early 1900s; at higher elevations, conifers are dominant. Soils have developed on relatively homogeneous, glacial till deposited about 14,000 years ago and derived predominantly from granodiorite and pelitic schist. Soils were sampled by horizon from 45 soil pits within a 12-hectare watershed. Long-term weathering rates were calculated as the loss of elements from soils relative to the parent material using Ti as an immobile element. The average long-term chemical weathering rate in the watershed (40 meq m^{-2} yr^{-1}) is similar to rates in other 10 to 15 ka old soils developed on granitic till in temperate climates. The soil parent material is chemically homogeneous, yet the weathering rates range from 21 to 65 meq m^{-2} yr^{-1} across the watershed, generally increasing with elevation due to changes in vegetation, soil water flow paths, and depth to impermeable bedrock. Feldspar weathering rates are greater at higher elevations at HBEF. Plagioclase weathering accounts for a significant amount (56-84%) of the calcium lost from the soils over the last 14,000 years, while the dissolution of apatite accounts for 15 to 32%. The present-day loss of base cations from the watershed greatly exceeds the long-term weathering rate providing additional support that the pool of exchangeable base cations in the soil continues to be diminished.

B41D MCC: Level 2 Thursday 0830h

Aqueous Microbial Geochemistry I Posters *(joint with H, OS, V)*

Presiding: **E Shock ,** Arizona State University**; L A Warren,** School of Geography and Geology, McMaster University

B41D-0913 0830h POSTER

Characterization of novel archaeal lineages associated with acid mine drainage in Iron Mountain, CA using anaerobic cultivation and cultivation-independent genomic analysis

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Iron Mountain in northern California, contains a pyritic orebody undergoing dissolution from mining creating extremely acidic (generally pH 0.8), warm (>40°C), and highly concentrated metal solutions, referred to as acid mine drainage (AMD). AMD communities are limited in the number of lineages that have been associated with them. The archaeal members of the mine community, in the past, have been restricted to the Thermoplasmatales order. The various clades within the Thermoplasmatales have been named the "alphabet plasma" (ie. Aplasma through Gplasma). The majority of them remain uncultured. Anaerobic media containing ferric sulfate and glucose has been successful in enriching and maintaining members of the "alphabet plasmas". Analysis of aqueous chemistry of these cultures shows a reduction of ferric iron, suggesting a subset of these archaea are capable of iron reduction. This may be a relevant part of iron cycling in the mine previously overlooked. Recently, another deeply branched archaeal group, named WTF1102, has been identified. Completely independent of all previously identified AMD lineages, its closest relative available in present databases is to that of the euryarchaeota group referred to as VAL1, which consists entirely of uncultured and poorly represented in sequences. Screening of the community genomic library constructed from the site revealed a contiguous fragment from two shotgun clones, totaling 4.4kb in length. These clones have been fully sequenced and contain two genes, a phosphatase and 16S rRNA. The 16S rRNA gene has a 515 bp long intron at 1102 (E. coli numbering) that contains an open reading frame which encodes for a ubitiquitin-like protein modifier. Phylogenetic analysis of the phosphotase amino acid sequence revealed it branches with that of other acidophiles, Thermoplasma and Ferroplasma. We are developing FISH probes to target the individual "alphabet plasma" and WTF1102. This work extends what we know about the diversity and metabolic capabilities of archaea in AMD.

B41D-0914 0830h POSTER

Rare Arsenic-Antimony-Sulphide Bio-immobilization and Bacterial S-layer Preservation in Siliceous Sediments from Champagne Pool Hot-Spring, Waiotapu, New Zealand

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Champagne Pool is a large (65 m diameter, 150 m deep) hot spring in the Waiotapu geothermal area of North Island, New Zealand. The spring discharges water of a mildly acid chloride type, with a pH of 5.2, a constant temperature of 75 °C and a silica concentration of 460 ppm. Siliceous sinter, loose sediments, and flocs suspended in the spring water are composed of opaline silica and metal-rich sulfides that contain many well-preserved, mineralized microbes. Detailed analysis by transmission electron microscopy and energy dispersive spectrometry has shown that bacterial cell wall and capsular material is preserved by the immobilization of high levels of As (up to 33 wt%), Sb (up to 60 wt%), and S (up to 20 wt%) in the organic matrix. Significant precipitate formation is absent (and when present only small microcrysts form), suggesting much of the As-Sb-S has accumulated through adsorption processes. When extensive biomineral precipitates are present upon the cell wall, they are composed of Al rich amorphous silicates. This suggests a 2-step biomineralization process whereby As and Sb sulfur complexes are adsorbed onto the cell surface polymers first, followed by inorganically driven precipitation of the supersaturated amorphous silica phase. Despite the lack of detailed preservation, biomineralization commonly preserves S-layers, an ordered mosaic of proteins on the outer surface of the cell wall. These are the finest ultrastructural details thus far found preserved by hot-spring biomineralization. Preserved S-layers exhibited either a hexagonal (p6) or square (p4) lattice structure with unit-unit spacing of 9.7 ± 1.6 nm. Because S-layer morphology varies considerably between species it can be used as a fingerprint to aid identification of microfossils. By considering both S-layer morphology and the hot-spring habitat (pH, Eh, temp etc) it is suggested the S-layers preserved here belong to *Clostridium thermohydrosulfuricum* or *Desulfotomaculum nigrifacans*. To determine possible mechanisms behind S-layer preservation, geochemical speciation calculations were undertaken to determine the probable inorganic species present in the hot spring water, using the REACT component of the Geochemists Workbench software package (GWB version 3.2.1). Mineral saturation indices were also calculated using this code. Results suggest that arsenic and antimony are present in the spring water as negative and neutrally charged thio or hydroxide complexes such as $HAs_2S_4^-$, H_3AsO_3 and $HSb_2S_4^-$. Furthermore, all As, Sb and S mineral phases were undersaturated. This explains the lack of notable As-Sb-S precipitate upon the cells and adds credence to the idea that the As-Sb-S phases may have been adsorbed onto the organic polymers. The observation that S-layers are preserved whilst other ultrastuctures are not may indicate a novel mechanism is involved in S-layer preservation at this hot-spring site. S-layers are dominated by amine groups which would be positively charged at the pH of the spring water. Although tentative, it is speculated the early adsorption of negative As-S and Sb-S complexes onto reactive amine groups on S-layers is paramount in the excellent preservation of these delicate ultrastructures.

