Influence of $CaCO_{3(s)}$ Grain Coatings on Contaminant Reactivity in the Hanford Vadose Zone

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Rationale and Objective

Rationale

- $CaCO_{3(3)}$ is an ubiquitous minor mineral phase in Hanford sediment (1-25%)
  - Detrital
  - Pedogenic
  - Waste-sediment reaction
- $CaCO_{3(3)}$ may impact contaminant retardation
  - Surface exchange
  - Co-precipitation
  - Passivation/blocking [Cr(VI), Tc(VII)]

Objective

- Define role of $CaCO_{3(s)}$ in cation and anion reaction processes in Hanford sediment using model systems, and pristine/contaminated sediments

Hanford Vadose Zone Carbonates

a. Coatings

b. Stringers

c. Nodules

General Experimental Approaches and Focus

Sorbates: $Cr(VI)O_4^{2-}$ Polyvalent contaminant immobilized as Cr(III). Reducible by α-Fe_3O_4

$Sr^{2+}(^{90}Sr)$ High inventory Hanford contaminant showing moderate retardation (by ion exchange?)

<u>Model System Studies</u> (Chambers and Brown)

Issue: Do $CaCO_{3(s)}$ grain coatings passivate mineral reductant systems?

- Synthetic Fe(II/III) oxides
- Magnetite isolates
- Surface microscopies and spectroscopies

<u>Sediment Studies</u>

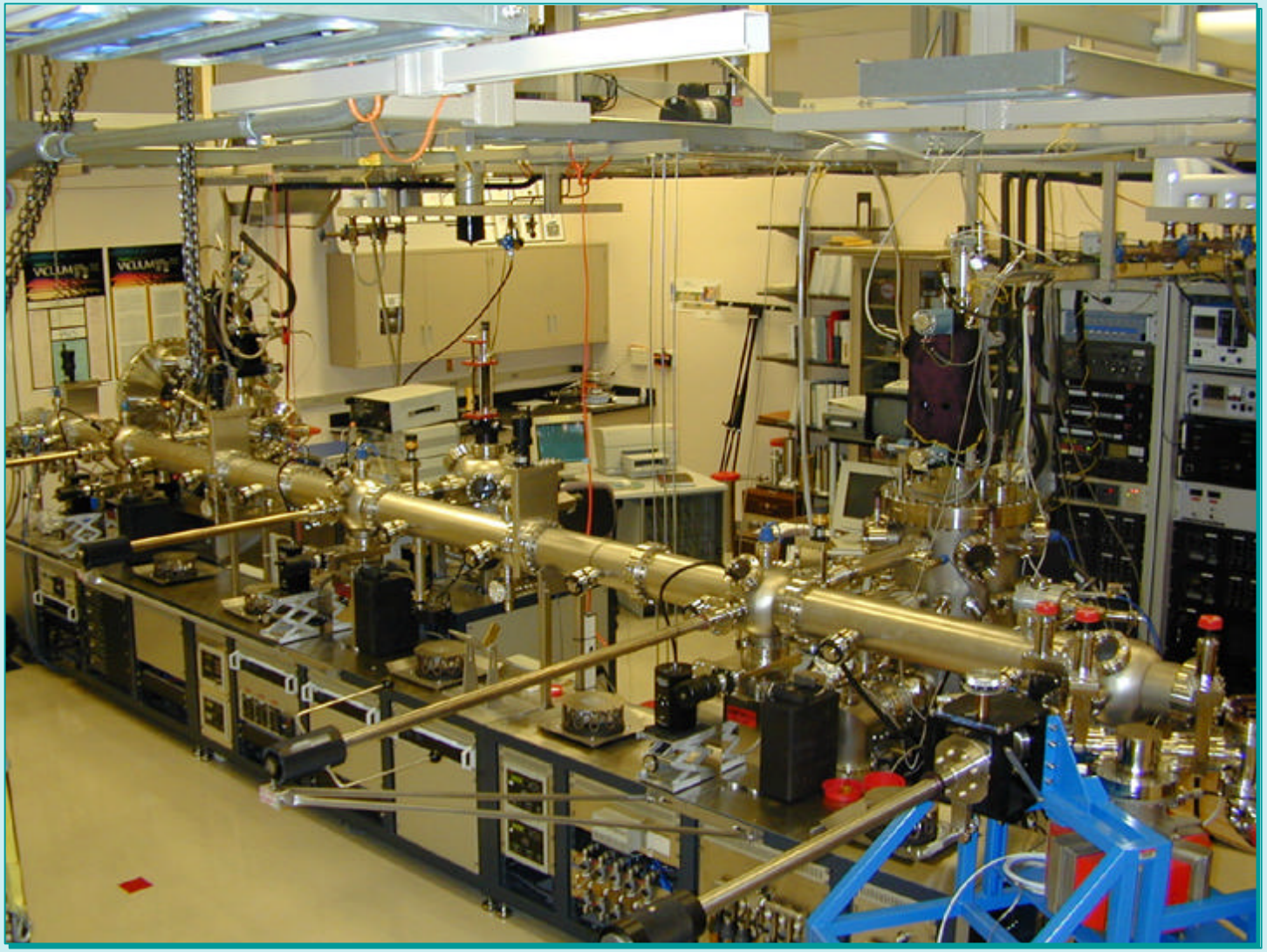
Pristine: How do carbonates of different geologic/geochemical origin effect contaminant reactivity?

- Sediments from different lithologies/formations
- Focus on Sr
- Microscopic $\rightarrow$ macroscopic reaction experiments

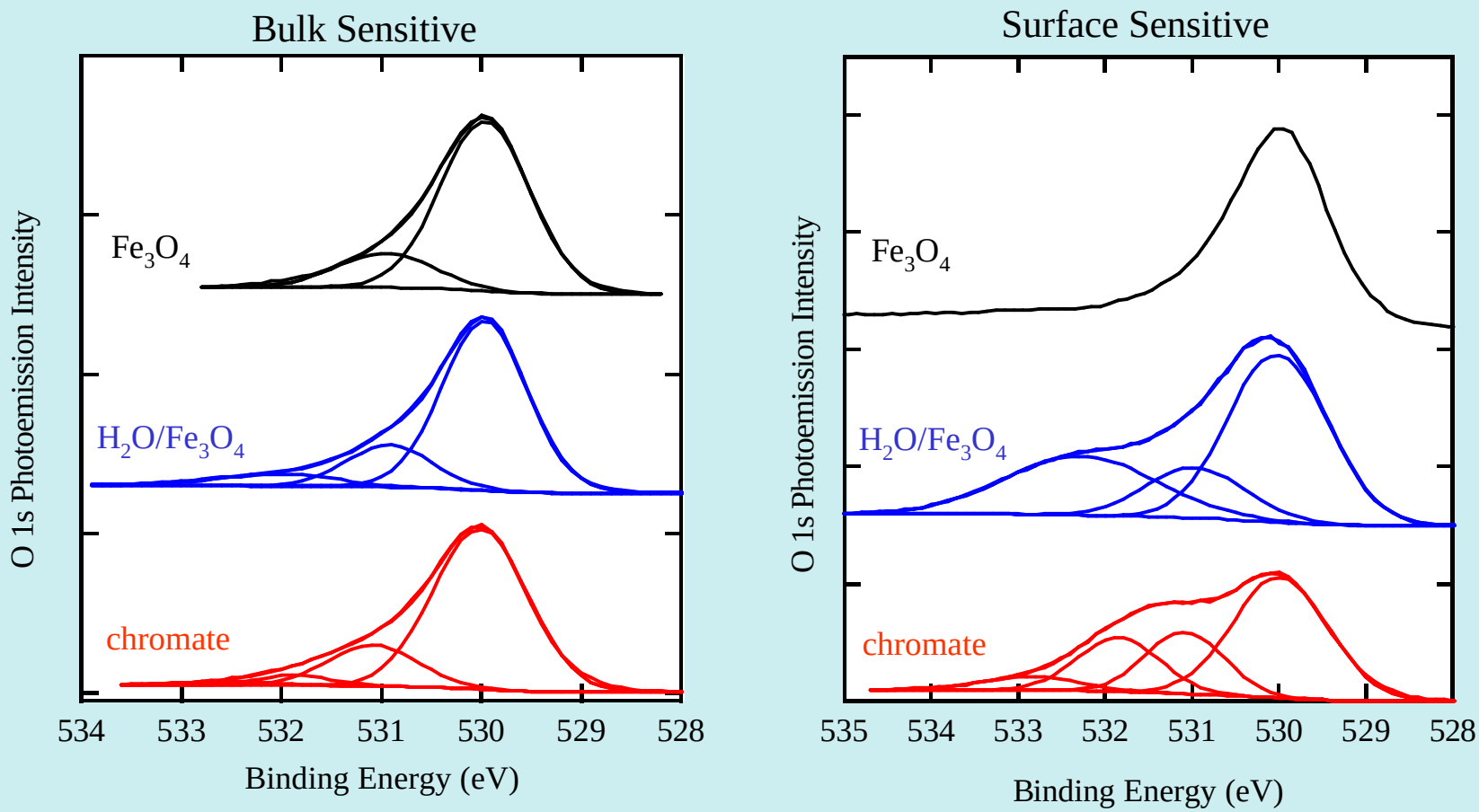
Contaminated: What are effects of waste-sediment reaction?

