

Volcanology, Geochemistry, and Petrology

V51A MCC: Hall C Friday 0830h

Applications of Synchrotron Radiation in Low-Temperature Geochemistry and Environmental Science I Posters (joint with H)

Presiding: P Fenter, Argonne National Laboratory; M Rivers, University of Chicago; N Sturchio, University of Illinois, Chicago; S Sutton, University of Chicago

V51A-1224 0830h POSTER

Local and Medium Range Order Around Fission Products in Inactive Waste Glasses: Implication for Glass Structure and Stability

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Borosilicate glasses are used to store high level nuclear waste in France (R7T7 glass). The structure of the glass around elements such as fission products controls important parameters as the homogeneity of the glass and/or the melted glass rheology. Data on the local and medium range order structure of these glasses could help improving the resistance toward leaching and/or irradiation, in relation with surface or geological storage of these vitrified wastes.

Due to the complex composition of these glasses (up to 30 oxides), chemically selective methods are required to understand the environment of elements. X-ray Absorption Spectroscopy (XAS) is, from this point of view, a powerful tool as it provides a direct access to the investigation of the structure around specific cations in this multicomponent amorphous material, to specify their role in the glass durability.

We will present different XAS studies (synchrotrons in LURE and ESRF, France) on the inactive amorphous analog for the R7T7 glass (the SON 68 glass). This report will illustrate the potentialities of this approach through the determination of the environment around fission products such as Zr, Zn and Mo. XAS shows the peculiarity of the sites occupied by these glass components of technological interest. Coordination numbers are shown to be systematically smaller than in crystalline compounds with close composition. Below the definition of the sites occupied by the chemical elements, XAS allows to detect some degree of medium range order which gives insight on the bonding of the site to the polymeric borosilicate network and allow to link precisely experimental data to theoretical calculations. Eventually, XAS is used to study the interaction between noble metals (Pd and Ru) and the glassy matrix. These elements are at the origin of small precipitates that induce changes in the melt viscosity. They occur as a result of the non-insertion of these elements in the glassy matrix. To accurate and precise structural interpretations, a direct comparison with MD calculations on simplified nuclear glass comprising 5 oxides, is performed.

V51A-1225 0830h POSTER

Periodic Density Functional Theory Calculations of Sr(II) and Zn(II) Adsorption onto the (110) Face of Rutile

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Periodic DFT energy minimizations were performed with Sr(II) and Zn(II) adsorbed onto the (110) face of rutile using the program CASTEP (Accelrys, Inc.). Ultra-soft pseudopotentials, an energy cut-off of 340 eV, the Generalized Gradient Approximation, and Perdew-Wang functionals were employed to calculate energies. A 3-layer thick slab of rutile (alpha-titanium dioxide) was relaxed in P2 symmetry with the central layer of atoms constrained to mimic the bulk experimental crystal coordinates. Both the Sr(II) and Zn(II) were surrounded by a solvation sphere of water molecules on the side opposite the rutile crystal face in order to approximate the water-mineral interface. Sr(II) was found to be stable in a quadridentate configuration bonded to two terminal Ti-OH oxygen atoms and two bridging (Ti-O-Ti) oxygen atoms with a distance of 2.5 Angstroms to the rutile surface. This configuration is essentially the same as that derived by Fenter and coworkers using X-ray standing wave (XSW) spectroscopy. Zn(II) was predicted to be stable in two configurations suggested by XSW spectroscopy: a monodentate complex to a bridging oxygen atom and a bidentate configuration bonded to two terminal Ti-OH oxygen atoms.

V51A-1226 0830h POSTER

XAS Monitoring of Zinc Scavenging in Layered Double Hydroxides (LDHs) and Phyllosilicates in Impacted Soils From Western Europe.

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Among trace metals, zinc is one of the most widespread in contaminated soils. Its phytotoxicity is well established and, as other trace metals, its mobility and bioavailability are strongly dependant of its chemical form (i.e. speciation). This parameter results from interactions between soluble species and reactive mineral and organic surfaces (phyllosilicates, hydrous Fe, Mn and Al oxides, humic substances) which cause the formation of sorption or surface-precipitation complexes.

