

EUG XI



Theme PCM

Physics and Chemistry of Earth Material

EUG XI



Symposium PCM1

Environmental Mineralogy
and Geochemistry –
The ‘Molecular Environmental Science’
Perspective

Convenors

David Vaughan

S. Clarke

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PCMI Environmental Mineralogy and Geochemistry

Sunday PM Session

PCMI : SUPm26 : G6 Molecular Environmental Science: Shedding New Light on Heavy Metal Pollutants in the Environment using Synchrotron Radiation

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Environmental pollutants are receiving increasing attention in the news media and in scientific publications because of their widespread occurrence and their potential harmful effects to humans and other organisms. Almost every day we see new reports about environmental problems such as arsenic pollution in drinking water in Bangladesh and in mine tailings in the Sierra Nevada foothills of California, lead in house paints, and plutonium and uranium in soils near nuclear materials processing plants. A new field referred to as Molecular Environmental Science has developed over the past few years to address these types of problems. Two of the key pieces of information needed to assess the potential danger of environmental pollutants are their chemical speciation at the molecular level and how they react with the surfaces of natural solids, which can sequester pollutant species or transform them to less toxic forms. Synchrotron-based x-ray absorption spectroscopy (XAS), in combination with other molecular-scale probes, can provide this information for a wide range of heavy metal and metalloid pollutants in complex environmental samples. Examples of synchrotron-based XAS studies of a number of environmental pollutants will be discussed and used to illustrate some of the important environmental issues faced by modern society.

PCMI : SUPm27 : G6 An X-Ray Absorption Fine Structure Spectroscopy Study of Iron(III)-Silica and Gallium-Silica Complexes in Aqueous Solution. Implications for the Hydrolysis and the Formation of Iron and Aluminum Oxy-Hydroxides and Silicates

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The influence of aqueous silica on iron(III) and gallium(III) hydrolysis in dilute aqueous solutions (mGa/Fe = 0.0001-0.01 m) was studied at ambient temperature using high resolution XAFS spectroscopy. Results show that in Si-free solutions at acid pH (pH<2.5) both Fe and Ga are coordinated with 6 oxygens of H₂O and/or OH groups in the first coordination sphere of the metal forming a distorted octahedron. With increasing pH (2.5<pH<5), these groups are progressively replaced by bridged oxygens (-O-), and polymerized Ga and Fe hydroxide complexes form via Ga/Fe-O-Ga/Fe chemical bonds. In these polymers FeO₆ and GaO₆ octahedra are linked together via their edges and double corners, similar to the structures of Fe and Ga oxyhydroxide minerals. At basic pH Ga exhibits a tetrahedral coordination corresponding to the Ga(OH)₄⁻ species, whereas Fe remains 6-coordinated and forms stable polynuclear hydroxide species similar to those at acid pH. In the presence of Si important changes both in Ga and Fe hydrolysis have been detected. At both basic and acid pH, Ga exhibits a tetrahedral coordination and forms stable gallium-silicate complexes, where it is bound to one or two silicons via oxygen bridges with average Ga-Si distances of 3.13±0.03 Å, similar to those determined in Ga-zeolites. The evolution of the average Ga-Si coordination numbers (a measure of the complex stability) as a function of pH and Si concentration is similar to that for Al-Si complexes (Pokrovski et al., 1998). Thus, as for aluminum, silicic acid greatly hampers Ga hydrolysis and enhances Ga mobility in natural waters.

The effect of aqueous silica on Fe(III) hydrolysis is different. The first atomic shell of Fe remains hexa-coordinated in the presence of aqueous silica although about 20% of total Fe is found to be tetrahedrally coordinated in very concentrated silica solutions (0.16 mol). Si atoms at about 3.18 ±0.05 Å are detected in the iron second coordination shell over a wide pH range (2.5<pH<12.5). Spectra analysis shows that silicic acid is likely to substitute for Fe octahedra at the corners linkages, forming stable Fe-Si polymer structures where Fe octahedra are shearing one to two edges, and each silicon tetrahedron is bound to two neighboring Fe octahedra via corners. These bidentate corner linkages for silica are similar to those found for arsenate (Waychunas et al., 1993; Manceau, 1995), selenate (Manceau & Charlet, 1994) and phosphate (Rose et al., 1996) adsorbed or co-precipitated with iron oxy-hydroxides. These new results imply that aqueous silica can poison iron hydrolysis/ polymerization and thus Fe oxyhydroxide precipitation in surficial environments, but its effect is less marked than in the case of Ga and Al. This different silica role in the hydrolysis of the two major metals (Fe and Al) and, consequently, their minor analogs (Ga, Cr, Ni...) allows better understanding of metals migration and fractionation in the earth's surface environments.

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PCMI : SUPm28 : G6 Influence of Mn and Cd Ions on Solution on the Aragonite-Calcite Transformation

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The interaction between inorganics pollutants on solution and the solid phases of soils and aquifers could result on precipitation and surface complexation phenomena. These processes produce the partial immobilization of the dissolved metals, modifying their transport properties. Most of the studies realized on this subject had dealt with the interaction between dissolved metals and calcite (Zachara et al., 1991; Stipp et al., 1992; Tesoriero et al., 1996; Prieto et al., 1997) since it is one of the most important constituents on soils, marine sediments and aquifers.

Aragonite, the second important modification of CaCO₃, is a common constituent of biogenic and abiogenic carbonates. Due to its metastability under Earth's surface conditions, it may transform into a more stable phase (calcite) by the reaction with aqueous solutions. The presence of cations that form MCO₃ calcite-type carbonates (Mn, Cd, Co, Ni, Zn) on the aqueous solution tends to accelerate the aragonite dissolution kinetics, and the subsequent crystallization of a (M,Ca)CO₃ solid solution (Böttcher, 1997). On this study we had investigated the transformation of aragonite crystals embedded in a silica hydrogel matrix, through which (Mn²⁺)_{aq} and (Cd²⁺)_{aq} had diffused. The experimental device consisted on a diffusion "cell" on which we introduced (110) and (001) aragonite sections with a width of 1 mm. The cells were filled with an aqueous solution of sodium silicate acidified with HCl (1N) until a pH of 5.5 was reached. After a few minutes the sodium silicate turns into a gel, embedding the aragonite crystals. Then we introduced, on a source reservoir connected with the gel, aqueous solutions of MnCl₂ (0.1 M and 0.2 M) or CdCl₂ (0.1 and 0.05 M). The gel is a porous medium which suppresses convection and advection, only allowing the diffusion of the ions which will reach the aragonite surface.

The interaction between the dissolved metals and the aragonite crystals results on a dissolution-precipitation process. The aragonite dissolution proceeds as the solid-solution (M,Ca)CO₃ nucleate on its surface. The process was followed using optic microscopy and the resulting transformation was estimated by XRD. The later method was used to determine the reaction kinetics and its influence on the sorption kinetics of the metals. The composition of the (Mn,Ca)CO₃ crystals was determined using X-ray dispersive energy microanalysis. The experimental results show that aragonite removes dissolved metals on a more effective way than calcite.