- In-situ calcium carbonate precipitation
- Speciation and mineral residence
- K_d and reaction prediction

Growth and Characterization of Metal-Oxide Surfaces



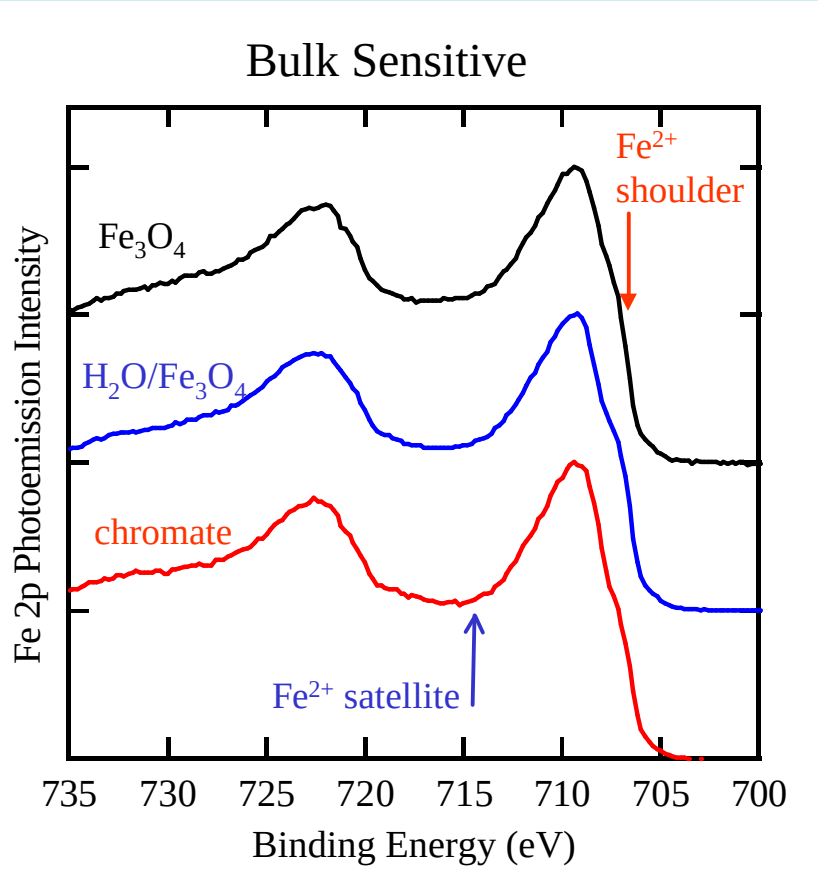
Adsorption of Aqueous H_2O and CrO_4^{2-} on Fe_3O_4

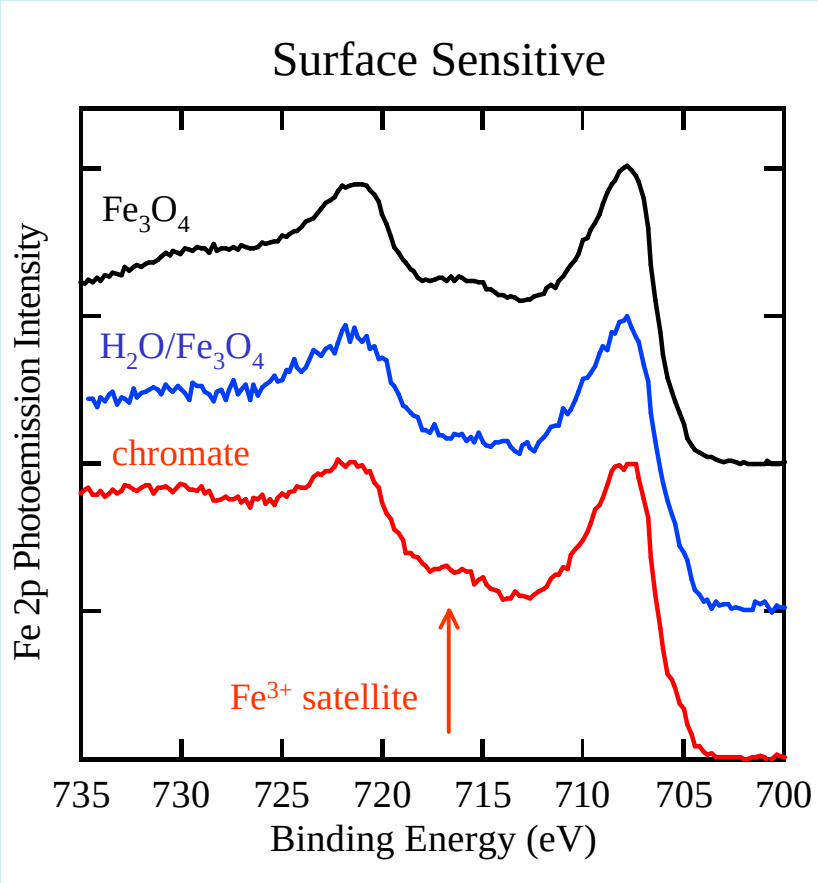


High resolution core-level measurements of the water reacted magnetite show a hydroxide peak with binding energy 2.3 eV above the primary O*1s*.

Chromate reacted magnetite exhibits an additional oxy-hydroxide peak 1.8 eV above primary.

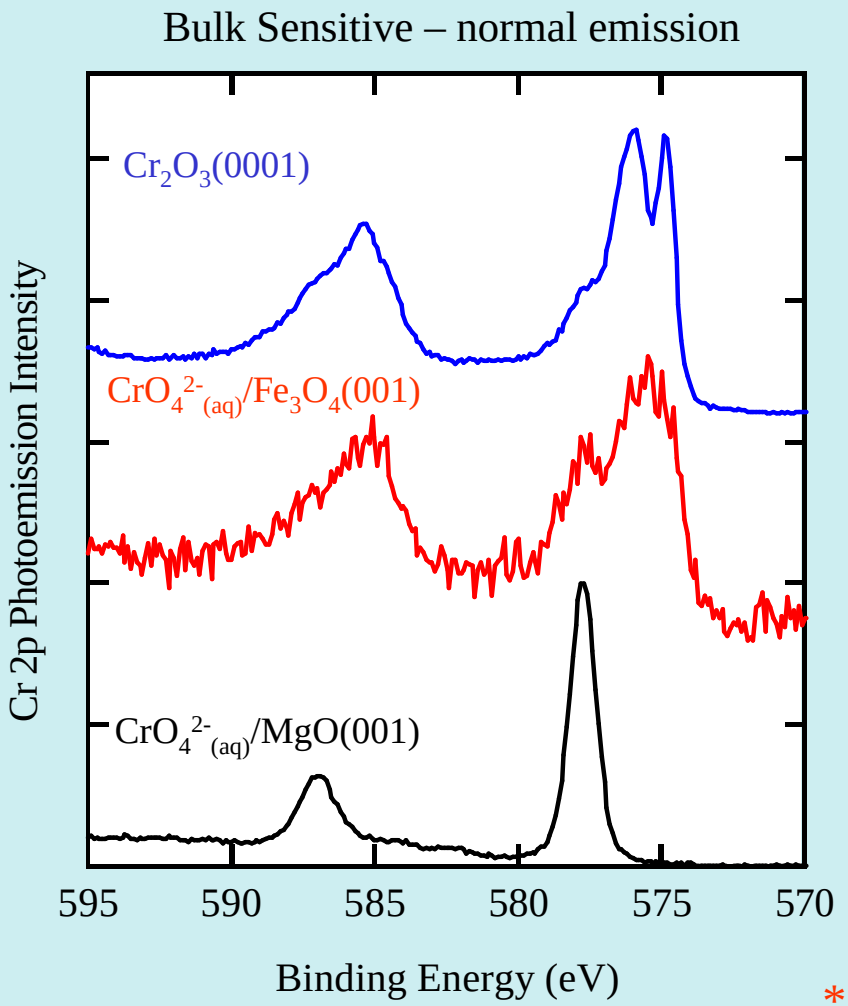
H_2O & CrO_4^{2-} Adsorption on Fe_3O_4/MgO(001) Fe 2p Photoemission





Slight increase in Fe^{3+}/Fe^{2+} ratio at surface in aqueous chromate reacted magnetite

Cr 2*p* Core-Level Photoemission



Synthetic Fe_3O_4/MgO(001) sample reacted with aqueous chromate solution then rinsed with H_2O

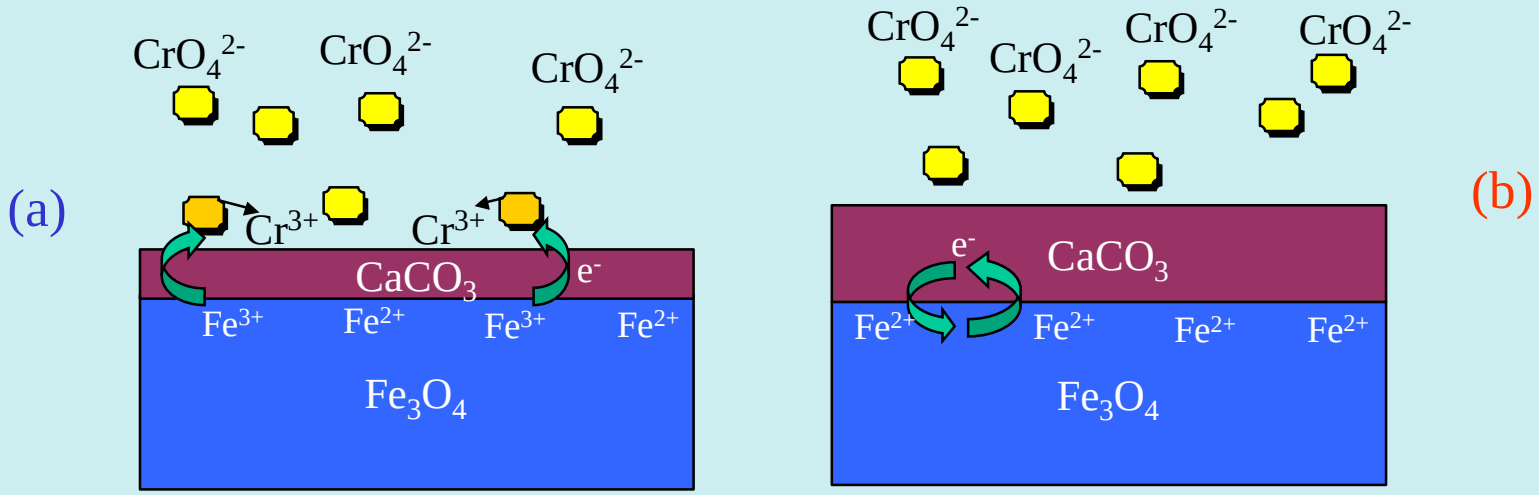
Cr(VI) reacts with Fe(II) at surface to form immobile Cr(III) species

Thickness of passivating layer (chromium oxyhydroxide*) self-limits at a total thickness of approximately 15 A° and prevents further reduction.

