

ENVIRONMENTAL AND SOIL CHEMISTRY OF CLAYS

Monday June 21, 2004

Environmental and Soil Chemistry of Clays	
10:00 – 10:20a	<p>PLUTONIUM TRANSPORT FOR 11 YEARS THROUGH A VADOSE ZONE SEDIMENT: INFLUENCE OF OXIDATION STATE. Daniel I. Kaplan^{*1}, Brian A. Powell², Deniz I. Demirkanli¹, Robert A. Fjeld², Fred J. Molz², Steven M. Serkiz¹, and Martine C. Duff¹</p> <p>¹Westinghouse Savannah River Company, Aiken, SC, 29808; ²Dept. of Environmental Engineering & Science, Clemson University, Clemson, SC, 29634</p>
10:20 – 10:40a	<p>URANIUM AND TRITIUM TRANSPORT IN VADOSE ZONE SEDIMENTS. D. Craig Cooper^{*1}, Mitchell A. Plummer¹, Don T. Fox¹, Ravi K. Kukkadapu², and Lawrence C. Hull¹</p> <p>¹Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID 83415 (coopdc@inel.gov); ²Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory, Richland, WA, 99352</p>
10:40 – 11:00a	<p>ARSENIC MOBILIZATION AND MINERALOGY OF ANOMALOUS SOILS FROM BRAZIL. Jaime W. V. de Mello^{1*}, Joseph W. Stucki², William R. Roy³, Jonathan L. Talbott⁴</p> <p>¹Soil Department, Federal University of Vicosa, MG 36570-000 Brazil; ²Department of Natural Resources and Environmental Sciences, University of Illinois; ³Illinois State Geological Survey; ⁴Waste Management and Research Center, University of Illinois</p>
11:00 – 11:20a	<p>INTERACTIONS WITH THE NONIONIC SURFACTANT Brij 35 INFLUENCE SORPTION OF ATRAZINE ON K- AND Ca-SMECTITES. Mark A. Chappell^{*1}, David A. Laird², Michael L. Thompson¹, and P. Evangelou³</p> <p>¹Iowa State University, Ames, IA; ²USDA-ARS National Soil Tilth Laboratory, Ames, IA; ³Deceased</p>
11:20 – 11:40a	<p>SORPTION OF TETRACYCLINE AND CHLOROTETRACYCLINE ON K- AND CA-SATURATED SOIL CLAYS AND HUMIC SUBSTANCES. Jutta R.V. Pils^{*1}, and David A. Laird²</p> <p>¹Iowa State University Ames, IA; ²National Soil Tilth Lab Ames, IA</p>
11:40 – 12:00p	<p>TECTONIC IMPLICATIONS OF SOIL CLAY MINERALOGY AND GEOCHEMISTRY IN A TROPICAL TERRACE SEQUENCE, COSTA RICA. Burch Fisher[*], and Peter Ryan</p> <p>Geology Department, Middlebury College, Middlebury, VT 05753</p>

Environmental and Soil Chemistry of Clays Poster Session	
5:00p	SEQUENCE STRATIGRAPHY OF THE EOCENE HUBER-DRY BRANCH INTERVAL IN THE GEORGIA COASTAL PLAIN. John A. Allen ^{*1} , Steven M. Holland ¹ , and Mack S. Duncan ² ¹ University of Georgia, Athens, GA 30602, ² J.M. Huber Corporation, Wrens, GA 30833
5:00p	FIFTY YEARS OF CLAY MINERALOGY DEVELOPMENT: REVIEW AND OUTLOOK. Joe B. Dixon Soil & Crop Sciences Dept., Texas A&M University, College Station, TX 77843 2474
5:00p	SIMPLE APPROACH TO REMOVE LEAD FROM WATER WITH CLAY. Carmen O. Melendez-Pizarro [*] , and Antonio S. Lara New Mexico State University, Department of Chemistry and Biochemistry, P.O. Box 3C, Dept. 30001, Las Cruces, NM 88003
5:00p	EVALUATION OF THE POTENTIAL FOR BIOREMEDIATION OF DEEPLY WEATHERED SOIL/SAPROLITE IN THE AREA 2, NABIR FRC SITE, TENNESSEE. Ji-Won Moon ^{*1} , Yul Roh ¹ , Tommy J. Phelps ¹ , David B. Watson ¹ , and Gyoo Ho Lee ² ¹ Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831; ² Korea Institute of Geoscience and Mineral Resources, Daejeon, 305-350, Korea.
5:00p	MINERALOGICAL-GEOCHEMICAL CHARACTERIZATION OF SEDIMENTS BELOW MANGROVE FORESTS AT THE RED RIVER MOUTH (AN EXAMPLE FROM NAM DINH PROVINCE/VIETNAM). Ngoc Thi Minh Nguyen ¹ , Mai Trong Nhuan ² , and Joern Kasbohm ¹ ¹ Institute of Geography and Geology, Ernst-Moritz-Arndt-University of Greifswald, Germany; ² Faculty of Geology, Hanoi University of Science, 334, Nguyen Trai Rd. Thanh Xuan Dist. Hanoi, Vietnam. <i>E-mail</i> : tn023510@uni-greifswald.de
5:00p	THE IONIC-COVALENT PARAMETER IN ION-EXCHANGE EQUILIBRIUM. Jacob G. Reynolds Washington Group International, Richland, Washington, 99352
5:00p	A WORKSHEET MODEL FOR ADSORPTION/DESORPTION OF IONS ON CLAY SURFACES. Giora Rytwo School of Environmental Sciences and Technology, Tel Hai Academic College, Upper Galilee 12210, Israel; MIGAL, Galilee Technological Center, Kiryat Shmona, Israel. E-mail: rytwo@telhai.ac.il ; http://www.migal.co.il/SoilEnvironmental.html
5:00p	AN INVESTIGATION OF THE IRON OXIDES AND CLAY MINERALS OF THE ANKARA CLAY. Zeynep J. Saglam ^{*1} , Asuman G. Turkmenoglu ² , and Warren D. Huff ¹ ¹ University of Cincinnati, Department of Geology, Cincinnati, OH 45221; ² Middle East Technical University, Department of Geological Engineering, Ankara, 06531 Turkey.
5:00p	BIOAVAILABILITY OF ORGANIC MATTER INTERCALATED INTO NONTRONITE CLAY. Gengxin Zhang [*] , Deb P. Jaisi, Hailiang Dong Miami University, Department of Geology, Oxford, OH 45056