B41D-0915 0830h POSTER

Sulfide as a Chemoautotrophic Electron Donor for Dissimilatory Arsenate Reduction in Mono Lake, California

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In aqueous systems, arsenic occurs as arsenate [As(V)] or as arsenite [As(III)], with the latter form being more toxic and mobile. Mono Lake, California is a meromictic soda lake (pH = 9.8; salinity = 70-90 g/L) with exceptionally high arsenic content (∼200 μM), a consequence of hydrothermal inputs combined with evaporative concentration. Previous work has shown that arsenic speciation changes from As(V) to the more reduced As(III) with vertical transition from the lake's surface oxic waters to its unmixed, anoxic bottom waters and that dissimilatory reduction is responsible for the observed change in arsenic speciation. Rates of *in situ* dissimilatory As(V) reduction measured by radiotracer (∼1- 6 μmol/L/d) were estimated to be significant enough to mineralize up to 14% of annual primary productivity. Subsequent lab-based investigations with As(V)-amended (∼1-2 mM) bottom water displayed significantly higher rates (150-260 μmol/L/d) of As(V) reduction and were not limited by the availability of organic electron donors such as acetate, lactate, malate and glucose. The focus of this study was to identify a natural source of electrons for As(V) reduction in Mono Lake. While Mono Lake contains plentiful dissolved organic carbon (∼7 mM) this material is usually refractory and resistant to bacterial oxidation. Alternatively, the anoxic bottom waters contain high concentrations of sulfide ions (∼1-2 mM) that could potentially serve as an electron donor for dissimilatory As(V) reduction. In a time course experiment with As(V)-amended Mono Lake bottom water, we observed oxidation of sulfide linked to the reduction of As(V) to As(III). This reaction did not occur in filter sterilized controls and sulfide loss did not occur in samples lacking As(V). In bottom water amended with additional sulfide (total = 6 mM) and As(V), we observed a linear relationship between rates of dissimilatory As(V) reduction and As(V) concentration. The highest rate observed under these conditions was ∼3 mmol/L/d, over 1000-fold higher than Mono Lake *in situ* rates. We isolated an anaerobic bacterium from Mono Lake bottom water, strain MLMS-1, that grows in mineral salts media by oxidizing sulfide to sulfate and reducing As(V) to As(III). MLMS-1 grew with a 4:1 stoichiometry of As(V) reduced to sulfide oxidized, indicating an 8 electron transfer. MLMS-1 aligned by 16S rDNA amplification and sequencing in the δ-Proteobacteria, being closely related to the sulfate-reducing bacteria of the genus *Desulfobulbus*. However, strain MLMS-1 does not grow with sulfate as an electron acceptor.

B41D-0916 0830h POSTER

Importance of Fe(II)-Hydroxide Complexes For the In-Situ Bioremediation of ARD Sites

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Enhancing the growth of heterotrophic bacteria such as Acidiphilium cryptum that are indigenous to acid rock drainage (ARD) sources is a potential strategy for in-situ inhibition of pyrite oxidation and acid formation. When biodegradable organic carbon was supplied to A. cryptum, oxygen was consumed by rapidly growing heterotrophs, and bacterial iron reduction observed, accompanied by increasing solution pH. A. cryptum (ATCC 33463) cells were incubated in well-aerated liquid media containing Fe2(SO4)3 and glucose at varying initial pH values from 1.5 to 3.5. No more than 1% of the added ferric iron was detected as soluble Fe3+ for any of the media, indicating that the A. cryptum cells were able to reduce precipitated ferric iron. No organic carbon consumption or iron reduction was observed in flasks incubated at pH 1.5 indicating that A. cryptum may not be able to grow at this low pH. In reactors where the initial pH was 3.5, the pH increased to approximately 5.5 during the experiment accompanied by a 0.4 gl-1 decrease in Fe(III) species after aeration stopped. In reactors where the initial pH was 2.5, final pH values were inconsistent between replicate experiments: pH decreased to 2.3 in one experiment and increased to 2.8 in the second. Dissociation of Fe(OH)2+ complexes at pH values near 2.5 could have acted as a buffer, minimizing pH change during iron respiration. The existence of Fe(OH)2+ complexes was investigated using O-square wave voltametry, a pulse polarography technique which allows for identification of metal complexes and estimation of complex stability constants. The presence of ferric hydroxide complexes at pH near 2.5 was confirmed by pulse polarography. When the initial pH was 3.5, the base neutralizing capacity of the solution decreased due to the replacement of Fe(OH)2+ by Fe(OH)3 resulting in the pH increase of over 2 units.