Zinc speciation was followed in three european soils (France, Switzerland and England) impacted by pyrometallurgical activities or sewage sludge adding and differing in mineralogical composition (silty, carbonaceous clayey and sandy). Because of the low concentration for zinc in these soils (between 300 and 2500 mg/kg), conventional mineralogical techniques such as Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) failed at localizing this element at the micron scale and at determining its speciation. X-ray Absorption Spectroscopy (XAS), combined with selective chemical extractions, yielded evidences for the incorporation of Zn²⁺ in Zn/Al-layered double hydroxides (Zn/Al-LDHs) and/or Zn-bearing phyllosilicates as well as its sorption onto hydrous iron oxides and humic substances. In a silty French soil and in a clayey carbonaceous Swiss one (pH ranging from 5.5 to 8.0), Zn/Al-LDHs and Zn-bearing phyllosilicates were the most abundant Zn-bearing components. Their relative proportions were related to pH conditions, Zn/Al-LDHs occurring mainly in the soils with the highest pH. In a sandy English soil (pH 6.5), Zn-bearing phyllosilicates were found together with zinc sorption complexes on hydrous iron oxides. The relative proportion of these two Zn chemical forms depends on the depth of sampling, Zn-bearing phyllosilicates occurring in larger amounts in deeper horizons.

The ubiquity of Zn/Al-layered double hydroxides (Zn/Al-LDHs) and/or Zn-bearing phyllosilicates in Zn²⁺ scavenging in impacted soils, added to the possible incorporation of a large range of transition elements (Cr, Mn, Co, Ni, Cu) in these structures, emphasizes their potential for in situ remediation techniques. However, comparative thermodynamic and kinetic data about these minerals are lacking and further laboratory studies are needed to fill this gap.

?Deceased, 26 October 1999

V51A-1227 0830h POSTER

Synchrotron-Based Studies of Manganese Oxide Biomineralization

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Natural Mn oxide colloids and grain coatings are ubiquitous in the environment and profoundly impact the quality of soils and soil solutions via their ability to degrade and sequester contaminants. These oxides are generated via oxidation of Mn(II) by freshwater and marine bacteria and have extremely high sorptive capacities for heavy metals. Mn oxides readily oxidize a variety of recalcitrant organic and inorganic compounds. The mechanism(s) and products of bacterial Mn(II) oxidation are therefore believed to have deep and wide-ranging roles in the environmental cycling of trace metals, organics, and carbon.

We have utilized X-ray absorption spectroscopy (XAS) and synchrotron-based in-situ transmission XRD (SR-XRD) to probe the structure of fully hydrated biogenic manganese oxides produced by spores of the marine bacterium, *Bacillus* spp., strain SG-1. Biogenic oxides were produced in the absence and then presence of co-metal solutes Co(II), which have high affinities for Mn oxides, but present contrasting redox properties and coordination chemistries, thus providing greater probe capability. The primary biogenic product is a poorly crystalline solid similar to delta MnO₂ in which Mn has an oxidation state close to 4+. The structure of the oxide is analogous to acid birnessite, but with fewer layer vacancies and greater local order around Mn(IV). Co(II) is oxidized to Co(III) and incorporated at Mn(IV) sites in the octahedral layer. The presence of Co(III) alters the stability and structure of the host Mn oxides. This observation, combined with the very high sorptive capacity of the Mn oxides, imply that bacteria can exert tremendous influence over Co cycling in impacted waters via Mn oxide biomineralization.

V51A-1228 0830h POSTER

Condensed Layer Ion Positions at the Rutile(110)-Water Interface with High Brilliance X-rays

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We have used the technique of X-ray Standing Waves to measure the adsorption structure of Sr²⁺ and Zn²⁺ ions at a condensed layer at the rutile (110)-water interface. We find that the heights of these ions do not change with the ionic strength of the solution over a wide range. For Rb⁺ and Br⁻ ions, XSW measurements at low concentration (<1mM [Rb⁺] or [Br⁻]) show no significant adsorption at the interface. Through the measurements in distinct crystallographic directions, XSW triangulation can uniquely locate the 3D ion positions at the interface. And we find the adsorption site of the Zn²⁺ is different from that of Sr²⁺ and Y³⁺. We have also extended our analysis of these results to provide a direct, model independent mapping of the elemental distributions. This is the first use of this approach to produce a three dimensional image of a surface adsorbate sites. And the results are consistent with the XSW triangulation.

Sorption of Zn(II) and Co(II) on Rutile Surfaces from 25 to 250 Degrees Centigrade by pH Titrations: Impact of X-Ray Standing Wave (XSW) and EXAFS Studies on Electrical Double Layer Models.