**Results agree with Kendelewicz et. al. (2000)*

Electron Transfer Interference

Carbonate coatings can interfere with the reduction of CrO_4^{2-} at the magnetite-water interface when they become thick enough.



(a) Thin carbonate coatings allow electron transfer

(b) Thick carbonate coatings inhibit electron transfer

Aqueous CrO_4^{2-} solutions are 50 μM Na_2CrO_4 with a pH 8

Deposition of Calcium Carbonate Films by Polymer-Induced Liquid Precursor (PILP)* Process

1) Immerse Fe_3O_4/MgO(001) film in 20 mM calcium chloride solution, containing 20 µg/ml of polymeric additive [poly-α,L-aspartate MW=8600].
2) Freshly crush 0.4 g ammonium carbonate powder and divide evenly between two containers with needle holes in top to allow for slow diffusion of ammonium carbonate vapor (NH_3 and CO_2 decomposition products).
3) Seal inside vessel for 24-36 hrs.
4) Extract sample and rinse in water followed by methanol.

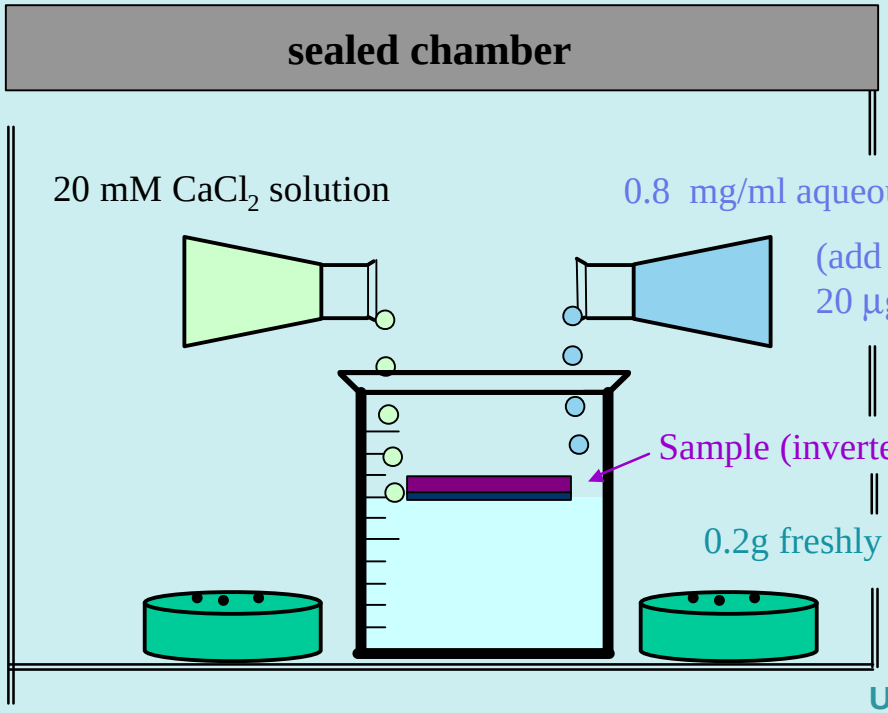
Polymer coats substrate & acts as a surfactant upon which Vaterite nucleates as a continuous film.

Calcite crystals nucleate on Vaterite layer.

With prolonged time, Calcite crystals continue to nucleate, but Vaterite growth self-limits.

20-24 hrs required to grow a few ML of Vaterite

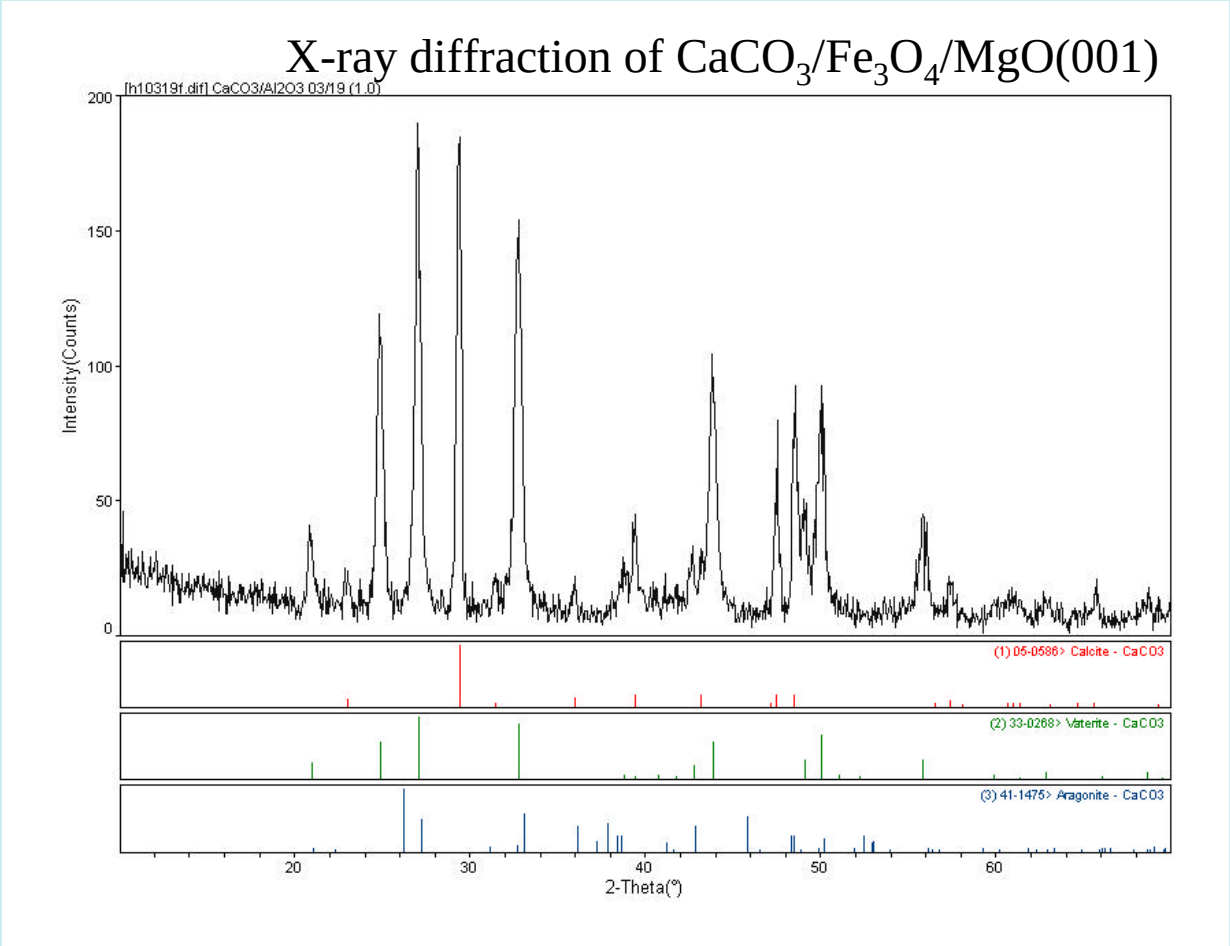
Calcite growth on Vaterite occurs much faster



*L.B. Gower *et. al.* *Journal of Crystal Growth* 210 (2000)

Solution Based Calcium Carbonate Growth by PILP

Calcium carbonate overlayers consist of continuous films, primarily vaterite, with patchy crystallites of Calcite. Little, if any, of the third possible polymorph, Aragonite, has been observed.

