MICROBIAL IMPACTS ON CLAY TRANSFORMATION AND REACTIVITY

Monday June 21, 2004

Microbial Impacts on Clay Transformation and Reactivity I	
1:20 – 2:00p	**BEHAVIOR OF IRON-REDUCING BACTERIA AT Fe(III)-OXIDE SURFACES.** Gill Geesey Department of Microbiology, Montana State University, Bozeman, MT 59717-3520
2:00 – 2:20p	**INTERACTION OF MITOCHONDRIAL CYTOCHROME C WITH HEMATITE (001) SURFACES.** Nidhi Khare*, Carrick M. Eggleston, and David M. Lovelace Department of Geology and Geophysics, University of Wyoming, Laramie, WY, 82071.
2:20 – 2:40p	**CONTROL OF Fe(III) SITE OCCUPANCIES ON MICROBIAL REDUCTION IN THE NONTRONITE STRUCTURE.** Deb P. Jaisi[1], Hailiang Dong[1], Dennis D. Eberl[2], and Ravi K. Kukkadapu[3] [1]Department of Geology, Miami University, Oxford, OH 45056; .[2]US Geological Survey, Boulder, CO 80303; [3]Pacific Northwest National Laboratory, Richland, WA 99352
2:40 – 3:00p	**EFFECTS OF BACTERIAL REDUCTION OF STRUCTURAL IRON ON THE INFRARED SPECTRA OF IRON-BEARING SMECTITES.** Kangwon Lee[1], Joseph W. Stucki[1*], and Joel E Kostka[2] [1]University of Illinois, Department of Natural Resources and Environmental Sciences, Urbana, IL 61801; [2]Florida State University, Department of Oceanography, Tallahassee, FL 32306
Microbial Impacts on Clay Transformation and Reactivity II	
3:20 – 4:00p	**NEW INSIGHTS INTO THE MOLECULAR MECHANISM OF BACTERIAL METAL RESPIRATION.** Thomas J. DiChristina School of Biology, Georgia Institute of Technology, Atlanta, GA 30332
4:00 – 4:20p	**DEGRADATION OF OXAMYL BY REDOX-MODIFIED SMECTITES: DISSIMILARITIES BETWEEN CHEMICAL AND BACTERIAL REDUCTION.** Fabiana R. Ribeiro*[1], Joseph W. Stucki[1], Peter Komadel[1,2], Amos Banin[3], Ido Negev[3], José D. Fabris[4], Karen A. Marley[1], Richard A. Larson[1] and Joel E. Kostka[5] [1]Department of Natural Resources and Environmental Sciences, University of Illinois, Urbana, IL 61801 USA; [2]Institute for Inorganic Chemistry, Slovak Academy of Sciences, SK-84536 Bratislava, Slovakia; [3]Department of Soil and Water Sciences, Hebrew University of Jerusalem, Rehovot 76100, Israel; [4]Department of Chemistry, Federal University of Minas Gerais, Belo Horizonte, MG 31270-901 Brazil; [5]Department of Oceanography, Florida State University, Tallahassee, FL 32306 USA *fribeiro@uiuc.edu
4:20 – 4:40p	**EFFECTS OF IN SITU MICROBIAL STIMULATION ON Fe PHASES IN A SUB-SURFACE SAPROLITIC SOIL: A VARIABLE-TEMPERATURE MÖSSBAUER SPECTROSCOPY STUDY.** Kangwon Lee[1], Joseph W. Stucki[*1], Joel E.Kostka[2], and Bernard A. Goodman[1] [1]Department of Natural Resources and Environmental Sciences, University of Illinois, Urbana; [2]Department of Oceanography, Florida State University, Tallahassee

4:40 – 5:00p	**BIOREDUCTION OF Fe IN SHALE-LIMESTONE SAPROLITE CONTAINING Fe(III) OXIDES AND Fe(II)/Fe(III) PHYLLOSILICATES.** Ravi K. Kukkadapu*[1], John M. Zachara[1], James K. Fredrickson[1], David W. Kennedy[1], Steven C. Smith[1,] and Hailiang Dong[2] [1]Pacific Northwest National Laboratory, Richland, WA 99352;[2] Miami University, Oxford, OH.
Microbial Impacts on Clay Transformation and Reactivity Poster Session	
5:00p	**SINTER MINERALOGY OF TERRESTRIAL HOT SPRING VENT, UZON CALDERA, KAMCHATKA, RUSSIA**. Jennifer E. Kyle*, and Paul A. Schroeder University of Georgia, Athens Georgia, 30602-2501
	INTERACTION BETWEEN VERMICULITE AND THE BACTERIUM *PSEUDOMONAS FLUORESCENS* STRAIN CHA0 AND ITS GENETIC DERIVATIVES. Barbara Müller Institute for Geotechnical Engineering, Swiss Federal Institute of Technology, 8093 Zürich, Switzerland

Tuesday June 22, 2004

Microbial Impacts on Clay Transformation and Reactivity Poster Session	
5:00p	**INTERACTIONS OF URANIUM WITH MIXTURES OF MICROORGANISMS AND KAOLINITE CLAY.** Toshihiko Ohnuki*[1], Takahiro Yoshida[1], Takuo Ozaki[1], Mohamad Samadfam[1], Naofumi Kozai[1], and Arokiasamy J. Francis[2] [1]Japan Atomic Energy Research Institute, Advanced Science Research Center, Tokai, Ibaraki 319-1195, Japan; [2]Brookhaven National Laboratory, Environmental Sciences Department, Upton, New York 11973, USA.

