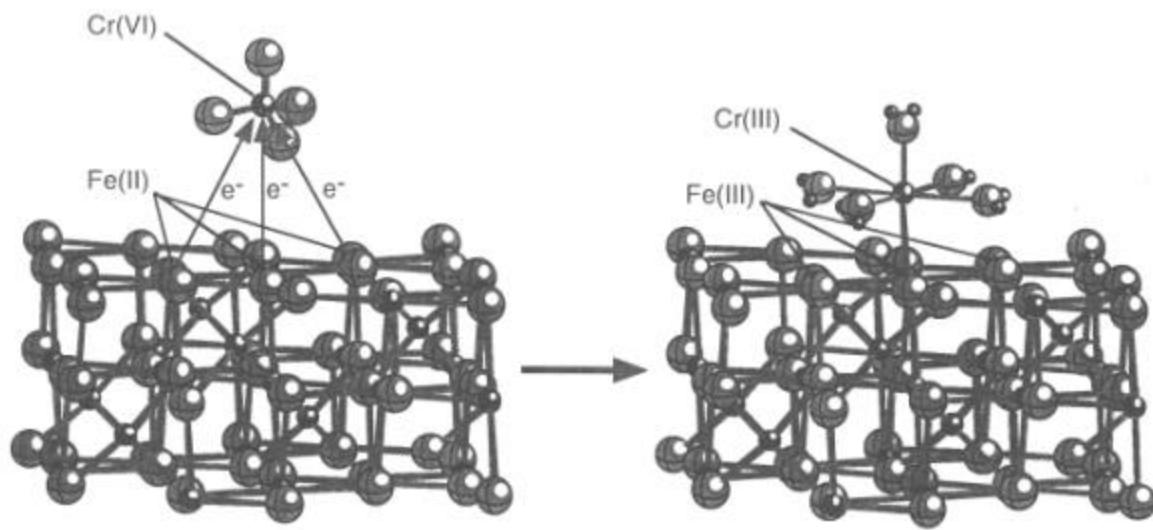


The Influence of Calcium Carbonate Grain Coatings on Contaminant Reactivity in Vadose Zone Sediments

S.A. Chambers¹, J.M. Zachara¹, T. Droubay¹, G.E. Brown, Jr.^{2,3},
T. Kendelewicz³, C. Doyle^{2,3}, S. Higgins⁴, and C.M. Eggleston⁴

1. *Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory -- Richland, WA*
- 2.. *Surface & Aqueous Geochemistry Group, Department of Geological and Environmental Sciences, Stanford University, Stanford, CA.*
3. *Stanford Synchrotron Radiation Laboratory - -SLAC, Stanford, CA*
4. *Department of Geology and Geophysics, University of Wyoming, -- Laramie, WY*



Approach

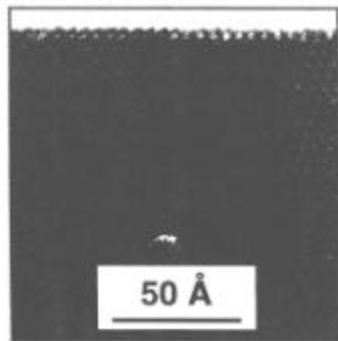
*control experiments
on model systems*

1. Gain understanding of (complex) Fe 2p photoemission lineshapes for model iron oxide film surfaces grown by molecular beam epitaxy --(Droubay & Chambers).
2. Chromate reduction on carbonate films grown from a metal organic precursor [Ca(thd)₂] on model magnetite film surfaces --(Droubay & Chambers).
3. Contaminant reactivity on carbonate films grown from solution and vapor deposition (Ca +H₂O + CO₂) on natural magnetite crystals, and dissolution of carbonate films regrown from solution with impurities -- (Doyle, Kendelewicz, Brown, Higgins and Eggleston).
4. Sorption of contaminants on carbonate coated Hanford sediments --(Zachara).

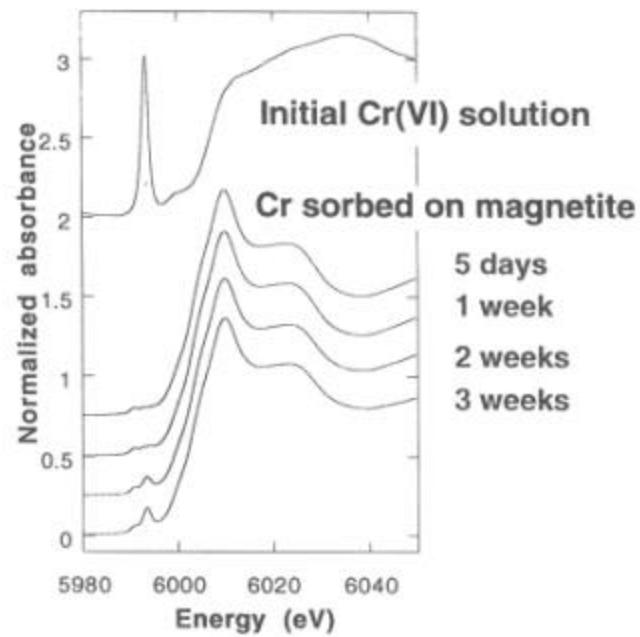
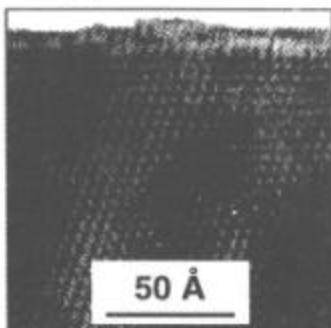
*experiments on
Hanford specimens*

Cr(VI) reduction by reaction with magnetite; magnetite surface passivation

Unreacted magnetite (Fe_3O_4)

