

American Chemical Society
Division of Geochemistry
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D. B. Kent, Program Chair

SUNDAY MORNING

The Gestalt of Porous Media: Understanding Chemical, Geochemical and Biogeochemical Reactions in Porous Media

G. D. Redden, Organizer Papers 1-8

SUNDAY AFTERNOON

The Gestalt of Porous Media: Understanding Chemical, Geochemical and Biogeochemical Reactions in Porous Media

G. D. Redden, Organizer Papers 9-15

MONDAY MORNING

Biogeochemical Redox Processes in Soils and Sediments

M. Ginder-Vogel, Organizer Papers 16-23

MONDAY AFTERNOON

Biogeochemical Redox Processes in Soils and Sediments

K. M. Campbell, Organizer Papers 24-29

MONDAY EVENING

Sci-Mix

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TUESDAY MORNING

Biogeochemical Redox Processes in Soils and Sediments

K. M. Campbell, Organizer Papers 30-35

TUESDAY AFTERNOON

Biogeochemical Redox Processes in Soils and Sediments

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Siderophores: From Biogeochemistry to Medical Applications

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The Gestalt of Porous Media: Understanding Chemical, Geochemical and Biogeochemical Reactions in Porous Media

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Biogeochemical Redox Processes in Soils and Sediments

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Siderophores: From Biogeochemistry to Medical Applications

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Siderophores: From Biogeochemistry to Medical Applications
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GEOC 1

Rates of U(VI) desorption from various grain size fractions of sediments from a contaminated aquifer as a function of bicarbonate concentration

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The kinetics of U(VI) desorption were studied with aquifer sediments collected beneath a former mill tailings site in Naturita, CO. Chemical variables included pH and bicarbonate and Ca concentrations. Batch experiments were performed on a <2mm sample and six size fractions ranging from <0.063mm to 1-2mm. For all samples, U(VI) desorption occurred in two major steps, an initial fast desorption (24 hr), and then slowing before reaching equilibrium after several weeks. Column experiments with tritium and bromide tracers were used to define the diffusion properties of intra-granular pore space and grain coatings. Diffusion from these physical regimes appears to be a rate-limiting process for slow U(VI) desorption. The relative abundances of U(VI) desorbed was 30-50% in the fast step versus 50-70% in the slow desorption step. Increased bicarbonate concentration increased the rate of U(VI) desorption in both steps, while the relative fractions in fast and slow steps remained nearly constant.

GEOC 2

Role of diffusion as a limiting kinetic factor affecting U(VI) release to a Hanford aquifer

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A groundwater plume containing uranium(VI) exists beneath the 300-Area at Hanford (WA, USA), due to continuing desorption from contaminated vadose-zone and saturated sediments coupled with dissolution of co-precipitated U(VI)-bearing mineral phases. Grain-scale morphology of the aquifer material suggests that intra-grain flow paths and mineral coatings, in which sorption complexes and

precipitates formed over years of waste disposal, provide a significant kinetic constraint that slows groundwater “flushing” of the sediments. Batch dissolution/desorption studies from five aquifer sediments were previously conducted in order to create an equilibrium and kinetic model for U(VI) release. The U(VI) release data is compared with tritium and bromide tracer diffusion from the sediments, following months of equilibration in packed columns with high concentrations of both tracers and elution with flow and stop-flow events. The intra-granular and mineral coatings regions represent a potentially long-term contaminant source, as U(VI) desorption from these regions appears to be a rate-controlling process.

GEOC 3

Intragranular diffusion as a kinetic control for uranium desorption from contaminated sediments

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U(VI) transport in contaminated systems can be limited by sorption to mineral surfaces. Sorption equilibrium is achieved rapidly in some cases, but is often kinetically limited by the diffusion of U(VI) through soil aggregates, grain fractures, and mineral coatings. Since sorption equilibrium is dependent on solution chemistry (pH, alkalinity, [Ca²⁺]), kinetics are influenced by the diffusion of U(VI) and other chemical species. This effect is not captured in models that generically lump physical and chemical kinetics. Results will be presented for a grain-scale diffusion model for contaminated sediments from Naturita, CO and Hanford, WA. High resolution tracer experiments reveal multiple diffusion zones with differing tortuosities. These results are being used to constrain a kinetic model that includes U(VI) surface complexation and component-specific diffusivities to test the dependence of U(VI) sorption kinetics on cross-diffusion of chemical species, with the goal of developing more accurate continuum-scale reactive transport models.

GEOC 4

Scaling of U(VI) and As(V) interactions with synthetic iron oxide-coated sand

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In this study, iron oxide-coated sands (IOCS) were synthesized and the interaction of uranium and arsenic with these synthetic sorbents were assessed. The iron content of the synthesized sands was 0.04%, 0.18, and 0.31%, respectively. The iron content and the measured specific surface area showed a positive and non-linear relationship. The U(VI) and As(V) adsorption isotherms of the three IOCS showed differences when normalized to Fe loading. However, when adsorption was scaled to their respective specific surface areas, the three sands exhibited similar adsorption isotherms. Furthermore, the pH edges on the three IOCS showed differences when normalized to iron content but showed similar adsorption when scaled to surface area. Published literature data sets and surface complexation models were used to support our results. These findings are significant in the understanding of U(VI) and As(V) interactions to Fe-dominated subsurface media.

GEOC 5

Alternative conceptual models of solution chemistry and resulting computer simulations of plutonium transport in the Savannah River Site vadose zone

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A fully-transient flow and reactive transport model has been developed to describe plutonium mobility in a series of 52-L field lysimeter experiments at the Savannah River Site. The present conceptual model assumes instantaneous sorption along with surface-mediated, first-order, kinetic redox cycling between the relatively mobile Pu(V) and immobile (or nearly immobile) Pu(IV) oxidation states. In this work, we present alternative conceptual models based upon known Pu solution chemistry and geochemical behavior which may be employed in the current reactive transport model with appropriate adjustments of the model parameters. These alternative conceptual models include: 1) Equilibrium distribution of Pu(IV) and Pu(V) based on $O_2(g)$ fugacity, 2) Kinetically controlled Pu(IV) and Pu(V) distribution based upon PuO_{2+x} dissolution, and 3) Mobilization of Pu(IV) due to complexation with dissolved organic matter. Analysis of these alternative conceptual models within the current reactive transport model framework and the ability to simulate observed transport behavior in the field lysimeters illustrate the problems associated with developing unique chemical reaction concepts in natural porous media. Results to date show how different reactive chemical models can produce the same or similar computer simulations when reaction parameters are used to fit the computer simulations to data.

Knowledge that this non-uniqueness is inherent in the so-called inverse problem (using data to derive parameter values in a model that is used to simulate the data) is not new. Using the SRNL Pu data sets, this non-uniqueness problem is illustrated in detail. One result is that modern computer modeling should be conceived more as an extension of the thinking process (computer-aided thinking) than as a classical predictive process. When applied properly, we view experiment combined with computer simulation-based analysis as a powerful methodology for extracting information from highly complex systems.

GEOC 6

Comparison of forced- and natural-gradient tracer tests to evaluate the rates of U(VI) desorption in a contaminated aquifer

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Several meter-scale tracer tests were conducted in a uranium-contaminated aquifer located at Naturita (CO, USA). Desorption of U(VI) was studied by injecting uncontaminated upgradient groundwater with Br tracer into a contaminated portion of the aquifer, using both forced- and natural-gradient experiments to vary rates of groundwater flow. The low concentration of U(VI) in the injected water caused a temporal decrease in U(VI) concentrations at downgradient multilevel observations wells with a gradual rebound in dissolved U(VI) concentrations. The decrease and rebound in U(VI) concentrations are affected by numerous chemical and physical factors, including fluid mixing, subsurface heterogeneity, groundwater flow rates, and experimentally-induced temporal changes in the chemical concentrations of U(VI), HCO₃, Ca, Na, and pH. Reactive transport model simulations are presented that describe the experimental observations and allow conclusions to be drawn about the relative effects of chemical and physical processes on U(VI) fate and transport in the Naturita aquifer.

GEOC 7

Capturing 3-D fluid configurations in porous materials

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Capturing three-dimensional fluid configurations in porous materials

Using confocal microscopy we monitor the evolution of fluid configurations during two-phase flow through a porous material under a variety of controlled conditions. The porous media is composed of slightly sintered, borosilicate glass beads that are 63 microns in diameter. The spatial and time resolution of confocal microscopy affords us the ability to collect three-dimensional images during flow experiments. During each flow experiment the flow rate is controlled and the pressure drop across the media measured. These tools allow us to capture the fluid morphology as it evolves through the media.

GEOC 8

Solute dispersion in geological porous media: Unifying pore network modeling, continuous time random walk theory and experiment

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Solute transport in geological porous media possesses spatial and temporal variations due to complex porous structure from pore scale upwards. This talk focuses on the advantages offered by a novel methodology that unifies pore network modeling, CTRW theory and experiment to describe solute dispersion.

A Lagrangian-based pore-scale network model is used to successfully predict the rich Péclet-number dependence of dispersion coefficient, D . In the asymptotic limit the model compares well with the experimental data in restricted diffusion, transition, power-law and mechanical dispersion regimes. However, prior to reaching the asymptotic limit, transport is non-Gaussian and D possesses temporal and spatial variation.

Probability density functions (PDF-s) of the pore-to-pore particle transit times are studied within the network throats and an excellent agreement is obtained with the CTRW theory. Based on the truncated power-law interpretation of PDF-s, the physical origin of the power-law scaling of D vs. Pe is explained for unconsolidated porous media, sands and a number of sandstones, arriving at the same conclusion from numerical network modelling, analytic CTRW theory and experiment.

The extensions to reactive transport and to the field-scale dispersion are discussed. Increasing heterogeneity and/or Péclet results in an increase of the length traveled by solute plumes before Gaussian behaviour is attained. These findings can have large implications on the field-scale dispersion where the range of solute velocities can be so high that the asymptotic behaviour might not ever be reached.

GEOC 9

Influence of microbial biofilms on reactive transport in porous media

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Understanding biofilm accumulation and its influence on transport and reaction in porous media is important in a number of environmental and industrial technologies including bioremediation, enhanced secondary oil recovery, abatement of saltwater intrusion, deep-subsurface sequestration of supercritical carbon dioxide, and biofouling of injection or recovery wells. The ability to understand and control biofilm growth in porous media is needed to optimize the efficacy of these technologies.

Laboratory studies were performed to evaluate the impact of biofilm accumulation on reactive transport in quasi 2- and 3-dimensional porous media reactors. *Vibrio fischeri* and *Cellulomonas* sp. (strain ES6) biofilms were established in continuous flow reactors under constant head and constant flow conditions. The impact of nutrient concentration, flow rate, and biocide challenges on porous media biofilm structure was evaluated by investigating changes in average pore velocity, permeability, and hydrodynamic dispersivity from tracer studies, combined with digital image analysis of bulk fluid dye tracers, *Vibrio fischeri* bioluminescence (as a measure for oxygen concentration), microbial vital stains, enumerations, microscopy, and biochemical analyses.