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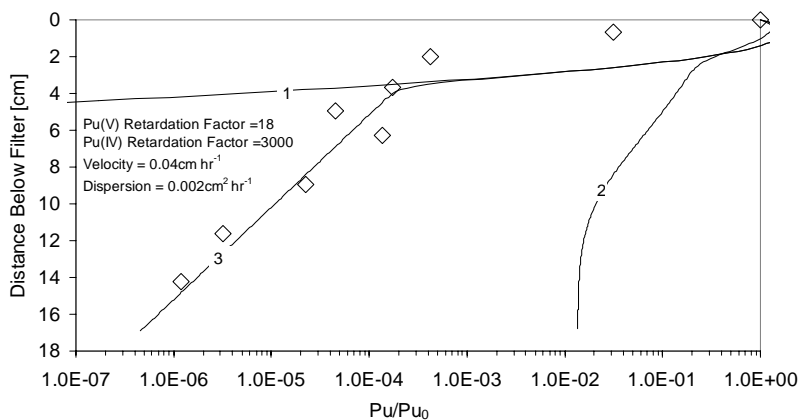
10:00AM

PLUTONIUM TRANSPORT FOR 11 YEARS THROUGH A VADOSE ZONE SEDIMENT: INFLUENCE OF OXIDATION STATE

Daniel I. Kaplan^{*1}, Brian A. Powell², Deniz I. Demirkanli¹, Robert A. Fjeld², Fred J. Molz², Steven M. Serkiz¹, and Martine C. Duff¹

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Lysimeter and laboratory studies were conducted to identify the controlling chemical processes influencing Pu(IV) mobility through the vadose zone. A 52-L lysimeter containing sediment from the Savannah River Site, South Carolina and solid Pu^{IV}(NO₃)₄ was left exposed to natural wetting and drying cycles for 11 years before the lysimeter sediment was sampled. Pu had traveled 10 cm, with >95% of the Pu remaining within 1.25 cm of the source (see below). Laboratory studies showed that the sediment could quickly reduce Pu(V) to Pu(IV) (the 1st order reduction rate constant, k'_{obs} , was 0.11 hr⁻¹). XANES spectra showed the presence of Pu(IV), based on edge energy. Plutonium(V) reduction was believed to be induced by microbes or various Fe-bearing minerals. Of particular interest was that this same sediment could be induced to release very low concentrations of sorbed Pu under oxidizing conditions, presumably by oxidation of sorbed Pu(IV) to the more mobile Pu(V) species. Transport modeling supported the contention that Pu oxidation occurred in the lysimeter sediment; the inclusion of an oxidation term in the model produced simulations that capture the Pu depth profile data. By not including the oxidation process in the model, Pu mobility was grossly underestimated by a factor of 3.5. Both oxidation and reduction mechanisms can play an important role in Pu transport through the vadose zone and should be considered when evaluating disposal of Pu-bearing wastes.



Normalized total Pu sediment concentrations (Pu/Pu₀) in the Pu^{IV}(NO₃)₄-amended lysimeter. Diamond symbols represent measured values. Simulation input values (k_o and k_r are the first-order rate constants for Pu(IV) oxidation and Pu(V/VI) reduction, respectively): (1) $k_o = 0 \text{ hr}^{-1}$, $k_r = 0 \text{ hr}^{-1}$; (2) $k_o = 1\text{e-}5 \text{ hr}^{-1}$, $k_r = 0 \text{ hr}^{-1}$; (3) $k_o = 1\text{e-}8 \text{ hr}^{-1}$, $k_r = 1.2\text{e-}3 \text{ hr}^{-1}$.

URANIUM AND TRITIUM TRANSPORT IN VADOSE ZONE SEDIMENTS

D. Craig Cooper^{*1}, Mitchell A. Plummer¹, Don T. Fox¹, Ravi K. Kukkadapu², and Lawrence C. Hull¹

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Groundwater resources in the Western United States are typically separated from the soil zone by a thick region of unsaturated sediments known as the vadose zone. This region is characterized by irregular fluid transport, and biogeochemical cycles that are strongly impacted by the composition of soil gas. Natural resource utilization and legacy waste from the Cold War have introduced contaminants into the Vadose Zone, and population growth is continually placing new stresses on limited groundwater supplies. Biogeochemical processes within the Vadose Zone are poorly understood, and proper utilization of this critical groundwater resource requires an increased understanding of the processes that control contaminant fate and transport in the vadose zone.

