

B32A-0110 1330h POSTER

Soil Organic Carbon Redistribution by Geomorphic Processes in an Undisturbed Zero Order Annual Grassland Watershed, California

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Despite the crucial role of soils in global carbon cycle, the sizes of soil organic carbon (SOC) pools and relevant fluxes are still in debate. We studied the extent which topography regulates SOC pools and fluxes through geomorphic processes (erosion, deposition, and episodic hollow evacuation) in an undisturbed zero order annual grassland watershed of Tennessee Valley California (site area: 100m×70m, MAP:760mm, MAT:16°C). We systematically measured soil thickness, bulk density, texture, carbon and nitrogen content to the depth of bedrock contact for 69 soil pits (and plant C inputs at 44 aboveground 25×25 cm quadrats) along diverging slopes (average slope: 28%) and in the adjacent hollow. We performed a high resolution (<1m) topographic survey of the area using a total laser station with centimeter scale accuracy. Survey data was used to create a topo map and calculate the 2 dimensional slope curvature using Kriging method. Over the diverging slope, in general, soil thickness (5 to 92cm) and SOC storage (3.8 to 17.0 kgC/m²) tend to increase downslope despite their significant variations with local topographic curvature. Hollow soils are thicker (71 to 270cm) and have higher SOC storage (17.5 to 28.6 kgC/m²). However aboveground plant C inputs in the upper hollow (75 to 187 gC/m²/yr) were not higher than those of diverging slope (42 to 336 gC/m²/yr), suggesting the importance of the burial and reduced decomposition rate of SOC eroded from adjacent slopes. By combining a diffusion soil transport law (which is a function of topographic curvature and soil thickness) and a carbon decomposition model, we determined the rate of SOC erosion losses from divergent slopes and reconstructed SOC storage in the hollow over time scale of 10k years. This empirically constrained model provides the mechanistic explanation of the observed topographic pattern of SOC storage.

B32B MC: Hall D Wednesday 1330h

Metals in Soil and the Environment (joint with H)

Presiding: K Dawson, University of Alabama

B32B-0111 1330h POSTER

Conditional Sampling for Measuring Mercury Vapor Fluxes

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Surface to atmosphere mercury fluxes are difficult to measure accurately. Current techniques include dynamic flux chambers and micrometeorological gradient and aerodynamic approaches, all of which have a number of intrinsic problems associated with them. We have adapted conditional sampling, a micrometeorological technique commonly used to measure other trace gas fluxes, to measure surface to air mercury fluxes. Our initial flux measurement campaign over an agricultural soil consisted of two one-week measurement periods, and was longer in duration than any previously reported measurement period. Fluxes during

both measurement periods ranged between 105.25 ng m⁻² h⁻¹ (evolution) and 34.95 ng m⁻² h⁻¹ (deposition) with an average evolution of 6.6 ng m⁻² h⁻¹. The data showed significant diurnal trends, weakly correlated with shallow soil temperatures and solar radiation. Poor conditions for micrometeorological techniques plagued the system throughout the measurement period, and increased uncertainty in the data collected. However, this initial trial run indicates that conditional sampling has much promise for the accurate quantification of both short and long-term mercury fluxes.

B32B-0112 1330h POSTER

Heavy Metals Concentrations in top Soils of Urban Areas (Naples Southern Italy) as an Indicator of Anthropogenic Origin.

