B21B-0713 0830h POSTER

Agent-Based Modeling of Physical Factors That May Control the Growth of Coccidioides immitis (Valley Fever Fungus) in Soils

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A model of the spread and survival of the fungus Coccidioides immitis in soil via wind-borne spore transport has been completed using public domain agent-based modeling software. The hypothetical model posits that for a successful new site to become established, four factors must be simultaneously satisfied. 1) There must be transport of spores from a source site to sites with favorable soil geology, texture, topographic aspect, and lack of biomass competition. 2) There must be sufficient moisture for fungal growth. 3) Temperature of the surface and soil must be favorable for growth. Finally, 4) the temperature and moisture must remain in favorable ranges for a long enough time interval for the fungus to grow down to depths at which spores will survive subsequent heat, aridity, and ultraviolet radiation of the hot, dry season typical of the Southwest U.S. climate. Using agent-based modeling software, a model was built so that the effects of combinations of these controlling factors could be evaluated using realistic temperature, rain and wind models. The rain probability and amount, temperature annual and diurnal variation, and wind direction and intensity were based on the weather records at Tucson, Arizona for the 107-year period from 1894 to 2001. Favorable ground was defined using a fractal tree algorithm that emulates a drainage network in accordance with observations that favorable sites are often adjacent to drainage channels. Numerous model runs produced the following five conclusions. 1) If any property is not isotropic, for example wind direction or narrow paths of rainstorms, parts of the favorable areas will never become colonized no matter how long the model runs. 2)The spread of sites is extremely sensitive to moisture duration. The amount of wind and temperature after a rain control the length of time before a site becomes too dry. 3) The distribution of wind and rainstorm direction relative to that of the favorable sites is a strong control on the spread of colonization. East-west winds across an area that has mostly north-south favorable sites restricts spread strongly. 4) Soil temperature was the least sensitive control in the model, although it does control the ultimate dormancy of a site. Fifth, the model results cover the spectrum of complete colonization of all favorable sites from a few source sites to none, one, or two new sites in three years of model simulation. This implies the probability of new sites depends on the four factors in a Bayesian way. These results indicate that the complexity introduced in the model from site favorableness, temperature, moisture, and duration of favorable temperature and moisture conditions is adequate to explain observed distributions of real sites.

B21B-0714 0830h POSTER

Variations in Particulate Organic Matter Across the Drake Passage

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Modeling studies have shown that the Southern Ocean plays an important role in the global carbon cycle and is a relatively large sink for anthropogenic CO2. The formation, sinking, and eventual burial of particulate organic matter (POM) is a crucial component of this cycle, which removes gaseous carbon from the short-term atmospheric system and deposits it in a long-term sedimentary system. This study analyses surface POM from five cruise tracks taken between 1997 and 2002 across the Drake Passage between 54.11 S and 67.22 S. We determine the relationship between the stable carbon and nitrogen isotopes of the POM from underway samples and the pCO2, temperature, and salinity of the surface water for these cruises. The d13C of these samples, a proxy for productivity, ranges from -18.13 per mil to -33.40 per mil, with the least negative values closest to South America. The isotope values become more negative further south, showing the highest levels of seasonal variability (11 per mil) around 65 S at the approximate location of the Antarctic Divergence. The d13N record, a proxy for nutrient utilization, shows an equally large range from -7.22 per mil to 8.64 per mil. Like the carbon isotopes, these nitrogen POM isotopes exhibit the highest values near South America. Between 54 S and 56 S, the values drop to -4 per mil and then show an increasing trend further southward, with a relative maximum at 65 S. The nitrogen POM isotopes show considerable seasonal variability throughout all five of the tracks studied here. We use this data to define the latitudinal and seasonal variation of these parameters, as well as address the significance of the seasonally varying locations of water fronts across the Drake Passage.

B21B-0715 0830h POSTER

Effects of Microbial Colonization, Liquid Flow and Textural Heterogeneities on Gas-Phase Transport in Unsaturated Systems

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Gaseous flow dynamics in unsaturated media were examined with respect to microbial colonization, liquid flow rates, and textural heterogeneities. A light transmission chamber consisting of two glass sheets mounted in an aluminum frame in front of a light bank was packed with translucent quartz sand and brought to unsaturated conditions. To visualize gas transport, carbon dioxide was introduced to the chamber at varying rates in combination with different liquid flow rates and textural inclusions. A methyl red pH indicator solution was used in conjunction with a liquid-cooled camera to monitor carbon dioxide concentrations and infer transport dynamics throughout the system. To explore whether gas-phase nutrients would stimulate microbial growth, acetate and ammonia vapors were pumped through a chamber inoculated with *Pseudomonas fluorescens* HK44. Naphthalene vapor pulses were used to induce bioluminescence, allowing imaging of responsive colonies.