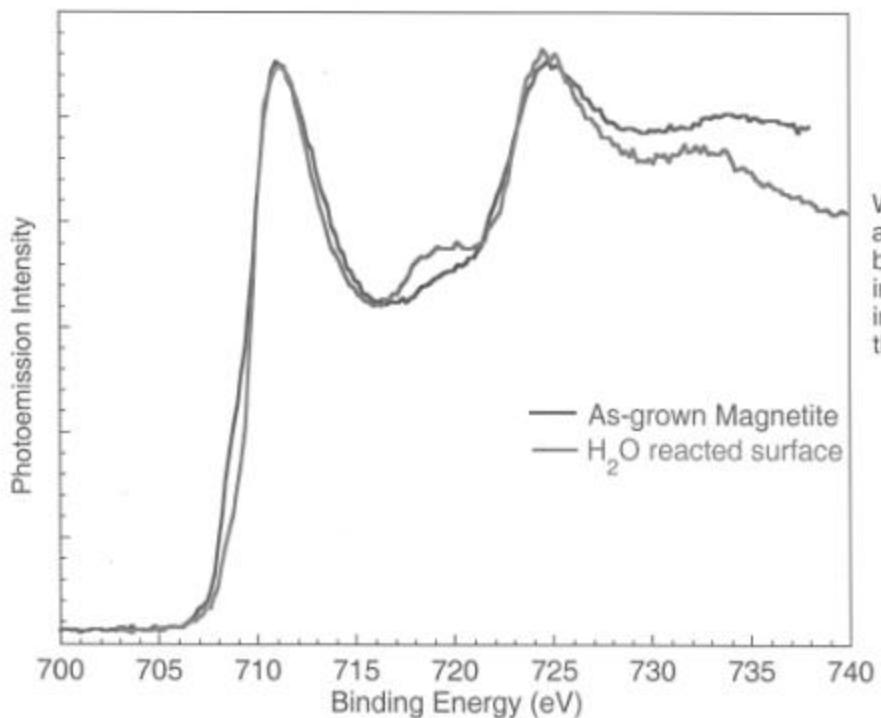


Cr(VI)-reacted magnetite
showing passivation layer

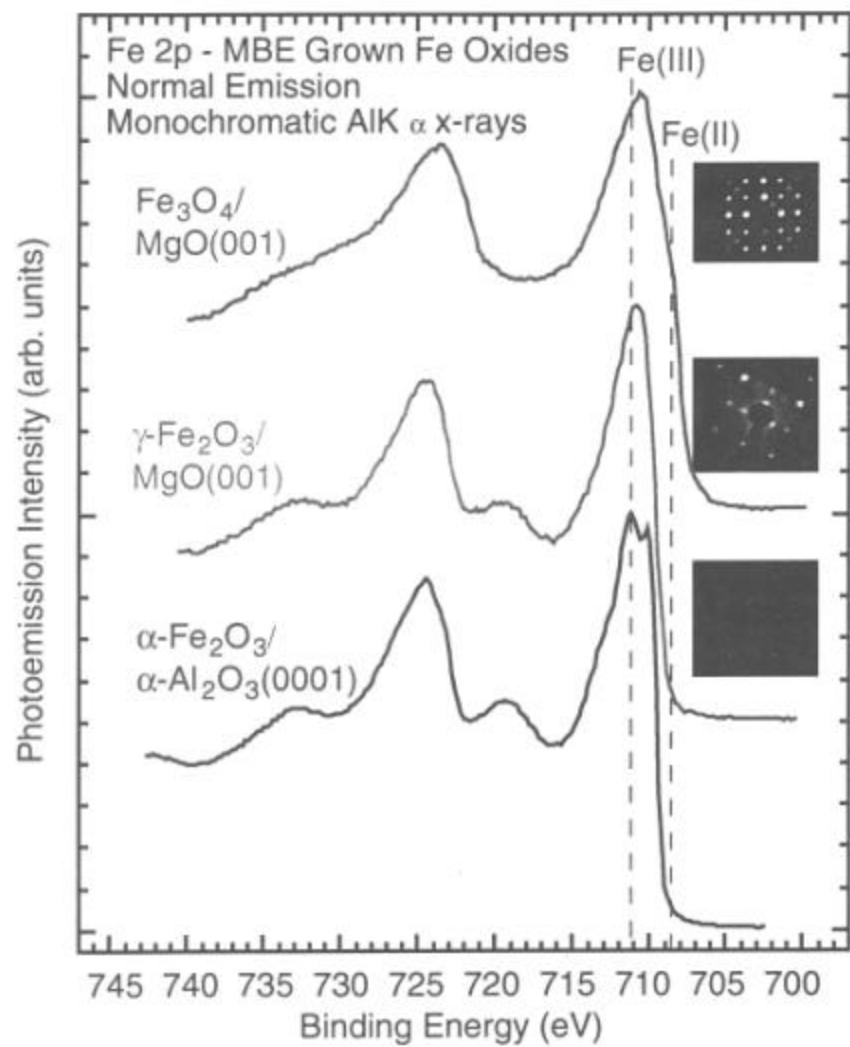


Reaction of liquid water with the Fe₃O₄/Mgo(001) surface

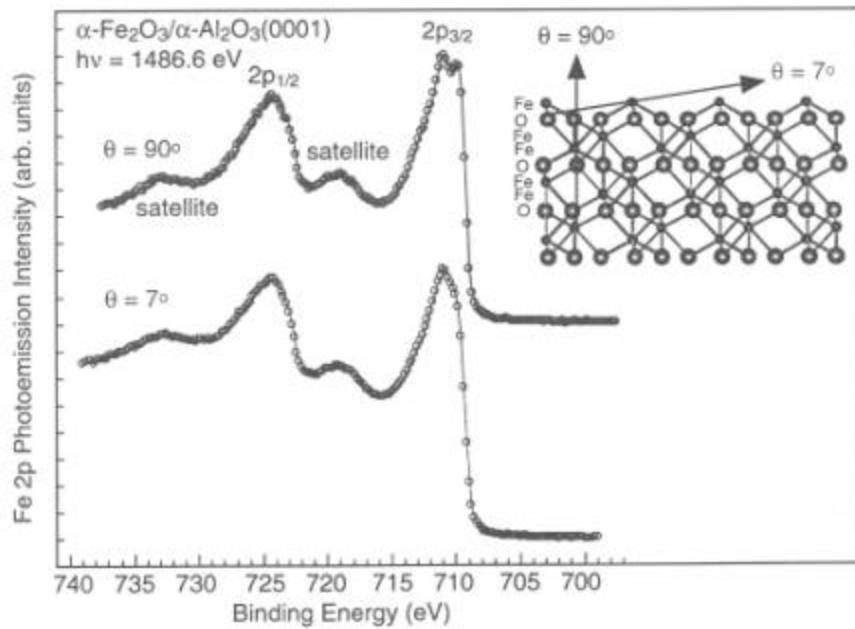
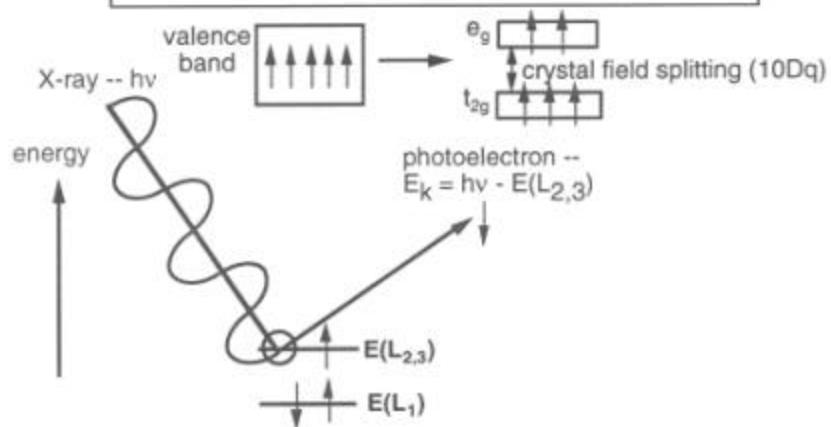
Glancing Angle Fe 2p core-level Photoemission



