Project 70121

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

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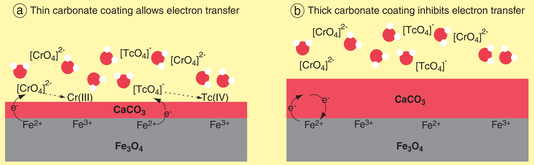
Objectives

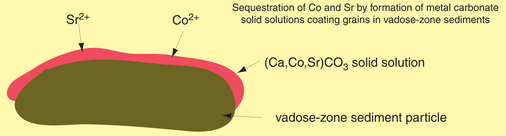
- To characterize natural carbonate grain coatings from the Hanford vadose zone in terms of composition, morphology, surface structure, and reactivity towards targeted contaminants, including Cr(VI), Tc(VII), Co(II), and Sr(II)
- To establish reaction mechanisms and modes of sorption of selected radionuclide/metal cations (Co^{2+}, Sr^{2+}) with carbonate coatings by investigating the molecular configurations of *ad*sorbed and *ab*sorbed contaminants, and how such configurations vary with relevant geochemical/waste scenarios and conditions
- To determine the effects of carbonate coating thickness and composition on substrate reactivity, emphasizing electron transfer reactions responsible for the reductive immobilization of $Cr(VI)O_4^{2-}$ and $Tc(VII)O_4^{-}$
- To identify carbonate coating growth mechanisms and rates on relevant mineral substrates approximating natural and waste-dominated aqueous conditions, and the influence of growth/recrystalization on "irreversible"

Hypotheses

(1) Carbonate coatings can interfere with the reduction of $[CrO_4]^{2-}$ and $[TcO_4]^{-}$ at the magnetite-water interface when they become thick enough

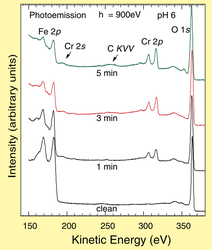


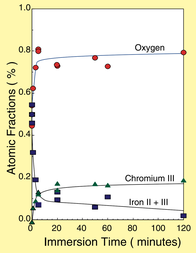
(2) Co and Sr can be sequestered at the magnetite-water interface by incorporation in metal carbonate layers

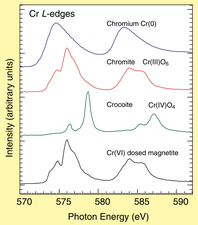


Background

A necessary starting point for testing the first hypothesis is to demonstrate that electron transfer reactions on magnetite surfaces can reduce aqueous chromate and pertechnetate. We have comprehensively investigated the reaction of pure water on the the magnetite and hematite surfaces [1], which is essential prior to investigating aqueous solutions interacting with these surfaces. As part of our first EMSP project (see EMSP poster by Chambers *et al.*), we carried out a detailed study of the reduction of aqueous chromate on magnetite (111) surfaces using a combination of x-ray photoemission and x-ray absorption spectroscopies, and showed that Cr(VI) is indeed reduced to Cr(III) relatively rapidly, but that the reduction reaction stops after ~20 minutes due to the formation of a passivating layer on the magnetite surface, through which electrons can't tunnel in laboratory time periods. The nature of this passivating overlayer was studied by O *K*-edge and Fe and Cr *L*-edge absorption spectroscopies [2] and was found to consist of an amorphous overlayer containing a Cr-oxyhydroxide outerlayer and a ferric oxyhydroxide innerlayer, with a total thickness of ~ 20 Å [3,4].





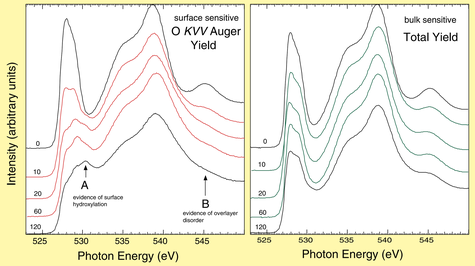


The figure at the top left shows Fe 2*p*, Cr 2*p* and O 1*s* core level photoemission spectra taken with a photon energy of 900 eV of magnetite(111) surfaces immersed in 50 M solutions of sodium chromate at pH 6. The figure at the top right shows atomic fractions derived from the intensities of these core levels. The attenuation of the Fe 2*p*, along with the growth in Cr 2*p* and O 1*s*, provides evidence of overlayer growth. It is clear that the overlayer growth retards the electron transfer reaction after ~20 minutes.

The figure to the left displays Cr *L*-edge spectra for a series of chromium standards with differing oxidation state. The lower spectrum is of a magnetite (111) surface reacted with a 50 M sodium chromate solution, and is typical of spectra obtained for Cr(III) sorbed to the magnetite surface.