B21B-0716 0830h POSTER

Influence of Pedogenic Iron-oxyhydroxides on the Ge/Si Weathering Tracer

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Germanium/silicon ratios are a promising tracer of the silica cycle in both marine and terrestrial environments. Prior work shows that Ge/Si ratios are fractionated by at least two distinct mechanisms in the weathering environment: sequestration of Ge by soil clay minerals and biological fractionation during plant phytolith formation. Ge may also be sequestered by pedogenic iron oxyhydroxides, resulting in a decoupling of the Ge and Si geochemical cycles. Ge/Si ratios in Hawaiian soils are high (3.5-25 μmol/mol) relative to the ratio in the basaltic parent rock (2.5μmol/mol). We are examining Ge behavior in a well-characterized climate gradient on the Hawaiian island of Maui to elucidate the relationship between Fe geochemistry and Ge/Si ratios. The Maui precipitation gradient is made up of 7 sites on the flank of Haleakala Volcano ranging in mean annual precipitation from 875 mm rain/year to 5066 mm rain/year (Schurr et al., 2001). All sites are developed on $\sim$400 ka parent material and are highly weathered (>80% Si loss relative to immobile Nb). Sites experiencing less than 3338 mm rain/year display characteristics typical of oxic, highly weathered basaltic soils. In these soils, Fe weathered from parent material is not mobile and accumulates as secondary Fe(III) minerals (ferrihydrite). The wetter sites (>3338 mm/yr) show evidence of extensive Fe reduction, resulting in mobilization and loss. Ge/Si ratios in relatively dry sites (<3338 mm rain/year) are as high as 21 μmol/mol, nearly 10 times higher than parent rock ratios. Fe-depleted horizons in the wettest sites have Ge/Si ratios as low as 3.5 μmol/mol. Reductive loss of Fe-oxyhydroxides results in a dramatic drop in Ge/Si ratios, suggesting that Ge is in part accumulating in the Fe oxyhydroxide component of soil. However, nearly Fe-free soils maintain Ge/Si ratios elevated with respect to parent material, consistent with partitioning of Ge into secondary soil alumosilicates. Regardless, the influence of pedogenic Fe-oxyhydroxides must be taken into account when using the Ge/Si system as a weathering tracer.

B21B-0717 0830h POSTER

Tracing Terrestrial Silica Cycling Using Ge/Si Ratios, Luquillo Mountains, Puerto Rico

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Ge/Si ratios are fractionated by several processes in the weathering environment, potentially providing insight on silicate weathering processes and providing a tracer of Si sources in streamwater. We are analyzing Ge/Si ratios in soils, soilwaters, streams, and plants from the USGS Luquillo Water, Energy and Biogeochemical Budgets research watershed in Puerto Rico in an effort to apply this tracer system to granitoid weathering in a tropical environment. This system has many features in common with our previous work in the Hawaiian Islands, but the mineralogy here is more complex and more globally representative. Bedrock is a quartz diorite pluton with a Ge/Si ratio of 2.4 μmol/mol. Soil and saprolite ratios range from 2.6 to 3.6 μmol/mol. Soil Ge/Si ratios are lower than ratios measured in basaltic soils due to the accumulation of primary quartz with a low (0.5 μmol/mol) Ge/Si ratio. Soil kaolinite has a Ge/Si ratio of 5.9 μmol/mol demonstrating preferential partitioning of Ge into secondary soil clays. Nine common plant species were sampled from the Luquillo site to investigate the role of plants in the terrestrial silica cycle. Many plant species contain abundant opal phytoliths (as much as 4.4 wt% SiO_2 in aboveground biomass). Consistent with our work in Hawaii, plant phytolith opal at Luquillo has very low Ge/Si ratios (0.05 to 0.6 μmol/mol). Recycling of phytolith opal likely explains surface (top 20 cm) maxima in soil-saprolite porewater [Si] profiles measured in lysimeter samples. Globally, most streams have Ge/Si ratios that vary with discharge and can be explained by mixing of a low-Ge/Si, high [Si] component, and a high Ge/Si, low [Si] component. Our prior work in Hawaii suggests that the low Ge/Si ratios commonly seen in streams reflect a contribution of plant-cycled Si that is particularly important at base flow. We will test this model with samples collected this fall by automatic streamwater samplers during storm events at two gauged stations in the Río Icacos basin.

