

V61B-1371 0830h POSTER

Magmatic Chimney Beneath Telaga Bodas Revealed by Magnetotellurics Profiling: A Case Study at the Karaha Bodas Geothermal System, Indonesia

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Karaha-Telaga Bodas is a partially vapor-dominated geothermal system located on the flanks of Galunggung Volcano in Java, Indonesia. Fumaroles, hot springs and a shallow acid lake occur at the southern (Telaga Bodas) end of the geothermal area. Enrichments in chloride, fluoride, and sulfur in the lake water and the presence of tourmaline, fluorite, and native sulfur at depth are related to the flux of magmatic gases. Here, temperatures as high as 350 degree C are found at depths of about 2 km. A magnetotellurics profile crossing the Telaga Bodas area is used to test for presence of a magmatic chimney, which is believed to be the source of the magmatic components. The profile was modeled on a grid having 248x48 cells with 46 closely spaced stations aligned along NW-SE direction. The TM mode and vertical H-field data were rotated to strike of 10 degree east and inverted with a 2-D algorithm which damps model departures from an a-priori 1-D structure. The dataset consists of 25 periods running from 0.01024 to 1024 seconds yielding an RMS of 2.3. Five distinctive resistivity features are recognized: (1) resistive thin layer at the surface (about 1.5 km asl); (2) conductive layers sloping to the NW and SE; (3) a slightly resistive region in the center encapsulated by the conductive layers; (4) a vertical conductive structure inside the slightly resistive region; and (5) a resistive basement starting from 2 km below sea level. The sloping conductive layers (< 10 Ohm.m) are interpreted as representing clay-rich and/or weathered layers that exist for cap rock over the geothermal system whereas the slightly resistive region in the center corresponds to altered volcanic rocks and the underlying intrusives. The width of these volcanic rocks varies from about 2 km at their top to about 5 km at their base. The chimney is represented by a vertical conductive structure (< 10 ohm-m) inside this slightly resistive region. The size of the chimney is about 1 km wide and 2.5 km high. The low resistivities are interpreted as representing the presence of advanced argillic alteration assemblages formed by interactions between magmatic sulfur dioxide and the surrounding geothermal waters. The profile suggests that the gases migrate upwards through a vapor-dominated magmatic chimney overlying a cooling intrusion.

V61B-1372 0830h POSTER

Possible earthquake-generated wave deposits near Yellowstone Lake: Clues into triggering mechanisms of a large hydrothermal explosion crater

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Yellowstone National Park has experienced numerous hydrothermal explosions in the past and there is no reason to suggest that such activity will diminish in the future. Craters and associated breccia deposits created from hydrothermal explosions are mapped as Holocene units throughout the Park, primarily within the 0.64-Ma Yellowstone caldera. The largest hydrothermal explosion crater in Yellowstone, referred herein as the Mary Bay explosion crater complex, has a diameter of 2 km by 1 km and is nested in Mary Bay in the northern basin of Yellowstone Lake, an area where extremely high heat flow values are measured. Formation of hydrothermal features in Yellowstone is related to convective meteoric hydrothermal fluid circulation above a magma chamber. Hydrothermal explosions result from accumulation and release of steam generated during

hydrothermal fluid ascent, possibly reflecting changes in confining pressure that accompany and may accelerate failure and fragmentation of overlying lithologies. Sealing of surficial discharge conduits due to hydrothermal mineral precipitation contributes to overpressuring and catastrophic failure.

Exposed in wave-cut cliffs along Mary Bay north of Yellowstone Lake is a sedimentary sequence, which gives insight into the history of the Mary Bay hydrothermal explosion event. A sequence of lake sediments overlain by the Mary Bay hydrothermal explosion deposit is separated locally by an unusual dark, well sorted, cross-bedded, fine-grained sand layer. This unit is 1.5 to > 2 meters thick and contains numerous small en echelon faults. We conclude that this sand represents a deposit from an earthquake-generated tsunami-like wave, which in turn triggered the explosion of the Mary Bay crater complex. The potential of an event like this occurring today is currently under evaluation.

V61B-1373 0830h POSTER

Hydrothermal Vents in Yellowstone Lake: Chemical Fluxes, Siliceous Deposits, and Collapse Structures

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The geochemistry of Yellowstone Lake is strongly influenced by sublacustrine hydrothermal vent activity. The hydrothermal source fluid is identified using Cl and dD data on water column and sublacustrine hydrothermal vent fluid samples.

Silica-rich hydrothermal deposits occur on the lake bottom near active and presently inactive hydrothermal vents. Pipe- and flange-like deposits contain cemented and recrystallized diatoms and represent pathways for hydrothermal fluid migration. Another major type of hydrothermal deposit comprises hard, porous siliceous spires up to 7 m tall that occur in 15 m of water in Bridge Bay. Bridge Bay spires are hydrothermal silica deposits formed in place by growth of chimney-like features from lake-bottom hydrothermal vents.

