

to have formed via the strictly anoxic pathway. The results presented here may provide aid in deciphering important, but still partially understood formation mechanisms and biochemical and geochemical roles of iron sulfides.

B12C-0804 1330h POSTER

The Effects of Microbial Fe(III) reduction on Clay Sediment Flocculation and Mineral Transformation

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This study was undertaken to investigate physicochemical properties of smectite associated with microbial reduction of structural Fe(III). Iron reducing bacterium, *Shewanella oneidensis* were inoculated with formate as the electron donor and smectite as the sole electron acceptor for the intervals of 3, 12, 24, and 48 hours in anaerobic chamber. The extent of Fe(III) reduction was observed to reach up to 9%. The control, containing microwave radiation heat-killed bacterial cells and M1 media plus formate, was prepared from the same smectite sample. Settling experiments were performed in anaerobic chamber for 1) the bioreduced nontronite samples which contain viable cells and biopolymers secreted by bacteria, with variable incubation time points, and 2) abiotic nonreduced controls having dead cells (no biopolymers). Furthermore, the separate set of incubation was prepared in aerobic condition where the microbial Fe-respiration does not prevail, but viable bacteria produced the biopolymers, and then suspended in a settling column in aerobic condition. Compared with abiotic nonreduced control, Micromeritics Sedigraph measured 2.3- m increase of mean aggregate size and a 30-times faster average settling velocity in the bioreduced nontronite suspensions. In addition, the aerobically inoculated nontronite (no Fe-respiration) shows a similar aggregate size distribution to that of an abiotic nonreduced control. Significant changes in physical properties of smectite induced by microbial Fe(III) reduction were directly observed using Environmental Cell Transmission Electron Microscope (EC-TEM). Particularly, neoformation of minerals in bioreduced smectite sample indicate that environmental factor such as bacterial activity should be considered as a geological variable for the mineral transformation studies. Neoformed Illite phase was identified in bioreduced smectite sample that challenge the conventional concept of smectite-to-illite transformation with far-reaching implications. In flocc architecture, several domains of smectite packets are glued by biopolymers secreted by bacteria, and the aspect ratio (thickness/length) of individual smectite particle increases from 0.11 to 0.18. We suggest that surface chemistry changes (more negatively charged on smectite surface) induced by microbial Fe(III) reduction more likely to promote the flocculation by adsorbing the cations which bridge the smectite particles and the biopolymers resulting in the increase of mean aggregate size.

B12C-0805 1330h POSTER

Investigations of Fe and Mn Bioreduction in Unconsolidated Clastic Sediments

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We studied the microbial reduction of Mn and Fe in sediments from Oak Ridge, TN, and the Hanford Site, WA. Bioreduction was by incubation of 1 g sediment in 10 ml of 30 mM pH 7 bicarbonate buffer with 7-9 x 10⁷ cells/ml of *S. putrefaciens* CN32 and 10 mM sodium lactate as electron donor. Solution chemistry was monitored during incubation and sediments were pasteurized before characterization. For the unconsolidated clay-rich saprolite from Oak Ridge, Fe reduction occurred after Mn reduction was essentially complete. In sediments from the Pliocene Ringold Fm. (Hanford), incubated under the same conditions, Fe reduction was

inhibited, and Mn(III/IV) was incompletely reduced. When Ringold sediments were incubated under conditions with greater available electron donor, more Fe was reduced after reduction of almost all of the available Mn(IV). Transmission and scanning electron microscopy and X-ray microprobe and XANES analysis of Ringold sediments were used to determine the spatial and temporal distribution of Mn. Initially, Mn(III/IV) was present as fragments of phyllosilicate minerals and as interlamellar precipitates with Fe oxides in micas and on silicate clast surfaces. The precipitates were botryoidal and chemically heterogeneous at the sub-micron scale. Precipitates within micas had expanded and deformed the sheet structure of each flake. With the lesser available donor, Mn reduction essentially ceased after 43 days of incubation, and the bulk Mn XANES spectrum indicated residual Mn(III/IV). X-ray microprobe mapping indicated all of the remaining Mn was associated with interlamellar and grain-surface iron oxides, and microXANES showed that the Mn valence within a single mica clast was heterogeneously distributed, and varied from Mn(III/IV) to Mn(II). At longer incubation times, the Mn nearer to the clast exterior tended to be more uniformly reduced than Mn in the interior. The Mn in clast interiors was apparently not readily bioavailable, but could act to buffer the sediment's redox capacity and re-oxidize Fe(II) produced during incubation. Re-oxidation was confirmed by dilute-acid extraction of poorly crystalline Fe(III) oxides.