Wednesday June 23, 2004

Microbial Impacts on Clay Transformation and Reactivity III	
1:20 – 2:00p	**CONTROLLED CULTIVATION: APPROACHES FOR DEBUGGING BIOGEOCHEMICAL RESEARCH.** Yuri A. Gorby Biological Sciences Division, Pacific Northwest National Laboratory, Richland, WA, 99352 USA
2:00 – 2:20p	**ROLE OF MICROBES IN PROMOTING THE SMECTITE TO ILLITE REACTION.** Jinwook Kim[*1], Hailiang Dong[2], Jennifer Seabaugh[2], Steven W. Newell[1], and D. D. Eberl[3] [1]Naval Research Laboratory, Seafloor Sciences Branch, Stennis Space Center, MS 39529, USA; [2]Department of Geology, Miami University, Oxford, OH 45056, USA; [3]U. S. Geological Survey, Boulder, CO 80303, USA
2:20 – 2:40p	**DISSOLUTION OF MICROBIAL REDUCED NONTRONITE IN A FLOW-THROUGH SYSTEM.** S.E. O'Reilly[1*], B.R. Bickmore[2], and Y. Furukawa[1] [1]Naval Research Laboratory, Seafloor Sciences Branch, Code 7431, Bldg. 1005, Stennis Space Center, Mississippi 39529; [2]Brigham Young University, Department of Geology, Provo, Utah 84602
2:40 – 3:00p	**REDUCTION OF STRUCTURAL Fe(III) IN NONTRONITE BY A THERMOPHILIC BACTERIUM.** Jennifer L. Seabaugh[*1], Hailiang Dong[1], Dennis D. Eberl[2], Jinwook Kim[3], Ravi K. Kukkadapu[4] [1]Miami University, Oxford, OH 45056; [2]U.S. Geological Survey, Boulder, CO 80303; [3]Naval Research Laboratory, Seafloor Sciences Branch, Stennis Space Center, MS 39529; [4]Pacific Northwest National Laboratory, Richland, WA 99352
Microbial Impacts on Clay Transformation and Reactivity IV	
3:20 – 4:00p	**NANOPARTICULATE SILICA COLLOID SIZE DISTRIBUTIONS ASSOCIATED WITH BACTERIAL CELLS.** F. Grant Ferris[*], and Elisabeth Magalhaes Department of Geology, University of Toronto, Toronto, ON Canada
4:00 – 4:20p	**MICROBIAL WEATHERING OF ORTHOPYROXENE AND CLAY FORMATION IN AN ARID ENVIRONMENT: A STXM AND HRTEM STUDY.** Karim Benzerara[*1], Tae-Hyun Yoon[1], Nicolas Menguy[2], Francois Guyot[2], Tolek Tyliszczak[3], and Gordon E. Brown, Jr.[1] [1]Surface & Aqueous Geochemistry Group, Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA; [2]Laboratoire de Minéralogie-Cristallographie, Universite Paris 7, Paris, France; [3]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA., USA
4:20 – 4:40p	**BIOGENIC DISSOLUTION OF SOIL PHOSPHATE MINERALS.** Javiera Cervini-Silva[*1], David Fowle[2], and Jillian F. Banfield[1] [1]Department of Earth and Planetary Sciences, University of California, Berkeley, CA 94720-3110, [2]Department of Geological Sciences, University of Windsor, Canada
4:40 – 5:00p	**EFFECTS OF SIDEOROPHORES ON Pb AND Cd ADSORPTION TO KAOLINITE.** Sarah E. Hepinstall, Patricia A. Maurice, and Benjamin F. Turner[*] Department of Civil Engineering & Geological Sciences, University of Notre Dame, Notre Dame, IN 46556

MONDAY JUNE 21, 2004

MICROBIAL IMPACTS ON CLAY TRANSFORMATION AND REACTIVITY I

1:20PM

BEHAVIOR OF IRON-REDUCING BACTERIA AT Fe(III)-OXIDE SURFACES

Gill Geesey

Department of Microbiology, Montana State University, Bozeman, MT 59717-3520

Cells of the Fe(III)-respiring bacterium *Shewanella oneidensis* MR-1 rapidly colonize surfaces of hematite and magnetite under flow conditions when these solid phase Fe(III)-oxides serve as the sole electron acceptor in the system. Significant differences were observed in the maximum cell density achieved on hematite (001), magnetite (111) and magnetite 100 surfaces. Maximum cell density appeared to vary with Fe(III) site density on the three surfaces with hematite (001) having the highest Fe(III) site density (4.2 nm^{-2}) and cell density and magnetite (100) having the lowest Fe(III) site density (1.4 nm^{-2}) and cell density. Silicon surfaces accumulated cells to a maximum density of approximately 1/3 that observed for the magnetite (100) surface, and decline to 50% of the maximum value after 5 days. The maximum rate of cell accumulation on the hematite (001) surface was not significantly different from that on either of the magnetite surfaces. However, the maximum rate of cell accumulation on magnetite (111) was significantly greater than that on magnetite (100). Instantaneous cell detachment rates were generally higher on magnetite (111) surfaces than the other two surfaces, although large variations at different sampling times precluded application of meaningful statistical analysis of the process. Mineral surface-associated cell production was determined by summing the number of cells that remained associated with the mineral surface and the cells that had detached from the surface after increasing periods of time. Hematite (001) and magnetite (111) exhibited similar mineral surface-associated production whereas cell production on magnetite (100) was approximately 50 times lower than that observed on the other two surfaces. The data suggest that bulk of the cells produced on all surfaces detached under the hydrodynamic conditions used in these studies. The data suggest that the fate of cells produced on a mineral surface is controlled by the properties of that surface. Electron transfer (ET) between a heme at the cell surface and the oxygen plane of the mineral surface was predicted to occur at a higher rate on hematite (001) and magnetite (100) than on magnetite (111). That magnetite (111) supported a cell higher accumulation rate and higher cell production than the other surfaces suggest that parameters other than ET control these aspects of cell behavior. These results suggest that complex and surface-dependent behavior of cells associated with different Fe(III)-oxides pose challenges to the establishment of mechanistic models of biological iron reduction.

INTERACTION OF MITOCHONDRIAL CYTOCHROME C WITH HEMATITE (001) SURFACES

Nidhi Khare*, Carrick M. Eggleston, and David M. Lovelace

Department of Geology and Geophysics, University of Wyoming, Laramie, WY, 82071.

Microbial Fe-reduction has been intensively studied, and outer-membrane c-type cytochromes have been implicated in electron transfer from the bacteria to Fe-oxide surfaces. The interaction of cytochromes with mineral surfaces for purposes of electron transfer is of interest not only for a better understanding of respiratory electron transfer pathways used by metal-reducing bacteria but also for in-vitro use of cytochromes and other biomolecules in contaminant remediation strategies and pharmaceutical industry. Horse heart ferricytochrome-c (Hcc), a water soluble mitochondrial cytochrome-c, has been well characterized and hence may be used as an analog to study the interaction of Fe-oxide surfaces with c-type cytochromes. Because it is thought that Hcc is optimized for electrostatic interaction with its physiological partners, we hypothesized that sorption to hematite will occur in the pH range where electrostatic attractions are greatest. The objective of this study was to characterize the interaction of Fe-oxide (hematite (001)) powders and single crystal surfaces with Hcc as a function of time, pH, and salt (KCl) concentration using both wet chemical sorption and atomic force microscopy (AFM).

Wet chemical sorption kinetics were characterized by adding 5000 μL of 0.1mM Hcc solution to hematite suspensions at 10mM KCl background electrolyte and equilibrating for 1, 5, 20, 65, and 120 h at pH 3, 7, and 9.5 at a temperature of 21°C. The pH (2-13) and salt concentration (10-500mM KCl) dependence was similarly studied by equilibrating for 20 h at 21°C. Horse heart ferricytochrome c sorbed on hematite within an hour, reaching near maximum sorption capacity. Although the amount sorbed varied with pH, the rate of sorption did not. At 20 h equilibration, Hcc sorption varied as a function of pH with most sorption occurring between pH 8 and 10. The isoelectric point of Hcc is about 10 while the isoelectric point for hematite varies between 8 and 9; hence, the relatively fast sorption kinetics and the narrow pH range of sorption (at pH values for which we would expect opposite charge on the Hcc and hematite) suggest an electrostatic mechanism of Hcc binding on hematite surfaces. Sorption between pH 8 and 10 was reversible as shown by 80 to 100% desorption on changing pH to 4 providing additional evidence for electrostatic binding. Sorption of Hcc on hematite at pH 3 and 9.5 varied with KCl concentration. At pH 3, sorption increased with increasing salt concentration while at pH 9.5 after an initial increase in sorption, there was a dramatic reduction at 500 mM salt concentration. Horse heart ferricytochrome c undergoes conformational changes with pH as well as with salt concentration. At pH 3 Hcc unfolds, but Cl^- ions are known to induce re-folding, consistent with the increase in Hcc sorption with KCl concentration at this pH. The reduction in Hcc sorption with KCl concentration at pH 9.5 is probably due to electrostatic screening effects. The AFM images showed that Hcc sorbed on hematite within minutes and sorption occurred at pH 4, 7, and 10 in agreement with the wet chemical results.