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PCMI : SUPm32 : G6 Variable Temperature XAS Studies on Uranyl(VI) Speciation in Nitrate-, Chloride-, Citrate- and Acetate-Bearing Solutions

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Recently we have used X-ray absorption spectroscopy to study the speciation of uranyl(VI) in aqueous solution with several environmentally relevant ligands (nitrate, chloride, acetate, citrate). We have varied pH range, ligand concentration and looked at complexation at temperatures between 25 and 250 °C.

Studies into the effect of temperature in the pH range 1-4 on the hydrated uranyl ion found that at low temperatures coordination is by 5 equatorial H₂O ligands with a mean U-OH₂ distance of 0.242 nm. Constrained refinements of the equatorial oxygen shell (see Allen et al., 1996) imply the existence of U-O interactions with two distinct distances. The coordination numbers of these two shells vary as a function of the pH, they may represent U-OH and U-OH₂ bonds. The species with 5 equatorial H₂O ligands is stable up to 160°C. Above this temperature there is a significant decrease in the number of equatorial H₂O ligands from 5 to 3. There is no apparent variation of the U-OH₂ distance. At 250°C and 1 M concentration of NO₃⁻ there are demonstrable interactions between the uranyl ion and nitrate groups. We found no clear evidence for the existence of polynuclear complexes.

Only UO₂Cl⁺_(aq) and UO₂Cl²⁺_(aq) species have been reported using spectrophotometric and chromatographic techniques at 25°C. Our studies demonstrate that as chloride concentration increases, the number of chloride ligands in the equatorial plane increases. At a pH of 1 and uranyl concentration of 0.1 M, the speciation changes from 5 equatorial H₂O ligands with U-OH₂ of 0.242 nm in chloride-free solutions to an average of 4 equatorial chloride ligands with U-Cl of 0.262 nm at 150°C in 5 M chloride. As temperature increases chloride ligands replace H₂O ligands even at low chloride concentrations e.g. in a solution of 0.1 M uranyl and 0.1 M chloride there is a 4:1 OH₂:Cl⁻ ratio at 25°C which changes to 1.5:3.5 at 215°C. This indicates that chloride species may be important in enhancing U mobility at high temperatures.

Our results for uranyl in acetate and citrate solutions show no evidence of any U-U interaction at U concentrations of 0.01-0.1 M and ligand concentrations of 0.05-5 M. With U concentrations of 0.1 and 0.05 M we find strong evidence of bidentate acetate coordination at room temperature at Ac:U ratios from 50:1 at pH's between 1.8 and 3.2. Our citrate data shows citrate coordination at room temperature over a wide pH range. No dimeric U species could be identified from the EXAFS alone. Variable temperature studies indicate that between 125 and 175°C changes in speciation occur, resulting in a complex equilibria. Above 200°C the speciation in acetate-bearing solutions appears to revert to UO₂(OAc)₂(OH₂)_{1.0±0.2}.

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PCMI : SUPm33 : G6 Structural Development of Amorphous Transition Metal Sulfides

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The structural and electronic properties of solid crystalline metal-sulfides have been widely studied; however, little information exists on the first amorphous phases formed from aqueous solutions and their structural and chemical relationships with the final stable crystalline minerals. The reactivities and properties of possible intermediate phases are not well established. Our previous studies of these systems have used X-ray Absorption Spectroscopy (XAS) to study the "dynamics" of precipitation in sulfide systems. For example, CuS initially forms a primitive amorphous structure (possibly derived from a wurtzite-type structure) which evolves into an amorphous covellite in around an hour (Patrick et al., 1998). Similarly, in the case of FeS, either hexagonally close packed or cubic close packed initial precipitates form, dependent on solution conditions, and develop via tetragonal FeS (mackinawite) to Fe₃S₄ (Lennie and Vaughan, 1996). Building on these studies we have used Energy-Dispersive Extended X-ray Absorption Spectroscopy (EDEXAFS) and Energy Dispersive X-ray Diffraction (EDXRD), which allow acquisition of spectra between 0.1-1 seconds in EDEXAFS and < 1 minute in EDXRD. Preliminary analyses show that, in the CuS at ambient temperatures, approximately 1 hour after initial precipitation, a short-range structural change occurs from an amorphous CuS precipitate to one with a more covellitic character. At temperatures above 40°C this 'covellitic' intermediate becomes more crystalline. The combination of these two techniques allows short range local structure and long range structural development to be followed over time, and the calculation of the rates of these transformations.

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PCMI : SUPm34 : G6 In Situ Atomic Force Microscopy Investigation of Mica Dissolution Mechanisms: Preliminary Investigation

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The reactions of biotite and muscovite dissolution were investigated by experiments in the liquid cell of an Atomic Force Microscopy at room temperature and pH=1. The morphological evolution of a freshly cleaved (001) surface and the chemical composition of the interacting solution introduced by peristaltic pump under high flow condition were analysed for 5 hours. AFM resolutions of the molecular periodicity consist with hexagonal-like arrangement interpreted to correspond to the tetrahedral sheets. When fluids are pumped, dissolution produces etch pit of stair-step pattern having the first step of 4.4 ± 0.6 Angstrom. The average velocity of step retreat has been estimated to be 180 and 120 nm/h for biotite and muscovite respectively, while pits deep with a rate of 0.4 and 0.3 nm/h respectively. The total (001) surface area remains constant during the reactions, while lateral surface (hk0) area of biotite increases 3 times faster than muscovite. This study suggests that the reactivity of mica basal (001) is 2 orders magnitude lower than lateral (hk0) and that steps formed during the edge attack of the (001) surface, correspond to the sum of tetrahedral and octahedral sheets of mica.

PCMI : SUPm35 : G6 Redox Conditions in a Hydrothermal System: An EPR Study

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The redox potential (Eh) is an important geochemical parameter because it has a strong influence on the mobility and complexation of metal cations in geological systems. *In situ* Eh measurements in such systems are often not possible, and therefore, most of the information on redox potentials is based on estimations from activities, pH and hydrogen gas concentrations or from the occurrence of redox-responsive minerals such as pyrite and pyrrhotite. All of these approaches can be utilized only if direct measurements of the chemical indicators are possible or redox-responsive minerals can be identified.

An analytical approach by which redox-sensitive trace elements structure-bound in clay minerals operate as redox indicators is proposed. The major problem with using trace elements is the precise determination of their oxidation states. Electron paramagnetic resonance (EPR) spectroscopy is a powerful methodology to detect metal centers (e.g. Fe(III), Cu(II), Mn(II), V(IV)) in specific redox stages. Difficulties can arise by the assignment of an EPR signal recorded from a multinatural sample to a specific mineral or a specific chemical form due to spectral superposition of paramagnetic species. It is possible to overcome this problem by the combination of a detailed mineralogical analysis and an experimental approach which is founded on the changes in EPR signals upon thermal and/or chemical treatments. This approach is based on the assumption that different mineral phases of a multi-mineral system differ in their thermal and/or chemical stability.