B41D-0917 0830h POSTER

Effects of Bacterial Respiratory Reduction Processes on the Transformation and Transport of Ferric Hydroxide Complexed Arsenic

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The mobility of arsenic in contaminated aquifers is primarily controlled by the presence of iron (hydr)oxides and sulfides. Under reducing conditions bacteria that can alter or produce these compounds will have a strong effect on the chemistry and hence the mobility of arsenic. Here we investigate how arsenic complexed with ferrihydrite is mobilized under dynamic flow conditions in the presence of anaerobic bacteria that can reduce As(V) and/or Fe(III) through dissimilatory processes. Ferrihydrite-coated sands were loaded with 200-300 mg Kg^{-1} As(V) or As(III) and inoculated with *Sulfurosprillum barnesii* strain SES-3 or *Bacillus benzoevorans* strain HT-1. The sands were packed into columns through which minimal ground water media was passed. In columns containing arsenite loaded ferrihydrite and SES-3, As(III) release was most intense initially when microbial activity was high and decreased thereafter. Similar results were observed with arsenate loaded ferrihydrite and SES-3, yet arsenate reduction to arsenite occurred prior to the onset of high Fe(II) in solution. These results suggest that arsenic release into the aqueous phase is stimulated by iron reduction and is not wholly dependent on arsenic redox transformations.

B41D-0918 0830h POSTER

Association of Eu(III) and Cm(III) With Halophiles

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Halophiles live in high ionic strength brine. The mechanisms of metal association with these microorganisms are poorly understood. In this study, we determined the distribution of Eu(III) and Cm(III) on halophiles, *Halomonas* sp. (WIPP1A) which was isolated from the Waste Isolation Pilot Plant (WIPP) repository in Carlsbad, US., *Halomonas elongata* (ATCC33173), *Halobacterium salinarum* (ATCC19700), and *Halobacterium halobium* (ATCC43214) and examined the coordination environment of Eu(III) adsorbed on the cells by time-resolved laser-induced fluorescence spectroscopy (TRLFS). The cells of *Halomonas* sp. and *H. elongata* were grown in media containing 10 - 15 w/v% and 3.5 - 30 w/v% NaCl, respectively. *Halobacterium salinarum* and *H. halobium* were grown in media containing 25 w/v% NaCl. The logarithmic distribution coefficient ($\log K_d$) was measured by using the cells at the late exponential phase. After washing the cells with the same concentrations of NaCl, the cells were mixed with 1×10^{-6} mol dm^{-3} Eu(III) and 1×10^{-8} mol dm^{-3} Cm(III) at pH 5 in the same concentrations of NaCl and $\log K_d$ of Eu(III) and Cm(III) was determined. For *Halomonas* sp. and *H. elongata*, $\log K_d$ was determined as a function of NaCl concentrations. The coordination environment of Eu(III) adsorbed on the cells was estimated by TRLFS. For TRLFS measurements, samples were prepared by adding cells to a solution of 1×10^{-3} mol dm^{-3} Eu(III) with the same concentrations of NaCl as the culture media. For *Halomonas* sp. and *H. elongata*, $\log K_d$ of Cm(III) was apparently larger than that of Eu(III) at all the NaCl concentrations examined. On the other hand, $\log K_d$ of Eu(III) and Cm(III) for *H. salinarum* and *H. halobium* was almost identical. Our previous study demonstrated that non-halophiles, *Chlorella vulgaris*, *Bacillus subtilis*, and *Pseudomonas fluorescens* show no preferences between these elements. Chemical properties of Eu(III) and Cm(III) are almost identical. Our findings suggest that the difference in $\log K_d$ of Eu(III) and Cm(III) for *Halomonas* sp. and *H. elongata* is reflected due to the slight difference in the affinity of Eu(III) and Cm(III) for the functional groups on the cell surface commonly present in the microorganisms of the genus *Halomonas*. The ligand field of Eu(III) on the halophiles was stronger than that on the non-halophiles, indicating that the coordination environment of Eu(III) on the halophiles is dense with the components of the outer cells surface.

