ABSTRACTS*
(Arranged alphabetically by first author)

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MESOPOROUS MATERIALS FOR ANALYTICAL SENSING AND SEPARATIONS OF ENVIRONMENTAL CONTAMINANTS

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Self-assembled monolayers on mesoporous supports have a number of properties that make them ideal for environmental sensing and separation application. The mesoporous silica structures are produced through a surfactant templated sol-gel process which endows them with large surface areas and a rigid open pore structure. A high density monolayer of selective complexing ligands can be bound to the silica surface. This organically modified silica nanostructure offers high capacity, rapid sorption kinetics, and interfacial chemistry easily tailored for a wide variety of analytes. We will discuss the advantages, challenges and limitations for using mesoporous materials for the analytical sensing and separations of environmental contaminates. Applications to heavy metals and radionuclides material will be presented.

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

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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 interfluve 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.

CHARACTERIZING PARTICLES FOR TOXICOLOGICAL STUDIES

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Comprehensive particle characterization is essential for any meaningful biological study of respirable particles. A simple XRD pattern and an obligatory BET measurement are insufficient. Excellent examples are the toxicological studies of respirable quartz particles of markedly different origins, which show markedly different biological activities. Naturally-occurring respirable quartz in the atmosphere appears to be markedly less toxic than the crushed quartz created in various man-made processes.

A current series of toxicological experiments studying are comparing the activity of quartz extracted from Wyoming bentonite, a surrogate for natural quartz with a crushed quartz, DQ12. This initial exploratory investigation shows markedly different values for a variety of measurements. These measurements include domain size, morphology, thermal response, surface area, and particle size, as well as chemical analysis and scanning and electron microscopy.

Preliminary toxicological results from a 28 day study show significantly lower quantitative and qualitative effects of the quartz separate vs. DQ-12. Underway is a more comprehensive 90 day study that will elucidate the data more fully, particularly the behavior of the inflammatory response. The study will examine the particles recovered from tissue throughout the experiment to determine any biologically induced changes in them. Of particular interest is the "fine particle effect," that can lead to a high initial inflammation that lessens over time.

These types of studies should always be a part of any toxicological study of particles.

REACTIVITY OF IRON OXYHYDROXIDE NANOPARTICLES

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Nanoparticle reactivity is critically important to the geochemical cycling of both natural and anthropogenic chemical species. Iron oxides and oxyhydroxides are common and important materials in the biogeochemical cycle of iron and other metals and molecular species, such as arsenic, at and near the Earth's surface. These materials commonly occur as nanoparticles in the 3-10 nm size range. Our work shows that rates of redox using quinones as reducing agents and iron oxyhydroxide nanoparticles as reductants are strongly particle size and phase dependent. Current results show that the surface area normalized rate of redox is substantially faster (as much as 18x) in experiments using ferrihydrite versus goethite nanoparticles. Reactions using ~9x70 nm and ~30x350 nm goethite particles show a surface area normalized rate of redox up to 4x faster using the smaller particles. In addition, growth experiments suggest the possibility of size dependent phase stability of goethite nanoparticles and show that goethite almost exclusively grows by oriented aggregation in environmentally relevant conditions (e.g., circumneutral pH and low ionic strength). Results from high-resolution transmission electron microscopy, X-ray diffraction, low-temperature magnetometry, Mössbauer spectroscopy, and X-ray photoelectron spectroscopy of the synthetic iron oxide nanocrystals before and after reduction will be presented.

THE FATE OF SMECTITE BEFORE BECOMING ILLITE IN BENTONITE EXPERIMENTS

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In 1997 at the end of a workshop dedicated to Victor Drits by the French CNRS Bernhard Kübler proposed that it would be a great help to follow the talks if the speakers would give their definitions of vermiculite, high-charged-smectite or illite at the beginning of their talks. As a matter of fact a look through literature reveals that most of these terms are operationally defined. The aim of our study was to investigate the fate of smectite during a possible smectite to illite transformation in bentonites. The question is then, is smectite just a passive partner in the reaction giving the ingredients for the new phase illite or is illite perhaps smectite with a higher charge? In the literature two ways are described to make illite from a bentonite smectite. One is to use KCl and high temperatures (>200°C) and pressures and the other is using KOH at low temperatures (<100°C). In our presentation we will focus on the experiments with KOH.

In the study SAz-1 smectite (source clay repository) is used with 1 M KOH at 80°C to look in detail at the evolution of the smectite. XRD measurements at 40% relative humidity revealed some changes in expandability of the smectite. The 001 reflection profile of smectite was modelled using the trial-and-error approach of Sakharov (1999). The results indicate that with increasing run time the number of non expandable layers with zero or one water layer increases and that the coherent scattering domain size of the smectite decreases. Infra-red spectroscopy of the reacted smectite suggests that there is no change from the initial clay. The dehydroxilation temperature showed a slight decrease from 619° to 605°C. STA measurements demonstrated that the cis-vacant character of the octahedral sheet remained nearly unchanged throughout the experiment. The layer charge showed a continuous increase from 0.3 to 0.42 eq/Si $(Si/Al)_4O_{10}$. The average layer charge distribution indicated the appearance of high charged smectite layers with a charge of $\sim$ 0.6 eq/Si $(Si/Al)_4O_{10}$ and the disappearance of the low charged layers. Above $\sim$ 0.6 eq/Si $(Si/Al)_4O_{10}$ the smectite collapsed irreversibly.

The reaction using bentonites did not proceed through mixed-layer illite/smectite intermediates. In our experiments illite behaviour originated from a smectite via an increase of the layer charge and the final closure of the structure at values above $\sim$ 0.6 eq/Si $(Si/Al)_4O_{10}$. A similar evolution can be found for smectites in KCl solutions (< 300°C). Recently Claret et al. (2004) showed that in sedimentary basins (Paris basin, Gulf coast) the smectite illitization can be described without illite/smectite intermediates being a combination of smectitic and illitic minerals of different proportions.

Sakharov, B. A., Lindgreen, H., Salyn, A. and Drits, V. A. (1999) Determination of illite-smectite structures using multispecimen XRD profile fitting. Clays Clay Miner., 47, 555-566.
Claret, F., Sakharov, B.A., Drits V.A., Velde B., Meunier A., Griffault L., Lanson, B. (2004) Clay minerals in the Meuse - Haute Marne underground laboratory (France): Possible influence of organic matter on clay mineral evolution. Clays Clay Miner. (accepted).

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

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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.

APPLICATIONS OF MICROBEADS AND NANOPARTICLES FOR BIOSEPARATIONS AND BIOSENSING

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The detection of microorganisms in environmental samples often requires extensive sample preparation for the purification and concentration of biomarkers (cells, proteins, or nucleic acids). In addition, approaches are needed for the rapid and sensitive detection of multiple organisms. This presentation will highlight some research at Pacific Northwest National Laboratory involving the use of microbeads and nanoparticles composed of materials such as silica, iron, and quantum dots for bioseparation and biosensing. Superparamagnetic microbeads that contain iron oxide nanoparticles are functionalized with antibodies and used for automated cell concentration from environmental samples, to enable the detection of only10 cells/mL. Porous silica microbeads are used for automated concentration and purification of RNA, to enable the simultaneous detection of microorganisms by mRNA analysis on microarrays. In additions, quantum dots are being developed for use as optical reporters to enable rapid and sensitive biodetection.

# SMECTITE ILLITIZATION IN ORGANIC RICH SHALE OFFSHORE MID-NORWAY

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The Spekk and Melke Formations transgressive mudstones found in the Haltenbanken area offshore Mid-Norway were deposited during the Upper Jurassic. These sediments have been subjected to continuous subsidence since deposition and constitute an excellent natural laboratory for studying diagenetic reactions.

X-ray diffraction analysis was carried out on 37 samples from 19 different wells. The mixed layer clay mineral components were identified before they were quantified using the software tool CLAY++ based on pattern fitting by a least-squares fit between the experimental XRD pattern and a suite of selected synthetic patterns generated in Mulcalc. The results from the curve fitting procedure indicate that the smectite to illite transformation occurs in distinct phases where pure smectite produces discrete illite, mixed layer illite/smectite (ML), quartz and possibly chlorite before the ML component produces illite, quartz and possibly more chlorite. The presence of detrital quartz makes it difficult to keep control on the authigenic quartz content. Anyhow, a slight increase in the quartz content is associated with the dissolution of smectite. Precipitation of quartz changes the local geochemical conditions, resulting in destabilization and dissolution of smectite and precipitation of mixed layer illite-smectite (I/S) phases, discrete illite, quartz and chlorite. There is no record of an increasing illite content in the I/S phase.

Based on this study the overall mineral reactions for the smectite to illite transformation can be summarized as follows:

$$smectite \rightarrow illite/smectite + illite + quartz + chlorite \rightarrow illite + quartz + chlorite$$
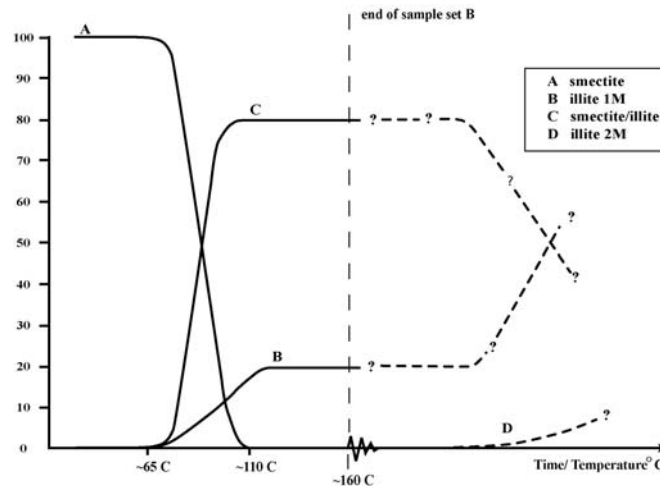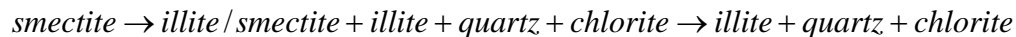
Cartoon of the change in relative abundance of the various smectitic and illitic mineral phases in the sample set. The dashed lines illustrate a postulation of further development of the smectitic and illitic material below 160 °C. The plateaus exemplify how the mineral assemblage seems to stay stable between the intervals where diagenetic processes take place.

SELF-CONSISTENT SELF-INTERACTION CORRECTED DFT STUDIES OF ANNITE

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We have recently developed a framework for the self-consistent calculation of self-interaction corrections (SIC) to pseudopotential plane-wave density functional theory (PSPW). The technique implements the original method due to Perdew and Zunger and combines two procedures: construction of maximally localized Wannier functions (MLWF, procedure due to Marzari and Vanderbilt and to Silvestrelli) and direct minimization of the DFT+SIC total energy functional. The technique developed can be employed in PSPW-DFT methods without adding significant expense. Furthermore, atomic forces and stresses are straightforward to implement, making it applicable to both confined and extended systems, as well as to Car-Parrinello ab initio molecular dynamic simulations. This method has been applied to several systems for which standard DFT methods do not work well.

We present here results from a recent study of the oxidation of annite in air. Some evidence exists that oxidation of annite will result in a charge states inside the single-particle band gap, associated with localized Fe^{3+} ion state. Such a state is typically the result of local distortion of the lattice leading to localization of the electronic wave function. So far, only small cluster models within Hartree-Fock approximation have yielded such a localized Fe^{3+} state. However, it is well known that the Hartree-Fock approximation unnecessarily favors localized states. In contrast, large-scale periodic DFT calculations using standard DFT functionals do not localize these types of states. It has been suggested that standard DFT functionals which are not self-interaction free tend to favor delocalized electronic states since self-interaction creates a Coulomb barrier to charge localization. Using or newly developed self-interaction corrected DFT method we have been able to obtain a significant degree of charge localization. Various aspects of this application and implications will be discussed.

EFFECT OF INTERLAYER CATION ON DEHYDROCHLORINATION OF POLYCHLORINATED ETHANES BY REDOX-MANIPULATED SMECTITE CLAY MINERALS

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Potassium fixation is an important process in clay soils and sediments. This paper reports the effect of Na^+-for-K^+ exchange in redox-manipulated Upton montmorillonite (Upton) or ferruginous smectite (SWa-1) on elimination reactions of pentachloroethane and 1,1,1-trichloroethane. Iron redox cycling in smectites were studied using reduced or reduced-reoxidized Upton or SWa-1 saturated with Na^+ or K^+ (Na^+-$Upton_R$ or Na^+-$Upton_{RO}$, K^+-$Upton_R$ or K^+-$Upton_{RO}$, Na^+-SWa_R or Na^+-SWa_{RO}, K^+-SWa_R or K^+-SWa_{RO}). Upon K^+-for-Na^+ exchange, Upton and SWa-1 showed incomplete reoxidation of structural Fe(II), possibly because of the collapse of superimposed clay layers precluding access to interlayer surfaces by the oxidizing agent. The transformation pathways of 1,1,1-trichloroethane and pentachloroethane depended on the oxidation state of the structural iron, and the nature of the clay and exchangeable cation. Regardless of the nature of the exchangeable cation, transformation of pentachloroethane was greater with SWa_R than with $Upton_R$, and with SWa_{RO} than with $Upton_{RO}$. Dehydrochlorination of pentachloroethane proceeded to a larger extent by K^+-$Upton_{RO}$ than by K^+-SWa_{RO}, but an opposite trend in reactivity prevailed when Na^+ was the exchangeable cation. The higher Fe(II) content in K^+-SWa-1 compared to K^+-Upton possibly contributes to impede reversible expansion of interlayer spacing upon reoxidation. Partially -collapsed, redox-manipulated smectites may owe their Brønsted-base behavior towards polychlorinated ethanes to more strongly adsorbed water at basal surfaces in the vicinity of octahedral Fe(II). Dehydrochlorination of 1,1,1-trichloroethane to 1,1-dichloroethene by SWa-1 occurred only with the K^+-SWa_R form, and, on a molar basis, led to a faster loss than observed for pentachloroethane with the same form of SWa-1. So, K^+ exchange led to increases in rates of transformation of pentachloroethane in mixed-valent SWa-1 and of 1,1,1-trichloroethane in SWa_R. In the case of pentachloroethane, these findings are opposite to the effect of K^+ on the reactivity of Fe(II) in SWa_R and $Upton_R$. Owing to the greater hydration energy of Na^+, K^+ may yield a lower water content adjacent to basal surfaces, and guarantee less energetic constraints for electron transfer between clay basal planes and 1,1,1-trichloroethane. Clearly, $E1_{cb}$ and E2 reactions of polychlorinated ethanes in redox-manipulated smectites occur at different clay sites. These findings add complexity to the effects of interlayer cations and surface-water on charge transfer from the clay to organic solutes in suspension.

BIOGENIC DISSOLUTION OF SOIL PHOSPHATE MINERALS

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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.

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

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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 $CaCl_2$ solutions (200 meq (+) L^{-1}), and then against dilute KCl or $CaCl_2$ 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 $CaCl_2$ 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 10^5 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 ≤ 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.

PROGRADE CHANGES OF PHYLLOSILICATE MICROSTRUCTURES IN LOW-GRADE PELITIC ROCKS AS CHARACTERIZED BY X-RAY PEAK-PROFILE ANALYSIS AND TEXTURE GONIOMETRY

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X-ray powder diffraction analysis reveals that the distribution of metapelitic zones in the Tertiary slate belt and pre-Tertiary metamorphic complex of Taiwan are limited by structural and/or stratigraphic boundaries. The variations in phyllosilicate crystallinity indices are continuous at the boundaries where ductile shear zones occur. Slates collected from the ductile shear zones of the Tertiary slate belt and from the schist belt of the pre-Tertiary basement invariably have epizone crystallinity values. The shear-zone slates that either display a set of well-developed disjunctive spaced cleavage or have a zonal crenulation cleavage show better crystallinity than those collected from the neighboring regions. Crystal thicknesses and lattice strains of muscovite and chlorite determined by X-ray peak-profile analysis (Voigt method) increase and decrease respectively with increasing grade in the slate samples. The studied chlorite generally has a crystal thickness similar to that of the intergrown muscovite but shows a better crystallinity, smaller lattice strain, and higher intensity of lattice preferred orientation (LPO), especially in anchizone rocks. The differences are minimal for epizone samples collected from the ductile shear zones and schist belt.

The LPO intensity as measured by X-ray texture goniometry increases with decreasing values of phyllosilicate crystallinity indices, following a linear trend with a few exceptions. In the ductile shear zones, the pole-figure patterns of samples having a zonal crenulation cleavage exhibit an elongated elliptic shape and have moderate LPO intensities nearly identical to those recorded for samples with a disjunctive spaced cleavage. In contrast, the pre-Tertiary slates that have a disjunctive spaced cleavage display circular pole-figure patterns with closely spaced intensity contours and very high LPO intensities (as high as 20 multiples of random distribution) and those that have a discrete crenulation cleavage show highly elongated or two-pole pole-figure patterns with reduced LPO intensities as low as 4 m.r.d. No systematic changes of crystal thickness and lattice strain were observed to be associated with any specific types of cleavage.

The aforementioned result collated with SEM observations collectively imply that the degree of crystallization/recrystallization was significantly enhanced in the ductile shear zones and pre-Tertiary metamorphic complex in which tectonic stress was effective at depths during metamorphic processes. Muscovite and chlorite showed different behaviors in response to tectonic stress and metamorphism with muscovite being able to store higher strain energy under anchizone conditions but recrystallizing rapidly in epizone. The development of disjunctive or crenulation cleavage occurred primarily through dissolution and transfer and/or rotation via grain boundary sliding with minimal lattice distortion and size reduction. The result also suggests that the use of LPO intensity as an indicator of metamorphic progress in low-grade pelitic rocks must consider microstructural changes produced by tectonic stress through time.

MOLECULAR CHARACTERIZATION OF STRONTIUM UPTAKE AND TRANSFORMATION WITH KAOLINITE REACTED AT HIGH pH

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Microscopic and molecular-level spectroscopic investigations were conducted to elucidate the chemical behavior of Sr in reacted purified specimen kaolinite (KGa-1) under extreme geochemical conditions at the Hanford Site in WA (0.05 M Al_T, 2 M Na^+, 1 M NO_3^-, pH~14, Cs^+ and Sr^{2+} present as co-contaminants). Time series batch experiments were conducted from 0 to 190 days, with initial Cs^+ and Sr^{2+} concentrations ranging from 10^{-3} to 10^{-5} M.

Chemistry, X-ray diffraction (XRD), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS) and diffuse reflectance infrared Fourier transform spectra (DRIFT) data revealed a pronounced reactivity and secondary phase precipitation during the reaction time. Dominant secondary phases identified in the kaolinite system after 190 days were cancrinite, sodalite and chabazite.

Synchrotron-based extended X-ray absorption fine structure (EXAFS) was used to characterize the local coordination environment of strontium in reacted bulk kaolinite samples. Strontium K-edge measurements were performed with sample loadings of 10^{-3} M Cs and Sr at room temperature and compared with published data.

Fitting results of kaolinite samples reacted for 1 and 7 days show that the local atomic structure around strontium is similar to the structure of crystalline $SrCO_3$, which was not detected by XRD or SEM. Results may imply small particle size for the $SrCO_3$ precipitate or a small amount of $SrCO_3$ that is below detection with XRD. Kaolinite samples reacted for 33 days indicate that the $SrCO_3$ phase is transient and is replaced by another secondary phase. Fitting results of kaolinite samples reacted for 93 and 190 days indicate that strontium mainly is associated with zeolite phase(s). These results suggest that strontium uptake from solution may occur initially by formation of a transient carbonate phase, followed by localization into secondary zeolite phases that form at later reaction times.

Present findings are of importance with respect to reliable risk assessment of contaminants under the leaking tanks, as well as for the development of sustainable environmental management and protection strategies. Furthermore, the knowledge gained of the chemical behavior of strontium at high pH and high ionic strength have implications for the development of future ^{90}Sr waste treatment technologies and in-situ remediation schemes.

AN INTERPRETATION OF OCTAHEDRAL ORDERING AND SITE OCCUPANCIES OF FE^{2+} IN MUSCOVITE AND ILLITE.

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Recent experimental and theoretical, structural models have been used to infer the site occupancies of Fe^{2+} in muscovite and illite and to account for their Mössbauer spectra. Octahedral site preferences have been discussed for Al, Fe^{3+} and Mg by several authors (e.g., Drits et al., 1997; Cuadros et al., 1999; Sainz-Diaz et al., 2003; Palin et al., 2004) but, to date, Fe^{2+} has not been considered. The model proposed for the dioctahedral sheet in glauconite by Dainyak et al. (1992) that recognizes illite-like and celadonite-like domains appears to be valid for phengitic muscovites and illites as well. The trans-vacant dioctahedral sheets are separated into exclusively Al-bearing and mixed-cation domains. The mixed-cation domains have symmetrically non-equivalent cis sites with different R^{2+} and R^{3+} preferences. A high ordering energy is predicted when R^{2+} fully occupies one of the two cis sublattices in the mixed-cation domains.

Inasmuch as muscovites and illites are essentially trans-vacant, octahedral cations occupy the two cis (M2) sites in mixed-cation domains. Each cis site has three nearest neighbors on the other cis sublattice. In the lowest energy configuration, Fe^{3+} forms clusters on the R^{3+} sublattice. In accord with previous studies, it is assumed that Mg^{2+} and Fe^{2+} are randomly distributed on the R^{2+} sublattice. With this ordering, the proportions of the different local environments of Fe^{2+} cations will be determined by the Fe^{3+}-content of the dioctahedral sheet and the sizes of the mixed-cation domains and Fe^{3+} clusters. Thus, in muscovite and illite the Fe^{3+}-rich clusters within the mixed cation domains encompass much less Mg^{2+} (and Fe^{2+}) than do the Fe^{3+}-poor regions.