A recent hydrothermal mudpool at the southwestern slope of the Rincón de la Vieja volcano in Northwest Costa Rica is used as an example to demonstrate the above experimental approach. The mudpool exhibits an argillic alteration system formed by intense interaction of sulfuric acidic fluids with wall rock materials.

Detailed mineralogical analysis revealed an assemblage with kaolinite, alunite, and opal-C as the major mineral phases. Electron paramagnetic resonance spectroscopy (EPR) showed three different redox-sensitive cations associated with the mineral phases. Cu⁺ is structure-bound in opal-C, whereas VO²⁺ and Fe³⁺ are located in the kaolinite structure. The location of the redox-sensitive cations in different minerals of the assemblage is indicative of different chemical conditions. The formation of the alteration products can be described schematically as a two-step process. In a first step alunite and opal-C were precipitated in a fluid with slightly reducing conditions and a low chloride availability. The second step is characterized by a decrease in K⁺ activity and subsequent formation of kaolinite under weakly oxidizing to oxidizing redox conditions as indicated by structure-bound VO²⁺ and Fe³⁺.

The detection of paramagnetic trace elements structure-bound in mineral phases by EPR provide direct information about the prevailing redox conditions during alteration and can, therefore, be used as additional insight into the genesis of the hydrothermal, near-surface system.

PCMI : SUPm36 : G6 Biofilm Effects on Hydraulic Conductivity: Experiments from the Microscopic to the Macroscopic Scale

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Fluid flow and pollutant transport in porous geological media (including soils, sediments and aquifers) are ultimately controlled by hydraulic conductivity. Growth and movement of bacterial consortia in these media may markedly reduce effective porosity and permeability by up to four orders of magnitude (Taylor and Jaffe, 1990; Beveridge et al., 1997). This reduction in hydraulic

conductivity has direct relevance to the efficiency of petroleum recovery, water abstraction, leachate migration and radionuclide transport. The considerable metal sorption capacity of bacteria and associated extracellular polymeric substances (EPS) also affect pollutant transport by presenting a sorptive interface to dissolved trace metals (Boult et al., 1997). Laboratory based simulations of porous media-microorganism interactions have tended to focus on bacteria grown under enriched nutrient conditions relative to natural systems (van Deventer and Bayve, 1992). However, such elevated nutrients may not reflect typical bacteria-supporting groundwater. Furthermore, critical problems in scaling system behaviour up from laboratory experiments to real environmental systems also exist.

For these reasons, an integrated programme which aims to characterise bacteria-mineral interactions and their effect on both physical (hydraulic conductivity) and chemical (metal sorption and bacterially mediated mineral formation) aspects of fluid flow and pollutant transport in porous media is underway. These experiments encompass measurements ranging from molecular to field scale. The effect of biofilm growth on porous media properties under geologically relevant solution nutrient conditions is being studied using a modified Constant Depth Film Fermenter (CDFS) and quartz sand columns. Pollutant transport and mineral precipitation at quartz surface-biofilm and at biofilm-solution interfaces is being studied with novel single-pass flow cells. Biofilm growth and reaction with trace metals is being quantified using spectroscopic techniques including X-ray reflectivity, X-ray Absorption Spectroscopy (XAS), Fourier Transform InfraRed (FTIR) spectroscopy, and confocal microscopy. Measurements of pollutant transport and hydraulic conductivity are also being made in a 500 g Tonne geotechnical centrifuge. The centrifuge data allow us to perform carefully controlled laboratory experiments which can be directly scaled up to field dimensions, thus providing the key link between microscopic processes and macroscopic system properties. Results obtained from this study will be used to improve models of reactive transport in porous media.

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PCMI : SUPm38 : G6 In Situ Synchrotron Studies of Hydrothermal Reactions in the CaO-SiO₂-H₂ System: Kinetics, Thermodynamics and Reaction Mechanisms of Gyrolite Formation

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The availability of high-energy, high-flux, synchrotron X-radiation is revolutionising the *in situ* study of hydrothermal reactions at elevated temperature and pressure as reactions can be studied dynamically allowing phase stability, kinetic, thermodynamic, and mechanistic data to be obtained for reactions taking place over a few hours. We have been studying hydrothermal crystallization and dehydration reactions for C-S-H minerals using these techniques. As well as being of significance in mineralogy and geology, man-made crystalline and disordered C-S-H phases are very widespread (e.g., in hydrated Portland cement and thermal insulation components) and the results therefore impact on fields ranging from environmental science, to materials science and technology, and to radioactive and toxic waste disposal.

In situ energy dispersive powder diffraction experiments were carried out on station 16.4 at the Daresbury Laboratory at temperatures ranging from 190 to 240°C. At every temperature, the sequence in which the various peaks appear, grow and decline illustrates that there are three distinct stages to this reaction. Firstly, within about 5 minutes, a poorly ordered C-S-H gel forms, followed after about 50 minutes by transformation of this to the intermediate Z-phase. After about 55 minutes, the Z-phase peak begins to transform to gyrolite, which is the final product within about 8 hours.

PCMI Environmental Mineralogy and Geochemistry

Sunday PO Session

PCMI : Supo01 : PO Experimental Study and Modelling Approach of Weathering Processes of Basaltic Rocks

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Reaction kinetics and reaction mechanisms were investigated by fitting peak area vs time data with an Avrami-type kinetic model which relates nucleation and growth phenomena to the kinetics of crystallization. The activation energy for growth of the C-S-H gel is about 47 kJ/mol which characterises the first stage of the reaction. During the transformation of C-S-H gel to Z-phase and of Z-phase to gyrolite, the activation energies for crystallization are significantly higher and range 73 - 87 kJ/mol. Crystallization of Z-phase and gyrolite occurs by a 2-dimensional, diffusion-controlled growth mechanism, for a decreasing nucleation rate.

The kinetic data from these experiments can be used to determine the crystallisation rate of gyrolite at temperatures similar to those expected in the near-field environment surrounding a radioactive waste site, 20°C (low level) to 100°C (high level). This shows that, despite the large error due to the extrapolation from high temperature, gyrolite could crystallise within the expected lifetime of a cementitious waste repository (~10,000 years). Therefore any model of waste-site evolution should take into account the crystallisation of C-S-H gel to gyrolite and other C-S-H minerals.

In situ synchrotron studies are ideal for providing this wealth of information for hydrothermal reactions of environmental significance.

Following some recent works on the hydrolytic mechanisms of the basaltic rocks alteration under humid tropical climate, we performed leaching experiments at laboratory, under controlled external conditions, on the most representative basaltic rocks of the Réunion island. These rocks represent the complete alkali basaltic trend, typical of the lava flows from the "Piton des Neiges" and the "Piton de la Fournaise".