B41D-0919 0830h POSTER

Production and Dietary Uptake of PUFA by Piezophilic Bacteria, Implications for Marine Biogeochemistry

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Polyunsaturated fatty acids (PUFAs) have been used extensively as proxies for determining the source and preservation of organic matter in marine sediments. However, the origin of polyunsaturated fatty acids in deep-sea sediments is not well understood; the ultimate source of PUFAs is only partially constrained. At issue is whether PUFAs in deep-sea sediments are derived from the primary production of the photic zone or from the in situ piezophilic bacterial production in the deep-sea, or both. In this study, we tested three deep-sea piezophilic strains, Shewanella violacea DSS12, Shewanella benthica DB21MT-2, Moritella yayanosii DB21MT-5, in biosynthesis and dietary uptake of PUFAs. These piezophilic bacteria were characterized by high abundance of unsaturated fatty acids (62-73% of total fatty acids). In particularly, polyunsaturated fatty acids (PUFA) were detected in all piezophiles examined, ranging from 8 to 27% of total fatty acids. M. japonica DSK1 produced 22:6n-3 (cis-4,7,10,13,16,19-docosahexaenoic acid, DHA), whereas the three Shewanella strains produced 20:5n-3 (cis-5,8,11,14,17-eicosapentaenoic acid, EPA) with trace amounts of DHA. The total concentrations of PLFA were higher in strains grown at low pressure (DSK1, 10 Megapascal or MPa, 26,983μg/g dry wt cells; DSS12, 50 MPa, 23,986 μg/g), and lower in strains grown at high pressure (DB6705, 85 MPa, 1,901μg/g; DB21MT-2, 100 MPa, 3,014 μg/g). When growth media were supplemented with arachidonic acid (AA; C20:4n-6), there was active uptake and cellular incorporation of AA in the hyperpiezophilic bacteria DB21MT-2 (14.7%) and DB21MT-5 (1.4%). No uptake was observed in DSS12. When cells were treated with antibiotic cerulenin, all three strains incorporated AA into cell membranes (13 to 19%). These results suggest that piezophilic bacteria can be an important contributor in producing and reworking of PUFAs in the deep sea, and that that caution must be exercised in using PUFAs in deducing sources of organic matter in the marine sediments.

B41D-0920 0830h POSTER

Biotransformation of pu(VI) by microorganisms

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The migration behavior of actinides in the environment due to microbial activity should be elucidated for estimating the potential hazards of geological disposal of high-level radioactive wastes. Actinides exist in the oxidation states, III, IV, V and VI in solution, and their chemical behavior differs each other. Actinides(V) and (VI) are more mobile than actinides(III) and (IV) in groundwater. In this study, we carried out the accumulation experiments of Pu(VI) by *Bacillus subtilis* and the mixture of B. subtilis and kaolinite to elucidate the role of microbes for the migration of Pu(VI). Accumulation experiments of Pu by *Bacillus subtilis*, kaolinite, and the mixtures were carried out for $4x10^{-4}$ M Pu(VI) solution containing 0.01 M NaCl with its initial pHs between 3.2 and 6.3. Concentrations and oxidation states of Pu in the solutions were determined at 48 hours after the exposure. Sorbed Pu by *Bacillus subtilis*, kaolinite, and the mixtures was extracted with 1:1 H_3PO_4 solution for 5 minutes to determine its oxidation states. Oxidation states of Pu were determined by UV/VIS spectrometry. After 48 hours of the contact with Pu(VI) solution, Pu accumulated *Bacillus subtilis*, kaolinite and the mixtures were separated from the Pu(VI) solution, then were contacted with a 1 M CH_3COOK solution to examine reversibility of the sorbed Pu. Approximately 17% of the initial concentrations of Pu(VI) was sorbed by *Bacillus subtilis* at pH 3.2 and the amounts of the sorbed Pu increased with increasing pH. Similar trend was observed for the sorption of Pu on kaolinite. The oxidation state of Pu sorbed on *Bacillus subtilis* and kaolinite was Pu(IV) and Pu(VI), respectively at 48 hours after the contact. Approximately 30 and 90% of the sorbed Pu was desorbed from *Bacillus subtilis* and kaolinite in a 1 M CH_3COOK solution. The amounts of sorbed Pu increased and the desorbed fractions by a 1 M CH_3COONa solution decreased with increasing content of *Bacillus subtilis* in the mixtures. Oxidation state of the sorbed Pu on the mixture was IV. These results indicate that Pu is accumulated on *Bacillus subtilis* through precipitation of insoluble Pu(IV) due to the reduction of Pu(VI), and Pu(VI) is reversibly sorbed on kaolinite. Pu is preferably sorbed on *Bacillus subtilis* in the mixture because of the stronger association of Pu(IV) with *Bacillus subtilis* than Pu(VI). It is concluded that microorganisms function important roles in the migration of Pu(VI) in the environments.