Mössbauer spectra of most muscovites and illites exhibit two Fe^{2+} doublets having quadrupole splittings of ~3.0 mm/s and ~2.1 mm/s. The former, which has the greater site fraction and narrower linewidth appears to represent a unique local configuration of Fe^{2+} surrounded by three Al nearest neighbors while the latter, whose splitting is smaller and more variable, appears to represent local environments of Fe^{2+} cations surrounded by from one to three Fe^{3+} nearest neighbors. Quadrupole splittings of Fe^{2+} cations will vary depending on the positions of Fe^{3+} cations relative to the crystal electric field gradient. Intermediate splittings observed in some muscovites and illites may result from cation disorder between the R^{3+}-rich and R^{2+}-rich sublattices.

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(Powerpoint presentation: http://defects.physics.wsu.edu/papers/CMS-04-Illite-Symp.pdf)

URANIUM AND TRITIUM TRANSPORT IN VADOSE ZONE SEDIMENTS

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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 $CO_2\backslash O_2$ gradient affect ^{14}C and ^{238}U 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 Ca^{2+} salts (e.g. NO_3^-, SO_4^{2-}) 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 ^{238}U moved only ~20-30 mm over a period of 18 months, and analysis of solid-phase ^{238}U in cores recovered from the column supports this prediction. As with ^3H, the model predicts that clay mineral AlOH sites accounted for most ^{238}U sorption. Independent confirmation of predicted ^3H and ^{238}U 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 CO_2 driven changes in pH and carbonate chemistry provide an important control on contaminant speciation and transport in vadose zone systems.

CANCRINITE AND SODALITE FORMATION IN THE PRESENCE OF Cs^+, K^+, Mg^{2+}, Ca^{2+}, or Sr^{2+} IN HANFORD TANK WASTE SIMULANTS

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High-level radioactive tank waste solutions at the U.S. DOE Hanford Site, Washington, have complex chemical compositions. Some of the tank waste leaked into the subsurface. It was reported that under simulated laboratory conditions, two feldspathoids, cancrinite and sodalite, formed when tank waste solutions contacted sediment minerals. Here, we investigated the effect of different cations, Cs^+, K^+, Sr^{2+}, Ca^{2+}, and Mg^{2+}, on mineral formation and transformation pathways under conditions mimicking Hanford tank leaks. We used sodium silicate to represent the dissolved silicate from sediments. We prepared a series of simulants that contain 0.5 M of aluminate, 1 M or 16 M NaOH, and the nitrate salts of the cations. The precipitates were monitored by X-ray diffraction, scanning electron microscopy, and X-ray energy dispersive spectroscopy. In the 1 M NaOH simulants, low concentration of Cs^+ (< 100 mM) did not affect the formation of lepispheric cancrinite and sodalite, whereas only highly crystalline cancrinite formed when Cs^+ was >250 mM. An unidentified feldspathoid or zeolite intermediate phase was observed in the presence of high concentration of Cs^+. The presence of K^+ did not alter but slowed down the formation of cancrinite and sodalite. The presence of divalent cations can lead to the formation of intermediate or stable silicates, aluminates, hydroxides or even aluminosilicates. Formation of these intermediate phases slowed down the formation of cancrinite and sodalite by consuming OH^-, silicate or aluminate. Compared with the concentrations used in this study, radioactive Cs^+ and Sr^{2+} in the tank solutions are much smaller than those used in our experiments, and released divalent cations from sediments likely precipitate out as hydroxides, silicates, or aluminates. Therefore, we do not expect that these monovalent and divalent cations affect the formation and transformation pathways of cancrinite or sodalite in the sediments underneath the leaked waste tanks.

STABILITY OF INCORPORATED Cs IN FELDSPATHOIDS, ZEOLITES AND ALLOPHANE FORMED IN HANFORD TANK WASTE SIMULANTS

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Cesium-137 is the major radioactive element in the high-level radioactivity waste tanks at the U.S. DOE Hanford site. Cancrinite and sodalite have been found as the neoformed stable mineral phases when Hanford sediments contacted the waste simulants. Allophane, Linde Type A (LTA) zeolite, and a 3-dimension-cross shaped feldspathoid or zeolite have been observed as the intermediate phases in our previous simulation experiments. We investigated the incorporation of Cs^+ and the stability of the incorporated Cs^+ in these metastable and stable minerals and short-range ordered materials. These materials were synthesized in the presence of $CsNO_3$, CsCl, or CsOH according to previous experiment results. Mineral phases were verified with X-ray diffraction and electron microscopic analyses. The incorporated Cs^+ was quantified by atomic absorption spectroscopy after digestion in 1 M HCl. Four hundred milligram of each mineral or short-range ordered material was exchanged three times with 0.25 M Ca^{2+}, 0.5 M K^+ or 0.5 M Na^+ at 80 °C, and three times with water at room temperature. For each time of ion exchange treatment, the solid and cation solution were in contact for 24 hours with 20 minutes shaking for every two hour interval. The solid was separated by centrifugation and mixed with fresh solutions. No morphology changes were found after the ion exchange treatment, yet crystal expansion by K^+ was detected by XRD on lepispheric sodalite and cancrinite. Very little (<2%) of the incorporated Cs^+ was replaced by the cations in a highly-crystalline cancrinite formed in the presence of CsCl, whereas 57% of Cs^+ was replaced by K^+ in another highly-crystalline cancrinite formed in the presence of $CsNO_3$. Cesium in lepispheric sodalite showed strong resistance to cation exchange, and less than 15% of the incorporated Cs^+ was replaced by the cations. Cesium in LTA zeolite, the 3-dimensional cross-shaped fledspathoid or zeolite, and allophone were rapidly replace by the cations, more than 98% of the incorporated Cs^+ was replaced by K^+ or Na^+ in LTA zeolite and the unidentified fledspathoid or zeolite. Potassium showed the strongest ability of replacing Cs^+, whereas Ca^{2+} showed stronger ability than Na^+ in lepispheric cancrinite and sodalite, but weaker ability than Na^+ in LTA zeolite, the 3-dimension-cross shaped feldspahtoids or zeolite, and allophane. Elemental mapping data support the ion exchange reaction and also indicate that ion exchange reaction occurred homogeneously in the bulk of the small particles. The stability of Cs^+ in the minerals more likely depends on the size of the apertures of the channels and cages in the feldspathoids and zeolites. Transmission electron microscopic analysis indicates structural stacking fault was not an important factor in controlling the stability of incorporated Cs^+.

NEW INSIGHTS INTO THE MOLECULAR MECHANISM OF BACTERIAL METAL RESPIRATION

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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.

FIFTY YEARS OF CLAY MINERALOGY DEVELOPMENT: REVIEW AND OUTLOOK

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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.

CHEMICAL ACTIVITY OF NANOPOROUS MgO

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The chemical activity of, and reagent transport on, nanoporous MgO films are probed using adsorption of various probe molecules. The MgO films employed in this study are grown via reactive ballistic deposition of Mg in the background of O_2 at low temperatures (< 300 K). The films have very high surface area (~ 1000 m^2/g) and high fraction of active, high energy binding sites. As such these films serve as an ideal platform for studies of the catalytic activity of MgO surfaces. The dynamics and kinetics of adsorbate displacement is explored by coadsorption of various weakly bound species (e.g. N_2/CO and N_2/O_2). The exchange of adsorbates between the adsorption sites and facile transport within the film is demonstrated. In case of chemisorption, the dissociation of HCOOH via two distinct channels is seen with H_2 + CO_2 and H_2O + CO formation. The overall reaction efficiency and selectivity between these two reaction pathways is determined. The adsorption on flat, high quality MgO(100) surfaces is used as a reference for comparison with the adsorption on nanoporous MgO films.

ILLITIZATION AS A CRYSTAL GROWTH PROCESS

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Studies of illitization in basins such as the Gulf of Mexico have shown that smectite-rich mixed-layer clays react progressively with depth to form illite-rich mixed-layer clays. At first, illite layers are randomly interstratified with smectite layers (R = 0 ordered); but at about 35% smectite layers the interlayering becomes ordered (R = 1, or IS ordered). This pattern of reaction is readily explained by nucleation of 2 nm thick elementary illite crystals while at the same time 1 nm thick smectite crystals dissolve. After smectite particle dissolution is complete, R = 1 ordering naturally appears at about 35 % smectite layers due to interparticle diffraction effects between adjacent elementary illite crystals that diffract coherently as stacks of two to three crystals. Thereafter, illlitization consists of illite crystal growth, with or without simultaneous nucleation of new illlite crystals.

To describe the growth of illite crystals, we (Eberl, Drits and Srodon, 1998, AJS, 298, 499-533) were led to formulate a new theory for crystal growth, because existing theories could not explain the available data. This theory starts with the observation that most minerals, including illite, commonly have lognormally shaped crystal size distributions (CSDs). The only simple mathematical method to generate such shapes by growth is according to the Law of Proportionate Effect (LPE): $X_{j+1} = X_j + \varepsilon_j X_j$, where X_j is the crystal thickness after j calculation cycles (or j increments of time), and ε is a random number that varies between 0 and 1. If this law is applied for several calculation cycles to many crystals, a lognormal CSD results. If nucleation is continuous with LPE growth, then an asymptotic CSD is formed. These are the two most common CSD shapes for illite crystals, with the asymptotic shape forming under conditions that favor higher levels of supersaturation, such as those found within wall rock in hydrothermal deposits, whereas the lognormal CSD forms within veins in such deposits. An α-β^2 diagram (where α is the mean of the natural logs of the crystal diameters, and β^2 is their variance) and the Galoper computer program can be used to simulate CSDs and reaction paths for illite and other minerals.

Use of the LPE to describe crystal growth has several interesting consequences: (1) crystals generally will grow at a rate in proportion to their diameter, even though such growth involves adding much more volume to larger crystals than to smaller crystals during the same time interval; (2) crystal growth has a random component (ε), which indicates that one can not predict accurately the growth rate for individual crystals, but only for the distribution of crystals--this inherent randomness also accounts for crystal growth dispersion; (3) the relative shape of a CSD generally is determined soon after nucleation, and then is maintained during proportionate growth; and (4) illite crystal growth appears to occur discontinuously (in jumps), rather than continuously with time.

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.

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 $^{\circ}$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.

ENVIRONMENTAL APPLICATIONS OF SYNTHETIC NANOPOROUS CERAMIC OXIDES.

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Surfactant templated synthesis of mesoporous ceramics provides a versatile foundation upon which to create high efficiency environmental sorbents. These nanoporous ceramic oxides condense a huge amount of surface area into a very small volume. The ceramic oxide interface is receptive to surface functionalization through molecular self-assembly. The marriage of mesoporous ceramics with self-assembled monolayer chemistry creates a powerful new class of environmental sorbent materials. These nanoporous hybrid materials are highly efficient sorbents, whose interfacial chemistry can be fine-tuned to selectively sequester a specific target species, such as heavy metals (*e.g.* mercury, cadmium and lead), and oxometallate anions (*e.g.* chromate, arsenate), and radionuclides (*e.g.* plutonium, cesium, pertechnetate). Details addressing the design, synthesis and characterization of SAMMS materials specifically designed to sequester species of importance to environmental clean-up, as well as evaluation of their binding properties are discussed.

STEREOSELECTIVE PHOTOOXIDATION OF SULFIDE BY USE OF CLAY-CHIRAL METAL COMPLEX ADDUCTS AS A PHOTOSENSITIVE ADSORBENT

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We have attempted the photooxidation of a prochiral sulfide by using a clay mineral modified by photosensitive chiral metal complexes, $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$. A sulfide used in this research has a chiral carbon. By identifying four kinds of prodcuts, both enantiomeric and diastereomeric selectivity were observed. We discussed the interactions among the chiral carbon center of a substrate, adsorbed metal complexes and a clay surface.

We used α-ethylbenzyl phenyl sulfide as a substrate. It has an asymmetric carbon. The sulfide is oxidized in two stages; a sulfide to a sulfoxide at the first stage and a sulfoxide to a sulfone at the second stage. Since a sulfur in a sulfoxide is chiral, two enantiomeric pairs are produced from the present substrate (Scheme 1) in which each pair is in diastereomeric relation (Figure1).
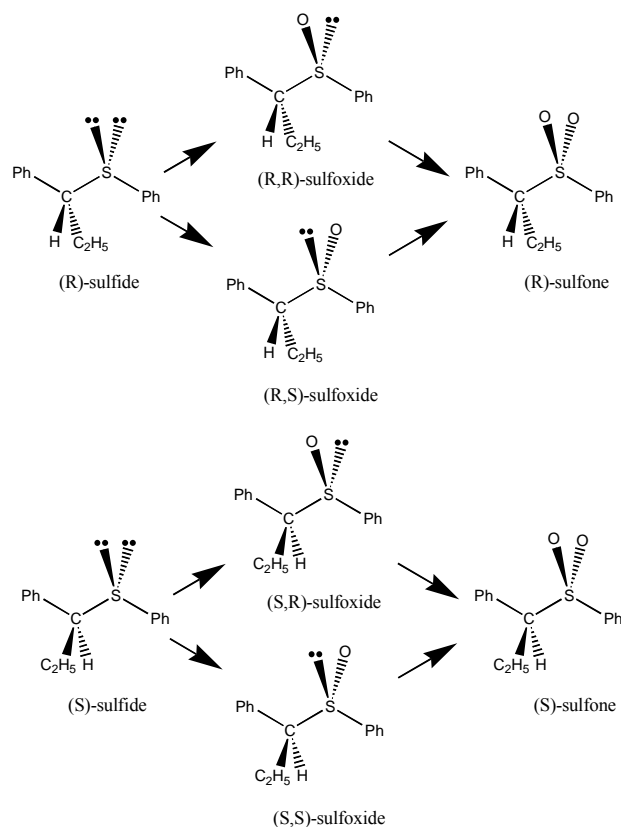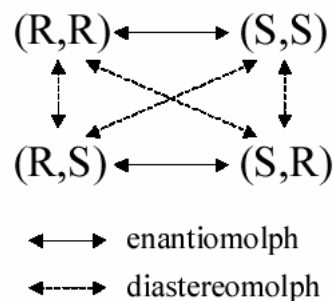

Scheme 1. Oxidation of α-ethylbenzyl phenyl sulfide

Figure 1. Stereomolph of the sulfoxide

CRYSTAL STRUCTURE OF BIRNESSITE: FROM WELL-CRYSTALLIZED TO HIGHLY-DEFECTIVE STRUCTURES

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Birnessite is a manganese oxide containing predominantly Mn^{4+} cations in layers of edge-sharing octahedra. Layer charge deficit arises from the presence of Mn^{3+} and/or vacant octahedra within layers and is compensated for by the presence of interlayer cations.

Despite the relatively low abundance of manganese, birnessite is ubiquitous in nature and is essential to the geochemistry of soils and oceanic nodules because of its remarkable cation exchange capacity, sorption, and redox properties. In particular, because of its high affinity for pollutants (heavy metals, organics, …) this mineral plays a pivotal role in their fate in contaminated environments.

This layered Mn oxide, that can be synthesized using various chemical routes, presents a high structural variability depending on the physico-chemical conditions of formation. The coupling of several characterization techniques, such as X-ray diffraction (monocrystal, or powder), X-ray absorption spectroscopy and electron diffraction, is often necessary to access structural details fundamental to understanding the reactivity for each variety. In particular, such coupling allows solving the structure of the layers and determining the origin of their charge. In addition, the stacking mode of the birnessite layers determines the structure of the interlayer region and the configuration of the sites available for cation adsorption.

Birnessite also exhibits random or well-defined stacking faults that are common in layered structures. The high proportion of such structural defects strongly reduces the efficiency of usual structure refinement methods, including the Rietveld method. One of the most effective ways to determine the actual structure of these defective systems is the calculation of XRD patterns using the mathematical formalism described in detail by Drits and Tchoubar (1990). This trial-and-error procedure allows determining, in addition to the structural information obtained for well-ordered birnessite varieties, the nature, abundance and distribution of the defects.

Even in the most defective structures, when the abundance of random stacking faults leads to the occurrence of extremely disordered structures without three-dimensional ordering (turbostratic stacking), X-ray diffractograms of birnessite exhibit noticeable modulations and relevant structural information, which includes not only unit-cell parameters but also the atomic coordinates and occupancies of the different sites, can be obtained.

Drits and Tchoubar (1990), X-ray Diffraction by Disordered Lamellar Structures. *Springer-Verlag*

SYNTHESIS AND SPECTROSCOPY OF DOPED OXIDE SEMICONDUCTOR NANOCRYSTALS

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Diluted magnetic semiconductor (DMS) nanostructures such as quantum dots (DMS-QDs), quantum wells, quantum wires, and epitaxial thin films are pivotal architectural elements in many proposed spintronics devices. This talk will present our group's recent advances in the development of direct routes for preparation of freestanding high-quality oxide DMS quantum dots, a target material recently shown to support high-temperature ferromagnetism in thin films. The application of magneto-optical spectroscopic methods (including magnetic circular dichroism and Zeeman spectroscopies) to study the electronic structural properties of oxide DMS-QDs will also be discussed. Finally, data addressing the influence of DMS length scales on high-T_C ferromagnetic ordering will be presented.

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

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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.

A COMPARISON OF THEORETICAL AND EXPERIMENTAL PROPERTIES OF THE ELECTRON DENSITY DISTRIBUTIONS FOR EARTH MATERIALS

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The electron density, ρ, is one of the most important properties of an earth material. It includes all of the information about the bonded interactions and structure together with important information about chemical reactivity[1-4]. However, despite its high information content, the extraction of information from ρ is a very difficult and nontrivial task. But, if headway is to be made in acquiring this information, it is crucial that we explore the extent to which the properties of an experimental model distribution for an earth material agree with those of a theoretical model distribution generated with first principles quantum mechanics.

Electron density distributions have been calculated and bond critical point, bcp, properties have been generated for a large number of earth materials.[5] As predicted by the theoretical calculations, the bcp properties observed for several materials correlate with the observed bond lengths. Those recently determined with essentially extinction and absorption free single crystal high energy synchrotron diffraction data agree with those calculated within 5%, on average, whereas those determined with lower energy single crystal diffraction data show substantial disagreements in several cases. The value of the electron density at the bcp is highly correlated with the strengths of the bonded interactions, providing a physical basis for Pauling's definition of bond strength.[6]

The Laplacian of an electron density distribution, $\nabla^2\rho$, is a powerful tool for locating regions of a material that are susceptible to electrophilic and nucleophilic attack. In the case of the silica polymorph coesite, theoretical and experimental $-\nabla^2\rho$ distributions show that the nucleophilic character of an O atom comprising a SiOSi bonded interaction increases in a regular way with decreasing angle. Further, the H positions in a H-bearing specimen were located on the basis of maxima in the distributions where the electron density is locally concentrated. The positions of the H atoms have been confirmed in a careful infrared spectroscopic study by Köch-Müller et al.[7] The H atoms in H- and Al-bearing stishovite were also successfully located on the basis of the maxima in the $-\nabla^2\rho$ distribution.

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CONTROLLED CULTIVATION: APPROACHES FOR DEBUGGING BIOGEOCHEMICAL RESEARCH

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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.

NMR CHARACTERIZATION OF THE STRUCTURE AND DYNAMICS IN MODIFIED CLAYS AND POLYMER/CLAY NANOCOMPOSITES

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To obtain clay-polymer nanocomposites, one of the critical steps is the surface treatment of the mineral. Surfactants are usually ion-exchanged with interlamellar cations of the negatively charged mineral, ensuring its dispersion within the polymer matrix. The interaction between a typical organic cation and the mineral surface should be modulated by the location of cation isomorphous substitution and the charge density of the clay. Accordingly, we have used Laponite, a commercial synthetic hectorite, and synthetic saponites of variable interlayer charge. These minerals have been characterized by ^{27}Al, ^{29}Si MAS and ^{23}Na 2D 3QMAS NMR [1]. The properties of the organically-modified clays are currently described by macroscopic techniques. We have used NMR spectroscopy in the solid-state to probe the structure, conformation and dynamics of the intercalated species.

After intercalation in Laponite, the properties of hexadecyltrimethylammonium ions are drastically changed compared to those of the pure organic salt. The ^{13}C CP MAS NMR spectrum of the hybrid compound indicates conformational flexibility of the surfactant hydrocarbon chain and the ^{13}C longitudinal relaxation times show high mobility of the alkyl chain [2]. Then, we have extended this study to a few surfactants intercalated in Laponite and synthetic saponites, showing how chain dynamics are perturbed. The charge density modulates the trans/gauche conformational ratio of the surfactant alkyl chain, providing a deeper understanding of the variation of the basal spacings from X-ray diffraction [3]. This ratio depends also on the location of cation isomorphous substitution in the clay. We have extended these studies to nanocomposites formed by poly(ε-caprolactone) and these modified clays.

Natural clays such montmorillonites are paramagnetic materials that prevent dynamic information from NMR relaxation data. However, the proton relaxation rate in the laboratory frame can be useful to characterize the montmorillonite dispersion within the polymer matrix [4], as proposed recently in the literature.

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ILLITE POLYTYPES AND DIAGENESIS SINCE HOWER et al. 1976

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Hower et al. published their seminal paper on illite diagenesis of the Gulf coast sediments in 1976. Earlier Hower authored and coauthored 2 papers in 1963 on illite polytypes and K-Ar ages of different size fractions with the observation that different illite polytypes are of different origin. Here we specifically look at how illite polytypes have enhanced our understanding of illite diagenesis.