We will summarize our work, focusing upon linking our improved understanding of the spatial and temporal dynamics of diffusive and advective transport, mixing, and the establishment of chemical gradients in biofilm-affected porous media with recommendations on how to develop improved environmental and industrial engineering technologies.

GEOC 10

Role of microbial exopolymeric substances from *pseudomonas aeruginosa* p16 and *pseudomonas putida* p18 on chromium speciation and sorption to heterogeneous soil surfaces

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Laboratory ion exchange and sorption experiments were performed to investigate the influence of exopolymers (EPS) extracted from *P. aeruginosa* P16 and *P. putida* P18 on Cr(III) binding with heterogeneous surface soils. The analysis of titration data performed at two different ionic strengths of 0.01 and 0.1 M NaCl using a non-electrostatic discrete ligand model suggests that the isolated EPS molecules are simple, and contain a uniform distribution of ligands with functional groups ranging from carboxylic to hydroxyl/phenolic groups. The analysis of ion exchange data shows that Cr(III) strongly binds with the carboxylic and phosphate groups of EPS molecules leading to the formation of a 1:1 Cr:EPS complex for P18 EPS and 1:2 Cr:EPS complex for P 16 EPS, respectively. XANES analysis at the Cr absorption edge confirmed that Cr added as Cr(VI) was reduced to Cr(III) by the bacteria and the addition of carbon sources such as glucuronic acid and galacturonic acid appeared to have little effect on the overall extent of reduction. EXAFS analysis was performed to determine the nature of the Cr bonding to EPS.

The results from laboratory sorption experiments indicate that bacterial EPS has a great influence on Cr(III) sorption to soils under a wide range of pH indicating that EPS may impact Cr mobility in subsurface systems.

GEOC 11

Fluid flow, solute mixing, and precipitation in porous media

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We have investigated how mineral-forming reactants can be transported and mixed in porous media to stimulate the nucleation, growth, and deposition of minerals. The research issues concern: (1) the nature of solute transport and mixing, (2) coupling between precipitation and permeability, and (3) the impact of precipitation on a mobile, contaminant metal.

Calcium carbonates are the model mineral phases, and strontium is the model contaminant. Two mixing geometries involve parallel flow or sequential addition of CaCl_2 and NaHCO_3 solutions. Experimental and modeling results (using smoothed particle hydrodynamics and continuum approaches) show narrow, self-focusing precipitation zones in the first case and transient deposition in the second. The effect of saturation states and $\text{Ca}^{2+}/\text{CO}_3^{2-}$ ion ratios on the rates of precipitation and the co-precipitation of Sr^{2+} were also studied and are discussed in terms of reaction kinetics vs. transport and mixing in porous media systems.

GEOC 12

Longterm release of Cs and Sr is consistent with control via feldspathoid dissolution in hydroxide-weathered Hanford sediments

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We examined the characteristics of contaminant release and porous media dissolution from Hanford Site (WA, USA) sediments that were subjected to hyperalkaline ($\text{pH} > 13$) $\text{Na-Al-NO}_3\text{-OH}$ solutions for 182 days under two pCO_2 regimes (undetectable at < 10 ppmv and atmospheric, 385 ppmv). Release was monitored in flow-through experiments conducted after removal of the hyperalkaline waste source and modeled using the reactive transport model CrunchFlow. After more than 500 pore volumes, sustained, long term release of Cs^+ and Sr^{2+} is consistent with control via feldspathoid dissolution. Reactive transport modeling indicates that while dissolution dominates at long times, it is also superimposed on early ion exchange processes, contributing to initial contaminant release. Quantification of nitrate precipitation into—and release from—neoformed precipitates suggests that elevated contaminant concentrations suppress feldspathoid formation. Changes in sediment characteristics (e.g., CEC and porosity) as a result of mineral dissolution will also be discussed.

GEOC 13

Redox transformations and transport of iodine in two geochemically distinct zones of a sand and gravel aquifer in Cape Cod, MA

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Radioactive forms of iodine (^{131}I and ^{129}I) are important components of radioactive waste. In this study, three tracer tests were performed in a sand and gravel aquifer in Cape Cod, MA in order to study the redox transformations and transport of iodine under different geochemical conditions. Results show that I^- was oxidized to both I_2 (up to 46%) and IO_3^- (up to 6%) in the oxic zone, with the extent of oxidation increasing with transport. A pulse of dissolved Mn was liberated from the sediments, providing evidence that Mn oxides were responsible for I^- oxidation. Iodate transport was retarded relative to a conservative tracer (Br) in the oxic zone. In the Fe-reducing zone, IO_3^- was quickly reduced to I^- without any observed production of I_2 intermediate. The results indicate the importance of considering the complex redox and sorption chemistry of iodine when predicting its transport in waste plumes.

GEOC 14

Chemistry of sulfate, sulfite, and sulfonate esters in faujasite X

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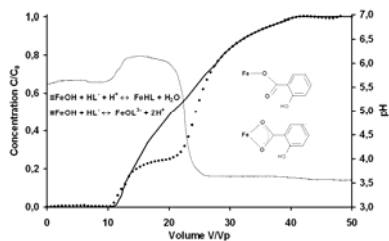
The zeolite sodium Faujasite X (NaX) has been shown to have nucleophilic character at oxygen atoms that are directly bonded to an aluminum atom in the framework, due to a delocalized anionic charge, which is stabilized by a sodium cation. We have successively shown that isocyanates, phosphorous acid esters, and alkyl halides are susceptible to chemistry with NaX. Esters based on sulfur acids are of interest due to their use in industrial processes, and the harm they can cause to the environment. Reactions between dimethyl sulfate (DMSate), dimethyl sulfite (DMSite), and methyl methane sulfonate (MMS) with NaX were conducted through an evaporative transfer technique allowing it to transfer from the gas phase into the cage of the zeolite. The results were analyzed using ^1H and ^{13}C high resolution liquid NMR, ^{13}C MAS solid state NMR, GC/MS, and IR spectroscopy.

GEOC 15

Reactive transport of salicylate in a goethite-coated sand column

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The salicylate sorption at oxide/water interface and correlation with the hydrodynamic transport parameters is the main objective of this study. For this purpose, the surface complexation reactions were examined under static and dynamic conditions by conducting batch and column tests, vibrational spectroscopy and modeling approach. Prior to salicylate sorption experiments, the surface properties of the synthesized Goethite-coated quartz were determined. Sorption isotherm, sorption edges, solid-to-solution ratio effect on sorption were studied and described using macroscopic models and the MINTeq database incorporated in PHREEQC-2. The hydrodynamic parameters of the column were determined by a non-reactive tracer injection using the Convection-Dispersion Equation. Column breakthrough curves displayed two steps at high flow rate (0.3 cm/min). On the basis of spectroscopic observations (Raman and IR), the mononuclear salicylate surface complexes (monodentate and/or bidentate) are identical at any height in the column. However, a binuclear monodentate complex is expected in batch. Assuming one type of site and two surface complexation reactions per site, the transport of salicylic acid in a goethite-coated sand column can be described by Surface Complexation Modelling.



GEOC 16

Molecular mechanism of bacterial metal respiration

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Metal-respiring bacteria occupy a central position in the biogeochemical cycles of metals and carbon, and serve as catalysts for a variety of other environmentally important processes including biomineralization, biocorrosion and bioremediation. Metal-respiring bacteria are presented, however, with a unique

physiological challenge at circumneutral pH: they are required to respire anaerobically on electron acceptors which are either highly insoluble (e.g., Fe(III)) and unable to enter the cell, or highly soluble (e.g., U(VI)) and reduced to insoluble end-products which precipitate inside the cell. To overcome these physiological problems, metal-respiring bacteria employ a variety of novel respiratory strategies not found in other bacteria, including 1) direct enzymatic reduction at the cell surface, 2) electron shuttling between the cell and metal surfaces, and 3) metal solubilization by bacterially-produced organic ligands followed by respiration of the soluble organic-metal compounds. The talk will highlight our latest findings on the enzymatic mechanisms of bacterial metal respiration.

GEOC 17

Respiration on amorphous iron oxyhydroxides by *Shewanella oneidensis*: Attachment and dissolution morphology

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The kinetics of dissimilatory iron respiration by bacteria and the factors that control the rate are important to a variety of globally significant environmental processes as well as the fate and transport of contaminants. In this work, the attachment and dissolution morphology of slides coated with amorphous iron (oxy)(hydr)oxide particles and exposed to the soil bacteria *Shewanella oneidensis* was examined using atomic force (AFM) and confocal microscopies. The dissolution morphology of the slides exposed to wild-type organisms is heterogeneous with dissolution features that are some tens of micrometers in size. This contrasts to the behavior of slides exposed to a small soluble electron shuttling compound with or without cells, where reductive dissolution is homogenous. Similarly, slides stained with either acridine orange or a live-dead dye (Invitrogen) and examined using confocal microscopy revealed that microcolonies of organisms form that are of a similar size and character to the dissolution features.

GEOC 18

Biogeochemical processes controlling the release of iron from marine sediments

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The solubility of iron in marine sediments is generally controlled by redox processes, either through the oxidation of ferrous iron by dissolved oxygen, the anaerobic respiration of iron oxides, or the chemical reduction by dissolved sulfides. Over the last decade, we have shown using voltammetric gold/mercury (Au/Hg) microelectrodes that ferric iron remains soluble in marine sediments when complexed by organic ligands. In this study, the seasonal transformation of soluble organic-Fe(III) complexes has been investigated using a benthic lander and conventional porewater extractions along the salinity gradient in an estuary of the South East of the United States. Our results reveal that soluble organic Fe(III) complexes can reach near millimolar levels in porewaters and that the flux of these complexes across the sediment-water interface probably contributes to the significant concentration of dissolved iron in the surface waters of this estuary. Seasonal variations suggest that sulfate reduction may indirectly control the release of iron from these sediments and thus the supply of an important nutrient to coastal waters.

GEOC 19

Fe(II) oxidation in coastal groundwaters: A multifactorial analysis of hydrogen peroxide yield across the intertidal zone

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Anoxic groundwaters are known to be significant sources of reduced Fe species to estuaries and the coastal ocean. We report hydrogen peroxide yield from Fe(II) oxidation across a range of solution conditions that represent the transition from fresh, organic rich groundwater to seawater. Hydrogen peroxide production is correlated against several species known to affect the kinetics of Fe(II) oxidation, including fluoride, sulfate, dissolved organic matter, chloride and total carbonate species. A multivariate, microscale, high throughput experimental approach is used to explore correlations between these factors acting individually and cooperatively (i.e. the effect of the natural organic matter/chloride interaction) on the yield of hydrogen peroxide. The yield of hydrogen peroxide from the oxidation of native Fe(II) in natural groundwater from coastal South Carolina is also discussed.