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Heavy metals pollution, which mainly originates from automobile exhausts and industry, is a serious danger for human health. The source and extension of heavy metals pollution in the top soils has been studied extensively in the past 30 years. The role of the soil processes in accumulating or mobilising metals is very important in environmental science due to the central position of the soil in the hydrological cycle and ecosystem. Concentrations of heavy metals in top soils, collected in green areas and public parks in metropolitan Naples area have been determined to provide information on specific emission sources. In addition to toxic metals, such as Pb, As, Cd, Cr and others, we have investigated the top soils as well for Pt group elements (PGEs), because since 1993 it is mandatory within EC for all new petrol driven motor vehicles to be equipped with Pt/Pd/Rh catalytic converter. In Italy this law has come into effect in 1998, but still is allowed to old vehicles use lead gasoline, though now the big majority of cars is equipped with Pt/Pd/Rh catalytic converters. Emission of abraded fragments of catalytic converters in vehicle exhausts will certainly determine environmental contamination with Pt group elements (PGEs), since many Pt complexes are highly cytotoxic and, in small dose, are strong allergens and potent sensitiser. The metropolitan area of Naples due to intense human activities and vehicles traffic is an interesting area to be monitored in order to check the pollution state of the soils. The geology of the area is prevalently represented by volcanics, erupted from the Upper Pleistocene to Recent by Mt. Somma-Vesuvius on the east and the Campi Flegrei fields on the west. To compile multi-element geochemical maps baseline we have sampled in situ and transported top soil for a total of 200 samples. The survey have been carried at about 200 sites covering an area of about 120 Km², with a grid of 0.5 x 0.5 km in the highly urbanised area and 1 km x 1 km in the sub urban areas. In each sampled site has been determined the pH (5.93- 8.21); and measured partial and total radioactivity (U, Th, K) using a portable scintillometer. All soil samples were analysed for 40 elements by ICP-MS and AES. The data for some of the harmful metals (as mg Kg-1) range as follows: Cd from 0.03 to 6.9, Cr from 0.8 to 189, Ni from 0.8 to 67, Pb from 17 to 2052, Co from 3 to 37, Hg from 0.01 to 2.6, Pt from 0.001 to 0.1, Pd from 0.002 to 0.052. The geochemical data, have been processed by means of GIS to compile geochemical single element distribution, R-mode factor analysis element associations and risk maps. The latter in particular, are useful to enhance areas potentially at risk for residential/recreational and commercial/industrial land use, following intervention criteria fixed by Italian

B32B-0113 1330h POSTER

Arsenite Oxidation by Anaerobic Bacteria in Mono Lake, California

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Mono Lake, California is a meromictic soda lake (pH = 9.8; salinity = 70-90 g/L) with exceptionally high arsenic content (200 μM) derived from hydrothermal sources. Previous work has shown that arsenic speciation changes from arsenate [As(V)] to the more reduced arsenite [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 (Oremland et al., 2000). Depth profiles of arsenic speciation indicate that a small amount of As(V) exists in the anoxic bottom waters, suggesting a constant resupply by microbial oxidation of As(III). Anaerobic microbial oxidation of As(III) to As(V) was first noted in arsenate-enriched anoxic bottom water amended with nitrate, where nitrate addition caused a rapid microbial re-oxidation of arsenite to arsenate (Hoefft et al. 2001). In following, we conducted time course experiments with As(III)-amended bottom waters supplemented with either 5 mM nitrate, Fe(III)-NTA or nitrite. Nitrate-amended waters formed As(V), while killed controls did not form significant amounts and 5 mM nitrate was completely reduced to 5 mM nitrite by the end of the incubation. Live samples amended with 5mM Fe(III)-NTA produced As(V) that exceeded production of As(V) in killed controls, while nitrite-amended waters formed As(V) in excess of killed controls after an initial lag. We isolated a pure culture, strain MLHE-1, that grows in minimal salts media by oxidation of As(III) to As(V) with the reduction of equivalent quantities of nitrate to nitrite. Strain MLHE-1 appears to be a chemoautotroph. These results demonstrate that the cycling of As(V) and As(III) can be sustained in the absence of oxygen. This has implications not only for the recycling of As(V) in Mono Lake's bottom waters, but also for the mobility of arsenic in aquifers as well.

Oremland, R.S. et al. 2000. *Geochim. Cosmochim. Acta* 64: 3073-3084. Hoefft, S.E. et al. 2001. *Geomicrobiol.* In press.

B32B-0114 1330h POSTER

Zinc Adsorption on Fe(II)/Fe(III) Substrates Produced by Microbial Reduction of High-Surface-Area Goethite, Medium-Surface-Area Goethite and Lepidocrocite

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A series of experiments were performed to investigate the influence of bacterial reduction on Zn²⁺ adsorption by Fe(III) oxyhydroxides. Lepidocrocite, high-surface-area (HSA) goethite, and medium-surface-area (MSA) goethite were synthesized with measured BET surface-areas of 75²/g, 225m²/g and 48 m²/g, respectively. Zinc adsorption isotherms were determined for the unreduced mineral phases at aerobic conditions from pH 5.5 to 7.5 in a matrix of artificial groundwater (AGW). The isotherm data for zinc adsorption onto HSA goethite were pH-independent over the studied pH range, with <5% variation in zinc adsorption. Isotherm data for lepidocrocite and MSA goethite showed pH-dependence with up to 65% variation in zinc adsorption over the pH and concentration range used.