Since Hower et al. (1976) illite polytype analysis improved significantly due to improvements in analytical and sample preparation techniques and by the help of computer modelling of X-ray diffraction patterns using e.g. WILDFIRE$^{©}$. Illite polytype analyses help decipher the age, origin, physical and chemical conditions of illitization, by quantifying the different illite polytypes and by characterizing the individual illite polytypes. The analysis includes a) the determination of the type of polytype, *2M₁, 1M* cis-vacant, *1M* trans-vacant and *1M$_d$* illite and b) the determination of the disorder in the *1M$_d$* illite consisting of %smectite, 60º and 120º rotations, cv/tv octahedral occupancy. In addition to a literature review we will present case studies of our own research that include: 1) Illite Age Analyses using Illite polytypes: Rb/Sr age dating of Upper Proterozoic shale of the Stangenes Formation (Varanger Peninsula, northern Norway) with a detrital age of 1.3 to 1.4 Ga and a diagenetic age of 365 to 376 Ma. 2) Physical and chemical conditions of illitization of the Campana Mahuida porphyry copper ore deposit in the Neuquén province of Argentina, where we were able to identify a high temperature illitization event forming *2M₁* illite, formed during the evolution of the ore deposits.

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WATER ON METAL OXIDES: AN EXPERIMENTAL PERSPECTIVE

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Water is perhaps the most important and most pervasive chemical on our planet. The influence of water permeates virtually all areas of biochemical, chemical and physical importance, and is especially evident in phenomena occurring at the interfaces of solid surfaces. The water – metal oxide interaction is of particular importance in fields such as catalysis, electrochemistry, photoconversion, geochemistry, adhesion, sensors, atmospheric chemistry, and tribology. Researchers in all these fields grapple with very basic questions regarding the interactions of water with oxide surfaces, such as how is water adsorbed, what are the chemical and electrostatic forces that constitute the adsorbed layer, how is water thermally or non-thermally activated, and how do coadsorbates influence these properties of water. The attention paid to these and other fundamental questions has been immense in recent decades. In this talk, a sampling of recent experimental findings in the literature on water – oxide interactions are presented with a focus on fundamental studies utilizing single crystal surfaces.

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 $22^{o}C$, 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 $PbH_3(DFO-B)^{2+}$ 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.

UV-PROTECTION CREAMS: FIRST RESULTS FOR SUBSTITUTION OF NON-NATURAL ADDITIVES BY CLAY MINERALS

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We used clay minerals to substitute for common compounds in UV-protection skin creams, e.g. TiO_2. Clay minerals are relatively inert in comparison to photocatalytic TiO_2 [Dunford et al., 1997, FEBS Letters 418:87-90]. Experiments from Elsner (2003; unpublished report) have demonstrated, that UV rays kill Escherichia coli bacteria colonies on skin covered by TiO_2-bearing sun creams. Previous work with clay minerals has mostly focused on Na-montmorillonite (Vicente et al., 1989, Clays Clay Miner. 37:157-163; Del Hoyo et al., 2001, Clay Miner. 36:541-546). Our investigations have been carried out with kaolins (from Saxonia/Germany), bentonites (Wyoming, Chambers, Nontronite Garfield), and clays (from Saxonia/Germany) to recognize advantageous factors. Clay samples were identified by XRD, TEM, XRF and their UV-absorption abilities were studied by UV-spectrophotometry from 250-400 nm (passing a 3 µm thick cream layer). The transmission data are shown for 3 wavelengths: 280 nm (beginning of UV B area), 300 nm (responsible wavelength for sunburning), and 400 nm (end of UV A area).

Sample	Fe_2O_3 (%)	Transmission (%) at Wavelength cream + 10 % clay			Transmission (%) at Wavelength cream + 20 % clay		
		280 nm	300 nm	400 nm	280 nm	300 nm	400 nm
Kaolins							
Wolfka	0,34	29,61	21,42	34,18	22,76	16,57	25,54
Caminau	1,25	27,07	18,71	30,51	23,11	16,06	25,26
Seilitz	1,29	33,17	28,35	42,85	23,66	19,03	33,90
Clays							
Teistungen	4,52	13,94	10,86	21,42	9,54	5,84	15,99
Teistungen (dithionite)	4,06	13,94	11,86	28,54	8,95	7,48	20,41
Thierfeld	7,89	7,29	7,02	15,08	4,06	2,06	8,53
Thierfeld (dithionite)	4,11	17,23	20,02	35,05	10,77	13,42	25,29
Bentonites							
Na-Wyoming	3,35	35,68	35,74	48,37	13,97	21,46	37,49
Garfield (nontronite)	31,79	23,41	13,77	36,65	5,48	3,72	23,41

The Teistungen and Thierfeld clays show the best results for decreasing the intensity of UV radiation. This property seems to be connected with the amount of Fe in these clays. Both clays are red colored and thus are not commonly suitable for pharmaceutical purposes. Fe-rich smectite (nontronite from Garfield) offers similar protection against UV radiation as demonstrated for Thierfeld and Teistungen. The absorption of Garfield nontronite greatly exceeds that of the commonly used Na-Wyoming bentonites.

CLAY MINERALOGY OF CORE SAMPLES FROM THE UZON CALDERA, KAMCHATKA, FAR EAST RUSSIA

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Uzon Caldera is an active geothermal area within the Kamchatka Peninsula of Russia. During the summer of 2003, the geochemistry of five active geothermal fields was extensively studied based on the presence of diverse microbial communities, as well as variable geochemical conditions. Within any individual field, pH-Eh-T° (which ranged from 2.2 to 5.9, +255 to -280, and 33 to 94°C, respectively) can vary from pool to pool such that adjacent pools, separated by only meters, can host different mineralized sediments and microbes. To investigate the effects of such variations on the alteration and mineralization of the dacitic gravel through which the geothermal fluids ascend, eight core samples were collected within and adjacent to pools. The cores were sub-sampled on the basis of color and textural differences, reflecting changes in fluid composition and mineralogy. Each sub-sample was size fractionated (<2 μm e.s.d., 2-45 μm, >45 μm) and subsequently analyzed by X-ray powder diffraction.

Elemental sulfur ± opal-A tends to dominate the uppermost portion of most cores (high Eh values) and are either mixed with, or grade downward into zones dominated by kaolin group and mixed layer illite/smectite minerals. In some cores, a sharp redox boundary exists and is characterized by a change in color from gray/green/white at the top to black at the bottom (low Eh). The black sediment is dominated by pyrite ± feldspar and lesser amounts of clay minerals. Results will be presented correlating the measured values of pH, Eh, and temperature, with mineralogy and pool water geochemical analyses.

BIOTITE AS A DISCRIMINATOR IN THE LATE ORDOVICIAN DEICKE, MILLBRIG AND KINNEKULLE K-BENTONITES

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Late Ordovician K-bentonites in eastern North America and northwestern Europe are characteristically clay-rich, but also contain primary minerals in the form of isolated and euhedral phenocrysts. Major and trace element analysis of whole-rock Ordovician K-bentonites indicates that the parental magmas consisted of a calc-alkaline suite ranging through andesite, rhyodacite, trachyandesite and rhyolite. The chemical compositions indicate a tectonomagmatic setting characterized by destructive plate margin volcanics. The Deicke and Millbrig K-bentonites are two of the most widespread and persistent of the many beds of altered volcanic ash that occur in Middle to Upper Mohawkian/Champlainian (= Lower to Middle Caradoc) strata of eastern North America. The Kinnekulle K-bentonite is the thickest and most widespread among the many K-bentonites in the Ordovician of Baltoscandia and it is generally present in sections having an apparently uninterrupted Johvian-Keilan succession. The possibility of a common source for these ash beds was suggested by Huff et al. (1992, Geology, **20**, 875). Additional information supporting this interpretation was recently presented by Saltzman et al. (2003, 9th Int'l Symposium on the Ordovician System, 137).

However, Haynes et al. (1995, Geology, **23**, 847) suggested that the proposed intercontinental correlation of the Millbrig and Kinnekulle beds is suspect. They suggested that the utility of the discriminant function analysis of whole rock compositions, which are obtained by neutron activation analysis for the correlation of K-bentonite beds, is not valid for large-scale regional or global correlations. They maintained that uncertainty results from the variable mobility of several major and certain trace elements during diagenesis might result in regional shifts in bulk composition. Haynes et al. (1995) studied the compositions of volcanically generated biotite phenocrysts that had survived diagenesis and concluded that they are more reliable as specific bed indicators than bulk rock composition. They reported a compositional difference between Kinnekulle and Millbrig biotites with respect to their FeO, MgO, Al_2O_3, MnO, and TiO_2 content. They further suggested that these variations represent separate eruptive events. However, Haynes et al. (1995) used data from only one Millbrig site in North America and one Kinnekulle site in Baltoscandia, so they failed to evaluate lateral variation as well as within bed variation in biotite compositions. Here we present a comprehensive study of K-bentonite biotite composition covering a more extensive geographic and stratigraphic range for these Ordovician beds. A total of 666 Kinnekulle biotite analyses, 97 Millbrig biotite analyses and 39 Deicke biotite analyses representing 32 separate localities provide the most comprehensive view to date of the nature and extent of internal compositional variability of these widespread Laurentian and Baltoscandian ash beds. The data show clearly that the Kinnekulle and Millbrig are multiple event ash beds, some parts of which are indistinguishable from one another. Published age dates are inconclusive as to the true ages of each bed and are thus permissive of a common age and a common origin.

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

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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.

INTERPLAY OF PROCESSES OF MINERAL TRANSFORMATION, STRAIN RECOVERY AND RECRYSTALLIZATION IN LOW-GRADE PELITIC ROCKS

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Microstructural evolution of potassium white mica and chloritic minerals in a prograde sequence of pelitic rocks (illite crystallinity indices = 0.17-0.58°Δ2θ) from the Gaspé Peninsula, Québec were investigated by scanning and transmission electron microscope (SEM and TEM) techniques. SEM data show that the microstructures change from a bedding-parallel microfabric with poorly-defined matrix crystal boundaries in the late diagenetic zone to two sets of well-defined fabric elements with two distinct groups of white mica compositions in the epizone.

TEM data show that potassium white mica and chloritic minerals charastically occur as small crystals with high defect densities in late diagenetic rocks. Potassium white mica is dominated by the $1M$d polytype. Bending of layer packets is common and often associated with dislocations and low-angle boundaries. Elimination of defects is in part due to transformation from corrensite to chlorite. Crystal size increases and defect density and randomness of crystal orientations decrease significantly with increasing grade. Aggregation of medium-size crystals, coalescence of layers associated with dislocations and low-angle boundaries, neoformation of small crystals sandwiched between strained crystals, and embracement of large, defect-free $2M$ by aggregates of small $1M$d potassium white mica crystals occur in anchizone rocks. Layer bending, dislocations, and low-angle boundaries are much more abundant in potassium white mica than in chlorite. Epizone rocks are dominated by large, defect-free crystals ($2M$ muscovite) and high-angle boundaries. Enclosure of medium- to large-sized euhedral crystals within quartz and albite is common.

TEM-measured crystal-size distributions of potassium white mica in samples of different grades have lognormal shapes but with a broad bump on the greater size side of the mode for anchizone rocks. The variance of the logarithms of the crystal dimension increases nearly linearly with increase in mean of the natural logarithms of the crystal sizes. The result appears to be consistent with surface-controlled growth of potassium white mica in open systems, but the studied rocks apparently do not represent isothermal systems affected by identical stress conditions. The data collectively suggest that the size and defect state of Gaspé potassium white mica and chloritic minerals were not governed by simple growth mechanisms but were modified by strain recovery and phase transformations in late diagenetic rocks, and by growth coarsening, layer coalescence (lateral aggregation), neoformation, and polytypic transitions associated with recrystallization in syntectonic prograde metamorphism.

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

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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 $Pu^{IV}(NO_3)_4$ 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.
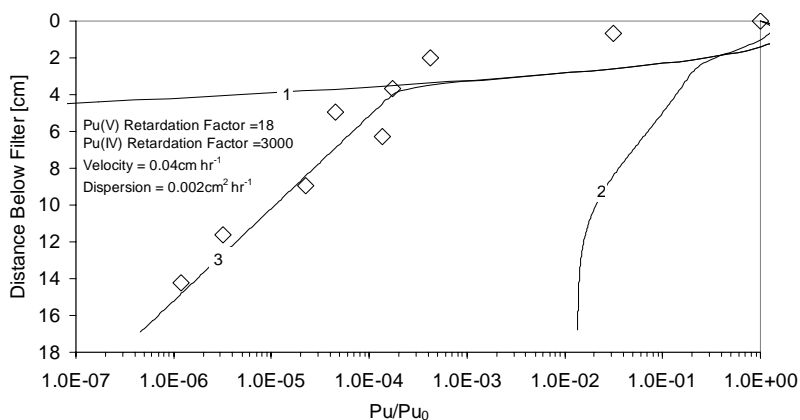
Normalized total Pu sediment concentrations (Pu/Pu_0) in the $Pu^{IV}(NO_3)_4$–amended lysimeter. Diamond symbols represent measured values. Simulation input values (ko and kr are the first-order rate constants for Pu(IV) oxidation and Pu(V/VI) reduction, respectively): (1) $ko = 0$ hr^{-1}, $kr = 0$ hr^{-1}; (2) $ko = $ 1e-5 hr^{-1}, $kr = 0$ hr^{-1}; (3) $ko = $ 1e-8 hr^{-1}, $kr = $ 1.2e-3 hr^{-1}.

SHORT TERM EXPERIMENTS WITH DIFFERENT BENTONITES IN SALINE SOLUTIONS

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Compacted bentonites are candidate materials for sealing elements of technical barriers in repositories for radioactive and chemical wastes. For a long term guarantee of such barriers we have to describe beforehand the possible alteration processes of applied bentonite in interaction with different types of solutions.

In Herbert et al. [2004, Appl. Clay Sci. (in press)] pyrophyllitization/kaolinitization was characterized as the main thermodynamic pathway of alteration in high saline solutions (low pH) for MX-80 bentonite. These results were valid mainly for "closed" reaction systems. This work also suggested that beidellitization, vermiculitization and illitization might occur in "dynamic" systems.

To test these predictions, short term experiments (20 days) were carried out with different bentonites (Belle Fourche, Pioche, Chambers, Otay; Garfield nontronite; Friedland IS-mixed layers). These experiments were conducted with powder samples in 1 n NaCl-solution (solid-liquid ratio = 1:4), at ambient temperature, and arranged in an overhead-shaker equipment (= "dynamic"). Experiments with compacted MX80-bentonite (dry density 1200 – 1300 kg/m³) in percolating 10% and 20% NaCl-solutions for 30 days (110°C) were also conducted to visualize possible alteration processes under more realistic conditions. Run products were characterized by X-ray diffraction and transmission electron microscopy (morphology, electron diffraction, element distribution).

After the short reaction time of 30 days smectite was still the main compound in the run products of compacted MX-80 bentonite and retained full expandability under ethylene-glycol solvation (16.9 Å). Montmorillonite was formed by Al-enrichment in the octahedral layers (as shown by TEM-EDX). This process decreased the layer charge. Otherwise, remarkable amounts of beidellite were identified by TEM. A small 10 Å-interference was seen but we could not distinguish between illite/brammalite neoformation or irreversible collapsed layers. Saline solutions increased the rate of changes for the mineralogical and technical parameters (hydraulic conductivity, swelling pressure) compared to distilled water.

***"Closed" System** (up to 600 days)*	
pyrophyllitization	*MX-80 bentonite*
***"Dynamic" System** (in 20 days)*	
unchanged	*Belle Fourche bentonite*
beidellitization	*compacted MX-80 bentonite*
vermiculitization	*nontronite of Garfield*
illitization	*Chambers bentonite completely to IS; Pioche bentonite partially; Otay bentonite in first steps*

It is possible to describe different rates of hydrolytic reactions for different montmorillonites in "dynamic" systems. Different rates should also be expected for different bentonites in a compacted design.

INTERACTION OF MITOCHONDRIAL CYTOCHROME C WITH HEMATITE (001) SURFACES

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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.

SINGLE ENZYME NANOPARTICLES

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We have developed single-enzyme nanoparticles (SENs), which dramatically stabilize alpha-chymotrypsin by surrounding each enzyme molecule with a porous composite organic/inorganic network of less than a few nanometers thick. The synthetic procedure, entailing enzyme modification and two orthogonal polymerization steps yields nanoparticles containing a single enzyme, which can be observed by transmission electron microscopy. In experiments with chymotrypsin, incorporation into the nanostructure dramatically increased the enzymatic stability. Furthermore, the nanoscale structure around the enzyme is sufficiently thin that it does not impose a significant mass transfer limitation on the substrate. We have also prepared SENs containing trypsin for the protein digestion in proteomic analysis. These nanoparticles can be further immobilized onto nanostructured matrices that provide a large surface area for attachment. Several examples of successful processing will be given in this presentation. These new nanostructures are very promising for many applications including biosensors, bioreactors, microfluidic devices, decontamination, remediation, antifouling, and protective layers.

ROLE OF MICROBES IN PROMOTING THE SMECTITE TO ILLITE REACTION

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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.

THE EFFECTS OF ALKALI METAL CATIONS ON KAOLIN SUSPENSION RHEOLOGY

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The effect of alkali metal cations on commercial kaolin suspension rheology was studied across a concentration range of 1.0 to 500 mM. The kaolin slurries were all dispersed with sodium polyacrylic acid (Na-PAA) at 0.2 mg/m^2 (the amount necessary for surface coverage). The critical coagulation concentration (CCC) was determined for Li^+, Na^+, K^+, Rb^+, and Cs^+ using viscosity measurements. Also, diluted suspensions (~10 vol.%) were prepared to examine the coagulation effects on kaolin suspensions at different pH levels (pH = 4, 7, and 9). Adsorption isotherms of cations on the kaolin were measured for all the samples. The critical coagulation concentration of M^+ was determined to be identical for Li^+, Na^+, K^+, Rb^+, and Cs^+, but the maximum viscosity scaled with ion size. In addition, the larger metal ions demonstrated significant specific adsorption on the surface of the clay modifying the viscoelastic properties of the coagulated system. Dispersion stability is eventually overcome by cation affects as the CCC is approached. The rheology of highly loaded suspensions is sensitive to combined alkali concentrations at the tens of millimolar level which is occasionally of concern for industrial ceramic production.

OUTCOMES OF THE SECOND REYNOLDS CUP IN QUANTITATIVE MINERAL ANALYSIS OF CLAY BEARING SAMPLES

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The first Reynolds Cup was initiated by colleagues from ChevronTexaco and the U.S. Geological Survey to stimulate the development of methods for quantitative mineral analysis of clay-bearing rocks (McCarty, 2002). After the results of the contest have been published at the 2002 CMS meeting in Boulder(CO), an "ad hoc" committee decided to continue with a second contest in 2004. This one is supported by the Deutsche Forschungsgemeinschaft (German Research Council), the Clay Minerals Society, the German-Swiss-Austrian Clay Group (DTTG) and the Commission on Powder Diffraction of the International Union of Crystallography. The second Reynolds Cup was announced at some mineralogical and crystallographical conferences in 2003 as well as at the DTTG homepage and to the CMS, MSA and IUCr Rietveld listservers in December 2003. The 60 sets each containing 3 mineral mixtures have been requested by the interested people in about 4 days after sending the start signal to the listservers. This indicates the great interest of the community in improving the analytical methods. The samples have been sent out to these 60 laboratories in 18 countries of 5 continents during the late December 2003. The only information given to the participants was that the compositions were designed to represent three different types of sedimentary rocks (mudstone, sandstone, saliniferous rock). The mixtures were prepared from pure mineral samples, obtained mainly from the collections of the Technical University Bergakademie Freiberg/Germany. Clean minerals were hand-picked from broken single crystals or separated by chemical treatment and size fractionation in the case of clay minerals. These reference minerals have been screened for purity by XRD and other techniques. All materials were broken to < 0.4 mm size for main components and to < 0.2 mm or < 0.1 mm for minor components of the planned mixtures. The air-dried material was weighted in for a total mass of 256 g of each mixture. These samples were homogenized by one day overhead tumbling in 800 ml glass bottles together with mixing balls. Then, the mixtures were split into 8 parts in an rotary sample splitter and recombined 5 times. After a further splitting run, the 8 splits were split again into 8 parts (now 4 g) using a micro-rotary splitter. In this way 64 4-g-units of each mixture were obtained. In order to check the homogeneity of the splits, 3 sample sets were taken randomly from these 64 units. Two of them were divided into two parts used for XRD and XRF analysis, respectively. The third sample was quartered to check the chance to take representative 1 g sub-samples also from a single sample set. Two of these quarters were also ground in a McCrone micronizing mill and XRD patterns were measured. No significant differences could be seen in the XRD patterns and in the XRF results for all these sub-samples. The participants had about four months (until May 1st) to carry out their analyses. All methods for phase identification and quantification were allowed. To avoid nomenclature problems during reporting and judging the results, some grouping of minerals was done in the same way as in the first contest. Again we used simply the sum of deviations from actual wt-% ("bias") as a criterion for the quality of the analyses. Details of the results are presented in this talk. The winner of the 2004 Reynolds cup is ... the whole clay community ☺!