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Experimental studies have been conducted on rutile powders (ca. 15 m²/g, 110 face dominant) in aqueous sodium trifluoromethanesulfonate (NaTr) solutions (0.03 and 0.30 molal) in a conventional glass-electrode autotitrator as well as a hydrogen-electrode concentration cell, which permits continuous pH-monitoring and sample removal for chemical analysis at elevated temperatures. The surface charge was determined in NaTr with and without 0.001 molal Zn or Co by pH titration, and separate experiments were conducted to determine the amount of metal ion adsorbed as a function of pH. These studies demonstrate that both cations are strongly sorbed, with the affinity for Zn being greater than that of Co. Ionic strength dependence of the sorption edges is very weak, and a combination of the two types of experiments indicates a proton release stoichiometry approaching 2:1 at high temperature. The pH of 50 percent adsorption for both ions decreases more rapidly with temperature than does the point of zero charge of the powder. X-ray Standing Wave measurements conducted on rutile 110 single crystal surfaces at the Advanced Photon Source (Zhang et al., this symposium) indicate that, at room temperature, Zn²⁺ binds predominantly as a monodentate species with surface oxygens bridged to two underlying titanium atoms. The zinc ions occupy positions equivalent to Ti lattice sites in the underlying crystal, resulting in a fixed distance of 3 above the Ti plane. Towle et al. (JCS, 1999, v217, 299) conducted EXAFS studies of Co²⁺ adsorption on rutile (110) and (001) single crystal surfaces and concluded that this ion also occupies an equivalent Ti site, though they could not distinguish between bridged and terminal sites. These geometrical constraints, coupled with proton binding constants predicted from our temperature-extended MUSIC model, are applied in Stern Layer EDL models. The synchrotron results provide unequivocal evidence for "inner sphere" adsorption at room temperature, presenting a challenge for modeling the observed strong increase in surface binding affinity with increasing temperature.

V51A-1230 0830h POSTER

The Utility of in situ X-ray Standing Wave Measurements to Help Constrain Surface Complexation Models

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Macroscopic ion adsorption data are typically rationalized with the aid of various Surface Complexation Models in which ion binding to surface functional groups is combined with various Electrical Double Layer (EDL) Models. However, model results are very loosely constrained with macroscopic data alone since many combinations of model parameters can adequately fit experimental data. X-ray standing wave (XSW) measurements help to greatly constrain possible model parameters since the location and bonding geometry of ions within the compact layer of the EDL can be precisely determined.

The utility of XSW in constraining Surface Complexation Models will be illustrated for the adsorption of Sr²⁺ on rutile. Macroscopic ion adsorption data are available for rutile powders (with the (110) crystal face dominant) from 25 to 250°C, and in 0.03 and 0.30m NaCl and RbCl media. Corresponding XSW measurements are available for single crystals of rutile terminated by the (110) crystal plane at 25°C. These XSW measurements indicate that Sr²⁺ is bound to 2 singly coordinated and 2 bridged surface hydroxyl groups in a tetradentate configuration, with the average distance from these groups being about 1.4 angstroms.

These XSW data can be accommodated by a MUSIC Model description of the rutile (110) surface combined with Stern based representation of EDL structure with the result that model fitting parameters for the rutile powder data are tightly constrained. Consequently, a major advantage of this combination of results is a more realistic description of EDL structure for the rutile (110) surface.

V51A-1231 0830h POSTER

Structure of the Hydrated Hematite (0001) Surface

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Chemical reactions at mineral surfaces play a major role in controlling the composition of surface and ground waters and strongly influence the transport of contaminant species. A key to understanding these reactions is detailed knowledge of the molecular-scale structure at the mineral-water interface. Of particular interest is the characterization of iron-(hydr)oxide surface structure and reactivity since these materials are often a dominant scavenger of contaminant species in aquatic systems. In this study we have investigated the structure of the hydrated α -Fe₂O₃ (0001) surface using crystal truncation rod (CTR) diffraction. The surface was prepared under heavily hydrating conditions which resulted in a predominantly hydroxyl terminated surface structure. Our results also suggest that the surface shows substantial relaxation of the surface atoms away from the bulk positions. Details of the surface model will be presented based on least-squares fits of the CTR data.

V51A-1232 0830h POSTER

EXAFS Study of Uranyl Complexation at *Pseudomonas fluorescens* Cell Surfaces

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Little is known about the roles of microbial biomass as a sink and source for uranium in contaminated aquifers, nor of the impact of bacterial biochemistry on uranium speciation in the subsurface. A significant role is implied by the high affinities of both Gram positive and Gram negative cells for binding uranyl (UO₂²⁺). In the present study, Extended X-ray Absorption Fine

Structure (EXAFS) spectroscopy was used to identify membrane functional groups involved in uranyl binding to the Gram negative bacterium *Pseudomonas fluorescens* from pH 3 to pH 8. Throughout this pH-range, EXAFS spectra can be described primarily in terms of coordination of carboxylic groups to uranyl. U-C distances characteristic of 4-, 5- and 8- membered rings were observed, as well as the possibility of phosphato groups. Both shell-by-shell fits and principle component analyses indicate that the functional groups involved in binding of uranyl to the cell surface do not vary systematically across the pH range investigated. This result contrasts with EXAFS results of uranyl sorbed to Gram positive bacteria, and suggests an important role for long-chain carboxylate-terminated membrane functional groups in binding uranyl.