B21C MCC: Level 2 Tuesday 0830h

Molecular Biogeochemical Processes of Terrestrial Environments V Posters

(joint with H, V, MR)

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

B21C-0718 0830h POSTER

Soil Microbial and Enzymatic Responses to Complex and Labile Nutrient Inputs

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Microbial extracellular enzymes are essential for converting complex organic compounds into smaller molecules that are available for plant and microbial uptake. However, enzyme production represents a substantial resource cost for microbes, and microbes may be under selection to produce enzymes only when benefits exceed costs. We predicted that soil enzyme activities would be highest when complex substrates were abundant, but available nutrients were scarce (large potential benefit from enzyme production). We also predicted that rates of nutrient and carbon mineralization would correspond to observed shifts in enzyme activities. To test these predictions, we added insoluble

and available carbon, nitrogen, and phosphorus substrates to soil incubations and measured enzyme activities, CO_2 respiration, microbial biomass, and nutrient mineralization. Labile carbon additions increased respiration rates and microbial biomass, while labile nutrient additions were taken up by microbes but did not increase respiration rates. Labile carbon + nitrogen additions increased acid phosphatase activity, while labile nitrogen additions suppressed aminopeptidase activity. Insoluble nutrients caused major increases in enzyme and microbial activities only when added in combination with complementary labile nutrients (e.g. insoluble carbon + available nitrogen and phosphorus). These results indicate that microbes respond to soil nutrient status by changing patterns of extracellular enzyme production. Such changes can allow microbes to access nutrients in complex molecules, but may be limited by the availability of resources to build enzymes.

B21C-0719 0830h POSTER

Desert Varnish: Relative and Absolute Dating Using Portable X-Ray Fluorescence

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Levels of manganese and iron measured *in situ* with a portable x-ray fluorescence instrument permit relative and absolute dating of desert varnish. This novel technique may have wide potential application to dating Pleistocene and Holocene events and geomorphic surfaces in dry climate settings. Desert varnish is a thin biogenic coating, enriched in Mn and Fe, found on rock surfaces in arid and semi-arid regions. The accumulation of varnish marks the passage of time since a fresh rock surface was created or exposed. Thus the varnish thickness reflects the age of the event that created the fresh surface, whatever the agent was, e.g., a rock fall, a fault movement, or an aboriginal artist. Past attempts to date rock varnish have been marked more by ambiguity or outright failure than by success. Our recent research suggests a practical and rapid method for dating varnish using a portable x-ray fluorescence instrument (PXRF). Varnish thickness encodes two distinct signals, metal and clay. The biogenic Mn and Fe record the passage of time, whereas the accumulation of clay particles is a more time-random process. X-ray fluorescence (XRF) can measure just the "metal thickness" of Mn and Fe in varnish. Earlier tedious microscope techniques focused on physical thickness that includes the noise associated with the clay component. XRF integrates the metal thickness of a broad area of varnish, which is seen to vary significantly in a thin-section traverse. Thus XRF provides a meaningful average thickness over a surface. A portable x-ray fluorescence unit provides rapid, non-destructive, *in situ* measurements. On outcrop a single analysis takes about 2 minutes and the varnish is not consumed or even disturbed. The hand-held PXRF instrument is simple to operate and relatively inexpensive ($ 30,000). PXRF analysis of varnish on independently dated materials yielded a substantive correlation between age and metal (Mn + Fe) thickness. This provided an initial validation of the technique for relative dating, and a cautious optimism for reliable absolute dating. Using that initial correlation as a thickness vs. age calibration has generated what appear to be reasonable ages on unrelated varnish "unknowns." Obvious applications of the technique include dating of petroglyphs by degree of repatination; assessment of rock-fall risks by dating old falls; dating motion from varnish development on fault scarps; and finding ages of geomorphic surfaces.

B21C-0720 0830h POSTER

Mechanisms of Biogeochemical Influence on Phosphorus Bioavailablity in Cold Terrestrial Ecosystems

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The Bonanza Creek LTER site along the Tanana River near Fairbanks, Alaska is a phosphorus-limited ecosystem. Our research combines microbiological and geochemical approaches to understand factors controlling phosphorus bioavailability at this site. Our first objective was to identify the phosphate minerals within the sediment and soils of vegetated islands in the river. Detailed electron microprobe studies revealed that the predominant inorganic phosphate source is fluorapatite. Thus, we are conducting microbial and abiotic experiments to evaluate the role of organic ligands in fluorapatite dissolution. Kinetic data are obtained in flow through reaction vessels as a function of apatite variety and ligand type. Batch experiments are used to investigate organic adsorption to apatite surfaces to test a hypothesized relationship between the propensity of a ligand to adsorb and its influence on dissolution rates. These data will contribute to understanding of biological impact on mineral weathering and nutrient cycling in terrestrial environments. At Bonanza Creek, and in many other soils, phosphorus released by apatite weathering is sequestered into secondary lanthanide, aluminum, and iron phosphate minerals. These represent important, highly insoluble phosphate reservoirs in some phosphorus-limited ecosystems. We have studied the selectivity of biogenic organic ligands in promoting mineral dissolution through strong metal ion complexation. Of particular interest are siderophores, which modeling results indicate have the potential to influence both iron and phosphorus bioavailability.