Incubation experiments were performed in which lepidocrocite, HSA goethite or MSA goethite served as the electron acceptor for the dissimilatory iron reducing bacterium (DIRB) *Shewanella alga* in a matrix of AGW under anaerobic conditions. The incubation bottles were sampled at various time intervals to establish the effects of progressive iron reduction on the zinc adsorption capacity of the solid material. Batch experiments were then conducted equilibrating AGW solutions of zinc with incubation experiment substrates to produce adsorption isotherms at various stages of reduction. The results of these experiments showed a decrease of about 10 to 15% in the adsorption capacity of the reduced substrate compared to the original HSA goethite. Incubation experiments for lepidocrocite only produced <1% reduction of Fe(III) after a period of several months. *S. alga* incubations containing MSA goethite have produced 4% reduction in Fe(III) after a period of approximately 5 months. Experiments are currently underway to determine the effects of bacterial reduction of the MSA goethite on Zn²⁺ adsorption. The data produced from these experiments will then be fit using the Freundlich and Langmuir adsorption models to predict the effect of bacterial reduction on the adsorption capacity of Fe(III) oxyhydroxides. The results of these experiments will improve our understanding of the biogeochemical processes that affect the mobility of metals in anaerobic groundwater systems.

B32B-0115 1330h POSTER

Effects of Air Pollutants on Lichens of the Idaho National Engineering Laboratory National Environmental Research Park

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The Idaho National Engineering and Environmental Laboratory is a (2300 square km) National Environmental Research Park that has been used for research and operational support of nuclear power. The Park includes scattered industrial operations and provides an ideal setting to study effects of industry on semi-arid environments. One of the facilities on the Research Park is the Idaho Nuclear Technology Center (INTEC). This facility reprocessed spent nuclear fuel from the US Navy, and its operations included heating acidic solutions to convert wastes to a solid form. The conversion released nitrogen oxides, low levels of other gases (including HF), and small amounts of solid particles through a facility stack. A fossil-fuel power plant also contributed airborne contaminants including sulfur dioxide.

A 1985 study identified the effects of INTEC operations on the health of lichens *Xanthoria polycarpa* (quantified using electrolyte leakage), on levels of trace metals in the lichens *X. polycarpa* and *Rhizoplaca melanophthalma*, and on the levels of trace metals in higher plants and soils. The study concluded that operations impacted the physiological health of *X. polycarpa* southwest of the plant, and that lead was significantly higher downwind of the plant relative to other locations. Effects of the plant were re-examined in 1999 as part of an Environmental Impact Statement to evaluate the environmental effects of measures available to deal with radioactive waste at INTEC.

Sulfur dioxide emissions from the facility decreased from approximately 375 tons/year to approximately 10 tons/year between the two studies. The re-examination of lichens showed that the measure of physiological health used in the previous study (conductivity of rinsates collected from lichen thalli) correlated well to the levels of potassium measured in rinsates collected from thalli. There, however, was no correlation between the levels of potassium/conductivity of such rinsates and the levels of total potassium in lichens or between levels of potassium/conductivity and macroscopic vigor of the lichens or between levels of potassium/conductivity in rinsates and chlorophyll ratios (another common indicator of the physiological health of lichens). This suggests that potassium levels in rinsates may not be a good indicator of physiological stress.

X. polycarpa abundance varied with direction from the facility. The species was lacking from background locations at Craters of the Moon National monument. Cover on dead *Artemisia tridentata* twigs varied between 2 and 5% downwind and crosswind for the predominant wind direction, but approached 75

Calcium levels in *R. melanophthalma* around INTEC were significantly higher than calcium levels in lichens from the background location at Craters of the Moon. This may reflect migration of the species to more buffered calcium carbonate substrates in response to acidified precipitation. Levels of calcium in *R. melanophthalma* fell between the two studies, possibly reflecting less substrate acidification during the later period. Lead was not significantly elevated during the second study, but mercury may be elevated downwind of the facility.