GEOC 20

Factors influencing the reactivity of metal-core iron nanoparticles in aqueous geochemical systems

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The chemistry of metal-core iron nanoparticles in aqueous systems differs from that of micron-sized or bulk iron primarily as a result of the key role played by the surface. The structure of the oxide shell, which forms at the surface and can account for the majority of the particle mass, controls the transfer of electrons between the aqueous phase and the metallic core and may offer unique sorption sites for contaminants, degradation products, and Fe(II) species. The dominance of the surface also means that significant changes in reactivity can be expected as a result of particle aging, interactions with solution constituents, and aggregation with other particles including clay minerals. This talk will explore the dynamic interplay between the surfaces of metal-core iron nanoparticles and the aqueous geochemical environment using the reaction with carbon tetrachloride as a measure of the changes that occur.

GEOC 21

Redox transformation of hematite mediated by biased bulk crystal conduction

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The biogeochemical cycle of iron in nature often involves redox interactions between dissolved abiotic or biogenic Fe(II) and Fe(III)-oxide and oxyhydroxide minerals. Some iron oxides are electrical semiconductors. Furthermore, they can exhibit a wide variety of stable crystallographic terminations, each with distinct pH-dependent surface charging behavior in solution. Using hematite as the example, we show that in certain solutions, unequal charging behavior between different hematite surfaces creates a bias across the crystal that can direct a current through the bulk. In this case, the current source is net oxidative adsorption of Fe(II) at (001) surfaces and the sink is net internal reduction of lattice Fe(III) to Fe(II) at edge surfaces. This transformation mechanism complicates the view of redox transformation of iron minerals, and introduces the

concept of coupled interfacial redox reactions occurring on different mineral surfaces mediated by bulk electron conduction.

GEOC 22

Effects of oxyanions and natural organic matter on the formation of Fe(II)-bearing secondary mineralization products resulting from the bioreduction of lepidocrocite

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The bioreduction of Fe(III) oxides may result in the production of a suite of Fe(II)-bearing secondary mineralization products (Fe(II)SMPs), including magnetite, siderite, vivianite, and green rusts. In an effort to better understand the effects of solution chemistry on the formation of particular Fe(II)SMPs of dissimilatory Fe(III) reduction, we examined the effects of a series of oxyanions and natural organic matter on the bioreduction of lepidocrocite by *Shewanella putrefaciens* CN32. The presence of arsenate, molybdate, phosphate, silicate, or tungstate resulted in the formation of carbonate green rust, while in the absence of these anions or with the addition of borate, magnetite formed. Similarly, the addition of citrate, humic and fulvic acids, or extracellular polysaccharides from *S. putrefaciens* CN32 resulted in green rust; however, magnetite formed in the presence of oxalate or gellan (an extracellular polysaccharide produced by the bacterium *Sphingomonas elodea*).

GEOC 23

Lead dioxide dissolution when both iron(II) and manganese(II) are present: Inhibition and catalysis

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Human activities govern the oxidation state and speciation of Pb entering soils and sediments. Here, we focus upon Pb^{IV} and its reduction to Pb^{II} . E° for the $\text{PbO}_2(\text{plattnerite})/\text{Pb}^{2+}$ half-reaction is 170 mV higher than that of $\text{MnO}_2(\text{birnessite})/\text{Mn}^{2+}$, and 510 mV higher than that of $\text{Fe}(\text{OH})_3(\text{amorph.})/\text{Fe}^{2+}$. Both Fe^{2+} and Mn^{2+} reduce and dissolve PbO_2 , but continued reaction is confounded by Fe^{III} and $\text{Mn}^{\text{III,IV}}$ (hydr)oxide products that coat PbO_2 surfaces. This inhibitory effect is more pronounced for iron than for manganese, and becomes more acute when PbO_2 loadings are decreased. Consider reactions at pH 6.0 in the presence of 20 μM Fe^{2+} or Mn^{2+} . When the PbO_2 loading is 200 $\mu\text{moles/L}$, initial rates of Pb^{2+} release are 3.7-times lower for Fe^{2+} than for Mn^{2+} . When the PbO_2 loading is 20 $\mu\text{moles/L}$, initial rates are 25-times lower for Fe^{2+} than for Mn^{2+} . When Fe^{2+} and Mn^{2+} are simultaneously added, the situation becomes more complex. At low Fe^{2+} concentrations and PbO_2 loadings, inhibitory effects arising from Fe^{III} (hydr)oxide formation control reaction kinetics. As Fe^{2+} concentrations are increased, $\text{Mn}^{\text{III,IV}}$ (hydr)oxides are reduced back to Mn^{2+} . By cycling between oxidation states, Mn effectively catalyzes the reduction of PbO_2 by Fe^{2+} .

GEOC 24

Real-time molecular scale redox kinetics at the mineral/water interface

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The kinetics of redox processes in natural systems are often characterized by a rapid initial reaction, on time scales of seconds to minutes, followed by a slower reaction. The rapid reaction may comprise a significant portion of the entire reaction. In many cases much of the initial reaction is completed before the first measurement can be made using traditional batch and flow techniques. It is important to measure initial reaction rates so that chemical kinetics rate parameters can be determined and reaction mechanisms can be elucidated. The use of real-time in-situ molecular scale techniques can be employed to measure rapid reaction processes. In this presentation, the use of rapid-scan attenuated total reflectance (ATR) Fourier transform infrared (FTIR) and quick x-ray absorption fine structure (QXAFS) spectroscopy will be employed to measure the redox kinetics of oxyanions at the mineral/water interface.

GEOC 25

Pyrite oxidation in abiotic and biotic environments

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Acid Mine drainage (AMD) is a significant environmental problem, that primarily results from the oxidation of pyrite, FeS₂. The process results in the acidification of the surrounding environment. The process is driven in large part by microbial (both autotrophic and heterotrophic) processes. Toward understanding these processes, studies have been conducted to investigate the interaction of bacteria, such as the chemolithoautotrophic species, *Acidithiobacillus ferrooxidans* and heterotrophic species, *Acidiphilium acidophilum* with pyrite. Surface science techniques capable of probing the oxidation of pyrite under both abiotic and biotic conditions have been used to shed light on the microscopic controls of pyrite oxidation in abiotic and biotic environments. Specifically, attenuated total reflection infrared spectroscopy, electron spectroscopies, and probe microscopies have been used to develop a surface picture of the oxidation process. The development of this picture has suggested potential ways to suppress AMD in the environment.

GEOC 26

Oxidation rate of pyrite in the presence of galena

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Pyrite oxidation is the most important process contributing to acid mine drainage, which affects many streams in coal-mining regions as well as gold and base-metal mining regions. Pyrite is often commingled in mine waste with other minerals, including sulfides. Here we examined the effect of the presence of galena on the rate of pyrite oxidation. On the basis of column experiments, we conclude that the presence of galena suppresses the oxidation rate of pyrite significantly, while the oxidation rate of galena increases. These results are consistent with the galvanic effect, in which galena is a sacrificial electron donor and protects pyrite from oxidizing. In this study we are explicitly studying if

contact between the two materials is necessary for the protection to take place. The implications of this work are far ranging as it shows that predicting rates of pyrite oxidation can be drastically affected by the presence of a second metal sulfide.

GEOC 27

Expanding the role of microbes in the oxidation of Mn(II)

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The oxidation of Mn(II) has sweeping environmental ramifications, impacting the fate and transport of contaminants, the degradation of carbon, the cycling of nutrients, and the function of anaerobic-based metabolisms. While the oxidation of Mn(II) by molecular oxygen is thermodynamically favorable at circumneutral pH, the reaction is kinetically limited in the absence of mineral surface or enzyme catalysts. In particular, oxidation of Mn(II) is catalyzed by the activity of microorganisms and has primarily been attributed to the enzymatic activity of a phylogenetically diverse group of bacteria. Here, we highlight alternative and important pathways for the oxidation of Mn(II) within surface environments. The role of photo-active metabolites in surface waters and the abundant and diverse community of Mn(II)-oxidizing fungi within surface soils will be discussed. This research reveals that Mn(II) oxidation pathways are more diverse than predicted and other abiotic and biotic forces have been underestimated in some systems.

GEOC 28

Inhibition of heterogeneous As(III) oxidation by hydrous Mn(IV) oxide by mineral surface alteration

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Heterogeneous oxidation of As(III) on the surface of manganese oxides has been well characterized; however, the surface chemistry of the oxidation reaction remains poorly characterized, particularly during the initial phase of the oxidation

reaction. Our methodology uses a novel flow-through column system packed with hydrous manganese(IV) oxide (HMO) coated sand. A 1 mM As(III) solution is introduced into the column, and the oxidation and retention of As on the HMO mineral surface is followed in real-time, using quick-scanning X-ray absorption spectroscopy (Q-XAS). We found that initially, only As(V) is retained on the mineral surface. However, eventually, As(III) is also retained on the HMO mineral surface. The retention of As(III) on the mineral surface coincides with the appearance of As(III) in the column effluent. Ex situ analysis of the reacted HMO, using HR-TEM, reveals the presence of an amorphous rind on the mineral surface, which may be responsible for As(III) retention, although the injection of 1 mM phosphate results in As(III) mobilization. Future studies will investigate As(III) oxidation by biogenic Mn(IV) oxides.

GEOC 29

Surface chemistry of Cr(III) oxidation and precipitation on Mn(IV) oxides

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The main soil components that oxidize Cr(III) to the more hazardous chromium species Cr(VI) are manganese oxides. With hydrous manganese oxide (HMO) and birnessite, Cr(III) may react in two steps: a first step in which Cr(III) sorbs to MnO₂ and exchanges its electrons, and a second step when a chromium hydroxide precipitate may form on the surface of the manganese oxide. Our primary goal in this study is to measure the kinetics of surface precipitate formation, to understand its effect on the Cr(III) oxidation rate, and to infer chemical mechanisms that are involved in steps 1 and 2. To address these questions, several spectroscopic and microscopic techniques were used in the study including quick XAFS, TEM, XPS, and SEM. Understanding the reactivity of chromium with manganese oxides from both a molecular spatial scale and a rapid temporal scale will help us predict the fate of chromium in the environment.

GEOC 30

Microbial reduction of uranium in the presence of nontronite and chlorite

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To assess the dynamics of microbially mediated U-clay redox reactions, we examined the reduction of uranium(VI) by *Shewanella oneidensis* MR-1 in the presence of iron(III)-rich nontronite NAu-2 or chlorite CCa-2. Bioreduction experiments were conducted with combinations and varied concentrations of U(VI), nontronite, chlorite and the electron shuttle AQDS. Abiotic experiments were conducted to quantify U(VI) sorption to nontronite or chlorite, the reduction of U(VI) by chemically-reduced (CBD) nontronite or chlorite, and the oxidation of U(IV) by nontronite or chlorite. Solids were characterized by X-ray diffraction, scanning electron microscopy, and X-ray absorption near edge spectroscopy. Essentially no U(VI) reduction was observed in incubations that contained CBD nontronite-Fe(II), while U(VI) was reduced by CBD chlorite-Fe(II). Bioreduction of U(VI) was primarily responsible for U valence cycling in these U-smectite systems and enhanced clay-Fe(III) reduction. Contrasting results obtained with nontronite vs. chlorite were explained by thermodynamic considerations and differences in reaction mechanisms.