B41D-0921 0830h POSTER

In situ bio-immobilization of Uranium and Technetium via indigenous soil microbes: preliminary study results

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Groundwater at Oak Ridge National Laboratory's Field Research Center (FRC) is contaminated with uranium and technetium, has pH as low as 3.3, and nitrate concentrations as high as 120 mM. The objective of this research was to determine if in-situ bio-immobilization is a viable treatment alternative for this water. A laboratory column packed with crushed limestone and bicarbonate was used to model in-situ pH adjustment. Denitrification and metal reduction were modeled with column experiments as well, using FRC sediment and ethanol as the electron donor. The limestone column maintained a pH of above 5 for nearly one hundred pore volumes without significant loss in hydraulic conductivity. The high nitrate (120 mM) column study provided rates of denitrification ($\sim$ 15.25 mM/day), ethanol utilization ($\sim$ 13 mM/day), and technetium reduction (120 pM/day) by indigenous microorganisms, while no uranium reduction was detected. Results of the low nitrate (3 mM) column experiment indicate that once the pH of FRC water is adjusted and nitrate is removed, uranium and technetium reduction, ($\sim$ 0.5 uM/day) and ($\sim$ 57 pM/day) respectively, proceed with ethanol as the electron donor. These preliminary findings demonstrate that microorganisms indigenous to FRC sediment are capable of reducing, and thus immobilizing uranium and technetium in small scale reactors. Intermediate scale models (3m long) were designed to simulate in-situ pH adjustment, nitrate removal, and radionuclide reduction, all in one continuous reactor. Preliminary data from the intermediate scale, high nitrate model indicates that nitrate, uranium, and technetium reduction are occurring. Large scale, in-situ bio-immobilization zones have the potential to prevent further radionuclide contamination of groundwater world wide.

B41D-0922 0830h POSTER

Impact of Calcium on Bacterial Reduction of U(VI) Under Advective Flow

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Due to mining and nuclear-production activities, uranium is now an environmental contaminant of great concern, the hazard of which can be diminished through

reduction of the oxidized species, uranyl, to reduced phases such as uraninite. Recent evidence, however, illustrates the importance of uranyl speciation on the extent of reduction. In the presence of calcium, a CaUO2-CO3 complex is the dominant aqueous species, greatly limiting abiotic and biotic reduction of uranium. This species is, in fact, the most stable form of U(VI) in waters equilibrated with atmospheric carbon dioxide levels and calcium concentrations $>$ 0.4 mM from pH 5 to 8. Here we explore the impact of calcium on uranium reduction rates and the concomitant biomineralization products of uranium and hydrous ferric oxide under dynamic flow conditions by a metal reducing bacterium, Shewanella putrefaciens. Using x-ray adsorption near edge structure (XANES) spectroscopy, we confirm the complete reduction of uranyl to the precipitated mineral uraninite in systems absent of calcium. While in contrast, minimal reduction transpires upon introduction of millimolar calcium concentration. Thus, calcium concentrations will have profound effects on bacterial reduction, and hence mobility, of uranium within surface and subsurface environments.

B41D-0923 0830h POSTER

Specific Detection and Direct Enumeration of Dehalococcoides sp. in a Chlorinated Solvent-Contaminated Aquifer

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Chlorinated solvents are among the most important groundwater contaminants since spills are very hazardous and difficult to clean up. Biological degradation is a promising remediation technology. *Dehalococcoides ethenogenes* strain 195 is the only known organism that is capable of complete reductive dehalogenation of tetrachloroethene to the innocuous product ethene. Hence, methods that detect and quantify this organism in environmental samples are needed to assess and potentially optimize bioremediation efficiency. The objective of this study was to directly enumerate *Dehalococcoides* sp. in a chlorinated solvent-contaminated aquifer using fluorescence in situ hybridization with recently developed 16S rRNA-targeting probes (Yang and Zeyer, 2003; AEM 69(5), 2879-2883)). The presence of *Dehalococcoides* sp. was verified qualitatively using PCR and sequencing. Furthermore, occurrence of *Dehalococcoides* sp. was related to concentrations of ethene, chlorinated solvents (PCE, TCE, cDCE, VC) and redox conditions. This study demonstrates the successful application of a novel tool to quantify *Dehalococcoides* populations directly in contaminated environments.

B41D-0924 0830h POSTER

Changes in Microbial Community Structure With Depth in a Simulated Vadose Zone Environment

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Little is known about how microbial processes affect contaminant transport in the vadose zone (bulk aerobic, nutrient poor, unsaturated). A combination of culture-independent and dependent methods was used to assess prokaryotic community structure in a large, meso-scale column reactor packed with soil from the Idaho National Engineering and Environmental Laboratories in southeast Idaho. Acridine orange direct cell counts, aerobic heterotrophic plate counts, denaturing gradient gel electrophoresis (DGGE), and 16S ribosomal DNA clone libraries were used to characterize the prokaryotic communities at four depths in the column: soil surface, 15cm, 168cm, and 192cm below the surface. No change in total cell count was seen with depth. Aerobic plate counts decreased with depth and number of colony morphologies seen increased from the surface to a depth of 15cm and decreased to 192cm below the soil surface. Extractable DNA concentrations increased between the surface and the 15cm sampling port but remained constant at the remaining depths. Polymerase chain reaction using eubacterial primers provided DNA for DGGE and the clone libraries. DGGE indicated the number of different community members and their relative abundances changed at each depth. Five of the 65 total bands seen were common to all four depths. Clone libraries were constructed for each depth. The number of different clones represented remained relatively constant between depths but the proportions of members present changed. At least 20 different known taxa were represented throughout the column. Aerobic and facultative anaerobic bacteria dominated the surface. A few *Clostridia* were also observed, likely as spores since they are obligate anaerobes. The 15cm depth was dominated by *Clostridia* and facultative anaerobes. Sulfate reducing bacteria and members of the genus *Aquaspirillum*, the genus *Flexibacter*, and the phylum *Verrucomicrobia* were present at all depths but co-dominated the two lowest depths. These changes in microbial community structure occurred along a gradient of decreasing oxygen and increasing carbon dioxide with depth. Mössbauer spectroscopy indicated that iron was lost from the system concomitant with the shift in microbial community structure towards facultative anaerobes. These data indicate that microbial processes within hypoxic microsites may be important in the upper 15cm, and that anaerobic microbial processes in general may be important within this simulated vadose zone environment.