The Cl concentrations indicate that Yellowstone Lake water is about 1 percent hydrothermal source fluid and 99 percent inflowing stream water and that the flux is about 10 percent of the total hydrothermal water flux in Yellowstone National Park. With recent swath-sonar mapping studies that show numerous new hydrothermal features, Yellowstone Lake should now be considered one of the most significant hydrothermal basins in the Park. Many lake-bottom hydrothermal vents occur in small depressions that are clearly imaged on multi-beam sonar, some of which are interpreted as collapse structures based on seismic reflection data. Sediments collected from such vents show chemical evidence of leaching of 60-70 wt. percent SiO₂, which may result in volume reductions up to 80 percent and provides a mechanism for vent structure formation.

V61B-1374 0830h POSTER

Equilibrium Distribution of Common Geologic Fluids in Anhydrite Aggregates

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Anhydrite rocks are commonly associated with salt domes where they are believed to form an impermeable caprock that arrests or traps migrating hydrocarbons. In addition, salt domes have been proposed as potential repositories for nuclear and toxic chemical wastes. In both settings, the most important consideration is the relative mobility of common geologic fluids within and through the anhydrite rocks.

The relative mobility of fluids in unfractured rock is directly related to the equilibrium distribution of the fluid, as predicted by the solid-fluid dihedral angle (Θ). In this study, anhydrite-fluid dihedral angles were measured for a series of anhydrite aggregate samples experimentally equilibrated with common geologic fluids. The starting material was a natural anhydrite aggregate (Wandflue) that was pre-annealed at

500°C and 100 MPa for 7 days to ensure an equilibrium texture and to remove unwanted volatile components (especially H₂S). The samples were then loaded with ~5 wt% of either water, 6M NaCl brine, or CO₂ (as silver oxalate powder) and run at 300°C to 600°C and 100 MPa for 1 day (brine, 600°C) to 2 weeks (CO₂). The anhydrite-fluid dihedral angles were measured from SEM images using NIH Image software and standard protocols.

The preliminary results indicate that in anhydrite aggregates under the conditions of our experiments, CO₂ fluids are unlikely to be interconnected ($\Theta > 60^\circ$), pure water may show some degree of interconnectedness ($\Theta \sim 60^\circ$), and brines are likely to be interconnected along three-grain channels ($\Theta < 60^\circ$), especially at lower temperature (300°C to 400°C). Additional experiments using mixed water-CO₂ and brine-CO₂ fluids are underway. However, the results to date clearly raise important questions as to the suitability of anhydrite rocks for retention of waste materials in a salt dome environment.

V61C MCC: 122 Saturday 0830h

Applications of Synchrotron Radiation in Low-Temperature Geochemistry and Environmental Science II (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

V61C-01 0830h INVITED

Quantitative analyses of pore-scale multi-phase flow processes: An application of synchrotron-based micro-imaging in the environmental sciences

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Our current understanding of groundwater flow and contaminant transport in the subsurface is, to a large degree, limited by existing measurement techniques. To correctly describe transport of contaminant species, it is essential to understand the interplay of advection, mechanical dispersion, and diffusion and their dependency on soil water distribution, degree of saturation, as well as gas-liquid phase contact characteristics. However, these pore-scale mechanisms cannot be measured with traditional experimental techniques. X-ray computerized microtomography provides non-invasive pore-scale observation of variables such as changing fluid phase content and distribution, as well as interfacial area and curvatures. We present results obtained at the microtomography facility at GSECARS (sector 13) at the Advanced Photon Source, Argonne National Laboratory. Samples of 6-7 mm diameter sand or glass bead packs were scanned at different stages of drainage and imbibition and with varying boundary conditions. We observed significant differences in fluid saturation and phase distribution for different boundary conditions, clearly showing preferential flow and a dependence on the applied flow rate. Individual pores, water/air interfaces and their curvatures as a function of pore-water pressure were resolved and the interfacial areas quantified using image analysis techniques. We plan to use this detailed information to verify existing pore-scale numerical models and to aid development of new modeling approaches dealing with contaminant flow and transport in the subsurface.

Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38.