The results allow to show a good correlation between the water chemistry and its geological environment (Hoareau and al., 2000). However, in order to better understand the precise mechanisms of alteration of the rocks by fresh water and the possible precipitations of secondary phases and clays minerals, we performed a numerical modelling of this leaching experiments.

We proposed some scenarii of basaltic rocks dissolution tested using the thermodynamic and thermokinetic model KINDIS (Madé, 1990, Madé and al., 1991). These different modellings are first constrained by the hydrochemical data collecting by surveying the natural springs of Réunion island. Thus, the numerical dissolutions have been performed so that the saturation states modelled are similar to the natural waters ones. The several tries of numerical modelisation match well with the experimental leaching results. The behaviour observed at laboratory for the cationic and anionic elements mobilities between rocks and aqueous phases are partially obtained with models. For a better fitting of the models, we have to consider on the same way the external parameters like temperature, rain intensity or carbon dioxide partial pressure with an humic origin ; the lithologic parameters like glass-crystals ratio, rocks mineralogy and the probable influence of the volcanic activity on the chemical evolution of the waters (lithostatic pressure, temperature, magmatic carbon dioxide partial pressure).

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PCMI : Supo02 : PO Development of the Application of Magnetic Micro-Sorbents for the Elimination of Hazardous Inorganic Contaminants from Natural Waters

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Inorganic contaminants in raw waters of drinking water supplies become more and more important in many countries. Respective contaminants are heavy metals like lead, zinc, copper, cadmium, mercury and nickel usually occurring as divalent cations and arsenic, selenium, antimony and chromium which are found as oxide anions. An additional contaminant is fluoride.

These contaminants can be eliminated by processes such as precipitation, membrane filtering and sorptions.

Adsorption of the contaminants onto commercially available ion exchangers and granular sorbents often is too slow to allow a satisfactory technical process. The only way to overcome the problem consists in an increase of the exchange surface by applying small particle sized adsorbents.

Micro-sorbents generally do not allow normal filter operations. Their application is only possible in combination with suitable reactors design and separation processes. As a consequence, the development of reactors and magnetic separator systems is necessary.

As mentioned sorbents in the form of micro-particles have several advantages compared to conventional sorbents particles with diameters of about 1 mm. The most important of these advantages are fast kinetics as well as better use of sorption capacity. In cases where the sorption only takes place at the particle surface the orders of magnitude higher specific surface of small particles is an additional advantage. However, the advantages of micro-particles have to be paid by the loss of the possibility to simply handle the particles in fixed beds. Even in the case of small flow velocities of a few meters per hour, the pressure drop will become unacceptable high. In addition there would be an increasing tendency for blockage and in the case of upstream operation there is also the danger of particle loss. In the case of magnetic micro-particles magnetic drum separators or high gradient magnetic separators could be efficiently used for this purpose.

This work will be focused on the development, modeling and testing of a novel process for the elimination of inorganic contaminants from water on the basis of magnetic micro-particles.

In a first step magnetic micro-particles will be produced based on iron(hydr)oxides, silicon-oxide, aluminum- and manganese-oxides. Especially new synthesis methods will be applied to mass-tailor the magnetic properties. The basic properties of these newly developed micro-sorbents will be examined. These are:

- exchange capacity - surface charging - sorption capacity - sorption kinetics - magnetic properties, such as initial permeability, remance, saturation magnetization

PCMI : Supo03 : PO Production and Characterization of Microporous Aggregates Made from Nano-Particles and the Attachment of Magnetic Minerals

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Heavy metals and other toxic compounds in aqueous media (e.g. ground water, deposit leachates) are a potential environmental risk. For the removal or reduction in concentration several in- and organic sorbents have been used. On one hand a high specific surface area is sought-after for reasons of efficiency, on the other hand small particles in the range of a few nano-meter have to be handled. This happens partly by filters or coating of filter substrates, but leads to the drawbacks entailed by this technique. A way out is the use of the magnetic properties of ironoxides, by applying magnetic fields on such particles suspended in aqueous media. These magnetic particles feature some drawbacks, such as low specific surface area and limited sorption behavior. A solution to this problems is the production of microporous aggregates from nanoparticles with mass-tailored sorption and manipulation properties for the subsequent processing. A selection of materials consists of Fe(hydr)oxides such as ferrihydrite, Al- and Tioxides, and microporous SiO₂ spheres.

These nano-particles form microporous aggregates, which span a huge range of sorbates due to their surface chemical properties. Furthermore, these sorbates are stored within the microporous structure of the aggregates. This possible homogeneous distribution within the aggregates and the kind of material may lead to a promising after treatment or recycling. The combination of this aggregates with magnetic particles for the magnetic separation technique allows the fine dispersion in aqueous media and thus increases the reactive surface area clearly in comparison to filter bed techniques.

In this work, microporous aggregates will be produced which have the following properties:

- broad spectra of surface chemical properties - different poresizes and poresize-distributions - magnetic properties for the manipulation in magnetic dc and ac fields - to allow different methods in the after treatment such as thermal, chemical, and physical processes

With that, aggregates are produced which leave their application range of water and groundwater protection far behind. Possible applications fields may lie in food technology, pharmacy and soil chemistry.

PCMI : SUpo04 : PO

Characterization of Kaolinite Polymorph Mixtures in Lateritic Weathering Profiles using *In Situ* Infrared Microspectroscopy on Polished Thin Sections

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Infrared microspectroscopy (IRMS) is employed for the first time to characterize lateritic weathering kaolinites directly on petrographic thin sections. In lateritic weathering profiles kaolinite is ubiquitous but presents heterogeneous crystal chemical patterns, even at a centimetre scale in a given facies. Most of previous spectroscopic techniques used to characterize kaolinite necessitates the separation of the clay fraction from the bulk soil sample. Such a procedure necessitates a grinding of the sample leading to an alteration of clays, that favors the extraction of small size rather than large size kaolinite. IRMS provides a unique mean to study *in situ* each clay fraction separately, that may relate to different processes at work during the long development of thick tropical weathering profiles.

