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Research Highlights

Heterogeneous Chemistry of Individual Mineral Dust Particles with Nitric Acid: A Combined CCSEM/EDX, ESEM, and ICP-MS Study

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The chemistry of individual mineral dust may play an important role in climate forcing and atmospheric chemistry and may need to be explicitly accounted for in climate models.

It has been reported that 50 percent of the global emission of tropospheric aerosol particles consists of mineral dust particles injected into the atmosphere, mainly from desert and arid regions. Mineral dust tends to originate from very specific areas in the Earth and then transports over very long distances, influencing climate and chemistry of the atmosphere on regional and global scales. Climatic effects of mineral dust include reflection and absorption of incoming solar radiation and impacts on cloud formation, cloud properties, and precipitation. Heterogeneous chemistry of mineral dust modifies both the gas-to-particle partitioning in the atmosphere and physicochemical properties of individual particles. An individual mineral dust aerosol may include a wide variety of individual minerals having different physical and chemical properties. Therefore, quantification of its global impacts requires information on dust emission sources and its transport, particle size, and compositional data, and a description of the processes that govern changes in particle properties as they evolve in the atmosphere. Dust mineralogy and its emission inventory, transport, and dry and wet removal have been included in a number of recent global

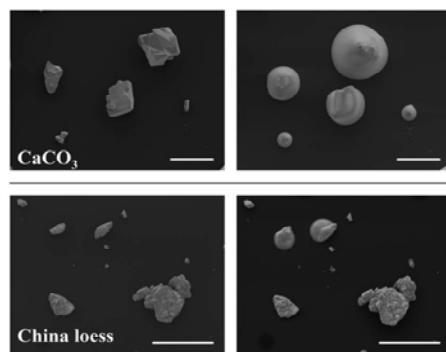


Figure 1. Secondary electron images of CaCO₃ and China loess particles (left) before and (right) after reaction with gaseous HNO₃ in the presence of water vapor.

and regional climate models. However, the atmospheric chemistry of dust is oversimplified in current models, where mineral dust is often considered as a single entity aerosol with a single kinetic parameter for reaction with a particular trace gas.

Particle hygroscopicity is a key property of atmospheric aerosol that is important in its impact on climate and the overall atmospheric environment. The ability of dust particles to serve as cloud condensation nuclei, their optical properties, and their heterogeneous chemistry are all coupled to the hygroscopic properties of mineral dust, which is typically considered a largely nonsoluble material. Indeed, mineral dust aerosol consists mainly of different nonsoluble soil minerals such as quartz, calcite, gypsum, and clays. However, as the mineral dust is processed or aged in the atmosphere, some of the particles may become substantially hygroscopic because of the presence of surface coatings. From a practical perspective, it is very difficult to assess the detailed mineralogy of mineral dust, its size- and composition-resolved heterogeneous chemistry, and its cloud formation abilities. An important first step may be the identification of the components of mineral dust that have the greatest atmospheric reactivity and impact on the Earth's chemistry and climate.

Towards this goal, we studied the heterogeneous chemistry of mineral dust with nitric acid aimed at identifying and characterizing particles of greatest reactivity and determining changes in their physicochemical properties. We use computer-controlled scanning electron microscopy with energy-dispersive X-ray (CCSEM/EDX) analysis to follow heterogeneous chemistry of calcium-containing particles within a diverse mixture of mineral dust particles extracted from authentic sand samples collected in different desert areas: China loess region (upper basin of the Huang River), Sahara, and coastal and inland Saudi Arabia. We used state-of-the-art environmental scanning electron microscopy to probe the hygroscopic behavior of mineral dust particles reacted with nitric acid.

The secondary electron images shown in Figure 1 demonstrate morphology changes observed for individual CaCO_3 and China loess particles following exposure to HNO_3 vapor. Particle images prior to reaction are shown on the left, and images after the exposure are shown on the right. Figure 1 (top) shows that the crystalline solid particles of calcium carbonate become enlarged and spherical in shape because of formation of the deliquesced calcium nitrate product. Figure 1 (bottom) demonstrates that a few of the China loess particles reacted with HNO_3 under the same conditions also show similar morphology changes. Manual EDX analysis and X-ray mapping of particles that showed a crystalline-to liquid transformation, as evidenced by a change in morphology, confirmed the presence of CaCO_3 in the original particles and consecutive formation of $\text{Ca}(\text{NO}_3)_2$ after reaction.

Figure 2 shows the elemental composition of a few hundred individual CaCO_3 and $\text{Ca}(\text{NO}_3)_2$ particles as a function of particle size determined by CCSEM/EDX. The elemental compositions of individual particles are expressed in terms of atomic ratios of oxygen/calcium and nitrogen/calcium. The red symbols in Figure 2 depict the oxygen/calcium and nitrogen/calcium elemental ratios for CaCO_3 particles exposed to HNO_3 .

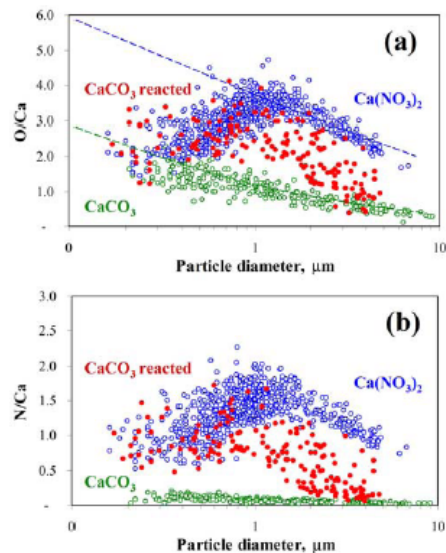


Figure 2. Elemental ratios of (a) oxygen/calcium and (b) nitrogen/calcium measured by CCSEM/EDX analysis, plotted as a function of particle size for CaCO_3 particles (green symbols) and $\text{Ca}(\text{NO}_3)_2$ particles (blue symbols). Data for CaCO_3 particles reacted with HNO_3 in the presence of water vapor (red symbols) are also included in the plots.

