13 element Ge detector)
- $L_3$ -edges
  - Limited  $k$  range (LREE)
  - Multielectron excitations?

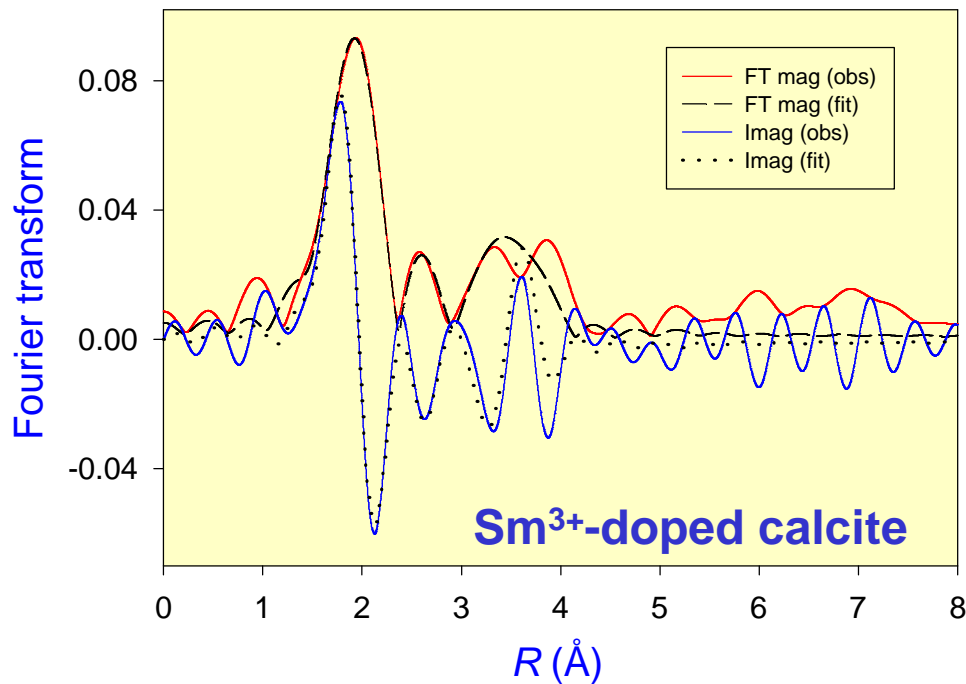




## $L_3$ -edge EXAFS – Fourier Transforms

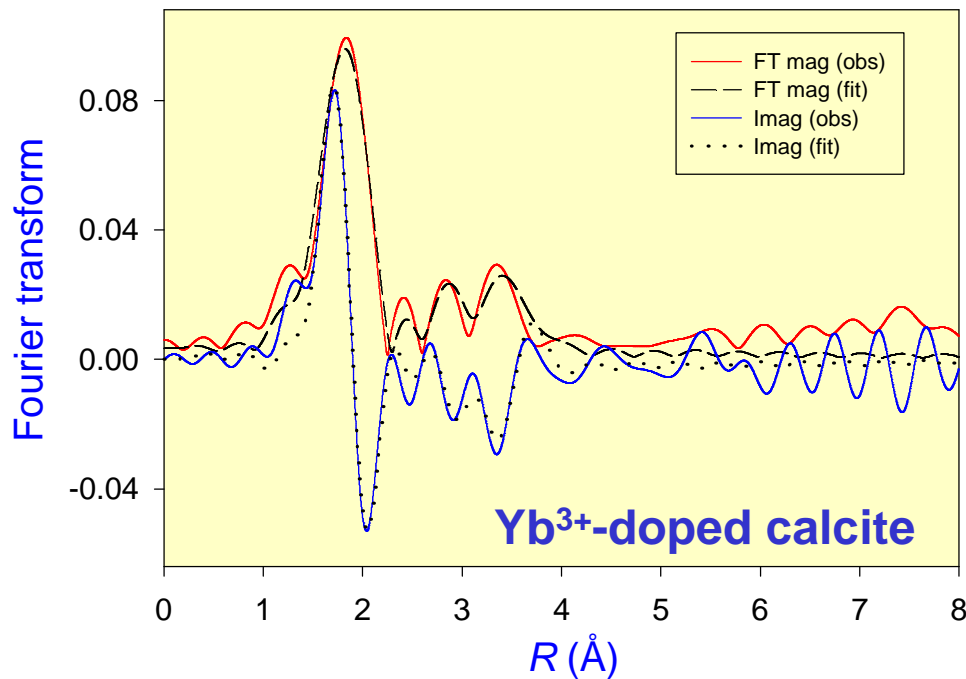