We have recently conducted a 2 year contaminant transport experiment utilizing a *mesoscale* unsaturated column (~3 m tall and ~1 m dia). The objectives of this experiment were to determine how gas phase chemistry and vadose zone microbiological processes in a natural CO₂/O₂ gradient affect ¹⁴C and ²³⁸U transport, and to develop conceptual models that can be used to predict how various remediation/management schemes may alter contaminant transport. While this work has been targeted toward addressing a specific DOE contamination problem, the results have implications for a range of scientific issues.

The sediments used in the experiment were a clayey-silt with many geochemical properties that are common in Western vadose zone systems. Clay minerals present the majority of reactive surfaces, and carbonate mineral dissolution appears to increase clay surface reactivity. Furthermore, dissolution of soluble Ca²⁺ salts (e.g. NO₃⁻, SO₄²⁻) may increase the degree of carbonate supersaturation and impact carbonate geochemistry. Tritium transport was approximately 1.4x slower than Br⁻ transport, and comparison with the water balance indicates ³H retention. Geochemical modelling indicates that ³H⁺ complexation with clay mineral AlOH sites can account for this difference. Geochemical modelling also indicates that ²³⁸U moved only ~20-30 mm over a period of 18 months, and analysis of solid-phase ²³⁸U in cores recovered from the column supports this prediction. As with ³H, the model predicts that clay mineral AlOH sites accounted for most ²³⁸U sorption. Independent confirmation of predicted ³H and ²³⁸U surface speciation is not yet available. These data indicate that clay minerals are a more important adsorbent than iron oxides in sediments from the Snake River Plain in Idaho, and CO₂ driven changes in pH and carbonate chemistry provide an important control on contaminant speciation and transport in vadose zone systems.

ARSENIC MOBILIZATION AND MINERALOGY OF ANOMALOUS SOILS FROM BRAZIL

Jaime W. V. de Mello^{1*}, Joseph W. Stucki², William R. Roy³, Jonathan L. Talbott⁴

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Arsenic biogeochemistry and its dynamics in the environment are considered to be related to iron oxide mineralogy and microbiological activity. In order to study the soil characteristics that affect As mobility, surface and sub-surface soil samples representing As-anomalous conditions were collected from three different gold-mine sites in Brazil. The samples were characterized by XRD and chemical analysis. The oxalate (Fe_o) and CBD (Fe_d) iron contents were determined on the < 2-mm fraction by AAS, and the soluble As contents were analyzed by equilibrating 5 g of soil with 2.5 mM $CaCl_2$ solution for 24 h, then the As contents in the soil solution were determined by ICP-MS. For some selected surface samples, the speciation for arsenite (As[III]) and arsenate (As[V]) was also performed by IC-ICP-MS. Initial results seem to indicate that the mobilization of As is independent of the amount of total As in the solid phase and of the Fe_o/Fe_d ratio. Soil mineralogy and organic C content apparently play the most prominent role. Comparing the mean total mobilized As with Fe_d for the three different sites indicates that As mobilization is roughly controlled by the Fe oxide content of the soil, as suggested by various authors, but a closer examination of the data from each site revealed the importance of other highly weathered clay minerals and organic matter. For example, the presence of gibbsite and significant amounts of well crystallized kaolinite in the soil from one of the gold-mine sites seemed to inhibit As mobilization into solution. On the other hand, the presence of micaceous minerals and small amounts of kaolinite seemed to favor more soluble As. An exception to this pattern was found in the raw ore material, which exhibited no significant As mobilization in spite of its greater As content, small kaolin content, and the virtual absence of gibbsite. In this case, however, the possible presence of sulfides could be responsible for the stability of As compounds. In the other gold-mine sites, As mobilization was greater in the surface horizon than in the sub-surface horizon in spite of similar Fe_d and total As contents, which may be attributed to differences in organic matter content. A possible exception that may raise some doubt about the dependence of As mobilization on organic matter was found in one set of surface samples from the same region, which had similar properties to each other in every respect, except As was mobilized in one but not in the other. We currently have no explanation for this. In general, we concluded that low-soluble As is related to the presence of gibbsite and goethite or to a lack of organic C in the solid phase. The apparent importance of gibbsite to As mobilization is revealing and has environmental significance because gibbsite should be more thermodynamically stable than Fe oxides, especially under conditions of reducing redox potential such as those found in waterlogged soils and lake sediments.

Acknowledgments: JWVM thanks CAPES (Brazil) for fellowship funding.

INTERACTIONS WITH THE NONIONIC SURFACTANT Brij 35 INFLUENCE SORPTION OF ATRAZINE ON K- AND Ca-SMECTITES

Mark A. Chappell^{*1}, David A. Laird², Michael L. Thompson¹, and P. Evangelou³

¹Iowa State University, Ames, IA; ²USDA-ARS National Soil Tilth Laboratory, Ames, IA;
³Deceased

Nonionic polyethylene oxide (PEO) surfactants like Brij 35 are commonly used in commercial herbicide formulations. Little is known about how the surfactants impact fate and efficacy of herbicides in soil environments. This work was conducted to determine how interactions among saturating cation (K and Ca), Brij 35, and air-drying treatments influence the sorption of atrazine on the reference smectite, Panther Creek (PC).