CONTROL OF Fe(III) SITE OCCUPANCIES ON MICROBIAL REDUCTION IN THE NONTRONITE STRUCTURE

Deb P. Jaisi[1], Hailiang Dong[1], Dennis D. Eberl[2], and Ravi K. Kukkadapu[3]

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A quantitative study was performed to understand the rate and extent of bioreduction of Fe(III) in different structural sites on two nontronite samples (NAu-1 and NAu-2) by a metal reducing bacterium *Shewanella putrefaciens,* CN32. The NAu-1 and NAu-2 (Source Clay Repository, IN) are relatively pure clays. NAu-1 and NAu-2 contain 16.4% and 23.1% of total iron in their structures with all iron as Fe(III). The 0.5-0.2 μm fraction of NAu-1 used in experiment contained a small amount of Fe-bearing Fe oxide (goethite) as revealed by Mossbauer spectroscopy. The <0.5 μm NAu-2 is very pure with no other Fe(III)-bearing minerals. The nontronite suspension of 5mg/ml in bicarbonate buffer was used in three different treatments. Except for control, experimental tubes were inoculated with 2.3×10^6 to 3.8×10^7 cells/ml with lactate as the electron donor and Fe(III) in the nontronite structure as the sole electron acceptor. The total and aqueous iron Fe(II) production with time were measured by Ferrozine assay. The release of major cations (Fe, Si, Al, Ca, and Mg) into solution during the iron reduction was measured by direct current plasma (DCP) mass spectroscopy. The bioreduced samples were analyzed using X-ray diffraction and Mőssbauer spectroscopy.

The extent of reduction was higher in AQDS treated samples than those without AQDS. Despite the similarity between the two nontronite samples, the extent and rate of reduction (Fe_{total}) were very different. The total reduction was only 16% in NAu-1 but 32% in NAu-2 in AQDS treated samples in 15 days. The reaction rate was also different: in NAu-1 only about 29% of the total reduction was attained in 46 hrs, but for NAu-2, it reached 73% to 85% of the total reduction for the same time. Observed aqueous iron (Fe_{aq}) was less than 1% of those measured by Ferrozine assay in both nontronites.

The XRD analyses showed that the average nontronite particle thickness in NAu-1 slightly increased from 2.1 nm to 2.5 nm with no apparent change in crystal size distribution. On the contrary, the average nontronite particle thickness in NAu-2 decreased from 7.6 nm to 3.4 nm as a result of reduction suggestion dissolution of nontronite layers. The microbial reduction also changed crystal size distribution from lognormal to asymptotic shape suggesting crystal growth mechanism of simultaneous nucleation and growth.

The Mőssbauer spectroscopic study of the unreduced nontronite samples showed that all Fe(III) in NAu-1 is located in the octahedral site, whereas Fe(III) in NAu-2 is located in both the tetrahedral and the octahedral sites. Mőssbauer data of the bioreduced NAu-2 revealed that there was a production of 32% Fe(II), which is consistent with the Ferrozine data. Furthermore, Fe(III) in one structural site was preferentially reduced to Fe(II), whereas Fe(III) in the other site partially remained after bioreduction .

These data collectively suggest that the higher degree and faster rate of reduction in NAu-2 is due to the presence of Fe(III) in multiple structural sites. One Fe(III) site is presumed to be more accessible to bacteria than the other one, resulting in different behaviors in the bioreduction.

EFFECTS OF BACTERIAL REDUCTION OF STRUCTURAL IRON ON THE INFRARED SPECTRA OF IRON-BEARING SMECTITES

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The redox state of structural Fe in smectites greatly alters clay surface chemistry. The present study was performed to investigate the effect of redox reactions by bacteria on the structure of three Fe-bearing smectites (Garfield, SWa-1, and Upton) using Fourier transform infrared (FTIR) spectroscopy. Redox treatments of the smectites included unaltered (oxidized), bacteria reduced, bacteria-reduced reoxidized, dithionite reduced (to a similar Fe(II) level as with bacteria), and dithionite-reduced reoxidized. Bacterial reduction was achieved by incubating the Na-saturated smectites with *Shewanella oneidensis* strain MR-1 in a minimal medium including 20 mM lactate. Reoxidation was carried out by bubbling O_2 gas through the reduced suspension. After redox treatment, the clays were washed 4 times with deoxygenated 5 mM NaCl. The samples were prepared either as a self-supporting film for O-H stretching and deformation bands or as a deposit on ZnSe windows for Si-O stretching bands and placed inside a vacuum cell with ZnSe windows. The spectra from microbially treated samples were compared with dithionite-treated samples having a similar Fe(II)/total Fe content. The changes observed in all three spectral regions (O-H stretching, O-H deformation, and Si-O stretching) for microbially reduced smectite were similar to results obtained at a similar level of reduction by dithionite. The O-H stretching band shifted from 3570 cm^{-1} to 3560 cm^{-1} in Garfield nontronite and from 3632 cm^{-1} to 3620 cm^{-1} in Upton montmorillonite. In ferruginous smectite, SWa-1, 3550 cm^{-1} shoulder became distinctive from 3577 cm^{-1} band. The O-H stretching band possibly lost intensity due to partial dehydroxylation. The Si-O band shifted to lower wavenumber also. In the O-H deformation region, 840-850 cm^{-1} band became very weak or disappeared. Upon reoxidation the bands shifted back toward their unaltered positions, but not completely, even though the Fe(III) oxidation state was restored. All microbially reduced clays retained a noticeable H_2O band at 3500-3300 cm^{-1} region due to H_2O trapped in the reduced clays and in the bacteria. This band was largely replaced by a broad band at ~ 2700 cm^{-1} when D_2O was inserted into the sample atmosphere. Replacement of OH with OD in inorganically reduced samples confirmed that the H_2O was primarily on the surfaces rather than in the structure of the clays. These observations indicate that bacterial reduction of Fe modifies the crystal structures of all three of these Fe-bearing smectites, and that the modifications are generally of the same nature with respect to structural vibrational modes as produced by dithionite reduction.