# Selected XAFS Fit Results



## Calcite:Sm<sup>3+</sup>

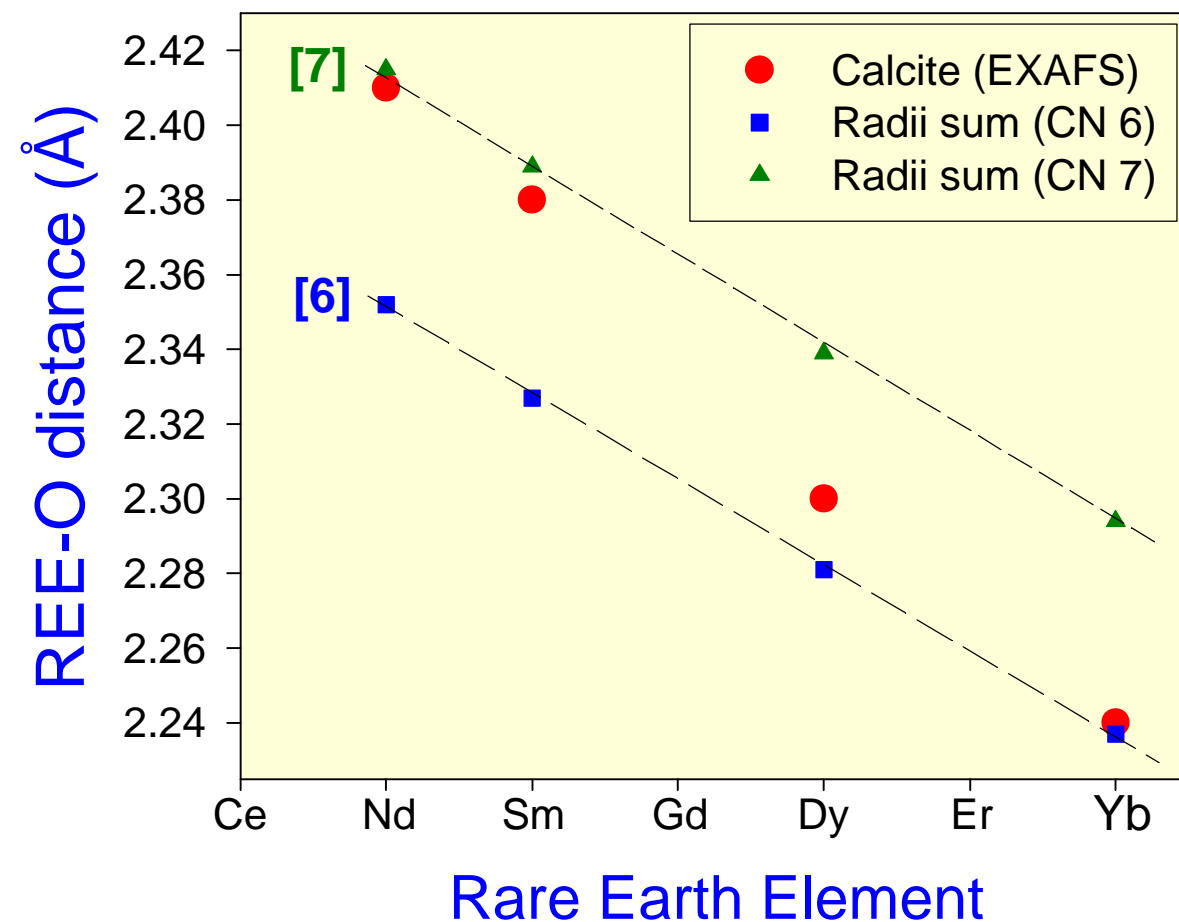
	$R$	CN	$\sigma^2$
Sm-O	2.38	8.3	0.009
Sm-C	3.24	6*	0.008
Sm-O	3.48	6*	0.012
Sm-Ca	4.09	6*	0.012