CLAY-ORGANIC MATTER INTERACTIONS IN THE SOIL ENVIRONMENT - 30 YEARS OF PERSONAL CONTRIBUTIONS AND PERSPECTIVES FOR FUTURE RESEARCH

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Most of the organic carbon in soils is associated with the clay fraction. The principal soil organic components are humic substances, which are usually classified as humin, humic acid and fulvic acid, based on their solubility in acid and alkali. Interactions of humic substances with clays form associations of widely differing physical, chemical and biological stabilities, which affect various soil properties. Among humic substances, fulvic acid (FA), soluble in both acid and alkali, is completely soluble in water at all pH values and is considered to be the most active fraction. The interaction of FA with clays, therefore, became the prime objective of the investigation. In collaboration with Morris Schnitzer the investigation was initiated about 30 years ago at what was then Soil Research Institute of Agriculture Canada. The results of this investigation indicated the following: 1) a FA solution is efficient in dissolving mafic minerals, due to its ability to complex metal ions, 2) the extent of FA adsorption on external mineral surfaces depends on the physical and chemical characteristics of the surface, the pH of the system and its water content, 3) once adsorbed on clays the solubility of FA in water of the FA decreases, 4) in some instances clays appear to behave as templates which change the nature of FA molecules from hydrophilic to hydrophobic, 5) expandable clay minerals can absorb FA in their interlayer sites as a function of pH of the system and the reaction is influenced by interlayer cation species, 6) the presence of FA retards crystallization of minerals, and 7) as an aggregate architecture, mineral - organic matter associations may play an important role in influencing living habitats in soils. These findings have been useful for explaining and understanding some phenomena occurring in soils. However, now looking back on this research, it is clear that much remains uncertain and unexplored. Some examples will be presented.

DIRECT DETERMINATION OF DEFECT STRUCTURES IN KAOLIN MINERALS BY HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (HRTEM)

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Near-atomic resolution TEM imaging (Fig. 1) has been successfully applied to determine the stacking defect structures in kaolin minerals, especially in kaolinite. The specimen studied is at mid-stage of the depth-related kaolinite-to-dickite transformation in a sandstone reservoir. Although electron radiation damage is a serious obstacle, a number of high-quality images were recorded on films, in which the tetrahedral and octahedral positions in a kaolinite unit layer were clearly resolved. Electron diffraction and high-resolution imaging of dickite showed that few stacking defects exist in this polytype. On the other hand, kaolinite crystals contain high density of stacking defects. These defects or stacking disorder are formed by mixture of the two kinds of lateral interlayer shifts, t_1 (approximately $-a/3$) and t_2 ($-a/3 + b/3$), between adjacent layers (Fig. 2). Disorder by the coexistence of B layer and C layer, or dickite-like stacking sequence was never observed. These results provide not only an unambiguous settlement for the long controversy of the defect structures in kaolinite, but also a new clue to understand kaolinite-to-dickite transformation mechanism.
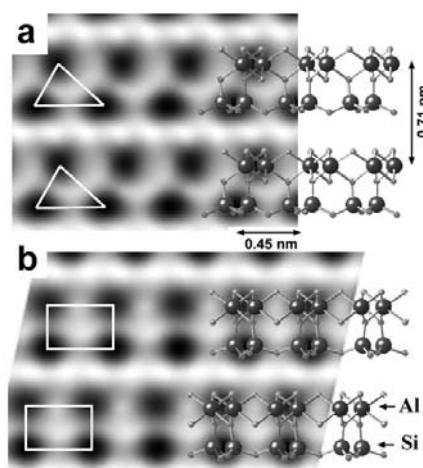

Fig. 1. Crystal structure and corresponding multi-slice simulated image of kaolinite, viewed down (a) [100] and (b) [110]. In the crystal structure model, Al and Si atoms are represented as large spheres and oxygen (hydroxyl) atoms
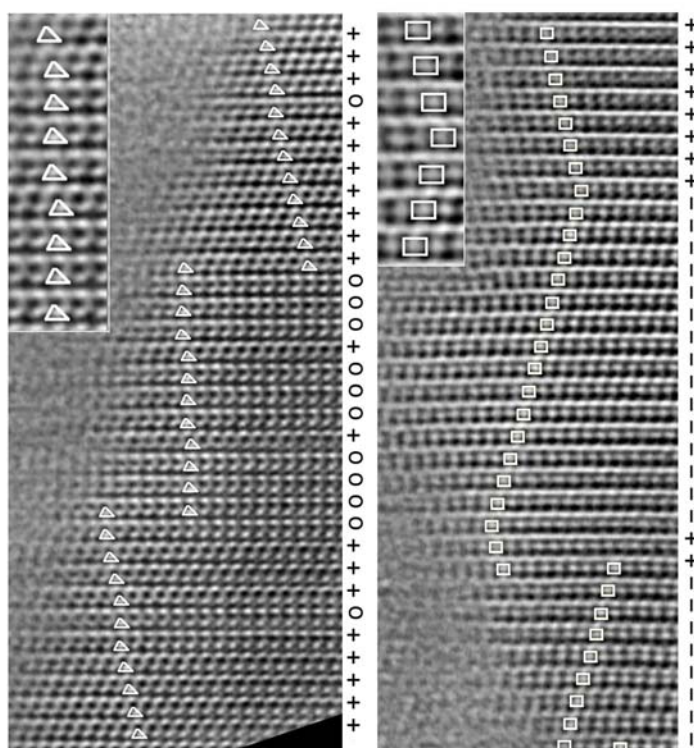

Fig. 2. Two filtered HRTEM images of disordered kaolinite. The marks of "o", "+" and "−" at the right of the figures indicate no-, left- and right-hand staggers respectively, from the under layer. The insets at the top-right are the magnified images of portions in the lower-magnified ones.

POLYTYPE AND MORPHOLOGY ANALYSES OF KAOLIN MINERALS BY ELECTRON BACK-SCATTERING DIFFRACTION (EBSD)

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Electron back-scattering diffraction (EBSD) technique has been applied to fine-grained kaolin minerals to determine the polytypes (kaolinite, dickite and nacrite) for individual grains and their crystal orientations in a scanning electron microscope (SEM). Kaolin particles dispersed on a flat substrate and carbon-coated were prepared for the EBSD analyses. Because kaolin minerals are prone to radiation damage by intense electron beam that is necessary to obtain EBSD patterns, the beam during pattern acquisition should be radiated on a certain specimen area with scanning mode. Kaolinite-dickite or nacrite are easily distinguished by trigonal or hexagonal symmetries around the [001]* direction respectively, of the Kikuchi bands corresponding to family reflections. Ordered dickite can be differentiated from kaolinite with a mirror plane passing the [001]* direction and characteristic Kikuchi poles.

As EBSD analysis is performed in a SEM, morphological characters can be corresponded to polytypes. Oriented overgrowth of dickite fragments on nacrite plates was found on a sample of hydrothermal origin. Ordered dickite always has euhedral shapes in a diagenetic kaolinite-dickite mixture specimen. Combination of EBSD and SEM observation enables morphology analysis for fine crystals as clay minerals. Lath-shaped diagenetic dickite is definitely elongated along the *a*-axis directions. Rhombohedral dickite consists of crystal planes with indices of {-111} as side-facets.
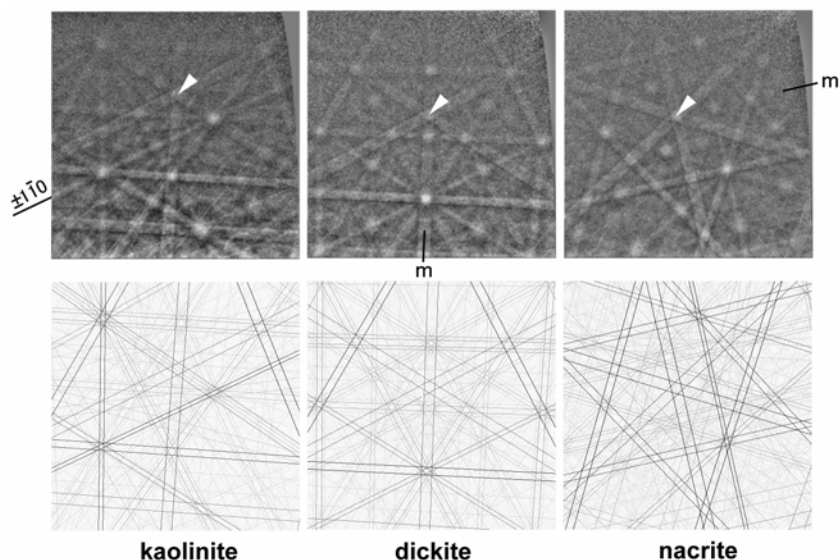
(Top) EBSD patterns from kaolinite, dickite and nacrite. (Bottom) Calculated Kikuchi patterns in the same orientation. The position corresponding to the [001]* direction is indicated with the arrowhead in each pattern.

QCM STUDIES ON ADSORPTION BY AN ION-EXCHANGE ADDUCT

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An ion-exchange adduct of Mg-Al layered double hydroxide and $[Fe(BPS)_3]^{4-}$(BPS = 4,7-diphenyl-1,10-phenanthroline disulfonate) was prepared by the coprecipitation method at various Mg(II)-to-Al(II) ratios ([Mg(II)]/[Al(III)] = 2/1, 3/1 and 4/1). The structures and adsorption properties of the materials were studied by XRD, TG and QCM (quartz crystal microbalance) measurements. LDH-[Fe(BPS)_3] was prepared by the coprecipitation method which was thought to be effective for a bulky anion. An aqueous suspension of an ion-exchange adduct was cast onto a gold-coated quartz electrode (an 1.33 cm^2 electrode area) and dried under air. The electrode was immersed in an aqueous solution. The change of mass was monitored by following resonance frequency (Δf) after adding organic liquid as an adsorbate under stirring. Mass change was calculated according the following Sauerbrey equation: $\Delta m = S\Delta f$ (S $=-17.7$ ng Hz^{-1}cm^{-2}). Figure 1 shows an example of the QCM measurements when acetonitrile was added to the water medium in which a QCM electrode was immersed. The saturated adsorption amount was calculated to be 9.21×10^3ng per 1 mg of the adduct. Similar experiments were performed for other kinds of organic molecules to examine any selectivity towards an adsorbate.
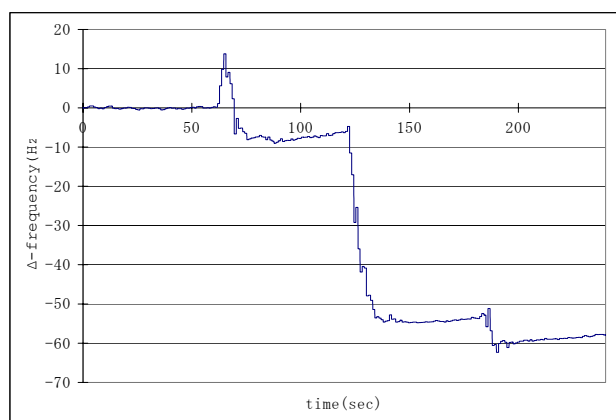

Figure.1 The frequency change of a QCM electrode coated with a cast film of an adduct of LDH (Mg/Al = 4/1) with $[Fe(BPS)_3]^{4-}$.
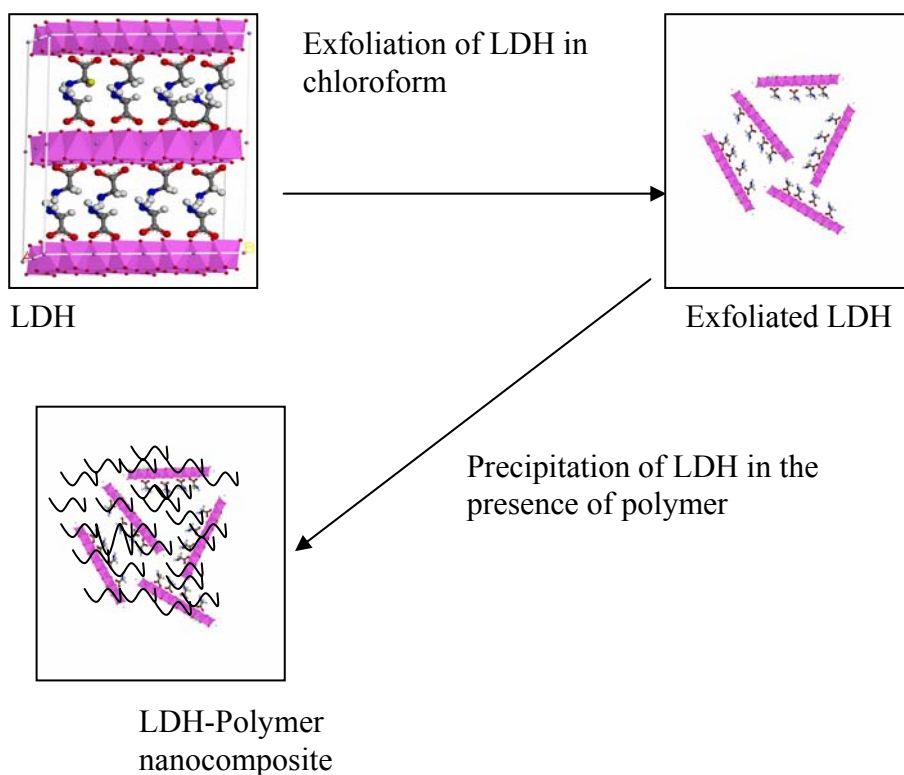
SYNTHESIS AND CHARACTERIZATION OF LAYERED DOUBLE HYDROXIDES (LDH)/POLYMER NANOCOMPOSITES

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Layered Double Hydroxides (LDHs) are a class of layered materials which are suitable for the preparation of nanocomposites, in which ultra fine nano-particles of LDH are homogeneously dispersed within a polymer matrix. Nanocomposites are prepared either by (i) intercalation of a polymer material between the layers of an inorganic material or (ii) by exfoliation of a layered material in a suitable solvent followed by precipitation in a polymer matrix.

Nanocomposites based on exfoliated Li-Al-glycine LDHs and polyethyleneglycol (PEG) are described in this presentation. The products have been characterised by PXRD, FTIR and HREM and the properties of the composite materials have been studied using thermogravimetry and by mechanical testing. Results suggest that the LDH plates are individually dispersed in the polymer matrix and that the properties of the composite materials are superior to the parent polymer, proving that the exfoliated clay state is effective in improving the properties of parent polymer.

LDH

Exfoliation of LDH in chloroform

Exfoliated LDH

Precipitation of LDH in the presence of polymer

LDH-Polymer nanocomposite

NANOSTRUCTURATION OF PYRIDINE GUEST MOLECULES ENTRAPPED IN THE TUNNELS OF SEPIOLITE

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Sepiolite is a naturally occurring fibrous phyllosilicate structurally with nanotunnels (3.7×10.6 Å in cross section). Sepiolite is previously heated at 120 ºC to remove selectively the zeolitic and surface bound water molecules, and then exposed to pyridine vapor at room temperature. Two kinds of pyridine molecules are evidenced in the broad line ^{2}H NMR spectra: (i) mobile surface pyridine molecules easily removed by heating at 90 ºC for a night, and (ii) rigid pyridine molecules trapped in the nanostructured tunnels of sepiolite and H-bonded with structural water. Upon further heating of the sample, the structural water is entirely removed along with some of the pyridine molecules. The ^{15}N chemical shielding parameters indicate that the remaining pyridine replaces the structural water and is coordinated directly to the edge Mg^{2+} sites.

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

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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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INVESTIGATING THE MOLECULAR INTERACTIONS OF OXYTETRACYCLINE IN CLAY AND ORGANIC MATTER: INSIGHTS ON FACTORS AFFECTING ITS MOBILITY IN SOIL

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Residual concentrations of tetracycline antibiotics in the environment have been found to contaminate surface, ground and drinking water, aquatic sediments and soils. This has also led to increased emergence of resistant strains of pathogenic bacteria that could potentially impact human health. The interactions of oxytetracycline with model clay adsorbents and organic matter were investigated as a function of suspension pH. The clay adsorbents used were the montmorillonite clay (SWy-2), Na-montmorillonite clay (Na-SWy-2), and hexadecyl trimethyl ammonium-montmorillonite clay (HDTMA-clay). The adsorption of oxytetracycline to the clay could be described by Freundlich type adsorption isotherms. It was observed that the adsorption of oxytetracycline in the natural and sodium forms of montmorillonite clay decreases with increasing pH in the order pH 1.5 > pH 5.0 > pH 8.7 > pH 11.0. This trend is consistent with cationic exchange interactions that are dominant at lower pH values when oxytetracycline has a net positive charge. On the other hand, hydrophobic interactions when oxytetracycline is zwitterionic (at pH 5.0) are predominant, as evident from the FT-IR spectrum of the HDTMA-clay adsorbed with oxytetracycline. The presence of large amount of dissolved organic matter (DOM) was also found to decrease the sorption of oxytetracycline on clay, suggesting that DOM may increase its mobility in the natural environment. Several mechanisms of interaction of oxytetracycline in clay are proposed based on the adsorption isotherms and the results from X-ray diffraction (XRD) and Fourier transformed infrared (FT-IR) analyses.

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

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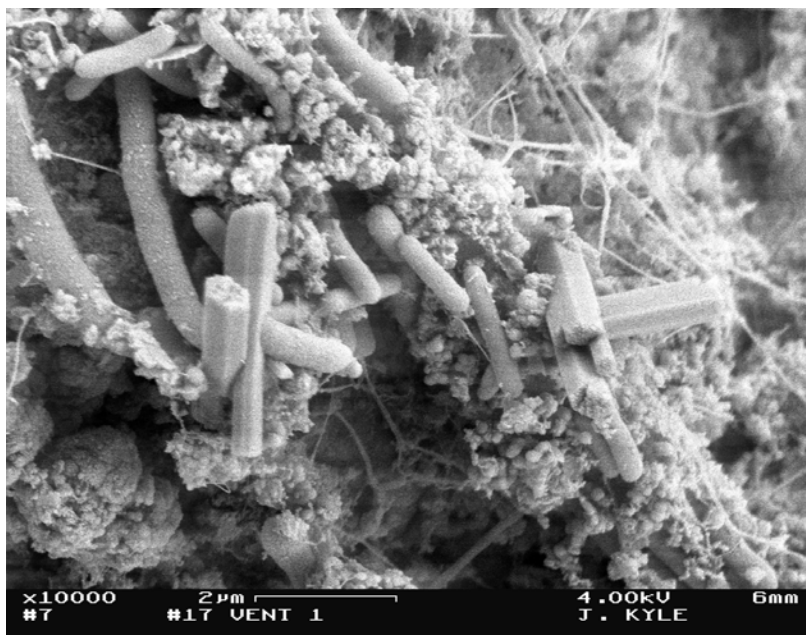
SEM micrograph of rod shaped microbes in close association with crystals on the sinter deposit from the rim of vent 1.

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.

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

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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.

IMMOBILIZED ENZYMES IN NANOPOROUS MATERIALS EXHIBIT ENHANCED STABILITY AND ACTIVITY

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Enzymes (proteins) are the nano-machines of cells. Unlike conventional catalysts, enzymes efficiently perform chemical reactions with extreme specificity under mild reaction conditions. In cells, molecular crowding provides enhanced protein stability and can induce order-of - magnitude enhancements in catalytic reaction rates compared to enzymes in solution. We recently demonstrated that enzymes can be artificially crowded through immobilization on surfaces to thereby increase their reaction rates and stability.

The focus of our research is to utilize proteins in combination with inorganic materials to create devices and materials with exciting new properties and capabilities. Proteins provide superior catalytic abilities over traditional inorganic type catalysts and the simplified reaction conditions of enzymes require less complex engineering than catalytic reactors. To overcome the inherent fragility of enzymes in solution, one focus of our research is to immobilize enzymes in functionalized nanoporous supports (FMS) that could mimic the stabilizing cellular microenvironment.

Nanoscale materials can be combined with enzymes to dramatically improve the durability of enzymes, create localized high concentrations of protein, and reduce costs by minimizing losses. A major caveat is that the enzyme immobilization reaction must not destroy catalytic activity. Studies within our lab have now demonstrated that at least three unrelated enzymes (organophosphorous hydrolase [OPH], glucose isomerase [GI], and glucose oxidase [GO]) linked to a mesoporous material engineered with cavities or pores sized slightly larger than the enzymes resulted in markedly enhanced thermal and chemical robustness of the enzyme without decreasing its catalytic abilities.

We've succeeded in immobilizing large quantities of 3 active enzymes in functionalized nanoporous materials. Our enzyme specific activity is actually higher once immobilized, consistent with 'molecular crowding' effects observed in cells. One of the enzymes we used, oganophosphorous hydrolase (OPH), inactivates chemical warfare agents. After immobilization in FMS, specific activity was double that of free enzyme; the immobilization efficiency was > 200%; and after 54 days of storage, the enhanced specific activity of the entrapped enzyme was still 167% that of free enzyme.

Our approach could be used to make more sensitive sensors, for decontamination, and to develop advanced separations based on the high specificity of protein-mediated interactions. We can produce large quantities of the materials, so it need not be limited only to research purposes.

SYNTHESIS ROUTES TO NANOMETER-SIZED IRON OXIDES

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Several methods have been shown to be useful for the synthesis of gram to kilogram quantities of nanometer-sized iron-containing materials. Among the techniques used in our laboratory are Rapid Thermal Decomposition of Solutes (RTDS), Modified Reverse Micelles (MRM), Rapid Expansion of Supercritical Solutions (RESS) and general solution techniques. The diverse materials produced can contain iron ranging from iron (0) to iron (III) with both single phase and multiple phase materials of the common iron oxides obtainable. Crystallite and agglomerate size can also be controlled across a wide range by varying processing and work-up parameters. This presentation will briefly describe the above synthesis methods with emphasize on the strengths and weaknesses for each technique.