Samples of Na-saturated PC (<2 μm) were K- or Ca-saturated by dialysis, first against concentrated KCl or CaCl₂ solutions (200 meq (+) L⁻¹), and then against dilute KCl or CaCl₂ solutions (10 meq (+) L⁻¹). The cation saturation process took 3 weeks. Sample handling effects were tested either by keeping the homoionic PC in suspension (never-dried treatment or ND) or by air-drying and then resuspending the homoionic PC samples in the dilute KCl or CaCl₂ solutions for seven days (air-dried treatment or AD). The surfactant's influence on atrazine sorption was evaluated by a batch equilibrium technique. PEO concentrations used in these experiments ranged from 0 to 6300 mg Brij 35 L⁻¹. Atrazine was first emulsified in aqueous Brij 35. Emulsified atrazine was then added to the PC clay suspensions (12.5 mg clay ml⁻¹ aqueous solution) and equilibrated for 24 hr.

Atrazine sorption on PC was negatively correlated with additions of Brij 35 up to 2100 mg L⁻¹. Greater suppression of sorption occurred for K-PC than Ca-PC. However, atrazine sorption "rebounded" somewhat with the addition of 6300 mg L⁻¹ Brij 35. Sorption studies of Brij 35 in the absence of atrazine revealed that the surfactant was very strongly sorbed on both K- and Ca-PC (on the order of 10⁵ mg kg⁻¹ clay). Higher adsorption maximums of Brij 35 were observed on air-dried clays. X-ray diffraction analysis of the clay suspensions (12.5 mg clay ml⁻¹ aqueous soln) showed that intercalation of Brij 35 reduced ND K-PC *d*-spacing from 1.88 nm to 1.35 nm, while minimal changes in *d*-spacing for ND Ca-PC were observed in suspensions. However, XRD analysis of oven-dried samples of ND Ca-PC systems revealed that the Brij 35 was present in the interlayers. Sedimentation experiments also revealed that Brij 35 induced flocculation of Ca-PC. Our results show that concentrations \leq 2100 mg of Brij 35 L⁻¹ suppressed atrazine sorption by effectively blocking atrazine's access to interlayer sorption sites. A model is proposed showing how increasing concentrations of Brij 35 first inhibited, then enhanced atrazine sorption.

SORPTION OF TETRACYCLINE AND CHLOROTETRACYCLINE ON K- AND CA-SATURATED SOIL CLAYS AND HUMIC SUBSTANCES

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Chlorotetracycline (CTC) and Tetracycline (TC) are used extensively for growth promoting and therapeutic purposes in livestock production. In order to elucidate the environmental fate of these drugs, batch equilibrium studies were conducted for K- and Ca-saturated soil clays and clay-humic complexes. Sorption isotherms indicate that Ca promotes sorption relative to K and that CTC is more strongly adsorbed than TC. Raising the pH of the Ca-clay-humic complexes from 5.4 to 7.0 decreased sorption of CTC and TC. Between pH 3.3 and 7.4 both CTC and TC are zwitterions. The greater sorption in the Ca-systems and the decreased sorption with increasing pH suggest that both charge neutralization and cation bridging contribute to sorption. Furthermore, both, TC and CTC are strongly sorbed on both soil clays and soil humic substances. However, TC and CTC are much more strongly sorbed on clays than on humic substances. Interactions between clays and humic substances significantly diminish sorption of TC and CTC on soil clay-humic complexes. The effect may be caused by competition between tetracyclines and humic substances for sorption sites, or by the structural organization of clay-humic complexes. Desorption studies show that little CTC is desorbed from soil components, but small amounts of TC may be desorbed from clay-humic complexes back to the soil solution.

TECTONIC IMPLICATIONS OF SOIL CLAY MINERALOGY AND GEOCHEMISTRY IN A TROPICAL TERRACE SEQUENCE, COSTA RICA

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Soils developed on Quaternary fluvial and marine fill terraces on the Pacific coast of Costa Rica display progressive changes in mineral assemblage, chemical composition and particle size with age. Soils range from poorly-developed, dark yellowish brown (10YR 3/4) inceptisols to lateritic, dark red (10R 3/6) oxisols in the oldest terraces. Mean annual precipitation is 3100 mm and mean annual temperature is 27 °C.

Clay minerals from active floodplains are predominately smectite with lesser 7 Å halloysite and traces of 10 Å halloysite. Soils on 5 – 10 Ka terraces at elevations < 30 m above mean sea level (MSL) exhibit similar clay mineral assemblages, with smectite decreasing at the expense of halloysite with age. Soils on 37 – 240 Ka (Sak et al. 2004) terraces 60 to 210 m above MSL consist of 7 Å halloysite with only traces of 10 Å halloysite and smectite. A 7 m soil profile sampled at 140 m above MSL is dominated by halloysite with traces of smectite present only at depths of > 5 m. Bulk mineralogy varies from a smectite-plagioclase-pyroxene-quartz assemblage in young terrace soils < 30 m above MSL to a halloysite-goethite-hematite-quartz-magnetite assemblage in terrace soils > 60 m above MSL. Chemical weathering and leaching results in rapid loss of soluble base cations, and residual concentration of Ti and Zr indicates mass losses of ~50% by chemical denudation.