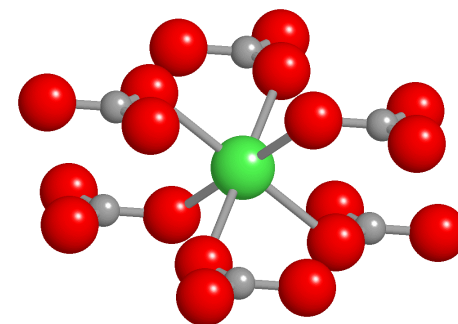
## Calcite:Yb<sup>3+</sup>

	$R$	CN	$\sigma^2$
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)

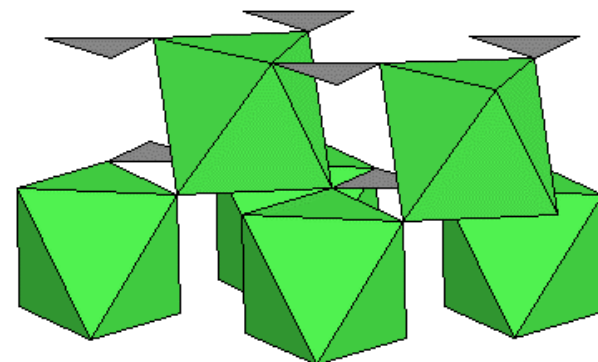


Ca octahedron  
in calcite

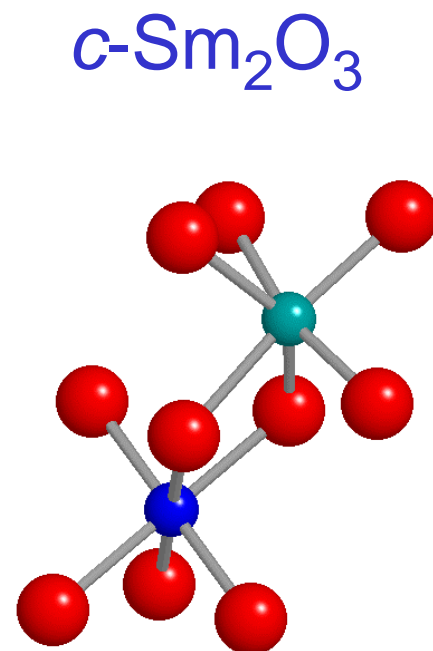
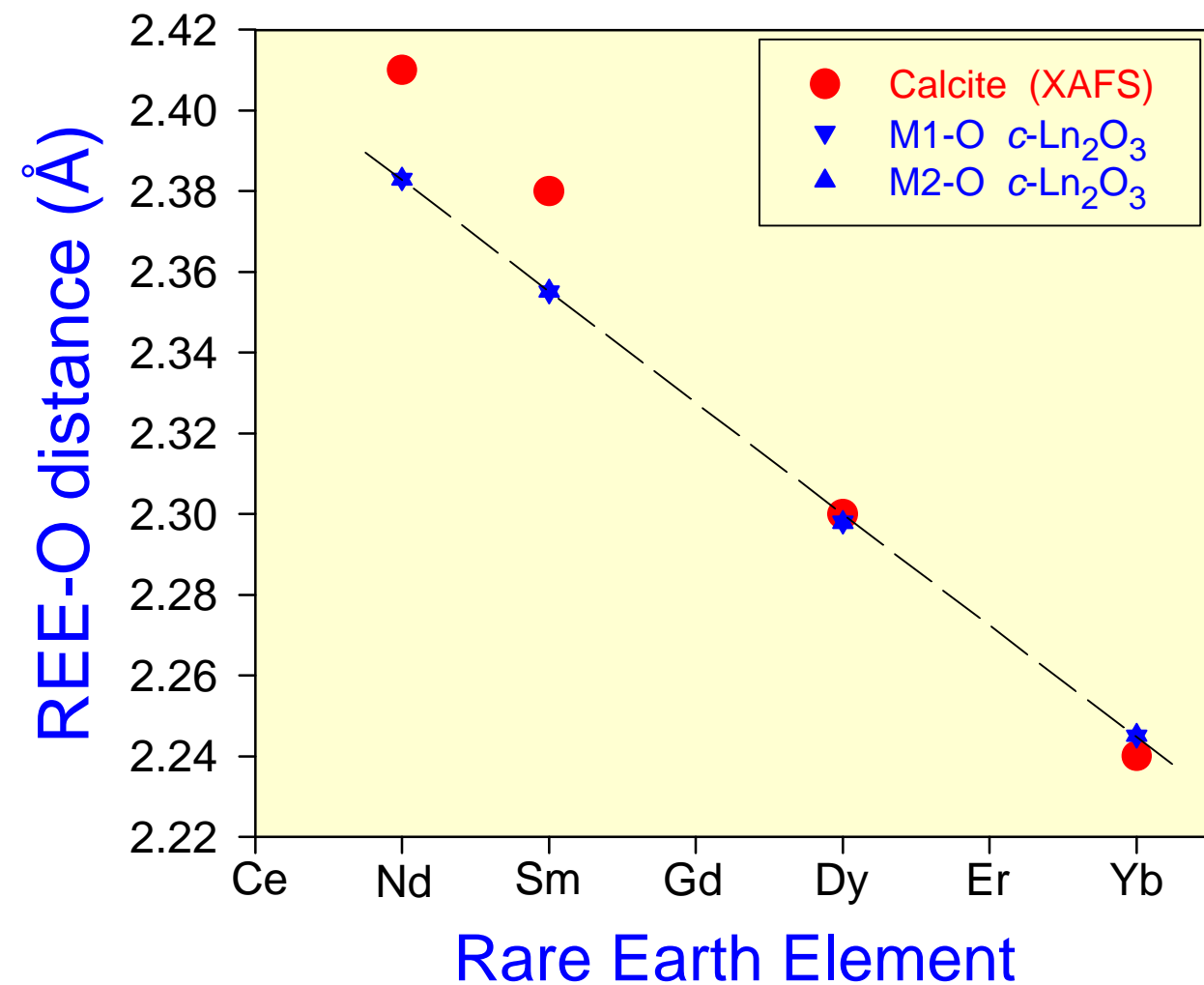