By applying IRMS to kaolinite of petrographical thin sections, four classical OH-stretching bands have been observed on the Fourier transform infrared (FTIR) spectra, at 3695, 3668, 3650 cm⁻¹ for the inner surface hydroxyls and 3620 cm⁻¹ for the inner hydroxyls, noted ν_1 , ν_2 , ν_3 , and ν_4 , respectively, plus a vibration band at 3595 cm⁻¹ standing for the octahedral substitution of Fe³⁺ for Al³⁺, noted ν_{Fe} . The intensity of ν_1 much varies from a kaolinite sample to another one. According to the clay size, further vibration bands are often needed to fit at best the FTIR spectra. Large size kaolinites of 10-20 μ m have FTIR spectra characterized by an additional band at 3680-3685 cm⁻¹ which is generally unresolved using classical IR spectroscopy and only depicted by dispersive Raman spectroscopy. The integrated intensity of the ν_2 band is larger than that of the ν_3 band, that characterizes well ordered kaolinites. Vibration bands at 3710, a splitting of the 3668 cm⁻¹ band into two bands at 3672 and 3666 cm⁻¹, and a band at 3615 cm⁻¹ were also depicted by curve fitting procedure. Small size kaolinites, ~2 μ m exhibit quite different FTIR spectra, with absence or weakness of the ν_2 OH-stretching band, but with an additional band at 3640-3645 cm⁻¹. Such FTIR spectra characterize poorly crystallized kaolinites, i.e., disordered kaolinites. It is suggested that, although the orientation of kaolinites, in particular the "booklets", can affect the relative intensities of the OH-stretching bands, the diversity of FTIR spectra observed also reflects the intergrowths of clay

PCMI : SUpo05 : PO

Structure and Crystallisation Behaviour of (Sr,Ba)HAsO₄·H₂O Solid Solutions

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Arsenic is widely distributed in nature. During the last decades, progressive use of arsenic in industrial processes (thermal powder, pesticides, ceramic, gold-mine tilling, etc) have provoked an increase of this toxic metal in water and soils. In aqueous environment, arsenic can exist in two oxidation states (As-III and As-V) as both inorganic and organo-metallic species. The reduced form (arsenite) is less common but more toxic and mobile than the oxidised form (arsenate). Several studies have been focused on removal of As-V from aqueous systems by adsorption on some geological materials such as ferrous and clay minerals. In spite of its environmental interest, crystallo-chemistry and crystallisation behaviour of arsenates are poorly known. In this work, nucleation and growth of crystals of (Ba,Sr)AsO₄·H₂O solid solutions were obtained in a double diffusion system. The reactants counterdiffuse through a column of porous silica hydrogel in a U-shaped tube (length 28 cm). The source reservoirs were filled with 8 cm³ of BaCl₂-SrCl₂ and Na₂HAsO₄ mother solutions. A set of experiments at isothermal conditions (25°C) with mother solutions of different concentration was carried out. Experimental details are described by Prieto et al., (1993). Before the diffusion starts, the gel column is a homogeneous medium with pH-5.5 and zero reactant

concentration. A limited solid solution between the two end-members (Sr and Ba arsenate) was observed. The two end-members of the solid solutions crystallise in the orthorhombic system, space group Pbc_a. The crystal structure of the barium arsenate (BaHAsO₄·H₂O) was solved and refined using by 1719 reflexions to a final R value of 0.05. Hydrogen atoms were located and included in the refinement. Unit cell parameters for barium arsenate are: a=7.7519, b=14.668, c=8.759, Z=8, D_c=3.939 mg/m³. The structure of the strontium arsenate end member shows unit-cell parameters slightly smaller. These parameters, previously determined by Binas (1962), were refined in the present work, as well as their evolution with the Ba/Sr content for intermediate (Ba,Sr)HAsO₄·H₂O solid solutions. Finally, the theoretical morphology of the Ba end-member was calculated from the structural data by the Donnay and Harker method (1937). Although this method is only an approximation, the results agree with the observed morphologies dominated by {010} with {111} and {021} as minor forms.

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Monday AM Session

PCMI : MOam02 : G6

Molecular-Level Speciation of Lead and Arsenic in Soils over Geochemical Anomalies

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Lead is a widespread pollutant often associated with airborne deposition from automobile exhaust, mining and smelting operations. Arsenic contamination of surface waters, sediments and soils both originate from natural and anthropogenic sources, especially acid-mine drainage. Once deposited in soils or in sediments, these elements can accumulate for hundreds of years and represents a potential environmental risk. In soils, the mobility and bio-availability of chemical elements is essentially driven by surface reactions involving mineral and organic components and metabolic reactions within living organisms, both strongly depending on key parameters as pH and Eh. Many laboratory works based on detailed EXAFS analysis have elucidated on the atomic scale, the sorption mechanisms which explain the strong affinity of Pb(II) for Fe- and Mn-(hydr)oxides and soil organic matter as well as of As(III) and As(V) ions for Fe-oxides. However, the question arises whether the mechanisms that control element mobility in laboratory experiments or even in soils contaminated during historical times also describe their long term behaviour in natural systems. The present communication aimed at comparing the molecular-level speciation of Pb and As in soils overlying geochemical anomalies and in soils impacted by human activities. The topsoils from natural anomalies exhibit Pb and As concentrations as high as those encountered in most impacted soils (from 100 to few thousands of mg/kg). These systems may be, therefore, considered as long term analogues for polluted soils, in terms of concentration levels. The main difficulty to investigate trace element speciation in such heterogeneous media as soils, comes from the fact that element often occurs in a wide variety of chemical forms in the same sample, including a myriad of possible sub-micron surface species unable to identify without using spectroscopic techniques. Our approach, which combined X-ray Absorption spectroscopy (EXAFS) with more conventional techniques, including μ XRD and Rietveld refinement, has offered the possibility to measure changes in metal(loid) speciation as a function of soil nature and soil horizons. Sorption processes appear to be key mechanisms in recently contaminated soils: Pb-organic matter complexes mainly control the mobility of Pb in acidic organic-rich topsoils, while Pb(II) mainly sorbs onto Fe- and Mn-(hydr)oxides in cultivated soils with low organic content. Besides, in-situ formation of sparingly soluble Pb-phosphates, mainly from the pyromorphite and plumbogummite family, appear to be the most efficient long term Pb-sequestration mechanism. First results on As speciation confirm the strong relationships between As and Fe geochemistry and suggest that, after dissolution of secondary iron-arsenate minerals, sorption of As(V) on iron (hydr)oxide surfaces represent the ultimate As species in topsoil horizons. Such data on toxic metal speciation provide important clues about long-term sinking processes in soils and may and could therefore help for optimising in-situ remediation strategies and land-use.

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PCMI : MOam03 : G6 Electrochemical Oxidation of Pyrite in Alkaline and Acid Electrolytes: An Investigation Employing Glancing Incidence X-Ray Absorption Spectroscopy and X-Ray Photoelectron Spectroscopy

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The decomposition of pyrite under oxidizing conditions is important both industrially and environmentally, the later particularly because pyrite is the major source of acid rock (mine) drainage¹. However, the fundamental mechanisms involved in the oxidative dissolution/decomposition of this mineral are not well understood, despite numerous investigations. This is because of the complexity of the decomposition reactions which may lead to a considerable variety of products: for example under acidic (A) and basic (B) oxygenated conditions products of decomposition may include

(A) pyrite + water, sulphate, elemental sulphur, soluble metal ions, metal deficient sulphides, polysulphides, protons, electrons
(B) pyrite + water, sulphate, oxides, (oxy)hydroxides, protons, electrons

The molecular scale reaction mechanisms, sequence of formation and predominant reaction products depends upon specific oxidation conditions (pH, Eh, ionic strength, dissolved gases).