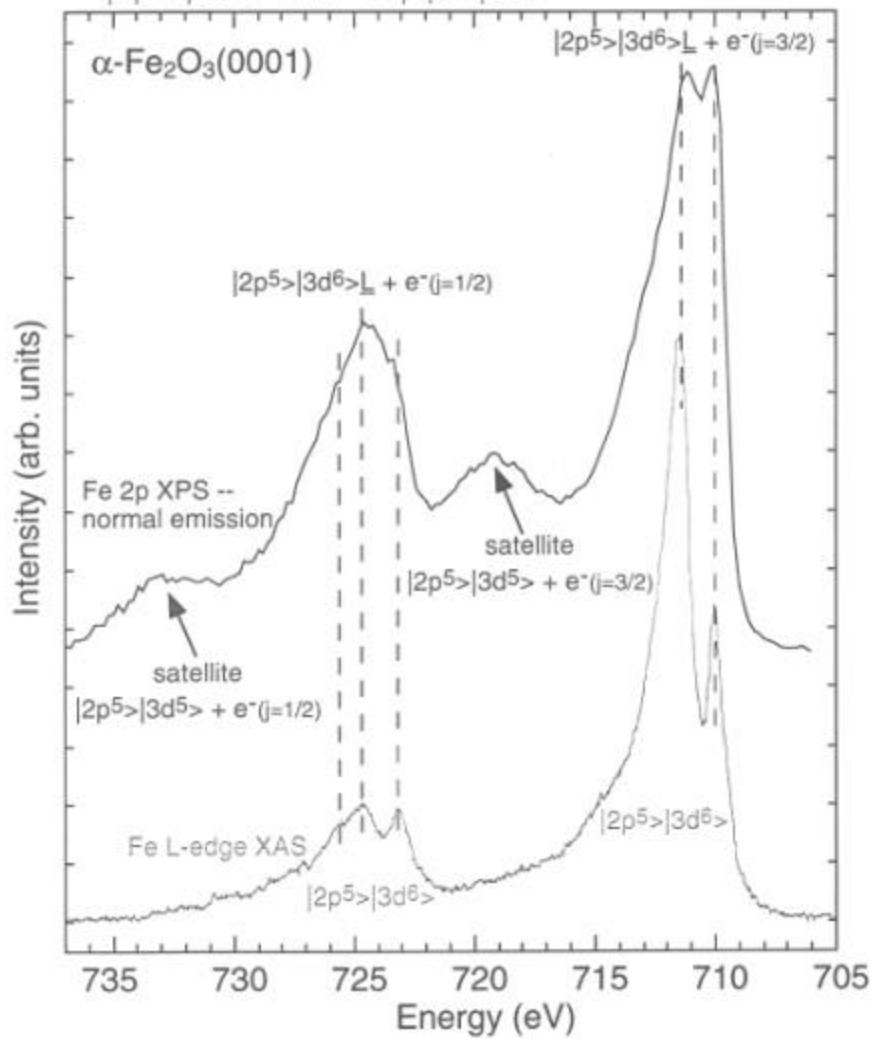
Water reacted surface exhibits a decrease in Fe(II) shown here by a decrease in the shoulder intensity (L3 edge) and an increase in the satellite ~718 eV attributed to the Fe(III) signal



Fe(III) in an octahedral field of O ligands

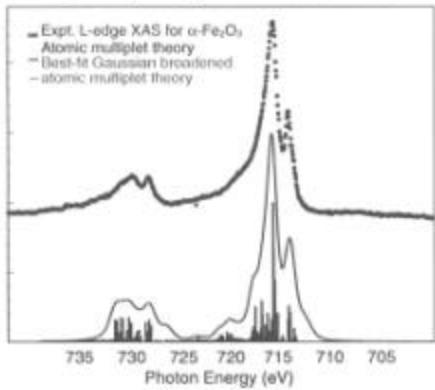


- Fe(III) 2p XPS --
 $|2p^6>|3d^5> + h\nu \rightarrow |2p^5>|3d^5> + |2p^6>|3d^6>_L + e^-$
- Fe(III) L-edge XAS --
 $|2p^6>|3d^5> + h\nu \rightarrow |2p^5>|3d^6>$

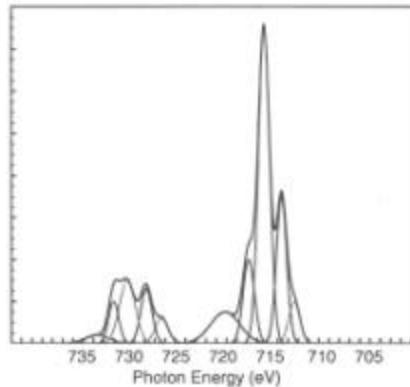


Surface Crystal Field Splitting from XPS, XAS and Multiplet Theory

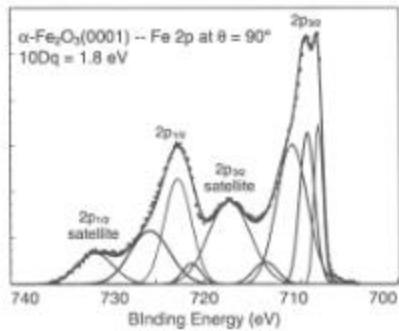
Step 1 -- Measure Fe L-edge XAS. Calculate all final-state multiplets resulting from the unpaired 2p e- interacting with a Fe(III) 3d⁵ L valence configuration, as distributed among the eg and t_{2g} orbitals split by the crystal field in the bulk.



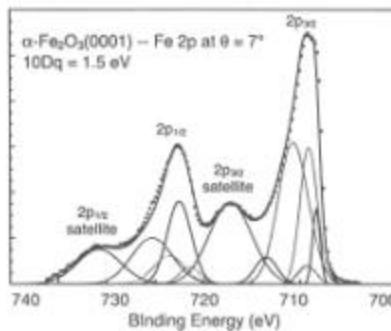
Step 2 -- Select the minimal subset of Gaussians required to fit the XAS. Refit, treating the peak heights and widths as adjustable parameters.



Step 3 -- Using the outcome of the XAS fit as a starting point, vary the multiplet peak intensities and widths to optimize the fit to the Fe 2p XPS at $\theta = 90^\circ$ (normal emission -- more bulk sensitive).