- Nd-O and Sm-O distances suggest 7-fold coord.
- Dy-O and Yb-O distances consistent with 6-fold
- Coord. differences supported by bond-valence sums

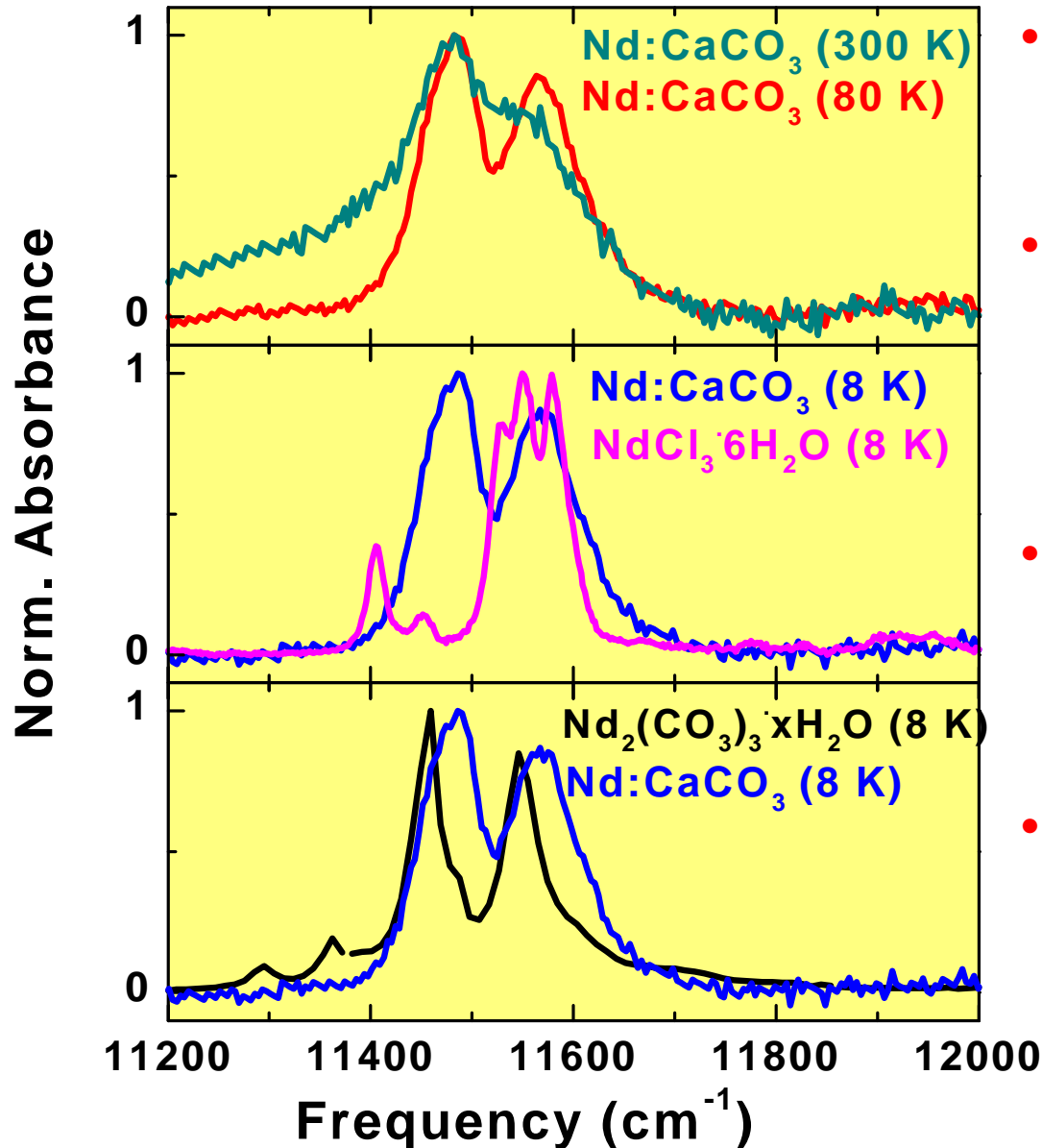
Corner-sharing  
topology  
in calcite



## Comparison with REE-O in lanthanide sesquioxides



# Optical Spectroscopy – Nd<sup>3+</sup> in Calcite



- Optical spectroscopy can distinguish different Nd<sup>3+</sup> crystal field environments
- Neodymium chloride and Neodymium carbonate phases are absent in Nd:CaCO<sub>3</sub> samples grown from solution
- Nd:CaCO<sub>3</sub> shows high degree of inhomogeneous broadening and no line sharpening below 80 K
- There is a broad, continuous distribution of crystal field environments for Nd<sup>3+</sup> in calcite.

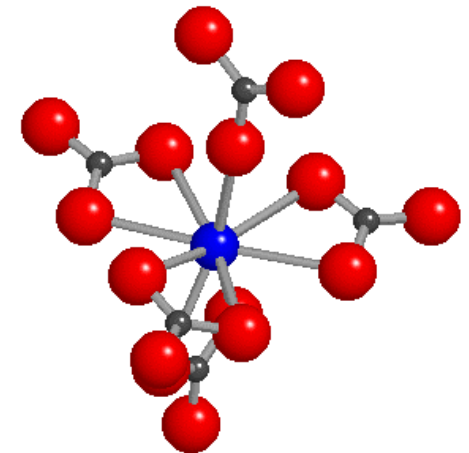
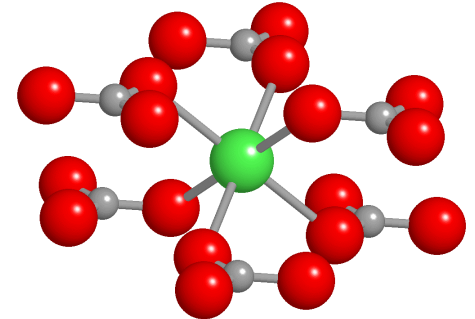
## Conclusions:

- LREE coordinated to 7 oxygens in Ca\* site
  - Bidentate  $\text{CO}_3$  ligation
  - Extra OH or  $\text{OH}_2$  ligand
- HREE coordinated to 6 oxygens in Ca site
- Some disruption of structure in higher shells
- Multiple crystal-field environments (Nd)