V51A-1233 0830h POSTER

Structure and Dynamics of Mineral/Water Interfaces: Molecular Dynamics Simulations of Clays and Clay-Related Phases

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The nanoscale structural ordering and the dynamics of water molecules at the mineral/water interfaces and in the interlayer regions of clays and other layered materials can affect the surface reactivity of these phases, their ability to adsorb and intercalate various solution species, and their swelling behavior. New developments in the synchrotron X-ray reflectivity measurements (Fenter et al., 2000; Cheng et al., 2001) have recently allowed experimental investigation of the atomic density oscillations in water adjacent to mineral surfaces, thus providing novel, nanoscale information about the structure of interfacial water. However, for many important phases, adequately large, clean and defect-free surfaces suitable for such measurements are difficult or impossible to obtain. Atomic density profiles calculated from molecular dynamics (MD) computer simulations can be directly correlated to the experimental information and also offer the ability to investigate materials for which experiments are not possible. Thus, a combination of the experimental and computational approaches can provide significant new quantitative insight into the atomic-scale interpretation of the observed interfacial phenomena and the effects of mineral surface structure and composition and the composition of the interfacial solution.

We have performed a series of MD simulations to study the structure, ordering, and dynamics of water molecules and a variety of dissolved aqueous species at the surfaces of kaolinite, pyrophyllite, montmorillonite, beidellite, brucite, portlandite, gibbsite, and several anionic clays (layered double hydroxides). The structure and composition of the substrate control the structure and molecular ordering of interfacial water, the effective diffusion rates of surface-sorbed species, their residence times, and translational and librational dynamics. At some surfaces, H₂O molecules donate hydrogen bonds to surface atoms and also accept H-bonds from the surface OH groups, thus developing a well interconnected H-bonding network within the interfacial layer of the aqueous phase in contact with the surface. However, at many surfaces H₂O molecules can only serve as either acceptors or donors of H-bonds, and in some cases H-bonding with the surface does not occur. The simulation results are in good qualitative agreement with experimental sorption, X-ray, and NMR measurements. An attempt has been made to simulate electron density profiles across the mineral/water interfaces that can be directly compared with synchrotron X-ray reflectivity observations.

V51A-1234 0830h POSTER

Microbial Reduction of Elemental Selenium to Selenide in Anoxic Sediments - A XANES Study

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Elemental selenium [Se(0)] is the dominant species of selenium present in anoxic sediments. The forms of Se in sedimentary rocks similarly contain high proportions of Se(0), but much of the Se is also in the form of metal selenides, Se(-II). It is not clear if the occurrence of these selenides is due to microbial reduction of Se(0), or a purely chemical process. In this study, we examined the Se redox state of San Francisco Bay sediments that were amended with chemically-formed amorphous Se(0) [Se(0)_{Chem}], biologically-formed amorphous Se(0) [Se(0)_{Biol}], chemically formed black crystalline Se(0) [Se(0)_{Black}] and selenite [Se(IV)] by analyzing the Se XANES spectra in the region 12620-12700 eV. Additions of lactate were used to stimulate activity, while formalin was used as a poisoned control. Samples of the sediment slurries were taken over a period of 95 d. The sediments were centrifuged and loaded into acrylic sample holders in an anaerobic chamber. The sample spectra were fitted with up to three standards with the R-Space X-ray Absorption Package. The standards providing the best fits to the samples were the Se(0) form added to the sediments, selenocystine, FeSe(-II), and Se(IV). For samples amended with Se(0)_{Chem}, first order Se(0) reduction rate constants ranged between 0.11 to 0.025 d⁻¹, and only slight stimulation was found in lactate amended samples. A slightly higher initial reduction rate constant was found for samples amended with Se(0)_{Biol}, while rapid reduction of Se(IV) to Se(0) and selenocystine was observed in the sample with Se(IV). No change in the Se(0) spectrum was observed for samples killed with formalin. The significant proportion of sedimentary Se(-II) as revealed by Se XANES spectra compared to freely soluble Se(-II) concentrations measured by ICP-MS or acid volatile Se(-II) indicates most of the reduced Se was present in the solid form. These results confirm our earlier findings that bacteria are capable of reducing Se(0) to Se(-II), and gives a microbial mechanism to explain the presence of selenides in sedimentary rocks.