Plots of terrace age vs. various measures of clay mineralogy and chemical composition produce parabolic curves consistent with rapid chemical weathering pre-37 Ka and slower rates of change from 37 – 240 Ka. These findings are significant because they (1) indicate that terraces 5-20 m above sea level are Holocene (5 – 10 Ka), (2) have potential to be applied to correlating terraces and uplift rates across tectonic blocks on the Pacific coast of Central America, and (3) appear to confirm age estimates of Sak et al. (2004) consistent with uplift rates that vary from 1 – 4 m/Ka over the time interval studied. This further suggests that the subduction of anomalous bathymetric features at the Middle America Trench is having a significant impact on fore-arc dynamics over a relatively small geologic time period.

Sak, PB; Fisher, DM; Gardner, TW; Murphy, K; Brantley SL. 2004. Rates of weathering rind formation on Costa Rican basalt. *Geochimica et Cosmochimica Acta*, Vol. 68, pp. 1453-1472.

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ENVIRONMENTAL AND SOIL CHEMISTRY OF CLAYS

POSTER SESSION

5:00PM

SEQUENCE STRATIGRAPHY OF THE EOCENE HUBER-DRY BRANCH INTERVAL IN THE GEORGIA COASTAL PLAIN

John A. Allen^{*1}, Steven M. Holland¹, and Mack S. Duncan²

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Sequence stratigraphic analysis of 19 sections in the Twiggs Clay and Irwinton Sand Members of the Dry Branch Formation reveals 4 previously undescribed depositional sequences. The lowest sequence boundary (SB) caps the Huber Formation and is characterized by 10 m of erosional incision, paleosols, and burrowed firmgrounds. Sequence A is composed of fluvial fill of the Albion Member (?), Clinchfield Sand Formation. The base of sequence B is a transgressive lag of bioturbated shell hash, quartz pebbles, and clay intraclasts. The TST of sequence B consists of bioturbated, smectitic clay with plant remains, inclined heterolithic bedding, and bioturbated, sandy channel fills collectively interpreted as a lagoonal environment within the Twiggs Clay Member. The HST of sequence B consists of heavily bioturbated shoreface sands of the Irwinton Member. Sequence C consists of coarse estuarine sands with abundant *Ophiomorpha* and large-scale cross bedding within channels incised up to 14 m into underlying deposits. Sequence C is assigned to the Irwinton Member and is capped by a SB with rooted kaolin lenses interpreted as interfluvial paleosols. Sequence D consists of estuarine coarse sands with *Ophiomorpha* burrows, large-scale cross bedding, and abundant large pebbles near its base. Sequence D is found within the Tobacco Road Formation (?) and fills channels incised more than 5 m into sequence C. The presence of major erosion surfaces at SBs, and the tendency for individual formations to straddle SBs and reflect multiple depositional environments, belies the simplicity implied by current lithostratigraphy.

FIFTY YEARS OF CLAY MINERALOGY DEVELOPMENT: REVIEW AND OUTLOOK

Joe B. Dixon

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This review of 50 years of progress in clay science was stimulated by development of a new book to replace the popular lab manual by M.L. Jackson (Soil Chemical Analysis-Advanced Course, 1956, 1973, 1985; republished by the Dept. of Soil Science, University of Wisconsin, Madison, WI). The new book, *Methods of Soil Analysis: Mineralogical Methods* edited by Richard Drees and Billy Kingery will be published by the Soil Science Society of America.

Jackson's career coincides rather well with most of the history of the Clay Mineral Society. Publication of books during the past 50 years and should be a useful indicator of the rate of publication we have grown to expect and may be helpful in planning publications and other activities for the future.

Many of Jackson's procedures remain the standard for soil mineralogical research and many topics researched by Jackson and his students (e.g. illite) are still being investigated. Other topics e.g. hydroxy-Al interlayers in vermiculite and smectite have been expanded to include nanocomposites. The database in soil mineralogy has continued to grow yet there still are many soil minerals that have not been thoroughly investigated with regard to soil structure, carbon sequestration, oxidation and reduction, pesticide behavior, and toxic metals. New methods continue to emerge, built on a firm foundation by Jackson and others. There is a current need for stronger science and engineering programs providing abundant challenge for future soil mineralogy research and instruction. The progress of clay science and technology will depend on how well we use the new methods, new theory, and new skills in attacking problems that continue to present themselves often with funds and support.

There are outside factors that influence our science too. Such as the advent of electronic processing of information and publications. Commercial electronic journals compete with journals published by scientific societies such as *Clays and Clay Minerals*. Clay minerals papers are being published in an ever-expanding assortment of journals brought on by political, technical, and scientific changes. *European Journal of Soil Science* is likely given new support by political changes. A recent review of common clay minerals revealed papers in the following journals: *Computational Materials Science*, *Earth and Planetary Science*, *Environmental Contamination and Toxicology*, *Materials Chemistry and Physics*, *Chemical Materials*, and *Environmental Pollution*. These changes in information science and practice portend an exciting future for clay science.