MONDAY JUNE 21, 2004

MICROBIAL IMPACTS ON CLAY TRANSFORMATION AND REACTIVITY II

3:20PM

NEW INSIGHTS INTO THE MOLECULAR MECHANISM OF BACTERIAL METAL RESPIRATION

Thomas J. DiChristina

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Metal-reducing members of the genus *Shewanella* respire anaerobically on a wide variety of compounds as terminal electron acceptor including oxidized iron [Fe(III)], manganese [Mn(IV)], uranium [U(VI)] and technetium [Tc(VII)]. The molecular mechanism of bacterial metal respiration, however, is poorly understood. A genetic complementation strategy has been followed to identify the genes and proteins required for anaerobic respiration on Fe(III), Mn(IV), U(VI) and Tc(VII). Four rapid screening techniques have been developed to identify respiratory mutants deficient in anaerobic respiration on each metal. Mutant subclasses (designated Fer, Mnr, Urr and Tcr, respectively) have been identified by the inability to respire anaerobically on a specific terminal electron acceptor, while retaining the ability to respire on all other compounds tested. Wild-type DNA fragments containing metal reduction-specific genes have been isolated by genetic complementation with a wild-type gene clone bank, and the metal reduction-specific genes have been identified by nucleotide sequence analysis. The metal-reduction-specific genes provide new insight into the molecular mechanism of bacterial metal respiration.

DEGRADATION OF OXAMYL BY REDOX-MODIFIED SMECTITES: DISSIMILARITIES BETWEEN CHEMICAL AND BACTERIAL REDUCTION

Fabiana R. Ribeiro*[1], Joseph W. Stucki[1], Peter Komadel[1,2], Amos Banin[3], Ido Negev[3], José D. Fabris[4], Karen A. Marley[1], Richard A. Larson[1] and Joel E. Kostka[5]

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The redox state of Fe in the structure of clay minerals profoundly affects the fate of agrichemicals, such as the pesticide oxamyl, and helps determine their efficacy for agriculture and their risk to the environment. Oxamyl degrades either by a redox pathway to produce N, N-dimethyl-1-cyanoformamide (DMCF) or by a base-catalyzed hydrolysis pathway to produce oxamyl oxime. Under neutral pH (7) conditions and in the presence of dithionite-reduced ferruginous smectite (SWa-1, 17% total Fe), oxamyl degrades rapidly, completely, and exclusively to oxamyl oxime (base hydrolysis pathway). At lower pH (3.5) the degradation is incomplete (92%) and 8% of the degradation product is DMCF. This result was surprising because the reduced smectite presumably has a high reduction potential, which *a priori* predicts the redox pathway and production of DMCF. The objectives of this study were, therefore, to better understand the observed degradation mechanism of oxamyl in the presence of reduced smectite, and to determine the potential for such degradation reactions to occur in nature. Degradation of oxamyl was investigated at low (3.5) and neutral (7) pH in the presence of dithionite and bacteria redox-modified SWa-1, Upton montmorillonite (3% total Fe), and the clay-size fraction of Givat Brenner soil (7% total Fe). Reaction of oxamyl with all dithionite-reduced clays at neutral pH produced exclusively oxamyl oxime; but, at lower pH, results were mixed. With Upton montmorillonite at low pH degradation was incomplete and the principal product was DMCF, unlike SWa-1 where oxamyl oxime was the major product and DMCF was only a minor product at low pH. The Givat Brenner soil clay, when dithionite-reduced at low pH, behaved much like SWa-1. Bacterial reduction also yielded a similar result to dithionite with all clays at circum-neutral pH, but at low pH bacteria-reduced SWa-1 altered oxamyl to a much lesser extent and the reaction product was mostly DMCF. Due to the lower structural Fe(II) produced by bacteria, the surface pH was probably lower. One anomaly to the above patterns was that the degradation with the soil clay at neutral pH was much greater than with SWa-1, despite more structural Fe(II) in SWa-1. In conclusion, the degradation product from oxamyl reaction with both reference and soil clays reduced to varying degrees by either dithionite or bacteria at circum-neutral pH is oxamyl oxime (base hydrolysis pathway). At low pH, SWa-1 degrades oxamyl via the base hydrolysis pathway due to the large Bronsted basicity at the clay basal surface created by the high structural Fe(II) content; whereas, the low-Fe(II) Upton and Givat Brenner clays allow the redox pathway to produce DMCF. Bacterially reduced clays degrade oxamyl to DMCF at low pH. At neutral pH the main product is oxamyl oxime and the soil samples degrade more oxamyl than the reference clay with higher iron content.

EFFECTS OF IN SITU MICROBIAL STIMULATION ON Fe PHASES IN A SUB-SURFACE SAPROLITIC SOIL: A VARIABLE-TEMPERATURE MÖSSBAUER SPECTROSCOPY STUDY

Kangwon Lee[1], Joseph W. Stucki[*1], Joel E.Kostka[2], and Bernard A. Goodman[1]

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[2]Department of Oceanography, Florida State University, Tallahassee

Bacterial reduction of Fe in oxides and clay minerals has been postulated as a method for sub-surface bioremediation, but little has been done to actually demonstrate it in the field. Because the potential for reduced-Fe minerals in sub-surface soils to promote immobilization of redox active metals such as U, Tc, Cr, and As is great, further investigation into this phenomenon was undertaken using sub-surface soils from the Field Research Center of the Department of Energy at Oak Ridge National Laboratory. The overall objective of this study was to determine the effects of biostimulation on the mineralogy and oxidation state of Fe in the soil. The principal method for evaluating changes in Fe mineralogy was variable-temperature Mössbauer spectroscopy between 4 and 298 K. Specific objectives were to ascertain the importance of carrying out the measurements over a range of temperatures from 4 K upward, to determine the change in Fe oxide content due to bioreductive dissolution, to measure the change in silicate Fe oxidation state, and to identify, to the extent possible, which Fe oxides are present in the resulting biostimulated cores. Biostimulation caused extensive dissolution of the Fe oxides in the soil, decreasing them from 64.5% of the total Fe to only 45.3%. The Fe(II)/Fe(III) ratio in the silicate phase simultaneously increased from 0.328 to 0.390, indicating that, in addition to dissolving Fe oxides, biostimulation also partially reduced the Fe in the silicate phase. Comparison of peak area ratios at 4 and 77 K revealed that measurement of the Mössbauer spectra at a sample temperature of 4 K is critical to obtaining reliable estimates of the relative amounts of Fe in oxide versus silicate phases. For example, the Fe distributed in the oxide phase in the original (unbiostimulated) soil was estimated from the 4 K spectra to be 64.5 % of the total Fe, whereas the corresponding value from the 77 K spectra was only 56.5%. After biostimulation, the estimates from 4 and 77 K were 45.3% and 31.2%, respectively. In both samples the 77 K spectra underestimated the amount of Fe in the oxide phases by a large margin compared to the 4 K spectra.