The data show that submicron CaCO_3 particles appear to react completely. Larger particles (1 to 2.5 μm) show lesser reaction extent, and finally, very large particles ($>2.5 \mu\text{m}$) remain either almost or completely unaffected by the reaction. The data obtained from this focused laboratory study suggest that a portion of each of the four mineral dust aerosol samples from specific source regions may exhibit substantial reactivity with gas-phase HNO_3 , leading to formation of hygroscopic $\text{Ca}(\text{NO}_3)_2$ -containing particles. Therefore, in the atmosphere, once $\text{Ca}(\text{NO}_3)_2$ particles are formed, they remain in the aqueous phase and never dry out, even over desert areas. These liquid particles may change the optical properties of mineral dust, serve as effective cloud condensation nuclei, and modify clouds as well. In addition, these modified particles may open up the possibility of new multiphase reaction chemistry. It follows that a significant fraction of the dust from these specific locations will change their physical and chemical properties when transported over polluted areas. These changes may have an important impact on climate forcing and atmospheric chemistry.

This research is discussed in further detail in Laskin et al. 2005.

Citation

Laskin A, TW Wietsma, BJ Krueger, and VH Grassian. 2005. "Heterogeneous Chemistry of Individual Mineral Dust Particles with Nitric Acid: A Combined CCSEM/EDX, ESEM, and ICP-MS Study." *Journal of Geophysical Research D: Atmospheres* 110(D10):D10208 (pages 1-15).

Development of Multipurpose Tags and Affinity Reagents for Rapid Isolation and Visualization of Protein Complexes

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Strategies are being investigated to develop reagents and technology for high-throughput processes that will foster rapid characterization of protein complexes in microbial cells. The end result will be data collection of time-dependent changes in protein complex formation in response to environmental conditions, providing a systems-level understanding of how microbes adapt to environmental changes. Ultimately, these strategies will help to optimize methods pertaining to efficient energy use, carbon sequestration, and environmental remediation

This research is being conducted to develop the necessary reagents and technology for high-throughput methods that will ensure rapid and quantitative characterization of protein complexes in microbial cells. We are investigating a strategy focused on the development of multiuse protein tags engineered around a tetracysteine motif (i.e., CCXXCC), which has previously been shown to provide a highly selective binding site for cell-permeable, arsenic-containing affinity reagents that can be used to identify and validate protein complexes in living cells. Use of novel affinity reagents that become fluorescent upon binding to engineered tags will permit quantification of expressed proteins and purification and stabilization of protein complexes. Ultimately, high-throughput data collection of time-dependant changes in protein complex formation in response to environmental conditions will be available, thus permitting a systems-level understanding of how microbes adapt to environmental change.

Important to our progress has been access to EMSL's High-Field Magnetic Resonance Facility. Nuclear magnetic resonance (NMR) spectrometry analysis has contributed to the production of cell-permeable orthogonal fluorescent probes by facilitating regular identification and characterization of synthesis pathways

and resultant products. NMR has also been implemented to investigate the structure, dynamics, and binding kinetics of peptide-reagent interaction.