B12D MCC: 3002 Monday 1340h Molecular Biogeochemical Processes of Terrestrial Environments III (joint with H, V, MR)

Presiding: J Cervini-Silva, University of California, Berkeley; J Chorover, University of Arizona

B12D-01 1340h

The Link Between Microbial Community Composition and Organic Matter Transformations in a Laboratory System

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The carbon cycle in aquifer systems is poorly understood. In particular, the role of prokaryotic and eukaryotic microbes in the cycling of organic matter (OM) has not been well documented. The goal of this work was to utilize stable isotopes in combination with geochemical and microbial methods to study microbially-mediated OM transformations in aquifers and aquifer sediments. A laboratory flow-through column experiment was conducted with sediment collected from a pristine, shallow, coastal plain aquifer. The groundwater medium was amended with low levels of isotopically labeled nutrients, 13C-acetate and 15N-ammonium. At pre-determined time points, DNA, RNA, and relevant biomarkers were isolated from the sediment and groundwater. The labeled nucleic acids were separated from non-labeled nucleic acids by ultracentrifugation and then sequenced to determine the composition of the actively-respiring microbial consortia. In parallel, the organic matter was analyzed by GC-MS and ESI-FT-ICR-MS. The incorporation of 13C and 15N was examined for both the aqueous phase and sediment bound microbial communities along with the dissolved and adsorbed OM. Analyzing both dissolved and adsorbed fractions enabled us to determine the relative importance of each on microbial activity and OM transformations. The incorporation of 13C and 15N allowed us to estimate residence times of different organic matter fractions and to answer fundamental questions about organic matter lability and microbial community dynamics in the subsurface environment.

B12D-02 1355h

Photochemistry of Dissolved Organic Matter in Arctic Surface Waters

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It has been shown that persistent organic pollutants (POPs), transported to the Arctic by long-range processes, can potentially contaminate Arctic surface waters and affect both local ecosystems and human health. Once deposited, the behavior of these pollutants is poorly understood; particularly the processes that govern their lifetime and concentrations within the water column. Here, we discuss the photochemical degradation of several halogenated organic pollutants (e.g., lindane, hexachlorobenzene) as mediated by natural dissolved organic matter (DOM). These experiments were conducted both in a controlled laboratory setting using an artificial sunlight simulator, as well as in situ in Alaskan surface waters near Toolik Lake. Our findings to date show high variability in the photodegradation rates of the target POPs and can be correlated to both their structure and the type of DOM present.

B12D-03 1410h

Molecular Simulation of Electron Exchange Between Ferrous and Ferric Iron in Hydrolyzing Aqueous Solutions

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We have constructed a molecular model for ferrous-ferric electron transfer in hydrolyzing aqueous solutions. The model is explored at two pH values, where the pH is defined by the influence of added protons on the ratios of the hydrolysis species of ferric iron. We find two important effects on electron transfer rates as a function of pH. First, it is shown that the barrier to electron transfer at any given ion separation increases with increasing pH due to the stabilization of ferric iron. A similar increase in the transfer barrier would result, for example, from increasing the dielectric constant, effectively pinning the electron on the ferrous ion. The second effect, which acts opposite to the first, is the decrease in the potential of mean force between the ferrous and ferric ions as the pH increases. These two contributions, of opposite sign, are of approximately equal magnitudes. Electron transfer reorganization energies for the hydrolysis species show a surprising degree of overlap, indicating that fluctuations in hydrolysis state can be viewed on a continuum with other solvent contributions to the reorganization energy. This continuum picture is odds with current interpretations of the pH dependence of the transfer rate, which ascribe the observed increase in rate with increasing pH to hydrogen atom transfer involving $Fe^{2+} \cdot FeOH^{2+}$, where the $FeOH^{2+}$ species present at vanishingly small concentrations.