A previous strategy to obtain accurate Fe oxide contents from 77 K spectra (because 4 K was inaccessible with available cryostats) was to remove superparamagnetic Fe oxides by acid ammonium oxalate treatment. To test the efficacy of this strategy, samples were submitted to the oxalate treatment and Mössbauer spectra obtained at both 4 and 77 K. In the biostimulated sample, the resulting distributions for Fe in the oxide phases were 42.5% and 35.4%, respectively. Results at 4 K revealed that the oxalate treatment removed only a small amount of the Fe oxide (45.3% decreased to 42.5%). The 77 K spectrum after oxalate treatment reported Fe oxide content to be about 35.4%, which differs significantly from the 4 K value of 42.5%. Hence, spectra at 4 K are essential. More work is needed to identify the specific Fe oxide minerals that are present, but at least three different components were detected.

Acknowledgments: Financial support from the DOE-NABIR and NSF Geochemistry Programs

BIOREDUCTION OF Fe IN SHALE-LIMESTONE SAPROLITE CONTAINING Fe(III) OXIDES AND Fe(II)/Fe(III) PHYLLOSILICATES

Ravi K. Kukkadapu*[1], John M. Zachara[1], James K. Fredrickson[1], David W. Kennedy[1], Steven C. Smith[1,] and Hailiang Dong[2]

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A <2.0-mm fraction of sediment containing 4.6-wt.% Fe (Fe_{TOT}) was incubated with *Shewanella putrefaciens* (strain CN32) under anoxic conditions with lactate as electron donor. The incubation was carried out in an HCO_3^- buffer at circumneutral pH. The sediment was obtained from a U.S. DOE experimental site (Oak Ridge Field Research Center) where *in situ* stimulation of dissimilatory Fe reduction is being studied as a potential approach to arrest the subsurface migration of mobile radionuclides [U(VI) and Tc(VII)]. Quartz, illite, and vermiculite dominated the sediment composition. Approximately 60 to 70% of the Fe_{TOT} existed in the silicate environment (illite and vermiculite; with Fe(II)/Fe(III) ratio of ~0.2) while the remainder was Fe(III)-oxide (primarily goethite), based on Mössbauer measurements.

Fe(III) bioreduction was not observed until essentially all of the hydroxylamine-HCl extractable Mn was reduced (10 days). The Fe(III) bioreduction was followed as a function of time (as determined by 0.5 N HCl extraction). Approximately 17% of the Fe_{TOT} was extracted from 60-day bioreduced samples. Almost all of the extracted Fe, which was Fe(II), remained associated with the bioreduced sediment. The Fe(II)/Fe(III) ratio (e.g., >0.6; 60 d) of the bioreduced samples was significantly higher than that of the unreduced sample. The superposition of Fe(II) from silicate and discrete biogenic Fe (if any) in the Mössbauer spectra made it difficult to identify the latter phase and follow changes in the Fe(II)/Fe(III) ratio of the residual silicate. A combination of chemical extractions (e.g., $CaCl_2 \cdot 8H_2O$, acid-ammonium oxalate [AAO], 0.5 N HCl) and Mössbauer spectroscopy (at various temperatures of the unreduced, reduced, and reoxidized samples—untreated and chemically extracted) was used to characterize the Fe phase(s) of the bioreduced samples. A significant portion of the Fe(II) in the bioreduced sample was readily oxidized in air. Very little Fe was extracted by $CaCl_2 \cdot 8H_2O$ (in PIPES-buffer), indicating that biogenic Fe was either precipitated or strongly adsorbed, or the increase in Fe(II) signal was mainly due to the bioreduction of silicate Fe(III). There was little evidence of the formation of siderite. Significant amounts of Fe(III) [along with some Fe(II)], however, was extracted by AAO. Fe(II) catalyzes Fe-oxide dissolution in the presence of AAO (Sulzberger et al., 1989). Combinedly, the data suggested that at least a portion of the Fe(II) in the bioreduced sample was associated with a phase(s) that was soluble in AAO. Additional experiments and Mössbauer measurements are underway for further characterization of the bioreduced sample to determine whether the increased Fe(II) signal in the Mössbauer spectra was primarily caused by discrete biogenic Fe-phase, adsorbed Fe, and/or the bioreduction of silicate Fe(III).

Reference

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MONDAY JUNE 21, 2004

MICROBIAL IMPACTS ON CLAY TRANSFORMATION AND REACTIVITY

POSTER SESSION

5:00PM

SINTER MINERALOGY OF TERRESTRIAL HOT SPRING VENT, UZON CALDERA, KAMCHATKA, RUSSIA.

Jennifer E. Kyle*, and Paul A. Schroeder

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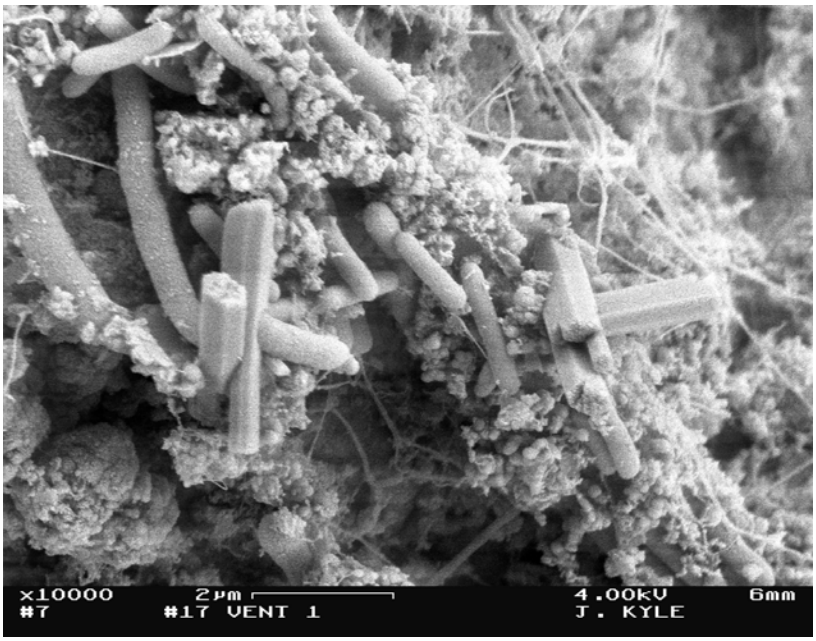
Sinter material was collected at two vents (designated Jenn's Pools) during a field expedition to the Uzon Caldera, in Kamchatka, far-east Russia. Vent outflow conditions were characterized with temperatures of 80-85 °C, pH 5.5, Eh –240 mV, and alkalinities of 220 units and 160 units for vent 1 and vent 2 respectively. Flow conditions of vent 2 pulsated at intervals that averaged 4.5 minutes. Gases emitted from the pool had values of 1800, 560, and 9600 ppmv for H_2, CO, and CH_4, respectively. Microbial mats were collected at the edges of the pools, with some preserved in 2% gluteraldahyde.

X-ray powder diffraction (XRD), energy dispersive spectroscopy (EDS), and scanning electron microscopy (SEM) studies reveal the dominant phases present are opal-A and elemental sulfur. Other phases identified by XRD and EDS include gypsum, pyrite, marcasite, opal-CT, cinnabar, barite, kaolin group minerals, andesine, quartz, jarosite, and magnetite. Textural analysis shows the sinters have light and dark laminations, with spicules of opal directed upward. SEM shows microbe morphologies are rod shaped and filamentous, and also the presence of spores. The premise for this work is to study the relationship between minerals and microorganisms and the biomineralization that result from this association. Biomineralization remnants record the existence of primitive life forms on Earth throughout history and perhaps other planets.