V51A-1235 0830h POSTER

Zn Speciation in two Fe-Mn Banded Systems

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We have used micro-EXAFS spectroscopy to study the speciation of Zn in two shallow-water Fe-Mn banded structures. One of the samples is from the Baltic Sea and contains anthropogenic Zn in a matrix which is believed to be banded due to annual oscillations in oxygen content, pH and other variables of water chemistry (Hlawatsch, et. al., 2002). The other sample, from Akayu Hot Springs off the coast of a volcanic island (Satsuma-Iwo Jima) at the southern tip of Japan, is a hardened biomat in which the compositional oscillations are at least partly due to bacterial action, and in which the Zn content is natural (Tazaki, 2000). By using a beam as small as 5 μm in diameter, we can look at details of metal distribution and speciation on a spatial scale much finer than the banding, which has wavelengths of order 100 μm. In both samples, the Zn is associated with the high-Mn layers, though the layer-to-layer contrast is lower in the Japan sample. However, the speciation of Zn is different in the two samples. The Baltic sample shows Zn only in one form - sorbed on a layered phyllosulfate resembling birnessite with Zn tetrahedrally coordinated and sorbed to vacant octahedral sites of the Mn layer. This species was also found in soil (Manceau et. al., 2000). The Japan sample also has tetrahedral Zn in birnessite-like phyllosulfate as well as Zn in at least two other forms. The phyllosulfate species is thus seen to be a ubiquitous sink for Zn in the environment. We will discuss some possible reasons for the differences and similarities of Zn speciation in these two systems.

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long-term environmental changes. *Chemical Geology*, 182 697-709.

Manceau A., Lanson B., Schlegel M.L., Hargé J.C., Musso M., Eybert-Bérard L., Hazemann J.L., Chateigner D., Lamble G.M. (2000) Quantitative Zn speciation in smelter-contaminated soils by EXAFS spectroscopy. *American Journal of Science*, 300, 289-343.

Tazaki, K. (2000) Formation of banded iron-manganese structures by natural microbial communities. *Clays and Clay Minerals* 48 511-520.

URL: <http://xrayweb.lbl.gov/uxas/index.htm>

V51A-1236 0830h POSTER

Synchrotron Spectroscopic Studies of the Reaction of Cleaved Pyrite (FeS₂) Surfaces with Cr(VI) Solutions

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Pyrite is one of the most common sulfide ores, and the separation of valuable sulfide minerals from it has been an area of considerable interest for a long time. This extraction has led to a large quantity of pyrite waste, typically remaining in mine tailings piles which can interact with oxygen and surface water. The oxidation of pyrite under these conditions leads to the commonly known environmental problem of acid mine drainage, with acidification of surface waters, and the release of potentially toxic metals remaining within the pyrite matrix. A microscopic understanding of this oxidation process is extremely important and has been the aim of a number of studies.

We apply the methods of synchrotron based surface science to this problem, utilizing surface sensitive photoemission and X-ray absorption spectroscopy to study the surface species present on the pyrite surface at the initial stages of oxidation. We have reacted pyrite surfaces with solutions containing chromate. Chromium exists in solution in two principal valence states, trivalent Cr(III) and hexavalent Cr(VI). Hexavalent chromium is itself considered an environmental problem due to its high toxicity and solubility, and thus mobility, whilst trivalent chromium is much less toxic and relatively insoluble. Hexavalent chromate is a strong oxidizing agent, and will react rapidly with the pyrite surface allowing the identification of oxidized iron and sulfur surface species. The possibility of using pyrite as a means of reducing chromate, and at the same time using chromate to passivate the pyrite surface to further oxidation through the buildup of a non-reactive iron-chromium (oxy)hydroxide layer will be investigated.

The work was performed on rods cut from a natural pyrite single crystal from the Logroño region of Spain. The rods were then fractured over a reaction vessel, producing a fresh (100) surface for each experiment. The pyrite surfaces were reacted with 50 μM Cr(VI) solutions for 5 minutes at pHs of 2, 4, and 7. Additional studies were performed at pH 7 with 50 μM Cr(VI) for durations of 1 minute to 38 hours, and with 5 mM Cr(VI) for 30 seconds. Photoemission and X-ray Absorption Near Edge Structure (XANES) spectroscopies were performed under UHV conditions at beamline 10-1 at the Stanford Synchrotron Radiation Laboratory (SSRL).

These studies show that chromate is an effective oxidizing agent for the pyrite surface and that oxidation products can be trapped on the pyrite surface under a reduced chromium layer. Sulfur 2p photoemission identified sulfate, sulfite and zero-valent sulfur species on the pyrite surface. The features due to sulfate and sulfite are broad and were fitted using a single broad envelope which may include contributions from disorder and varying degrees of hydration. Iron 2p photoemission and L-edge XANES showed that very minor amounts of iron (III) remain on the surface indicating that this species is rapidly lost into solution. The chromate was reductively sorbed onto the pyrite surface forming a (oxy)hydroxide layer which ultimately passivates the surface towards further chromium reduction or pyrite oxidation.