GEOC 31

Nanoscale size effects on uranium (VI) adsorption and surface-mediated reduction by iron(II) on hematite nanoparticles

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The high surface area to mass ratios of hematite nanoparticles can increase the extents of surface reactions that affect the environmental biogeochemistry of pristine and contaminated environments. Surface reactions of interest include uranium(VI) adsorption and surface-mediated reduction by iron(II). In order to understand nanoscale effects on these surface reactions, hematite nanoparticles with diameters of 10, 50, and 200 nm were synthesized using gas phase methods. Uranium(VI) adsorption to the three sizes of hematite particles was evaluated over the pH range of 3-11. Surface complexation modeling provided a quantitative reaction-based framework for evaluating the size effects. EXAFS spectroscopy was used to study the differences in the coordination environments of surface-associated uranium species. Rates of U(VI) reduction by adsorbed Fe(II) were investigated in batch experiments. The reduction was interpreted as a

pseudo-first-order reaction with respect to the activity of the adsorbed U(VI) with an excess of Fe(II) relative to U(VI).

GEOC 32

Structural identity and reactivity of biogenic UO₂

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Biogenic UO₂ is important for its anticipated role as an in-situ waste form for subsurface uranium contamination at U.S. DOE sites. A remarkable property of this material is its tendency to form nano-scale crystals, down to ca 1 nm diameter. It has been speculated that nano-scale size induces substantial lattice strain, destabilizing nano-biogenic UO₂. We have systematically characterized biogenic UO₂ using EXAFS, in-situ synchrotron powder diffraction, TEM, and continuous-flow dissolution measurements. Surprisingly, the biogenic UO₂ lattice was found to be unstrained and structurally homologous to stoichiometric UO₂, suggesting that surface energy is relatively modest in comparison to the particle total energy. This conclusion is reinforced by the finding that the solubility of nano-biogenic UO₂ is very similar to that of bulk stoichiometric UO₂ under reducing conditions. These results provide a clear structural paradigm for this complex natural material and a scientific basis for describing its reactivity in the subsurface.

GEOC 33

Uranium association with iron minerals in alluvial sediments

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In field-experiments, the nature of bioavailable Fe mineral(s), e.g., Fe-oxides and/or clays, and site-specific coupled geochemical, hydrological and microbiological conditions under which these Fe-minerals are biotransformed play a significant role in aqueous U(VI) attenuation from the contaminated groundwaters. Samples of a naturally bioreduced zone from the U.S. DOE Integrated Field Challenge Site (IFC) at Rifle, CO, exhibit U-containing framboidal pyrite and magnetites, based on SEM-EMP micrographs and measurements. Framboids existed in different sizes and microcrystal morphologies with varying internal porosities and U contents. This is the first report of U-containing framboidal pyrite at a contaminated site. Various analytical, spectroscopic and microscopic studies are being utilized to elucidate the origin (abiotic or biotic), and role of these Fe-minerals on U sorption, reduction and solid phase speciation. The new knowledge will be valuable to better predict the flow and reactive transport process models of natural attenuation of uranium in suboxic alluvial aquifers.

GEOC 34

Hard X-ray absorption spectroscopic and microscopic investigations of redox transformations at microbial surfaces

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The biogeochemical cycling of Fe is driven largely by microbial activity, particularly where Fe redox cycling by microorganisms is a significant component of carbon cycling and energy flux. The microenvironment within, at, and adjacent to actively metabolizing cell surfaces can be significantly different from the bulk. Additionally, the behavior of contaminants in such microenvironments can affect the macroscopic fates of contaminants. We have developed and used x-ray (micro)(spectro)scopy (~100 nm resolution) to investigate Fe and U

biogeochemical transformations at microbial cell surfaces. Results include 1) characterization of the chemical speciation of U in natural subsurface sediments before and after biostimulation, 2) identification of the distribution and average valence state of U relative to cells adhered to iron hydroxide films, 3) identification of the co localization of U and Fe in extracellular structures, and 4) identification of partially reduced iron precipitates within cells. Results of these studies will be presented.

GEOC 35

Biogeochemical differences in pilot-scale bioremediation treatment plots undergoing iron reduction or sulfate reduction in a uranium-contaminated aquifer

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Prolonged removal of uranium from groundwater, now described as a third phase in the field-scale biostimulation experiments at the Rifle IFC, is preceded by an iron reduction phase (Phase I) and a sulfate reduction phase (Phase II). In phase I, acetate is added to the contaminated aquifer and stimulates the predominant growth of *Geobacteraceae*, which are dissimilatory iron-reducing bacteria also responsible for the majority of uranium reduction and removal from the groundwater. In phase II, acetate continues to be supplied to the aquifer, sulfate reduction begins to dominate and uranium removal efficiency decreases. Pilot-scale investigation of the mechanisms involved in phase III revealed that sulfide accumulation in the sediment may not be directly linked to the ongoing removal of uranium from groundwater. The microbial community associated with the post-biostimulation sediment was investigated.

GEOC 36

Quantum chemical modeling of biologically-mediated U(VI) reduction

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The reduction of U(VI) in the environment is a desirable consequence because U(IV) is less soluble and can form the mineral uraninite. Bacterially-mediated reduction of U(VI) has been explored as a cost-effective method of remediation for uranium-contaminated sites. This work focuses on the two-electron reduction of U(VI) to U(IV) via an organic ligand. Quantum chemical methods are used to track the reaction path and relative thermodynamic stability of the species involved. Comparisons to experimental observations of this reaction are discussed as well as implications for chemical remediation of U-contaminated sites that mimic this biological process. Principles of sub-surface metal reduction reactions are highlighted in this example that are likely to be pivotal in understanding similar metal reduction reactions.

GEOC 37

Soil mineral solubility, mineral suspension composition and pH effects: Does it affect carbon dioxide hydrate formation?

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Carbon dioxide hydrate formation presents an interesting phenomenon because it could form different proportions of the carbonic species. In this study, we controlled the pH of the soil mineral suspensions (montmorillonite, kaolinite, and pyrite) prior to the dissolution of CO₂ through the addition (100-700 µL) of 2M NaOH and 2M HCl. Based on our formation studies, there is a certain pH range with each soil mineral in which carbon dioxide hydrate is observed to form. Our study suggests that the additional driving factor which can influence the formation of carbon dioxide hydrates is pH. In an effort to identify chemical species that could potentially affect CO₂ hydrate formation, we used a batch speciation modeling (PHREEQC) to assess the geochemical interaction of CO₂ in soil mineral suspensions with and without electrolytes (NaCl, CaCl₂) under 30 bar and 0.3°C.

GEOC 38

Influence of the diffusive boundary layer on the solute dynamics in the sediments of a seiche-driven lake: A model study

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The diffusive boundary layer plays an important role for mineralization and reoxidation processes in highly reactive sediments. We used modeling to identify the different effects of the DBL and to quantify their impact on solute dynamics. An increase of the diffusive boundary layer thickness from 0.25 to 1.5 mm decreased the oxygen uptake into the sediment from 15 to 9.5 mmol m⁻² d⁻¹. The reoxidation of iron and manganese in the sediment decreased by up to 45 % (from 7.2 to 3.2 μmol m⁻² d⁻¹ for manganese) at the same time. We also found that processes in the deeper layers of the sediment which are inhibited by the presence of oxygen show low sensitivity to a changing DBL thickness under steady state conditions. However, fluxes of nitrogen species periodically deviated by more than 60 % when an oscillating DBL thickness with periods of less than 6 h was modeled dynamically.

GEOC 39

Aggregate-scale spatial heterogeneity in mineral formation driven by dissimilatory iron reduction of ferrihydrite under diffusive conditions

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Chemical species distribution in structured soils can be strongly localized due to mass-transfer limitations and redox gradients within soil aggregates. We used novel aggregate-based flow-through experiments with ferrihydrite-coated sands inoculated with *Shewanella putrefaciens* strain-CN32 and reactive transport modeling to investigate controls on small-scale iron transformation. Transitioning from advection- to diffusion-controlled mass transfer, the observed spatio-temporal evolution of secondary mineralization products of ferrihydrite reduction contrasts with reported magnetite formation in advection-dominated regimes. Goethite/lepidocrocite were dominant products, with siderite also present, within diffusion-controlled aggregates. Moreover, their spatial distribution varied at a scale of few mm, owing to diffusively controlled supply of lactate or O₂ (supplied in the solution surrounding the aggregate) and efflux of Fe(II) and bicarbonate (produced in the aggregate). Our findings demonstrate the large spatial and temporal variation in biotransformation rates and distribution patterns of iron phases within soil aggregates characterized by a transition between advective and diffusive transport domains.

GEOC 40

Quantum chemical modeling arsenic (III,V) adsorption and oxidation on manganese oxides

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Mn(III,IV)-oxides strongly regulate arsenic mobility, toxicity and bioavailability by oxidizing arsenite (As(III)) to arsenate (As(V)) in the natural environment. Here we used quantum chemical calculations to investigate the adsorption and oxidation of arsenic (As(III) and As(V)) on the surface of Mn(III, IV)-oxides. Several possible electron transfer processes were modeled and adsorption affinities between arsenite/arsenate and Mn(III)/Mn(IV) oxides were compared. The results help explain certain arsenite oxidation behavior, such as 1) possible arsenite oxidation pathways, electron transfer or substitution mechanism? 2)inhibition mechanisms of arsenite oxidation by arsenate, and 3) the role of Mn(III) in arsenite oxidation. A better understanding of arsenite oxidation will help predict arsenic fate and transport of arsenic in the environment.

GEOC 41

Thermodynamic modeling of contaminant fate in subsurface environments

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Experimental assessment of contaminant reactivity and transformation pathways in the subsurface is highly time- and money-consuming. The objective of this project is to develop a predictive tool based on thermochemical properties that can be used to screen contaminants such that reactivity and potential breakdown products can be identified. However, especially for many new and emerging contaminants, properties that govern their fate in natural environments and under different physical and chemical conditions are unknown. As a first approach, density functional theory (DFT) was used to derive thermochemical parameters relevant for predicting chemical reactivity such as free energies of formation and reaction, bond dissociation energies, and HOMO/LUMO energies. Quantum-mechanical predictions via both atomization energies and isodesmic reactions were compared to Group Additivity estimates. Calculated and experimentally

validated parameters are subsequently related to lab and field data to delineate the predictive model.

GEOC 42

Fe(II)-bearing secondary mineral formation following the bioreduction of synthetic and natural Fe(III) oxides and oxyhydroxides

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The bioreduction of Fe(III) oxides and hydroxides may result in the production of a suite of Fe(II)-bearing secondary mineralization products (Fe(II)SMPs), including magnetite, siderite, vivianite, green rusts, and ferrous hydroxy carbonate. In an effort to better understand the factors controlling the formation of specific Fe(II)SMPs, we examined the Fe(II)SMPs formed from the bioreduction of a series of natural and synthetic Fe(III) oxides and oxyhydroxides (including akaganéite, ferroxhyte, ferric green rust, ferrihydrite, goethite, hematite, lepidocrocite, and maghemite) by *Shewanella putrefaciens* CN32. The rate and extent of Fe(II) production as well as the type(s) of Fe(II)SMPs formed were affected by Fe(III) mineralogy as well as the presence or absence of electron shuttling compounds and phosphate.