B32B-0116 1330h POSTER

Surface Characteristics and Reactivity for Nickel of Synthetic Mn Oxyhydroxides Exposed to Varying Regimes of Wet and Dry Conditions

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In acid mine drainage systems where pH values are commonly below 4, i.e. where Fe oxyhydroxides were

typically be positively charged, other mineral surfaces may play a more significant role in metal sorption. Our group has been investigating the biogeochemical processes controlling metal transport from mine tailings around Sudbury (ON). From these field investigations, it has become evident that Mn oxyhydroxides play a key role in retention of metals in surface tailings seepage streams. These surface seepage streams are typically shallow and show great variation in the extent of water coverage of the streambed. Thus, there are periods when significant border areas are dried out. Variable wetting and drying of these small, reactive minerals is likely to affect their surface characteristics and thus alter their sorptive capacities for metals. The objectives of this laboratory study were to evaluate: the surface characteristics of synthetic Mn oxyhydroxides under three regimes designed to simulate hydrologic conditions that Mn oxyhydroxides experience in our field site (1., wet, freshly precipitated; 2., dry (dried for 19 days at 37 deg. C); and 3., wet-dry cycle (three cycles of dried at 37 deg. C for 72 hours, followed by hydration for 72 hours for a total of 19 days)); and the relative sorptive capacities of these three Mn oxyhydroxides for nickel.

Mn oxyhydroxides were synthesized by oxidizing Mn²⁺ with permanganate. Once precipitated, the fresh Mn oxyhydroxides were separated into three aliquots for the three hydrologic regimes. The wet sample was immediately titrated; while the dry and wet-dry cycle samples were placed in the oven for their respective drying times. Samples were also taken from each Mn oxyhydroxide sample for mineralogical identification by X-Ray diffraction (XRD). All titrations were carried out using a Mettler Toledo DL70 automatic titrator under N₂ atmosphere. All titration solutions were made up in an anaerobic chamber and degassed for 10 minutes under N₂ once assembled in the titration system, prior to titration of the Mn oxyhydroxides. Titrations were carried out in 0.1 M ionic strength medium (KNO₃). Titration results were modelled using a linear programming method (LPM) to determine pK_a values and binding site densities. The respective sorptive capacities for Ni, of the three Mn oxyhydroxide regimes were also evaluated in sorption batch experiments. Triplicate experimental systems were set up for each Mn oxyhydroxide using 0.1M Ni at three pH values: 2, 4 and 6. The batch systems were shaken and the pH monitored over an 18 hour equilibration time. Ni concentrations were then analysed by ICP.

Results of these experiments indicate differences in surface characteristics of the three Mn oxyhydroxide systems. All show a strong site around pH 2. However the number and types of surface sites varied amongst the three treatments. Further, their relative reactivities for Ni also varied. In general, the dried Mn oxyhydroxides appeared to sorb the most Ni of the three treatments. Results of these experiments will be presented and their implications for metal reactive transport in the field site discussed.

B32B-0117 1330h POSTER

Mercury loss from the forest floor during wildland fire

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Gaseous elemental mercury in the atmosphere is transferred into a forest environment by wet or dry deposition onto the forest floor, creating a repository of mercury that is bound to organic carbon. During forest fires, biomass burning and soil heating can release mercury by vaporization and combustion. The USGS is conducting research to quantify mercury sources and sinks in forested ecosystems including mercury emissions during and after wildland fire. Concurrently, we are developing sampling and analytical techniques that will standardize sample and data collection. Samples of forest floor material and organic soils were collected before and after a prescribed burn at 10 sites in a northern hardwood/pine forest in Minnesota and at 18 sites in a black spruce/feathermoss forest in interior Alaska. In Minnesota, all of the forest litter and duff, originally 1-4 cm thick, was burned from four of the samples sites, exposing bare mineral soil. The calculated average mercury emission from burned organic material varies from 0.001 to 0.005 g Hg/m² of area burned. In Alaska, about 1/3 of the forest floor, originally 20 cm thick, was consumed by the fire, with losses of approximately 0.001 g Hg/m². In both studies, the calculated mercury emissions are highly dependent on the original nature of the forest floor and fire severity. These two studies indicate a significant global source of mercury emissions during wildfires.