We utilized synchrotron based PES and XAS to show that chromate is reductively sorbed at the pyrite surface, and that the pyrite oxidation products can be observed under a chromium (III) containing layer. These preliminary results indicate that reacting pyrite with Cr(VI) may play the dual role of reducing chromate and passivating pyrite surfaces towards oxidation.

V51A-1237 0830h POSTER

Structure of the Fluorapatite (100)-Water Interface by High Resolution X-ray Reflectivity

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For more than two decades it has been noted that a complete understanding of the surface chemistry and dissolution dynamics of the apatite-water system requires direct observation of interfacial structure at the molecular scale. Here we provide the first results on the structure of the apatite(100)-water interface using high resolution x-ray reflectivity. The specular x-ray reflectivity from a natural growth surface of Durango fluorapatite was measured at beamline, 11-ID-D (BESSRC-CAT, Advanced Photon Source). The natural growth surface exhibits a uniform crystallographic termination corresponding to the unit cell border of the apatite crystal. Atomistic model of the interfacial structure were obtained by comparing the experimental results with calculated reflectivities and optimized through non-linear least-square fitting, in which the structural parameters were selected to be both physically and chemically plausible. The derived structure indicates the presence of a surface hydration layer at the apatite-water interface which is formed through the adsorption of water molecules on the solid surface.

V51A-1238 0830h POSTER

Carbon K-Edge Scanning Transmission X-ray Spectromicroscopy (STXM) of Uranium Binding to Bacterial Cells

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The sorption of uranium by bacteria was studied by interrogation of the C K-absorption edge using scanning transmission x-ray spectromicroscopy (STXM). The unique imaging and spectroscopy capability of STXM was used to elucidate the chemical environment of C in the bacterial cell. Washed whole cells and cell wall preparations of bacteria commonly found in soil environments including *Pseudomonas fluorescens*, *Bacillus subtilis*, the facultative anaerobe *Shewanella putrefaciens* and the strict anaerobe *Clostridium* sp. were exposed to uranyl nitrate at pH 5. After washing to remove potential surface precipitates and non-bonded uranium the cells and walls were dried onto TEM grids. Standards (uranyl salts and organic complexes), bacterial cells unexposed, and U-exposed cells were analyzed by STXM at 280-310 eV with the C K-edge x-ray absorption near-edge spectroscopy (XANES) examined for evidence of U in the C coordination environment. Principle spectral features of the bacteria included the 285 eV C=C and 288 eV C=O 1s-π* resonances due to the major C function groups that comprise the bacterial cell wall. There was no change in peak position of 1s-π* spectral features for whole cells or cell walls when U was present. This indicates that U does not exert an influence on the electron resonance of C when bonded as carboxylate species at the bacterial cell surface. This finding is supported by the analysis of uranyl citrate and uranyl alanine standards. The extended x-ray absorption fine structure spectroscopy region of the C K-edge of bacterial cells exposed to U shows slight changes in spectral features at >290 eV. Other absorption edges accessible by soft x-ray spectroscopy were examined; U was detected at its N_V (736.2 eV) and N_{IV} (778.3 eV) edges however there was poor resolution of U associated with the bacteria. Analysis at the O K-edge (529 eV) provided evidence for metal-ligand interaction and forms

the basis for further study to gain a molecular-level understanding of actinide-bacterial cell association using soft x-rays.

V51A-1239 0830h POSTER

EXAFS Analyses of Innersphere Surface Complexations of Arsenate and Silicate on Natural Hydrous Ferric Oxides

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X-ray absorption spectroscopy (EXAFS) was used to determine the near range order of three elements (Fe, As, Si) on the surface of hydrous ferric oxide (HFO) from thermal water scales. Fe K-edge EXAFS analyses of the 2nd shell show a better fit including Si as backscattering neighbor. Validation of the Si-Fe bond was obtained by Si K-edge EXAFS spectra, where the light absorber element is surrounded favourably by much heavier second-shell elements. Least-squares fitting of the second-shell Fourier-filtered EXAFS spectrum in the k-range of 5-11 Å⁻¹ yields in a Si-Fe distance of 3.10-3.13Å, and a Si-Si distance of 3.00Å. Both these interatomic distances and the coordination number N = 2 obtained for the Si-Fe shell are consistent with the formation of a corner-bridging bidentate binuclear (²C) surface complex on the HFO surface. The Si-Si bonds and existence of a vibrational band at 964 cm⁻¹ in the infrared spectrum indicate polymerisation of the silicate on the HFO surface (Tommaseo & Kersten). As K-edge XANES analyses showed the As present in form of arsenate scavenged by the HFO phase. As and Si K-edge EXAFS analyses revealed both elements to compete for ²C surface complexation sites. A mean As-Fe distance of 3.03Å indicate an approx. equal distribution of arsenate between ²C (3.24Å) and another ¹E (bidentate mononuclear surface complexation) sites (2.84Å). The average Fe-(O,OH) bond length of 2.09Å is compatible with a high proportion of distorted surficial Fe^{III}(O,OH)₆ octahedra in the colloidal HFO precipitates of the scale deposits. The slight distortion of the Fe^{III}(O,OH)₆ octahedra is consistent with the apparent strong binding of the ¹E arsenate surface complexes (Manceau, 1995). The adverse effect of silicate would therefore be overpredicted without surface complexation models constructed to account for both surface functional groups. The Si K-edge EXAFS data provide also a basis for explaining at the molecular level the poisoning of HFO particle growth and the slowing down of the transformation of HFO to crystalline goethite. The inhibition of crystal growth by both oxoanions form a kind of passivation layer which protects HFO from recrystallization and concomitant release of part of the arsenic upon otherwise rapid ageing in the thermal waters.