ELECTRICAL CONDUCTIVITY SPECTRA OF SMECTITES AS INFLUENCED BY SATURATING CATION AND HUMIDITY

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Electrical conductivity is an important soil property related to salinity, and is often used for delineating other soil properties. The purpose of this study was to examine the influence of smectite properties on the complex electrical conductivity spectra of hydrated smectites. Four reference smectites were saturated with Ca, Mg, Na, or K and equilibrated at four relative humidities (RH) ranging from 56 to 99%. X-ray diffraction was used to determine fractions of the various smectite layer hydrates (0 to 4 layers of interlayer water molecules) in each sample. A vector network analyzer was used to determine the real component of the complex electrical conductivity spectra (σ') for frequencies (f) ranging from 300 kHz to 3 GHz. Values of the d.c. electrical conductivity (σ_0), the frequency where the slope changes in the spectra (f_r), and the slope at the high frequency end of the spectra (n) were determined by fitting σ' to $\sigma'(f) = \sigma_0 (1 + f/f_r)^n$. Both σ_0 and f_r increased with the total amount of water, the amount of interlayer water, and for saturating cations in the following order; K<Mg <Ca<Na. The opposite trends were observed for n. Values of these parameters were influenced by the type of smectite, but the trends were not consistent for the effect of layer charge. The results indicate that interlayer water in smectites contributes to the electrical conductivity of hydrated smectites, and that polarization of water by local electrical fields has a substantial influence on the complex electrical conductivity spectra of smectites. The accuracy of salinity estimates for soils and sediments that are based on conductivity measurements may be adversely affected unless the effects of hydrated clays on electrical conductivity are considered. Example conductivity spectra are shown below.
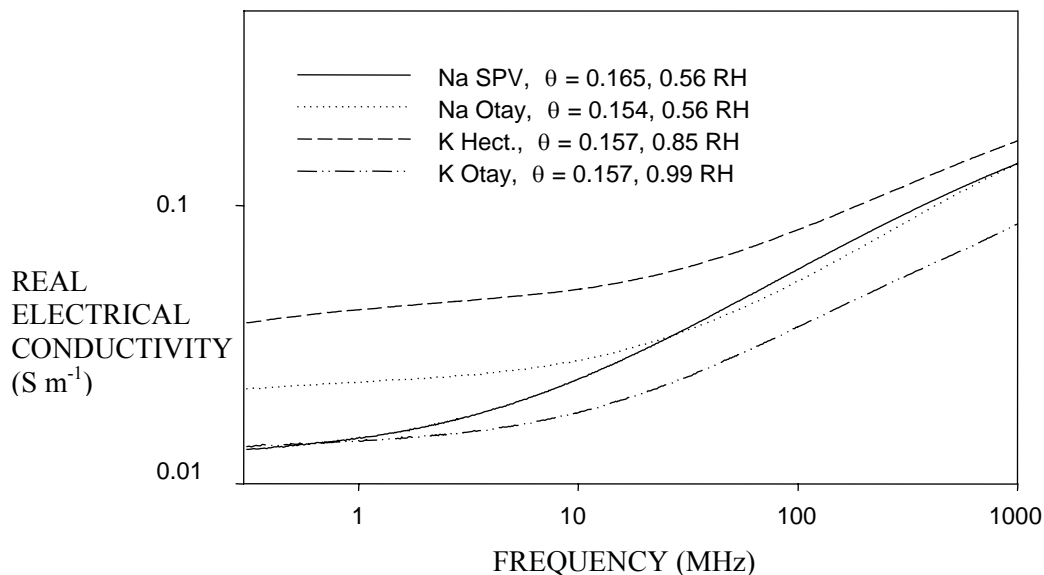
BASAL REFLECTIONS OF A STABLE ISOTOPIST: REVEALING THE SECRETS OF FLUIDS, CLIMATE & CRYSTAL CHEMISTRY FROM THE CLAY ARCHIVE

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Presently or formerly of The Basal Reflections Society, Department of Earth Sciences, *The* University *of* Western Ontario, London, ON Canada N6A 5B7

The use of stable hydrogen and oxygen isotopic analysis to determine the origin and evolution of clay minerals was revealed in seminal papers by Savin & Epstein, Lawrence & Taylor, and Sheppard *et al.* in the late1960s and early 1970s. They taught us about the relationships among temperature and the isotopic compositions of clay minerals and water. My research group has exploited this elegant foundation ever since.

H- and O-isotope results for diagenetic illite, smectite and kaolinite record the basin-wide Eocene influx of meteoric water into sandstones of the Western Canada sedimentary basin, and its impact on hydrocarbon distribution. H- and O-isotope analyses of secondary chlorite and illite mark multiple episodes of rock-water interaction along the Precambrian-Paleozoic unconformity in the Appalachian basin. Hot basinal brines, driven westward by Taconic orogenic events, controlled chlorite formation. Illitic clays formed later from local meteoric water during basement reactivation related to distal Acadian and Alleghanian orogenic activity. We have also used the H- and O-isotopic compositions of pedogenic clay minerals from Cretaceous paleosols as a climate archive. These values are a proxy for paleo-precipitation, whose isotopic compositions, in turn, can be related to temperature. In Holocene systems, grass phytoliths (opal-A) also preserve O-isotope compositions that can be related to humidity. There have also been practical applications. For example, steam is injected into oil sands to facilitate hydrocarbon recovery. Changes in the H- and O-isotope compositions of reservoir clays can be used to trace the extent and temperature of contact with the injected fluid.

Isolation of clay minerals without changing their stable isotopic compositions is a practical challenge to the analyst. The classic 'Red' and 'Blue' texts of Professor Jackson describe most common methods used in clay separation. We have evaluated most these procedures for their isotopic consequences. Stable isotopic study of clays also depends upon reliable knowledge of clay-water fractionation factors. Patience is a virtue in measurement of clay-water fractionation factors at low temperatures. Our studies of gibbsite, for example, produced reliable O- and H-isotope fractionation factors only after years of growth. Post-formational isotopic exchange of clays with ambient fluids is also of concern. It affects different clays differently, in ways still being discovered. For example, 1.0nm halloysite demonstrated significant oxygen (in addition to hydrogen) isotopic exchange at room temperature, a feature largely absent from the 0.7nm variety. A still greater challenge to interpreting clay stable isotopic results is the chance that some clay minerals inherit part of their compositions from precursors. Experiments involving transformation of berthierine (1:1) to saponite (2:1) suggest that the prudent clay isotopist no longer can ignore the possibility of such behaviour.

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.

ARSENIC MOBILIZATION AND MINERALOGY OF ANOMALOUS SOILS FROM BRAZIL

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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/F_{ed} ratio. Soil mineralogy and organic C content apparently play the most prominent role. Comparing the mean total mobilized As with F_{ed} 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.

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

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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 form 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.

A REVIEW OF THE FRICTIONAL STRENGTH OF MONTMORILLONITE

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Montmorillonite is a common constituent of the accretionary wedges and downgoing sediments of subduction zones, and it has also been identified in core samples from drillholes into active strike-slip fault zones. Knowledge of the frictional properties of montmorillonite may be critical to understanding the behavior of such faults. Unfortunately, many of the published data on montmorillonite friction are contradictory, with reported values of the coefficient of friction, μ (= shear stress/effective normal stress) ranging from 0.06 to 0.78. We propose that this wide variation is partly a function of the large difference in strength between thoroughly dried ($\mu \geq$ 0.7) and water-saturated ($\mu \leq 0.3$) montmorillonite. Petrographic examinations indicate that dry montmorillonite gouge undergoes frictional processes such as abrasion, wear, and fracture during shear. In contrast, shear of water-saturated montmorillonite gouge is concentrated in thin films of water that are adsorbed onto the (001) surfaces of the platy grains. Our recent laboratory investigations suggest that water-saturated shear strength of layer-structure minerals increases with the strength of the bonding of the polar water molecules to the (001) surfaces, and the relative weakness of water-saturated montmorillonite may be largely owing to its small layer charge. Published values of μ for montmorillonite under (deionized) water-saturated, equilibrated conditions increase regularly from 0.06 at effective normal stresses <1 MPa to 0.30 at ≈300 MPa. The direct correlation of μ with effective normal stress is characteristic of sheet-silicate gouges, and it is attributed to decreasing thickness of the surface water films with increasing normal load. In contrast, μ of common framework silicates such as quartz exhibits little pressure sensitivity below about 200 MPa effective normal stress and then decreases with further increases in effective normal stress (Byerlee's law). Increasing salinity of the pore fluid has the same effect on the shear strength of montmorillonite as increasing effective normal stress, due to reduction in double-layer thickness of adsorbed water. Most of the published strength data for montmorillonite fall outside the trend of water-saturated, equilibrated samples on a plot of μ versus effective normal stress. The data that are stronger than the water-saturated results for a given set of experimental conditions may have been only partially saturated, whereas those that are weaker appear to be caused by inadequate drainage and consequent build-up of excess internal pore pressure that was not alleviated over the duration of the experiments. These results highlight the hazards of interpreting fault-zone behavior based on experiments that do not represent natural conditions. For example, the use of unsaturated clay rheology in modeling subducted sediment wedges in megathrust environments could lead to erroneous predictions of fault strength.

SOLID-STATE NMR STUDIES OF THE TRANSFORMATION OF CLAY MINERALS IN THE ENVIRONMENT

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Environmental mobilities of radionuclides (such as ^{137}Cs and ^{90}Sr) are governed by their interactions with natural soil particles in the saturated and unsaturated zones at Department of Energy waste sites (*e.g.* the Hanford Site). High surface area aluminosilicate clay minerals are a component of the natural soils beneath the leaking waste tanks at these sites, and serve as possible radionuclide sorbents. However, due to the characteristics of the contaminant medium (high pH, high Al, and high ionic strength), clay minerals are susceptible to transformations during exposure to tank waste leachates. To gain a better understanding of fundamental processes taking place in the vadose and saturated soil environments in these affected areas, we are currently studying the transformation of clays under specific chemical conditions that mimic the composition of contaminant solutions.

In a first set of studies, specimen clay samples are reacted for varying time periods (up to one year) with simulated tank waste leachate (STWL) solutions containing fixed concentrations of (nonradioactive) Cs and Sr co-contaminants (at levels of 10^{-3}, 10^{-4}, and 10^{-5} M). Mineral dissolution and transformation are followed with solution analysis, x-ray diffraction, solid-state nuclear magnetic resonance (NMR), and a number of other analytic methods. We report here results from ^{27}Al magic-angle spinning (MAS) NMR, ^{29}Si MAS NMR, and ^{1}H/^{29}Si cross-polarization MAS (CPMAS) NMR, and we evaluate these results along with those of other parallel analytic studies. A number of neophases are identified through these analyses, and the use of solid-state NMR at multiple fields allows for superior resolution of resonances from different species. Ultimately, solid-state NMR results offer a powerful way to quantify the reaction kinetics.

Further reaction and interaction mechanisms are also important in these systems. The sorption of strontium in clay minerals and zeolites in particular is not well understood, although various spectroscopic techniques (EXAFS, XAS) have been implemented in an attempt to discern both the coordination of strontium species as well as the degree of hydration. While solid-state NMR is one of the most effective techniques for developing a molecular-level understanding of cation sorption, the low gyromagnetic ratio and low natural abundance of the NMR-active strontium isotope make it difficult experimentally to acquire and interpret solid-state ^{87}Sr NMR spectra. Therefore, additional studies have been designed to (a) identify the effects of strontium on the kinetics of neophase formation and (b) probe the coordination environment of strontium nuclei trapped in these phases using solid-state NMR. Simulated neophases have been generated by seeding a model Hanford waste solution with colloidal silica in the presence of varying concentrations of cesium, strontium, and iodine. Aluminum, silicon, and sodium MAS NMR are used to follow the kinetics of neophase formation and the impact of the strontium concentration on these kinetics. NMR methods for probing strontium nuclei will also be discussed, offering useful experimental approaches for the direct NMR analysis of strontium in neoformed precipitates and other systems of environmental importance.

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

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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.

INTERLAYER CATION ARRANGEMENT AND HYDRATION SHELLS IN SODIUM AND CALCIUM MONTMORILLONITE OBTAINED BY MONTE CARLO SIMULATIONS

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Today the interlayer structure of montmorillonite is simulated by computer experiments (e.g. Monte Carlo, MC). Early MC simulations focussed on the 1D-distribution of interlayer species perpendicular to the 2:1 layers and reproduced the well-established layer-wise arrangement of water molecules. Recently, more attention is drawn to the precise arrangement of interlayer species in 3D. However, no detailed picture of the interlayer structure has been proposed until now.

In the present study, we placed strong emphasis on position, orientation and geometry of cationic hydration shells, but also on structure of water layers and distribution of cations on the 2:1 layer surface. We performed MC simulations of a montmorillonite at two different layer spacings (sodium one- and two-layer hydrate and calcium two- layer hydrate). The relative arrangement of the 2:1 layers was equally chosen for all three, i.e. it was independent of the degree of expansion.

In the sodium one-layer hydrate, cations have a quadratic planar hydration shell. The diagonals of the square are rotated (~15°) with respect to the crystallographic a,b axes. This is deduced from paired hydrated cations. In the sodium two-layer hydrate, some cations stay coordinated to the 2:1 layer, their hydration shell is extended to a tetragonal pyramid. The rotation angle is preserved. Sodium ions detached from the 2:1 layer are octahedrally coordinated with six water molecules. The octahedron is lying parallel to the 2:1 layers with two of its triangular sides. All the extracted bond lengths compare well with literature data.

In the calcium two-layer hydrate, the cations are coordinated to the 2:1 layer and are found in/over the pseudo-hexagonal structural element of the 2:1 layer. In many examined cases, the first hydration shell is a pentagonal pyramid with its base parallel to the 2:1 layer. This geometry is in good agreement with recent simulation data on hydrated calcium in solution (pentagonal bipyramidal coordination).

All three simulations give clear indications of a superstructure caused by the ordered distribution of interlayer cations. This is evidenced from the cation-cation radial distribution functions.

FACTORS AFFECTING THE DESORPTION OF CADMIUM FROM GOETHITE

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Cadmium is perhaps environmentally the most significant heavy metal in soils. Bioavailability and fate of Cd entering in soils is usually controlled by adsorption-desorption reactions on Fe oxides. Adsorption of Cd on soil colloids including Fe oxides has been extensively studied but Cd desorption from soil minerals has received relatively little attention. Some factors that affect Cd adsorption on goethite include pH, temperature, aging and presence of inorganic and organic ions. This research was conducted to study the influence of pH, temperature, aging, desferrioxamine B and oxalic acid on Cd desorption from goethite.

Two batch experiments were conducted to evaluate Cd desorption with 0.01 M $Ca(NO_3)_2$ from goethite. In the first experiment, Cd desorption was observed at 20, 40 and 70 °C in combination with aging for a period of 16 hours, 30, 90 and 180 days using goethite with Cd adsorbed from initial Cd concentrations of 20, 80 and 180 µM. Cadmium desorption for all these treatments was measured at pH 5.5 and 6.0. In the second experiment, Cd desorption was determined separately in the presence of 300 µM desferrioxamine B (DFOB), 200 µM oxalic acid (OA) and the combination of two at 25 °C. For the second desorption experiment goethite samples which adsorbed Cd from initial Cd concentrations of 180 and 300 µM at pH 6.0 were used.

At the lowest amount of initially adsorbed Cd and equilibrium pH 5.5, Cd desorption decreased from 71 to 17% with aging from 16 hours to 180 days and the corresponding decrease at pH 6.0 was from 32 to 3%. There was a substantial decrease in Cd desorption with increase in equilibration temperature. For example, in goethite with the lowest amount of initially adsorbed Cd after 16 hr and at equilibrium pH 5.5, Cd desorption decreased from 71 to 31 % with increase in temperature from 20 to 70°C. Dissolution of Cd adsorbed goethites in 1 M HCl, after 15 successive desorptions with 0.01 M $Ca(NO_3)_2$, indicated that approximately 60% of the Cd is surface sorbed.

Cadmium desorption increased in the presence of DFOB, OA and DFOB + OA. The dissolution of goethite in presence of DFOB possibly increased Cd desorption whereas a decrease in equilibrium pH from 6.0 to 4.8 was the main factor for increased Cd desorption in the presence of OA.

CONVENTIONAL AND UNCONVENTIONAL ZEOLITES: THERMODYNAMICS OF FORMATION, HYDRATION AND ION EXCHANGE

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Microporous molecular sieves, including zeolites sensu stricto, are important in nature and technology for catalysis, ion exchange, and water retention. Natural zeolites (clinoptilolite and others) are important in backfill and surrounding strata for nuclear repositories such as Yucca Mountain. Synthetic silicotitanate and niobate molecular sieves have been designed to have high selectivity of cesium over sodium and of strontium over calcium. Liquid tank wastes at Savannah River and Hanford sites, rich in sodium, aluminum, silicon, and nitrate, precipitate sodalite and cancrinite phases as unwanted products. The thermodynamics of these three classes of systems have been studied by high temperature oxide melt solution calorimetry. The interplay of thermodynamic and kinetic factors in the formation of these materials, in ion exchange, and in their calcination to dense ceramics is summarized.

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%, P_2O_5: 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 degradates the mangrove ecosystem and is also characterized by the dispersion of nutrients (N: from 0.07 to 0.05%, P_2O_5: 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

SYNTHESIS OF COLLOIDAL Mn^{2+}:ZnO QUANTUM DOTS AND HIGH-T_C FERROMAGNETIC NANOCRYSTALLINE THIN FILMS

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Using direct chemical synthesis to produce oxide diluted magnetic semiconductors free from impurity phases, we have synthesized high quality, colloidal Mn^{2+} doped ZnO nanocrystals in DMSO. Synthesis of these nanocrystals was monitored by electronic absorption and electron paramagnetic resonance (EPR) spectroscopies. Under aerobic reaction conditions, $Zn(OAc)_2$ prevents the oxidation of Mn^{2+} by O_2 towards manganese oxide impurities. Internally doped Mn^{2+}:ZnO nanocrystals of relatively spherical shape and uniform diameters were produced after removing Mn^{2+} ions from the surfaces of the as-prepared nanocrystals using dodecylamine. Simulations of the highly-resolved X-band and Q-band EPR spectra of the surface cleaned nanocrystals confirms substitutional doping of Mn^{2+} in the ZnO nanocrystals with homogeneous speciation. Spin coat processing of these Mn^{2+}:ZnO colloids yielded thin films exhibiting above room-temperature ferromagnetism with saturation moments up to 1.35 μ_B, about an order of magnitude higher than any previously reported saturation moment at room temperature for Mn^{2+}:ZnO. The low temperature solution synthetic technique effectively prevents impurity phase segregation, a common concern of higher temperature vacuum deposition techniques, therefore ensuring the observed ferromagnetism is intrinsic to Mn^{2+}:ZnO.

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INTERACTIONS OF URANIUM WITH MIXTURES OF MICROORGANISMS AND KAOLINITE CLAY

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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 4×10^{-6} M or 4×10^{-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 4×10^{-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.

DISSOLUTION OF MICROBIAL REDUCED NONTRONITE IN A FLOW-THROUGH SYSTEM

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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.

PROBING OXYANION ADSORPTION MECHANISMS AT THE MINERAL/WATER INTERFACE WITH MOLECULAR-SCALE TECHNIQUES

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Many different oxyanions are found in the soil environment, and the chemistry of these oxyanions is quite varied. Oxyanions are studied for both agronomic and environmental reasons by soil chemists. Some oxyanions such as phosphate and sulfate are essential nutrients for plant growth and are found in relatively high concentrations in soils. Other oxyanions such as borate and molybdate are micronutrients. They are essential for plant growth at low concentrations but become toxic at higher concentrations. The range between deficiency symptoms and toxicity is usually quite narrow. A third group of oxyanions, such as arsenate, arsenite, selenate, selenite, and chromate are frequently studied because they have little agronomic use and are instead detrimental to human health. Understanding the mechanisms by which these oxyanions react with mineral surfaces is vital for predicting their bioavailability, toxicity, and transport in natural systems.

The environmental soil chemistry program at University of Saskatchewan uses an array of advanced spectroscopic techniques to determine the nature of interactions between oxyanions and soil components. Several types of X-Ray Absorption Spectroscopy (XAS) have been utilized as well as Attenuated Total Reflectance (ATR) FTIR spectroscopy. While the mechanisms of adsorption are unique to both the sorbate and sorbent being studied, there is a recurring theme in that is quite significant.

In many cases, more than one adsorption mechanism can be seen to occur simultaneously. In systems where only adsorption is occurring, then both outer-sphere and inner-sphere complexation are often observed at the same time. This distribution of outer-sphere and inner-sphere surface complexes has been seen with sulfate, selenate, and borate on iron oxides. Reaction conditions such as pH, ionic strength, surface structure of sorbent, and reactant concentration have all been shown to influence the relative distribution of the simultaneously occurring sorption complexes. Therefore it is necessary to conduct spectroscopic studies at a wide range of reaction conditions to truly understand the reactivity of oxyanions. It is also important to account for outer-sphere complexation of oxyanions when attempting to describe their adsorption with surface complexation models.

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.

IN-SITU XRD MEASUREMENTS OF INTERLAYER SWELLING OF CLAYS

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The swelling phenomenon of clays is one of the most important topics in the engineering and environmental work. Swelling is a time dependent volume increase involving physicochemical reactions with water. There are two categories of swelling. The inner and intracrystalline swelling is a process whereby the exchangeable cations in the interlayer and at the surface of clay minerals build one to four discrete hydration shells. At higher water content, the formation of non solvated (non bound) water is observed. The osmotic (intracrystalline) swelling results from the difference in the ion concentrations close to the clay mineral surfaces and in the pore water.

The ionic composition influences the extent of swelling, due to the different hydration energies of the cations, which depends from ionic size and valence. Furthermore the swelling behaviour of clayey soils and rocks depends strongly on the mineralogical composition, i.e. on the type and quantity of clay minerals encountered and on the content of further minerals which show swelling behaviour caused by recrystallisation processes. The fabric and density of clays determines the time dependent swelling behaviour. Understanding the effects of cation valence, cation hydration energy and clay layer charge provides a model to calculate the swelling pressure.