The figures below show surface- and bulk- sensitive O *K*-edge spectra of Cr(VI)-dosed magnetite surfaces (left and right, respectively). The growth of the "A" feature is indicative of increasing hydroxylation of the surface, whilst the dissapearance of the "B" feature, due to O-O nearest neighbor multiple scattering,

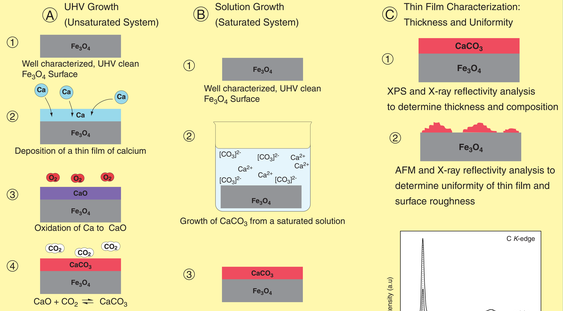
O *K*-edge NEXAFS



Coating Thickness

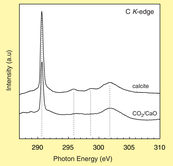
A direct test of our first hypothesis also requires the growth of carbonate phases on metal oxide surfaces. Our initial approach has involved the reaction of CO_2 with metal oxide surfaces under carefully controlled conditions to determine if carbonate coatings form. The Hanford vadose zone undergoes periods of saturation and unsaturation with respect to water, and CO_2 levels may greatly exceed ambient atmospheric pressures, implying that both aqueous and non-aqueous mechanisms of carbonate formation may play roles in the formation of carbonate coatings. Here we present results of our x-ray photoemission and x-ray absorption studies of carbonate formation in both unstaurated and aqueous systems.

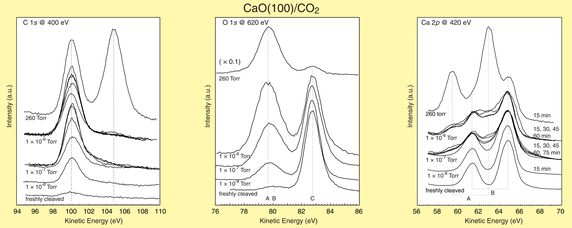
Growth and Characterization of $CaCO_3$ Thin Films on Magnetite

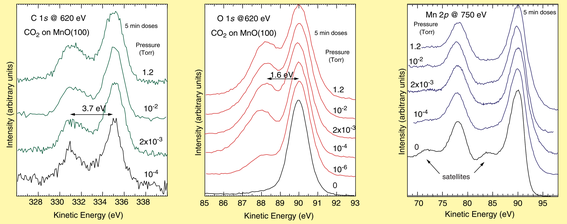


Unsaturated Systems

Here we present photoemission and C NEXAFS data for the reactions of CaO (upper) and MnO (lower) with CO_2. CaO provides a good model system for carbonate formation [5], and aids the interpretation of the spectra of carbonates on more environmentally relevant substrates, such as MnO.

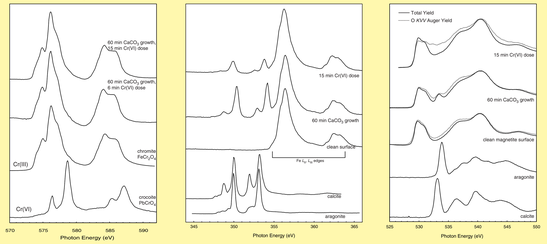






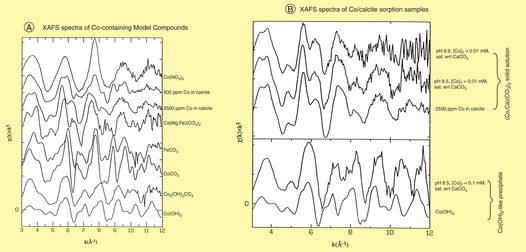
Aqueous Systems

The figures below show preliminary results for calcium carbonate growth from solution onto magnetite (111) single crystal surfaces, and the effects of Cr(VI) dosing. The Cr *L*-edge spectra (left) for doses of both 6 and 15 minutes show no sign of Cr(VI) on the surface, indicating that the carbonate layer formed has not reached sufficient thickness to retard the reduction of Cr. Ca *L*-edge spectra (middle) show changes between carbonate deposition and Cr dosing, which may provide evidence for dissolution/reprecipitation. O *K*-edge spectra (right) are complicated by contributions from the substrate, coating, and possibly a Cr-oxyhydroxide layer, however Auger yield data following Cr dosing show good agreement with data for Cr dosing on clean magnetite surfaces, where Cr-oxyhydroxide layers were observed. It should be noted that at this stage of the work, we have not characterized the uniformity of our carbonate coatings. Until such time, our interpretation of the results is tentative at best.