SEM micrograph of rod shaped microbes in close association with crystals on the sinter deposit from the rim of vent 1.

INTERACTION BETWEEN VERMICULITE AND THE BACTERIUM *PSEUDOMONAS FLUORESCENS* STRAIN CHA0 AND ITS GENETIC DERIVATIVES

Barbara Müller

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It has been known for a long time that bacteria can alter the properties of the clay minerals. In an ongoing study we have analyzed the influence of *Pseudomonas fluorescens* strain CHA0 on the chemical, mineralogical and mechanical properties of the clay mineral vermiculite affected by microbial activity. These interactions include the changes in chemical (e. g. minor and trace element content), mineralogical (X-ray diffraction pattern, water content, grain size distribution, intracristalline swelling, cation exchange capacity, layer charge, exchangeable cations, specific surface) and mechanical parameters (soil mechanical behavior, e g. swelling, rheology, compressibility, plasticity and shear strength) of the clay mineral vermiculite. Mechanisms of the interactions will be determined by using genetic derivatives of strain CHA0, derivatives modified in the production of metabolites.

So far, determination of the major, minor and trace element content, water content, grain size, X-Ray diffraction pattern, intracrystalline swelling with glycerine, layer charge, CEC, exchangeable cations, BET surface and rheology provided the necessary information about the differences between pure vermiculite, vermiculite suspensions containing the nutrient medium and vermiculite suspensions containing the nutrient medium and the bacterium *Pseudomonas fluorescens* strain CHA0.

We found that the aerobic bacterium *Pseudomonas fluorescens* strain CHA0 causes changes in trace element composition, grain size, agglomeration of vermiculite grains as evidenced by smaller BET surfaces, beginning dissolution as shown by SEM and ESEM studies and enhanced viscosity of the bacteria containing slurries. Vermiculite in contact with bacteria contained significantly less Zn and V, but the same amount of e. g. Fe and Cu, compared to vermiculite from bacteria free slurries after two weeks of experiment run time. The bacteria therefore seem to take up the trace elements Zn and V.

Layer charge, intracrystalline swelling and CEC were not affected by the microbial activity, nor did the bacteria count for the exchange of potassium against sodium in the vermiculite. The microbes inhibited the last process during the first stage of the experiments, however increasing run time favors this exchange as well.

TUESDAY JUNE 22, 2004

MICROBIAL IMPACTS ON CLAY TRANSFORMATION AND REACTIVITY

POSTER SESSION

5:00PM

INTERACTIONS OF URANIUM WITH MIXTURES OF MICROORGANISMS AND KAOLINITE CLAY

Toshihiko Ohnuki[*1], Takahiro Yoshida[1], Takuo Ozaki[1], Mohamad Samadfam[1], Naofumi Kozai[1], and Arokiasamy J. Francis[2]

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Microorganisms can affect the mobility of actinides in the environment from the geological disposal of radioactive wastes. Little is known about the U sorption by microorganisms-mineral mixtures, although sorption of U by clay minerals or bacteria has been extensively studied and much has been learned about the bacterial uptake mechanisms. In this study, we determined the accumulation of uranium (VI) by a mixture of *Bacillus subtilis* and kaolinite to elucidate the role of microbes on U(VI) mobility. A mixture consisting of 100 mg of *B. subtilis* and kaolinite was exposed to $4x10^{-6}$ M or $4x10^{-4}$ M U(VI) in 0.01 M NaCl at pH 5. Contents of *B. subtilis* were ranged from 0 to 5% in the mixtures. After 48 h the mixtures were separated and the concentration of U in solution was determined. The solids were extracted with 1 M KCl solution for 24 h to determine the association of U with the mixture. The mixture exposed to $4x10^{-4}$ M U was analyzed by transmission electron microscope (TEM) equipped with EDS. Accumulation of U by the mixture increased with an increase in the amount of *B. subtilis* in the mixture at both U concentrations examined. Almost all of the U associated with the kaolinite without the bacteria was removed when extracted with 1 M KCl solution. However, in the presence of *B. subtilis* the amount of U extracted decreased with an increase in the amount of bacteria in the mixture. TEM-EDS analysis showed that most of accumulated U was associated with *B. subtilis*. These results suggest that the bacteria have a higher affinity for U than the kaolinite clay mineral because they possess several different functional groups capable of binding U and that the bacteria can immobilize significant amount of uranium.

WEDNESDAY JUNE 23, 2004

MICROBIAL IMPACTS ON CLAY TRANSFORMATION AND REACTIVITY III

1:20PM

CONTROLLED CULTIVATION: APPROACHES FOR DEBUGGING BIOGEOCHEMICAL RESEARCH

Yuri A. Gorby

Biological Sciences Division, Pacific Northwest National Laboratory, Richland, WA, 99352 USA

Extracellular and cell surface components of bacteria significantly influence biogeochemical processes, including sorption and valence transition of dissolved metal ions, solid phase metal oxides, and metals bound or otherwise associated with structured clay minerals. Environmental conditions directly influence metabolic and physiological processes in bacteria, including the composition and reactivity of cell surface components involved in biogeochemical processing of minerals. Surprisingly, technologies that enable the monitoring and control of environmental parameters and thereby reduce the list of unknowns that contribute to the complexity of biogeochemical reactions are commonly excluded from biogeochemical research. This presentation provides examples of how controlled cultivation technologies advance our understanding of fundamental and practical aspects of metal-microbe interactions, with particular emphasis given to the metal reducing bacterium *Shewanella oneidensis* strain MR-1.

ROLE OF MICROBES IN PROMOTING THE SMECTITE TO ILLITE REACTION

Jinwook Kim[*1], Hailiang Dong[2], Jennifer Seabaugh[2], Steven W. Newell[1], and D. D. Eberl[3]

[1] Naval Research Laboratory, Seafloor Sciences Branch, Stennis Space Center, MS 39529, USA, [2] Department of Geology, Miami University, Oxford, OH 45056, USA, [3] U. S. Geological Survey, Boulder, CO 80303, USA

The smectite-to-illite (S-I) transformation is closely related to hydrocarbon maturation, geopressuring of shale, formation of growth faults, and changes in pore-water chemistry. The S-I transformation occurs approximately concomitant with maturation of petroleum during sediment diagenesis. The degree of S-I transformation is used frequently as an independent geothermometer to allow reconstructions of the thermal and tectonic history of sedimentary basins. Numerous studies have emphasized temperature, pressure, and time as geological variables in either solid state or dissolution-precipitation S-I transformation mechanisms, but none of them has taken into account the role of microbes. Here, using high resolution transmission electron microscopy (HRTEM), and X-ray diffraction (XRD) we demonstrate that microorganisms can promote the S-I transformation via reduction of structural Fe(III) in smectite. This observation is significant because bacteria can transform smectite to illite at room temperature and one atmosphere within 21 days. This S-I reaction typically requires conditions of 300-350°C, 100 mPa, and 4-5 months in the absence of microbial activity. Therefore, these results, which challenge the conventional concept of the S-I transformation and of reaction kinetic models, have far-reaching implications.