GEOC 43

Iron (hydr)oxide controls on (bio)reductive transformation of nitroaromatic compounds

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This study investigated the impact of hematite, magnetite and ferrihydrite in the presence and absence of the electron shuttling compound anthraquinone-2,6-disulfonate on the (bio)reduction of 2,4,6-trinitrotoluene (TNT). The studies were conducted with *Cellulomonas* sp. ES6 or ferrous chloride as the reducing agent. Strain ES6 reduced both TNT and Fe minerals at increased rates in the presence of AQDS. The production of surface-associated Fe(II) and changes in Fe mineralogy were found to influence the rate, extent, and transformation pathway of TNT reduction. While the initial TNT reduction step was faster in the presence of the less (bio)reducible hematite, more reduced metabolites of TNT reduction were observed in the presence of ferrihydrite and magnetite. Ferrihydrite and magnetite both showed higher concentrations of surface associated Fe(II) than hematite. Secondary hematite was formed in systems containing ferrihydrite indicating that the greater extent of TNT reduction was due to Fe(II) not to secondary mineral formation.

GEOC 44

Methylarsenate sorption to aluminum oxide

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Inorganic arsenic has been extensively studied during past decades, yet only a limited amount of research has been done on organoarsenical species, especially monomethylarsenate (MMA) and dimethylarsenate (DMA). Methylarsenates are as toxic as inorganic arsenic and have been extensively used as herbicides for a long time. There is not much information available about methylarsenate behavior in soil, especially in regards to bioavailability or reactivity. Like inorganic arsenate, methylarsenates seem to interact with metal oxide mineral particles due to their negative charges at an environmentally relevant pH. To enhance the knowledge of methylarsenate species in the environment, MMA and DMA sorption behaviors to aluminum oxide are being investigated. For molecular scale sorption mechanism studies, FTIR and X-ray adsorption spectroscopy are used to examine sorption complex formation between methylarsenate and aluminum oxide.

GEOC 45

Quantifying the influence of adsorption on cation, phosphate, and arsenic concentrations in field reactive transport experiments investigating Fe(II)-coupled denitrification in groundwater

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Field reactive transport experiments that involved serial injections of nitrate into an anoxic, Fe(III)-reducing zone of a non-calcareous aquifer showed extensive denitrification coupled to dissolved and adsorbed Fe(II) oxidation over short transport distances. The rate of Fe(II)-coupled denitrification increased with repeated injections of nitrate. Fe(II) adsorption on the sediments was extensive and hydrous Fe oxide (HFO) generated during Fe(II) oxidation significantly increased adsorption of Fe(II), as well as adsorption of wastewater-derived phosphate and geogenic arsenic. Thus, solute adsorption must be accounted for in reactive transport simulations of the impact of Fe(II)-coupled denitrification on solute concentrations. Variable major cation concentrations and pH caused variable Fe(II) adsorption during transport. Simulating phosphate, As(V), and possibly As(III) concentrations during the experiment also requires accounting for the impact of variable chemistry on adsorption. Surface complexation models calibrated using laboratory experimental data can be used in reactive transport simulations to account for these impacts.

GEOC 46

Surface saturation effects in solid phase bacterial iron reducing kinetics

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Microbially mediated reduction of iron oxides can control the fate and transport of contaminants, and influence organic and inorganic biogeochemical nutrient cycling in the subsurface environment. To date, less study has explored solid phase iron reduction kinetics of geobacter species, the dominant surface-bound iron reducing microorganisms in most natural sediments, than shewanella species. Shewanella most likely uses a fundamentally different mechanism of electron transfer. In this study, batch scale experiments investigate the solid phase iron reducing kinetics of *G. sulfurreducens* growing on poorly crystalline ferrihydrite-coated sand, using acetate as an electron donor, under different biomass to iron content ratios. These experiments also study the effect of AQDS, an electron shuttle, on the relationship between biomass and mineral content. For a constant mineral content, the results show a log-linear relationship of biomass versus iron reduction rate, which changes to a linear relationship in the presence of AQDS.

GEOC 47

Birnessite formation and its transformation in acid media

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Birnessite formed in acid media has a similar hexagonal structure to biogenic manganese oxide. The formation of acid birnessite and its transformation through redox reactions involving MnO₄²⁻ and concentrated HCl in boiling solution were investigated by XRD, XAFS and TEM. The results show that the long range structure of acid birnessite produced in varying HCl concentrations is similar to each other. However, their local structures, such as amount of vacancy sites, composition and Mn oxidation state, are different. With increasing HCl concentration or reaction time, the average oxidation state of Mn, the molar ratio of K/Mn and the amount of vacancy sites in the acid birnessites decreased. Acid birnessite was gradually converted to pure 2×2 tunnel structured cryptomelane in the higher HCl concentration solution.

GEOC 48

Subsurface transport and biogeochemistry modeling at IFC site, Oak Ridge, TN

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Saprolite collected at the DOE Oak Ridge Field Research Center (ORFRC) in east Tennessee exhibits a low, highly buffered pH with large concentrations of Al, Ca, Mg, Mn, Co, Ni, U and Tc. Uranium is one of the major contaminants of concern and its mobility depends highly on geochemical characteristics associated with the subsurface media. Batch, column, and field experiments have been carried out and simulated to investigate the geochemical processes that control contaminant mobility and bioremediation. An ORFRC regional scale model was developed for the Integrated Field-Research Challenge (IFC) project to analyze the field-scale flow and transport processes needed to evaluate

natural attenuation and various remediation scenarios at the geochemically complex site. Future research will extend the ORFRC model to the entire DOE Y-12 Plant to perform modeling of the watershed scale contamination issue to help assess long-term risks associated with infrastructure decontamination & decommissioning (D&D) and site remediation.

GEOC 49

Using solid-state NMR and computational chemistry to investigate the reactive surface sites on clay minerals

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Understanding environmental reactions such as weathering and cycling of elements requires the determination of aluminosilicate dissolution and precipitation rates. Layered aluminosilicates such as clay minerals react faster on their edges compared to their basal planes. To understand clay surface reactivity, reactive species such as hydroxyl groups must be quantified. Solid-state nuclear magnetic resonance (NMR) spectroscopy has been paired with *ab initio* and density functional calculations to investigate reactive hydroxyl species and their relation to clay surface reactivity and structure. Clay minerals were treated with (3,3,3-trifluoropropyl)dimethylchlorosilane (TFS), which binds selectively to reactive hydroxyl sites. Quantification of ^{19}F spins in the TFS-treated samples from ^{19}F MAS NMR peak intensities provides a sensitive measure of the number of reactive hydroxyl sites. Within the Center for Environmental Kinetics Analysis at PSU, molecular-level information obtained from NMR and computations will be compared to measurements from a field site and used to inform field-scale models.

GEOC 50

Insight into siderophore and reductant dependence in iron acquisition from hematite by *Pseudomonas mendocina ymp*

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Pseudomonas mendocina ymp was shown by Hersman *et al* to produce a siderophore, possibly in conjunction with a reductant, to aid in iron acquisition from mineral. To further probe this interaction, we constructed a *P. mendocina* mutant incapable of siderophore production, and restricted direct access of the bacteria to the mineral with dialysis tubing. We show here that the siderophore is

required for iron acquisition; its loss abolished the bacteria's ability to grow on hematite. While the addition of an external reductant could partially restore growth, only addition of external siderophore resulted in wild-type growth. Interestingly, the amount of siderophore needed for complementation was far less than that secreted by the microbe. A reductase was found in the supernatant prior to peak siderophore production, suggesting a possible iron mobilization role. Two Fur-regulated, flavin-dependent reductases were identified in the *P.mendocina* genome; they have been isolated by chromatography, and are under investigation.

GEOC 51

Regulation of siderophore, siderophore receptor, and reductant in iron acquisition from hematite by *Pseudomonas mendocina ymp*

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To further probe the interaction of bacteria, siderophore, and mineral, we constructed a *Pseudomonas mendocina* mutant incapable of siderophore production, and restricted direct access of the bacteria to the mineral with dialysis tubing. We show here that the siderophore is required for iron acquisition; its loss abolished the bacteria's ability to grow on hematite. Surprisingly, the likely siderophore receptor is regulated directly by iron availability, rather than amount of siderophore in the medium. While the addition of an external reductant could partially restore growth, only addition of external siderophore resulted in wild-type growth. Interestingly, the amount of siderophore needed for complementation was far less than that secreted by the microbe. A reductase was found in the supernatant prior to peak siderophore production, suggesting a possible iron mobilization role. Two Fur-regulated, flavin-dependent reductases were identified in the *P.mendocina* genome; one is up-regulated in the absence of iron and is under investigation.

GEOC 52

Mass transfer across the capillary fringe under transient conditions

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Transverse vertical dispersion is essential for mass transfer of solutes across the capillary fringe. Flow patterns and/or transient conditions enhance dispersion in this transition zone. In order to examine the impact of transient conditions on transport of soil gases or volatile compounds across the capillary fringe, basic mass transfer parameters have to be quantified and compared to those under stationary conditions. 2D-tank experiments are conducted measuring mass transfer of the compounds of interest as a function of horizontal flow velocity of the water, grain size and grain size distribution, porosity, as well as water table fluctuation amplitude and frequency. In the zone of varying extension of the capillary fringe, pore water velocity and hydraulic conductivity change according to saturation. This has an impact on water, solute and gas transport from the soil surface to the aquifer, but also on transport of volatile compounds from the aquifer to soil gas.

GEOC 53

Effect of dynamic chemical conditions on the desorption and transport of U(VI) through sediments from a contaminated aquifer

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Elution of U(VI) from columns packed with sediment size fractions (<2mm) was studied as a function of pH and alkalinity. The sediments were collected from a uranium-contaminated aquifer located at Naturita (CO, USA). Flow interruptions indicate that reaction rates and mass transfer processes play a significant role in the release of U(VI). When the bicarbonate concentration of the influent was increased, the rate of release of U(VI) also increased; however, the mass of total U(VI) eluted was similar to a parallel experiment in which the alkalinity remained constant. In both experiments, the total mass of U(VI) eluted was similar to that determined in batch extractions with bicarbonate/carbonate solution at pH 9.5. Modeling approaches using a reactive transport model which incorporates chemical reaction rates and mass transfer rates are discussed. Reaction rates measured in batch and column experiments will be evaluated to determine if some upscaling of pore-scale reaction rates is necessary to simulate behavior in the columns.

GEOC 54

Microbially induced formation of mobile Cu(0) and CuS nanoparticles in a contaminated floodplain soil

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Floodplain soils are important sinks and/or sources for metal contaminants in river systems. Understanding the speciation and mobility of trace metals in periodically flooded soils is therefore of utmost importance. In microcosms, we investigated the behavior of Cu, Cd, and Pb in a metal-contaminated soil during 50 days of flooding, inducing anoxic conditions. The concentrations of dissolved Cu, Cd, and Pb in the pore water decreased strongly due to metal sequestration in poorly soluble sulfide minerals. In contrast, we observed a pronounced increase in colloidal Cu, Cd, and Pb in the pore water, peaking after 4 days for Cu and 10 days for Cd and Pb. TEM and XAFS investigations of the colloids revealed that metallic copper (Cu(0)) particles were formed on suspended bacterial cells during the first days of flooding. Sulfate reduction subsequently led to the transformation of Cu(0) particles into CuS hollow-spheres and formation of CuS nanoparticles from solution. Mechanisms and environmental implications of mobile metal colloid formation under reducing conditions will be discussed.