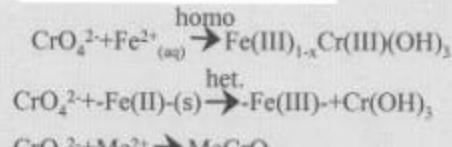
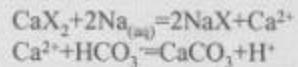
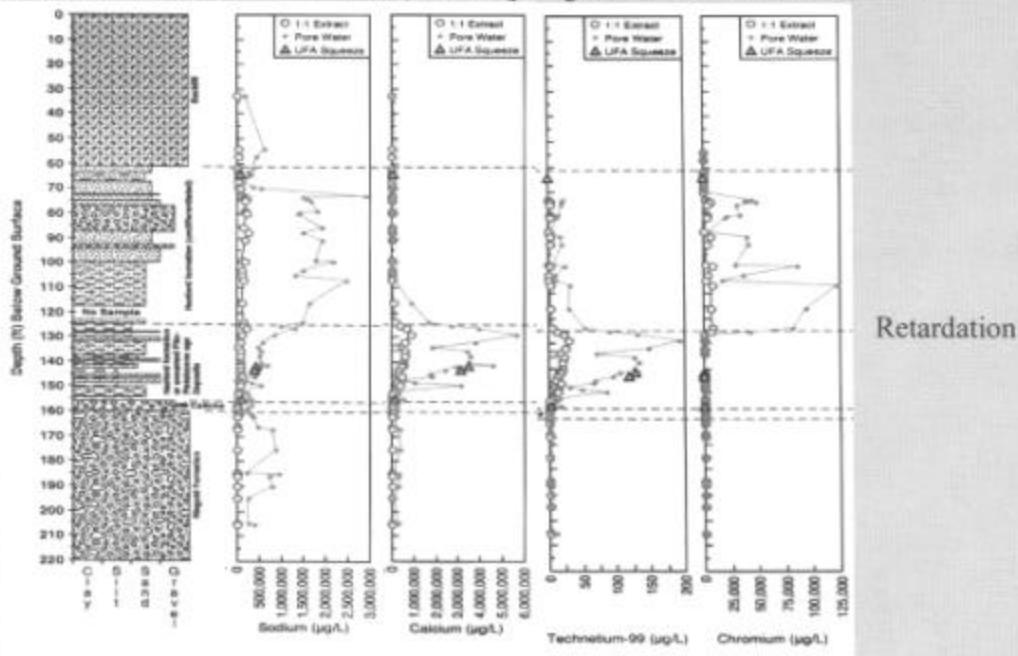
Step 4 -- Repeat step 3 for the Fe 2p XPS at $\theta = 7^\circ$ (grazing emission -- more surface sensitive), this time treating the crystal field splitting (10Dq) for the surface as an adjustable parameter.



Attenuation of CrO₄²⁻ from Tank Waste in the Hanford Vadose Zone

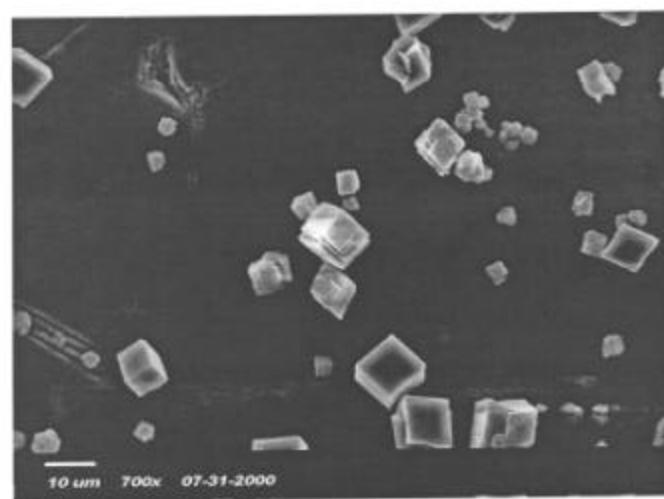
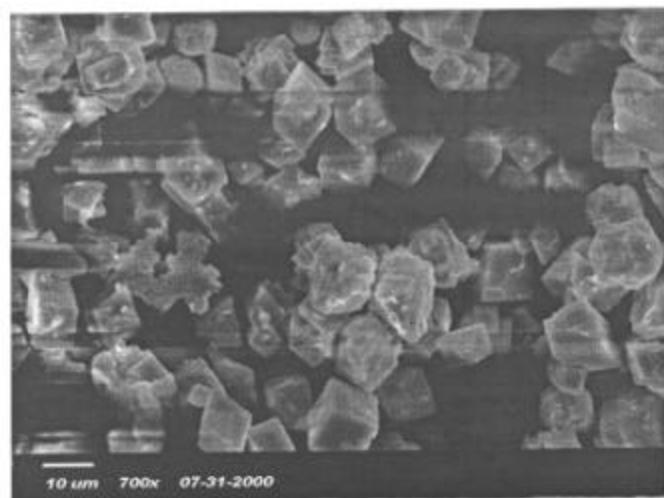
WMA S-SX Core 299-W23-19