In the present work electrochemical techniques have been used to control Eh: in addition such methods enable control of the amount of charge passed and hence the thickness of any reaction product layer. Direct information on the products forming at the pyrite surface and the thickness and variations as a function of depth beneath the surface, have been obtained using the techniques of Glancing Incidence X-ray Absorption Spectroscopy (GIXAS) and X-ray Photoelectron Spectroscopy (XPS). GIXAS is simply X-ray Absorption Spectroscopy in glancing incidence geometry, where by controlling the incident X-ray angle you also control the depth that the X-ray beam penetrates into a surface.

For example, pyrite samples oxidised at +600 mV (vs Ag/AgCl ref electrode) in a pH 8.4 (0.1 M NaNO₃) produced an iron oxide/hydroxide phase at the surface as shown by XPS analysis. This is in agreement with GIXAS data for a depth of 27.2 Å ±0.5, which shows both iron-sulphur and iron-oxygen first shell backscatterers. GIXAS further reveals that the iron-oxygen contribution is substantially diminished by 70 Å ±15 from the surface and has disappeared completely by 155 Å ±30. No sulphate was detected on the sample following passing of a moderate amount of charge (Q) specifically Q = 60 mC cm⁻². When Q = 120 mC cm⁻² sulphate could be detected. For pyrite oxidised at +600 mV (vs Ag/AgCl ref electrode) in a pH 4 NaNO₃ solution XPS analysis reveals the presence of both an iron oxide/hydroxide phase and sulphate even at low charge (Q = 60 mC cm⁻²). GIXAS analysis does not in this case give separate oxygen and sulphur shells surrounding iron but a broadened peak indicating disordered iron-sulphur-oxygen phases. Also presented are results from SEM, AFM, PIXIE and RBS techniques showing that the reaction proceeds via discontinuous islands of reaction products.

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PCMI : MOam04 : G6 Speciation of As by XAFS Spectroscopy in Si-Bearing Fe Hydroxide Precipitates

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Thermal water of the Wiesbaden spa contains over 100 ppb As, predominantly in form of arsenite. Si-bearing hydrous ferric oxide (HFO) precipitates found on the wellhead stone of the "Kochbrunnen" spring contains up to 0.2 wt.-% of As. The purpose of this work was to determine the structure of these X-ray amorphous precipitates by measurement of

EXAFS spectra at both Fe and Si K-edges, and As speciation in these precipitates by As K-edge XANES and EXAFS. Fe spectra are characterized by a small pre-edge peak due to 1s-3d transitions indicating octahedral Fe-III coordination. Fe EXAFS spectra can best be fitted by a short range order close to that of α -goethite, with both edge- and corner-sharing octahedra. The second RDF peak is broadened and has a shoulder on its right side. This characteristic pattern results from the contribution of a next nearest Fe atomic shell. However, fits based on two iron shells only, the first one at 3.03 Å characteristic of edge-sharing octahedra and the second at 3.44 Å for corner sharing octahedra, were not satisfactory. A much better fit especially at low k-values is obtained by considering additional Si atoms at a mean distance of 3.43-3.45 Å. This would correspond to a Fe-O-Si-Fe double scattering path generated within the second shell, with the shortest Fe-Si bond at about 3.10 Å as corroborated also by Si EXAFS data. The position determined at half height jump of the As K-edge (first derivative XANES peak) reveals that this element is present predominantly in the tetrahedral coordination of arsenate, with oxygens at a mean distance of 1.68 Å. Aeration and drying of the samples showed no influence on the position of the XANES peak. For the second coordination shell, a good EXAFS fit is obtained using both 2.83 Å and 3.26 Å As-Fe contributions corresponding to a bidentate mononuclear complex and a bidentate binuclear complex, respectively. As-Fe distances are much shorter across edges than corners. The adsorption of arsenate on the mineral surface causes two expanded Fe bonds resulting in a distorted octahedron with a mean bond length of 2.13 Å. Formation of both Si and As surface complexes is expected to retard the cross-linking of Fe chains during crystal growth, thus stabilizing the amorphous HFO structure. Moreover, the tight association with Si can increase the stability of colloidal Fe hydroxo complexes by the following reaction: $(\text{HO})_3\text{Si-OH} + \{\text{Fe}(\text{H}_2\text{O})_6\}^{2+} = (\text{HO})_2\text{Si-O}\{\text{Fe}(\text{H}_2\text{O})_5(\text{OH})_2\}^+ + \text{H}_2\text{O}$. Such positively charged colloids might serve as a substrate for the effective arsenate (co)precipitation from thermal waters. On the other hand, the results evidence for the first time directly competitive surface complexation of both As and Si.

PCMI : MOam05 : G6 Evolution of Mineral-Fluid Interfaces Studied at Pressure with Synchrotron X-Ray Techniques

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The development and use of new techniques and *in situ* reaction cells has been an important part of recent advances in mineral surface chemistry. Nonetheless, it has remained extremely difficult to study the evolution of the surface while under pressure. Since pressure is a key variable in geological systems, we have developed an experimental approach that has allowed us to directly measure changes in surface quality (at the angstrom scale) of mineral surfaces that are under pressure. Our immediate aim is to further the understanding of the phenomenon of pressure solution. Experiments with *in situ* reaction cells were completed at the Daresbury Laboratory Synchrotron Radiation Source. A perspex anvil was used both to transmit pressure to the mineral surface and as an X-ray transparent medium for the incident X-ray beam. Changes in intensity of the specularly reflected beam and of the diffusely scattered portion of the beam were monitored. Surfaces of single crystals of calcite and halite were analyzed under the following conditions: 1) dry and at ambient pressure, 2) dry and at elevated pressure (either 10 or 30 bar), 3) in contact with an undersaturated solution at elevated pressure, and 4) in contact with a saturated solution at elevated pressure. Perhaps our most important result is that interface structure can be analyzed with X-ray scattering under pressure. In order to accurately model transmission of X-rays through a bulk medium with an arbitrary index of refraction an algorithm for analysis of the data was formulated based on the Fresnel equations and on a surface roughness model. The change in surface roughness (σ) for the calcite surface at 30 bars pressure in an undersaturated solution was: $d\sigma/dt = 6.3 \times 10^{-5} \text{ A s}^{-1}$. This is consistent with previous measurements of calcite roughening at ambient pressure and can be accounted for purely by chemical dissolution. The roughening rate for calcite in a saturated solution was too small to measure over

3.75 days at 30 bar. In-plane topography was also stable. However, in a long term experiment, halite in a saturated solution appeared to roughen slightly at 30 bar with a roughening rate of $d\sigma/dt$ less than or equal to $7.5 \times 10^{-7} \text{ A s}^{-1}$.