B21C-0721 0830h POSTER

Iron Redox Transformations And Phosphorous Cycling In Tropical Soils

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We are investigating the hypothesis that in highly weathered tropical soils iron oxidation-reduction reactions may mediate phosphorous solubility. In these soils phosphorous may be removed from the plant-available soil pool by sorption to Fe(III) oxides and by precipitation with Fe(III) to form insoluble minerals. The reduction of iron during episodic anoxic conditions has the potential to release phosphorous in a plant available form. We aim to explore the factors controlling Fe reduction and to evaluate the role of Fe reduction in P solubilization. Soil samples were collected along a toposequence (ridge-slope-valley) in the Luquillo Experimental Forest, Puerto Rico. Besides precipitation, the valley soils receive additional water through subsurface and upland runoff. These soils are poorly-drained and, therefore, periodically saturated with water, which creates anoxic conditions. Two series of incubation experiments were carried out on air-dried and freshly-sampled valley soils. During a 14-day incubation period, increasing production of Fe(II) was detected in both types of soil sample. We also found positive correlations between the concentrations of soluble Fe(II), pH, and soluble P. In general, the total amounts of Fe(II) and P produced were higher in the air-dried soil, mainly due to differences in microbial activity. To examine further the factors controlling Fe reduction and P solubilization, we are performing soil incubation experiments in the presence of "electron shuttle" compound (AQDS). SEM and STXM techniques will be applied to detect the formation of Fe(II) secondary minerals.

B21C-0722 0830h POSTER

Outer Sphere Adsorption: Speciation and Implications for Mineral Dissolution

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Organic substances such as low molecular weight (LMW) acids and humic substances are ubiquitous in many natural settings. In environments such as soils and sediments, organic materials commonly strongly adsorb to minerals such as metal oxyhydroxides, thereby influencing their physicochemical behavior. In particular, a number of studies undertaken in recent years have shown that organic substances that adsorb in an inner sphere fashion (ie., through a ligand exchange process, resulting in a direct organic - metal cation bond) can dramatically enhance the dissolution behavior of a range of metal oxyhydroxides. In this study, we have examined the effect of outer sphere adsorption (ie., adsorption in the absence of direct ligand - metal cation bond formation) of a simple LMW anion, maleate, on the dissolution behavior of corundum - a model metal oxyhydroxide. Combined macroscopic adsorption results, ATR-FTIR spectroscopy and dissolution data indicate that under acidic conditions, the outer sphere binding of maleate strongly inhibits mineral dissolution, presumably by blocking and protecting surface sites against attack by dissolution-enhancing species present in solution. The potential implications of these results are discussed in light of other recent spectroscopic findings, which indicate that common macromolecular organic substances such as fulvic acid also predominantly bind in an outer sphere manner on mineral oxyhydroxide surfaces.

B21C-0723 0830h POSTER

Molecular Simulations of a Model Humic Substance

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Atomistic simulations can be used to explore the molecular scale interactions that govern the formation of organo-mineral complexes in soils, complexes that in turn control the size and turnover of soil C pools. A suitable model organic molecule, featuring properties and behavior typical of the recalcitrant portion of soil C in humic substances, is needed for these simulations. The latest iteration of the Schulten model of dissolved organic matter (DOM) was modeled under both dry and hydrated conditions, and as a carboxyl-deprotonated, Na- or Ca-saturated complex, using the COMPASS force field with energy minimization and molecular dynamics algorithms. This large molecule (10,419.3 Da) possesses a flexible, porous structure and a distribution of functional groups appropriate to humic substances. When dry and densely packed, the DOM molecule has a bulk density value within the range measured for natural humic substances, but its Hildebrand solubility parameter lies just outside the range of experimental estimates. A model IR spectrum calculated from this structure was comparable to experimental spectra. When surrounded by water molecules, the DOM molecule goes through conformational adjustments, resulting in the concentrating of polar groups in exterior regions, as has been predicted for pseudomicellar structures. In order to simulate humic substances under more typical aqueous conditions, the carboxyl groups of the DOM molecule were deprotonated, and hydrated Na^+ or Ca^{2+} was added to balance charge. These model metal-humic complexes were more porous, had greater solvent-accessible surface areas, and formed more H-bonds with water than the protonated, hydrated DOM molecule, due to intrusion of the cation hydrates. Our simulations indicated that, relative to Na^+, Ca^{2+} is both more strongly bound to carboxylate groups and more fully hydrated, evidently due to the higher charge of the divalent cation. The Ca-DOM complex also featured fewer H-bonds than the Na-DOM complex, perhaps because of reduced orientational freedom of both the organic moieties and the water molecules after interaction with Ca^{2+}. The DOM molecule mimics the behavior of natural humic substances under the conditions investigated, and therefore, may be considered suitable for use in simulations of organo-mineral complexes.