SIMPLE APPROACH TO REMOVE LEAD FROM WATER WITH CLAY

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Lead is problematic in drinking water obtained from underground wells, even along the U.S.-Mexico border. Lead is a big concern because it creates neurological damage. Simple and appropriate means to remove lead from water are needed for this type of contamination in family and municipal wells. In addition, industrial wastewater that involves lead processing will eventually contaminate the potable groundwater. Even the plumbing is highly suspect in lead contamination: "more than twenty times above action levels of 15 ppb lead" in Washington D.C. [C&EN, March 2004].

Many and varied approaches are being attempted to remove lead from water; additionally, another avenue is to use clays to sorb lead. For our region, New Mexico/Texas/Mexico, the most appropriate solution would be to use local clay in its most available and unprocessed form. The overall method should also be uncomplicated in order to have a product that extracts and concentrates the lead in a form that is safer and easier to manage by the citizens. A local clay from New Mexico, Berino clay, was used "as is"; i.e., the clay without purification or modification was used for this project. It was nonetheless characterized. The clay was tested in two forms: pH 4 and pH 10. Standard lead solutions (1 ppm to 100 ppm) were prepared, and ICP was used for quantitation of lead in the aqueous phase. The solutions were exposed to clay and the solutions tested periodically for lead and other typical clay exchange cations. For the solution at pH 10, lead was removed from the water; however, the lead existed in two other forms: as a precipitate and absorbed onto the clay. A net balance analysis (to include ICP analysis of the acid extractions from the clay) accounted for all of the lead, and exchanged ions from the clay were found in larger concentrations. On the other hand, for a similar concentration of lead, the clay at pH 4 also removed the lead; there was no precipitate, and all of the lead was detected sorbed on the clay (digest to ICP). In both cases, all of the lead is "accounted for" with mass balance considerations. For cases when precipitation was involved, the lead was removed from the water to concentration levels below detection limits (0.046 ppm). The non-precipitation cases lowered the levels of lead in the aqueous phase to approximately 0.5 ppm (more adsorption was expected with a longer extraction time). Another noticeable feature of this sorption process with clays is that removal of lead from the aqueous phase is faster when precipitation at pH 10 co-exists (3 grams of clay at pH 10 in 100 ml of 10 ppm lead took approximately five days to reach levels of indiscernible concentrations). A similar sorption at pH 4 without precipitation of lead took approximately 12 days to decrease concentrations to 0.5 ppm. Clays have potential to remove lead in batch processes for potable use in homes and small municipal applications.

EVALUATION OF THE POTENTIAL FOR BIOREMEDIATION OF DEEPLY WEATHERED SOIL/SAPROLITE IN THE AREA 2, NABIR FRC SITE, TENNESSEE

Ji-Won Moon*¹, Yul Roh¹, Tommy J. Phelps¹, David B. Watson¹, and Gyoo Ho Lee²

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Site characterization is an essential initial step in deciding if bioremediation is a feasible remedial alternative at hazardous waste sites. The objective of this study was to characterize U-contaminated soils and deeply weathered saprolite at Area 2 of the Natural and Accelerated Bioremediation (NABIR) Field Research Center (FRC) site, Oak Ridge, Tennessee. A typical geologic profile at Area 2 consists of about 6 meters of reworked fill and saprolite at the surface underlain by 2 meters of intact saprolite with weathered bedrock below the saprolite. Physicochemical and mineralogical characteristics including pH, cation exchange capacity, oxalate-(*o*), CBD-(*c*), and nitric acid-(*n*) extractable elements, and mineralogy, as well as groundwater composition were characterized to assess the nature and extent of contamination at Area 2. Concentrations of U (up to 291 mg/kg in U_o, 273 mg/kg in U_c, 453 mg/kg in U_n) were closely related to low soil/saprolite pH (ca. 4~5), high ECEC_{w/o Ca} (64.7~83.2 cmol/kg), amorphous manganese content (Mn_o, up to 800 mg/kg), and the clay minerals present (i.e. illite). The pH of the fill material ranges from 7.0 to 10.5, whereas the pH of the saprolite ranged from 4.5 to 8. Uranium concentration is highest (~ 300 mg/L) at ~ 6 m below land surface near the saprolite/fill interface. The pH of groundwater at Area 2 tends to be between 6 and 7 with U concentrations of about 0.9 ~ 1.7 mg/L. These site specific characteristics of Area 2, which has lower U contamination levels and more neutral groundwater pH compared to NABIR FRC Areas 1 and 3, indicate that with appropriate addition of electron donors and nutrients bioremediation of U by metal reducers may be possible.

MINERALOGICAL-GEOCHEMICAL CHARACTERIZATION OF SEDIMENTS BELOW MANGROVE FORESTS AT THE RED RIVER MOUTH (AN EXAMPLE FROM NAM DINH PROVINCE/VIETNAM)

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In tropical littorals, the progress of formation, development and degradation of mangrove forests is separating landscape into 3 sedimentary environments (low tidal zone, high tidal zone, aquaculturally used areas) distinctively for geomorphology, hydraulic conditions, anthropogenic impacts and geochemical properties as well.