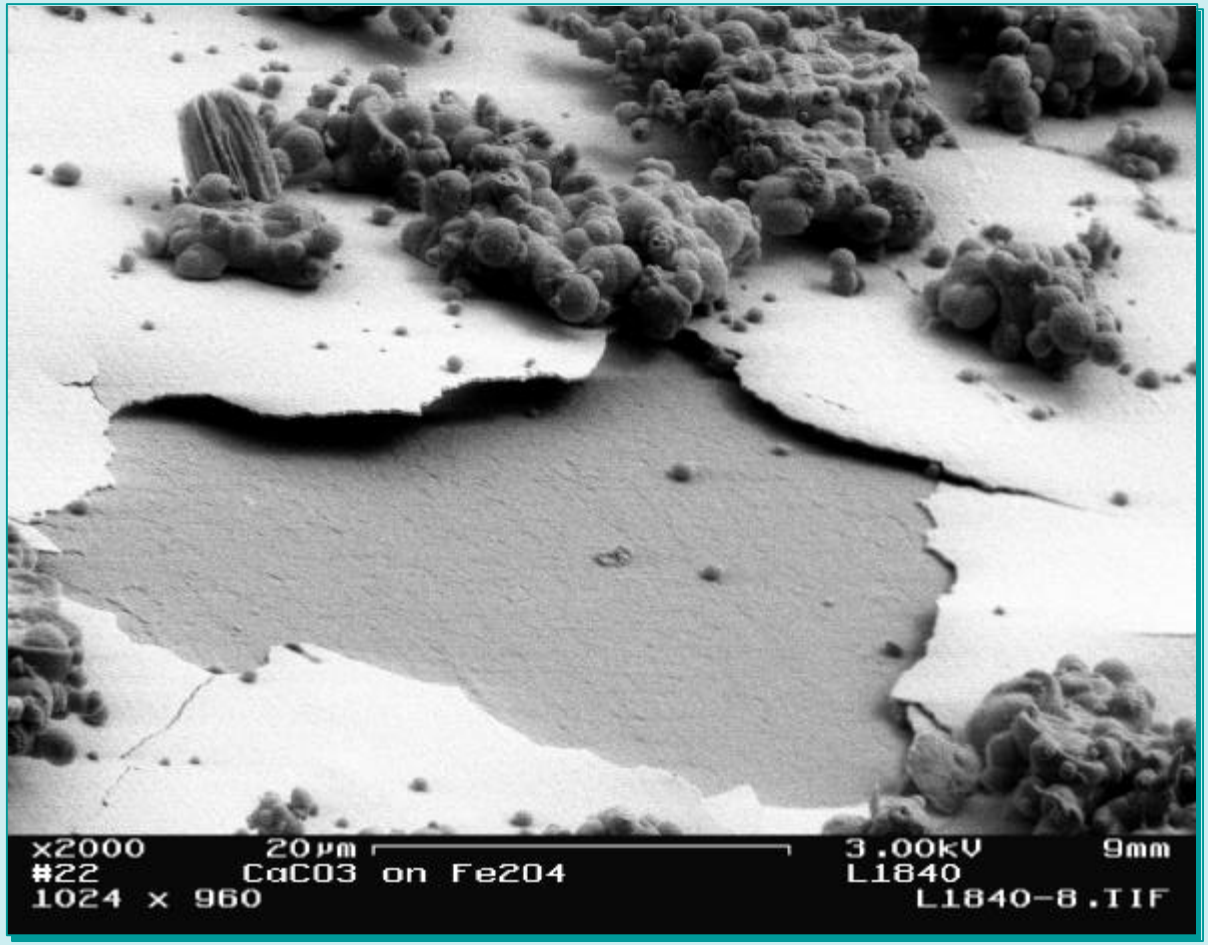


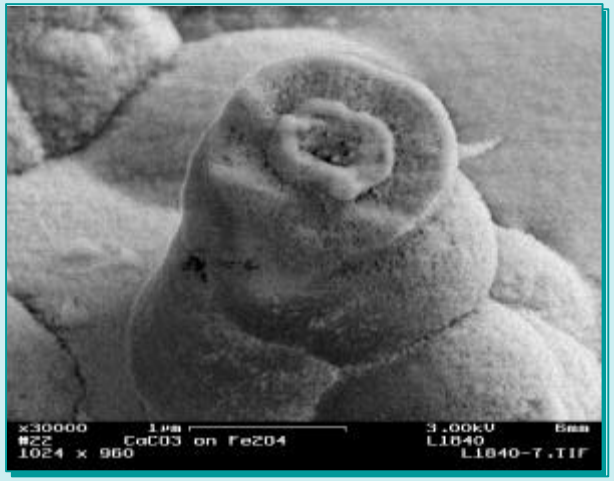
Calcite:Vaterite concentration (1:1 shown) increases with immersion time. Suggestive of calcite formation at defect sites.

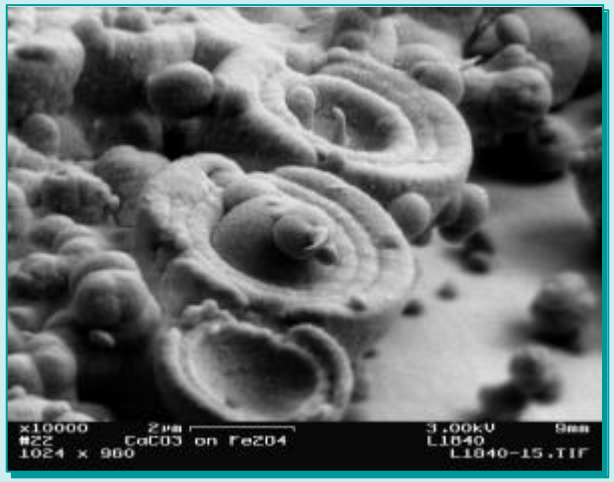
Film ⟶ Vaterite
Crystallite ⟶ Calcite

Three polymorphs of calcium carbonate ($CaCO_3$) Calcite, Vaterite, Aragonite

Carbonate Film Morphology - SEM

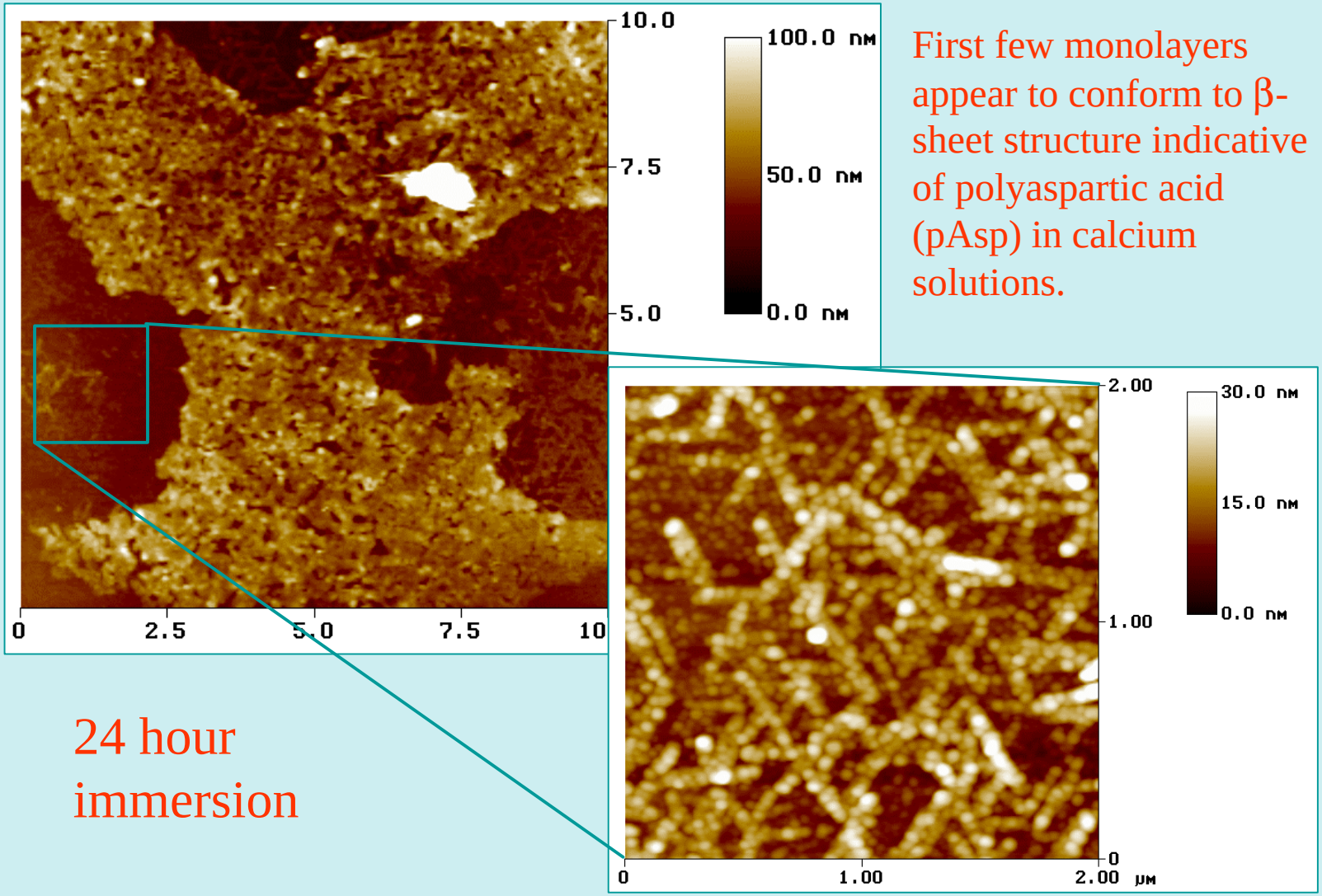






Molecular chirality of +*L*-aspartic acid leads to macroscopic chirality of calcium carbonate

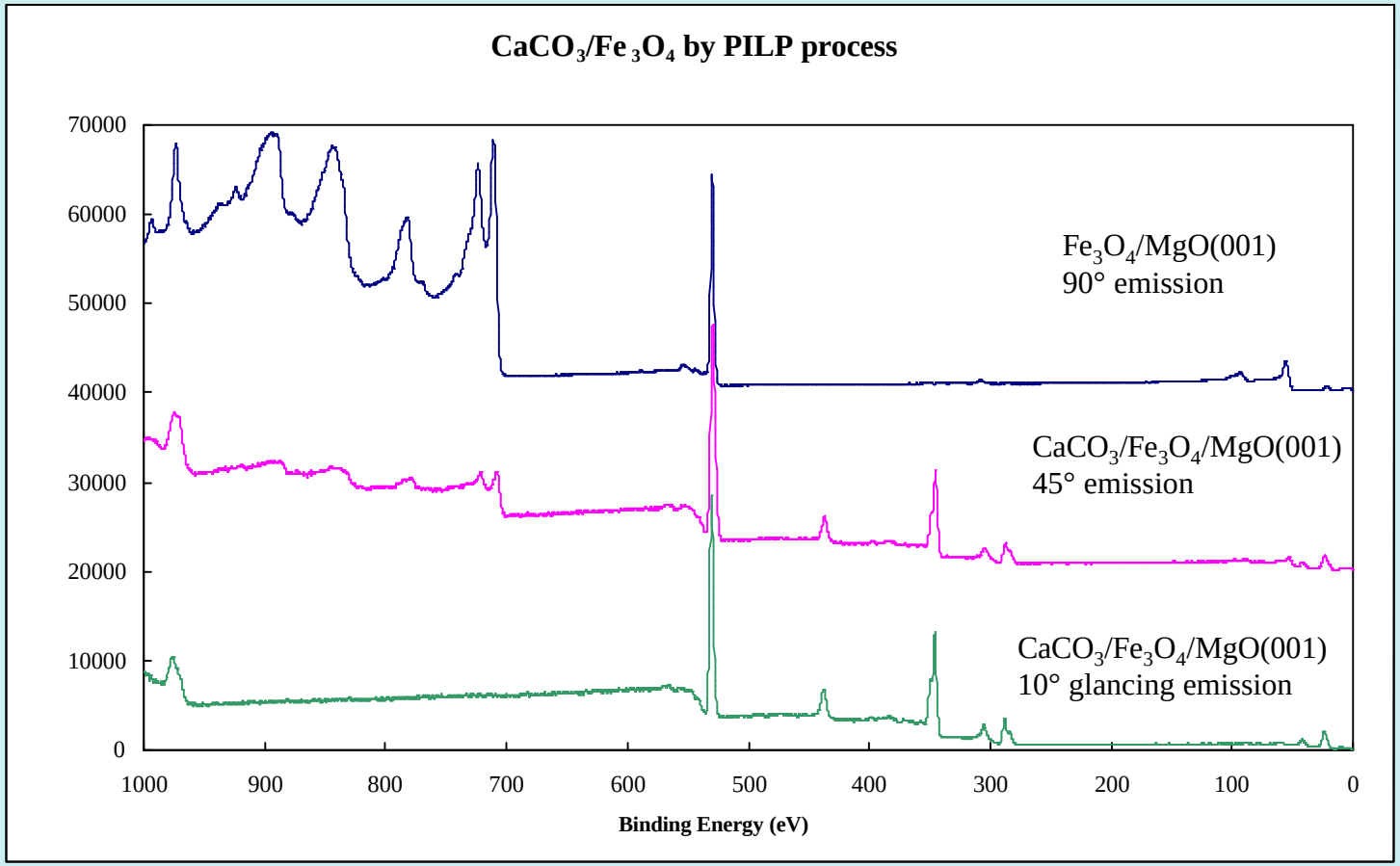
Initial Growth of Carbonate via PILP Process



First few monolayers appear to conform to β-sheet structure indicative of polyaspartic acid (pAsp) in calcium solutions.