URL: <http://www.er.dtu.dk/homepages/dw>

V61C-02 0850h INVITED

EXAFS Characterization of Uranyl Interaction at the Calcite-Water Interface

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Recent studies using X-ray absorption and luminescence spectroscopies have demonstrated uptake and incorporation of uranyl by calcite. X-ray microprobe studies on uranyl-reacted calcite single crystals reveal that uranyl exhibits preferences for specific surface sites. These preferences are likely expressed upon adsorption of uranyl species at the calcite-water interface. We have used X-ray absorption fine structure (EXAFS), combined with luminescence spectroscopy, to characterize the interactions of uranyl carbonate species with the calcite surface in the pH range 7.4-8.3. To minimize the potential for dissolution or precipitation, solutions were pre-equilibrated with reagent calcite powder for 3 weeks, with pH stabilizing at 8.3. For other experiments, the pH was adjusted initially to achieve a final pH of 7.4 after aging for 3 weeks. Uranyl carbonate solution was added to the pre-equilibrated suspensions to achieve initial U(VI) concentrations ranging from 5 μ M to 5 mM. Suspensions were filtered to recover the calcite, but were kept moist to retain the sorbed complexes at the calcite-water interface. Multiple EXAFS spectra were collected using a multi-element Ge detector at beamline 12-BM at the APS and analyzed using standard methods.

Fourier transforms (FT) of the spectra contain features corresponding to two axial oxygens and a shell of equatorial oxygens, as well as weaker features at higher R. For suspensions having initial U(VI) concentrations from 5-100 μ M, a shoulder is observed in the FT on the high-R side of the equatorial oxygen, and fitting suggests minor splitting of this shell. For higher initial U(VI) concentrations, including the highest U(VI) concentration, 5 mM, the splitting becomes more pronounced. Weak features in the FT at higher-R can be fitted with backscattering from carbon, oxygen, and calcium shells, although fits without calcium provide nearly the same agreement.

Luminescence spectroscopy reveals the presence of multiple uranyl species sorbed on the calcite from suspensions with 100 μ M U(VI) and lower concentrations. The presence of multiple species may account for the splitting of the equatorial coordination indicated by EXAFS. For higher U(VI) concentrations, the luminescence results are consistent with formation of a schoepite-like precipitate. Understanding the complex interactions of uranyl at the calcite-water interface requires complementary data from multiple techniques.

V61C-03 0910h INVITED

Illumination of Cation Sorption Mechanisms on Muscovite Using X-ray Reflectivity

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Detrital phyllosilicates and clays are major sorbents for contaminants, natural organic matter, and nutrients in soils and sediments, yet our knowledge of sorption mechanisms is largely based on data obtained at the macroscopic scale. Synchrotron-based X-ray reflectivity is used to determine the structure of sorbates with respect to the mineral surface and, in contrast to X-ray

Absorption Spectroscopic techniques, provides comparable information concerning the distribution of water. The unique ability to characterize water structure illuminates the inner-sphere or outer-sphere nature of sorbed cations.

We used high-resolution in-situ X-ray reflectivity measurements at BESSRC-CAT, Advanced Photon Source, to characterize the sorption of K, Cs, Ca, and Ba from chloride solutions onto the basal surface of muscovite. X-ray reflectivity data were collected through the specular reflection condition and converted to electron density profiles perpendicular to the interface by applying atomistic structural models that included surface relaxation, sorbate concentration and position, water structure, and surface roughness.

Cations were attached to the basal surface dominantly in the first adsorbed layer, which has the highest electron density of the solution phase. Derived heights above basal oxygens for K (1.67(6) Å) and Cs (2.15(9) Å) differ by the difference in their crystallographic radii and correspond closely to values in bulk K- and Cs-micas. Heights for Ca (2.5(1) Å) and Ba (2.04(5) Å) follow the trend for hydrated radii and deviate from the trend for crystallographic radii. All derived heights imply that no separate water layer exists between the sorbates and mineral surface. Interpretations of electron density profiles indicate the presence of cosorbed water or possibly, for divalent cations, cosorbed chloride. Water layering above the sorbed cation layer and minimal relaxation of the bulk muscovite were observed.

V61C-04 0930h INVITED

Probing Selenium-Ion Distributions and Changes in Redox-State at Biofilm/Mineral Interfaces by Coupling Long-period X-ray Standing Wave and XANES Measurements

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Metal sorption and precipitation reactions at biological as well as mineral surfaces are important controls on metal speciation and bioavailability in natural environments. When highly hydrated biofilms form on mineral surfaces, numerous competitive and synergistic effects are predicted to occur. Experimentally, it is challenging to determine where the sorbed metal ions are localized, the relative affinity of the biological vs. mineral surface sites, or to monitor biomineralization reactions or changes in metal speciation that may also occur. A large part of the difficulty is due to the low concentrations of sorbed ions, the small length-scale of the biofilm-mineral interface, and the complex interplay between microbially-catalyzed redox transformations vs. sorption and/or transport processes.