Combined experimental studies were carried out on bentonite (MX80 Wyoming and Montigel Sudchemie) as a model clay: isothermic water adsorption measurements in a gravimetric apparatus of McBain type, swelling pressure measurements in an adapted oedometer apparatus, and interlayer swelling studies with XRD at various relative humidity.

Results of in-situ XRD studies of interlayer swelling d(001) will be presented for homoionic montmorillonite. The montmorillonite were exchanged with Cs^+, Na^+, Sr^{2+}, Ca^{2+}, Al^{3+} (related enthalpy of hydration from 276 to 4665 kJ/mol). The measurements were performed in a sample chamber (Anton Paar TTK450) mounted on a Bruker AXS D8. The relative humidity (RH) was achieved by mixing wet and dry pressure air at 26°C (Sycos H). The sample temperature (26.0 ± 0.2°C) was controlled by circulating water in the double chamber wall and the sample stage. Firstly the oriented samples were dried in vacuum oven (12h at 65°C). After that the XRD measurements were carried out in programmed cycles in the RH range $1-80 \pm 0.2\%$ (stabilization and equilibration time of RH within 60 min).

EPR STUDIES OF COPPER EXCHANGED SMECTITE AND THE BEHAVIOUR UPON HEATING

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Movement of small cations (e.g. Li^+, Cu^{2+}) from the interlayer into the 2:1 layer of montmorillonite upon heating is a well-known phenomenon (Hofmann & Klemen 1950, Heller-Kallai & Moser 1995). However, the position of the cations after migration is not yet clarified. EPR spectroscopy is helpful in monitoring the hydration state and the location of exchangeable d-ions (e.g. McBride & Mortland 1974, Mosser et al. 1997, McBride 1982, Karakassides et al. 1999, Emmerich et al. 2001). The aim of the present work is to improve the knowledge of interaction mechanisms of montmorillonite with heavy metal cations under wet conditions at temperatures up to 100°C, the fixing of heavy metals in the crystal structure of montmorillonite and its effects on the clay characteristics.

Homoionic Cu^{2+}-exchanged samples were prepared by washing the <2 μm fraction of bentonite from Linden (Bavaria) with a chloride solution (Emmerich et al. 1999). Air dry samples or suspension with mass content of 10% of these clays were altered in a water steam atmosphere in stainless steel autoclaves at 55 or 90°C up to six month. Samples were characterized by XRD and EPR. Electron Spin Resonance spectra of randomly oriented powder samples of Cu^{2+}-rich montmorillonite were recorded with a X-Band ESR-spectrometer (Bruker ESP 300E) at room temperature after allowing samples to soak humidity in an atmosphere of 75% relative humidity.

EPR spectra of Cu^{2+}-rich montmorillonite showed two peaks at g = 2.15 and 2.05 which are characteristic for $[Cu(H_2O)_6]^{2+}$ and $[Cu(H_2O)_4]^{2+}$, respectively, on interlayer positions. The intensity ratio of both peaks moved in favour of the signal at 2.15 after short time alteration (seven days), whereas the peak at 2.05 regained intensity after six months. Dry and suspension samples that were altered in a steam atmosphere at 90°C as well as at 55°C showed a similar behaviour.

EPR spectra show that the amount of fully hydratable Cu^{2+}-ions on interlayer positions depends on increasing time of treatment at lower temperatures. The reduction of concentration of $[Cu(H_2O)_6]^{2+}$ at interlayer positions is a reversible process at lower temperatures. The Cu^{2+}-cations are fixed by occupying hexagonal cavities of the tetrahedral sheet (Karakassides et al. 1999) and not strongly in previously vacant sites in the octahedral sheet (Mosser et al. 1997).

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A COMPARISON OF FIBROUS CLAYS AND FIBROUS AMPHIBOLES AS INDUSTRIAL MINERALS

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The identification of fibrous clays and fibrous amphiboles are compared using their near-infrared (NIR) and fundamental OH bands. A palygorskite clay from Los Angeles Co. is included along with a new source of richterite from Trinity Co. and a new source of eckermannite from Placer Co.

The dominant NIR bands of Two Crows sepiolite, at 4324 cm^{-1} and 4363 cm^{-1}, are comparable to those of talc, at 4323 cm^{-1} and 4365 cm^{-1}, and that of palygorskite, at 4503 cm^{-1} is close to that of muscovite, which ranges from 4505 cm^{-1} to 4550 cm^{-1} with varying Al_2O_3 content. Richterite, with NIR bands at 4320 cm^{-1} and 4211 cm^{-1}, is also similar to eckermannite, with bands at 4320 cm^{-1} and 4208 cm^{-1}. Their fundamental bands also are similar with the strongest bands at 3729 cm^{-1}. The fundamental OH band shift of these alkali amphiboles is about 55 cm^{-1} from those of actinolite, at about 3674 cm^{-1}. The XRD spectra of richterite and eckermannite are similar to those of actinolites.

Tremolite and richterite are thermally stable to about 1045°C, whereas sepiolite and palygorskite are stable to about 820°C. The fibrous clays may hold large amounts of Pb and As whereas the fibrous amphiboles seldom contain either.

Concerning the use of these fibrous minerals, no adequate methods have been established for determining the relative health hazards from mining, fabrication, and use of these different fibrous minerals.

SYNTHESIS AND APPLICATIONS OF OXIDE NANOCLUSTERS AND NANOCLUSTER-ASSEMBLED MATERIALS[†]

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We have developed a nanocluster deposition system, which combines a new kind of sputtering-gas-aggregation cluster beam source with an atom beam from magnetron sputtering. A highly intense and very stable beam of oxides (such as ZnO, ion oxides) nanoclusters has been produced. Core-shell nanostructured Fe/ Fe oxides nanoclusters can be also synthesized. Monodispersive cluster size range is between 2 to 100 nm. Usually the deposition rate is as high as 5 Å/s. The cluster concentration in the film is adjusted through the ratio of cluster and atomic beam deposition rates, as measured *in situ* with a rotatable quartz microbalance. This system is used to deposit simultaneously or alternately cluster films, mesoscopic films or multilayers, and offers the possibility to control independently the incident cluster size and concentration, which is of interest for fundamental research and industry applications. Nanocrystalline structures of single clusters have been studied by AFM, XRD and HRTEM. Magnetic properties of clusters and cluster-assembled materials have been investigated by using SQUID and MFM techniques. We found the photoluminescence of ZnO nanoclusters at room temperature is size dependent, changing from 3.13 to 3.45 eV that is important for photoelectronic devices. Fe/Fe oxide core-shell nanoclusters for biomedical and environmental applications will be discussed.

SYNTHESIS AND CHARACTERIZATION OF CLAYS AND ORGANOCLAYS FOR THE SELECTIVE ADSORPTION OF N-NITROSAMINES

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N-Nitrosamines are among the most toxic compounds in tobacco smoke. Seven of the top ten tumorigenic compounds in tobacco smoke are N-nitrosamines. These compounds can reach the respiratory tract, lungs and alveolar tissue within the lungs. The high incidence of cancer among tobacco smokers is proof enough that these compounds are not trapped by the common cigarette filter. The goal of this research is to study the adsorption of N-nitrosamines onto sodium exchanged clays and organoclays.

Clays and organoclays were used as adsorbent materials in order to trap/sorb the carcinogenic N-nitrosamines. The large surface area, known potential to adsorb organics and ease of modification of clays makes them suitable materials. A major contributing factor for the selective adsorption of N-nitrosamines is the natural charge of clay particles. For these reasons, two smectite clays (STx-1 and SAz-1) of differing cation exchange capacities were selected as N-nitrosamine adsorbent materials. For purpose of specific adsorption, clays were modified with a homologous series of tetra-alkylammonium cations in order to study the alternate adsorption interactions between these modified clays and the N-nitrosamines. The changes in surface area, basal spacing, thermal and carbon/nitrogen elemental analysis indicated the presence of new porous and non-porous organoclay materials. Models were proposed to describe the adsorption of N-nitrosamines. The proposed models include ion-permanent dipole and additive London dispersive attractive forces, these to include surface, multi-sided, and pore interactions.

Besides the characterizations noted above, adsorption processes were characterize by Infinite Dilution Inverse Gas Chromatography. This will facilitate the understanding/proposing mechanisms for the adsorption of N-nitrosamines on the clay adsorbent materials. This technique was used to calculate the enthalpy, entropy and Gibbs free energy for the N-nitrosamine/clay adsorbent interaction. The enthalpy range for the adsorption of N-nitrosamines onto sodium homoionic clays and organoclays is -41 to -87 kJ/mol and -60 to -90 kJ/mol, respectively.

Theoretical calculations for the structural and molecular dimensions of the clay adsorbent materials and N-nitrosamines, respectively, were used to complement the proposed adsorption models. The structural dimensions and physicochemical properties of the clay materials were correlated to develop topographical models. These models were subsequently further correlated to molecular dimensions of the N-nitrosamines in order to complement the proposed adsorption mechanisms – natural sodium clays, porous and non-porous organoclays. Experimental and theoretical results indicate that clays and organoclays are effective in adsorbing and even selectively trapping N-nitrosamines.

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.

IRON-BEARING COMPOUNDS FORMED DURING AGING OF RESIDUES FROM INDUSTRIAL KAOLIN LEACHING: A <u>VARIABLE TEMPERATURE</u> MÖSSBAUER STUDY

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The industrial beneficiation of kaolin involves removal of iron (oxyhydr)oxides and other impurities that impart unwanted colors to the kaolin, which depreciate its commercial value, particularly to the paper industry. While the beneficiation process creates a better kaolin product, it also yields a waste residue for which environmentally proper and commercially viable disposition has proven difficult. The chemical leaching process often requires the addition of metallic zinc and sulfuric and phosphoric acids, causing the leachate to be highly acidic and hazardous to the environment. In order to render the residue less harmful, the industry instituted a neutralization step in which calcium oxide is added. The residue is then transferred to an open pond and allowed to evaporate. During this step the Fe also reprecipitates. As the pond evaporates, the dry residue accumulates and the Fe oxides begin to age and transform to more stable Fe-rich compounds. Stockpiles of these residues are increasing and methods for disposing of rather than just storing them is becoming increasingly important. In order to accomplish this goal, a better understanding of the properties and behavior of the residue is needed.

The purpose of this study was to identify the Fe oxides that are present in the residues and characterize their transformations during aging. Kaolin reject materials from an industrial plant in Brazil were studied by ^{57}Fe Mössbauer spectroscopy, including samples from residues aged for different periods of time. The kinetics of the Fe reactions are relatively slow and the most stable Fe oxides can only be accurately detected after a long aging time. Although data obtained with powder x-ray diffractometry, thermogravimetry, and scanning electron microscopy provided indispensable information about the crystal structure and morphology of these materials, Mössbauer spectroscopy proved to be an especially powerful technique to identify and help trace the inter-conversion mechanisms of the Fe-bearing species. In some samples, differential chemical dissolution was performed prior to Mössbauer analysis in order to distinguish between well-crystallized and poorly crystallized Fe oxide forms, enabling a more precise characterization of the Fe compounds. Mössbauer data handling with quadrupole splitting distribution was also utilized to enhance identification of the hydr(oxides) in the residue samples. At the initial aging step of the residue, the only (oxyhydr)oxides were lepidocrocite and akaganeite. Goethite and hematite were the main Fe-rich compounds found in the most aged residue.

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

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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.

CHARGE TRANSPORT IN MICAS: AN AB INITIO MODEL OF $Fe^{II/III}$ ELECTRON HOPPING AND THE EFFECTS OF SUBSTITUTIONAL DEFECTS

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Phyllosilicate minerals, such as clays and micas, often comprise an important electron source in subsurface geochemical environments. The presence of oxygen limits the availability of reduced metals such as Fe^{II} in solution or sorbed on mineral surfaces. However, Fe^{II} can persist over long periods in these environments in the form of structural constituents in phyllosilicate minerals. Therefore, the rate oxidation of structural Fe^{II} to Fe^{III} in phyllosilicates can at times dictate the availability of electrons for redox reactions in the local environment. Phyllosilicate minerals, even those bearing a large fraction of structural Fe^{II}, are poor electrical conductors. However, charge transport, likely by electron hopping through valence alternation of $Fe^{II/III}$ cations, has been demonstrated. Presumably, the process of oxidation of structural Fe^{II} would be progressive, involving rapid oxidation of outermost Fe^{II} sites with a relatively slow inward advance of an oxidation front. Central to this process is the effective accessibility of Fe^{II} electrons in the phyllosilicate mineral structure and, thus, the electron hopping mobility in the lattice.

The two principal $Fe^{II/III}$ electron exchange reactions underlying charge transport in the octahedral sheet of ideal end-member annite were modeled using a combination of ab initio calculations and Marcus electron transfer theory. A small polaron model was applied which yielded electron hopping activation energies that agree well with the limited available experimental data. A small ab initio cluster model successfully reproduced several important structural, energetic, and magnetic characteristics of the M1 and M2 Fe sites in the annite octahedral sheet. The cluster enabled calculation of the internal reorganization energy and electronic coupling matrix elements for the M2–M2 and M1–M2 electron transfer reactions. The M2–M2 electron transfer is symmetric with a predicted forward/reverse electron hopping rate of $10^6 \, s^{-1}$. The M1–M2 electron transfers are asymmetric due to the higher ionization potential by 0.46 eV of Fe^{II} in the M1 site. The electronic coupling matrix elements for these reactions are predicted to be small and of similar magnitude, suggesting the possibility that the coupling is essentially direction independent among hopping directions in the octahedral sheet. M1 Fe sites are predicted to be efficient electron traps and charge transport should occur by nearest-neighbor electron hops along the M2 Fe sublattice.

MASS AND CHARGE TRANSPORT IN LAYERED DOUBLE HYDROXIDE MODIFIED ELECTRODES

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Recent results of our study of charge transport in thin films of a redox active Ni-Al-Cl LDH will be presented. Impedance measurements show that the charge-transfer resistance of Ni-Al-Cl films decreased dramatically upon oxidation of nickel, from more than 10^6 Ω for un-oxidized films to less than 60 Ω in films oxidized to Ni$^{2.5+}$. At low frequency, the impedance of the oxidized films was dominated by mass transport. Effective diffusion coefficients estimated from the low frequency impedance varied between 1 and 5 x 10^{-9} cm^2/s. For Mg-Mn-CO$_3$ films, partial oxidation of the Mn(III) sites resulted in a similar drop in charge-transfer resistance. However, the charge-transfer resistance increased up to nearly its initial value in Mg-Mn-CO$_3$ films in which the manganese had been fully oxidized to Mn(IV).

Mass measurement using an electrochemical quartz crystal microbalance showed that the Ni-Al-Cl films lost mass on oxidation and gained mass on reduction. Impedance measurements at the resonance frequency of the LDH coated quartz crystals show that Sauerbrey's equation was valid for this system. The sizes of the mass change depended on the pH and composition of the electrolyte solutions. In a pH 8 potassium borate buffer, an apparent mass per mole of electrons transferred (MPE) of only 6 g/mol was obtained. Compensation for the positive charges generated by oxidation of the LDH's Ni(II) sites appear to occur by loss of protons from the LDH lattice accompanied by the loss of some water from the interlayer spaces. In pH 8 potassium borate buffer containing 4 mM Na$^+$ the MPE increased to 19 g/mol, suggesting that, in the presence of sodium, charge neutralization shifted from gain/loss of protons to intercalation/de-intercalation of sodium ions. Addition of [Fe(CN)$_6$]$^{4-}$ or [Mo(CN)$_8$]$^{4-}$ to the electrolyte solutions caused mass increases due to the intercalation of the heavy anions in the LDH films. Oxidation of the adsorbed anions resulted in reversible mass drops. Charge neutrality was maintained by desorption and re-adsorption of the electrolyte cations.

The cyclic voltammograms of [M(bpy)$_3$]$^{2+}$ (M = Os, Ru and Co) solutions at Ni-Al-Cl LDH modified electrodes were recorded. For [Os(bpy)$_3$]$^{2+}$, the cathodic peak current obtained with the Ni-Al-Cl coated electrode was 50 times larger than with the unmodified substrate. Addition of a small amount of [Ru(bpy)$_3$]$^{2+}$ resulted in an additional 2-fold increase in the size of the [Os(bpy)$_3$]$^{2+}$ reduction peak. Addition of [Ru(bpy)$_3$]$^{2+}$ to a solution of [Co(bpy)$_3$]$^{2+}$ produced a similar increase in the [Co(bpy)$_3$]$^{2+}$ reduction peak. In mixtures of all three cations however, the enhancement of the [Co(bpy)$_3$]$^{2+}$ voltammetric wave was suppressed at the expense of the [Os(bpy)$_3$]$^{2+}$ wave. These results were unexpected. These cationic species had not been expected to interact with the positively charged layers in LDH films.

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-µm and < 2-µm 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 Fe^{3+} resonance, whereas Fe^{2+} resonances were not detected. According to the isomer shift and quadrupole splitting (Δ) values, Fe^{3+} 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

THEORETICAL APPROACH ON VIBRATIONAL AND CRYSTALLOGRAPHIC PROPERTIES OF DIOCTAHEDRAL 2:1 PHYLLOSILICATES

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The octahedral cation ordering of dioctahedral 2:1 phyllosilicates was studied taking into account two-species and three-species of cations (Al/Fe/Mg), which were relevant to clay compositions found in nature, that can represent different natural (smectites, illites, Fe-rich montmorillonites, nontronites, celadonites) and synthetic clay minerals, by means of Monte Carlo simulations based only on theoretical models. Most systems exhibit short-range order at low temperature. The ordering of the octahedral cations is highly dependent on the cation composition. In general, a segregation tendency of Fe and dispersion tendency of Mg is observed. In samples with a high Fe content and low Al content, the Fe cations form globular clusters, whereas they form linear clusters in samples with high Fe content and significant Al content. The low long-range ordering level in the Fe distribution in the octahedral sheet is similar in illites and smectites, but the relative population of unclustered Fe cations in smectites is higher than in illites according experiment. Quantum-mechanical calculations based on Density Functional Theory (DFT) approximation were performed on smectite and illite samples confirming these results.

This ordering is studied also within the *cis*-vacant/*trans*-vacant polymorphism of these minerals. These configurations can be distinguished from one another experimentally by X-ray diffraction and thermal analysis, but with great difficulty and only semi-quantitative accuracy. *Trans*-vacant and *cis*-vacant configurations were distinguished and studied for smectites and illites with different cation substitutions in octahedral and tetrahedral layers and in the interlayer space at the quantum-mechanical level. The energy differences between the *cis*-vacant and *trans*-vacant configurations for a certain composition are lower than the energy changes produced by the relative cation distributions and ordering process in the octahedral and tetrahedral sheets.

Spectroscopic methods are a very useful experimental tool for studying cation distributions in octahedral sheet of these minerals, especially the IR frequencies of OH groups. Vibrational frequencies of the OH groups, ν(OH) and δ(OH), were calculated at First Principles level reproducing the experimental values. The vibrations of the OH groups depend significantly on the nature of the cations which they coordinate, and also on the interactions of the H atom with the tetrahedral O atoms that surround the OH group. For a certain MOHM', different OH frequencies can exist depending on their structural environment. Therefore, a wider range of vibrations should be taken into account experimentally, especially in the assignment of frequencies and determination of relative intensities with the deconvolution analysis method. This theoretical approach can be a useful tool for a predictive application of crystallographic and vibrational properties that cannot be determined experimentally in these clay minerals.

FIRST-PRINCIPLE STUDY ON POLYTYPE STRUCTURES OF 1:1 DIOCTAHEDRAL PHYLLOSILICATES

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Kaolinite ($Al_4[Si_4O_{10}](OH)_8$) is a 1:1 dioctahedral phyllosilicate (layered aluminosilicate) with little, if any, isomorphous substitution. The polytype structures of the three 1:1 dioctahedral phyllosilicates found in nature, kaolinite, dickite and nacrite, have been investigated. The calculations were performed using the plane-wave pseudo-potential software CASTEP. The calculated structural parameters, including the orientation of the OH groups, for the three polytypes are in good agreement with experimental data as shown Table 1. In particular, for kaolinite and dickite, the three-inner surface OH groups were predicted to be oriented nearly perpendicular to the (001) plane. In contrast, one of the inner surface OH groups of nacrite was predicted to be nearly parallel with respect to the (001) plane.

Table 1. Orientation of OH groups with respect to the (001) plane

Angle(degree)	Kaolinite C site	Kaolinite (ref a)	Dickite	Dickite (ref b)	Nacrite	Nacrite (ref c)
O-H	70.8	73.2	74.0	75.5	54.3	50.3
O-H	67.8	60.2	54.5	51.9	62.5	65.9
O-H	52.2	68.2	61.5	74.1	58.7	56.8
O-H(inner)	-8.9	0.4	-8.6	-1.3	-23.7	-18.6

(ref a) Bish, D.L.(1993). Clays and Clay Minerals, 41, 738-744.
(ref b) Bish, D. L. and Johnston, C. T. (1993). Clays and Clay Minerals, 41, 297-304
(ref c) Zheng, H. and Bailey, S.W. (1994) Clays and Clay Minerals, 42, 46-52.