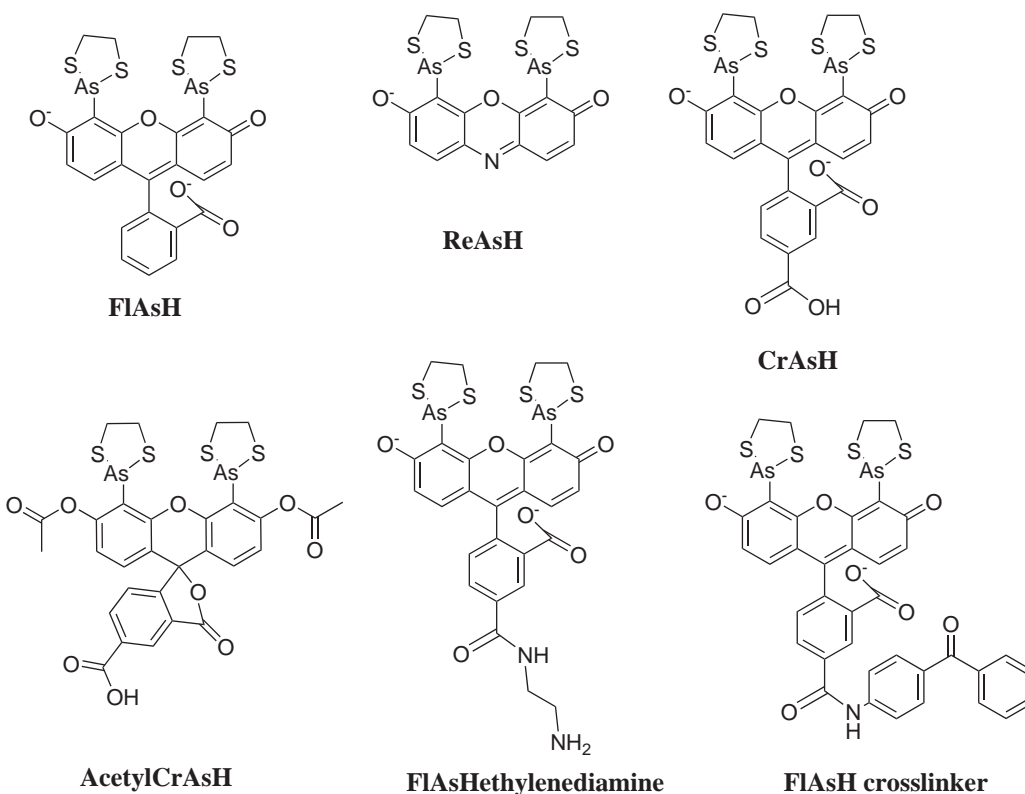


Figure 3. Sample fluorescent probe compounds characterized using FIAsh dye.

This research is currently in a synthesis-intensive phase to optimize the fluorescent dye and tag pair by sensible design and synthesis of new dyes and screening of the tetracysteine peptide library. Research is also underway to expand the applications of the FIAsh dye (a **F**luorescein **A**rsenic **H**elix binder, see Figure 3 for structure) to study protein-protein interactions. By taking advantage of the large increase in the fluorescence signal associated with binding the proposed fluorescent affinity reagents to the protein tag, it will be possible to use online detection to monitor affinity isolation of protein complexes and rapidly identify the proteins in the complex by using mass spectrometry.

Ultimately, these methods will permit optimization of useful metabolic pathways to fulfill U.S. Department of Energy goals involving efficient energy use, carbon sequestration, and environmental remediation.

Several papers that describe in detail our successful work in this area include Chen et al. 2005a and b and Mayer et al. 2005.

Citations

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Chen B, MU Mayer, and TC Squier. 2005b. "Structural Uncoupling Between Opposing Domains of Oxidized Calmodulin Underlies Enhanced Binding Affinity and Inhibition of the Plasma Membrane Ca-ATPase." *Biochemistry* 44(12):4737-4747.

Mayer MU, L Shi, and TC Squier. 2005. "One-Step, Non-Denaturing Isolation of an RNA Polymerase Enzyme Complex Using an Improved Multi-Use Affinity Probe Resin." *Molecular Biosystems* 1(1):53-56.

Proteomics Analysis of Potential Bioterrorism Agents

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This work will identify therapeutic targets for the causative agents of typhoid fever and smallpox. The methodologies developed should dramatically reduce the time required to characterize and respond to emerging infectious agents and bioterror threats.

Infection and pathogenicity are complicated, highly integrated processes that are unlikely to depend on any one protein product because of the availability of redundant pathways within the physiological repertoire of a pathogen. A systems biology approach that uses high-throughput global proteomics is being employed to identify new more effective vaccines and therapies.

In the past year, EMSL's High-Performance Mass Spectrometry Facility, in collaboration with Dr. Fred Heffron and Dr. Scott Wong of Oregon Health & Science University, have generated the data for foundational mass and time tag databases for *Salmonella typhimurium*, *Salmonella typhi*, Vaccinia virus, and Monkeypox virus. These extensive data resources will be used to allow for higher-throughput and reduced sample requirements for future proteomic measurements.

The most extensive of these databases has been developed for *Salmonella typhimurium*. This database has been initially data mined to compare to known biology and to identify previously unknown biology. Some of the most interesting results from comparing growth conditions are highlighted in a manuscript expected to be submitted later this month. These growth conditions include a typical logarithm growth state, a stationary growth state, and a growth condition that is meant to mimic an infectious environment. These results also give the research team a baseline as the experimental results of *Salmonella typhimurium* in a host cell environment become more complex.

Ongoing projects include analysis of *Salmonella typhimurium* and *Salmonella typhi* with various regulators of pathogenesis knocked out by mutagenesis. For Vaccinia and Monkeypox viruses, future efforts are meant to characterize more complex portions of the viral lifecycle.

This work was funded by the National Institute of Allergy and Infectious Diseases through interagency agreement Y1-AI-4894-01.

Formation of Cadmium Nanowires on Ion-Cut Surfaces of $\text{Cd}_2\text{Nb}_2\text{O}_7$

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Nanowires of semiconductors and metals are of technological interest due to their potential applications in many fields, including electronics, magnetics, optoelectronics, thermoelectrics, and photonics. Use of these materials versus their bulk counterparts will not only allow for device miniaturization, but also may improve device performance or create new functions. We describe a novel method for the synthesis of crystalline cadmium nanowires without involving either templates or a “seeded” structure.

Irradiation of a $\text{Cd}_2\text{Nb}_2\text{O}_7$ single crystal using 3.0-MeV He^+ ions at and below room temperature has been performed and formation of nanowires on the ion-cut surfaces was observed, as shown in Figure 4. The 70-degree-tilted view of the nanowires reveals a variety of diameters, lengths, and shapes. The wires are randomly distributed on the ion-cut surfaces; they can be as long as several tens of microns with diameters ranging from less than 100 nm to nearly 1 μm . Some of the wires have a granular knob at the top of the nanowire [Figure 4(a)]; both straight and curved wires are abundant [Figure 4(b)]. In general, the sidewalls of the thin wires are relatively smooth and their diameters are uniform, while the thicker wires have a “ridged” surface. The insert of Figure 4(b) shows a side view of a broken wire. The composition of the nanowires was determined by energy dispersive X-ray spectroscopy. The niobium concentration throughout the nanowires is below the detection limit, although the niobium peak is stronger than that of cadmium in the original $\text{Cd}_2\text{Nb}_2\text{O}_7$ crystal. The nanowires formed primarily as metallic cadmium under these conditions, and their surfaces subsequently became oxidized when the sample was exposed to air, since cadmium can be readily oxidized under ambient conditions. The backside of the exfoliated layer was also analyzed using energy dispersive X-ray spectroscopy, and the results show that it consists primarily of niobium and oxygen with no detectable cadmium.