Long-period X-ray standing wave (XSW) techniques are well-suited to determining the vertical distribution of metal(oid) species within biofilms overlying mineral surfaces. We will discuss experiments where Se fluorescence yield profiles are used to compare the affinity of Burkholderia cepacia biofilms for binding Se(IV) and Se(VI) species relative to underlying α -Al₂O₃ substrates over three orders of magnitude in [Se]. In addition, we will discuss how coupling the XSW experiments to grazing-incidence, spatially-resolved Se K-edge XANES spectroscopy can be used to differentiate between the oxidation state of the Se complexes localized within the biofilm vs. the mineral surface. This approach is used to monitor changes in the relative distributions of Se(VI), Se(IV) and Se(0) species as a function of time and proximity to the mineral surface.

The long-period XSW data show that selenite preferentially binds to the oxide surfaces, particularly at low [Se]. When B. cepacia is metabolically active, B. cepacia rapidly reduces a fraction of the Se(IV) to the red elemental Se form. In contrast, selenate is preferentially partitioned into the B. cepacia biofilms at all [Se] tested due to a lower affinity for binding to the mineral surface. XANES spectra show that rapid reduction of selenate by B. cepacia to Se(IV) and Se(0) species subsequently results in a vertical segregation of Se species at the B. cepacia/ α -Al₂O₃ interface. Elemental Se accumulates within the biofilm with the Se(VI), whereas selenite intermediates preferentially sorb to the underlying oxide surface.

V61C-05 0950h INVITED

Direct Crystallography of Trace Elements in Minerals Using X-ray Standing Waves

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We present a new synchrotron-based X-ray crystallography method for directly profiling the atom distribution structures of trace elements within minerals. This method makes use of the facts that an atom distribution within a unit cell can be expanded as a Fourier series of multiple-order components, and that the coefficient of each Fourier component (both amplitude and phase) can be acquired experimentally by an X-ray standing wave measurement. This method derives atom distribution structures by means of a direct mathematical inversion, without resorting to structural modelling and interpretation. It is therefore completely model-independent.

We prove the validity of this new method by using it to quantitatively reproduce the lattice atom structures (K, Si, and Al) of muscovite in the (001) direction of the crystal. We then use it to determine the distribution structures of the Fe, Mn, and Ti impurities within the muscovite unit cell in the (001) direction.

V61C-06 1030h

Investigations of Arsenic and Iron Interactions in Environmental Systems Using Synchrotron Radiation Techniques

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Understanding the reactions of arsenic with iron oxide is of critical importance to predicting the environmental cycling and bioavailability of this toxic element. Arsenic is strongly adsorbed on most of the common iron oxide surfaces such as hydrous iron oxide (ferrihydrite), goethite, and lepidocrocite. In addition to surface binding reactions, co-precipitation of arsenic with iron oxide also removes dissolved arsenic from solution. We investigated arsenic binding to iron oxide in a variety of different environmentally relevant systems including batch reactions with synthetic Fe(III) oxides, flow-through column experiments with corroding zero-valent iron as a groundwater remediation material, and sequestration during formation of an Fe(III) precipitate (plaque) on the root surfaces of two aquatic plants (Phalaris arundinacea (reed canarygrass) and Typha latifolia (cattail)). The mechanisms of arsenic binding were investigated using X-ray absorption spectroscopy and X-ray fluorescence microtomography. Arsenate (As(V)) and arsenite (As(III)) form inner-sphere surfaces complexes on ferrihydrite, goethite, and lepidocrocite with As-Fe inter-atomic distances indicative of predominantly bidentate binuclear complexes. Zero-valent iron corrosion causes in-situ Fe(II) oxide formation and both As(V) and As(III) are strongly adsorbed and occluded by the mixed Fe(II) oxide products. Iron plaque of both P. arundinacea and T. latifolia consisted predominantly of ferrihydrite with lesser amounts of goethite and minor levels of siderite. X-ray fluorescence microtomography results suggested that root surface arsenic generally corresponded to regions of enhanced Fe levels.

V61C-07 1045h

Time-Resolved Structural Analysis of Cation Exchange Reactions in Birnessite Using Synchrotron XRD

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Birnessite ((Na,Ca,Mn²⁺) Mn₇O₁₄·2.8H₂O) is a layered Mn-oxide with a 7.2Å spacing between the Mn octahedral sheets. Since birnessite is an abundant phase in soils, desert varnishes, and ocean nodules, it plays a significant role in soil and groundwater chemistry. Experiments by Golden et al. (1986,1987) have demonstrated that Na-birnessite (hydrated birnessite) readily exchanges Na⁺ for a variety of other cations, including K⁺, Mg²⁺, Ca²⁺, Ba²⁺, Ni²⁺, and Sr²⁺. In light of its high cation exchange capacity, birnessite is industrially important for ion and molecular sieves and cathodic materials. In addition, birnessite serves as a precursor in the synthesis of todorokite, which has a 3x3 tunnel structure and is used as an octahedral sieve.