B21C-0724 0830h POSTER

Properties of Distinct Biofilm Communities at an Acid Mine Drainage Site

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The Superfund site at the Richmond Mine in Redding, California contains microorganisms that greatly contribute to the generation of the mine's characteristic acidic, metal-rich environment. Rather than dispersed as single cells, these microorganisms are often found in biofilm communities. Several visually distinct biofilm communities exist in the mine, and they have been previously analyzed by FISH. The different communities are likely to be a reflection of the different microenvironments within the mine. Here, we compare other aspects of these distinct biofilms to better understand how these organisms thrive in their microenvironments. First, we have analyzed the polysaccharides present in the different biofilm samples, since polysaccharides are prominent components of the matrix which holds the biofilms together. Second, we have monitored how resilient the biofilms are to changes in temperature and pH, and to the presence of detergents. Third, since some biofilms have a characteristic pink hue thought to be due to the presence of cytochromes, we have also studied the heme-containing proteins in the pink biofilm samples. And last, we have used ICP-AES, UV-VIS, HRSEM, ATR-FTIR and XRD analyses, to compare the ability of different biofilms to sequester metals including As, Zn, and Fe, which may also have implications in toxicity and metal mobility in water bodies and sediments.

B21C-0725 0830h POSTER

Structural Study Of Nickel- And Zinc-Doped Layer Type Manganese Oxides

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In order to understand better the mobility of trace elements in soils it is necessary to characterize the interactions of these elements with the reactive mineral components of soils. We have studied the intercalation processes of Zn and Ni in the oxide phases birnessite [layer type Mn(III,IV)O_2 oxide] and lithiophorite [MnO_2-$Al(OH)_3$ mixed-layer oxide], which are found in ferromanganese nodules common in lakes, shallow marine environments, and the oceanic floor. Previously Manceau, Lanson and coworkers have demonstrated that nickel is sequestered in soil ferromanganese nodules by substituting for Mn^{3+} in the manganese oxide sheet of lithiophorite and for Li^{+} in the $Al(OH)_3$ sheet. In birnessite, on the other hand, they found that Zn atoms are adsorbed in the interlayer above and below vacant octahedral sites, either tetrahedrally and/or octahedrally coordinated. In our studies, Zn and Ni doped lithiophorite and birnessite with varying concentrations of the doped metals were synthesized in the laboratory to avoid the inherent complexity of natural samples. Different types of synthesis procedures had to be chosen for the birnessite and lithiophorite samples in order to insert the two metals into the structures of these phases. This reflects the differing insertion behavior of Zn and Ni and the corresponding different varieties of doped Ni and Zn in the birnessite and lithiophorite structures. Structural characterization of the Zn and Ni doped manganese oxides was performed with help of X-ray diffraction and EXAFS spectroscopy to determine precisely in which form and in which place in the structure the metals occur. The higher quality of the EXAFS spectra (k-values up to 16 $Å^{-1}$) of our synthetic samples in comparison to those of natural samples allowed us to resolve interatomic distances that differed by less than 0.12 Å. For example, Ni is octahedrally coordinated, sharing edges with the Mn octahedra in the birnessite structure at two slightly different Ni-Mn distances. Independently of its doping concentration, Zn was found to be tetrahedrally coordinated in both of the oxides investigated. The only exception to this trend was observed after replacing in the synthesis procedure for lithiophorite a certain percentage of Li by Zn. In that case Zn can be intercalated in the structure both tetrahedrally and octahedrally coordinated.

B21C-0726 0830h POSTER

Interaction of Strontium With the Calcite Cleavage Surface

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The interaction of Sr^{2+} and carbonate minerals is an important component in our overall understanding of the cycling and sequestration of trace metals in terrestrial environments. For example, uptake of ^{90}Sr by carbonates has significance for the subsurface migration of radioactive contaminants. Past work has confirmed the general inhibition of calcite dissolution in the presence of Sr^{2+}, and has suggested that Sr^{2+} may inhibit dissolution by (1) incorporation at kink sites associated with etch pits or (2) precipitation of a secondary phase at the crystal surface. However, these studies have fallen short of resolving the processes of Sr^{2+} inhibition at a mechanistic level. We have used atomic force microscopy (AFM) and vertical scanning interferometry (VSI) to examine calcite crystal dissolution in the presence of Sr^{2+} over a wide range of dissolved carbon concentrations. Although we do see a decrease in dissolution rates with increasing strontium concentrations, we do not see a change in etch pit morphology at solution pH 8-9, or significant precipitation of a secondary phase at concentrations of 25 μM Sr^{2+}. At higher concentrations (250 μM Sr^{2+}), our experimental results do suggest that Sr^{2+} may produce variable inhibition through new nucleation not necessarily related crystallographically with the cleavage surface. These relationships in conjunction with complementary work on the interactions of Mg and Mn with calcite will enable us to develop a general model for the incorporation of trace metals during dissolution of the pure solid.