MESOZOIC HYDROTHERMAL ILLITES IN THE ALTERED SOULTZ-SOUS-FORETS GRANITE, FRANCE

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This study presents petrographic, crystallographic and K-Ar results for hydrothermal illites of the altered Variscan granite of the EPS-1 drilling in Soultz-sous-Forêts, France. The drilling, situated in the Rhine Graben basin, is part of the "hot-dry-rock" project designed to explore geothermal heat as an energy resource. Based on XRD, SEM, HRTEM and K-Ar isotopic investigations of 8 different grain size fractions of four key samples collected from the lower parts of the borehole (below 1550 m levels), we demonstrate a Mesozoic age for illite formation. These well crystallized, pure illite phases are highly concentrated in phyllitic hydrothermal veins, and are present in smaller quantities within the matrix of the pervasively altered granite. The predominant mineral within the veins is an euhedral, $2M_1$ illite polytype variety, formed by both neocrystallization in pore spaces and as direct replacement products of feldspars (both plagioclase and K-feldspar). K-Ar ages of the various grain sizes yield a mixture of ages ranging between 211 and 280 Ma for these illites. In contrast, the host rock granite samples contain an addition generation of fibrous illite crystallites, mainly grown as replacement of plagioclase and minor K-feldspar. Here, the finer fractions (0.2-2 micron) yield a larger age span, ranging between 95 and 195 Ma, whereas the coarser fractions yield ages as old as 255 Ma. A mixture of illite phases of varying ages is also indicated by the complex crystallite thickness distributions (CTDs) determined using the program "MudMaster". The vein-illites reveal a size distribution close to log-normal for the most abundant 2-4 micron fractions. However, for the finer grain sizes, the distributions becomes progressively non-lognormal. In contrast, the illites of the host rock granite yield both asymptotic shapes (> 1 micron sizes) and non-lognormal shapes (< 1 micron sizes). Our results imply, that the late Eocene to the present-day development of the Rhine Graben rift system had no or little effect on the formation of hydrothermal illites at these depths in the Soultz-sous-Forêts granite.

SULFUR ISOTOPE AND POTASSIUM-ARGON ANALYSIS OF MINERALS FROM THE TURPLU HALLOYSITE MINE, BALISIKER REGION, NORTHWEST TURKEY

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Halloysite deposits situated between metamorphic dolostones and volcanic rock contacts within the Sakarya Tectonic zone of NW Turkey are potentially important economic deposits. Sulfur isotope and potassium-argon studies have been conducted to aid in the development of geochemical and structural models, which are needed to explain the mineralization pathways and spatial distribution of coexisting halloysite and alunite clays.

Potassium analysis of nearly pure alunite by inductively coupled plasma yielded a value of 6.47 weight percent. Argon analysis performed by isotope dilution procedures and noble gas mass spectrometry yielded a $^{40}Ar_{rad}$ value of 0.23 nl/g ($\%^{40}Ar_{air}$ = 85.3). A K-Ar age of 0.9 ±0.1 Ma is calculated for the alunite. Preliminary K-Ar analysis of the neighboring andesite in the region yielded dates ranging from 18.4 – 21.4 ±0.6 Ma for the whole rocks and 20.9 – 23.4 for biotite separates. The younger apparent whole rock andesite ages are attributed to excess atmospheric argon, with the biotite ages interpreted to more accurately reflect the age of volcanism.

Stable sulfur isotope studies were conducted using the minerals pyrite, alunite, gypsum, and jarosite (all identified by X-ray powder diffraction). $\delta^{34}S$ values are reported relative to the C.D.T. standard. Pyrite, collected from the adjacent altered andesite, had $\delta^{34}S$ values that ranged from 0.5 to 1.5 $^o/_{oo}$. One sample each of gypsum and jarosite were analyzed. Both have a similar value of 3.0 $^o/_{oo}$. Alunite $\delta^{34}S$ values ranged from 4.2 to 7.8 $^o/_{oo}$.

A preliminary sequence and timing of mineralization is hypothesized. Triassic collision of Gondwana and Laurentia in the paleo-region of NW Turkey took place comtemporaneously with depostion of marine limestones. Subsequent subduction and volcanism occurred during the period of 20 to 24 Ma. Regional extension and hydrothermal alteration is partially constrained to have occurred around 1.0 Ma, although it is likely that these processes started several millions of years early. Extension and hydrothermal activity in the surrounding region persist to the present. Closed system differences in $\delta^{34}S$ for coexisting sulfides and sulfates evolved from magmatic fluids under a reducing pathway (i.e., H_2S/SO_4 = 5) in the termperature range of 200 to 300°C predict a pyrite-alunite $\delta^{34}S$ difference in the range of 25 to 30 $^o/_{oo}$. The maximum difference between $\delta^{34}S$ pyrite and alunite values observed at Turplu is 7.3 $^o/_{oo}$. This difference is consistant with a hypothesis that hydrothermal fluids may have mixed with a marine sulfate source in the temperature range of 200 to 300°C.

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

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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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THE ROLE OF ILLITE AND I-S NEOMINERALIZATION IN FAULT ZONES

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Clay neomineralization and fabric development greatly influence the behavior of faults through directly weakening caused by the low strength of clay minerals as well as through modification of the permeability structure of fault zones. Moreover, the ability to quantify fault-related changes in illite polytypism and changes in the abundance of discrete illite and I-S provide the means to directly date fault rocks through the use of Illite Age Analysis (IAA).

Illite polytypism is quantified using WILDFIRE whereas discrete illite and I-S are quantified using NEWMOD. Transmission electron microscopy (TEM) analyses of samples complement powder X-ray diffraction analyses. As with earlier studies, we observe only the $2M_1$ and $1M_d$ illite polytypes using TEM selected area electron diffraction (SAED). Therefore, in contrast to previous studies of polytype quantification which are based on mixtures of $2M_1$, $1M$ and $1M_d$ polytypes we mix $2M_1$ with $1M_d$ with varying probability of a zero rotation (a probability of 1 defines classic $1M$ illite). This allows us to account for diffuse spots observed on SAED patterns from $1M_d$ illite in our samples, which indicate that stacking is not turbostratic, but instead has limited periodicity.

Along the Moab Fault, a normal fault in southern Utah with a maximum throw of ~960 m, the most intensely deformed fault rocks are enriched in $1M_d$ illite while less intensely deformed rocks adjacent to these are enriched in I-S. As the permeability of I-S is less than that of discrete illite, the I-S neomineralization acted as a seal that confined fluids to the active portion of the fault zone, thereby providing a mechanism by which elevated fluid pressure would have weakened this fault. IAA of $1M_d$ illite-rich gouge samples and less intensely deformed I-S rich samples yield ages of ~60Ma, which represents the youngest period of activity along this fault preserved in the sedimentological record.

IAA ages from the Late Mesozoic/Early Tertiary Sevier thrust belt in western North America often yield ages of ~50 Ma regardless of their position in the hinterland-foreland progression or their location along strike. The record of synorogenic sedimentation confirms that this was the youngest period of activity along these faults, which indicates that older faults continue to play a role in orogenic evolution despite the development of younger faults.

JOHN HOWER WAS RIGHT: ILLITE-SMECTITE AS A PALEOGEOTHERMOMETER

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Fifty years have passed since Kubler and Weaver first observed that 001 XRD peak of illite changes systematically with depth and ascribed this change to improving "crystallinity" at higher temperatures. In the late sixties the nature of this change was described in terms of layer ratio and ordering in mixed-layer illite-smectite and the techniques for measuring this ratio were developed. In 1979 Hoffman and Hower first proposed to use % smectite (%S) in illite-smectite in shales as a paleogeothermometer. Based on the then available field evidence they suggested that the transition from random to ordered interstratification takes place at about $100^{o}C$ and from the nearest-neighbor to longer range ordering at about$170^{o}C$. In the following years some investigators followed this approach but many criticized it, proposing instead various kinetic expressions, relating %S to a number of factors besides temperature (time, chemistry of pore water, type of ordering, chemistry of original smectite).

Despite very abundant literature on the smectite illitization in shales accumulated since Hower's time, its validity for solving this controversy remains limited for two reasons:
1) the %S measurement in shales is difficult and the numbers have to be examined critically before using them;
2) the burial history of investigated section often is not reported, so only the present-day temperatures and not the maximum paleotemperatures are available.

The examination of the published data, taking these two aspects into account, makes the present author believe that John Hower was right. Particularly convincing is the evidence of Price and McDowell (Clays Clay Miner. 41:134-147, 1993), who found randomly interstratified clays in Proterozoic shales from the Lake Superior basin, which have never been deeply buried. The %S profile of the East Slovak Basin (Sucha et al., Clay Miner. 28:243-253, 1993) is used in the following studies to calibrate paleotemperatures.

Three regional studies of the present author and his coworkers seem to support Hower's paleogeothermometer and suggest that it is more reliable than widely used organic indices:
1) The Cambrian clays of Estonia, which have never been buried more than 1000 m contain ca. 20%S illite-smectite, and this occurrence was used as an argument in favor of low-temperature time-dependent illitization. Organic indices support this conclusion. However, K-Ar dating of illite-smectite from Estonian bentonites revealed short-lasting illitization event, coincident with the Caledonian orogeny (ca. 390-400 Ma).
2) The Carboniferous shales of the Upper Silesia Coal Basin contain R>0 illite-smectite at the present-day erosional surface, which is inconsistent with R_o data for never deeply buried E part of the basin. K-Ar dating indicates Cretaceous heating event in the E part and the apatite fission track (AFT) dating supports IS against R_o evaluation of the paleotemperatures ($>125^{o}C$).
3) %S in the Oligocene shales of Podhale flysh basin evolve gradually NW to SE from >60 to <15%S. 110-120°C paleotemperature isoline based on %S is coincident with the line of total resetting of the detrital AFT ages ($125^{o}C$). Ro numbers are erroneous because of overwhelming detrital vitrinite contamination.

MOLECULAR-LEVEL INVESTIGATION OF METAL INTERACTIONS WITH CLAY MINERALS

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Clay minerals have tremendous sorption capacities for cations, and thus play a major role in the biogeochemical reactions occurring in natural systems. Metal cations, such as copper and lead, are selectively adsorbed by clay minerals in the environment. The goal of this project is to characterize copper reaction mechanisms with clay minerals under varying equilibrium conditions. To accomplish this we probed the molecular environment of sorbed Cu using X-ray absorption fine structure (XAFS) spectroscopy, electron paramagnetic resonance (EPR) spectroscopy, and X-ray diffraction (XRD). The variables studied include ionic strength and background electrolyte, pH, clay mineral type, and reduction state. The clay minerals studied were a Wyoming montmorillonite, Llano vermiculite, and reduced South African (Palabora) vermiculite. At low ionic strength and in the presence of no background electrolytes, Cu sorption mechanisms on all clay minerals were dominated by outer-sphere complexation, confirming that classic cation exchange processes are occurring. However, in the presence of Ca or K background electrolytes at high ionic strengths (0.1 M) inner-sphere complexation was the predominant reaction complex. The type of inner-sphere complexation mechanism varied depending on the clay mineral species. On montmorillonite small surface precipitates were observed, on Llano vermiculite monodentate adsorption on the edge sites were occurring, and on the reduced SA vermiculite Cu was adsorbing over the ditrigonal cavities present on the basal planes to satisfy the reduced positive charge associated with structural iron reduction. Our results did not reveal the formation of extensive layered double hydroxides or metal-clay neosynthesis products that have been reported in the literature for Ni, Zn, or Co. Our results provide new information on the reaction processes by which metals can interact with clay minerals, and will aid in designing remediation strategies, predicting bioavailability, and monitoring and managing contaminated sites.

MOLECULAR SIMULATIONS OF HYSTERESIS IN CLAY SWELLING

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It is known for several decades that certain types of clay minerals (i.e. smectites) have the capability of swelling. Charge compensating counter ions in the interlayer space attract water molecules, forming up to four layers. Related to this layer formation, swelling occurs stepwise and depends on the type of clay mineral, counter ion, and thermodynamic variables. Interestingly, clay swelling shows hysteresis: the swelling pathway is different from the shrinking pathway. Experimentally, this hysteresis is observed as a function of the salt concentration, temperature, and relative humidity. There is little consensus about the explanation of clay swelling hysteresis[1].

We used Molecular Dynamics simulations to study montmorillonite swelling hysteresis at constant volume, temperature, and water chemical potential. In particular, we focused on the swelling and shrinking of one- and two-layer hydrates, respectively. The atomic interactions between the clay mineral, cations, and water molecules (TIP4P model) are described with Lennard-Jones and Coulombic potentials. Insertions and deletions of water molecules are carried out with a Configurational Biased Monte Carlo scheme[2]. We systematically varied the basal spacing, type of counter ion, water chemical potential (related to the relative humidity), temperature, and external pressure to simulate the effect on clay swelling hysteresis. By sampling the pressure normal to the clay layers during the simulation, we calculated the free energy as a function of the basal spacing.

The minima in our free energy profiles indicate stable layer spacings, which are in agreement with experimentally measured spacings of one- and two-layer hydrates. With increasing relative humidity, the free energy of the two-layer hydrate becomes lower than the free energy of the one-layer hydrate. However, a free energy barrier between the one- and two-layer hydrates blocks the swelling. According to our simulations, this free energy barrier explains clay swelling hysteresis and therefore does not support other hypothesizes like irreversible rearrangements in the clay mineral structure[1]. Our simulations also predict a new form of hysteresis. At a given temperature and relative humidity, an increasing external pressure on the clay mineral induces shrinking. The original state is recovered at significantly lower external pressure[3]. Swelling for different types of counter ion occurs in the following order: $Li^+ > Na^+ > K^+$. The relative humidity needed to induce swelling and shrinking is lower for small counter ions, because they are more easily hydrated.

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UNDERSTANDING LAYER CHARGE DETERMINATION BY THE ALKYLAMMONIUM METHOD USING MOLECULAR SIMULATIONS

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Layer charge is one of the most important properties of 2:1 clay minerals[1]. Besides the fact that layer charge is a criterion for the classification of these minerals, it also determines the ion exchange properties and therefore the ability to adsorb all kinds of surfactants. The alkylammonium method can be used to measure the layer charge by measuring critical carbon chain lengths. Although this method has several advantages over other methods, its accuracy is questionable and the results are not completely understood[1,2,3].

We performed NP_zT molecular simulations of alkylammonium ions intercalated in three types of swelling clay minerals (Bentonite, Cheto montmorillonite, and Vermiculite) as a function of the carbon chain length in the range H_3NC_6 to H_3NC_{18}. We used Molecular Dynamics for moving the alkylammonium molecules and a Monte Carlo scheme to adjust the basal spacing, treating the clay layers as rigid bodies. For correct sampling of the phase space, a Configurational Biased Monte Carlo (CBMC) scheme was implemented to regrow[4] the alkylammonium molecules during the simulation. We used the united atom OPLS force field with rigid bonds, flexible bending and torsion angles, and inter- and intra-molecular interactions. Throughout the simulations we quantified the configurations of the alkylammonium ions in the interlayer space by sampling the average positions of the atoms and the tilt-angle with respect to the normal of the clay surface.

Our simulated molecular configurations of layered alkylammonium ions in Bentonite and Cheto montmorillonite confirm theoretically suggested structures[1]. On the other hand, several alkylammonium ions in Vermiculite adopt a tilted configuration. Our calculated basal spacings of all three types of clay are in agreement with experimentally measured basal spacings[2]. For Bentonite and Cheto montmorillonite we calculated energetically favorable intermediate basal spacings between those of monolayers, bilayers, and pseudotrilayers, probably caused by a subtle balance between enthalpic and entropic effects. In combination with layer charge heterogeneity, these intermediate spacings make the layer transitions more gradual and might explain peak broadening in X-Ray Diffraction patterns[3].

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OF CLAYS, COLLOIDS, AND COMPOSITES

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I decided on the above title for my Bailey Lecture because of its factual simplicity. That is, clays can behave as layered minerals, charged colloids, or particulate fillers of composite materials. The title also has a certain resonance with the theme of CMS2004: "Gorges, Clays, and Coulees". Other than that this lecture is by and large a recollection of my interest and research in clay science.

I was introduced to clay mineralogy in 1960 when I was an honours student in soil science at the University of Adelaide, Australia. Because of his own interest in the swelling potential of soil clays, my superviser (J.P. Quirk) suggested that I looked into the relationship between layer charge density and swelling ability of montmorillonite. My subsequent PhD thesis, jointly supervised by J.P. Quirk and D.J. Greenland, was concerned with the swelling (in water) of montmorillonite-organic complexes. Over the years many other scientists, including S.W. Bailey, have directly or indirectly influenced the direction of my research. My interest in, and involvement with, clays and clay minerals culminate in the recent compilation of the *Handbook of Clay Science* in collaboration with my co-editors, F. Bergaya and G. Lagaly.

Here I will outline some developments and advances in clay research that have occurred over the past 4 decades, with special reference to the clay-organic interaction. Wherever appropriate, I will give examples of practical applications, and point out potential research topics. Since much of the information is taken from the work of other people, I am acting as both spectator and player.

VOC SORPTION BY HYDROPHOBIC ZEOLITES, AND THE EFFECTS OF CONFINED WATER

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Volatile Organic Compounds (VOCs) can pose environmental problems in surface water and groundwater if left untreated. Recent studies of liquid and gas phase adsorption of VOCs (e.g., trichloroethylene [TCE] and methyl tertiary butyl ether [MTBE]) revealed some anomalous behavior in "hydrophobic" microporous zeolites. At very low concentrations the relatively small pore zeolite, silicalite-1, outperformed the larger pore material, a de-aluminated zeolite Y (DAY), even though both were about equally hydrophobic. It was speculated that the interference of water was responsible for the unexpected results.

The structure of water in confined spaces could be quite different from that of the bulk fluid. Therefore, a model for water confined in cylindrical micropores was developed, and will be discussed briefly. The equation of state accounts for fluid-fluid, fluid-wall, and hydrogen bonding interactions.

This model was used to analyze the density of water inside the micropores as a function of: a) the fluid density outside the pores, b) the pore radius, and c) the fluid-wall interaction affinity. The behavior of confined water in the presence of bulk <u>liquid</u> outside the pores was quite interesting: The model predicts that water should exist in a vapor-like state in the small pore silicalite, but could exist as a liquid phase in zeolite DAY.

More recent Molecular Dynamics calculations have provided supporting evidence for the existence of a liquid-like structure in zeolite Y, but a much less structured phase in the silicalite pore system. Therefore, the presence of a structured liquid-like water phase is predicted to disrupt the sorption of VOCs in some cases, but not in other cases.

HIGH-RESOLUTION CHEMOSTRATIGRAPHIC CORRELATION OF THE LOWER SILURIAN (LLANDOVERY) OSMUNDBERG K-BENTONITE IN BALTOSCANDIA AND NORTHERN EUROPE

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The Lower Paleozoic stratigraphic record in Eastern North America and northwestern Europe contains numerous altered volcanic ash beds (Huff et al., 1998). These ash beds exhibit a variety of mineralogical and chemical characteristics that can serve as useful fingerprints for recognizing them on regional scale.

The Lower Silurian Osmundsberg K-bentonite is a widespread ash bed that occurs throughout Baltoscandia and parts of northern Europe. Ordovician and Devonian K-bentonites in North America and Europe have been subjected to relatively numerous investigations in recent years, whereas only a few ash beds of Silurian age have been subjected to investigation. Because of its potential significance for stratigraphic and paleovolcanological application, the sections containing the Osmundsberg K bentonite beds were investigated to determine if chemical composition of these beds can be used as a basis for high-resolution chemostratigraphic correlation on a regional scale and geochemical data were applied to the interpretation of the tectonomagmatic setting of the source volcanoes produced Osmundsberg.

Fifteen Osmundsberg K-bentonite samples and twenty-six samples of accompanying beds from twelve different localities were analyzed for major and trace elements and the data statistically treated using discriminant function analysis to determine if the trace element data provides a unique chemical fingerprint for the Osmundsberg K-bentonite beds. Comparison with the correlation model drawn by Bergström et al. (1998) based on biostratigraphic evidence show that results from two independent techniques are generally in agreement.

Identification and classification of K-bentonites using statistical analysis is a useful stratigraphic tool, which can be most helpful where conventional methods are inadequate such as the absence of a good biostratigraphic control as in this case. Results demonstrate the unique and identifiable chemical fingerprint for the Osmundsberg K-bentonite does exist and can provide an additional stratigraphic tool for local and regional correlation of these K-bentonites.

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QUANTITATIVE RIETVELD PHASE ANALYSIS OF SMECTITES USING A SINGLE LAYER APPROACH

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The quantification of clay minerals is a frequent task in geosciences, engineering and oil industry. Among the XRD techniques, the Rietveld method is widely accepted to be a suitable tool for quantitative phase analysis (QPA). Very precise results can be obtained for materials containing well ordered phases like cement clinker, ceramics and some types of rock samples. Because the Rietveld method uses discrete Bragg peaks, it is apparently unable to calculate diffraction patterns of strongly disordered layer structures. The smectite group represents an excellent example of extreme disorder in layer stacking, the so-called turbostratic disorder. For such materials, the sharp *hkl* spots in reciprocal space smear to continuous *hk* rods in c^* direction. A way to approximate these rods by series of spots is the construction of a cell that is elongated in c^*, filled only by one layer at the bottom. This approach results in *hkl* reflection series with unusual high *l* that sum up the well-known asymmetric *hk* bands of turbostratically disordered materials. The resulting unrealistic *00l* series must be sorted for "true" reflections (with $l = n$ times the elongation factor) to reproduce the rational basal series. Additional line broadening parameters have to be introduced for the *00l* to correctly approximate the thickness of the stacks as well as for the *hkl* to approximate the diameter of the *hk* rods. Scale factors must be corrected for the partial filling of the cell. Such formulations can be done with the help of the structure interpreter language in the BGMN Rietveld program. We used the atomic positions of Tsipursky & Drits (1984) for the dioctahedral 2:1 layers and a cation-water complex in the interlayer space in a ten times elongated cell to calculate the diffraction pattern of montmorillonite. In a first trial, the mean chemical composition was taken from chemical analysis of a < 0.2 µm fraction of a white bentonite. The powder pattern of this material could be modeled very well. In order to check the reliability of this approach for QPA, mixtures of montmorillonite, kaolinite, illite and quartz have been prepared. Standard powder patterns were collected and analyzed. Lattice parameters for all phases, some occupation factors, complicated *hkl* dependent broadening of the kaolinite, preferred orientation parameters as well as a 5th degree background polynomial, sample displacement and zero point parameters, all together 56 to 73 parameters, were refined automatically without any user intervention. The results are encouraging: All concentrations could be reproduced to not more than ±3 wt-% difference from the correct values. We obtained only moderate complementary deviations of the montmorillonite and illite concentrations from their actual values, possibly caused by the insufficient description of the disordering features of the illite component. The calculation time required for a single cycle is in the magnitude of a few seconds. Routine powder patterns of real sedimentary samples, containing up to 10 detectable minerals, could be analyzed by refining of 87 parameters in about 10 minutes using a 2 GHz personal computer. In further work, the model will be adapted to trioctahedral smectites. Additionally, the chance to refine reliable occupation factors of the octahedral and of the interlayer positions will be checked out.