We monitored cation-exchange reactions in birnessite by time-resolved X-ray powder diffraction with a simple flow-through cell at the National Synchrotron Light Source. The flow-through cell was developed by Lee and Parise at SUNY-Stony Brook, and this work represents its first application to Mn oxides. A series of synthetic Na-birnessite samples were saturated with chloride solutions containing dissolved K⁺, Mg²⁺, and Ba²⁺, ranging from 0.1M to 0.001M. Powder X-ray diffraction patterns were collected every ~3 minutes.

The synchrotron experiments revealed that complete cation exchange occurs within three hours, and significant modifications of the arrangements of interlayer cations and water molecules accompany the exchange. Specifically, the replacement of Na by Mg resulted in the continuous growth of a discrete buserite-like phase with a 10Å layer spacing, while replacement of Na by K and Ba retained the 7Å spacing. K replacement of Na resulted in gradually decreasing peak intensity and peak merging. The Ba exchange yielded an abrupt decrease in diffraction intensities followed by a more gradual lattice change over the last 2 hours. Rietveld analysis led to the first determination of the structure of Ba-birnessite in space group C-1. With a final chi-squared parameter of 1.540, the refined lattice parameters were a = 5.178(2)Å, b = 2.850(3)Å, c = 7.320(5)Å, α = 89.512(1)°, β = 102.989(6)°, and γ = 89.893(6)°. However, the lattice parameters of the fully exchanged Ba-birnessite indicate that Ba substitution causes the unit cell to be more monoclinic.

V61C-08 1100h

Trace Metal Sequestration by the Manganese Oxidizing Bacterium *Pseudomonas putida*

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Bacterial cells are an important source of chemically reactive surfaces in freshwater and soil environments. *Pseudomonas putida* strain MnB1 cells, like many gram negative bacteria, present an outer membrane studded with phosphate groups and carbohydrates as well as a billowing biofilm of extracellular polysaccharides to the surrounding microenvironment. The cell outer membrane and the biofilm possess functional groups that complex trace metals. During certain growth phases *P.*

putida is also a manganese oxidizing bacterium, causing the cells to coat themselves in Mn(IV) oxide. Therefore, in addition to the cell outer membrane and associated biofilm, trace metals may sorb to the biogenic Mn oxide. To explore the relative contributions to trace metal sorption by the bacterial cells and biogenic Mn oxide, zinc and nickel were added to suspensions of bacterial cells with three different conditions: cells in the absence of Mn, cells in the process of Mn oxidation and cells with preformed biogenic Mn oxide. Adsorption isotherms were measured to quantify Zn and Ni sorption to *P. putida* in the presence and absence of biogenic Mn oxide. Zinc and Ni K-edge EXAFS spectra were measured to determine how and where the metals were binding to the bacterial cells and biogenic Mn oxide. The Zn and Ni adsorption isotherms exhibited two plateaus. The metal complexation was dependent on concentration with Zn having a higher affinity for phosphate and Ni for carboxyl functional groups. The preformed biogenic Mn oxide has high affinity for Zn and Ni and the bacterial surface contributed little to metal removal from solution under these conditions. However, if the metal is present in solution while Mn oxidation is occurring the bacterial cell surface influences greatly the overall removal of metal. Manganese oxidizing bacteria such as *P. putida* contribute to environmental metal sequestration by catalyzing the production of Mn oxide minerals, and the bacterial cells are themselves reactive environmental surfaces.

URL: <http://mnbiooxides.ucsd.edu/sciapps.shtml>

V61C-09 1115h

Trace Metal Sequestration by and Structure of Mn Oxide Produced by *Pseudomonas putida*

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The structure of the manganese oxide produced by *Pseudomonas putida* strain MnB1, and the sorption mechanism of zinc at the surface of the biogenic manganese oxide, were studied by X-ray diffraction and Mn- and Zn-K edge EXAFS spectroscopy. The X-ray diffraction pattern exhibits a broad basal reflection and asymmetrical hk0 bands characteristic of turbostratic birnessite. The average number of layers in birnessite particles and the lateral dimension of the MnO₂ layers were estimated from the size of coherent scattering domains in the c* direction and in the ab plane. XRD simulations showed that the relative intensity and shape of the 200 and 020 reflections are sensitive to the amount of interlayer Mn and, therefore, can be used to constrain the composition and structure of the interlayer space. Both XRD and Mn K-edge EXAFS data are consistent with a structural model in which the interlayer space is devoid of manganese, all Mn atoms being located within the birnessite layer. Mn-Mn distances obtained by the two techniques are identical (2.84 Å), and typical of pure Mn⁴⁺ manganese layers. The lack of Mn³⁺ within the manganese layer suggests that the deficit of structural charge from the biogenic birnessite arises from vacant octahedral sites (V). Zn-O and Zn-Mn EXAFS distances are consistent with the formation of tetrahedrally coordinated Zn complex on the face of vacant layer octahedral sites, i.e., with the formation of a tridentate corner-sharing interlayer complex ([H₂O]-IVZn-3Olayer-V-3Mnlayer). This [IV]TC complex was observed at low and high surface coverage, and this result contrasts with that obtained for abiotic hexagonal birnessite (HBI), in which Zn formed a [IV]TC complex at low surface coverage and a [VI]TC complex at higher coverage (Manceau et al., 2002). The structural reasons for this difference will be discussed, and it will be shown that the [IV]TC complex is the main binding form of Zn in natural phyllosilicates.