In order to characterize the atomic-scale structure by transmission electron microscopy, several nanowires on the ion-cut surfaces were placed on a copper grid with a thin formvar support film that was coated with a few atomic layers of carbon. Figure 5 shows a typical nanowire of ~ 80 nm in diameter. There appear to be two faceted faces at the tip of the wire, suggesting that the wire is a single crystal. The insert of the figure shows a selected-area electron diffraction (SAED) pattern for the area marked on the wire. The bright spots in the diffraction pattern, which are grouped with dashed lines, confirm that the nanowire in this region is monocrystalline. Assuming that the wire has the same structure as bulk cadmium, the diffraction maxima are from the (02-23) and (10-13) planes, as indicated in the SAED insert of Figure 5. The two symmetric, but faint, spots indicated by arrows might originate from the thin CdO shell of the nanowire, which is consistent with the nanowire composition.

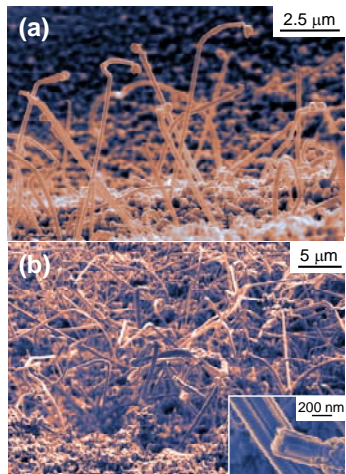


Figure 4. (a) 70-degree-tilted view of short nanowires on an ion-cut surface. (b) General view (70-degree-tilted) of an ion-cut surface containing nanowires. The irradiation dose for (b) is greater. Insert to (b) shows the side view of a broken nanowire.

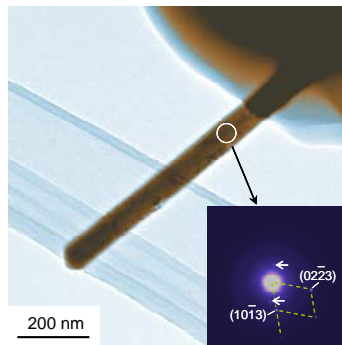


Figure 5. Transmission electron microscopy micrograph for a single nanowire. Insert is the SAED image for the nanowire. The diffraction pattern suggests that the nanowire is a single crystal. The two arrows point to faint diffraction maxima that may have resulted from the CdO layer on the surface of the nanowire.

During the irradiation of $\text{Cd}_2\text{Nb}_2\text{O}_7$, implanted helium and perhaps some O_2 accumulate at the peak in the irradiation-induced vacancy concentration and near the projected range of the implanted helium. Prior to surface exfoliation, there is a gas accumulation and bubble formation stage that forms a blister-like structure in which the upper surface layer begins to separate from the underlying substrate and bows outward under the high gas pressure. At this stage, there is high compressive stress on the inside of the top layer; as a result, the phase-separated, soft metallic cadmium is believed to be extruded as wires through the pores in the material. Such cadmium wires may also be simultaneously pulled from the inner top layer because the bond strength at the interface between the metallic cadmium and the underlying substrate is much stronger than that of the metallic cadmium within the residual niobium and niobium-oxide in the decomposed top layer; consequently, some of the thick cadmium wires may be strong enough to survive the pulling process. In addition, a probable volume expansion induced by amorphization of $\text{Cd}_2\text{Nb}_2\text{O}_7$ under these ion irradiation conditions could increase the pressure on the cadmium inclusions in the decomposed material and enhance the extrusion of the soft cadmium through pores. Thermal expansion of cadmium from 140 to 295 K might also contribute to the extrusion process, since the coefficient of linear thermal expansion for cadmium ($30.8 \times 10^{-6} \text{ K}^{-1}$ at 298 K) is much larger than that for niobium ($7.3 \times 10^{-6} \text{ K}^{-1}$ at 298 K). Mechanistically, a single-crystal structure can result from a strain-anneal process driven by the large strain produced by the extrusion process. The granular knob [Figure 4(a)], which has a similar composition to the crater surface, is apparently a mass of material that is pulled off the crater surface as the cadmium nanowire is extruded away from the

original surface. The observed surface ridges (striations or grooves) on the surface of the thick wires [Figure 4(b)] appear to result from the extrusion or pulling process through the large and irregular pores.

Effect of Zr Substitution for Ti in $Gd_2Ti_2O_7$ Pyrochlore: Ti 2p and O 1s NEXAFS Study

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Pyrochlores have a broad range of potential for different technological applications such as: catalysts, fluorescence centers, both cathode and electrolyte materials in solid-oxide fuel cells, oxygen-gas sensors at high-radiation environments, and as host matrices for the immobilization of actinide-rich wastes. In this work, we investigated the structural properties of these materials before and after ion beam irradiation.