DISSOLUTION OF MICROBIAL REDUCED NONTRONITE IN A FLOW-THROUGH SYSTEM

S.E. O'Reilly[1*], B.R. Bickmore[2], and Y. Furukawa[1]

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Nontronite evolution due to microbial reduction of structural iron over time by *Shewanella oneidensis* has been examined using a flow-through system enclosed in an O_2-free environment. Surface chemical changes, along with microbially induced structural and mineralogical changes, affect the sorption and flocculation properties of nontronite in the aquatic environment, which in turn can affect important environmental processes such as sediment transport and contaminant transformation. Flow-through experimental systems with in-line pH monitoring capabilities were utilized to facilitate the microbial reduction under controlled solution conditions, and to monitor the kinetics of Fe speciation. Major system ions such as Mg, Al, and Si, among others, as well as organic acids indicative of microbial activity such as lactate and acetate, were also monitored. The flow-through system allows the time-dependent characterization of aqueous products in a system free of product build-up while supplying the constant concentrations of nutrients. The solid products were also examined at the end of each run with a combination of advanced microscopic and spectroscopic techniques, including transmission electron microscopy (TEM), selected-area electron diffraction (SAED), energy dispersive X-ray spectroscopy (EDS), and atomic force microscopy (AFM). After 7 days, a significant amount of structural Fe(III) in nontronite was reduced to Fe(II). The effluent solution analyses indicate that approximately 0.012 % of Si and 0.42 % of Mg present in the original solid phase had been transferred to the solution phase by the end of the 7 day experiment, whereas the solution concentration of Fe was minimal and Al was below detection limits; solution concentrations of Fe/Si, Mg/Si, and Al/Si were not stoichiometric after 7 days. The TEM, SAED, and EDS analyses show the precipitation of secondary nanoparticles, including crystalline and amorphous silica phases (formed under conditions undersaturated with respect to amorphous Si and imogolite), siderite, vivianite, and a Ca-rich, unidentified phase. In addition, AFM analyses of nontronite particle morphologies suggest that their dissolution is, in fact, stoichiometric. These results indicate that the change in nontronite surface chemistry due to microbial reduction, which was previously inferred from changes in flocculation properties, is due to an increase in nontronite layer charge as Fe is reduced, as well as the formation of secondary nanoparticles with diverse surface chemical properties.

REDUCTION OF STRUCTURAL Fe(III) IN NONTRONITE BY A THERMOPHILIC BACTERIUM

Jennifer L. Seabaugh[*1], Hailiang Dong[1], Dennis D. Eberl[2], Jinwook Kim[3], Ravi K. Kukkadapu[4]

[1]Miami University, Oxford, OH 45056; [2]U.S. Geological Survey, Boulder, CO 80303; [3]Naval Research Laboratory, Seafloor Sciences Branch, Stennis Space Center, MS 39529; [4]Pacific Northwest National Laboratory, Richland, WA 99352

A study was undertaken to investigate the extent and rate of reduction of structural Fe(III) in nontronite (NAu-2) by a thermophilic bacterium *Bacillus infernus* strain TH-23. Nontronite NAu-2 occurs in the Uley Graphite Mine on the Southern Eyre Peninsula in South Australia (Keeling et al. 2000). It was obtained from the Source Clay Repository of the Clay Minerals Society. The < 0.5 μm size fraction used in this experiment and was a relatively pure dioctahedral smectite, containing trace amounts of quartz and no other Fe-bearing minerals, as indicated by XRD. All Fe in structure is in the form of Fe(III), which can be found in both octahedral and tetrahedral sites (Keeling et al., 2000; Gates et al., 2002).

Despite the high temperature and pressure of the deep subsurface, microbial activity has been found (Ghiorse and Wilson, 1988). *Bacillus infernus* was isolated 2,700 m below the surface in the Taylorsville Triassic Basin in Virginia (Boone et al. 1995). This organism is both strictly anaerobic and thermophilic. It can respire using both Fe(III) and Mn(IV) as electron acceptors.

MS growth medium was used for the experiment in addition to lactate as a substrate. In selected treatments, antraquinone-2,6-disulfonate (AQDS) was included as an electron shuttle to facilitate electron transfer. The controls were identical to the treatments except that there were no cells. Fe(II) production at various time points was determined by Ferrozine assay. Fe(III) in NAu-2 was the only electron acceptor. Residual and biogenic solids were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and Mössbauer spectroscopy .

The extent of reduction was greater in the presence of AQDS. According to Ferrozine analysis, the maximum amount of Fe(III) reduced in NAu-2 structure was 18% and was reached in 24 hours. In the experiment without AQDS, there was a reduction of 14% of the structural Fe(III) in NAu-2. XRD analysis of the bioreduced NAu-2 showed a decrease in the nontronite crystalline thickness from 6 nm to 3.4 nm. Microbial reduction also changed the crystal size distribution from lognormal to an asymptotic shape suggesting a crystal growth mechanism of simultaneous nucleation and growth. TEM analyses suggest the presence of a small amount of biogenically produced minerals. Initial characterizations appear to suggest the presence of siderite and vivianite. Preliminary Mössbauer spectroscopy results suggest that the tetrahedral Fe(III) was preferentially reduced relative to the octahedral Fe(III). More extensive characterizations of these minerals are underway.

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Gates, W. P., Slade, P.G., Manceau, A., Lanson, B. (2002) Clays Clay Miner., 50(2), 223-239.
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Keeling, J. L., Raven, M. D., Gates, W. P. (2000) Clays Clay Miner., 48(5), 537-548.

WEDNESDAY JUNE 23, 2004

MICROBIAL IMPACTS ON CLAY TRANSFORMATION AND REACTIVITY IV

3:20PM

NANOPARTICULATE SILICA COLLOID SIZE DISTRIBUTIONS ASSOCIATED WITH BACTERIAL CELLS

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The diameters of spherical silica colloids associated with bacteria in transmission electron microscopic images of geothermal sediment samples were measured to gather data sets for particle size distribution (PSD) analyses. A parallel series of measurements were compiled from each TEM image for silica colloids that were spatially separated from the bacterial cells. In total, 20 particle size data sets were generated from a digital TEM library with images from 7 different geothermal localities, and 3 experimental studies of bacterial silicification. Statistical evaluation of the silica PSDs was done using the nonparametrics and distribution fitting modules of STATISTICA (version 6.0). In all cases, the measured discrete PSDs were fit well by an asymmetrical extended gamma (Pearson Type III) distribution. Such positively skewed PSDs develop commonly in response to nucleation followed by particle growth and ripening. Comparison of the first four central moments of the PSDs (i.e., mean, variance, skewness, and kurtosis) revealed progressively increasing differences between those measured on versus away from bacterial cells. Mean particle diameters ranged from 10 to 300 nm, depending on the sample origin, but there was little difference between those on or away from the bacteria (R=0.96). Conversely, the variance of the PSDs away from bacterial cells was 23 % greater than that associated with bacteria (R=0.97), while the skewness and kurtosis were ca. 50 % and 80% lower, respectively. These data confirm that, despite similar mean values, PSDs of silica colloids away from bacterial cells are broader and more gaussian in shape than PSDs on bacteria. At the same time, minimum particle size values on bacteria remain up to 70% smaller than those away from cells (R=0.91). The implication is that silica colloids associated with bacteria are stabilized (i.e., rendered more insoluble) in the interfacial space near cells and are thus less prone to dissolution and aggregation, which normally promotes the growth of larger silica particles.