⁹⁹Tc, Ca²⁺, and CrO₄²⁻ in groundwater indicative of tank waste

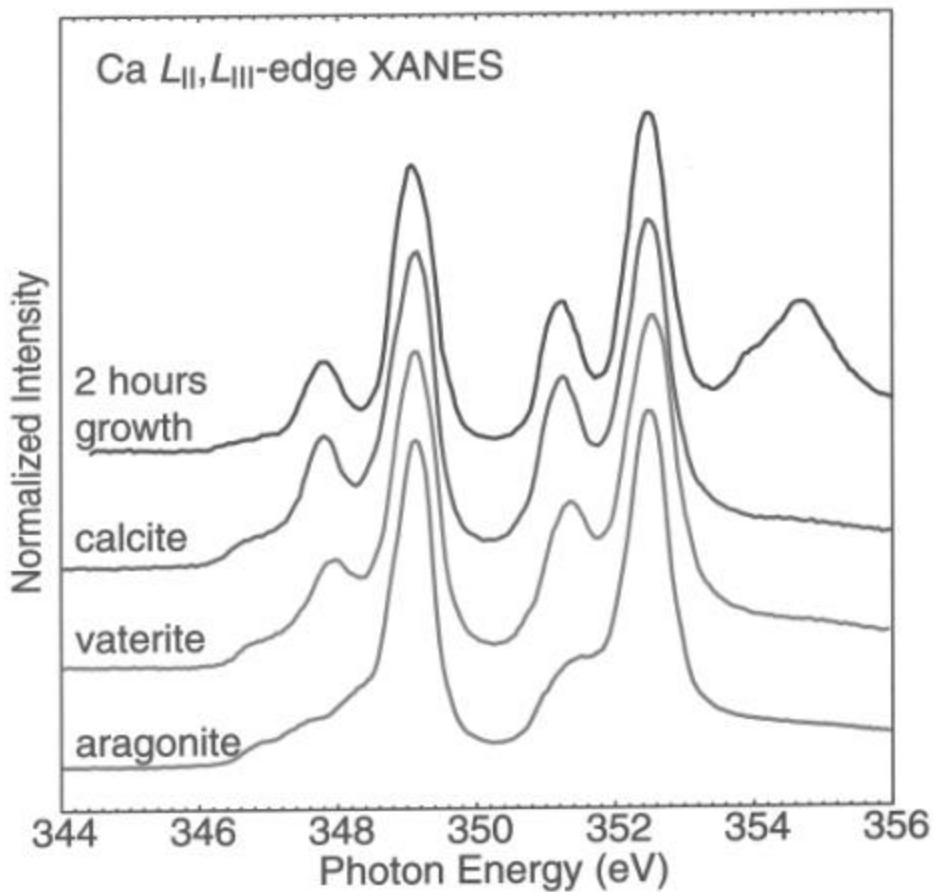


Pacific Northwest National Laboratory

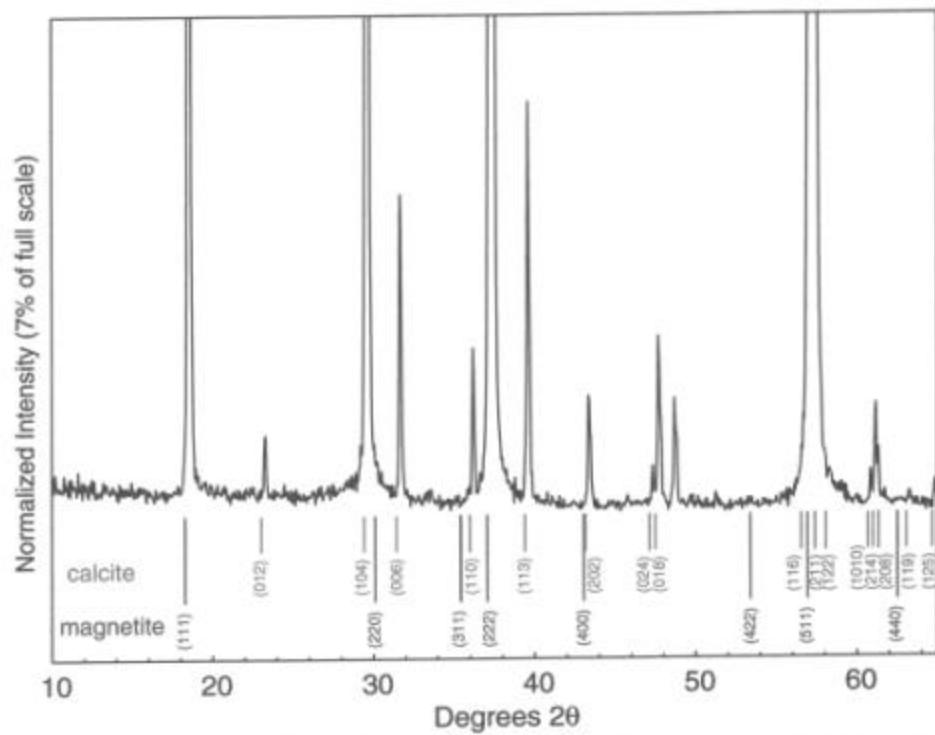
Battelle



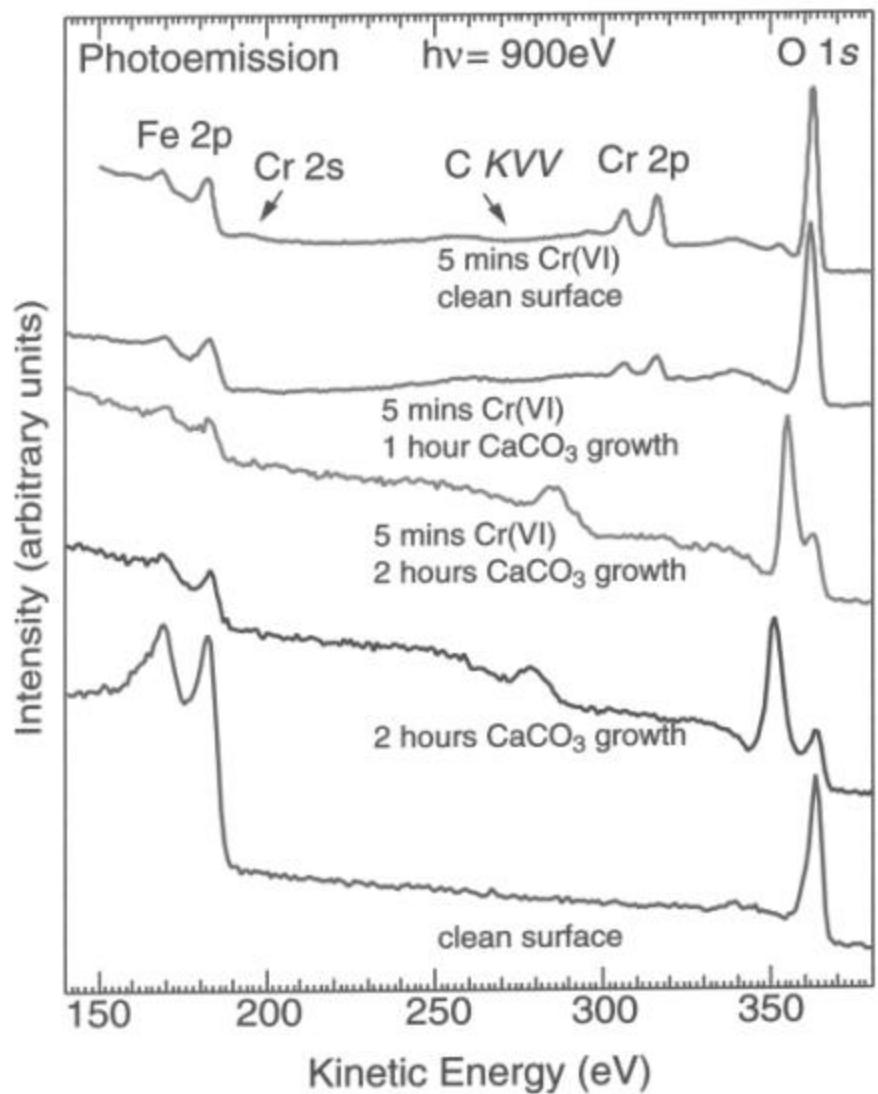
SEM micrographs of CaCO_3 films grown for two hours on magnetite (111). The upper is as-grown, while the lower was taken following dosing the surface with chromate.