Sediments in these 3 environments were classified as muddy silt, with quartz, feldspar, Fe-hydroxides mainly allocated in the coarser fraction and kaolinite, halloysite, di- and trioctahedral vermiculite, beidellite, chlorite and spread varieties of illite-smectite mixed layer minerals (from 40– 90% of illitic layers), dioctahedral vermiculite-smectite mixed layers allocated in fractions <2 µm. The clay matter is characterized by XRD and TEM, TEM-EDX and electron diffraction.

The mineralogical-geochemical information from sediment records of these environments in Nam Dinh coastal region, south of Red River mouth, was used to reconstruct the sedimentary evolution during the progress. The formation and development of mangrove forests are accompanied by medium wave and water circulation, but intensive sedimentation. This process (from low tidal to high tidal phase) is geochemically characterized by accumulation of fine sediments (clayey material) and nutrients (N: from 0.06 to 0.07%, P₂O₅: from 0.17 to 0.19%, humic acid: from 0.97 to 1.41%, C_{organic}: from 0.57 to 0.83%) as well as heavy metals (e.g. Pb: from 97 to 105 ppm, Zn: from 123 to 127 ppm). The formation and development of mangrove forests, which make sedimentary environment more favorable for storing toxic elements, contribute much to the protection of marine environment.

Degradation of mangrove ecosystem is caused by limitation of sediment supplying, water circulation, cutting mangroves and massive destroying their roots as well as removing the sediment to make shrimp pond. The using of mangrove forest in high tidal zones for shrimp cultivation is accompanied by accumulation of coarse sediments, pyrite, quartz, feldspar and sulfurs (S_{pyrite}: from 0.07 to 0.13%, S_{total}: from 0.21 to 0.28%, S_{reduction}: from 0.13 to 0.18%). The shrimp cultivation degrades the mangrove ecosystem and is also characterized by the dispersion of nutrients (N: from 0.07 to 0.05%, P₂O₅: from 0.19 to 0.06%, humic acid: from 1.41 to 0.94%, C_{organic}: from 0.83 to 0.55%) and by removing of toxic heavy metals from sediment to pond water (amount in sediment: Cu: from 119 to 89 ppm, Pb: 105 - 87 ppm, Zn: 127 – 94 ppm). Once the shrimp ponds degraded, it would be difficult not only to maintain high productivity of aquaculture, but also to replant mangrove forest.

Key words: geochemistry, Red River, sediment, mangrove, clay mineral

THE IONIC-COVALENT PARAMETER IN ION-EXCHANGE EQUILIBRIUM

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Ion-exchange equilibrium in clays has been extensively studied and modeled for industrial and environmental applications. The quantitative version of the Hard-Soft Acid Base model (HSAB) has been used to describe the ion-exchange equilibrium for alkali cations on clays (Xu and Harsh, 1990. *Soil Sci. Soc. Am. J.*, Vol. 54:1596-1601). The HSAB model, however, was not effective for describing the ion-exchange behavior of monovalent thallium and silver ions. In this study, an offspring of the HSAB model, the Ionic-Covalent (I-C) parameter is correlated to the monovalent ion-exchange data of Xu and Harsh (1990). The I-C parameter differs from HSAB theory in that the charge and coordination environment of the metal ions are considered in I-C parameter. The results show that the I-C parameter is well correlated with the Vanselow selectivity coefficients for exchange between sodium and other monovalent ions (including thallium and silver) in smectite suspensions. The I-C parameter was less successful at describing ion-exchange equilibria in vermiculite suspensions, but was still a small improvement (for thallium and silver) over the original HSAB theory. Neither model considers factors such as ligand-ligand interactions, or polymerization of silver in the clay interlayer. Nonetheless, the I-C parameter is useful for rationalizing and estimating ion-exchange equilibria trends in clays.

A WORKSHEET MODEL FOR ADSORPTION/DESORPTION OF IONS ON CLAY SURFACES

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Adsorption processes are considered to be very important, since they determine the amounts of nutrients, metals, pesticides, and other organic chemicals retained on the sorbent. The use of adsorption/desorption models to predict scenarios, is essential to evaluate critical concentrations of chemicals before they became an environmental or agricultural hazard. Predicting the behavior of reactive solutes in complex systems requires an accurate description of the sorption. While in the case of a single component adsorbed by clay minerals, the retention can be estimated from relatively simple models, in the case of multi-component systems with several interacting species, the processes can only be described with models accounting for the chemical reactions between the matrix and the species in the solution. One of the major problems with such multi-component adsorption models is the large array of adjustable parameters that are employed to fit the experimental data to the calculation. This led to the conclusion that one model is about as good as another, as long that the adjustable parameters are correctly set. In this study we present a worksheet, interactive version of a Gouy-Chapman-Stern adsorption model, which can evaluate the *simultaneous* adsorption and the equilibrium concentration of up to six different inorganic or organic cations. This is achieved by using only two adjustable parameters for each cation in the system: (1) the coefficient for the formation of a neutral complex, and (2), the coefficient of the formation of a charged complex. Those two parameters remain unchanged even upon changes in temperature, sorbent concentration, ionic strength, etc. The model used for this study solves numerically the electrostatic Gouy-Chapman equation for the relevant suspension in each experiment or sample. All cations in the suspension, with their respective valencies, are considered, and their spatial distribution as a function of the distance from the adsorbing surfaces is accounted. This allows evaluation of the surplus of each cation and the depletion of each anion in the double layer region. Changes in the actual surface charge density of the adsorbing surfaces that occur due to the specific cation binding are iteratively considered while solving the equations.