B21C-0727 0830h POSTER

The acid-base titration of montmorillonite

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Proton binding to clay minerals plays an important role in the chemical reactivity of soils (e.g., acidification, retention of nutrients or pollutants). If should also affect the performance of clay barriers for waste disposal. The surface acidity of clay minerals is commonly modelled empirically by assuming generic amphoteric surface sites (>SOH) on a flat surface, with fitted site densities and acidity constant. Current advances in experimental methods (notably spectroscopy) are rapidly improving our understanding of the structure and reactivity of the surface of clay minerals (arrangement of the particles, nature of the reactive surface sites, adsorption mechanisms). These developments are motivated by the difficulty of modelling the surface chemistry of mineral surfaces at the macro-scale (e.g., adsorption or titration) without a detailed (molecular-scale) picture of the mechanisms, and should be progressively incorporated into surface complexation models. In this view, we have combined recent estimates of montmorillonite surface properties (surface site density and structure, edge surface area, surface electrostatic potential) with surface site acidities obtained from the titration of alpha-Al_2O_3 and SiO_2, and a novel method of accounting for the unknown initial net proton surface charge of the solid. The model predictions were compared to experimental titrations of SWy-1 montmorillonite and purified MX-80 bentonite in 0.1-0.5 mol/L $NaClO_4$ and 0.005-0.5 mol/L $NaNO_3$ background electrolytes, respectively. Most of the experimental data were appropriately described by the model after we adjusted a single parameter (silanol sites on the surface of montmorillonite were made to be slightly more acidic than those of silica). At low ionic strength and acidic pH the model underestimated the buffering capacity of the montmorillonite, perhaps due to clay swelling or to the interlayer adsorption of dissolved aluminum. The agreement between our model and the experimental data illustrates the complementarity of molecular and macro-scale descriptions of the clay reactivity.

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Bacterial Reduction of Uranium in Mineralogically Heterogeneous Media: Impact of Mn- and Fe-oxides.

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Dissimilatory reduction of uranium can have a profound impact on the transport of uranium within surface and subsurface environments. The rate and extent of biological uranium reduction, and stability of reduced uranium phases, will be influenced by sediment mineralogy. Both Fe- and Mn-oxide phases have the potential to retard U(VI) reduction and may even serve as oxidants of reduced U phases such as uraninite. Mn-oxides in particular may serve as oxidants of uranium. Here we examine the rate of uranium reduction in the presence of Fe- and Mn-oxide coated sands and the spatial relationship of both products and reactants, inclusive of bacterial cells. Solids were characterized using X-ray absorption and Raman spectroscopies while spatial relationships between minerals and microbes were resolved using electron microscopies and X-ray microspectroscopy. The presence of birnessite decreases the rate and extent of biological uranium reduction while ferrihydrite only retards the rate of reduction. Uranium reduction rates also vary with birnessite concentration. During in-situ bioremediation aqueous uranium concentrations and uraninite stability will be partially determined by subsurface mineralogy.

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Spectroscopic Studies of Competitive Adsorption Between Suwannee River Fulvic Acid (SRFA) and Various Low Molecular Weight (LMW) Organic Anions at Mineral -Water Interfaces

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Natural Organic Matter (e.g., humic and fulvic acids) and LMW organic anions (e.g oxalate, maleate, and phthalate) are important components of natural soil and aquatic systems and play key roles in the transport and sequestration of trace metals due to their ability to form strong complexes with pollutant ions and/or positively charged mineral particle surfaces. Using in-situ ATR FTIR spectroscopy with flow-cell capability, we have investigated the competitive adsorption of SRFA for binding sites on the boehmite surface relative to various LMW organic anions forming inner-sphere (e.g., oxalate) or outer-sphere (e.g., maleate) surface complexes. At similar concentration ratios, inner-sphere oxalate surface complexes dominate boehmite surface binding sites with respect to outer-sphere surface complex-forming ligands such as fulvate and maleate. However, we also observed that outer-sphere type ligands (e.g., fulvic acid and maleate) with higher concentrations can induce desorption of inner-sphere oxalate surface complexes or inhibit inner-sphere oxalate surface complex formation.

B21C-0730 0830h POSTER

Iron chemistry of Hawaiian rainforest soil solution: Biogeochemical implications of multiple Fe redox cycles