B12D-04 1425h

The Effects of Microbial Surface Attachment on the Dissolution Kinetics of Plagioclase Feldspar

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The rate of mineral dissolution can be influenced by the attachment of microbes to a mineral surface. We have previously reported the effect of *Shewanella oneidensis* (MR-1) biofilm formation on the dissolution kinetics of calcite, dolomite and rhodochrosite, where the organisms completely control dissolution kinetics by recognizing high-energy surface sites overlying screw dislocations and attaching to those sites, inhibiting the opening of etch pits and significantly retarding dissolution. Note that calcite and dolomite are not known to possess nutritional significance for MR-1; and while this facultative anaerobe can reduce both Mn and Fe, our experiments were all conducted with aerobic organisms. In recent experiments, we have observed that this inhibitory effect requires the cells to be alive; dead cells do not prevent the opening of etch pits and subsequent dissolution of the carbonate crystals under conditions in which they would otherwise dissolve. Now

we report on the effects of the MR-1 biofilm formation on the more slowly dissolving end-member plagioclase feldspar, anorthite (CaAl₂Si₂O₈). The influence of organisms on feldspar weathering rates, in particular the Ca-rich plagioclases, has been the subject of considerable interest because of their crustal abundance and role in the maintenance of atmospheric CO₂. (Schwartzman and Volk, 1989; Schwartzman, 1995 and others). Our methodology of direct observation of microbial attachment, biofilm propagation and effects on mineral dissolution provides a quantitative measure of biological contribution to weathering of single crystal minerals for subsequent use in biogeochemical modeling.

B12D-05 1440h

Mineral Surfaces and Their Implications for Microbial Attachment: Results from Monte Carlo Simulations and Direct Surface Observations

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Mineral surfaces in contact with aqueous solutions form the interface at which microbial attachment and development is likely to occur and reactions will progress. Therefore, it is key to understand how microbes attach to crystal surfaces, and how they eventually impact mineral reaction kinetics. A prerequisite for any attempt to define these processes is the understanding and quantification of surface area. For practical reasons, we use the total surface area, even if we agreed that it would be more correct to use the reactive surface area, which is understood to be a fraction of the total. Surprisingly, recent computer based Monte Carlo (MC) simulations of mineral dissolution reactions have indicated that this concept might be flawed. The following questions elucidate this conclusion: How large is the reactive surface area? AND: How reactive is it? The first answer will be given in units of surface area, the second answer, however, can not be given in this unit. This has the unfortunate consequence that the reactivity term is embedded within the rate constant itself. A comparison of reactive versus total surface area implies that one part of the surface is reactive while the other is not. This concept is arbitrary and otherwise incorrect, as shown by analytical techniques like AFM and VSI that provide spatially resolved information. Additional evidence comes from model calculations that indicate that every locus the crystal surface has a certain reactivity. Expressed in terms of a MC model, these reactivities are expressed as probabilities; - otherwise, parts of the surface would be inert. Focusing at the molecular scale, we understand that each surface molecule has a certain probability to leave the structure and that every adatom has a probability to become a new member of the structure. The probabilities for the processes to occur depend, beside other factors, on the energy configuration at each location. Therefore, it is the number, type, and distribution of surface sites that define the average reactivity of a crystalline surface at any given time. This insight has large implications for a number topics: (1) reactive surface area can not be expressed solely in units of area, (2) nor can it be compared directly with total surface area. (3) Even more important, the distribution of sites at a given surface have the inherent potential for dynamic change. Therefore, we can not expect a unique rate for a dissolution process, but a range of rates. This conclusion is in agreement with many very well constrained experimental results. An attempt to model microorganisms on mineral surfaces and their interactions should address this problem because all interactions occur at the molecular scale. For example, *Shewanella* MR-1 attaches to specific sites at carbonate surfaces, i.e., the outcrops of line defects. By blocking these sites MR-1 modifies the reactivity of the surface and therefore the dissolution or growth kinetics.

B12D-06 1455h

Molecular Modeling of Biogenic Manganese Oxides Using ab Initio Density Functional Theory

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Layer type manganese oxides with short-range crystalline order (birnessites) are produced by many species

of bacteria. Deposits of these oxides form a highly reactive catalytic surface that plays a major role in the destruction and sequestration of organic compounds and metals. Biogenic oxides also contain vacant Mn(IV) sites; these sites, with their associated negative charge, are the probable main cause of the high sorptive reactivity of the oxide surfaces. In order to acquire a deeper understanding of the molecular mechanisms involved in these processes, a model of a biogenic oxide was built and its structure was optimized using the CASTEP three-dimensional periodic system computational package. The resulting crystal structure shows good agreement with EXAFS data from crystals formed by a strain of the common soil and freshwater bacterium, *Pseudomonas putida*. The greatest challenge in modeling Mn oxides (like other transition metal oxides) comes in dealing with the electronic factors that lead to their magnetic and catalytic properties: they are highly correlated systems where the spin must be taken into account in order to obtain accurate predictions of their properties.