## Implications:

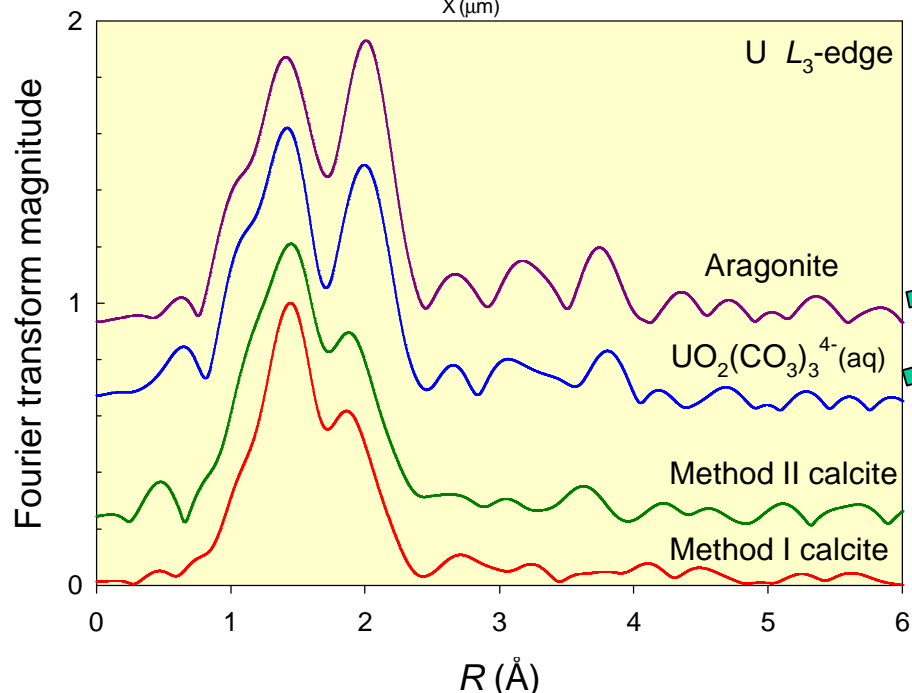
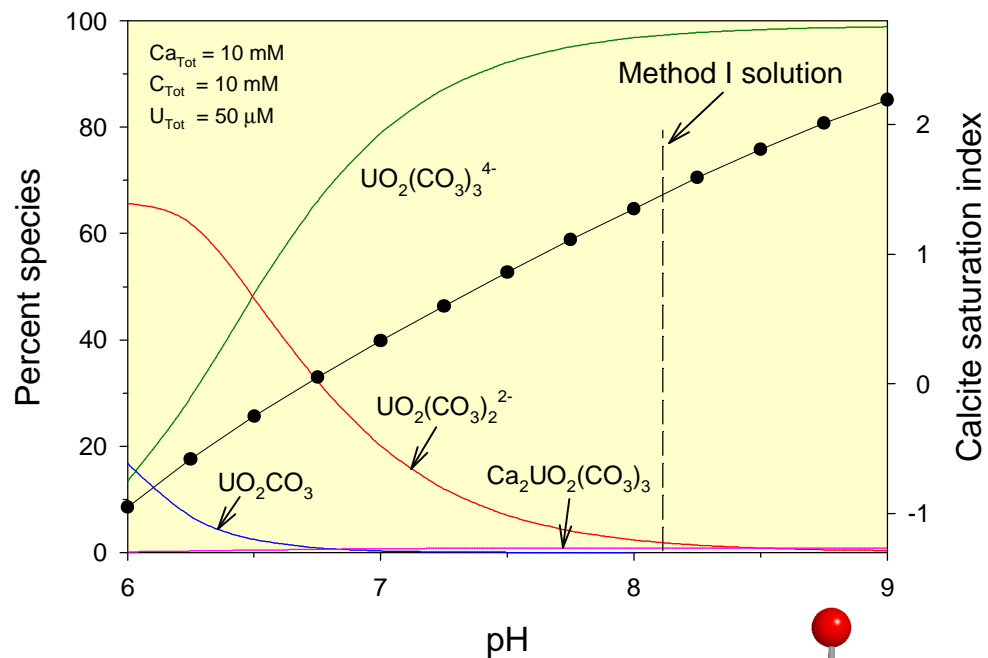
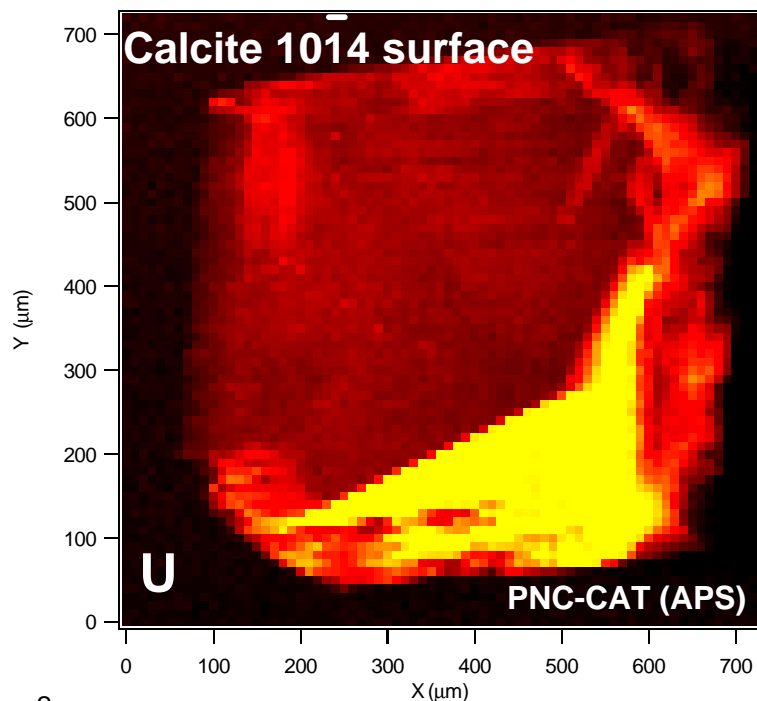
- $\text{REE}^{3+}$  strongly taken up by calcite ( $\text{An}^{3+}$  ?)
- Local defect structure(s) for Nd, Sm ( $\text{An}^{3+}$  ?)
- Increased energetics, solubility (?)
- Difference in charge compensation mechanism for L/H REE (?)
- Effect on  $K_d$  and long-term retention (?)