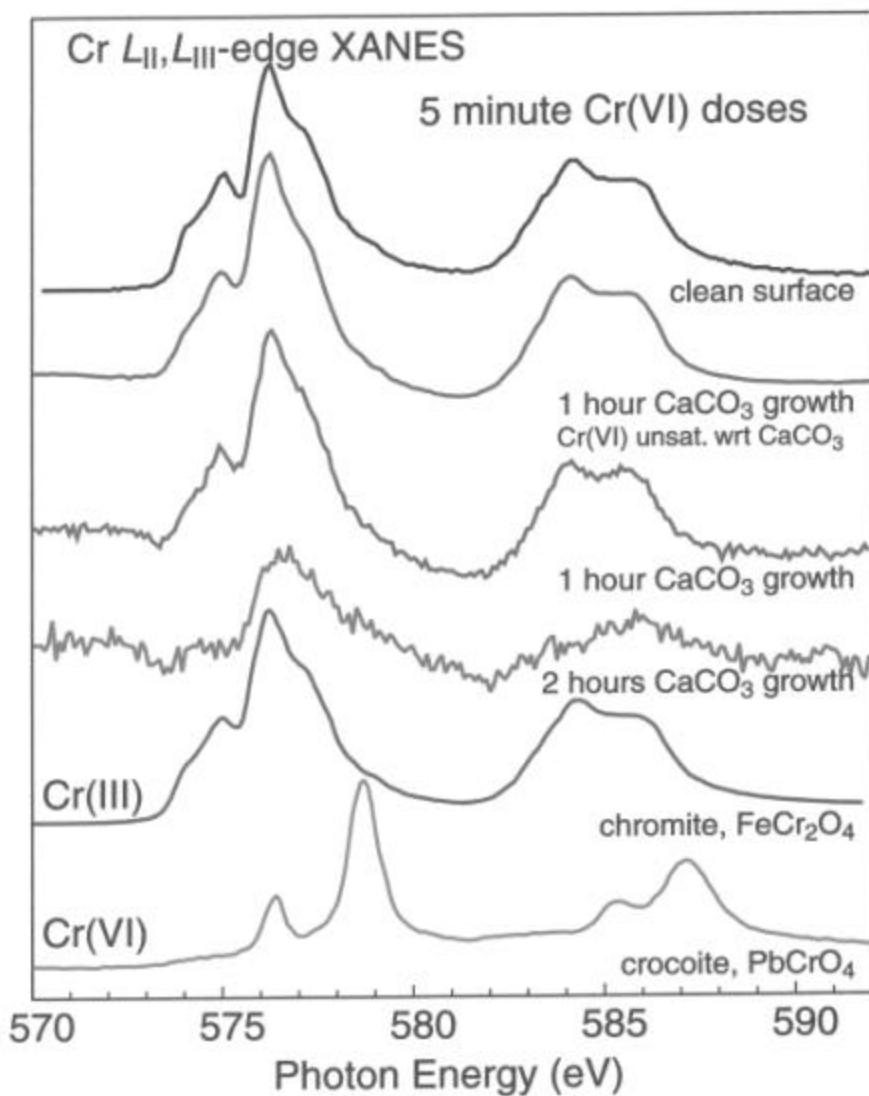
Ca $L_{\text{II}}, L_{\text{III}}$ -edge XANES spectra of carbonate coatings grown on magnetite (111), and of the calcium carbonate polymorphs calcite, vaterite, and aragonite.



Powder X-ray diffraction pattern of a calcium carbonate coated magnetite (111) sample. The reflections for calcite and magnetite are shown. The data was collected using Al $K\alpha$ radiation.



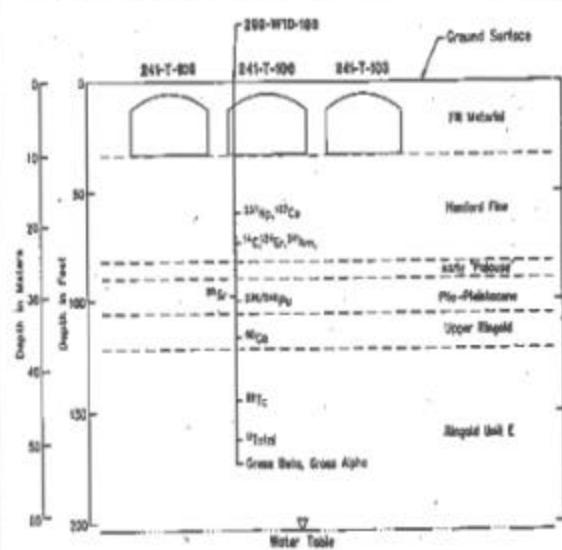
Photoemission spectroscopy showing surface composition progressing from clean to carbonate coated to Cr(VI) dosed surfaces



Cr $L_{\text{II}}, L_{\text{III}}$ -edge XANES spectra of Cr(VI) dosed, clean and carbonate coated magnetites, and model compounds for Cr(III) and Cr(VI).

A Role for CaCO_3 in the Retardation of $^{60}\text{Co}^{2+}$ and $^{90}\text{Sr}^{2+}$?

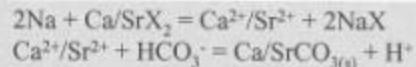
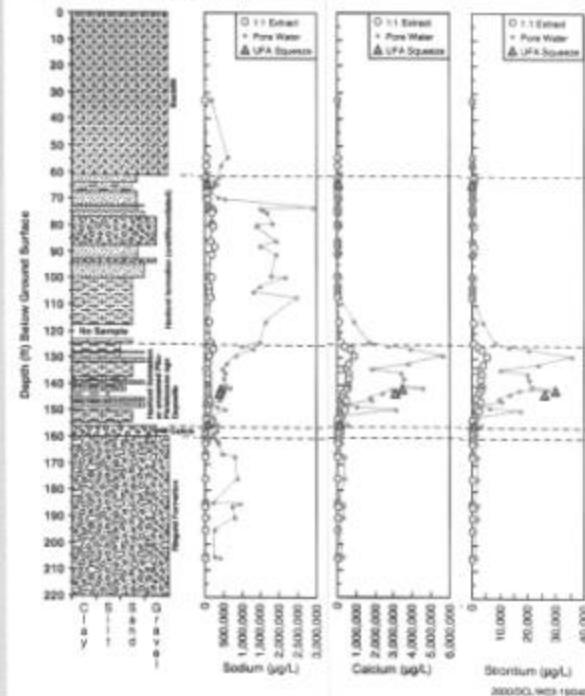
T106 B-Plant/ BiPO_4 Wastes



Deep penetration of ^{90}Sr and ^{60}Co beneath T-106

- depletion of the cold ^{88}Sr pool/high Na
- aqueous complexation (EDTA, diethyl-hexyl phosphoric acid)
- retardation mechanism with CaCO_3
 - + waste-precipitated
 - + plio-pleistocene