24 hour immersion

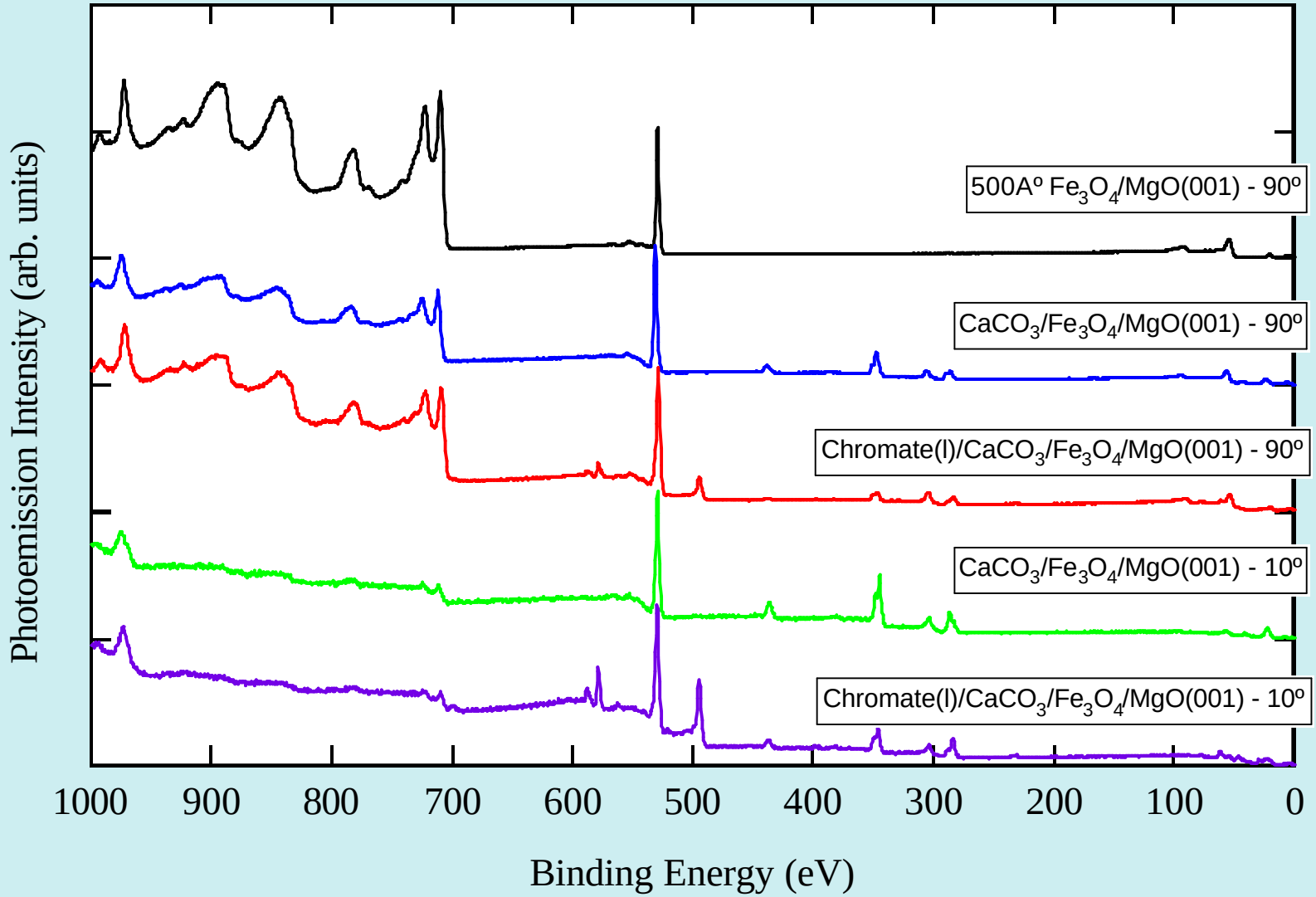
Photoemission Evidence of Continuous Film



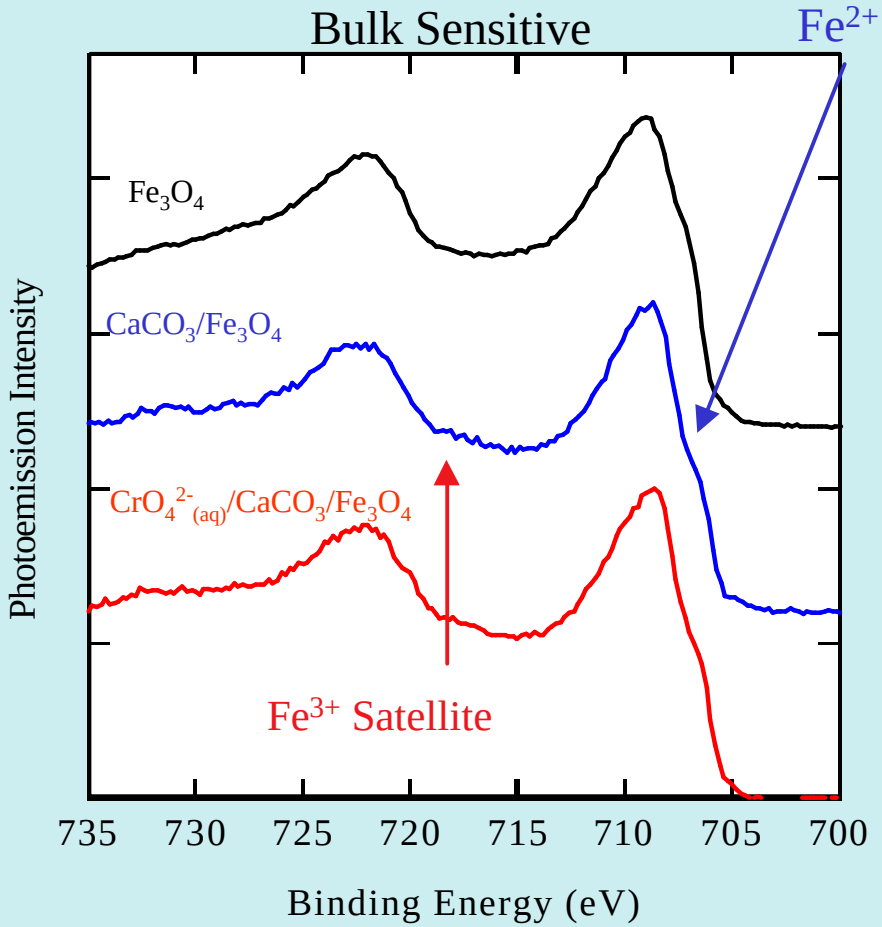
As XPS surface sensitivity increases ⟶ Fe 2p core-level disappears

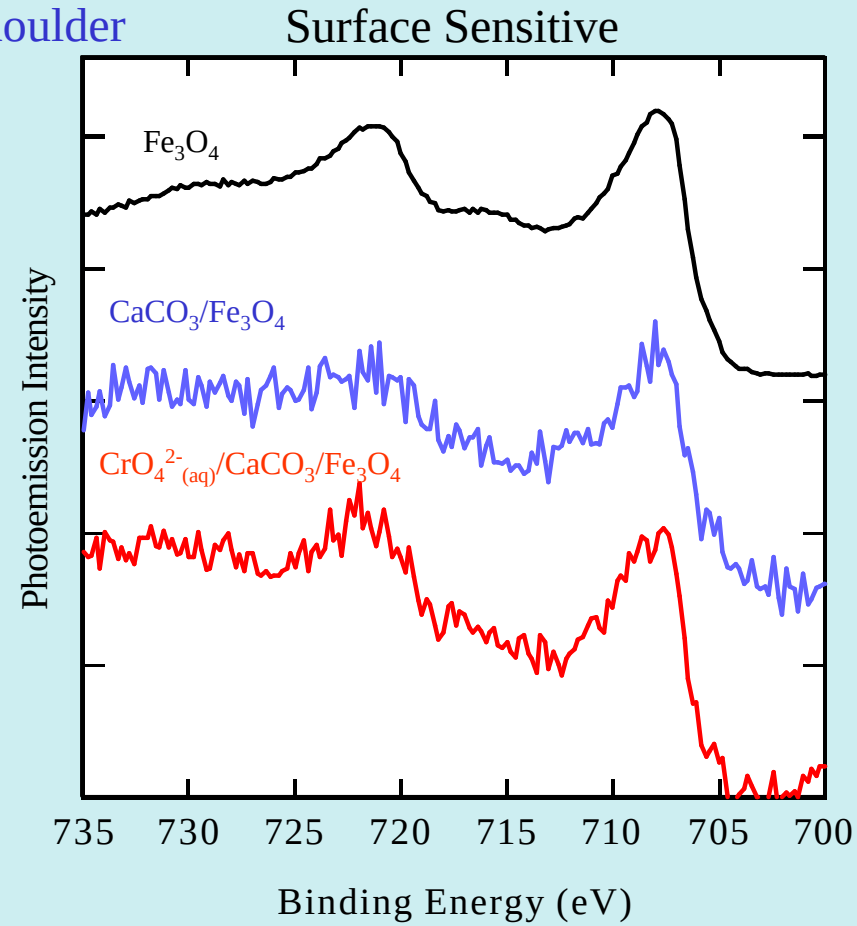
Small-area XPS unable to find region (>10 μm) devoid of calcium