Manceau, A., Lanson, B., and Drits, V.A. (2002) Structure of heavy metal sorbed birnessite. Part III. Results from powder and polarized extended X-ray absorption fine structure spectroscopy. *Geochimica et Cosmochimica Acta*, 66, 2639-2663.

V61C-10 1130h

X-ray Spectroscopic Investigation of the Distribution and Speciation of Uranium in Contaminated Sediments From the DOE's Hanford Site

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Extensive uranium contamination of the subsurface at the Department of Energys Hanford site has occurred through the leakage of significant quantities of high-level nuclear waste. Over 25 tons of uranium have been spilled into the vadose zone in the 200 and 300 Areas at the site, with sizable groundwater plumes present or developing. An understanding of the speciation and distribution of uranium in the vadose zone is needed to predict the future migration of uranium into groundwater. We have applied synchrotron-based x-ray spectroscopic techniques to characterize the speciation of uranium in contaminated sediments from under tank BX-102 in the 200 Area, and from disposal ponds and areas adjacent to waste storage areas in the 300 Area. X-ray fluorescence microprobe (μ -XRF) studies of BX-102 samples shows uranium distributed heterogeneously, occurring in discrete particles <5 mm in diameter. X-ray absorption near edge structure (XANES) spectroscopic studies demonstrate that >95% of the uranium occurs as U(VI) in all samples. In the BX-102 samples, extended X-ray absorption fine structure (EXAFS) spectroscopy suggests that the primary uranium species is an uranophane-group mineral, most likely boltwoodite. Two samples from the 300 area also contain uranium primarily as an uranophane-group mineral, whereas one sample contains a mixture of phases, and one appears to contain primarily adsorbed U(VI). These differences may reflect different waste sources and water exposures. These studies suggest that an uranophane-group mineral is the primary phase controlling the geochemistry of U at the Hanford site. X-ray microdiffraction studies of these samples will also be presented.

V61C-11 1145h

Atomic Scale Mechanisms Governing the Alteration of Inactive Nuclear Wastes: a Multi-Element XAFS Study

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We present a direct determination of the evolution of the local atomic structure at the interface between a nuclear glass and the leaching solution at 90C, as a function of the alteration conditions, up to the formation of gels and alteration products. Synchrotron radiation XAFS data complement the analysis of the evolution of the surface composition. Among the elements investigated, some of them such as Fe and Zn exhibit a coordination change, since the early stages of alteration. However, as Fe participates to the formation of a ferrihydrite-like local structure as Zn is incorporate in a T-O-T phyllosilicate. By contrast, Zr only changes coordination under open system conditions, as it retains the same local structure as in the pristine glass under alteration in near-saturation conditions. EXAFS data indicate that in the former case, Zr forms a poorly ordered oxy-hydroxide, as in the latter it remains connected to the silicate network while trapping charge

compensating elements such as Ca. Network formers, such as Al and Si, retain their tetrahedral coordination in the alteration layer and subsequent gel. As for Zr, this will help retain charge compensating cations, such as Ca or Sr in the alteration gel. Our data indicate that distinct mechanisms participate to the formation of the gel layer, but that they do not participate to the same extent to the long term stability of the glass/gel interface.

V61D MCC: 106 Saturday 0830h

Contemporary Chemical Geodynamics I (joint with T)

Presiding: J N Kellogg, University of South Carolina; **R L Rudnick**, University of Maryland

V61D-01 0830h

The Chemical Composition of the Earth and its Envelopes

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Radiogenic isotopes systematics have led to a model for the structure of the Earth with a continental crust, a mantle, divided into a depleted mantle (40%) and a primitive mantle (60%), and a core. These two mantles have been mixed up through geological time and form now, separated by the 670 km discontinuity, an upper depleted mantle and a lower mantle, partially depleted. This model gave also the distribution of the different parent/daughter chemical ratios in the different envelopes (Rb/Sr, Sm/Nd, U/Pb, etc).

Another approach, using systematic comparisons of characteristic chemical ratios like (Mg/Al, K/U, Rb/Sr, Ti/Sr), has shown that the Bulk Earth belong to the carbonaceous meteorites trend and has thus permit to determine composition of the Earth (Allège et al, 2002).