299-W23-19 Redox Wastes



Hanford Vadose Zone Carbonates

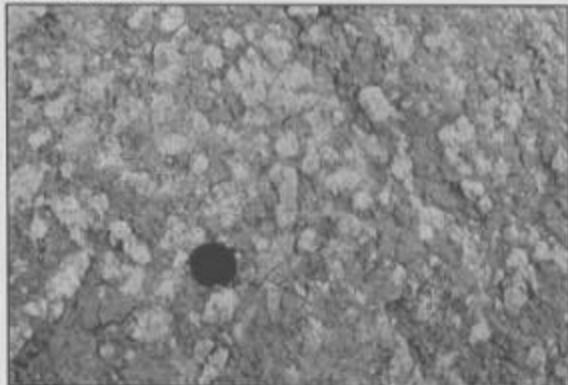
a. Coatings



b. Stringers



c. Nodules

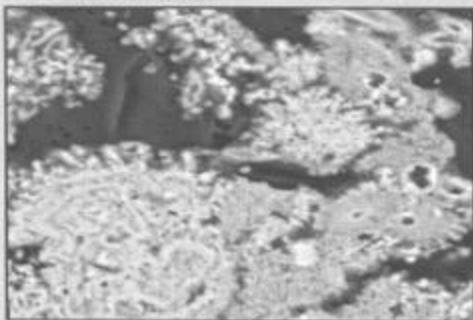


Battelle

Pacific Northwest National Laboratory

Elemental Composition of Hanford Caliche

a. backscatter



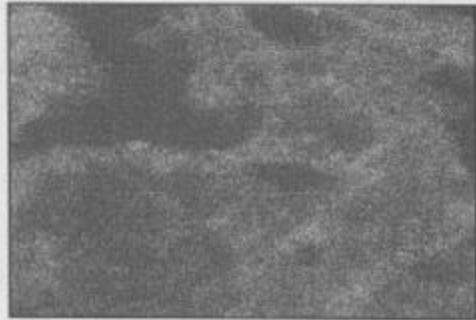
10.0 μm

b. Ca^{2+}



10.0 μm

c. Si



10.0 μm

d. Sr^{2+}



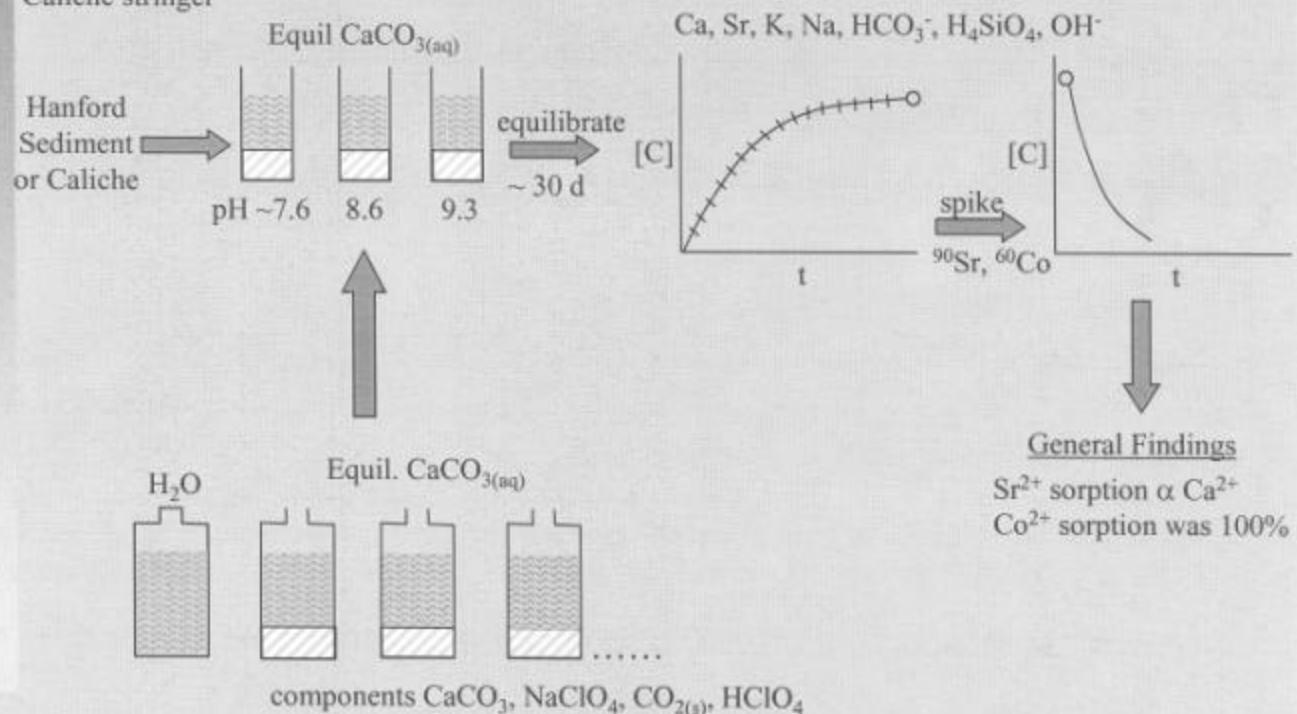
10.0 μm

Battelle

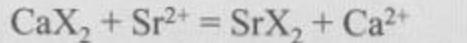
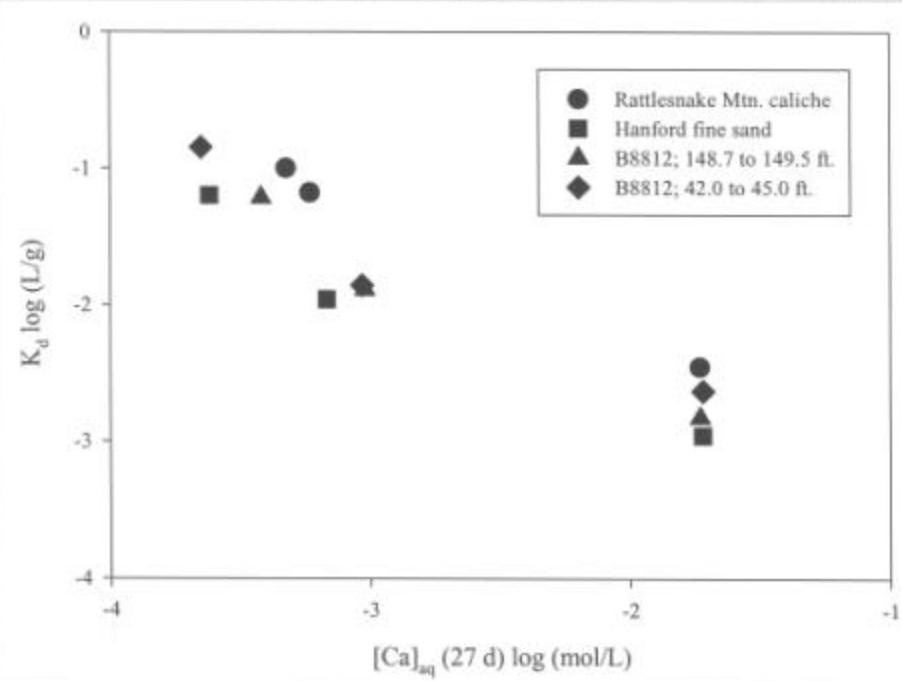
Pacific Northwest National Laboratory