Octahedral coord.  
in calcite

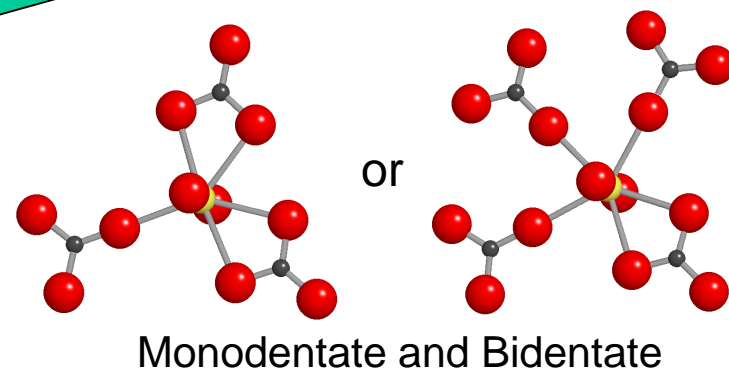
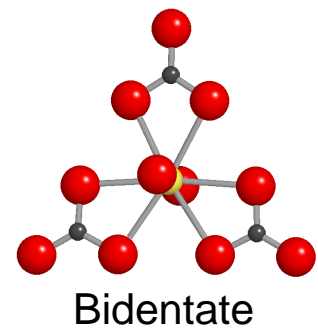


Bi- and monodentate  $\text{CO}_3$   
ligation in  $[\text{Nd}_2(\text{CO}_3)_8]$   
anion (Bond et al., 2000)

# 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  $\text{CO}_3^{2-}$  (?)
- 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