Aqueous Chromate Reaction on Fe_3O_4/MgO(001)



High-Energy Resolution Fe 2*p* Photoemission

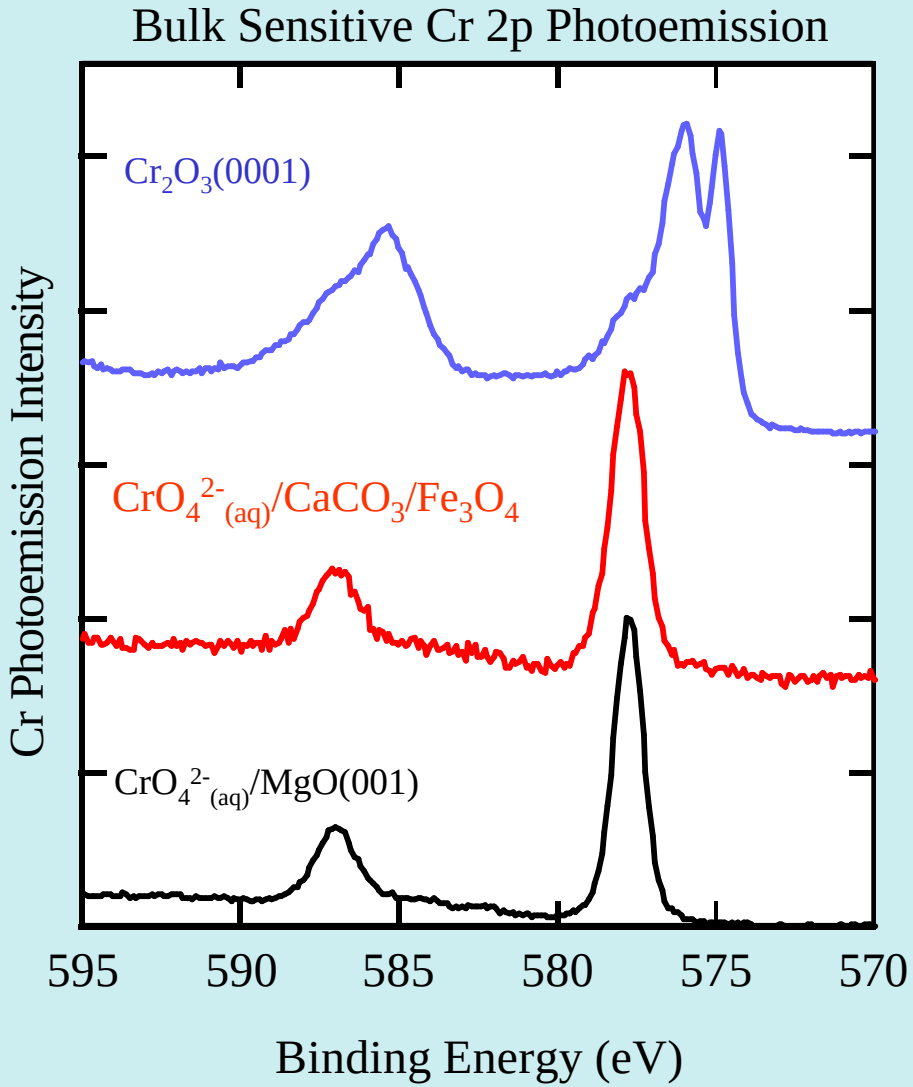




After solution-based growth of $CaCO_3$, slight increase in Fe^{3+} concentration seen by decrease of Fe^{2+} shoulder and increase of non-charge transfer satellite.

Lineshape of carbonate covered & reacted magnetite is very similar to surface-sensitive XPS of Fe_3O_4 films reacted with liquid water

Electron Transfer Interference by Carbonate Film



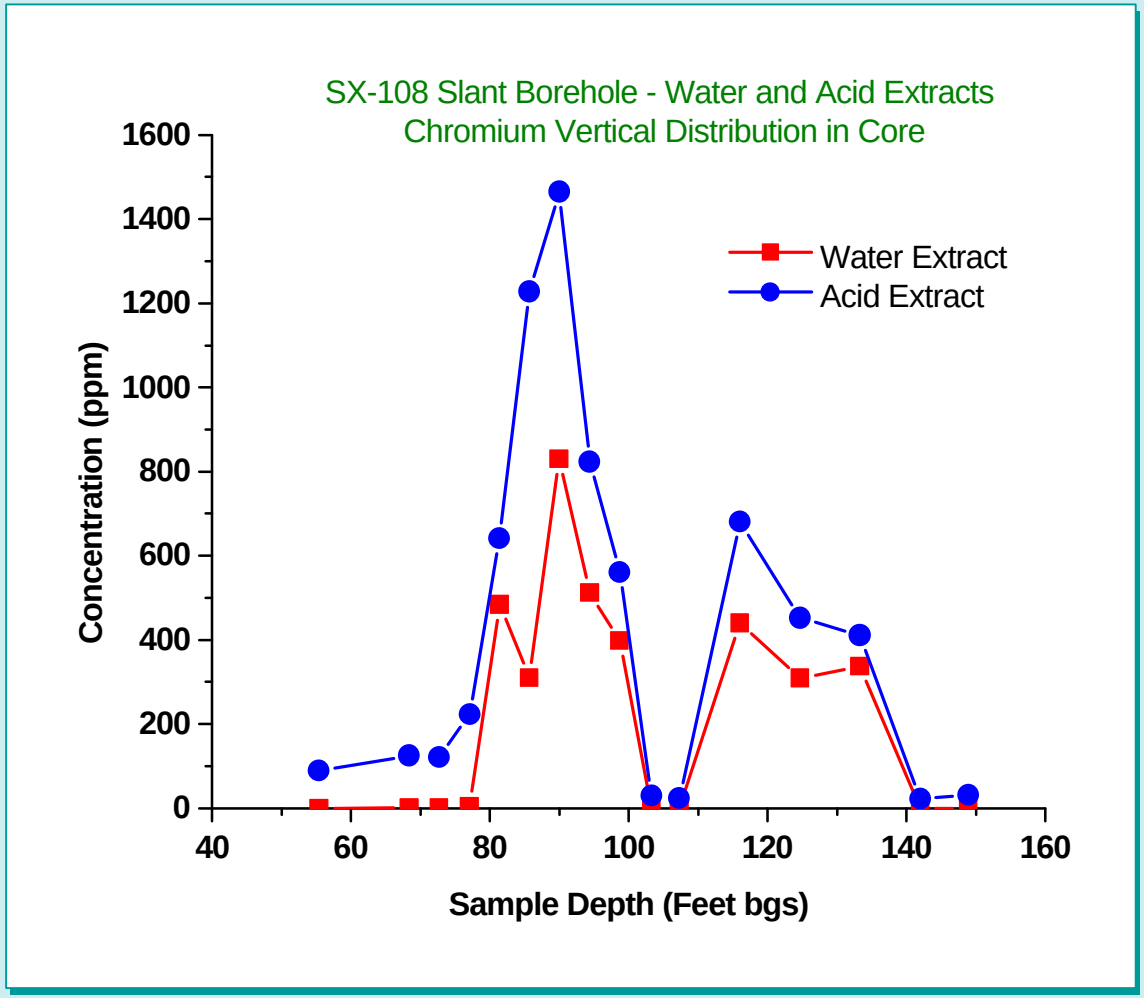
Thin (<25A°) calcium carbonate layer prevents electron transfer between aqueous Cr(VI) and surface Fe(II) atoms

Bulk and surface sensitive photoemission geometries dominated by Cr(VI) lineshape and show little, if any, Cr reduction at the surface