B41D-0925 0830h POSTER

Partitioning of Sr^{2+} into Calcite Precipitates Induced by Bacterial Ureolysis in Artificial Groundwater.

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A suite of experiments were performed to investigate the partitioning of Sr^{2+} (to mimic the radionuclide ^{90}Sr) between calcite and groundwater, in response to the hydrolysis of urea by *B. pasteurii* under simulated in-situ aquifer conditions. Three duplicate experiments were performed at 25°C over 8 days in microcosms inoculated with *B. pasteurii* ATCC 11859 and containing an artificial groundwater (AGW). The AGW composition was based upon the aqueous chemistry of the metal and radionuclide contaminated Snake River Plain Aquifer, Idaho,USA. Microcosms also contained 25 mM urea, and 1 mM of Sr as a contaminant treatment. Control experiments were run with non urea hydrolyzing bacteria, *B. subtillus*. Control experiments exhibited little change in pH, and dissolved ammonium and Ca^{2+} concentrations. Conversely during experiments inoculated with *B. pasteurii*, ammonium production increased asymptotically, peaking two days into the experiment when approximately all urea had been hydrolyzed. The production of ammonium and bicarbonate from urea hydrolysis caused an asymptotic increase in pH from 6.5 to 9.1 one day into the experiment. Dissolved Ca^{2+} and Sr^{2+} decreased asymptotically from the beginning of the experiment, and was accompanied by the development of solid precipitates identified as calcite by X-Ray diffraction. This caused an asymptotic decrease in the saturation state of calcite (S) after one day of the experiment. Specific rate constants were derived for calcite precipitation and critical saturation state from the time course data following a second-order chemical affinity based law. Calcite precipitation rate is fundamentally controlled by, and exhibits a positive association with S. Mass balance indicates the percentage of total Sr (dissolved and in calcite) incorporated into the calcite precipitate increases rapidly to 59 % after two days of the experiment, and increases less rapidly thereafter to a maximum of 67 %. Corresponding measured distribution coefficients (D_{Me}) exhibit a positive association with S and calcite precipitation rates. Therefore D_{Me} is greatest after one day of the experiment (D_{Me} maximum = 0.39), which corresponds to the highest S and calcite precipitation rate, and decreases thereafter (D_{Me} minimum = 0.16) as S and calcite precipitation rate decreases. Therefore the extent of Sr incorporation into calcite precipitates resulting from the hydrolysis of urea by *B. pasteurii* appears to be a primary function of precipitation rate, which is controlled by S. The median D_{Me} determined by this study (0.22) is greater than previously published coefficients for Sr in calcite by up to an order of magnitude. This demonstrates the potential of calcite precipitation by bacterial ureolysis as a remediation strategy for ^{90}Sr in calcite saturated aquifers.

B41D-0926 0830h POSTER

Insight From EXAFS and the Multi Site Complexation Model (MUSIC) Into the Discrepancy Between SCM-Predicted and Experimental pH-Dependent Ni Sorption to Hydrous Manganese Oxyhydroxide

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Hydrous manganese oxyhydroxides (HMO) are receiving increasing attention from both geomicrobiologists, due to the importance of microbial catalysis in their formation, and trace element geochemists, due to their importance as trace metal sorbents in a wide number of environments. Accurate models of the mechanisms of trace metal sequestration in association with HMO are thus required for an overall understanding of metal reactive transport. We have examined the utility of a surface complexation model to describe pH-dependent Ni sorption to synthetic HMO, a layered oxide comparable in structure to microbially-catalyzed Mn oxide. Surface complexation models (SCM) have successfully reproduced metal and proton binding curves to a number of geochemically relevant solids, including bacteria and mineral surfaces. However, because these models are derived from potentiometric titrations, they have intrinsic limitations; very high and very low proton affinity sites cannot be characterized. Results from our study indicated that Ni sorption to HMO could not be described by assuming Ni sorption to the SCM-derived proton binding sites. Ni sorption capacity of the solid far exceeded proton binding capacity at low pH values. Examination of the Ni-sorbed HMO samples with EXAFS indicated that the discrepancy between Ni sorption and proton binding could not be ascribed to the precipitation of a separate Ni solid phase. Rather, all at pH values examined (2.0, 4.0 and 6.5) Ni sorbed above/below layer vacancies in the MnO_6 octahedral layers of HMO, as interlayer tridentate corner-sharing complexes. At circumneutral pH (6.5), Ni also substituted directly for structural Mn. A theoretical pK_a spectrum was derived for HMO using the multi site complexation model (MUSIC) and proton affinity constants for surface functional groups relevant for Ni sorption, as constrained by EXAFS, were identified. Ni sorption as an interlayer complex occurred at sites with very high proton affinity, thus accounting for the under-prediction of Ni sequestration at low pH by the SCM. These results indicate that prediction of Ni sequestration to HMO requires the integration of molecular level speciation of Ni with theoretical and experimentally derived surface modeling approaches. Further, the results of this study are likely to have far reaching implications for modeling trace metal interactions with a number of important sorbent surfaces.