B32B-0118 1330h POSTER

Dissimilatory Reduction of Elemental Selenium to Selenide in Sediments and Anaerobic Cultures of Selenium Respiring Bacteria

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Selenium contaminated environments often contain elemental Se (Se⁰) in their sediments that originates from dissimilatory reduction of Se oxyanions. The forms of Se in sedimentary rocks similarly contain high proportions of Se⁰, but much of the Se is also in the form of metal selenides, Se⁻². It is not clear if the occurrence of these selenides is due to microbial reduction of Se⁰, or some other biological or chemical process. In this investigation we examined the possibility that bacterial respiratory reduction of Se⁰ to Se⁻² could explain the presence of the latter species in sedimentary rocks. We conducted incubations of anoxic sediment slurries amended with different forms of Se⁰. High levels of Se⁰ (mM) were added to San Francisco Bay sediments in order to enhance the detection of soluble HSe⁻, which was precipitated with Cu²⁺ then redissolved and quantified by ICP-MS. Concentrations of HSe⁻ were highest in live samples amended with red amorphous Se⁰ formed by either microbial reduction of Se⁺⁴ ("biogenic Se⁰") or by chemical oxidation of H₂Se(g) ("chem. Se⁰"); very little HSe⁻ was

formed in those amended with black crystalline Se⁰, indicating the general lack of reactivity of this allotrope. Controls poisoned with 10% formalin did not produce HSe⁻ from additions of chem. Se⁰. Reduction of both forms of red amorphous Se⁰ to HSe⁻ occurred vigorously in growing cultures of *Bacillus selenitireducens*, an anaerobic halophile previously isolated from sediments of Mono Lake, CA. Up to 73% and 68% of red amorphous, biogenic Se⁰ or chem. Se⁰, respectively, was reduced to HSe⁻ during growth of *B. selenitireducens*, (incubation time ~ 200 hrs): oxidation of lactate to acetate as well as cell density increases indicated that a dissimilatory reduction pathway was likely. Reduction was most enhanced when cells were previously grown on elemental sulfur or Se⁺⁴. In contrast to the growth experiments, washed cell suspensions of *B. selenitireducens* exhibited no HSe⁻ production when amended with red amorphous or black Se⁰; however, they could convert up to 34% of added Se⁺⁴ to HSe⁻ after its complete reduction to Se⁰ first occurred. These findings indicate that reduction of Se⁰ in sediments to HSe⁻ or metal selenides is a bacterial dissimilatory process, that explains the presence of selenides in some sedimentary rocks.

B32B-0119 1330h POSTER

Metal Transport, Heavy Metal Speciation and Microbial Fixation Through Fluvial Subenvironments, Lower Coeur d'Alene River Valley, Idaho

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The lower Coeur d'Alene River Valley of northern Idaho is the site of extensive lead and zinc contamination resulting from both direct riverine tailings disposal and flood remobilization of contaminated sediments derived from the Coeur d'Alene mining district upstream. Variations in the hydrologic regime, redox conditions, porosity/permeability, organic content and microbial activity results in complicated metal transport pathways. Documentation of these pathways is a prerequisite to effective remediation, and requires accurate analysis of lateral and vertical variations. An analytical approach combining sequential extraction, electron microscopy, and microanalysis provides a comprehensive assessment of particulate speciation in this complex hydrologic system. Rigorously controlled sample preparation and a new sequential extraction protocol provide unprecedented insight into the role of metal sequestration in fluvial subenvironments. Four subenvironments were investigated: bedload, overbank (levee),

marsh, and lacustrine. Periodic floods remobilize primary ore minerals and secondary minerals from upstream tailings (primarily oxyhydroxides, sulfides and carbonates). The bedload in the lower valley is a reducing environment and acts as a sink for detrital carbonates and sulfides moving downstream. In addition, authigenic/biogenic Fe, Pb and Zn sulfides and phosphates are common in bedload sediments near the sediment/water interface. Flood redistribution of oxide, sulfide and carbonate phases results in periodic contaminant recharge generating a complex system of metal dissolution, mobilization, migration and precipitation. In levee environments, authigenic sulfides from flood scouring are quickly oxidized resulting in development of oxide coated grain surfaces. Stability of detrital minerals on the levee is variable depending on sediment permeability, grain size and mineralogy resulting in a complex stratigraphy of oxide zones mottled with zones dominated by detrital and authigenic carbonate and sulfide phases. Marshes subjected to periodic sub-aerial exposure/flooding are even more complex and dominated by authigenic and biogenic mineralization. Lacustrine environments are dominated by nanocrystalline inorganic and biogenic sulfide minerals in the upper third of the contaminated sediment column with increasing amounts of silt sized detrital sulfides (especially sphalerite) closer to the premining surface.

