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## Recent Work

### Title

Molecular structure of water absorbed on a mica surface

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## B21B-0702 0830h POSTER

## Alginic Acid Accelerates Calcite Dissolution

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Accelerated carbonate weathering through biological activity affects both geochemical cycling and the local pH and alkalinity of terrestrial and marine waters. Microbes affect carbonate dissolution through metabolic activity, production of acidic or chelating exudates, and cation binding by cell walls. Dissolution occurs within microbial biofilms - communities of microorganisms attached to stone in an expolymer matrix. We investigated the effect of alginic acid, a common biological polymer produced by bacteria and algae, on calcite dissolution using a paired atomic force microscopy/flow-through reactor apparatus. The alginic acid caused up to an order of magnitude increase in dissolution rate at  $3 < \text{pH} < 12$ . Additionally, the polymer preferentially binds to the obtuse pit steps and increases step velocity. We propose that the polymer is actively chelating surficial cations reducing the activation energy and increasing dissolution rate. The role of biologically produced polymers in mineral weathering is important in the protection of cultural heritage materials and understanding of marine and terrestrial systems.

## B21B-0703 0830h POSTER

## Arsenic Cycling Within Bangladesh Sediments: Evidence for an Oxidative Front Causing Solid Phase Repartitioning

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Arsenic is a contaminant in the groundwater of Bangladesh and has resulted in the exposure of millions of people to drinking water above the World Health Organization standard. Solid concentrations of arsenic within the aquifer sediments typically do not exceed world averages, and, therefore, the question arises as to why arsenic is partitioned in the solution rather than the solid phase. To address this question we have obtained well-preserved deep-sediment cores from the Munshiganj District of Bangladesh. Spectroscopic analyses have been conducted to determine the speciation of arsenic, iron, and sulfur within the sediments. Additionally, laboratory studies of the sediments, in conjunction with those on model compounds, have been performed to isolate plausible desorption mechanisms of arsenic and to define the underlying chemical processes controlling arsenic cycling. Our work points to a complex cycling of arsenic in which an oxidative front has caused destruction of arsenic-bearing sulfides (which appear preserved during transport and sediment deposition!) and the concomitant repartitioning of arsenic onto oxidized solids, primarily those of Fe. Subsequent to repartitioning on ferric (hydr)oxide mineral surfaces, microbial reductive dissolution of such phases, stimulated by injection of labile carbon, has led to the concomitant release of arsenic into solution. The entire cycle implies an additional (and previously dismissed) step in the release of arsenic into Bangladesh groundwater. As a consequence, minimizing the drawdown (and thus the oxidative front) or utilizing deeper wells may provide water that is less contaminated with arsenic.

## B21B-0704 0830h POSTER

## Role of Water on the Fate of Organics in Reduced-Smectite Suspensions

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Clay mineral surfaces serve as a reaction site where interacting organic molecules undergo acid-base and redox transformations. Upon activation of the clay surface, water plays a key role in determining the mechanisms of transformation of adsorbing organics. The focus of this presentation will be on the reaction mechanisms of pesticides, and chlorinated and nitro aliphatics, at clay surfaces which have been modified through chemical or biological oxidation-reduction reactions. The outcome of this study indicates that the oxidation state of structural Fe in the clay strongly influences organic compounds hydration. A mechanism consistent with linear free energy relationships presented herein corresponds to organic compound hydration as the limiting step for adsorption and transformation by redox-manipulated smectites.

## B21B-0705 0830h POSTER

## Molecular Structure of Water Adsorbed on a Mica Surface

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The molecular structure of water adsorbed on micaceous minerals (2:1 layer-type aluminosilicates) has long been of widespread interest because of its crucial role in geochemical and biological processes. Early conceptualization of this structure imputed to it an icelike character because of its longer relaxation times when compared to bulk liquid water and its potential for epitaxy with the hexagonal array of oxygen atoms on the basal surfaces of mica and 2:1 clay minerals. These speculations have received support periodically from experimental and modeling studies, but recent spectroscopic data suggest that the hydration water on micaceous minerals is more disordered and more labile than ice Ih. Monte Carlo simulations of hydration water on the mica (001) surface under ambient conditions revealed water molecules bound closely to the ditrigonal cavities in the surface, with a lateral distribution of approximately one per cavity, and water molecules (interposed between  $\text{K}^+$  counter ions) in a layer situated about 2.5 Å from a surface O along a direction normal to the (001) plane. The calculated water O density profile was in quantitative agreement with recent x-ray reflectivity measurements indicating strong lateral ordering of the hydration water but liquidlike disorder otherwise.