LITERATURE

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V51B MCC: Hall C Friday 0830h

Metamorphism, Ultrahigh Pressure Metamorphism, and Diamonds Posters

Presiding: S Sorensen, Smithsonian Institution; L A Taylor, University of Tennessee

V51B-1240 0830h POSTER

Deformation, Fluid-Rock Interaction, and REE Equilibration in Eclogite and Garnet Amphibolite

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The intensity of fluid-rock interaction and deformation within an accretionary wedge vary over time. Both could affect trace element equilibration between slab protoliths and exotic components. We studied REE in garnet, epidote, apatite and titanite. These minerals, and 7 host samples of relatively dry, coronitic and mylonitized eclogite from the Monviso (M) and Voltri (GdV) massifs in the Alps, and of fluid-rich, less- and more-mylonitized eclogite from the Franciscan Complex (FC), California, were analyzed by LA-ICP-MS. INAA mineral and rock data for clinopyroxene-bearing and migmatitic garnet amphibolites from the Catalina Schist (CS), southern California, compare an extremely fluid-rich setting.

Whole-rock-normalized plots and budgets show that these 4 minerals contain most of the REE in the rocks. Chondrite- and whole-rock-normalized REE patterns show garnets depletion of LREE relative to HREE. The REE patterns of other minerals vary more. Most complement garnet, with LREE-richer, HREE-poorer patterns, but LREE abundances and fractionations also reflect the assemblage. For example, retrograde epidote from one dry Alpine eclogite shows the LREE of former apatite; epidote in another sample shows garnet-like LREE. Deformed samples yield similar results to coronitic ones. These features suggest closed system partitioning of REE among garnet, epidote, and apatite on the thin section scale, and preservation of protolith REE contents. Fluid-rich FC samples yield similar conclusions. In contrast, migmatitic CS garnet amphibolites, which manifest intense fluid-rock interaction, show trace element disequilibrium among garnet, titanite, and apatite. This probably reflects lack of equilibration with very REE-rich hydrothermal epidote.

During high P/T metamorphism, in both fluid-poor and fluid-rich terranes (M, GdV, F), deformation neither creates nor enhances disequilibrium REE distributions amongst garnet, epidote, apatite, and titanite in eclogite. However, extremely fluid-rich migmatitic garnet amphibolites (CS) testify to both disequilibrium and bulk REE addition. Only extreme fluid-rock interaction greatly disturbed REE systematics of slab rocks from these paleosubduction zones.

V51B-1241 0830h POSTER

The effects of deformation mechanisms on thermobarometry of plagioclase-bearing metamorphic rocks.

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The development of Garbenschiefer texture (large, radiating hornblende porphyroblasts) in the Greiner zone of the Eastern Alps resulted from complex interactions between deformational and metamorphic processes (Steffen et al. 2000, *GSL spec pub* 186). These interactions produced a wide variety of matrix plagioclase zoning types, even within individual samples. An understanding of the nature and timing of the processes responsible for the formation of plagioclase zoning relative to equilibration with other phases is critical to the accurate interpretation of thermobarometric calculations.