B41D-0927 0830h POSTER

Limits of Microbial Photosynthesis in Hot Spring Ecosystems

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The limits of microbial photosynthesis are determined by many environmental factors including light availability, temperature, pH, flow rate, nutrient abundance, chemical composition and the presence or absence of other microorganisms. In an effort to determine which factors have the greatest influence on the limits of photosynthesis, we conducted a field study in the summer of 2003 at Yellowstone National Park. At more than 75 locations temperature, pH, conductivity, and sulfide measurements were made in the field, and at many of these locations samples were collected for major and trace element measurements and organic analyses. Temperatures ranged from 32 to 93°C, conductivities from 790 to 11500μS, *in situ* pH from 1.87 to 8.97, and total sulfide concentrations from 1850μg L^{-1} to below detection ($\sim$2μg L^{-1}). These data indicate that the previously established upper temperature limit for photosynthesis of 73°C is reached in many

alkaline hot springs, but that upper temperature limits decrease with decreasing pH below ~7. As an example, we found no strong evidence for photosynthesis above 45°C at pH ~2. In several locations, photosynthesis appears to be suppressed despite temperatures and pH values that permit photosynthesis elsewhere. Preliminary results indicate that salinity variations are not responsible for suppression of photosynthesis, but that sulfide concentrations may be. Studies of five hot spring outflow channels, together spanning pH values from 2.5 to 8.6, show that photosynthesis appears once sulfide concentrations drop to < 20% of the source values. In one channel where total sulfide varies by only a factor of two over more than 100 m of flow, we found no evidence of photosynthesis despite temperatures ranging from 60 to 35°C and mild pH values of 5.8 to 6.5. These observations lead us to propose that photosynthesis becomes possible after a large decrease in initial sulfide concentration. Although abiotic processes (degassing, mineral precipitation, surface reactions) may explain decreases in total sulfide concentrations, preliminary results suggest that rates of microbial sulfide oxidation determine whether hot spring habitats become suitable for microbial photosynthesis. Alternatively, once sulfide concentrations decrease below some threshold level sulfide oxidizers may be outcompeted by photosynthesizers.

B41D-0928 0830h POSTER

Effects of Siderophores on Metal Adsorption to Kaolinite

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Siderophores are metal-complexing ligands with high affinities for Fe(III), produced by many microorganisms in Fe-deficient environments. Siderophores can also form strong complexes with other metals such as Pb and Cd; hence, siderophores may play an important role in controlling metal mobility in porous media. This study compared the effects of siderophores desferrioxamine-B (DFO-B), desferrioxamine-D (DFO-D1), desferrioxamine-E (DFO-E), as well as siderophore-like ligand acetohydroxamic acid (aHA) on Pb and Cd adsorption to kaolinite (KGa-1b) at pH 4.5 to 9, in 0.1 M $NaClO_4$, at 22 °C, in the dark. At pH > 6.5 all of the siderophores plus aHA, inhibited Pb adsorption, with inhibition increasing in the order aHA < DFO-D1 < DFO-B < DFO-E. At lower pH, all four ligands slightly enhanced Pb adsorption. These ligands also inhibited Cd adsorption at high pH, but had little or no effect at low pH. These results suggest that siderophore effects on metal mobility through porous media are likely to be complex and variable with pH.

B41D-0929 0830h POSTER

Isotopic Analyses of a new Cold Seep locality, Guenoc Ranch, Great Valley Group, Northern California

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A new Mesozoic cold seep limestone locality has been discovered in Great Valley Group (GVG) forearc strata of the Guenoc Ranch, bordering southeast Lake and northern Napa counties, northern California. Numerous scattered outcrops occur over 4 km, of which one petroliferous deposit (extending across 1.8 km) has been analyzed in detail. Petrographic and paleontologic observations indicate that this limestone unit formed via cold seep related processes during deposition of the GVG. Petrographic observations show clotted microbial and detrital micrite, pyritic corrosion surfaces, burrows, foraminifers, wood fragments, as well as fibrous, yellow, and sparry calcite; all of which are components typical of hydrocarbon seep deposits in the GVG. Lucinid and solemyid bivalves are also present, as are both large and small worm tubes, gastropods, and a Campanian (?) ammonite. The petrographic and paleontologic analyses strongly suggest that the Guenoc material resulted from venting methane. Carbon and oxygen isotope analyses are also being performed on the various micrites and cements seen in the Guenoc thin sections to add credence to the cold seep origin. Preliminary isotopic values for carbon and oxygen fall into the known range for cold seeps found within the GVG and worldwide. Generally, $\delta^{13}C$ values have been found to vary from seep to seep, ranging anywhere from -110 per mil to -20 per mil. Assuming no post-depositional alteration has occurred, values heavier than -20 per mil can still indicate a partial influence of venting methane on the carbon being incorporated into the carbonate. If post-depositional alteration has occurred however, the results of the isotopic data are inconclusive until further analyses are performed to ascertain the degree of alteration.