Of the potential applications for pyrochlores, the use in solid-oxide fuel cells and as host matrices for actinide-rich wastes are receiving increasing attention because recent studies show that the isovalent substitution of zirconium for titanium in $Gd_2Ti_2O_7$ increases the oxygen ionic conductivity by ~ 4.5 orders of magnitude at 875 K and the radiation resistance by ~ 5 orders-of-magnitude increase in radiation tolerance. Recent experimental studies concluded that the cation disorder and anion Frenkel defects are the main cause for dramatic increase in oxygen ion conductivity and radiation tolerance in $Gd_2Zr_2O_7$. We have investigated structural properties of pure and irradiated single and polycrystalline $Gd_2Ti_2O_7$ single crystal and $Gd_2(Ti_{1-y}Zr_y)_2O_7$, using site-sensitive near-edge x-ray absorption fine structure (NEXAFS) and X-ray photon spectroscopy (XPS). XPS measurements suggest that the charge state shift of 1.6 eV in the O 1s binding energy between the oxygen anions in 48f and 8b sites results from a lower electron density on oxygen with shorter gadolinium-oxygen (8b, 0.221 nm) compared to longer gadolinium-oxygen (48f, 0.254 nm) bonds. NEXAFS measurements were carried out at beam lines 6.3.2 and 9.3.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory.

The Ti 2p and O 1s NEXAFS of TiO_2 (rutile), $Gd_2(Ti_{1-y}Zr_y)_2O_7$ ($y=0.0-1.0$), $SrTiO_3$, yttria-stabilized zirconia ($y-ZrO_2$), and Gd_2O_3 are shown in Figures 6(a) and (b), respectively. Although the Ti 2p NEXAFS show exactly the same features for both single crystal and polycrystalline $Gd_2Ti_2O_7$, isovalent substitutions of zirconium for titanium in $Gd_2Ti_2O_7$ produce significantly different spectra. The notable observation found in Figure 6(a) is that the splitting of the e_g states, which indicates the degree of distortion from octahedral site symmetry decreases with increasing zirconium substitution in $Gd_2(Ti_{1-y}Zr_y)_2O_7$. The energy separation between the d_{z^2} and $d_{x^2-y^2}$ orbitals is found to be 1.0 eV, 0.8 eV, 0.6 eV, and 0.4 eV for $Gd_2(Ti_{1-y}Zr_y)_2O_7$ with $y=0.0, 0.25, 0.5, \text{ and } 0.75$, respectively. Similarly, the energy separation amounts to 1.2 eV for TiO_2 . In contrast, titanium in $SrTiO_3$ occupies perfect octahedral symmetry and hence the transitions to e_g states show no splitting; however, the profile is slightly unsymmetrical. Thus, curve fitting the transitions to e_g states of $SrTiO_3$ with two Gaussians produces an energy separation of ~ 0.5 eV, which is very close to that of $Gd_2(Ti_{1-y}Zr_y)_2O_7$ with $y=0.75$, suggesting no distortion in the TiO_6 octahedron, as in $SrTiO_3$. In addition, the magnitude of the transitions to e_g states relative to the transitions to t_{2g} states increases with increasing

zirconium substitution in $\text{Gd}_2(\text{Ti}_{1-y}\text{Zr}_y)_2\text{O}_7$. Thus, these results clearly show that the titanium retains its octahedral site symmetry, however, the distortion present in the TiO_6 octahedron decreases with increasing zirconium substitution for titanium in $\text{Gd}_2(\text{Ti}_{1-y}\text{Zr}_y)_2\text{O}_7$.

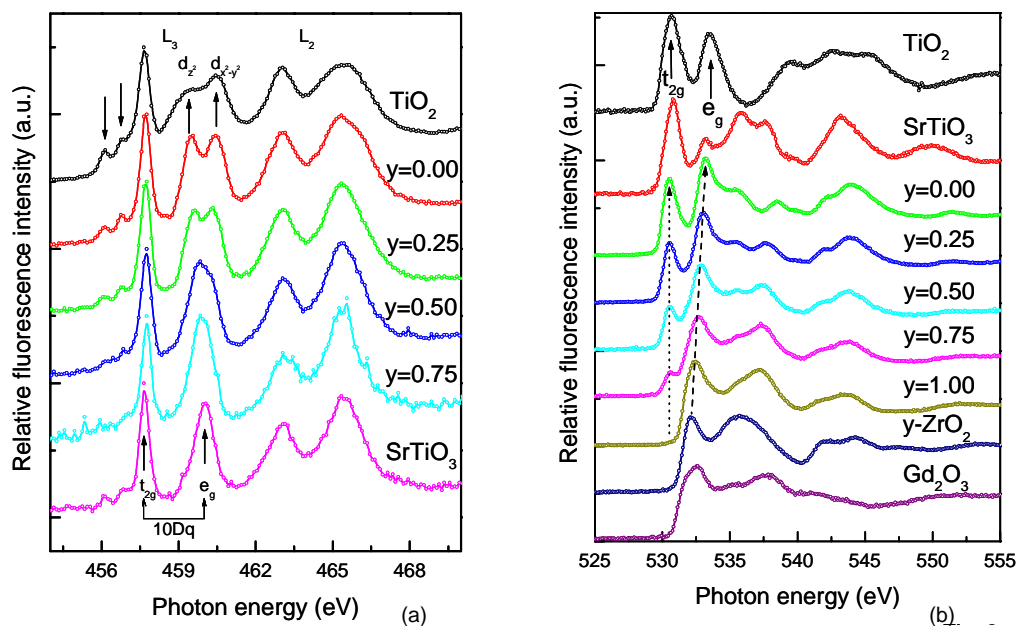


Figure 6. (a) Ti 2p NEXAFS for TiO_2 (rutile), $\text{Gd}_2(\text{Ti}_{1-y}\text{Zr}_y)_2\text{O}_7$ ($y=0.0, 0.25, 0.5, \text{ and } 0.75$), and SrTiO_3 ; (b) O 1s NEXAFS for TiO_2 (rutile), SrTiO_3 , $\text{Gd}_2(\text{Ti}_{1-y}\text{Zr}_y)_2\text{O}_7$ ($y=0.0, 0.25, 0.5, 0.75, \text{ and } 1.0$), yttria-stabilized zirconia ($y\text{-ZrO}_2$), and Gd_2O_3