GEOC 55

Elucidating cadmium speciation and bioavailability in Thai paddy soils

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The fluctuation of Eh and pH during rice cultivation due to alternating flooding and draining of paddies can alter Cd chemistry (e.g., speciation, mobility and bioavailability). This research aims to explore the speciation and bioavailability of Cd under an alternating-flooding/draining system in Thai paddy soils highly contaminated by Zn mine discharges using novel synchrotron techniques, SEM-EDX, and a stirred-flow approach. Bulk XAFS data indicate several species of Cd with CdCO₃ as the predominant species in both dry and flooded soils. X-ray microfluorescence images show that Cd tends to localize with Ca and Mn after flooding, while Cd does not appear to be correlated with specific elements in the dry soils. Stirred-flow studies reveal less than 15% of Cd is released. Elucidating

Cd speciation and bioavailability in Thai paddy soils is critical for developing and implementing best management practices.

GEOC 56

Iron mineral transformation in a permeable reactive biowall: Column and field experiments

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Iron- and sulfur-reducing conditions are generally created in permeable reactive barrier (PRB) systems constructed for groundwater treatment, which usually leads to formation of FeS phases. FeS has been shown to play an important role in TCE degradation and metal removal in these engineered systems. This study uses acid volatile sulfide (AVS) and chromium reducible sulfur (CRS) as probes to investigate FeS formation and transformation in a column and PRB field study dealing with TCE remediation. Solid-phase Fe speciation results show most Fe is reduced after extensive operations. S-partitioning measurements show that AVS and CRS coexist in all samples, with the conversion of AVS to CRS being most significant in locations with potential oxidants available. SEM/EDX shows FeS, Fe₃S₄ and FeS₂ formation in the column system, however, only pyrite formation was confirmed by XRD. Failure of FeS/Fe₃S₄ identification by XRD may be due to low crystallinity of these precursor phases. The polysulfide pathway is probably the primary mechanism of FeS transformation in the system, with S⁰ intermediate species formed through H₂S oxidation.

GEOC 57

Process-level heterogeneity controlling the fate of arsenic

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Dissolved concentrations of arsenic within pore-waters of soils and sediments are controlled by a composite of biogeochemical reactions. Generally, arsenic binds strongly to soil/sediment solids under aerated conditions; under anaerobic condition, aqueous concentrations generally increase, a phenomenon attributed to reduction of iron or arsenic. We show that reduction of arsenate to arsenite nearly universally increases the lability of arsenic, thus stimulating its migration within surface and subsurface environments. Iron reduction, conversely, can either increase or decrease the retention and lability of arsenic depending on the initial iron phase, the rate of reaction and resulting Fe(II) concentration, and the extent of reduction. Owing to heterogeneity within soils and sediments, the fate and transport of arsenic, and other elements, becomes dependent on coupled physical-biogeochemical processes that vary at the micron-scale.

GEOC 58

Microbial mineral weathering for nutrient acquisition releases arsenic

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Tens of millions of people in Southeast Asia drink groundwater contaminated with naturally occurring arsenic. How arsenic is released from the sediment to the water remains poorly understood. Here we show in laboratory experiments that phosphate-limited cells of *Burkholderia fungorum* mobilize ancillary arsenic from apatite as a by-product of mineral weathering for nutrient acquisition. The released arsenic does not undergo a redox transformation but appears to be solubilized from the apatite mineral lattice during weathering. Analysis of apatite from the drainage basin indicates elevated levels of arsenic. The rate of arsenic release is independent of the initial arsenic concentration and occurs at phosphate levels observed in Bangladesh aquifers. We also demonstrate the

presence of the microbial phenotype that releases arsenic from apatite in Bangladesh sediments. These results suggest that microbial weathering for nutrient acquisition could be an important mechanism for arsenic mobilization.

GEOC 59

Arsenic remobilization from paddy soils during monsoon flooding in Bangladesh

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Bangladesh relies heavily on groundwater resources, often containing high concentrations of arsenic, for the irrigation of dry season rice. An estimated 1360 tons of arsenic are thus transferred to arable soils in Bangladesh each year, creating a potential risk for crop production and human health. Irrigation with As-rich groundwater leads to an enrichment of As in the topsoil, but long-term accumulation is partly counteracted by As mobilization during monsoon flooding. As leaching into the subsoil, diffusion into the floodwater and microbially mediated As volatilization have been hypothesized as possible pathways for As mobilization from the topsoil. Here we present soil porewater and floodwater profiles from flooded paddy fields near Sreenagar (Munshiganj, Bangladesh) which clearly show reductive dissolution of As-bearing Fe(III)(hydr)oxides and subsequent As diffusion into floodwater to take place over the entire duration of monsoon flooding. As release into floodwater was quantitatively significant compared to the annual input of As via irrigation.

GEOC 60

Leachate transport and arsenic mobilization in a sublandfill aquifer

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Arsenic has been shown to be mobilized from sediments underlying a landfill by reducing, leachate-affected groundwaters. Contaminant transport was examined by using statistical correlations between aqueous and hydrogeologic parameters; elevated groundwater concentrations of contaminants (e.g. arsenic and landfill leachate tracers) were found associated with large grain sizes, high velocities of a purposefully injected tracer, and low electromagnetic induction, all indicating high contaminant concentration in large-grained, fast-flow regions. Observations indicate that tracer velocity is the most robust predictor of the aqueous geochemistry of the relevant groundwaters. The data support the conceptual model that landfill leachate predominantly affected more highly conductive regions leading to greater mobilization of sediment arsenic in these regions.

GEOC 61

Effect of storage time on the dynamics of As speciation and transformation in heterogeneous biosolid material

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Land application of poultry litter introduces high concentrations of trace elements (Cu, Zn, and As) into the soil and water systems. The most common source of As is an organic arsenical, roxarsone. Regulations regarding litter amendments entail strict application timelines, thus requiring litter to be stored for extended periods of time. Poultry litter was collected from a controlled poultry house experiment, and stored up to one year. Arsenic distribution and speciation of litter was determined using X-ray Absorption Spectroscopy conducted at beamline X26A at the National Synchrotron Light Source at Brookhaven National Lab. The use of X-ray Absorption Near Edge Structure spectroscopy demonstrated that storing litter results in degradation of roxarsone into inorganic degradation products. Other synchrotron techniques including μ -X-ray Diffraction and X-ray Fluorescence provided information about As distribution; its strong relationship with divalent trace metals; and identified crystalline compounds present in the litter samples.

GEOC 62

Microbial iron transport: A lesson in coordination chemistry

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Transferrin maintains free human serum ferric ion concentration at 10^{-24} M. Pathogenic bacteria compete against this thermodynamic limit through clever coordination chemistry to obtain iron from their human host. It is difficult to overestimate the significance of iron as a limiting nutrient in microbial growth: enhancement of pathogenicity of 4 to 7 **orders of magnitude** are seen when iron is supplemented. Powerful and selective iron chelators (siderophores) are produced and secreted in response to iron deficiency. These are taken up by membrane transporters. Spectacular advances have taken place in recent years in understanding the recognition and transport processes involved in siderophore-mediated iron acquisition and will be briefly discussed. Other topics will be siderocalin, a protein of the human innate immune system which specifically interrupts siderophore mediated iron transport of pathogenic bacteria, and the stealth siderophores produced by pathogens such as anthrax to evade this protein.

GEOC 63

New marine siderophores: Structure and reactivity

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Differences in the transition metal ion composition of the oceans and seas may play a significant role in the adaptation of a microbe to its chemical environment. While, iron is an essential micronutrient for marine microbial growth, other metal ions may affect the iron uptake process. The low level of iron in the surface water of much of the world's oceans is well recognized as a factor limiting microbial growth. To acquire iron many bacteria growing aerobically secrete siderophores. We are finding that marine bacteria produce new siderophores with interesting properties. Many of the siderophores are photoreactive, which is a distinguishing characteristic that likely plays a significant role in the biogeochemical cycling of iron in the ocean. Many of the siderophores are also produced as a suite of amphiphilic peptides or amphiphilic citrate-derived head groups, with varying fatty acids that also likely plays a significant role in the iron acquisition process. However in the Black Sea, where the chemical composition differs substantially from the open ocean, the microbial siderophores differ substantially. Consequences of the structural differences and transition metal reactivity are under investigation.

GEOC 64

Multiple roles of siderophores: From iron acquisition to metal homeostasis

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Siderophores (or “iron carriers”) are low molecular-weight ligands with a high metal affinity excreted by bacteria and other organisms. They are important for iron acquisition, as they capture iron from unavailable forms and deliver it to the organism. But the role of siderophores is not restricted to iron uptake. In the external medium of the nitrogen-fixing bacteria *Azotobacter vinelandii*, the excreted “siderophores” (which are really “metallophores”) bind other metals (such as Mo, V, W) in addition to Fe. The metal complex with the metallophore is unavailable unless the bacteria activate the appropriate transport systems, which are highly specific. The binding of metals by metallophores in the medium allows the bacteria to tightly control their metal uptake depending on whether the metal is needed for growth or toxic. This work may have important implications for our understanding of the terrestrial nitrogen cycle, as the nitrogenase enzyme, which is responsible for N₂-fixation, requires iron, molybdenum and/or vanadium at its active center. The finding of new mechanisms for the uptake for Mo and V in nitrogen-fixing bacteria suggest that the bioavailability of these metals could control N₂-fixation rates in soils, where their bioavailability is reduced because of low solubility, low concentration, or binding to minerals and organic matter.

GEOC 65

Taking the bite out of bidentate siderophores: New enzymatic targets for antimicrobials

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Successful antimicrobials target pathways that are necessary for and, where possible, unique to the pathogen. Finding appropriate targets is particularly challenging for eukaryotic pathogens, those that inhabit hard to reach cellular compartments, or those that rapidly develop antimicrobial resistance. Fe acquisition offers an attractive set of targets in each case. Amine-hydroxylating, flavin-dependent monooxygenases are critical constituents of siderophore biosynthetic pathways, adding “teeth” to form the bidentate chelating moiety of

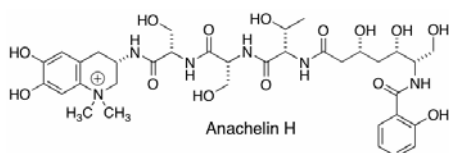
hundreds of hydroxamate siderophores. The enzymes are encoded by mutually homologous, essential genes in many pathogens, including *Aspergillus fumigatus* (eukaryotic), *Mycobacterium tuberculosis* (phagosome-dwelling), and drug resistant *Klebsiella pneumoniae*. Enzymes from these organisms appear to operate by a novel mechanism. Structure-activity relationships and a set of inhibitors are defined. Release of the iron from the siderophore's "bite" often requires reduction of iron(III). Characterization of the siderophore-targeting reductase from *Mycobacterium tuberculosis* reveals a second avenue for targeting the iron-acquisition pathway of this pathogen.