URL: [http://www-esd.lbl.gov/GEO/aqueous\\_geochem/index.html](http://www-esd.lbl.gov/GEO/aqueous_geochem/index.html)

## B21B-0706 0830h POSTER

## Landscape Influences on Organic Matter Export From a Midwestern Watershed

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In an effort to characterize relationships between landscape processes and organic carbon export, molecular and stable isotope approaches have been applied to particulate, colloidal, and dissolved organic matter samples from Big Pine Creek watershed; an agriculturally-dominated watershed located in west-central Indiana, USA. Preliminary results from multiple sites within the watershed show that organic matter from this 850 km<sup>2</sup> watershed is qualitatively similar to samples collected from larger rivers in the western hemisphere, suggesting that small to mid-sized watersheds can play a prominent role in terrestrial organic carbon export. Moreover, carbon-normalized yield data

and bulk stable isotope data from the study area show that relationships between export and stream discharge can be dependant on the size fraction of the organic matter. Dissolved organic matter tends to behave linearly with discharge while particulate organic matter responds in a logarithmic manner. Finally, bulk stable carbon isotopes of samples taken from Big Pine Creek show dramatic shifts from base flow to storm flow conditions showing a shift in organic matter sources during flood events. Taken together, these results show that upland conditions can play an important role in the quantity, quality, and source of organic matter exported from terrestrial systems.

## B21B-0707 0830h POSTER

## The Influence of Siderophores Produced by Alkaliphilic Microorganisms on Iron and Metal Contaminant Speciation and Solubility

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Halomonas campisalis strain 4A has been identified as capable of producing siderophores under halo-alkaliphilic growth conditions. Because of the scarcity of iron under the alkaline conditions in which Halomonas campisalis thrives, we hypothesize that the siderophores secreted by Halomonas campisalis and other alkaliphilic bacteria will have a stronger affinity for binding and solubilizing ferrous iron than siderophores produced by mesophilic bacteria. Siderophore production by Halomonas campisalis was confirmed through the use of the chrome azural S (CAS) agar plate method which showed a red-orange halo around the bacterial colonies indicative of siderophore production. The siderophores were found to be produced under conditions of both high salinity and pH with a salt concentrations ranging from 0.4 - 1.8 M NaCl and pH ranging from 8 - 11. The siderophores produced have been determined to be of the hydroxamate class via the Csáky method. A negative response to the Arnow assay indicated that the siderophore produced does not contain any catechol moieties in its chemical structure. It was found that maximum siderophore production was equivalent to approximately 400 mM desferrioxamine and occurred during mid stationary phase. Similar results were found at pH 8, 10 and 11. A purification scheme was developed that involved an initial extraction of the siderophore from the growth medium into benzyl alcohol followed by precipitation with diethyl ether. Additional purification was achieved via ion exchange chromatography and size exclusion chromatography. Final purification was achieved via HPLC. The structure of the purified siderophore was analyzed via LC/MS/MS equipped with an ESI source. To date, few studies have included the siderophores produced by microorganisms capable of tolerating highly saline and alkaline environments. In addition to unique structure and high affinity for iron, it is further hypothesized that siderophores from alkaliphilic bacteria will also have a corresponding higher affinity to heavy metal and radionuclide contaminants, thus increasing the mobility of these metals in subsurface environments and influencing contaminant fate and transport. Future work will examine the stability constants for complexes of various metals including uranium with the Halomonas campisalis siderophore.

## B21B-0708 0830h POSTER

## Effects Of Fungal-Mineral Interactions On Chemical Weathering And Denudation Processes - Observations From Experimental Ecosystems

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