PCMI : MOam08 : G6 Interaction of Metals in Solution with Alumina Surfaces Studied with Electronic Structure Simulations

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First-principles studies using quantum mechanical calculations have been performed for a range of metal ions on the hydroxylated (0001)-Al₂O₃ surface, with the aim of gaining an understanding of the general principles affecting geometry, electronic structure and energetics of adsorption in the presence of water. The adsorption of such metal ions as pollutants onto mineral surfaces plays an important role in their dispersion in the natural environment and in possible remediation strategies. Theoretical approaches have started to be applied to these systems, but only recently have computational resources been sufficient for these complex problems.

Electronic structure calculations have been successfully applied to many problems of solvated ions, surfaces and bulk minerals, although different methods have evolved which are each best suited to certain problems. Here we use Hartree-Fock (HF) and density functional (DFT) theories, the latter in both periodic and cluster formulations, and with both plane-wave and localised orbital basis sets for the periodic calculations. The variations between results using these methods indicate both their strengths and weaknesses and which results, from their consistency, can be taken to be most reliable.

In particular, the role of -OH groups in determining the preferred adsorption site of metal ions and the effect of water molecules have been investigated. The bare (0001)-Al₂O₃ surface exhibits a large relaxation compared to the bulk geometry, so deviations from this surface structure are easily identifiable.

PCMI : MOam09 : G6 Etch-Pit Honeycombs on Weathered Feldspar Surfaces: Catalytic Reactors for the Origin of Life?

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Potassium feldspar crystals in plutonic acid igneous rocks and gneisses ubiquitously develop sub-regular arrays of edge-dislocations forming loops around albite extension lamellae, during cooling from ~400°C. The dislocations form an intersecting orthogonal array, one set parallel to b, the other close to c, spaced 300-700 nm apart. During modern weathering in acid pore waters dissolution proceeds rapidly (relative to normal crystal surface) down dislocation cores, leading to tubular 'honeycombs' extending >50 μm beneath crystal surfaces, individual tubes being <500 nm wide at the surface, <80 nm within the crystal. Mechanical degradation of the crystal surface, during which the crystal breaks into flakes parallel to lamellae, is an important factor in natural feldspar dissolution. In modern soils, honeycomb surfaces are inhabited by bacteria, some filamentous, strikingly similar in dimensions to the surface etch-pit arrays, and to the earliest known microbes (3.5 Ga) from the Pilbara supergroup.

The honeycombs have considerable potential to act as catalytic reactors for biogenesis. Typical cleavage surfaces will have $2\text{-}3 \times 10^6$ pits mm^2 , and a nominal mm^2 of feldspar surface will provide $\sim 130 \text{ mm}^2$ of actual surface area. Granitoids appeared early in the Archaean (>4 Ga Acasta gneiss) and surface water was present at 3.8 Ga (Itsaq gneiss complex). A 10 km^2 granite outcrop would provide 4×10^{18} potential reactors. Silica-rich layers, a few unit-cells thick, perhaps with zeolite structures, could provide organophilic surfaces able to catalyse the formation of long

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polymers, and the tapered tips of dissolution pits might provide optimum sites for the accumulation of aligned polymers. We speculate that in the prebiotic Earth, alkali feldspar honeycombs would frequently occur in contact with a reservoir of diverse organic molecules in a 'primordial broth'. Oligomers could accumulate in the reactors, protected from the dispersive effects of flow and from ultraviolet radiation. Periodic desiccation could have led to high concentrations, minimizing the possibility of hydrolysis. Reactors normal to crystal surfaces would have communicated laterally through the narrower connecting tubes, and ever more complex polymeric molecules could have spread through the honeycomb zone. Somewhere, in some set of reactors on or near the surface of the early Earth, with the tubes acting as precursors to cell walls, a self-organised, autocatalytic set of minimal reactions able to support large self-replicating polymers arose, and colonized the mineral surface. Possibly, protective lipid lids to tubes evolved, extended into the broth in search of nutrients, and ultimately detached from the mineral substrate to give the first truly independent, unicellular life.

PCMI : MOam10 : G6 Heavy Metal Distribution in Surface Sediments of the Protected Wetland el Kelbia (Tunisia)

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Sebka El Kelbia is a protected wetland western center of Tunisia. Till now it was rather preserved but increasing industry and urbanisation have a harmful effect on this fragile environment. In order to preserve this existing natural wetland it is important to know the effect of the different anthropic activities. Therefore it is necessary to detect the actual pollution in sediments in relation with the anthropic activity, but also to point out the influence of natural phenomena in the extension of the pollution.

Only few studies concern heavy metals distribution in marine or lacustrine sediments from Tunisia (Ben Henda, 1997; Darragi et al., 1998; Khedhiri, 1998; Rais, 1992) and this work is the first one devoted to the geochemistry of Sebka El Kelbia.

Our aim is to check heavy metals distribution in the sediments in function of location of the major pollution sources, and the changes depending on the season.

Data on chemistry and mineralogy were collected at dry and wet seasons and at different locations and depths in the sediments. A data-processing program was then used for multidimensional statistical analysis (principal component) to underline affinities between elements and minerals.

Sebka El Kelbia surface sediments have a low heavy metals content compared to tunisian polluted lakes. The overall content is considered to be natural. The most enriched zone is related to river El Hallouf and the industrial site of Kondar. However, the contamination threshold is not reached and no major anomaly was detected in these sediments. The space distribution in metals is similar for all except Cd. Principal component analysis results show the following trends: - Fe, Pb, Ni, Mn, Cu and Zn seem to have the same origin and are strongly related to clays which could be their major adsorption; - Cd is strongly related to carbonates and seems preferentially fixed on them.

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PCMI : MOam11 : G6 The Interaction of U with the Calcite Surface: Batch Sorption and Synchrotron X-Ray Standing Wave Studies

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Characterisation of radionuclide mobility in the environment is a major goal in applied geochemistry. In natural solutions, uranium behavior is strongly controlled by its complexation with carbonates. Atomic-scale determination of the processes occurring during interaction between aqueous species and crystal surfaces can now be approached by using synchrotron X-ray techniques.

In this study, adsorption of uranyl-carbonate complexes at the surface of calcite was investigated by using batch sorption and synchrotron X-ray standing wave (XSW) measurements. Artificial solutions containing various amounts of U (0.1 to 30 µg/mL) were used for reactions with either freshly cleaved calcite surfaces or with calcite powders, during various reaction times (ranging from 1 to 60 min). EDTA was added to the solutions to insure that no U-bearing phase precipitated before the reaction with calcite. Calculations of the U-speciation in the initial solutions showed that more than 95% of the U was complexed with EDTA, whereas $\text{UO}_2(\text{OH})^+$ and UO_2^{2+} represented a few percent. However, reaction path calculations showed that the U speciation changed as soon as the solutions reacted with calcite, to reach 100% of $\text{UO}_2(\text{CO}_3)_2^+$ complexes. The linear sorption isotherms obtained and the reproducibility of the results indicate that the uptake of U on the calcite was controlled by a specific surface reaction in our system.