Sequestration

To test Hypothesis 2, we have carried out a study of the interaction of aqueous Co(II) with high surface area powdered $CaCO_3$ using batch uptake experiments (pH values of 7.4 to 8.9, Co concentrations of 0.01 to 0.1 mM, calcite saturation, and times of hours to one week) and Co K-edge EXAFS measurements on the reaction products [6]. Our EXAFS results indicate three dominant modes of Co sorption, depending on experimental conditions: (1) precipitation of a $Co(OH)_2$ phase, (2) dissolution of calcite followed by co-precipitation of a $(Co,Ca)CO_3$ phase containing structural regions with dolomite-like ordering of Co and Ca and regions with random (calcite-like) ordering of Co and Ca, and (3) precipitation of trace amounts of $CoCO_3$ with a calcite-like structure within more complex microstructures similar to those of mode (2). The EXAFS spectrum of a cobaltian calcite model compound containing 2500 ppm Co (see the figures below) is representative of a $(Co,Ca)(CO_3)_2$ solid solution similar to that formed when 0.01 mM Co is reacted with calcite at pH 8.5 in a calcite-saturated solution (see Figure B below). At 0.1 mM Co, under otherwise similar conditions, a $Co(OH)_2$-like precipitate forms (Figure B). These results indicate that Co(II) can be sequestered in carbonate or hydroxide phases depending on Co concentration and other solution variables.



A separate EMSP poster by Eggleston *et al.* on the application of hydrothermal atomic force microscopy applied to calcite growth on surfaces is closely related to this work, and is part of the overall EMSP project.

Publications from Stanford EMSP Work

[1] T. Kendelewicz, P. Liu, C.S. Doyle, G.E. Brown, Jr., E.J. Nelson, and S.A. Chambers (2000), Reaction of Water with the (100) and (111) Surfaces of Fe_3O_4, *Surf. Sci.*, (in press)

[2] T. Kendelewicz, P. Liu, C.S. Doyle, G.E. Brown, Jr., E.J. Nelson, and S.A. Chambers (1999), X-ray adsorption and photoemission study of the adsorption of aqueous Cr(VI) on single crystal hematite and magnetite surfaces, *Surf. Sci.*, **424**, 219-231

[3] T. Kendelewicz, P. Liu, C.S. Doyle, G.E. Brown, Jr., Reaction of Cr(VI) aqueous solution with (111) surfaces of magnetite, *Surf. Sci.* (submitted).

[4] G.E. Brown, Jr., S.A. Chambers, J.E. Amonette, J.R. Rustad, T. Kendelewicz, P. Liu, C.S. Doyle, D. Grolimund, N.S. Foster-Mills, S.A. Joyce, S. Thevuthasan (2000), Interaction of Aqueous Chromium Ions with Iron Oxide Surfaces, *ACS Symp. Ser.* (in press).

[5] C.S. Doyle, T. Kendelewicz, X. Carrier, G.E. Brown, Jr. (1999), The Interaction of Carbon Dioxide with Single Crystal CaO(100) Surfaces, *Surf. Rev. Lett.*, **6**, 1247-1254

[6] N. Xu, G.E. Brown, Jr., G.A. Parks, M. F. Hochella, Jr. (2000), Co(II) Sorption at the Calcite-Water Interface: II. X-ray Absorption Fine Structure Spectroscopy Study, *Geochim. Cosmochim. Acta* (submitted)

Acknowledgments

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

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Office of Science and Office of Environmental Management
Environmental Management Sciences Program

STATUS AND ORGANIZATION

Project initiated in October 1999. Funding divided between three groups, each displaying separate posters:

PNNL (here)
Epitaxial oxide synthesis (Chambers), and characterization/contaminant reaction studies with Hanford subsurface carbonates (Zachara)

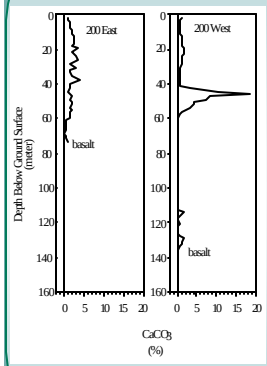
Stanford University
Synthesis of carbonate coatings on oxide surfaces and spectroscopic study of surface complexation and electron transfer reactions of Cr, Co, Sr, and Tc (Brown)