In pH-neutral subenvironments within the wetlands and lateral lakes of the lower Coeur d'Alene River Valley, microbial fixation plays a critical role in sequestering metals. Complex metal oxyhydroxide phases provided via flood recharge to river edge, marsh and lacustrine environments rapidly dissolve upon encountering anoxic conditions. Microbial activity is extremely effective in removing heavy metals from the water column, producing a nanocrystalline biofilm substrate characterized by ZnS (sphalerite) and non-stoichiometric PbS, FeS, and mixed metal sulfides. These solid phases are inherently unstable, and the sequestered metals become readily available through changes in redox or pH conditions, particularly dam-controlled annual fluctuations in base level, or during removal by bottom-feeding aquatic water fowl. The recognition of the inherent complexity and instability of microbially produced sulfidic material in a pH-neutral environment has important implications for remediation efforts utilizing wetland filtration methods.

B32C MC: 135 Wednesday 1330h

Biological Mineralization: Early and Extreme Environments II (joint with OS, P, PP, MR)

Presiding: P M Dove, Virginia Polytechnic Institute and State University; J J DeYoreo, Lawrence Livermore National Laboratory

B32C-01 1330h INVITED

Detection of Bacterial Magnetofossils with Ferromagnetic Resonance and Rock Magnetic Techniques

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Intracellular biomineralization of magnetite is a biochemical process used by members of the Bacteria, Protist, and Animal kingdoms, and the fossil remains of this process on Earth (termed magnetofossils) have been documented in sediments as old as the 2 Byr Gunflint Chert. Magnetofossils 4 Byr old have also been reported from carbonates in the Martian meteorite ALH84001; if this interpretation is correct, they represent the oldest evidence for life yet found.

Past techniques for identification of bacterial magnetofossils have relied on the use of particle extraction and high-resolution electron microscopy (HRTEM). Because these techniques are time-consuming and fairly complex, they are not appropriate for screening large volumes of sediments on Earth and could not be used remotely on a Martian lander. For this reason, we have been testing a variety of ferromagnetic resonance and low-temperature rock magnetic techniques to determine if they are capable of identifying correctly rock samples known to contain abundant magnetofossils. An instrument capable of making such a determination, if deployed on the Martian surface, could be extraordinarily valuable for selecting samples for return to Earth. Several features of the ferromagnetic resonance

(FMR) spectra have signatures only displayed by pure samples of magnetite from the magnetotactic bacteria, and from samples known to contain abundant magnetofossils. These unique features apparently arise from the elongated shape and narrow size distribution of the single-domain magnetite produced by these bacteria. Preliminary results from ALH84001 carbonates also have these features. We are also currently obtaining FMR spectra and low-temperature rock magnetic data on samples of Archean and Early Proterozoic sediments from Australia to search for older evidence of intracellular magnetite biomineralization on Earth.

B32C-02 1345h

MINERAL BIONIZATION - SURFACE CHEMICAL MODELING OF THE EMERGENCE OF LIFE

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The earliest stages in entering an RNA-world require natural mechanisms that are capable of selective concentration of simple aldehydes from dilute solution in the environment (4), furthermore phosphorylation of the sequestered aldehydes (2) and their catalytic condensation to form, selectively, tetrose- (threose) or pentose- (ribose) phosphate (3); the latter representing the R in RNA.

A variety of common positively charged sheet structure minerals (mixed valence double layer metal hydroxide minerals such as hydroxalcalite and green rust) have proven to be remarkably capable of performing these crucial tasks under simplified natural conditions (1). These prebiotic model reactions have demonstrated plausible closure of the gap, previously thought to preclude the natural formation of nucleoside phosphates, the backbone components of the information carrying genetic material.

Pioneering research by other workers (5) has demonstrated the feasibility of necessary further steps in the chain toward functional RNA; mineral (montmorillonite) catalyzed oligomerization of nucleotides, the formation of complementary RNA strands (6) and the enzymatic activity of RNA (ribozymes). These contributions have placed the initially conjectured concept of an initial RNA-world on an experimental footing.