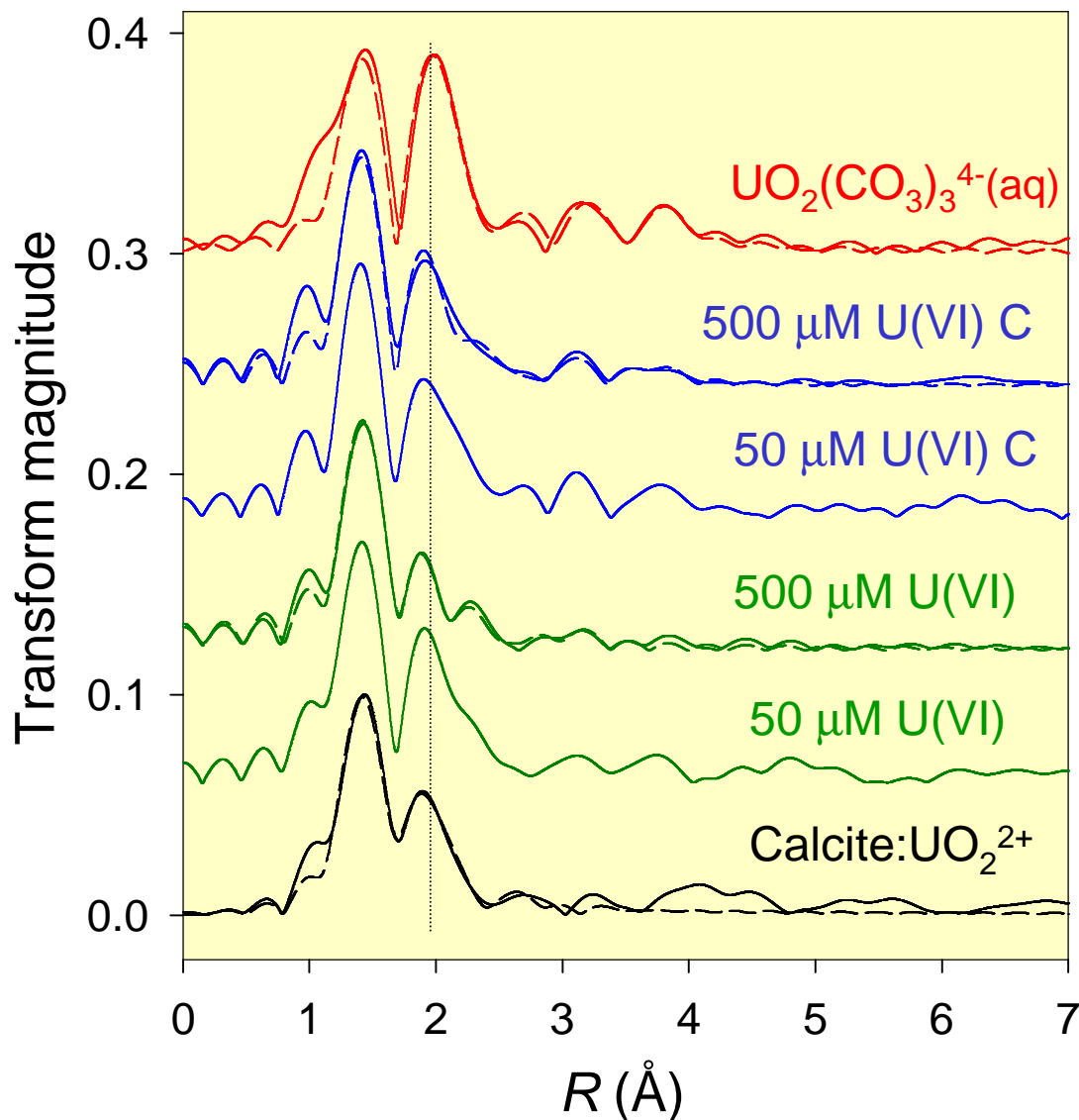
Present work: evaluate sorption complexes at calcite surface [ $f$  (loading, pH)]

### Method:

- Calcite suspension equilibrated at  $\log P(\text{CO}_2) = -3.5$  (eq. pH = 8.28)
- U(VI) concentrations: 50 and 500  $\mu\text{M}$  (undersat. w.r.t. rutherfordine, schoepite)
- U(VI) added w/ and w/o additional  $\text{CO}_3^{2-}$  (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  $\text{U-O}_{\text{eq}}$  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 mM (no  $\text{CO}_3$ ); ppt?
- $\text{U-O}_{\text{eq}}$  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  $\text{UO}_2^{2+}$  by calcite via coprecipitation, adsorption, and possibly surface precipitation. Significant  $\text{Ln}^{3+}$  uptake.
- Adsorbed  $\text{UO}_2^{2+}$  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
- $\text{CrO}_4^{2-}$ ,  $\text{Sr}^{2+}$  coprecipitation with calcite
- Predictive capability and applications