The location of the U atoms adsorbed at the calcite (104) cleavage surface was examined with the XSW technique. Measurements were performed at the Advanced Photon Source on crystals reacted for 90 sec with U solutions (13 to 30 µg/mL U). Using the $\text{L}\alpha$ peak of U, five XSW measurements on the (104) Bragg reflection of the calcite surface were performed. The coherent fractions obtained range from 0.14 to 0.65. The coherent position values are consistently between 0.80 and 0.88, with a mean value of 0.84 ± 0.02 . This position corresponds to a distance between the U atom and the calcite (104) plane of $2.55 (\pm 0.06)$ Å. The coherent coverage calculated from the coherent fraction and the total coverage ranges from 0.03 to 0.2 monolayer. The position of the adsorbed U was independent of solution U concentration. The significant deviation of the U coherent position from the Ca^{2+} coherent position (= 0 or 1 for the (104) Bragg reflection) indicates that a substitution of Ca^{2+} by UO_2^{2+} is not the main mechanism probed here. In contrast, the distance between the adsorbed U atoms and the (104) cleavage plane of $2.55 (\pm 0.06)$ Å suggests that the U adsorption at the calcite surface could correspond to a surface complexation of the uranyl-carbonate complex with the longitudinal axis of the uranyl ion parallel to the calcite (104) plane.

PCMI : MOam12 : G6 Non-Dissociative Adsorption of Water at the Surface of Zircon: A Clue for the Origin of its Resistance to Dissolution

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Zircon is a mineral known to be highly resistant to dissolution in many geological processes, including weathering, metamorphism and anatexis. Since surface properties are known to control the dissolution rates of silicates, the properties of the surface of zircon were studied in order to better understand its high resistance to dissolution. We have investigated the interaction of aqueous species with the (100) face of zircon using first-principles quantum mechanical calculations. Adsorption energy of molecular water on the Zr Lewis site is 1.27 eV per molecule whereas the energy of dissociative adsorption is only 0.84 eV per molecule. The non-dissociative adsorption of water is thus strongly preferred with respect to the dissociative adsorption on the (100) face of zircon. Such behavior, which is related to the weak ability of the surface structure to relax, is changed by a 5 percent increase of the surface cell para-

eters. From our theoretical results, we propose that the exceptional resistance of zircon to dissolution may be related to the strong acidity of the Zr-O-Si bridging oxygen atoms, which promotes the associative adsorption of water on the (100) surface of zircon.

PCMI : MOam13 : G6 Parallel Computational & Experimental Studies of the Morphological Modification of Calcium Carbonate

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It is known that the specific crystallographic form of an inorganic crystalline material will determine its physico-chemical properties, e.g. solubility, catalytic activity, optical properties. Thus, there is the potential for functionally optimising crystalline solids through the use of additives and dopants, which can selectively change the habit to a specific morphology. Although the design and activity of tailor-made additives is now well established, a predictive link between habit and functionality has yet to be systematically investigated.

The objective of the present study was to use a wide range of additives to provide a well-defined directory of crystallographic forms. In this presentation we will concentrate on the first stages of the project; the morphological modification of calcite through the addition of dopant cations.

These experimental studies parallel computational studies of the solid state. The morphologies of crystalline materials can now be predicted using computer modelling based on lattice and surface energy minimisation techniques. However, both of these methods rely heavily on the availability of accurate interatomic potentials to map the cohesive forces within the material. Molecular ionic materials exemplified by carbonates and phosphates pose a particular problem since both the bonded and non-bonded interactions have to be accounted for in any potential model. There is, therefore, a need to address this issue and develop suitable potentials.

This paper will show that the morphology of calcite has been predicted successfully and its modification through the interaction of divalent cations modelled. The successful prediction of the crystal morphology of calcite is a crucial step towards understanding the controlled formation of this material generating predictive models for future studies of structure-property-function relationships in both inorganic and inorganic materials.

PCMI : MOam14 : G6 Structural Characterisation of Natural Actinides (Th and U) in Natural Ceramics and Analogues: XANES and EXAFS Studies on Natural Zircons

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Natural zircons (ZrSiO_4) show variable degrees of radiation damage. These minerals are considered as natural analogues for industrial for high-activity nuclear (Chakoumakos et al., 1987; Ewing et al., 1987; Weber, 1990; Hess et al., 1998). Industrial ceramics for nuclear wastes and natural analogues have both accumulated α -doses greater than 10^8 α /mg. The samples were previously characterised using x-ray diffraction, electronic microprobe analyses and SEM/TEM imaging. XANES/EXAFS spectra at the Th and U-L_{III} edges were collected at ESRF (Grenoble, France), on the new undulator beamline ID26 (Gauthier et al., 1999; Signorator et al., 1999).

In crystalline zircon (originally metamorphic, annealed at 1200°C), the oxygen first neighbours around Th are at an average inter-atomic distance similar to that measured in crystalline thorite: 2.41(5) Å (Taylor and Ewing, 1978). Similarly, we measured Th-Si pairs at 3.16(5) and 3.90(5) Å, as observed in crystalline thorite. In contrast to thorite structure, we have detected Zr 4th neighbours around Th. The EXAFS-derived Th-Zr distance (3.74(5) Å) is the closest to the Zr-Zr distance in zircon (3.64(5) Å) than the Th-Th

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distance in thorite (3.90(5) Å). Above 4Å around Th, oxygen 5th and 6th neighbours are observed at a distance similar to that measured around Zr in crystalline zircon. So, the substitution mechanism of Th in crystalline zircon suggests considering, not just a simple ionic replacement mechanism, but instead, a larger structural unit. i.e., ThO₈Si₂Si₄ moieties to replace ZrO₈Si₂Si₄ within the zircon structure.

In metamict zircon, the local structure around Th (including 4th neighbours) is not similar to that observed in crystalline. Atoms around Th are located at an average inter-atomic distance similar to that measured in crystalline thorite. In contrast to Th in crystalline zircon, no Zr 4th neighbours are detected at 3.70(5) Å. Instead, Th neighbours are measured at 3.90(5) Å. Several radiation-damaged zircons from different locations were studied. The local environment around Th changes from sample to other. It varies from a structure completely metamict to almost crystalline.

We analysed XANES data collected at the U-L_m edge for several zircons. Some edges (zircons from USA, Madagascar...) are shifted to higher values in energy by 6eV, as compared to that of uraninite (UO₂) which is a model for U(IV). Such a shift in energy position is characteristic of the presence of U(VI). The XANES spectrum is also characteristic of the uranyl group, U(VI)O₂²⁺. Uranyl groups cannot partition easily onto the bulk zircon, so, these moieties result from the oxidation of the original U(IV), probably related to the radiation damage and subsequent weathering. In spite of metamict state of some zircon (Naegy, Sri-Lanka, etc...) no oxidation of U(IV) is detectable. Therefore, U in such material is stable as U(IV).

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