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Iron (Fe)-oxides are important sorbents for nutrients, pollutants and natural organic matter (NOM). When flucutations in soil oxygen status exist, Fe can cycle through reduced and oxidized forms and thus greatly affect the aqueous conc. of nutrients and metals. We are examining the influence of oscillating oxic/anoxic conditions on Fe-oxide formation and biogeochemical processes (microbial community composition, and carbon, nutrient and trace metal availability). Our work makes use of a natural rainfall gradient ranging from 2.2 to 4.2 m mean annual precipitation (MAP) on the island of Maui, Hawaii, USA. All sites developed on a 400ky basaltic lava flow and comprise soils under similar vegetation. Solid phase Fe concentration and oxidation state vary systematically across this rainfall gradient with a sharp decrease in pedogenic Fe between 2.8 m and 3.5 m MAP that corresponds with an Eh of 330 mV (1-yr ave.). Fe isotopic composition and Fe-oxide associated rare earth elements (REE) also suggest a shift from ligand-promoted to redutive Fe dissolution with increasing rainfall. To examine the effects of multiple Fe oxidation/reduction cycles, we constructed a set of redox-stat reactors that maintain Eh values within a set range by small Eh-triggered additions of oxygen. Triplicate soil slurry reactors are subjected to redox (Eh) oscillations such that Fe is repeatedly cycled from oxidized to reduced forms. During our current experiment, we measure pH and Eh dynamics and monitor the distribution of Fe(II) and Fe(III), major ion and anion concentrations, a range of trace metals including the REE, and total organic carbon (TOC) in three Stokes-effective particle size fractions (<0.45 mm, <0.1 mm, and <0.02 mm) by cascade centrifugation and a <3000 MW fraction isolated via ultra-filtration. Each sample is then sequentially extracted in dilute (0.5 M) HCl and acid-ammonium oxalate. Concurrently, CO2 release is measured and DNA fingerprinting is used to track changes in the microbial community. Prior to implementing the rigorous sampling procedure above, we completed two preliminary reactor experiments focusing only on Fe distribution between aqueous, HCl, and oxalate extractions. These experiments illustrated (1) a distinct threshold for Fe oxidation at 350 mV in the soils (pH 5) and (2) multiple redox cycles increased the HCl-extractable Fe(III) fraction relative to initial conditions. Unexpectedly, this increase occurred predominantly during reducing cyclesperhaps indicating a weakening of Fe-oxide structures during initiation of reducing conditions or oxidation of Fe(II) by NO3. By integrating Fe analysis with trace metal and microbial characterization in triplicate reactors, we will verify this increase in HCl-extractable Fe(III), and assess the impacts of Fe redox oscillation on biogeochemical processes.

B21C-0731 0830h POSTER

Production of Hydrolysable Tannin-Like Structures During the Microbial Demethylation of lignin: An Assessment Using13C-Labeled Tetramethylammonium Hydroxide Thermochemolysis.

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Phenolic compounds in soils are important mediators of microbial activity, metal mobility, soil redox, and soil organic matter building processes. Direct tannin input and the microbial decomposition of lignin in litter and soil are important contributors to this pool of phenols. The ability to accurately assess the relative differences in lignin decay (which are initiated by demethylation and side chain oxidation) among synapyl, coniferyl, and p-coumaryl components of detrital lignin requires the ability to determine microbial demethylation within the complex soil residues. Differentiating between hydrolysable tannins and contributions from advanced lignin decay can be problematic for many of the most common molecular techniques such as alkaline CuO oxidation, pyrolysis GC, and tetramethylammonium hydroxide thermochemolysis because of either the masking effects of derivatizing agents, oxidative damage to ortho-phenols or low volatility of lignin monomers. In this study we investigate lignin demethylation and polyhydroxyl-aromatic production in BC and C horizons of sandy forest soils dominated by oak, the A horizon from a red spruce forest, and controlled microbial inoculation studies of woody tissue using in-line 13C-labeled tetramethylammonium hydroxide thermochemolysis. Both white-rot and brown-rot decay resulted in syringyl demethylation, with the latter exhibiting more aggressive demethylation chemistry, while coniferyl monomer demethylation was essentially restricted to brown-rot decay. In a typical brown-rot sequence demethylation of syringyl components occurs more rapidly than coniferyl units within the same tissue and lower molecular weight fragments are likewise more demethylated than lignin monomers containing the full glycerol side chain. Demethylation of both methoxyl groups in the syringyl monomer is evident in soil horizons as well as laboratory inoculations. The latter may suggest demethylation after lignin depolymerization. Low molecular weight syringyl and coniferyl monomers are from 25-50 % demethylated in surface litter and decrease in demethylation content with depth while unoxidzed lignin monomers with the full side chain exhibit little demethylation in surface horizons and increase in demethylation with depth. Application of this technique will greatly aid in the determination of soil organic matter cycling and the comparative roles and lifetime of hydrolysable tannins and highly altered lignin in soils.