Combining these two types of data with elemental ratios measured in surface rocks as well as in pristine ultramafics, we have developed a global model using a general inversion procedure to compute the chemical composition of the different reservoirs of the Earth (i.e. Continental crust, Mantles and Core).

The results have important geologic consequences on the formation of the core, the origin of OIB and the energetics of the Earth. The composition of the different reservoirs also establish an important chemical relationship between the position of an element in Mendeleeff table and its geologic distribution, leading to a new geochemical classification of the elements.

V61D-02 0845h

High precision Pb isotopes in Indian Ocean MORB

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Several studies have shown that MORB from the Indian Ocean have different isotopic characteristics compared to those from the Pacific or Atlantic Oceans. A particular Pb isotope feature of Indian Ocean MORB is their high ²⁰⁸Pb/²⁰⁴Pb ratio compared to those from the Pacific or North Atlantic. These isotope differences have been interpreted as reflecting the presence of an old recycled component or lithospheric delamination in the Indian MORB reservoir.

We present Pb triple spike data on MORB from three Indian spreading centers - South West Indian Ridge (SWIR), Central Indian Ridge (CIR) and South East Indian Ridge (SEIR) - and from the Rodriguez

Triple Junction (RTJ). All samples have been previously analysed for major and trace elements and Sr, Nd and Pb isotopes. Our purpose is to use high precision Pb data 1) to investigate the Pb isotope relations between the three spreading centers and 2) to find whether differences in ²⁰⁷Pb/²⁰⁴Pb can also be resolved between Indian, Pacific and Atlantic MORB.

So far, Pb isotope measurements have been obtained on CIR and SWIR, and those on SEIR and RTJ are on going. Samples from Atlantis FZ II (SWIR) have lower Pb isotope ratios (²⁰⁶Pb/²⁰⁴Pb= 17.47-17.94, ²⁰⁷Pb/²⁰⁴Pb= 15.41-15.47, ²⁰⁸Pb/²⁰⁴Pb= 37.17-37.65) than CIR-MORB (²⁰⁶Pb/²⁰⁴Pb= 18.30-18.70, ²⁰⁷Pb/²⁰⁴Pb= 15.50-15.57, ²⁰⁸Pb/²⁰⁴Pb= 38.18-38.73). In both Pb isotope spaces, CIR and Atlantis FZ II MORB define two different linear arrays with distinct slopes. The ²⁰⁷Pb/²⁰⁴Pb-²⁰⁶Pb/²⁰⁴Pb slopes correspond to model ages of 1.97 (CIR) and 2.15 Ga (Atlantis FZ II), and values of $\kappa=5.14$ and 3.62, respectively.

Our new Pb isotope data allow us to distinguish two Pb isotope domains, CIR and SWIR, while previous data show large scatter and overlap. Furthermore, the influence of the Réunion plume is reflected in the gradual increase of Pb isotope ratios along the CIR with proximity to the hotspot. Comparison of Indian MORB with those from East Pacific Rise (EPR) and South Atlantic [1] show that Pb isotope ratios increase in the order: EPR < South Atlantic ~ CIR < SWIR for ²⁰⁷Pb/²⁰⁴Pb and EPR < South Atlantic < SWIR < CIR for ²⁰⁸Pb/²⁰⁴Pb.

1. Galer, S.J.G., et al., Eos Trans. AGU, Fall Meet. Suppl., Abstract., 2001. 82: p. F1403.

V61D-03 0900h

Regional Heterogeneity Within the Icelandic Mantle Revealed Through High-Precision Pb Isotope Data

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We report high-precision Pb-isotope data for > 120 neovolcanic lavas from Iceland that were analysed on an Axiom double focusing MC-ICP-MS, using a ²⁰⁷Pb-²⁰⁴Pb double spike to correct for instrumental mass bias. The external reproducibility of Pb isotope ratios determined for the standard SRM981 was ± 100 ppm (DS corrected) and replicate analyses of samples have a similar reproducibility. The study encompasses all the neovolcanic rift and off-rift zones, including alkalic and tholeiitic picrites, basalts and rhyolites. We observe a similar range in ²⁰⁶Pb/²⁰⁴Pb to published conventional TIMS results, but with a significant reduction in the ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb variation at a given ²⁰⁶Pb/²⁰⁴Pb value. Some scatter in ²⁰⁷Pb/²⁰⁴Pb still remains, which probably reflects real small-scale heterogeneities. The anomalously high ²⁰⁷Pb/²⁰⁴Pb values previously reported for Oraefajokull are confirmed here. For geographically restricted areas such as Reykjanes, Theistareykir and each of the Icelandic alkaline centres, we observe tight coherent linear data arrays in ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb vs ²⁰⁶Pb/²⁰⁴Pb that are interpreted as binary mixing lines, although each array is offset from the others such that more than four end-members are required.