Four plagioclase types are preserved in the Greiner Zone: (1) Coarse (50-200 micron), concentric zoned plagioclase (cores: An5-20; rims: An25-35) with high dislocation densities that accommodated strain via Regime 2 dislocation creep. (2) Fine-grained plagioclase (20-75 microns) with low dislocation densities that experienced moderate amounts of grain-boundary diffusion creep (GBDC, a grain-size sensitive, fluid-mediated strain accommodation process); plagioclase 2 shows chaotic zoning with rim compositions of An15-40. (3) Chemically homogeneous (An30-35) and dislocation-free plagioclase that experienced pervasive GBDC. (4) Homogeneous (An30-35), 30-200 micron plagioclase that formed during late hbl breakdown. Model pressures calculated from An+Ab+Act = Gro+Pyr+Parg+Qtz equilibria at 575°C using rim compositions of each plagioclase type are (1) 6-7 kbar, (2) 3-7.5 kbar, (3) 3-4.5 kbar and (4) 3-4.5 kbar. Only the plagioclase 1 pressures agree well with other estimates for these rocks. Despite the high diffusion rates associated with GBDC, 'new?' and 'relic?' plagioclase 2 compositions are randomly distributed and it is not possible to determine a priori which compositions represent equilibrium with other mineral phases. Regime-3 dislocation creep is also likely to produce scattered P-T results. Plagioclase 3 values likely reflect ongoing plagioclase GBDC after growth of other minerals ceased, and are hence spurious. Plagioclase 4 values may represent conditions of the hbl-out reaction. P-T and P-Tt-path calculations are thus sensitive to changes in deformation mechanism during metamorphism. Understanding the deformational processes that prevailed during metamorphism (determined from grain size and shape, chemical zoning patterns, and dislocation density) is an essential precursor to selection of appropriate mineral compositions for P-T calculations.

V51B-1242 0830h POSTER

Evolution of Himalayan Metamorphism and the Genesis of Inverted Metamorphic Gradients: Evidence From the Sutlej Valley, NW India

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An inverted metamorphic gradient is commonly preserved where the high-grade Greater Himalayan Crystalline Sequence (GHCS) overthrusts the Lesser Himalayan foreland. This structural break (the Main Central Thrust, or MCT) is a key feature of Himalayan tectonics, generally considered to have taken up at least 200-300 km of shortening since the Early Miocene. The timing of displacement along the MCT and its relationship with inverted metamorphism is debated, with existing temperature inversion models requiring either (a) post-metamorphic faulting along young shear zones; (b) continual or episodic syn-metamorphic thrust development; or (c) single phase pre- to syn-metamorphic thrusting and subsequent thermal relaxation. Here, we use the P-T-t evolution of individual rock samples to study the contrasting histories of the GHCS and LHS units and deduce the relationship between metamorphism and thrusting.

The Sutlej River Valley exposes an inverted metamorphic succession consisting of a 9-km thick amphibolite-facies core (the GHCS), structurally underlain by greenschist and amphibolite-facies Lesser Himalayan Sequence (LHS) metapelites which preserve garnet-in, staurolite-in and kyanite/sillimanite-in isograds. The GHCS displays kyanite-in and sillimanite-in isograds, with migmatization at the top of the sequence. A major thrust-zone (interpreted as the MCT) separates the LHS from the GHCS.

The application of rim-thermobarometry to Sutlej samples identifies both the inverted metamorphic gradient in the LHS and GHCS units, and the inherent frailty of cation-exchange thermobarometers when studying high-grade rocks that have been subjected to subsequent retrograde diffusion. The construction of pseudosections and contouring of mineral composition isopleths, however, identifies the PT-paths that both units have taken, allowing a detailed reconstruction of the burial and uplift histories of the units that constitute the MCT-zone. Pseudosections in the systems KFMASH and MnKFMASH suggest that upper regions of the GHCS reached an early (pre initiation of MCT slip?) kyanite-grade peak, before undergoing decompression to ≈ 0.7GPa and further heating to ≈ 750°C. Staurolite-grade LHS samples, however, reached a syn-kinematic peak of ≈ 650°C, before subsequent decompression and cooling. This suggests that (a) whilst GHCS metamorphism was early, LHS metamorphism is intrinsically linked with the MCT; and (b) MCT-zone activity was either prolonged, or the thrust was reactivated after a period of quiescence, as suggested for the central Nepalese Himalayas by Catlos *et al.*, 2001.

V51B-1243 0830h POSTER

Geology of the Acasta Gneiss Complex in Slave Province, northern Canada: Appreciating new geological evidence of the oldest rocks in the world

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We made three types of geological and sketch maps in the Acasta Gneiss Complex in western Slave Province in 2000 and 2002. One is 1:5,000 geological map of 8x8 km² whole region, second is 1:1,000 geological map of 2x2 km² main area, and others are 1:100 to 1:10 sketch maps of many geological critical areas. In addition, we collected about 1,000 rock samples all over the Acasta Gneiss Complex. The Acasta Gneiss Complex comprises mainly of Gray Gneiss, White Gneiss, and Foliated Granite, with many apatite and basaltic intrusions. Gray Gneiss occurs as enclaves within White Gneiss and Foliated Granite, in the range from 3x1 km² to 10x10 km² in scale. They form block, boudin