Initial Sorption/Exchange Experiments

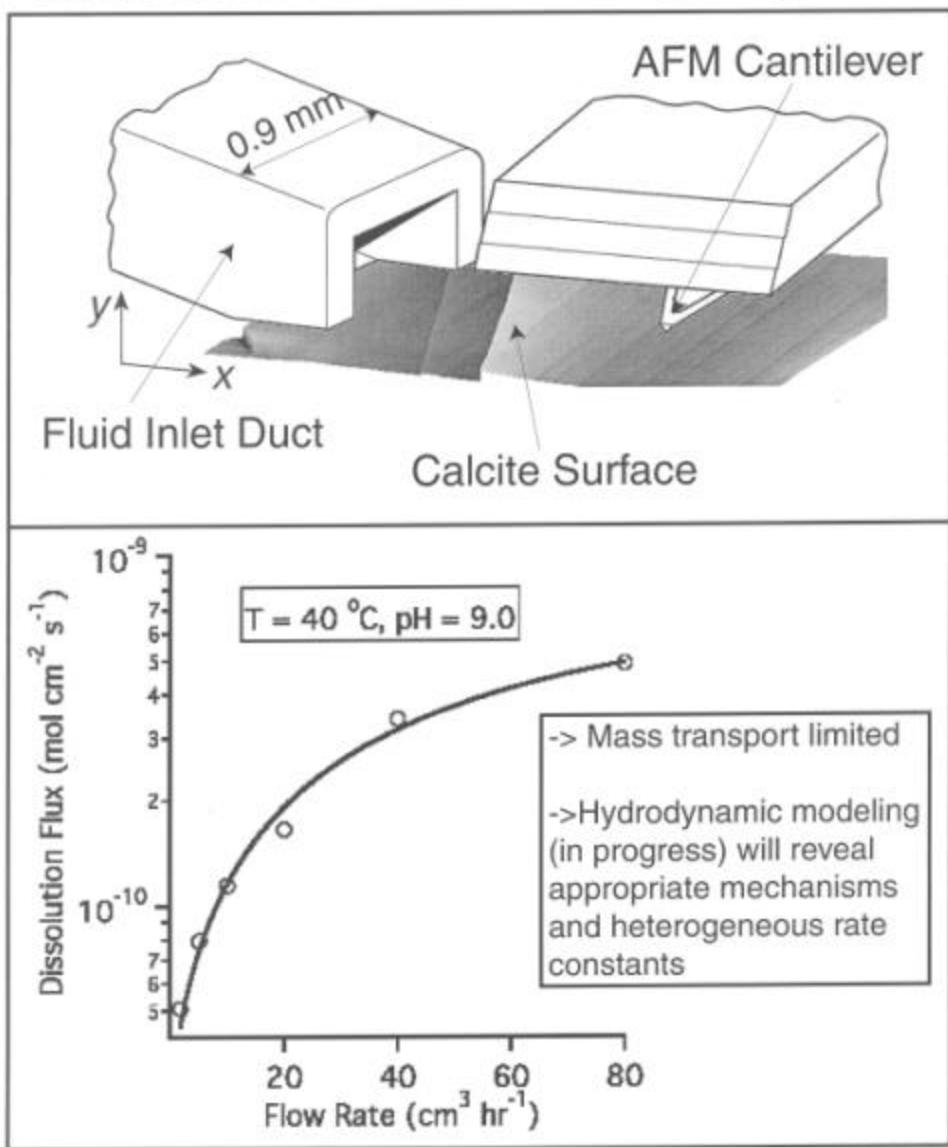
Calcereous sediment (WMA S-SX, 42-45')
Plio-pleistocene sediment (WMA S-SX, 148-149')
Caliche stringer



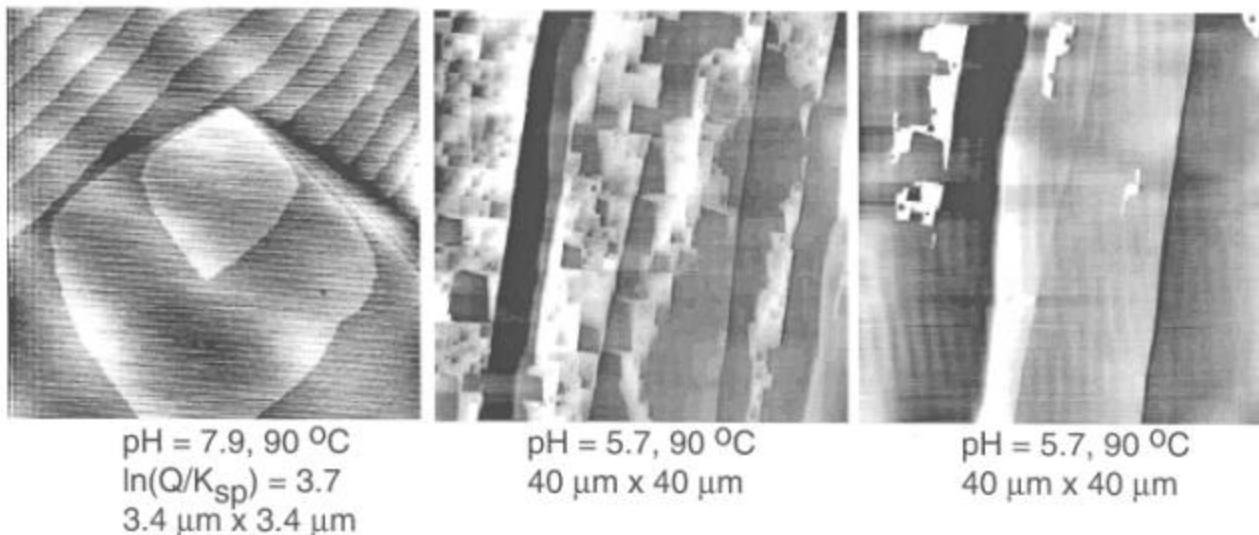
Distribution Coefficient (K_d) of Sr²⁺ With Hanford Calcereous Subsurface Materials



Dissolution Kinetics of Calcite at Elevated Temperatures with Well-Defined Hydrodynamics



Growth of Magnesite in the Presence of Fe(II) Impurities and Subsequent Dissolution of the Precipitated Layers



Defects in the new overlayer results in the overlayer dissolving more rapidly than the original magnesite crystal

Carbonate overlayers grown in the Hanford vadose zone that contain impurities may dissolve at a higher rate than carbonates pre-existing in the vadose zone

Future Work

CrO₄²⁻

- Further mechanistic studies on CaCO₃ veneering
 - heterogeneous electron transfer
 - CaCO₃ passivation
- Macroscopic chemical reaction studies
 - magnetic and micaceous fractions
 - sediments with precipitated CaCO₃

Co²⁺/Sr²⁺

- Mechanistic studies of precipitation/dissolution
 - temperature and minor element effects
- Exchange and coprecipitation experiments with Hanford calcites
 - thermodynamics/kinetics
 - speciation
- In-situ speciation studies of contaminated sediments from T-106
 - plio-pleistocene, center of mass