Transitions labeled as t_{2g} and e_g in O 1s NEXAFS for TiO_2 , SrTiO_3 , and $\text{Gd}_2(\text{Ti}_{1-y}\text{Zr}_y)_2\text{O}_7$ result from transitions to the final states, $\text{Ti}^{4+}: 3d(2t_{2g})^1\text{-O}^{2-}: (1s)^{-1}2p^6$ and $\text{Ti}^{4+}: 3d(3e_g)^1\text{-O}^{2-}: (1s)^{-1}2p^6$, respectively, where $(1s)^{-1}$ denotes a hole in the O 1s shell [Figure 6(b)]. The energy separation between t_{2g} and e_g states amounts to 2.8 eV, 2.7 eV, and 2.5 eV for TiO_2 , $\text{Gd}_2\text{Ti}_2\text{O}_7$, and SrTiO_3 , respectively, which is a direct measure of the ligand field strength of TiO_6 octahedron. O 1s NEXAFS of polycrystalline $\text{Gd}_2(\text{Ti}_{1-y}\text{Zr}_y)_2\text{O}_7$ show only the transitions from oxygen anions located in the 48f oxygen sites, which are coordinated to both Ti^{4+} and Gd^{3+} ; hence, gadolinium-oxygen also contributes to intensity in the vicinity of e_g states (533.3 eV) of TiO_6 octahedron in $\text{Gd}_2\text{Ti}_2\text{O}_7$. Further, the intensities of the transitions to t_{2g} and e_g states of TiO_6 octahedron decrease, and the oxygen ions coordinated to zirconium increasingly contribute to the intensity in the vicinity of the transitions to e_g states in addition to titanium-oxygen and gadolinium-oxygen. However, this transition shifts systematically towards lower energy with increasing substitution of zirconium for titanium in $\text{Gd}_2(\text{Ti}_{1-y}\text{Zr}_y)_2\text{O}_7$. Thus, a systematic shift towards lower energy of the transition at 533.3 eV for $y=0.0$ to 532.5 eV for $y=1.0$ shows an increase of zirconium coordination from 6 to nearly 8 with increasing substitution of zirconium for titanium in $\text{Gd}_2(\text{Ti}_{1-y}\text{Zr}_y)_2\text{O}_7$.

Graphene Nanostructures as Tunable Storage Media for Molecular Hydrogen

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Graphene nanostructures can be used as a new media for more effective molecular hydrogen storage.

Many methods have been proposed for efficient storage of molecular hydrogen for fuel cell applications. However, despite intense research efforts, the twin DOE goals of 6.5 percent mass ratio and 62 kg/m³ volume density (Schlapbach and Zuttel 2001) have not been achieved either experimentally or via theoretical simulations on reversible model systems. Carbon-based materials, such as carbon nanotubes, have always been regarded as the most attractive physisorption substrates for the storage of hydrogen. Theoretical studies on various model graphitic systems, however, failed to reach the elusive goal. Here and in recent work from the *Proceedings of the National Academy of Science* (Patchkovskii et al. 2005), we show that insufficiently accurate carbon–H₂ interaction potentials, together with the neglect and incomplete treatment of the quantum effects in previous theoretical investigations, led to misleading conclusions for the absorption capacity. A proper account of the contribution of quantum effects to the free energy and the equilibrium constant for hydrogen adsorption suggest that the DOE specification can be approached in a graphite-based physisorption system. The theoretical prediction can be realized by optimizing the structures of nano-graphite platelets (graphene), which are lightweight, inexpensive, chemically inert, and environmentally benign. The interaction of nonpolar H₂ molecules with physisorption substrates in a graphitic system is mainly the London dispersion. Accurate calculations including treatment of electron correlations on model systems, such as polycyclic aromatic hydrocarbons (e.g., benzene and coronene), indicate that H₂ molecules have adsorption energies between 4 and 7 kJ/mol (Tran et al. 2002; Hübner et al. 2004; Heine et al. 2004) at an equilibrium distance of $d \approx 3 \text{ \AA}$ (Figure 7). These binding energies are small and entropic, and quantum effects cannot be ignored at practical temperatures ($\approx 200\text{--}300 \text{ K}$). The estimated limit of accuracy of our calculations at $d \approx 8 \text{ \AA}$ is within $\pm 25\%$. Even considering this large margin of error, we conclude that an H₂ storage enhancement material approaching, or possibly even exceeding, the DOE specification can be produced by encapsulating molecular hydrogen in graphite layers with an appropriate interlayer spacing. All MP2 and CCSD(T) computations were performed with the NWChem (Straatsma et al. 2005) program package.