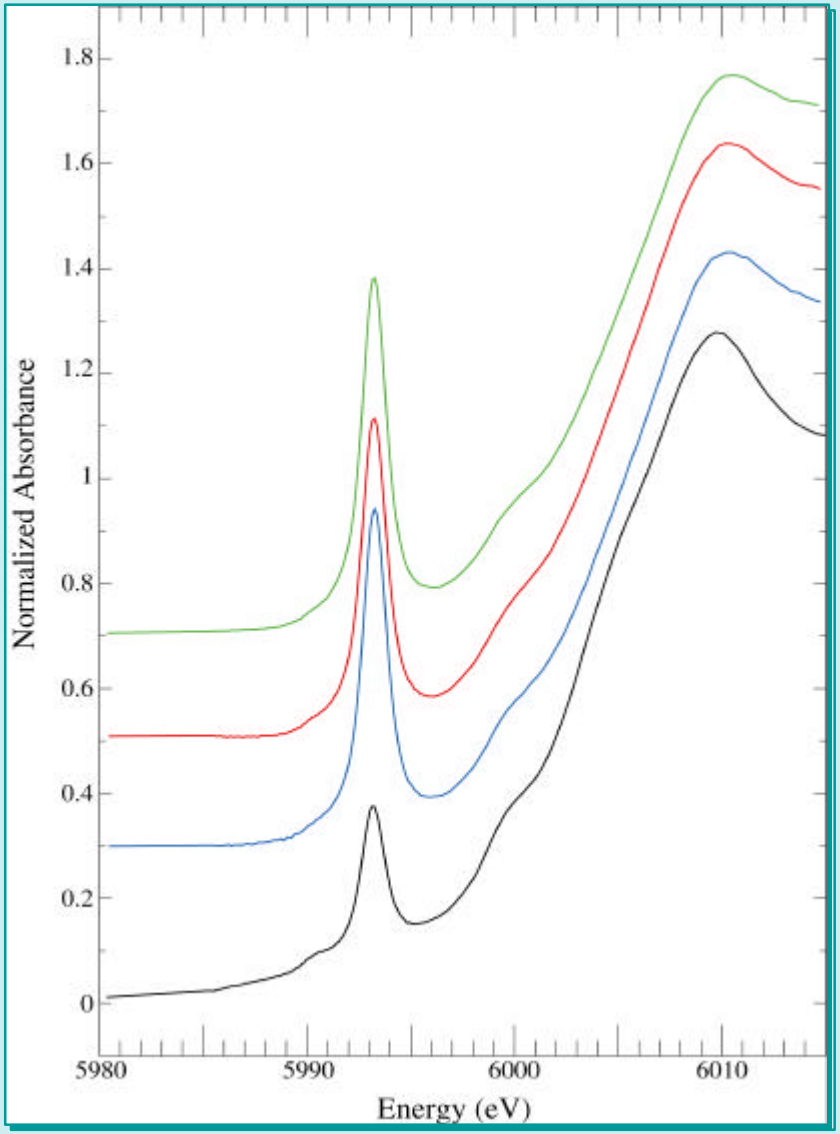
Results of Model System Studies

- Calcium carbonate films (vaterite) were prepared by a polymer-induced liquid precursor (PILP) process
  - Polymer coats surface and acts as a surfactant for vaterite growth
  - XPS of the Fe 2p core-level shows an increase of the Fe(II)/Fe(III) ratio consistent with an aqueous growth environment
- Reductive immobilization of Cr(VI) occurs at the surface of magnetite [Fe_3O_4/MgO(001)] resulting in a passivating chromium oxyhydroxide layer (15 A°)
- Thin (~20A°) calcium carbonate layers prevent electron transfer between the CrO_4^{2-} and Fe_3O_4/MgO(001)

Chromium in Water and Acid Extracts from SX-108 Core



Normalized Cr Pre-Edge Regions of the SX-108 Contaminated Sediment Samples (EMSP)



Results of Cr(VI) Determination from XAFS "Pre-Edge" Heights

Sample	Pre-Edge Position (eV)	Normalized Pre-Edge Height	% Cr(VI)
41-09-39-6AB	5993.24 ± 0.04	0.614	58.5
41-09-39-7ABC	5993.24 ± 0.04	0.681	68.6
SX-108-8A	5993.27 ± 0.04	0.641	62.6
SX-108-7AB	5993.18 ± 0.04	0.374	27.4

Conceptual Model

+ $[OH^-]$

<u>Chlorite</u>

$(Mg,Al,Fe)_{12}[(Si,Al)_8O_{20}](OH)_{16}$ →

<u>Biotite</u>

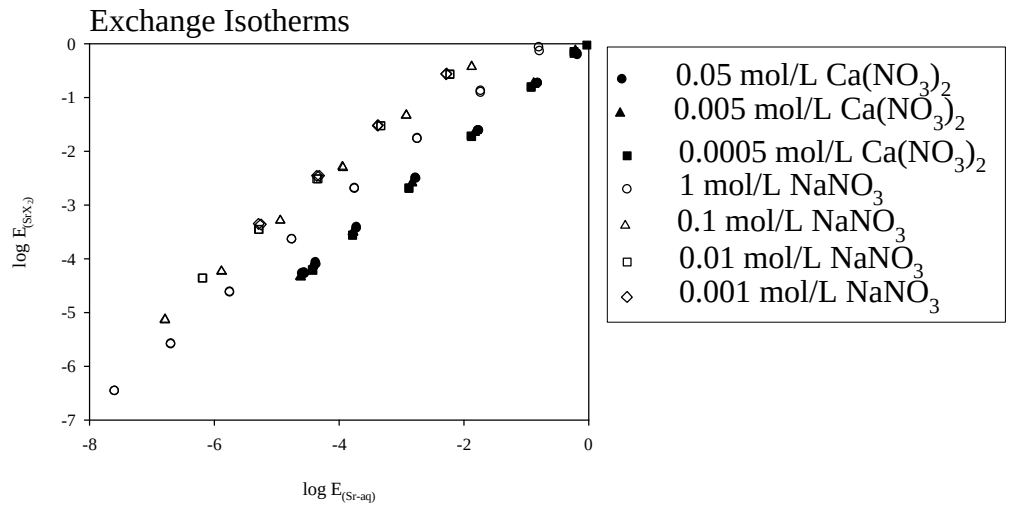
$K_2(Mg,Fe^{2+})_{6-4}(Fe^{3+},Al,Ti)_{0-2}[Si_{6-5}Al_{2-3}O_{20}](OH,F)_4$ →

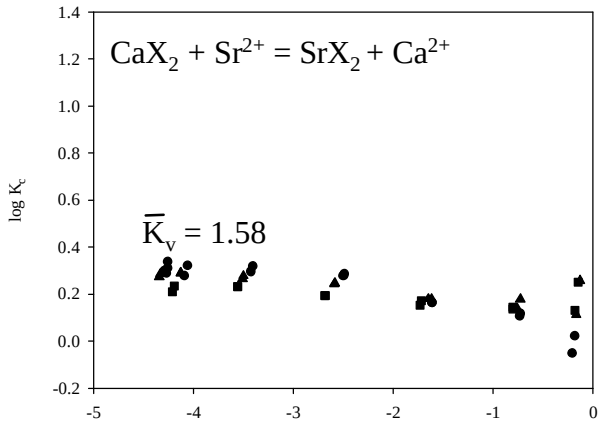
<u>Ilmenite</u>

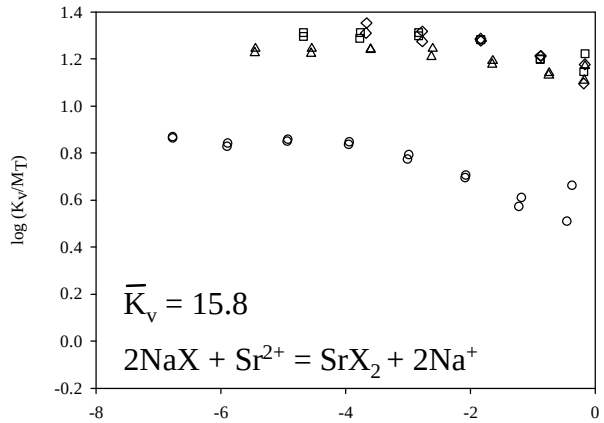
$FeTiO_3$ →

$$3Fe^{2+} + CrO_4^{2-} + 8H_2O = 4Fe_{.75}Cr_{.25}(OH)_3 + 4H^+$$

Sr^{2+} Exchange Behavior of Hanford Fine Sand Composite



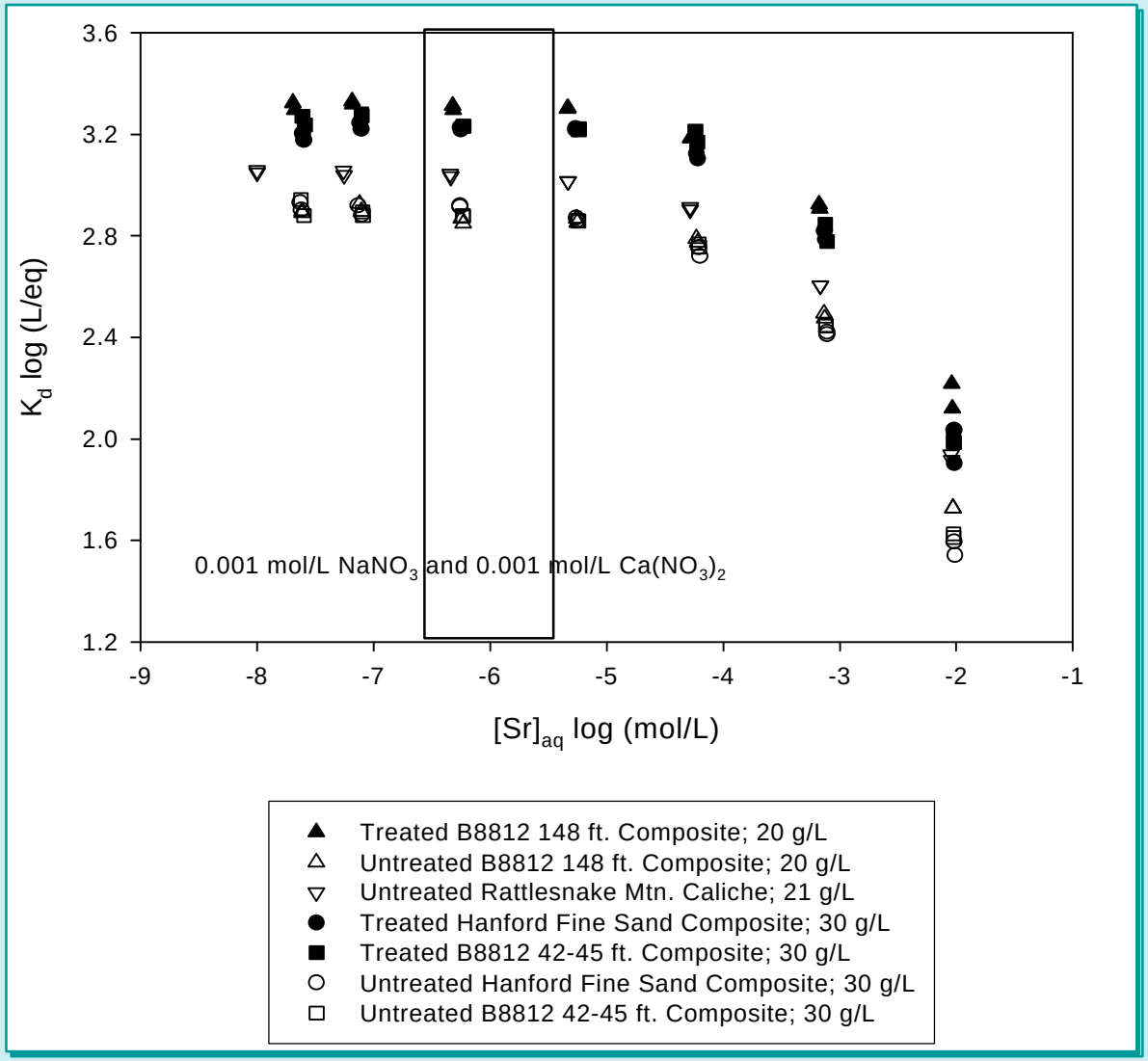




$$K_v = \frac{N_{SrX_2}(Ca^{2+})}{N_{CaX_2}(Sr^{2+})}$$

$$K_v/M_T = \frac{N_{SrX_2}M_{Na}^2}{N_{NaX}^2 M_{Sr}}$$

Strontium Sorption on Selected Hanford Sediments
(Untreated and Sodium Acetate Extracted)