B41D-0930 0830h POSTER

What explains the sulfur isotope fractionation observed in the aquifer system of Puebla Valley, Mexico?

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Puebla Valley, Mexico is located in the central part of the Trans Mexican Volcanic Belt and is surrounded by 3 large volcanoes: Popocatepetl (active since 1994), Iztaccihuatl (extinct), and Malinche (dormant). The aquifer system of the Valley contains at least two productive units: an unconfined aquifer formed mainly of alluvial and volcanic deposits and a second, confined aquifer, which has chemically distinct water that is sulfur-rich, high in CO_2, and high in alkalinity. There is a current debate about the origin of the sulfur-rich water, which is being used, after treatment, to lessen the deficit of water supply to the city of Puebla (with a population of approximately 1.5 million). Sulfate and sulfide species in water from the confined aquifer have an average sulfur isotope fractionation difference of 24.6 %. This fractionation is, at least in part, the result of bacterial sulfate reduction as evidenced by testing for bacteria with BART kits. Molecular analysis to identify the specific bacteria is underway. However, analysis of carbon isotopes of dissolved CO_2 (with average delta ^{13}C of 4.4%) and $^3He/^4He$ with average ratios of 2.1 for specific wells, located in the upper aquifer and characterized by having low sulfate but also rich in CO_2 and alkalinity, suggest a possible magmatic component. The carbon and helium isotope analysis of water from the confined aquifer is currently underway.

B41E MCC: 3014 Thursday 1020h

Regional-Scale Isotopic Interactions Between the Biosphere and the Atmosphere II *(joint with A, H, OS, GC)*

Presiding: **D Pataki,** University of Utah**; J Ehleringer,** University of Utah

B41E-01 1020h INVITED

Selective Logging Disturbance And Isotopic Composition Of Repired CO2 In Western Amazonia, Brazil

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Understanding the controls of gas exchange in primary and disturbed forests within the Amazon Basin is central to understanding the global carbon cycle, since tropical forests account for 40% of the carbon stored globally in terrestrial biomass. Stable isotope ratio analyses (13C, 18O) of atmospheric CO2 provide useful information regarding the balance between photosynthetic carbon gain and respiratory carbon loss in rainforest ecosystems and of the stomatal constraints on photosynthetic gas exchange. One useful isotopic parameter we have measured is the carbon isotope ratio of all respiration emerging from the ecosystem (del13Cr). Our recent observations suggest a direct relationship between logging activities and del13Cr values in these forests. Logging activities at the LBA site in Santarem, Para, began with the removal of lianas before the dry season and afterward selective logging. This logging activity opened the forest and resulted in a 4per mil shift in del13CR. During the following wet season (2002/2003), eddy covariance measurements at the logged site reported increased ecosystem gas exchange. Coincident with this increase in net ecosystem exchange, we observed a decrease in del13CR consistent with a decreased stomatal limitation on photosynthetic gas exchange in the logged forest.

B41E-02 1035h

Temporal variability in 13C of respired CO2 in a pine and a hardwood forest subject to similar climatic conditions

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The temporal variability in the 13C of ecosystem (äCr), soil (äCs) and foliage (äCf) respired CO2 were contrasted in a 18 m tall evenly aged loblolly pine forest and in a 35 m tall unevenly aged mature second growth deciduous mixed hardwood forest in North Carolina, USA, over a two year period. These two sites are located within a kilometer of each other and are subject to identical climatic and edaphic conditions. äCr varied in response to time lagged vapor pressure deficit (VPD) at both forests. However, the response of äCr to VPD was more dynamic at the pine relative to the hardwood. äCr at the pine forest varied from -31.0 to -26.4 per mill and at the hardwood forest from -26.0 to -27.0 permill during the growing season. äCr at the hardwood forest was 13C enriched during the growing season, on average, by 1.4 permill relative to äCr at the pine forest for the same time periods. Three factors influence these results. Canopy height and composition were different between the two sites, and also at the pine forest äCr values generally were more similar to äCf values, while at the hardwood forest, äCr values were more similar to äCs values. At the hardwood forest, the temporal variability in äCs was less that of äCf and buffered changes in the äCr. The results indicate that within a forest mosaic the vegetation structure needs to be considered for predicting realistic äCr values. Inclusion of a temporally and spatially variable äCr into the atmospheric inversion models will lead to a more realistic estimate of the partitioning of the global carbon uptake into oceanic and terrestrial sinks. Because äCr within each ecosystem varies in response to VPD in a predictable fashion, a variable äCr can be incorporated to better constrain atmospheric inversion models.

B41E-03 1050h

Disequilibrium of $^{13}CO_2$ fluxes between photosynthesis and respiration in North American temperate forest biomes

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