GEOC 66

To live and let die in The Big Blue

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Harmful algal blooms in both freshwater and marine environments pose significant challenges for humans, livestock and aquatic food webs. Over the last 50 years, several authors proposed that small molecule iron chelators (siderophores) could be responsible for such blooms,[1] but these studies were never evaluated on a chemical, molecular level. In this communication, we present that the iron chelator anachelin, isolated from the cyanobacterium *Anabaena cylindrica*,[2] is promoting the growth of cyanobacteria while concurrently decreasing the growth of competing phytoplankton (green algae). This dual mode of action (growth promotion and allelopathic activity) is caused by two different fragments of anachelin, as shown through chemical synthesis and biological evaluation. Anachelin thus constitutes a natural product hybrid blending two bioactivities in a single compound. [1]G. E. Fogg, D. F. Westlake, *Verh. Int. Ver. Limnol.* 1955, 12, 219; T. Murphy, D. Lean, C. Nalewajko, *Science* 1976, 192, 900; C. J. Matz et al., *Can. J. Bot.* 2004, 82, 436. [2] Isolation: H. Beiderbeck, K. Taraz, H. Budzikiewicz, A. E. Walsby, *Z. Naturforsch., C: J. Biosci.* 2000, 55, 681; Y. Itou, S. Okada, M. Murakami, *Tetrahedron* 2001, 57, 9093. Synthesis: K. Gademann, Y. Bethuel, *Angew. Chem. Int. Ed.* 2004, 43, 3327. K. Gademann, Y. Bethuel, *Org. Lett.* 2004, 6, 4707.



GEOC 67

Role of microbes in attenuation and mobilization of arsenic at the Lava Cap Mine Superfund site, Nevada County, CA

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Iron-oxidizing, iron-reducing, and arsenic-reducing microbial communities at the Lava Cap Mine Superfund site (Nevada City, CA) were investigated using culturing, chemical, and spectroscopic techniques to understand the interplay between processes that attenuate and mobilize arsenic (As) in surface waters. Sheaths formed by bacteria of the genus *Leptothrix* physically support a community of ferrous iron-oxidizing bacteria suspended in the water column. This community induces the precipitation of ferric (hydr)oxide which has a high sorptive capacity for As (1000 to > 10,000 mg/kg As, dry-weight). Several lines of evidence including: (1) high dissolved As in overbank sediment porewater relative to creek and pond sediment porewater, (2) most-probable number estimates of iron- and arsenic-reducing bacteria, and (3) spectroscopic evidence for As adsorption on biogenic ferric (hydr)oxide suggest that reductive dissolution of biogenic As-rich iron (hydr)oxide may be an important process leading to arsenic mobilization in shallow waters where *Leptothrix* blooms are seasonally abundant.

GEOC 68

In situ analysis of biogeochemical arsenic transformations

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The reactivity and transport of arsenic (As) in the environment is controlled to a large extent by its speciation. Oxidation of arsenite (As^{III}) is rapidly catalyzed by certain bacteria and soil minerals, producing the less toxic and less mobile arsenate (As^V) species. Rapid-scan attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy has been used to collect *in situ* kinetic data for oxidation of As^{III} to As^V. Using a rapid-scan technique, IR spectra are collected every 2.55 seconds (24 scans, 8cm⁻¹ resolution). Through observation and analysis of IR bands corresponding to arsenate (As^V), rapid chemically-controlled As^{III} oxidation is observed via Mn-oxide minerals. Also, the data reveal

oxidation of As^{III} is followed by rapid binding of As^V to Mn-oxides, at least in part, through surface bound Mn^{II}. The binding of As^V, and Mn^{II}, leads to surface passivation of the mineral phase and prevents further oxidation from occurring. Analysis of first-order rate kinetics revealed 95% transformation of As^{III} to As^V in < 3 min ($t_{1/2}$ < 1 min). Research is ongoing to examine reaction rates and effect on cell surface composition during bacterially catalyzed As^{III} oxidation by the As-oxidizing bacteria *Alcaligenes faecalis* and *Pseudomonas fluorescens*.

GEOC 69

Biological processes controlling the fate of arsenic

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Iron and arsenic reduction are important geological processes leading to the release of arsenic from sediments. Metal-reducing bacteria are thought to mediate these reactions. We are currently developing a geo-microbiological model that describes the complex regulation of iron and arsenate reduction pathways using a metal-reducing bacterium, *Shewanella* sp. ANA-3. We have shown that the arsenate respiratory reduction (*arr*) and *mtr/omc* pathways are primarily responsible for solid phase arsenate and iron reduction, respectively. We have also characterized several proteins that are important for regulating these pathways. Both iron and arsenate reduction are regulated in response to a universal signaling molecule, cyclic AMP (cAMP). However, the *arr* pathway is further regulated in response to arsenite, which is the predominant form of arsenic in anaerobic environments. Bioinformatic analysis of microbial genome sequences has also lead to additional insight into biological pathways that influence arsenic mobilization.

GEOC 70

Lightning-induced phosphorus redox biogeochemistry?

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Phosphorus is generally viewed as a redox-insensitive element, with orthophosphate (HPO₄²⁻) the dominant inorganic P species. Here we report the first occurrence of reduced P as phosphite (HPO₃²⁻) in soils struck by lightning, which forms glassy materials called fulgurites. Phosphite has been found by ³¹P NMR in five fulgurites of varied composition from across the US, and is not

present in soil adjacent to the fulgurites. While fulgurite formation is not a common phenomenon, a large suite of microorganisms are capable of utilizing phosphite as their sole phosphorus source, which implies that other sources of reduced phosphorus may be (or have been) available for life. We discuss other possible sources of reduced P, and the abiotic oxidation pathways of phosphite. The abiotic oxidation of phosphite leads to pyrophosphate and triphosphate formation, and the presence of these compounds in soils may be due in part to oxidation of reduced P.

GEOC 71

Lightning driven soil reduction as observed in fulgurites

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On average, lightning strikes the Earth's surface at a rate of ~65 times per second [1], dissipating up to 10^9 J per flash. Some areas of Florida, which experiences more frequent lightning strikes than any other area in the United States, are struck at a rate of $20\text{-}50\text{ km}^{-2}\text{ yr}^{-1}$. Cloud-to-ground lightning strikes affect local geochemistry through production of fulgurites, glassy material resulting from the fusion of sand, soil, or rock. Extreme reduction in Fe, Si, and C compounds has been observed in these materials [2]. Oxygen loss during volatilization drives reduction of silicates to metallic silicon and silicon-iron alloys such as iron silicides [1]. We present an overview of soil alteration, specifically the reduction of Fe, Si, C, and P compounds due to this significant but overlooked geochemical process. [1] Sheffer A., Ph. D. Thesis, U of Arizona (2007), [2] Essene and Fisher, Science 234 (1986).

GEOC 72

Understanding host-pathogen interactions: Mycobacteria within macrophage cells

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A promising avenue to the control of tuberculosis is limiting iron acquisition by the pathogen. Mycobacterium tuberculosis produces non-ribosomal peptide mycobactins during periods of iron limitation. Full virulence has been shown to require production of these siderophores. Like its deadlier cousin M. tuberculosis, Mycobacterium paratuberculosis is known to survive assault from the immune system by living within macrophage lysosomes. We have shown that mycobactin J, produced by mycobacterium paratuberculosis, localized to lipid droplets upon

metal binding within macrophages. We have also shown that mycobactin J causes large disruptions to cellular metabolism, including decreased protein production and changes in several major metabolic pathways. This lecture will describe our current efforts to understand the roles of siderophores in pathogenesis and host response.

GEOC 73

Sorption of iron from siderophore complexes by Mn oxides

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Siderophores are chelating agents produced by terrestrial and marine biota to increase ferric iron bioavailability. Recent work has suggested that Mn(III) may affect siderophore-mediated iron transport, but little is known about the potential for Mn(III,IV) oxides to scavenge iron from aqueous complexes. To probe the interactions of layer-type manganese oxides with aqueous Fe-siderophore complexes, the sorption of ferrioxamine B [Fe(III)HDFOB^+] to synthetic and biogenic birnessite was examined. The Mn(III,IV) oxides greatly reduced the aqueous concentration of Fe(III)HDFOB^+ . EXAFS spectra suggest that the dominant fraction of Fe(III) associated with the Mn(IV) oxides is specifically adsorbed to the mineral structure at multiple sites, thus indicating that the Fe(III) is displaced from the siderophore complex. These results indicate that manganese oxides, including biominerals, may sequester iron from soluble ferric complexes; thus, we conclude that the sorption of Fe-siderophore complexes may play a significant role in the biogeochemical cycling of iron in diverse environments.

GEOC 74

Siderophores as drug delivery agents: Application of the “Trojan Horse” strategy

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The outer membrane permeability barrier is an important resistance factor of bacterial pathogens. In combination with other factors like drug inactivating enzymes, target alteration and efflux, it can increase resistance dramatically.

A strategy to overcome this membrane mediated resistance is the misuse of bacterial transport systems. Most promising systems are those for iron transport. They are vital for virulence and survival of bacteria in the infected host, where iron depletion is a defense mechanism against invading pathogens.

We synthesized biomimetic siderophores as shuttle vectors for active transport of antibiotics through the bacterial membrane. Structure activity relationship studies resulted in antibiotic siderophore conjugates (SAC) highly active against problematic resistant pathogens, which play a crucial role in destructive lung infections in cystic fibrosis patients and in severe nosocomial infections. The mechanism of action and the uptake of the compounds via specific iron siderophore transport routes was demonstrated. Selected drug candidates were investigated for their in vivo efficacy in animal models. The novel SAC were active against systemic *Pseudomonas aeruginosa* infections in mice and show low toxicity.

GEOC 75

Structural characterization of marine fungal siderophores

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Iron is required for growth of most microorganisms. The insolubility of iron at near neutral pH under aerobic conditions is thought to limit growth of microorganisms in vast areas of the oceans. Like their terrestrial counterparts, the marine bacterial species studied thus far have been shown to produce low-molecular-weight iron(III)-binding compounds called siderophores to acquire iron. Marine fungi, however, have not been extensively studied. To date, one marine fungal siderophore has been structurally characterized. Thus, we are working to identify the structures of siderophores produced by marine-derived fungi. The structure of a novel citrate-derived siderophore produced by the marine fungus *Cunninghamella elegans* ATCC 36112 and preliminary results for a series of fungal strains from Antarctica will be discussed.