$$K_d = f(K_{T1}, K_{T2})$$

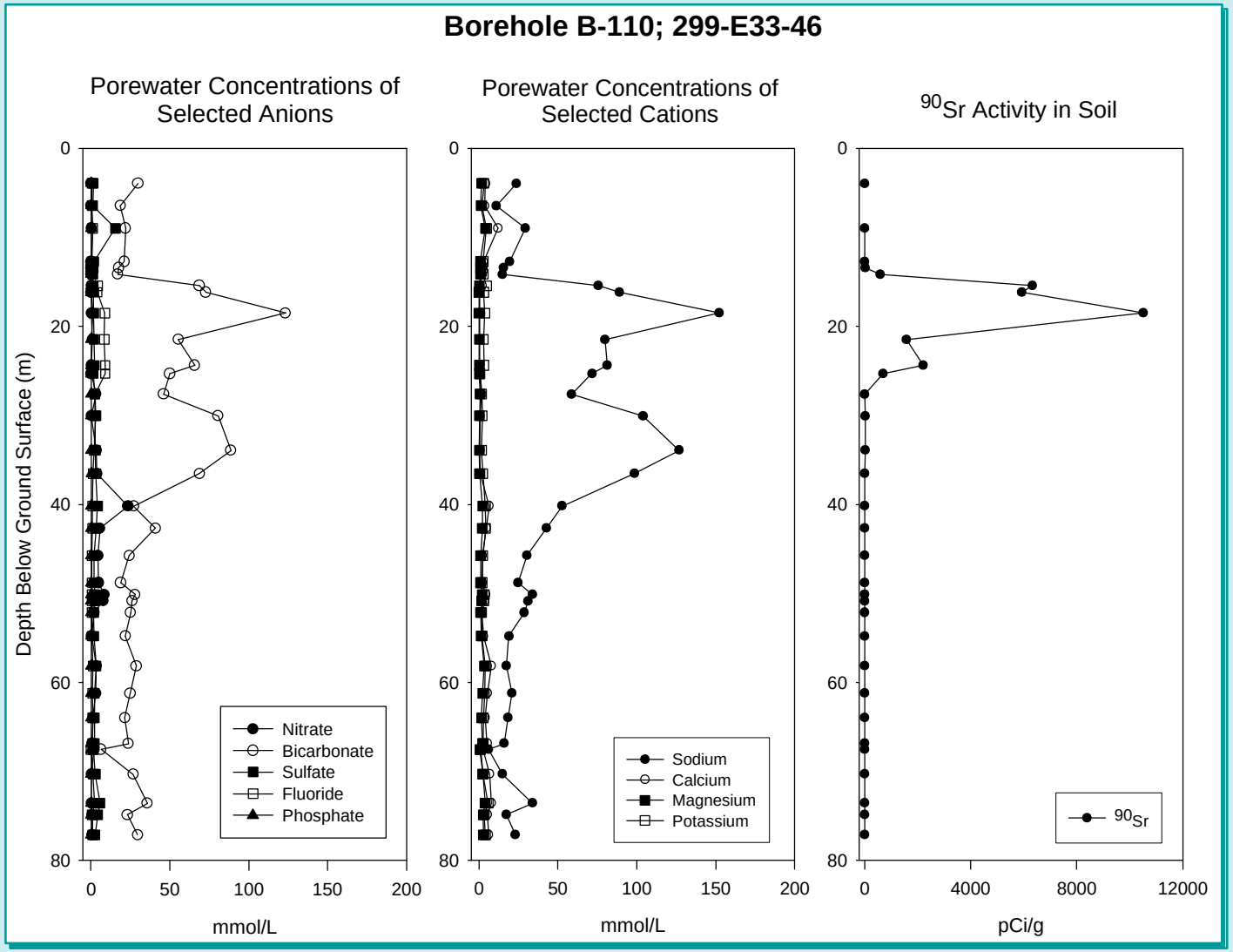
$$4NaX + Ca^{2+} + Sr^{2+} = 4Na^{+} + CaX_2 + SrX_2$$

$$K_{T1} = \frac{(Na^{+})^4 N_{SrX_2} N_{CaX_2}}{N_{NaX}^4 (Sr^{2+})(Ca^{2+})} = K_{ex}(Na\text{-}Sr)K_{ex}(Na\text{-}Ca)$$

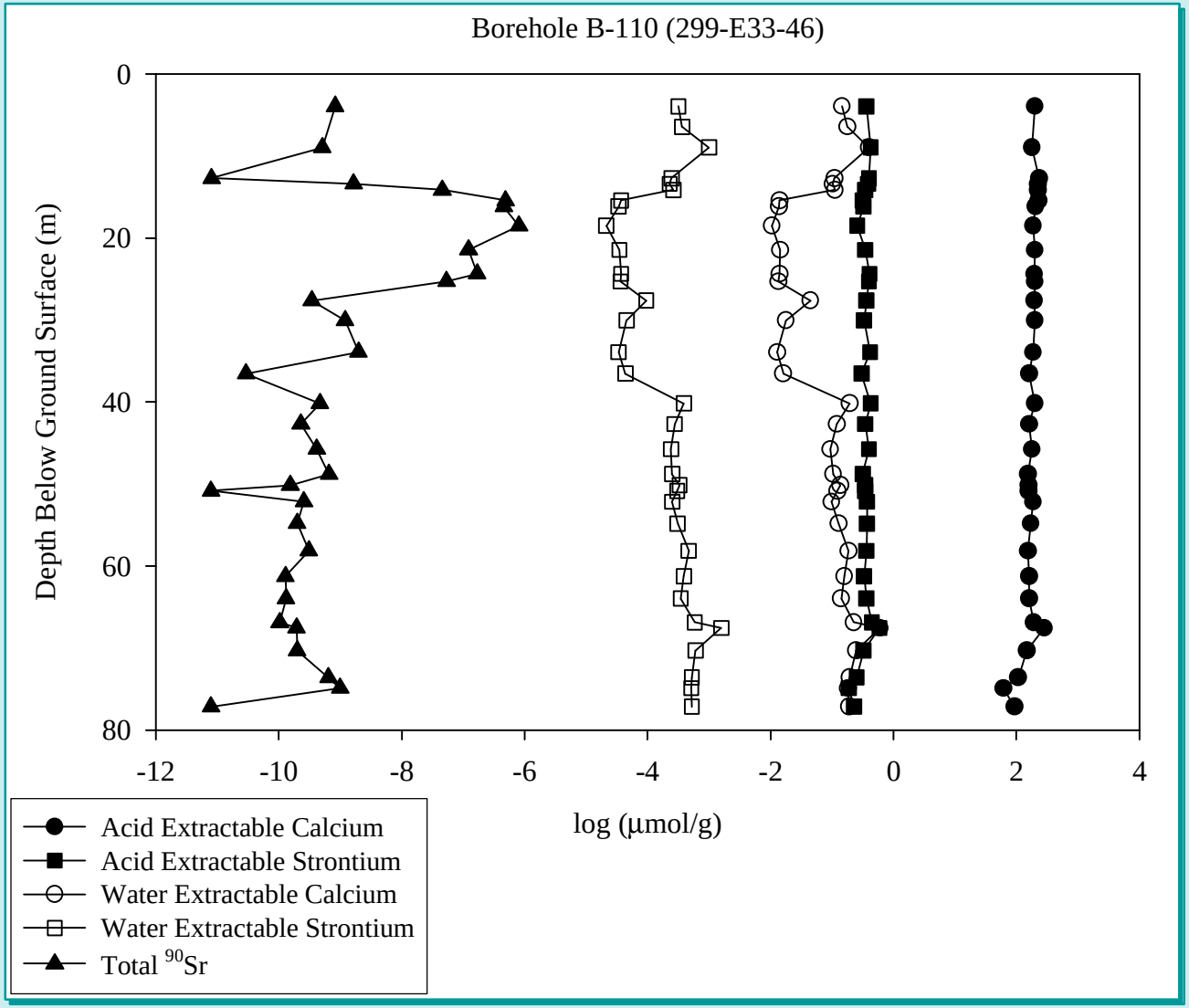
$$2Na^{+} + 2CaX_2 + Sr^{2+} = 2NaX + 2Ca^{2+} + SrX_2$$

$$K_{T2} = \frac{N_{NaX}^2 (Ca^{2+})^2 N_{SrX_2}}{(Na^{+})^2 N_{CaX_2}^2 (Sr^{2+})} = K_{ex}(Ca\text{-}Sr)/K_{ex}(Na\text{-}Ca)$$

Characterization Data from the B-BX-BY Tank Farms



Characterization Data from the B-BX-BY Tank Farms



Research Products

Scientific Findings and Insights

- Role of $CaCO_3$ on vadose zone contaminant reactivity. Effects evident
  - Passivation of reductant surfaces
  - Decrease cation binding
- Properties of $CaCO_3$ resulting from different formational processes
  - Coatings, etc.
- Strategies to model and describe anion and cation reactions in calcareous sediments

Contributions to Hanford

- Analyses (by XAS and other techniques) and study of contaminated materials provides new conceptual models of the reaction network
- Improved numeric models for $^{90}Sr^{2+}$ adsorption and Cr(VI) reduction (ICWO)
  - Hypothesis testing
  - History matching and future projections