University of Wyoming
Variable temperature scanning probe microscopy (SPM) study of calcite precipitation/dissolution mechanisms (Eggleston)

SCIENTIFIC ISSUES

- How does the surface and bulk geochemical behavior of vadose zone zone carbonates compare to pure calcite, which has been relatively well studied?
- What minor substituents and morphologic features of vadose zone carbonates influence growth/dissolution and adsorption/desorption?
- What is the relative importance of surface complexation to and coprecipitation of ^{90}Sr within vadose zone carbonates as compared to ion exchange on small quantities of vermiculite and smectite?
  - What is the balance between direct reactions of ^{90}Sr with the isotopic exchange between $^{86/87}Sr$ is vadose zone carbonates?
- Do carbonates coat other reactive sedimentary phases such as rutile and magnetite preventing or modifying their reaction with Tc(VII) and/or Cr(VI)?

ENVIRONMENTAL MANAGEMENT ISSUES



- Dilute and concentrated waste streams been discharged to the Hanford vadose zone from cribs, specific retention basins, and leaked tanks.
- The vadose zone contains low but significant concentrations of calcium carbonate (left). Calcium carbonate is reactive with many released contaminants (e.g., $^{90}Sr^{2+}$, $^{60}Co^{2+}$). Calcium carbonate is unreactive toward others (e.g., CrO_4^{2-}, TcO_4^-) and may block reactive sites on sediment minerals.
- Waste water-sediment interactions have precipitated calcium carbonates beneath leaked single shell tanks entraining contaminants and other macroions (e.g., Mg^{2+}).
- Devising interim corrective measures and long term remedial action/closure plans for the tank farms requires that credible projections be made of the future migration of in-ground contaminants. Such projections require that geochemical reactions with the carbonates be explicitly considered.

NATURE OF VADOSE ZONE CARBONATES

- Detrital
  - Lithogenic fragments deposited with the sediments (~1-5 mass %)
- Pedogenic
  - Present and relic calcic soil horizons spanning a continuum in development (5-35 mass %)
- Waste Induced
  - High Na (> 1 mol/L) in leaked high level wastes (HLW) displace Ca^{2+} and Mg^{2+} from the ion exchange phase (X; vermiculite/smectite) inducing Mg-calcite precipitation $Ca_{1-y}Mg_yX_2 + 2Na^+ + HCO_3^- = 2NaX + Ca_{1-y}Mg_yCO_3 + H^+$
- Elevated temperatures of leaked HLW (> 50°C) encourage precipitation

HANFORD VADOSE ZONE CARBONATES

Typical Forms of Calcite Accumulation

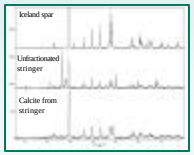
- Coatings on gravel bottoms and within sand

- stringers and layers in silt

- Nodules in clay and paleosols

Two field samples of calcium carbonate were selected for characterization and chemical reaction study. One is a calcite/caliche stringer similar to the middle photograph above, and the other is a calcite-coated sand from the Hanford formation (~20 m deep) obtained by RCRA coring near the S-SX tank farm in 200 W. Properties of the caliche stringer are shown below.

XRD of Hanford Carbonates

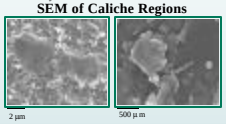


- The stringer (middle trace) is composed of quartz and calcite, with some mica, vermiculite, and feldspar.
- The calcite from the stringer (bottom) shows peak broadening relative to Iceland spar (top), indicative of small crystal size and crystallite disorder.

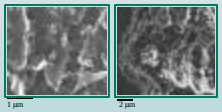
Optical Micrograph of Caliche Stringer

- The stringer exhibits complex structure with porous (biege) and dense (white) regions and inclusions of aluminosilicate soil material.

SEM of Caliche Regions

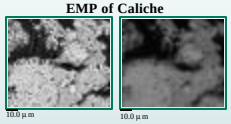


- The dense regions of the caliche are composed of calcite-cemented tabular, 100 nm $CaCO_3$ crystallites. Rhombohedral morphology was not observed.

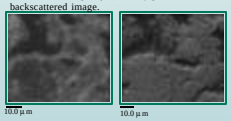


- The porous regions also contained tabular $CaCO_3$ crystallites, but porosity was induced by irregular cementation (left) and biogenic features (right).

EMP of Caliche



- A 30 µm thin section was analyzed by electron microprobe. The backscattered image (left) showed pore spaces (black) and porous, radial $CaCO_3$. The Ca elemental map (right) closely paralleled the backscattered image.