Remaining problems include the initial transfer of information to spontaneously forming RNA, sufficient to convey biofunctionality (7). Also in this central problem mineral surface interactions may be speculated to play a natural role; a question that is open to experimental verification.

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B32C-03 1400h

Genomic Analysis of the Archaeon *Ferroplasma acidarmanus*: New Insights Into the Evolution of Arsenic Resistance

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Arsenic resistance allows microbes to live in As-rich solutions and in proximity to As-bearing minerals and thus, to impact dissolution and precipitation reactions. As-resistance is a characteristic of both Bacteria and Archaea. In some cases, it is conferred by the acquisition of a plasmid, in other instances the genes are located on the chromosome. Through analysis of newly acquired genomic data for the highly arsenic-resistant, iron-oxidizing extreme acidophile *Ferroplasma acidarmanus* and genomic data for other organisms we can gain insight into the mechanisms, origin, and evolution of genes that confer arsenic resistance. The deduced protein sequences of all known arsenic resistance genes were compiled from genomic and protein databases. Sequence alignments and phylogenetic analyses were performed. Comparisons of arsenite efflux pump (ArsB) and 16S rDNA phylogenies indicated a parallel evolutionary history for the two genes. Results indicate that the As(III) efflux pump was present in the ancestor common to the Bacterial and Archaeal domains.

This pump, conferring resistance to arsenite, was probably important to early life living in metal-rich environments. Previous work has shown that the gene encoding for ArsA, an ATPase that increases the efficiency of arsenic efflux, clearly arose via gene duplication. *Ferroplasma* and related Thermoplasmatales group organisms contain a pre-duplication subunit of uncertain function. ArsA phylogeny shows two separate and distinct lines of evolution for the chromosomal- and plasmid-based proteins. This study provides the first evidence of metal resistance developing early in the evolution of life and gives new insights into the evolutionary history of the arsenic resistance proteins.

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Ancient bacterial diversity in mid-Cretaceous black shale: DNA records of oceanic euxinic paleoenvironments

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A record of the history of the planet Earth is hidden in the subsurface biosphere, like the annual rings of an old tree. From limited evidences retrieved from underground, one can infer the geographical, geological and biological events that occurred throughout Earth's history. Biosphere in oceanic subsurface and terrestrial subsurface environment has been already recognized as the biggest microbial world. Recent progress in approaching deep biosphere revealed that numerable microbial populations were consistently present in the drilling core samples and aquifers recovered from deep subsurface environment. However, the microbial community structures and the relationship between their habitats and geological events have been poorly proved. Molecular phylogenetic analyses have been becoming powerful tool for investigating the naturally occurring microbial communities. Using a combination of culture independent molecular phylogenetic analyses, we sought to recapture the indigenous microbial community of ancient oceanic habitats recovered from a continental drilled core of black shale deposited 100 million years ago.

We recovered the drilled core sample of black shale from the continental margin at Serre des Castets, the southern part of France. The recovered black shale contained one phosphate-accumulated strata, defined as a part of the mid-Cretaceous OAE (Oceanic Anoxic Events). Indigenous DNA was extracted from the several axis parts of the core, then bacterial ribosomal RNA genes (rDNA) was amplified by PCR. The molecular approaches such as the terminal-restriction fragment length polymorphism (T-RFLP) fingerprinting analysis, phylogeny analysis of rDNA clone libraries and the phylogenetic analysis of representative rDNA sequences revealed that the genetic signals from mid-Cretaceous black shale were almost similar to bacterial habitats at deep-sea floor sediments. Furthermore, a number of rDNA clone within the delta-subclass (sulfur-reducing bacteria) and epsilon-subclass (sulfur-oxidizing bacteria) of Proteobacteria class was prominent at the phosphate rich OAE strata. The redox-front type rDNA structure of oceanic bacterial habitats are observed at the euxinic water discharging sites such as the deep-sea cold seep and hydrothermal vent in present oceanic environments. These genetic rDNA signatures probably associated with the microbial habitats occurring at 100 million years ago, serves as potential geomicrobiological evidence reflecting novel records of the oceanic paleoenvironment in the Cretaceous period.

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Ubiquity of Deep-Sea Hydrothermal Vent Archaea in the Global Subsurface Biosphere

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