GEOC 76

Siderophores, surfaces, and metals: How siderophore structure affects exchange rates

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Each siderophore can be characterized by the number, identity and arrangement of its Lewis Base groups. Ways in which siderophore properties affect equilibrium speciation in solution have long been established. Less is known, however, about the effects of siderophore properties on rates of ligand exchange reactions in solution ($ML + Y \rightarrow MY + L$) and ligand-assisted desorption ($>S-M + Y \rightarrow MY + >S$). Our objective is to use comparisons among synthetic aminocarboxylate ligands as the basis for predicting rates for aminocarboxylate siderophores such as mugineic acid and avenic acid. Starting with $Ni^{II}(IDA)^0$, for example, yields rates of Ni^{II} capture by CDTA and EDTA in solution that are nearly equal. Starting with $Ni^{II}(NTA)^-$, in contrast, yields rates of capture by CDTA that are more than two orders-of-magnitude lower than rates obtained with EDTA. Two factors are relevant: (i) $Ni^{II}(NTA)^-$ has one less aquo-coordinated position than $Ni^{II}(IDA)^0$, making entry of the second ligand more difficult (ii) The cyclohexane ring that CDTA possesses but EDTA lacks makes it more difficult to align free Lewis Base groups with available coordination sites. Ligand-assisted desorption is distinct from metal capture in solution because adsorption differs from complex formation in important ways. Most importantly, only one side of the adsorbed metal is accessible, and bridging of the ligand to neighboring surface sites is possible. Rates of Ni^{II} desorption by IDA, for example, are considerably lower than rates of desorption by EDMA ($H_2NCH_2CH_2NHCH_2CH_2C(O)O^-$). The only difference is that a carboxylate group has been replaced by an amine group.

GEOC 77

Structure-stability relationships for trace metal complexes of desferrioxamine B

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Desferrioxamine B (DFOB) is a linear trihydroxamate siderophore widely used in chelation therapy which is found naturally in both terrestrial and aquatic environments. Although the role of DFOB in mediating Fe uptake by microbes has long been appreciated, it is now becoming clear that siderophores engage in a diverse chemistry with environmentally-important trace metals and that a richer paradigm is required to comprehend their behavior in Nature. We have employed a variety of techniques, including X-ray absorption and resonance Raman spectroscopies along with geometry optimization based on density functional theory, to elucidate the molecular structures of the aqueous complexes of DFOB with the metals Co, Cu, Ga, Mn, Ni, and Zn. The results permit some broad generalizations to be made about the relationship between structure and stability for trace metal-DFOB complexes. Of particular interest are the very stable complexes formed with trivalent Co, Fe, and Mn, which figure importantly in marine biogeochemistry. Our results lead us to suggest that siderophore evolution as a bacterial response to oxygenation occurred not only because of sharply decreasing concentrations of Fe(III) in the oceans, but also of Co(III).

GEOC 78

Utilization of microbial iron assimilation processes for the development of new antibiotics

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Pathogenic microbes have rapidly developed resistance to all known antibiotics. To keep ahead in the “microbial war,” extensive interdisciplinary effort is needed. Resistance develops primarily to overuse of antibiotics that can result in alteration of microbial permeability, alteration of drug target binding sites, induction of enzymes that destroy antibiotics (ie, beta-lactamases) and even cause efflux of antibiotics. A combination of chemical syntheses, microbiological and biochemical studies will demonstrate that the known critical dependence of iron assimilation by microbes for growth and virulence can be exploited for the development of new approaches to antibiotic therapy. Iron recognition and active transport relies on the biosyntheses and use of microbe-selective iron chelating compounds called siderophores. Our studies demonstrate that siderophores and analogs can be used for

- Iron transport-mediated drug delivery (“Trojan Horse”).
- Induction of iron limitation (Development of new agents to block microbial iron assimilation).
- Converting microbe-induced chemistry of iron into a process that is lethal to microbes.

Special attention will be given to the discovery of new anti-tuberculosis agents from studies of mycobacterial siderophores.

GEOC 79

Speciation of heavy metals (Pb and Cd) with siderophores and the metal/siderophore/kaolinite system

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Siderophores are low molecular weight organic ligands synthesized by aerobic microorganisms to acquire Fe under Fe stress conditions. In addition to Fe (III), siderophores can complex many other metals such as Pb and Cd. Solution speciation of Pb and Cd has been examined with commercially available trihydroxamate siderophore desferrioxamine B (DFO-B). Results indicate systematic changes in the speciation of Pb and Cd with change in pH. The XAFS observed structure did not always match thermodynamic modeling, which validates the need for direct spectroscopic evidence.

In the presence of DFO-B, bulk sorption studies indicated that Pb sorption is enhanced in the presence of DFO-B around pH 6 and inhibited above pH 6.5. This was confirmed by x-ray fluorescence measurements. Extended XAFS study clearly indicated unwrapping of DFO-B molecule at the surface. Our study has unambiguously recognized it as a "Type A" ternary complex. As opposed to Pb, DFO-B inhibits adsorption of Cd on kaolinite. XAFS results do not suggest any ternary complex formation with Cd. These results and their implications will be discussed.

GEOC 80

Antibacterial responses mediated by siderophore-binding proteins: Siderocalins

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Siderocalin, a member of the lipocalin protein family, functions in anti-bacterial responses by participating in the general iron-depletion strategy of the innate immune system. However, rather than sequestering iron directly, Siderocalin

binds to bacterial siderophores and ferric siderophore complexes. The profound susceptibility of Siderocalin KO mice demonstrates the importance of this defense. Through extensive biochemical experiments, we have precisely defined Siderocalin's specificity for two families of siderophores, from enteric bacteria or mycobacteria, and revealed the mechanism enabling its highly degenerate binding specificity. The association of alternate siderophore biosynthesis and siderophore modifications with virulence can now be understood in terms of Siderocalin's specificity: these alternate siderophores escape Siderocalin binding and allow pathogens to acquire iron around this defense. We have identified two additional candidate 'siderocalins' in a search for complementary specificities that may be useful therapeutics, as well as undertaken the rational, computational redesign of Siderocalin itself. Siderocalin likely also exerts pleiotropic functions, involving apoptosis and tumorigenesis, possibly by functioning as a secondary iron transporter (after transferrin), through an, as yet, unidentified endogenous siderophore activity. To explore these additional activities, we are characterizing the interactions between Siderocalin and its putative cell-surface receptor, the 24p3R.

GEOC 81

Membrane ferric-siderophore trafficking in *Pseudomonas aeruginosa* followed by fluorescence

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To acquire iron, *Pseudomonas aeruginosa* secretes a major fluorescent siderophore, pyoverdine that chelates iron and shuttles it into the cells via the specific outer membrane transporter, FpvA. We took advantage of the fluorescence properties of pyoverdine and the efficient FRET between donor tryptophans in FpvA and pyoverdine to follow the fate of siderophore during iron uptake. Our findings indicate that apparently iron reduction is required for the dissociation of Pvd-Fe and that this dissociation occurs in the periplasm. Afterwards, pyoverdine is recycled to the medium, still competent for iron chelation and transport. The fluorescent properties of pyoverdine were used also to study the mechanism, which regulates the metal specificity of the pyoverdine pathway. Our data indicate that the metal specificity of siderophore outer membrane transporter FpvA is apparently large for the binding step at the cell surface and only selective for the uptake process.

GEOC 82

Biocoordination chemistry of iron siderophore complexes

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We will review critical aspects of the biocoordination chemistry of siderophores as they relate to the dissolution, mobilization, transport, and delivery of iron to microbes. Siderophores are selective sequestering agents for iron(III) and this selectivity manifests itself in the form of a high and specific Fe(III) binding constant (K). The magnitude and specificity of K is controlled by the Fe(III) binding moieties and how they are incorporated into the siderophore structure (architecture and denticity). Siderophore complex structure also influences cellular recognition, the kinetics and thermodynamics of iron release, and the Fe(III)/Fe(II) redox potential. We will explore the significance of the influence of pH fluctuations on iron(III) binding (K, pFe) and redox (E) properties of the iron-siderophore complex. This will include a discussion of the importance of pFe variations with pH and possible reasons why some environmental microbes excrete multiple siderophores. We will also discuss the significance of a low redox potential and the role of pH and coupled equilibria in a redox facilitated iron release mechanism. Examples will be taken from our laboratory for siderophores and siderophore mimics with hydroxamic acid, catechol, hydroxypyridinone and other mixed Fe(III) binding moieties.

GEOC 83

Siderophore promoted iron oxide dissolution: Photochemistry and dark reactions

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Bacteria, fungi, and grasses exude siderophores under iron limiting conditions to increase the bioavailability of iron oxides. Here we report the results of lepidocrocite (γ -FeOOH) dissolution experiments in the presence of siderophores where the suspensions have been irradiated with a solar simulator under variable pH and ionic strength conditions. These results are compared to dissolution experiments conducted in the dark. We employed two siderophores that form soluble iron complexes with contrasting photostability: DFOB forming photostable complexes and aerobactin forming complexes that undergo photolysis under irradiation. Dissolution rates are accelerated in irradiated

systems compared to dark experiments in the presence of both siderophores. Furthermore, photoreductive dissolution of iron oxides in the presence of oxalate is accelerated in the presence of DFOB. We interpret these results considering ionic strength and pH effects and based on FTIR surface spectroscopic information. Also, we compare the results with analogous experiments conducted with citrate which we use as a model compound bearing some of the same functional groups that impart photoreactivity to soluble aerobactin complexes.

GEOC 84

Roles of redox-active “antibiotics” in iron acquisition and microbial physiology

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Iron is an essential nutrient for most bacteria. However, under aerobic conditions, bioavailable iron is extremely limiting because iron is either present as insoluble Fe(III) minerals, or bound to host proteins. Consequently, bacteria must develop strategies to acquire iron over a distance; this may be particularly relevant for bacteria living in biofilms. One strategy is to produce diffusible iron-binding siderophores. Alternatively, some bacteria produce diffusible redox-active small molecules (e.g., phenazines) that may function as electron shuttles to facilitate iron acquisition by reductively dissolving Fe(III). Here we characterize the ability of phenazines to reduce Fe(III) minerals and reveal that reactivity can be predicted based on phenazine redox properties and structure. Using a genetic approach, we further show that phenazine and siderophore production facilitates *Pseudomonas aeruginosa* biofilm development, possibly via their abilities to promote iron acquisition. Because phenazines are versatile redox-active molecules, we examine their roles as oxidants and reductants in biofilms.

GEOC 85

Salmochelin, the overlooked catecholate siderophore of Salmonella

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The detection of salmochelin has a curious touch. It was found around 1970 as the result of a 30 years search for a protective “vitamin” against Salmonella infections in mice. A partial structure of the substance called pacifarin was published in 1985. In 2003 the siderophore was rediscovered in a search for the function of the iron regulated *iroNEDCB* operon. The operon encoded the *IroB* protein with a predicted glucosyltransferase activity. Indeed a hydrophilic siderophore was isolated and characterised as a twofold C-glucosylated enterobactin which was called salmochelin. This siderophore is a major siderophore of Salmonella. Studies by different labs showed that salmochelin in vivo is not bound by siderocalin, a protein which is produced in inflammation and which suppresses growth of certain bacteria by binding with high affinity iron-catecholate siderophores. With the glucosylation of enterobactin these pathogenic bacteria evade the innate immune response of their host.