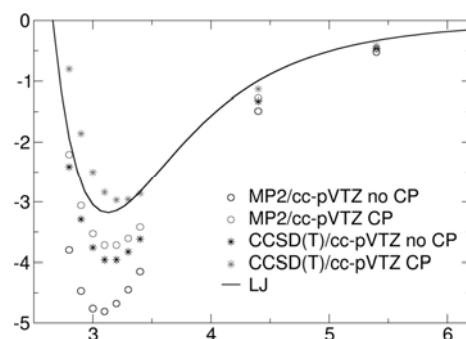


Figure 7. H₂/benzene interaction potentials are calculated using high-level *ab initio* methods.

Citations

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Quasiperiodic Trajectories in the Unimolecular Dissociation of Ethyl Radicals by Time-Frequency Analysis

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Studies of ethyl radical dissociation processes performed using direct dynamics are helping researchers to understand combustion processes.

Ethyl radical is an important intermediate in hydrocarbon crackers and combustion processes (Warnatz 1984), playing a central role as the principal precursor to ethylene through loss of a hydrogen atom. Detailed experimental studies in the relevant high-energy regime had previously worked with the assumption of statistical behavior (Hanning-Lee et al. 1993; Feng et al. 1993). Two recent studies (Gilbert et al. 1999; Amaral et al. 2001) of the dissociation dynamics of ethyl have found that highly excited radicals can dissociate with a fast and a slow component, with the slower component decaying four to five orders of magnitude more slowly than predicted by Rice–Ramsperger–Kassel–Marcus theory (Hase et al. 1979), even though the ~5-eV excitation energy far exceeds the 1.6-eV barrier to dissociation. We seek to investigate the anomalous and unexpected kinetic behavior by means of classical trajectory calculations on a full 21-dimensional, calibrated density-functional theory potential surface for C₂H₅. The 410 direct dynamics classical trajectories were integrated with a step size of 0.1 fs for a maximum of 2 ps, or up to a C₂H₄+H center-of-mass distance of 8.0 bohr, whichever came first. The calculations were carried out with a custom version of NWChem (Straatsma et al. 2004). Only 78 percent of the trajectories of ethyl radicals prepared in a microcanonical ensemble with 120-kcal/mol excitation energy above the zero-point energy and zero total angular momentum dissociate to form C₂H₄+H. The remaining hot ground-state ethyl radicals have a lifetime of \approx 2 ps, during which a time-frequency analysis finds them trapped for extended periods of time in long-lived quasiperiodic trajectories. These calculations support the experimental observation that the dissociation of highly excited ethyl radicals to ethylene and a hydrogen atom can occur much more slowly than predicted by statistical rate theories.

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Fast Electron Correlation Methods for Molecular Clusters in the Ground and Excited States

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A new method allows for highly accurate predictions of large-scale molecular clusters.

The factorial or high-rank polynomial dependence of computational costs with respect to system size is one of the most undesirable features of modern electronic structure theories (Kohn 1995; Head-Gordon 1996). When the system size refers to the volume of a molecule, worse-than-quadratic dependence is argued to be non-physical in view of the two-centre nature of Coulomb interactions. The physically correct asymptotic computational cost dependence is, in fact, believed to be linear for extensive quantities (e.g., total energies) and constant for intensive quantities (e.g., excitation energies). By choosing spatially localized functions as a basis set, we can devise *fast* electronic structure methods, the computational cost of which scales in a physically correct fashion (Kutteh et al. 1995; Lee et al. 1996; Strain et al. 1996; White et al. 1996; Challacombe, 1999). These fast electronic structure methods have the binary-interaction energy expression of (Kitaura et al. 1999):

$$E = \sum_{i < j}^n (E_{ij} - E_i - E_j) + \sum_i^n E_i, \quad (1)$$

where E_i is the total Hartree–Fock (HF) energy of unit i immersed in the electrostatic field of all the other $n-1$ units and the field is determined, prior to evaluating equation (1), by adjusting the electron density of each unit so that it becomes self-consistent with the field.

Likewise, E_{ij} is the total HF energy of dimer unit i and j in the electrostatic field created by all the other $n-2$ units. We combine this binary-interaction method in the dipole approximation with electron-correlation methods ranging from many-body perturbation theory [MBPT(2) and MBPT(3)], coupled-cluster theory [CCSD and CCSD(T)] to density functional theory and with excited-state methods from configuration-interaction singles theory, equation-of-motion coupled-cluster theory (EOM-CCSD) to time-dependent density functional theory. We also consider the inclusion of important three-body Coulomb, exchange, and correlation contributions exactly in what we call the ternary-interaction method. We apply these methods to calculate the binding energies of a small water cluster [(H₂O)₃], the energy differences among isomers of large water clusters [(H₂O)₂₀], the energy difference between the zwitterionic and neutral forms of glycine in water [(C₂NO₂H₃)(H₂O)₇ and (C₂NO₂H₃)(H₂O)₈], the lowest singlet $\phi^* \leftarrow n$ excitation energies and their solvatochromic shifts of small [(CH₂O)(H₂O)₂] and large [(CH₂O)(H₂O)₃₀ and (CH₂O)(H₂O)₈₁] formaldehyde–water clusters (Figure 8). The largest calculation is performed at the EOM-CCSD level with the aug-cc-pVDZ basis set for a cluster containing 247 atoms.



Figure 8. The structure of hydrated formaldehyde [(CH₂O)(H₂O)₈₁] is calculated using a new approach.

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What is the Fate of N₂ Gas Produced by Microbial Denitrification?