IN-SITU MONITORING OF SOLUTION–CLAY REACTIONS BY WET-CELL X-RAY DIFFRACTION (WC-XRD) TECHNIQUES

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A flow-through reaction cell (wet-cell) has been developed for the routine investigation of solution – fine powder reactions by X-ray diffraction analysis (Warr and Hofmann, 2003). This device is ideal for studying both short-term hydration, and long-term alteration reactions of clays in solution. In this contribution some examples will be presented from the hydration of Ca-and Na-montmorillonite in natural solutions (ground- and sea-waters), and from the hydrothermal alteration (85°C) of Mesozoic repository shales under the influence of strongly alkaline solutions produced by alteration of concrete. The wet-cell device is considered to be a new and useful tool for investigating clay applications in the disposal of nuclear waste material, as well as many other geoscientific problems.
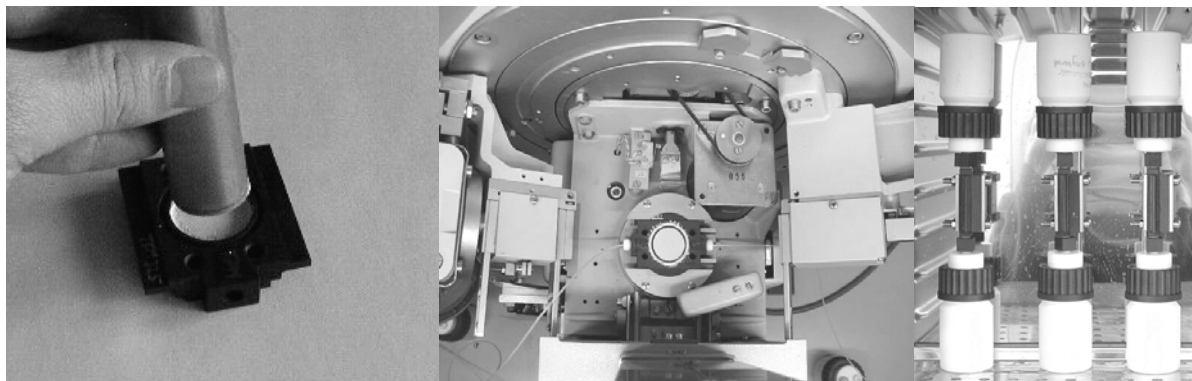
Wet-cell X-ray diffraction techniques used to monitor solution-clay reactions of compacted powders. *Left*: Pressing of a bentonite powder into the wet-cell device. *Middle*: In-situ X-ray diffraction measurement of the wet-cell experiment with teflon hoses attached. *Right*: Percolation of solutions through the sealed wet-cell device at 85°C in an air-oven.

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SOME APPLICATIONS OF EPR SPECTROSCOPY TO MINERALS, FOR THE NON-EXPERT

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I intend here to introduce the audience to the utility of electron paramagnetic resonance (EPR) spectroscopy in mineralogy, in particular to the art and science of extracting information from powdered samples. The audience will remember that EPR requires the presence of species with one or more unpaired electrons. The technique is extremely sensitive, dependent on the spectral linewidths at hand, capable of detecting down to 10^{-9} molar concentrations of such electrons. Variables include the sample temperature (T = 1 to 800 K), and the microwave frequency applied (ν = 1000 and these days up to ca. 500,000 MHz).

There are well over a 100 magnetic point defects in alpha-quartz now known and characterized. After their complex single-crystal EPR spectra are measured and analyzed, these data can be transformed by computer simulation to predict powder spectra. A library of such spectra, for various T and ν, is being produced and made available, and will enable quick identification of impurity and defect species in any samples containing quartz particles. Some special spectra, e.g., involving Ge(3+), Ti(3+) and Fe(3+), will be illustrated in this talk.

Attention will be paid to the complex art of determining from EPR the nature and local electrical symmetry of magnetic defects, and will be illustrated using our results on Gd(3+) in fluorapatite. In addition, the EPR characteristics of Mn(2+), as quantitatively measured by us, will be cited as offering a fine standard for comparison with other clays.

OPTICAL, MAGNETIC AND ELECTRONIC PROPERTIES OF NATURAL AND SYNTHETIC FELDSPATHOIDS

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Synthetic semi-condensed zeolites or feldspathoids with compositions and structures based on naturally-occurring minerals provide a superb systems for controlling the key, application-oriented, electronic properties. Examples taken just from the sodalite system include pigments such as lapis lazuli / ultramarine, $Na_7[AlSiO_4]_6\{S_3\}$, photochromic materials such as hackmanite $Na_8[AlSiO_4]_6\{S, Cl\}$, magnetic properties, as in the transition metal based danalites, $M_8[BeSiO_4]_6.X_2$, M = Mn, Fe, Co, X = S, Se, Te, and electronic properties of the framework expanded semiconductors e.g. $Cd_8[AlO_2]_{12}.X_2$ X = S, Se, Te. Once materials such as the cancrinites, and other semicondensed zeolite topologies, such as the ABW and JBW types, are considered together with possible allied metal substitutions into the aluminosilicate frameworks, the range of feldspathoid-type materials with potentially useful applications grows very rapidly. This paper will initially discuss the properties of several naturally occurring feldspathoids/zeolites of this type and then show how chemistry can be used to improve upon Nature to control a specific optical, magnetic or electronic property of interest. So, for example, methods of producing improved synthetic ultramarines from natural and synthetic clays and zeolites will be discussed along with results of recent studies on synthetic photochromic hackmanites and danalites. The physical properties of these materials will be discussed in terms of the feldspathoid framework acting as "spacer" that controls the interactions between the embedded cations and anions, see Figure.
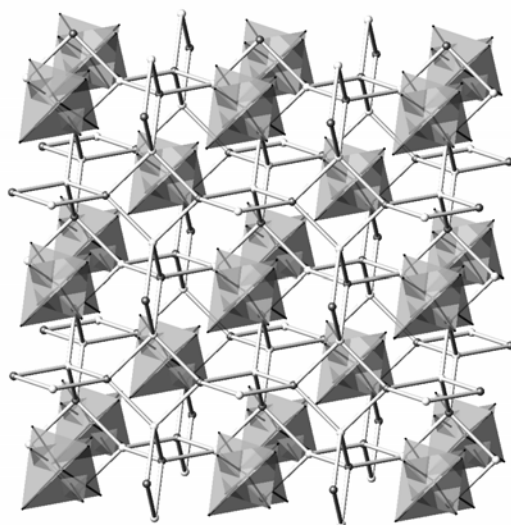

Figure. The structure of a sodalite of the type $M_8[TO_2]_{12}X_8$ shown as interpenetrating M_4X_4 blocks (polyhedra) separated by the TO_2 framework.

STABLE ISOTOPIC EVIDENCE FOR METASTABLE ILLITE GROWTH IN A MATRIX OF NON-EQUILIBRIUM SMECTITE

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There can be significant differences in the isotopic composition of clay minerals when separated into different size fractions. This has very important implications for the interpretation of bulk isotopic data. By studying the reaction path and crystal growth patterns of illite/smectite (I/S) we might use the isotopic range of the different size fractions to infer the geologic evolution of a sample. The smallest illite crystals represent the earliest, nucleated in equilibrium with paleofluids. During burial, larger illite crystals grow and may incorporate elements from later, hotter fluids. Because larger crystals grow faster than smaller crystals (Law of Proportionate Effect), the volume of the later growth overwhelms the isotopic record of the first nucleated crystal.

A hydrothermal experiment was conducted to examine stable isotopic variations during illitization of smectite. Standard SWy-1 (K-sat) was reacted to illite at 300°C, 100 MPa in a series of sealed Au-capsules that were sequentially quenched in order to examine mineralogical and isotopic changes during reaction progress. Each capsule contained a 1:1 wt. ratio of <0.2µm SWy-1 to water containing 1000 ppm each of isotopically labeled Li and B. Boron substitutes for Si in the tetrahedral layers of illite, and Li enters the octahedral sites, therefore by examining the isotopic changes associated with crystal growth, we can evaluate the timing of cation exchange associated with different crystallographic sites. The fluid isotopic composition was changed after 30 days of reaction in order to test the hypothesis that small crystals record the earlier fluid composition.

Within the run products sampled after 30 days, we observed a 4-5‰ decrease in δ^7Li and $\delta^{11}B$ as the size fraction increased from <0.2µm to the largest crystals grown (>2.0 µm). The stable isotopic values of the smaller crystals may represent metastable equilibrium during R1 reaction progress. However, during R3 ordering, after the fluid composition was changed, the amount of illite crystallized with the new fluid far outweighs the earlier growth, resulting in no discernable difference in the isotopic composition of the different size fractions.

The isotopic composition of the mixed-layered I/S reflects illite fundamental particles growing in metastable equilibrium with the fluid, in a matrix of smectite that is out of equilibrium with the fluid and therefore masks the equilibrium isotopic record. By separating illite fundamental particles from the matrix of smectite, we might use the isotopic information of different size fractions (representing different periods of growth) to deduce fluid and/or temperature changes over time within a single sample.

THE ORIGINS OF PORE SHAPES IN MESOPOROUS SILICA THIN FILMS

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The synthetically tailored morphologies of mesoporous silica thin films are important for the successful application of these materials to sensing, separations, and catalysis. Sol-gel methods using surfactant templates can produce a variety of mesopore morphologies. One such morphology, composed of long cylindrical micelles aligned parallel to the substrate, is particularly useful for analysis of the stresses that produce the pore shapes. In thin film applications, the drying and calcining stresses deform the micelles from circular to elliptical, and then to somewhat rectangular cross sections if the films are of sufficient thickness. A linear elastic model using an effective medium concept is proposed to describe this morphology evolution in terms of a minimal set of parameters: the film's Poisson ratio and its thickness strain. The circular to elliptical transition (for thinner films) is verified by comparison to independent experimental data. The elliptical to rectangular transition (for thicker films) involves an increasing pressure in the nearly incompressible liquid polymer that fills the micelles. This pressure leads to a departure from the plane stress conditions normally assumed for thin film analysis, and causes localized failures in the silica matrix that will limit the range of mesopore aspect ratios that is attainable in these materials. Limitations and predictive capabilities of the model are discussed.

SMECTITES FOR TAILORED APPLICATIONS

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Nanosized synthetic particles are a main focus in nanotechnology. Already natural nanoparticles, such as clay minerals are frequently used in nanocomposites. Many of these applications are not aware of the great variety clay minerals possess in structure and properties. Hence, the full potential of these particles for low-cost nanofillers is not regarded.
A comprehensive classification is necessary to take advantage of structural features offered by different 2:1 layer structures and to tailor nanofillers.

Until now classifications (Grim and Kulbicki, 1961, Schultz, 1969, Brigatti, 1983) disregarded the dehydroxylation behavior, which means that the structure of the octahedral layer of smectites remained unconsidered. Although the cis- and trans-vacant character of dioctahedral smectites is known for a long time a manageable method to determine this property was lacking for smectites until recently because of their turbostratic disorder. Drits et al. (1995) showed that the dehydroxylation temperature of all dioctahedral 2:1 clay minerals is related to the structure of the octahedral sheet. Trans-vacant minerals dehydroxylate at 500°C and cis-vacant varieties at 700°C. Mixed types also exist which show two dehydroxylation peaks.

Within the types of the common classification systems there are smectites which can not be assigned to any type of the nomenclature. Therefore, we propose to combine a systematic description and trivial names. The systematic name should describe layer charge, octahedral structure, tetrahedral charge, Fe-content and type of mineral like "high charged cis-vacant beidellitic _ montmorillonite" taking into account rules of IMA and AIPEA to characterize montmorillonites definitely. Trivial names like "Cheto-type montmorillonite" taking into account common classification systems as mentioned above can be used if their octahedral cation distribution allow this. Various data of smectites were collected from literature and the evaluation of our system was started. However, in many cases, data sets from literature do not provide all required information. Therefore, a series of 32 samples is under examination. First results indicate a relation between iron content, location of charge and dehydroxylation temperature. Cross checks like K^+- and Li^+-test will serve as additional tools for characterization.

Brigatti (1983) Clay Minerals, 18, 177-186.
Drits, Besson and Muller (1995) Clays and Clay Minerals, 43, 718-731.
Grim and Kulbicki (1961) The American Mineralogist, 46, 1329-1369.
Schultz (1969) Clays and Clay Minerals, 17, 115-149.

PHASE CHANGE OF CATALYSTS DERIVED FROM DEOXYCHOLATE PILLARED-HYDROTALCITE-TYPE CLAY AND IMPACTS ON NO$_X$ REDUCTION FROM STATIONARY SOURCES

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Selective catalytic reduction (SCR) of NO by NH_3 forming nitrogen and water is the commercial technology for removing nitric oxides in power plants. Clay is intensively interesting for this technology. In this study, catalysts from a hydrotalcite-type clay were prepared and used for SCR of NO by NH_3 over excess oxygen. Deoxycholate pillared-hydrotalcite-type clay (DA-clay) was synthesized by hydrothermal method. It showed over 99% N_2/N_2O selectivity at all testing temperatures. The change in structure, phase transition, surface morphology, and surface area of pillared-clay upon temperature were studied by XRD, TGA, SEM, and BET techniques. The characterization results showed that this pillared-clay has different thermal transition behaviors in the different stages of calcination temperatures, which affected to the SCR activity. The magnesium-aluminium mixed oxide phase from pillared-clay calcined at 500°C, which possessed Brønsted acid sites and high surface area, gave higher activity than the others.

SOFT X-RAY SPECTROMICROSCOPY AND ATR-FTIR STUDY OF CLAY MINERAL-NATURAL ORGANIC MATTER SUSPENSIONS

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Colloid-facilitated transport of contaminants has been suggested as one of the primary transport mechanisms in subsurface waters. Moreover, interactions between colloid components (e.g., clay minerals, humic acids, and bacteria) are thought to play an important role in determining colloid stability and the transport of adsorbed pollutant species. In this study, we have combined soft x-ray spectromicroscopic methods and ATR-FTIR spectroscopy to investigate interactions between natural colloid components such as clay minerals and Suwannee river humic acid. STXM (scanning transmission x-ray microscopy) and XANES (x-ray absorption near edge structure) measurements have been performed on these systems under *in-situ* condition at the Advanced Light Source on the new Molecular Environmental Science beamline 11.0.2. Using STXM image stacks obtained at both the Al K- and C K-edges, we can identify nm-sized clay mineral particles associated with humic acid under hydrous conditions. Additionally, ATR-FTIR spectroscopic measurements were also conducted to investigate molecular-level interactions between these components under various pH and concentration ratio conditions. These FTIR results will also be discussed.
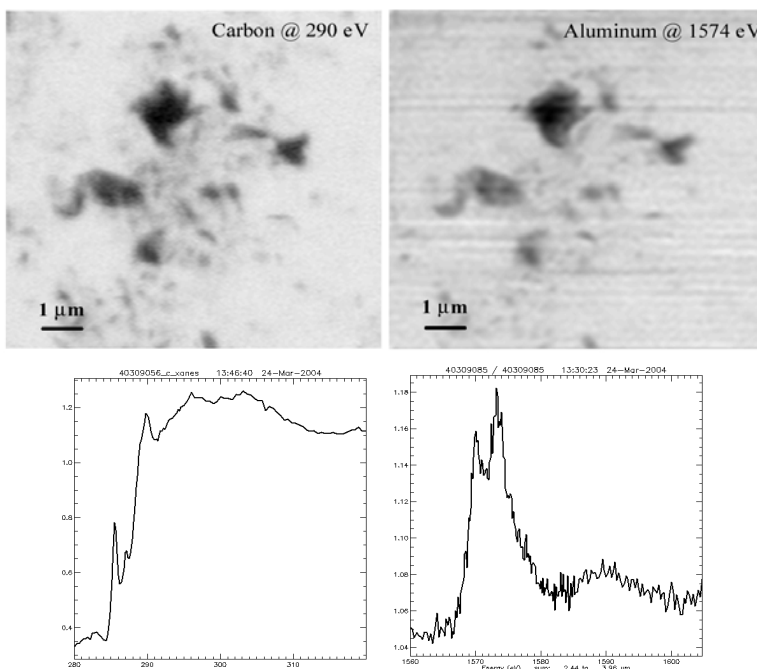
C K-edge (left) and Al K-edge (right) STXM Images and XANES Spectra of Montmorillonite (sAz) + Suwannee River Humic Acid Mixtures at pH =2.5

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 shutter anthraquinone-2,6-disulfonate (AQDS). The 0.5-2-μm 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.

Brigatti, M. F. et al. (1999). "Effects of exchange cations and layer-charge location on cysteine retention by smectites." Clays and Clay Minerals **47**(5): 664-671.

Kaden, J. et al. (2002). "Cysteine-mediated electron transfer in syntrophic acetate oxidation by cocultures of Geobacter sulfurreducens and Wolinella succinogenes." Archives of Microbiology **178**(1): 53-58.

IRON OXIDE SUPERPARAMAGNETIC NANOPARTICLES FOR TUMOR DIAGNOSIS AND THERAPEUTICS

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Major challenges in practical use of magnetic nanoparticles as MRI contrast agents include particle magnetic properties, biocompatibility and dispersity, and specific uptake of particles by the cells. We address these problems by (1) developing novel and low cost synthetic processes to synthesize well-dispersed nanoparticles; (2) developing surface modification techniques to produce a smart and integrated nano-bio-system consisting of nanoparticles coupled with PEG-linked ligands to conjugate surface receptors of tumor cells. In this system, the PEG is used as a linker or spacer between the nanoparticles and diagnostic agents to prevent the nanoparticles from agglomeration and improve biocompatiblity. Use of small ligands to target specific cells facilitates particle internalization by cells. In this study, nanoparticle uptake into tumor cells is visualized using fluorescence and confocal microscopy, and quantified using inductively coupled plasma emission spectroscopy (ICP). Surface modification is characterized by Fourier transform infrared (FTIR) and X-ray photospectroscopy (XPS). Our results showed that derivatized particles were internalized into the cancer cells much more efficiently than unmodified nanoparticles. This research provides a framework on which many material surfaces can be modified to meet the needs of variety of biomedical applications.

IRON NANOPARTICLES FOR SITE REMEDIATION: SYNTHESIS AND CHARACTERIZATION

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Nanoscale iron particles represent a new generation of remediation technologies that could provide cost-effective solutions to some of the most challenging environmental cleanup problems. Nanoscale iron particles have large surface areas and high surface reactivity. Equally important, they provide enormous flexibility for in situ applications. Research has shown that nanoscale iron particles are very effective for the transformation and detoxification of a wide variety of common environmental contaminants, such as chlorinated organic solvents, organochlorine pesticides and PCBs. Modified iron nanoparticles, such as catalyzed and supported nanoparticles have been synthesized to further enhance the speed and efficiency of remediation. Field tests have demonstrated promising prospective of the nanoparticles for in situ treatment of contaminated soil and groundwater. In this presentation, recent developments in both laboratory and pilot studies will be discussed. Main topics include: (1) synthesis and characterization of supported and unsupported nanoscale iron particles, (2) laboratory evaluation of the nanoparticles for the transformation of common soil and groundwater contaminants, and (3) field demonstration of the nanoscale iron particles for source control and groundwater treatment.

PRELIMINARY STUDIES ON THE SEPARATION OF DIAGENETIC ILLITE FROM DETRITAL MINERALS IN SEDIMENTARY ROCKS FOR Ar ISOTOPE DATING

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The dating of sedimentary rock has in part been hampered by the problem of completely separating diagenetic from detrital illite. Taking the clay minerals collected from the P-T boundary of Changxing area, ZheJiang Province, China as examples, this article introduces the procedure of separation of diagenetic from detrital minerals, including the preparation of suspension and the separation by high speed centrifuge of four samples. All the grain size fractions are analyzed by X-ray diffraction(XRD). XRD shows that impurities, such as quartz, potassium-feldspar, albite, calcite and dolomite, decrease gradually with the decreasing grain size and there are no detectable impurities in the <0.2μm fraction. Especially, the content of mixing I/S in some grain size fractions is 100%, which show that the separation is relatively successful. In addition, we dated some fractions of these four samples by K-Ar dating method and find that the age(~230Ma) of the fractions containing more detrital materials(18-31%) approaches the age of the strata while the age(~190Ma) of the fractions containing little detrital materials(0-5%) are younger than the age of the strata. Of course, these are not the last conclusions and we need further study on the reproducibility of these results and their reasons.