MICROBIAL WEATHERING OF ORTHOPYROXENE AND CLAY FORMATION IN AN ARID ENVIRONMENT: A STXM AND HRTEM STUDY

Karim Benzerara[*1], Tae-Hyun Yoon[1], Nicolas Menguy[2], Francois Guyot[2], Tolek Tyliszczak[3], and Gordon E. Brown, Jr.[1]

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The microbial alteration of a Mg-Fe orthopyroxene reacted for 70 years under arid conditions was studied by High-Resolution Transmission Electron Microscopy and Scanning Transmission X-ray Microscopy. An electron transparent cross section of the interface between a single microorganism and an orthopyroxene grain was prepared with a focused ion beam-SEM system. Electron energy loss spectroscopy (EELS) and Near Edge X-ray Absorption Fine Structure microspectroscopy allowed us to unambiguously identify the organic carbon and the iron oxidation state at the nanometer scale. A 100 nm deep depression was observed in the orthopyroxene adjacent to the microorganism rather than below it, suggesting enhanced dissolution of the pyroxene mediated by the microbe. In contrast, an Al- and Si-rich amorphous altered layer was observed beneath the microorganism. This aluminosilicate altered layer is consistent with decreased pyroxene dissolution rates just beneath the microorganism relative to the closely adjacent area containing the etch pit, showing the complex effects of the microorganism on silicate dissolution processes. Casey et al. (1993) observed a gel-like layer at the surface of Mg-Fe-olivines in laboratory dissolution experiments and hypothesized that such leached layers are suitable locations for topotactic growth of phyllosilicates on primary silicate minerals. Our TEM observation of a nm-sized clay particle in the amorphous layer growing in epitaxial relationship with the orthopyroxene under natural conditions is consistent with this hypothesis.

Casey, W. H., Westrich, H. R., Banfield, J. F., Ferruzzi, G., and Arnold, G. W. (1993) Leaching and reconstruction at the surfaces of dissolving chain-silicate minerals. *Nature* **366**, 253-256.

BIOGENIC DISSOLUTION OF SOIL PHOSPHATE MINERALS

Javiera Cervini-Silva[*1], David Fowle[2], and Jillian F. Banfield[1]

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The productivity of many terrestrial ecosystems is controlled or limited by the available phosphorus. Within these ecosystems nearly all of the biologically available P reservoir is derived via the weathering of apatite [$Ca_5(PO_4)_3.(OH,F,Cl)$]. After the initial weathering of apatite, the secondary mineralization of highly insoluble lanthanide phosphate minerals remains as important phosphorous repositories in soils. Although these phases can be dissolved via biologically-mediated pathways, the current view of the global P cycle is that microbial reactions do not lead to dramatic increases in available P unlike the terrestrial nitrogen and carbon cycles. However, this gap in the global P cycle may simply be the result of a poor mechanistic understanding of the biotic and abiotically mediated dissolution mechanisms. In this manuscript we show that ubiquitous ligands that may have high activities in soils namely ascorbate, citrate, oxalate, and humic acids facilitate the dissolution of rhabdophane $CePO_4.H_2O$ at $3 < pH < 8$. Dissolution experiments under far-from-equilibrium conditions show that the most effective biogenic ligand in releasing P is oxalate (rate of P release R_P is as high as 5.8×10^{-9} mol m^{-2} s), followed by citrate (3.3×10^{-9} mol m^{-2} s), and humic acids (1.6×10^{-9} mol m^{-2} s) and ascorbate (3.6×10^{-10} mol m^{-2} s). The effectiveness of oxalate and citrate in releasing P surpasses that by commercial EDTA (2×10^{-9} mol m^{-2} s). Optimum pH for dissolution is dependent on speciation and redox properties. Evidence of non-congruent dissolution, and μ-XRD and ATR-FTIR analyses of weathered phosphate minerals samples indicate cerium dissolution and oxidation. In parallel work we show that the formation of nanocrystalline ceria CeO_2 following weathering of $CePO_4.H_2O$ by catecholate accelerate oxidation reactions, including the formation of humic material, decarboxylation to CO_2, and partial oxidation to soluble organic acids [Cervini-Silva and Banfield, (in review)]. In the present manuscript we show that ligand-controlled electron transfers facilitate the formation of CeO_2. To date, oxidation of Ce^{3+} has been identified to occur enzymatically. Our findings show that simple organic ligands accelerate cerium oxidation, a previously unrecognized process of cerium biogeochemical cycling that may exert key controls and provide new linkages between the phosphate and organic carbon cycles in terrestrial ecosystems.

EFFECTS OF SIDEOROPHORES ON Pb AND Cd ADSORPTION TO KAOLINITE

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Siderophores are Fe(III)-specific organic ligands synthesized by aerobic microorganisms in Fe-deficient environments. In addition to Fe (III), siderophores may complex other metals such as Pb and Cd; hence, siderophores may influence metal mobility in soils. This study compared the effects of the trihydroxamate siderophores desferrioxamine-B (DFO-B), desferrioxamine-D (DFO-D1), desferrioxamine-E (DFO-E), and the monohydroxamate siderophore-like ligand acetohydroxamic acid (aHA) on Pb and Cd (excepting DFO-E) 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, all of the studied ligands decreased Pb adsorption to kaolinite: aHA by 5 to 40% and DFO-B, DFO-D_1 and DFO-E by 30 to 75%. The studied ligands decreased Cd adsorption to kaolinite at pH > 8: aHA by 5 to 20% and the trihydroxamates by as much as 80%. The decreased adsorption of Pb and Cd was due to the competition between the ligands in solution and the kaolinite surface for the metals. However, we also observed evidence that siderophores may, in some instances, enhance adsorption. For example, enhancement of Pb adsorption in the presence of DFO-B at pH 4.5 to 6.0 might have been due to adsorption of the doubly positively charged $PbH_3(DFO\text{-}B)^{2+}$complex, which is present in solution within this pH range. Spectroscopic investigations of Pb adsorption to kaolinite in the presence and absence of siderophores is ongoing. Overall, results of these experiments show that siderophores tend to inhibit metal adsorption to kaolinite at intermediate to high pH. However, enhanced adsorption sometimes may occur at lower pH, a phenomenon that requires further study.