Two simple scenarios were used to demonstrate the efficiency of the worksheet model (1) Na/Ca exchange and comparison to Gapon convention, (2) increased adsorption of organocations upon increasing the concentration of the inorganic cations in the solution. Both examples, which were widely elaborated in the past, are accurately described using the model, without any change on adjustable parameters found in previous studies.

The model presented here manages to deliver predictions that fit very well with measured results. The advantage of the model is its availability and flexibility. As it can be obtained from the internet as a worksheet version, it can be easily adapted for use by any researcher.

AN INVESTIGATION OF THE IRON OXIDES AND CLAY MINERALS OF THE ANKARA CLAY

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‘Ankara Clay’ is the name used to describe the red-reddish brown silty claystone- mudstone-shale lithologies of the Late Pliocene Yalincak Formation, which is commonly found around the Ankara, Turkey region. Early studies indicated that the ‘Ankara Clay’ was deposited in a fluvial setting and is an erosional product of the ‘paleosol’, a relict Red Mediterranean soil found in this region. In addition to analytical techniques such as petrographic, chemical, XRD and SEM-EDS, Mössbauer Spectroscopy was also utilized to investigate the crystal chemical properties of both iron oxides and clay minerals present in Ankara Clay. Mössbauer Spectroscopic Analysis was carried out at room temperature on both untreated and dithionite-citrate-bicarbonate (DCB) treated samples of the < 2-mm, < 53- μ m and < 2- μ m particle size fractions. Results indicate that, the associated iron oxides are hematite, maghemite and ilmenite. Red-colored amorphous iron oxide phases commonly occur as well. The sextet component observed in the Mössbauer spectra of particular size fractions is attributed to the existence of hematite and/or maghemite. The doublet component is attributed to iron containing 2:1 layer dioctahedral clay minerals. A low isomer shift (δ) value is assigned to Fe³⁺ resonance, whereas Fe²⁺ resonances were not detected. According to the isomer shift and quadrupole splitting (Δ) values, Fe³⁺ can be in both octahedral and tetrahedral sites. The non-clay minerals are plagioclase, calcite, quartz and Fe-, Ti- and Mn-rich pyroxene. The clay minerals are mixed-layer illite /smectite, illite, smectite, chlorite and kaolinite. It is thought that these clay minerals and iron oxides are the products of the hydrolysis of pyroxene of the parent rock under humid-temperature climates.

Key words: Ankara Clay, Iron oxides, Red Mediterranean soils, Mössbauer spectroscopy

BIOAVAILABILITY OF ORGANIC MATTER INTERCALATED INTO NONTRONITE CLAY

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Bioavailability of organic matter adsorbed onto soil and sediments is an important determinant of its fate and impact. In modern marine sediments, adsorption of organic matter onto clay mineral surfaces plays a fundamental role in the burial and preservation of organic carbon. In terrestrial environments and remediation applications, smectite clay has been used to immobilize organic pollutants. Adsorbed organic compounds may or may not be available for biodegradation. Currently, there is little direct evidence to demonstrate that adsorbed organic matter is readily available for microbial degradation without desorption into solution.

We investigated the bioavailability of cysteine intercalated into the nontronite interlayer. Cysteine is an essential amino acid for many living microorganisms and can be found especially in the electron transfer proteins. Cysteine was made into the interlayer region of a nontronite clay (NAu-2, Source Clay Repository of CMS), which was previously saturated with cupric chloride cations (Brigatti et al., 1999). X-ray diffraction analysis and infrared spectra indicated cysteine was intercalated into the nontronite interlayer. Our experiment was specifically designed to test if the structural bound cysteine (in the interlayer) can be made bioavailable by microbial reduction of Fe(III) in the nontronite structure (possibly through dissolution of the nontronite structure). *Shewanella putrefaciens* strain CN32, a Fe(III)-reducing bacterium, was inoculated with lactate as the electron donor and Fe(III) in the nontronite structure as the sole electron acceptor in bicarbonate buffer with presence of an electron shuttle anthraquinone-2,6-disulfonate (AQDS). The 0.5-2- μ m fraction of NAu-2 was used in the experiment and was found by X-ray diffraction to be pure with no other Fe minerals. Cysteine concentration was quantified using a photometric test system based on Ellmann's reagent (Kaden et al., 2002). The bacteria reduced, within 19 days, 25% of Fe(III) in cysteine intercalated nontronite with less than 1% release of cysteine into solution. During the same period, in abiotic (uninoculated) controls with 5% Fe(III) reduction, intercalated cysteine was not released into aqueous solution. The bacteria reduced 34% of the Fe(III) in NAu-2 without intercalated cysteine and reduced 22% of Fe(III) when 20 mM cysteine was present in the buffer, suggesting that free cysteine in solution was able to reduce Fe(III) in nontronite.

In summary, cysteine from the nontronite interlayer was not released during microbial reduction of Fe(III) in the nontronite structure. This would have important implications for organic matter preservation in clay minerals during burial and diagenesis. But more data are necessary to confirm these initial results by performing more experiments using a wide variety of organic matter.

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