- The $CaCO_3$ contained Si, with accumulation in porous surface regions (left). Sr (right) also concentrated in Si-rich, porous regions.

OBJECTIVES AND APPROACH

- Determine microscopic reactions, factors, and phenomena controlling contaminant flux to and from vadose zone carbonates

$$\frac{d[C]}{dt} = F \text{ (vadose zone carbonate properties)}$$

For both sorption and desorption of HLW contaminants where
C = ^{60}Co, ^{90}Sr, $^{99}Tc(VII)$, Cr(VI)

Sorbates

Cations: Co^{2+} ($\Delta r^{2+} = 0.35$) and Sr^{2+} ($\Delta r^{2+} = 0.16$) where $\Delta r^{2+} = r(VI)_{Ca^{2+}} - r(VI)_{Me^{2+}}$

1.) Surface exchange and complexation

$CaX + Me^{2+} = MeX + Ca^{2+}$ $\quad K_{ex}$
$CO_3H + Me^{2+} = CO_3Me^+ + H^+$ $\quad K_{cmplx}$

2.) Co-precipitation/coupled substitution

$CaCO_{3(s)} + Me^{2+}_{(aq)} = MeCO_{3(CaCO3)} + Ca^{2+}_{(aq)}$

$$K_d = \left(\frac{X_{MeCO3}}{X_{CaCO3}}\right)\Big/\left(\frac{m_{Me}}{m_{Ca}}\right) = \left(\frac{K_{CaCO3}}{K_{MeCO3}}\right)\left(\frac{\gamma_{Me}}{\gamma_{Ca}}\right)\left\{\exp\left(\frac{-\Delta\mu}{RT}\right)\right\}$$

(Experiment: X_{MeCO3}/X_{CaCO3}, m_{Me}/m_{Ca}; Theory: K_{CaCO3}/K_{MeCO3}, γ_{Me}/γ_{Ca})

γ = aqueous activity coefficient
$\Delta\mu$ = difference of chemical potential of $MeCO_3$ in $CaCO_3$ from $MeCO_3$

3.) Isotopic exchange

$^{90}Sr + {}^{8687}SrCO_3 = {}^{90}SrCO_3 + {}^{8687}Sr$

Anions: $Tc(VII)O_4^-$ and $Cr(VI)O_4^{2-}$

1.) Surface passivation of heterogeneous reduction

$3Fe_3O_{4(s)} + mCaCO_{3(s)} + TcO_{4(aq)} + (1+n)H_2O + H^+_{(aq)} \neq$ magnetite

$4Fe_2O_{3(s)} + mCaCO_{3(s)} + TcO_2{\bullet}nH_2O_{(s)} + Fe(OH)_{3(s)}$ maghemite

2.) Co-precipitation

$3Fe_3O_{4(s)} + mCaCO_{3(s)} + TcO_{4(aq)} + 3H^+ = 4Fe_2O_3 + (m-1)\,CaCO_3 + Ca^{2+}_{(aq)} + TcOCO_{3(s)} + Fe(OH)_{3(s)}$

Variables

- Temperature (10-50° °C)
- I (0.001 to 5')
- Electrolytes (Na^+, K^+, Ca^{2+}, Mg^{2+})
- pH (8.5 to 11+)
- Ω (low to high)

Materials

- Carbonate +/- core samples from Hanford and Ringold formations
- Samples representative of detrital carbonates and calcic soils at different development stages
- Mg-calcite from waste induced precipitation
- Magnetic mineral fraction (illmenite/rutile) from Hanford and Ringold formations

Experimental Systems

- Batch stirred flow reactors
- Unsaturated flow apparatus

Instrumentation

- Electron microscopy (FESEM, HRTEM)
- Microprobe (electron, X-ray, Auger, SIMMS)
- Synchrotron (SSRL, APS; XAS and XAS microspectroscopy)

EXPECTED RESULTS AND PRODUCTS

- Insights on the geochemical reactivity of different carbonate types in the Hanford vadose zone for key inventory ($^{90}Sr^{2+}$, $^{60}Co^{2+}$) and risk driver (CrO_4^{2-}, TcO_4^-) contaminants
  - detrital
  - caliche
  - coatings
  - waste induced

  and controlling features: morphology, minor substituents, surface structure, etc.
- Microscopic kinetic models of calcium carbonate mediated reactions for linkage with reactive transport codes
  - adsorption
  - coprecipitation
  - passivation of heterogeneous reduction

  to allow improved predictions of future in-ground concentrations and migration
- Fundamental insights on reaction mechanisms and controlling molecular phenomena (through linkage and collaboration and Brown and Eggleston)