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Effects of Metal Oxides on a Fungal Laccase Activity and Catechol Transformation

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The transformation of naturally occurring phenols to humic polymers is generally catalyzed by various phenoloxidases commonly present in soil. Some poorly crystalline metal oxides and hydroxides may also participate in these reactions. In this study, catechol (0.1 M) was incubated with a fungal laccase (950 unit/mL) in the presence of poorly crystalline minerals (ferrihydrite; 50 mg/mL: birnessite; 1 mg/mL: aluminum hydroxide; 50 mg/mL) to examine the interaction between these soil components under field conditions. Birnessite had an inhibitory effect on the laccase-mediated transformation of catechol (by up to 40%). Enzyme inhibition was possibly caused by the rapid production of humic-like polymers by birnessite. An additional inhibitory effect was caused by Manganese ion released from birnessite as it oxidized catechol (up to 70% loss in enzyme activity). In contrast to birnessite, aluminum hydroxide had an additive effect on the disappearance of catechol despite the rapid adsorption of the enzyme by this mineral (Xm=6.18μg/mg). Apparently, the adsorbed laccase retained some enzyme activity. Ferrihydrite also had an additive effect on catechol transformation. However, as compared to aluminum hydroxide, ferrihydrite adsorbed less laccase (Xm=0.89μg/mg) and more humic-like polymers. Unlike birnessite, aluminum hydroxide and ferrihydrite released negligible amounts of metal ions. In conclusion, under field conditions, phenoloxidase activity may be diminished by the presence of birnessite, but the presence of either ferrihydrite or aluminum hydroxide is less likely to inhibit enzyme activity, and may even enhance substrate transformation.

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FTIR Spectroscopic Study of Mn(II) Oxidizing *Pseudomonas putida* GB1 Biofilms on ZnSe, Ge, and CdTe Crystal Surfaces

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Pseudomonas putida strain GB1 is an aerobic, gram-negative bacterium capable of gaining energy from the biological oxidation of Mn(II). The increased kinetics of Mn(II) oxidation resulting from this microbial catalysis is known to contribute to the formation of Mn(IV) oxides in natural waters. Environmental conditions, including aqueous and surface chemistry, greatly affect the macromolecular composition and surface adhesion behavior of bacteria. For example, the chemistry of GB1 biofilms forming on crystal surfaces is expected to vary with Mn(II) concentration in solution. We used Fourier transform infrared (FTIR) spectroscopy to probe the formation of GB1 biofilms on the surfaces of negatively-charged IR transparent ZnSe, Ge, and CdTe crystal windows. Bacterial adhesion experiments were carried out both in the presence and absence of Mn(II)(aq) with FTIR windows suspended in a bioreactor comprising GB1 cells in a mineral growth medium at pH 7.6 and 30°C. After 85 h, windows were removed from the reactor and IR spectra were collected. Oxidation of Mn(II) was confirmed via leucoberbelin blue (LBB) indicator and the appearance of Mn-O stretches in biofilm IR spectra. Transmission FTIR spectra do not reveal detectable effects of crystal type on biofilm composition, but do indicate changes in chemistry resulting from introduction of Mn(II). In the presence of Mn(II), spectra of biofilms show higher relative intensity in the carbohydrate region (specifically 1160, 1052 cm^{-1}). A down frequency shift in the P=O absorbance was also observed (1240 to 1222 cm^{-1}). These results indicate a modification of bacterial cell/biofilm composition resulting during biological oxidation of Mn(II). The CdTe transmission window permits measurements to low wavenumbers (<600 cm^{-1}) and a peak at 588 cm^{-1} was observed when bacteria were surface-adhered in the presence of Mn(II). This peak, which has been attributed to Mn-O stretching vibrations, may provide an index of Mn oxide crystal growth. Scanning electron microscopy (SEM) images of the transmission crystal surfaces show similar bacterial coverage for each treatment. Transmission electron microscopy (TEM) of the bioreactor suspension revealed needle-like clusters of Mn oxide crystals in association with GB1 biomass and extracellular materials.

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Transport of Colloid-Associated Arsenic and Mercury: Column Experiments and Microscopic, Spectroscopic, and Chemical Analyses of Colloidal Material

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Heavy metal contaminants in aqueous solutions can be transported as dissolved or particle-associated species. While transport of dissolved species has received more attention, under certain conditions, transport of heavy metals associated with colloidal particles is also significant. Important issues to address are (1) the physicochemical conditions under which colloidal particles are mobilized, (2) the nature of the colloidal particles and the way(s) in which heavy metals are associated with them, and (3) the extent of particle-associated heavy metal transport. In this study, bench-scale column experiments were performed to demonstrate particle-based transport of arsenic and mercury from a calcined ore obtained from the inoperative Sulphur Bank mercury mine in the Northern California coast range. The calcines were exposed to organic acids and electrolyte as a means of simulating environmental perturbations that commonly cause mobilization of colloids in similar matrices. The arsenic and mercury species associated with the mobilized particles were characterized using Hg L(III)- and As K-edge x-ray absorption fine structure (XAFS) spectroscopy, scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), and analytical transmission electron microscopy (ATEM). Most of the mobilized arsenic and mercury was in particulate forms, comprising As(V)-Fe(oxy)hydroxide surface complexes or coprecipitates, As(V)-substituted jarosite ($KFe_3(SO_4,AsO_4)_2(OH)_6$), HgS (cinnabar and metacinnabar), and corderoite ($Hg_3S_2Cl_2$).

URL: http://pangea.stanford.edu/research/saag/aaron.htm