B12D-07 1510h

Cesium Interactions With Illite in the Presence of Bacterial Exudates

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Biogeochemical processes in the rhizosphere can significantly alter chemical reactions between contaminants and soil minerals. Several strains of bacteria that exude aluminum-chelating compounds were isolated from the rhizosphere of crested wheatgrass (*Agropyron desertorum*) collected from the Idaho National Engineering and Environmental Laboratory (IN-EEL). We examined the effect of exudates from the rhizosphere bacteria on cesium desorption from illite. The exudates from some strains of rhizosphere bacteria significantly enhanced Cs desorption from illite. In addition, Cs desorption from illite increased with increasing concentration of exudates from one selected bacterial strain. There was no obvious relationship between Cs desorption and the Al-chelating ability of the exudates. Both mobilization of Al from illite and changes in the density of frayed edge sites on the illite were monitored as a function of exudate type and concentration. Results suggest that exudates from rhizosphere bacteria may play an important role in Cs interactions with illite and, therefore, could alter Cs availability in micaceous soils.

B12D-08 1525h

Studies On The Influence Of Soil Components On Adsorption-Desorption Of Hazardous Organics And Their Insitu Biodegradation

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Currently approximately 155 cubic yards of soil is contaminated with hazardous organics at Patancheru Industrial area (Hyderabad, India). These hazardous organic contaminants are frequently part of hazardous waste disposed on land and the study of waste site interaction is the key to assess the potential for offsite and onsite contamination. In the present study the authors report the results on the adsorption, soil leaching potential and persistence of phenol, p-nitrophenol, 2,4-dichlorophenol and 4, chloro-2, nitrophenol which are the common constituents of the hazardous waste generated. The role of soil components like organic matter, clay, iron and aluminium oxides in the adsorption capacity has been studied. Desorption isotherms of soil adsorbed hazardous organics exhibited hysteresis at high initial concentration indicating the degree of irreversibility of adsorption-desorption process. Leaching potential of the hazardous organics decreases with their increasing hydrophobicity and soil organic matter content while their persistence in terms of half life time (DT50) increases. Insitu biodegradation has been carried out by developing mixed culture systems which can

degrade the phenols to complete mineralisation by utilizing them as the sole source of carbon and their corresponding biodegradation kinetic constants were evaluated. Based on the above data generated preparation of hazardous waste dumpsites with suitable soil surface having high holding capacity for organics and their insitu biodegradation by mixing with specific bacterial cultures enriched from different soils can be exploited as a cost effective technology for reclamation of contaminated sites.

B12E MCC: 3014 Monday 1340h

Disturbance, Climate, and Management Impacts on Carbon Budgets of Forested Ecosystems II

(joint with A, GC)

Presiding: K A Hibbard, Oregon State University; M Apps, Canadian Forest Service; D J Barrett, CSIRO Plant Industry

B12E-01 1340h INVITED

Fire and Carbon in Canadian Forests

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Fire is the major stand-renewing agent in Canadian forests, affecting carbon sources and sinks. On average over the past 40 years, about 27 Tg carbon have been emitted directly through combustion of Canadian forest fires annually, but in some years, this can be over 100 Tg carbon. The overall impact is much greater because fire-killed vegetation decomposes and releases carbon through heterotrophic respiration. In addition, very young successional vegetation that replaces the burned forest is usually a weaker carbon sink until the forest canopy develops. The magnitude of these post-fire effects has not been well quantified, but models suggest that it is of a similar magnitude to the direct combustion emissions. Post-fire carbon fluxes are being measured using eddy covariance as part of FLUXNET-Canada on a chronosequence of burned forests. These long-term measurements, in conjunction with short-term aircraft measurements and modelling are helping to reduce the uncertainty in our estimates of the effect of fire on the forest carbon balance. The impact of fire on forest carbon is expected to become more important in the future since global circulation models and regional climate models suggest that the area burned could double in Canada under a 3xCO₂ climate. This will be caused by warmer and drier conditions throughout much of the country. Although climate is a main driver of fire, landscape and fuel changes also need to be considered. Ongoing research is aimed at evaluating the potential to mitigate fire through landscape modifications and other fire management options. However it is most likely that we will need to adapt to the economic, social and ecological impacts of fire in a changing climate.

B12E-02 1355h

Climatic Variability, Fire Regimes and Carbon Dynamics in Dry Forest Ecosystems of the Western US

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Historical variability of fire regimes in the western Americas is associated with climatic phenomena such as ENSO. We describe the relationship between fire occurrence and interannual to decadal climatic variability (Palmer Drought Severity Index [PDSI],