One of the most striking features of these new data is the offset in $\Delta 8/4$ Pb between lavas from localities NE and SW of the assumed plume axis. This offset is very similar to that observed between lavas from the two volcanic trends in Hawaii. In Iceland, lavas from each region fall on broad distinct arrays with their most radiogenic compositions represented by alkaline lavas from Snaefell-Oraefajokull (NE) and Eyjafjöll-Torfajokull, respectively. Furthermore, both regions seem to link up compositionally (including Sr, Nd & He isotopes) as well as physically with the adjacent Kolbeinsey and Reykjanes ridges. There is a crude negative correlation between ³He/⁴He and both $\Delta 7/4$ Pb and $\Delta 8/4$ Pb, opposite to that observed for Hawaiian lavas. However, at this stage the extreme He-Pb isotopic composition of alkaline lavas may bias our observations. In conclusion, our extensive high precision Pb isotopic data set resolves local mixing relationships, regional chemical provinces and correlations with ³He/⁴He, and demonstrates that the Pb isotope variations cannot simply be explained in terms of just two or three end-member components.

V61D-04 0915h

High-Precision Pb Isotope Systematics of Basalts from the Kerguelen Archipelago: New Insights on the Kerguelen Plume Components

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The number and origin of components involved in mantle plumes continues to be a subject of intense debate amongst geochemists. New analytical techniques are now allowing for a more refined analysis of individual oceanic islands. About 60 samples of Kerguelen Archipelago basalts (MgO > 2.3 wt.%) were re-analyzed for their Pb isotopic compositions by MC-ICP-MS (Nu Plasma 015). We carefully selected the samples on the basis of their Sr-Nd-Hf and Pb (TIMS) characteristics in order to cover the range of age, geographic and compositional variations observed on the archipelago.

These new high-precision Pb isotopic compositions (2σ ima: 100-150 ppm for ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb and 150 ppm for ²⁰⁸Pb/²⁰⁴Pb) reduce the total range of ²⁰⁷Pb/²⁰⁴Pb variations among Kerguelen basalts by a factor of 2. This provides an important new perspective on Kerguelen plume systematics and allows for the clear distinction of three groups: the 29-25 Ma tholeiitic-transitional basalts, the 25-24 Ma mildly alkalic basalts, and the <10 Ma more evolved, alkalic lavas and intrusions. This age and compositional evolution also corresponds to a geographic trend, where the older basalts are closest to the Southeast Indian Ridge (~300-400 km) while the mildly alkalic basalts are further away. The younger, more evolved alkalic rocks occur mainly in the same areas as the mildly alkalic basalts. These alkalic rocks result from lower degrees of melting and their distinctly lower ²⁰⁶Pb/²⁰⁴Pb (and ¹⁷⁶Hf/¹⁷⁷Hf) together with their significantly younger age indicate some interaction with the older Kerguelen Plateau. These important differences clearly reflect a Miocene change of regime of the Kerguelen plume (Mattioli et al., JP, 2002).

Among the flood basalts that cover >80% of the Kerguelen Archipelago, the mildly alkalic basalts of the 24 Ma Crozier volcanic section stand out with distinctly higher ²⁰⁶Pb/²⁰⁴Pb. The isotopic compositions of the Crozier basalts are interpreted as representative of those of the Kerguelen plume. These basaltic magmas had little, if any, interaction with either the surrounding depleted mantle or the Kerguelen Plateau during ascent, either because their magma conduits became isolated or/and because by 24 Ma, the Southeast Indian Ridge was too far away. Our study confirms that the high-precision Pb isotope systematics of basaltic lavas represent an excellent tool to decipher components in major mantle plumes, as has also recently been shown in Hawaii (Eisele et al., G3, submitted; Blichert-Toft et al., G3, submitted).

V61D-05 0930h

A New Type of Model for Understanding Lead Isotopic Heterogeneity in the Earth's Mantle

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Using an extended version of the conventional geochemical reservoir model, we investigate the meaning of the Pb isotope data in oceanic basalts. Our method, previously used to study the Nd and Sr isotopic systems, allows us to model not only the mean isotopic ratios, but also the distribution of those ratios within the reservoirs.

Owing to low chemical diffusion rates, subreservoirs that are created by mass transport into and out of the mantle effectively exist as distinct geochemical entities for all time. By tracking these subreservoirs, we obtain a model of the full range of isotopic values represented in the mantle. Using results from numerical calculations of mixing, we also track the length scales associated with each subreservoir. Applying simple statistics, we obtain the distribution of expected measurements as a function of the stirring time, effective melt fraction, sampling volume, and mass transport history.