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Understanding the fate and transport of nitrogen gas produced in situ by microbial reduction of nitrate is important to evaluating the potential effectiveness of uranium and technetium bioremediation processes.

At DOE's Natural and Accelerated Bioremediation Research's Field Research Center (FRC) at Oak Ridge National Laboratory, researchers are investigating the possibility of using native microbial communities to create anaerobic and reducing conditions that favor the bioreduction of uranium and technetium to their less soluble and mobile forms. However, the high levels of nitrate co-contamination at this site (and many other sites) inhibit microbial uranium and technetium bioreduction. Once nitrate is removed, uranium and technetium reduction occur rapidly. Thus, by stimulating the activity of indigenous denitrifying organisms, nitrate can be reduced to nitrogen allowing metal-reducing organisms to reduce uranium and technetium. However, nitrate concentrations at the site are very large (up to 200 mM) and there is concern that the large quantities of nitrogen gas produced during denitrification will clog the pore space of the treated aquifer. Thus, understanding the fate and transport of nitrogen gas produced *in situ* is important to evaluating the effectiveness of uranium and technetium bioreduction.

In order to facilitate an understanding of fate and transport of nitrogen gas, a series of experiments at EMSL were conducted to mimic conditions in the field. A two-dimensional flow cell was packed with a mixture of FRC sediments. The lower half of the flow cell (through port 4) contained sediment from the shallow groundwater aquifer at the site. The upper half (ports 5-8) contained crushed limestone bedrock. Microbial activity was stimulated by a series of electron donor additions similar to those used in field experiments. For each addition, a synthetic groundwater solution amended with 300 mM of ethanol and 150 mM of nitrate was injected into the inlet of the flow cell. Water samples were collected at eight locations within the flow cell, and at the outlet. Hydraulic conductivity was measured before and after each ethanol addition. Aqueous and gas-phase saturations were measured using EMSL's dual-energy gamma imaging system, and samples were analyzed using ion chromatography and gas chromatography. Successful stimulation of the *in-situ* denitrifying microbial community was observed by the consumption of injected ethanol and nitrate, by the production of a denitrification by-product (NO₂), as well as by the visual observation of gas bubbles in the chamber.

In May 2005, the system was flushed to remove residual ethanol and nitrate and a test was conducted to quantify rates of ethanol and nitrate consumption, while at the same time quantifying gas production. This involved injection of a measured quantity of synthetic groundwater prepared as before. Samples were collected and the system was scanned daily so that the development of denitrification, production of intermediates, and the extent and location of N₂ gas formation within the pore space could be measured. At the end of the test, the system was destructively sampled to quantify the effects of donor additions on the microbial community.

Figure 9 shows a three-dimensional representation of the flow cell over the course of the 15 days that the experiment was run. Nitrate concentration, initially at ~150 mM, was nearly completely reduced in the lower biostimulated portion of the flow cell within ~ six days. Gas saturation of the pore space rapidly increased

and reached a maximum saturation of about 17 percent within the lower portion of the flow cell. Theory predicts that ~1.8 L of nitrogen gas will be produced by the complete denitrification of 150-mM nitrate. Measured gas saturations were much smaller, and observations confirm that, although substantial gas is produced, only a small portion is trapped within the pore space, while most is released to the sediment pack surface. The effect of gas production on the hydraulic conductivity of the sediment pack was very small. The quantity of organisms produced and the composition of the microbial community is currently being analyzed.

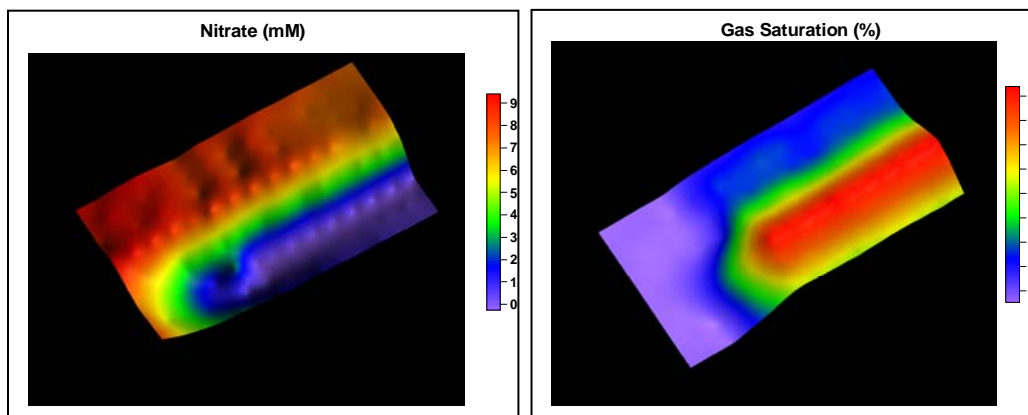


Figure 9. Plot of nitrate concentration and gas saturation (%) over the course of the 15-day experiment for each of eight ports.

Awards and Recognition

None

Professional/Community Service

Voluntary Protection Programs Participants' Association. The 21st Annual National Voluntary Protection Programs Participants' Association (VPPPA) Conference was held August 19-25, 2005, in Dallas, Texas. Among those attending was EMSL researcher Nancy Isern, the research and development co-chair of PNNL's Voluntary Protection Program (VPP). The National VPPPA conference provides a forum for the exchange of ideas related to the VPP, a nationwide program dedicated to continuous improvement in worker safety and health. In addition to various workshops focusing on management leadership, employee involvement, worksite analysis, hazard prevention and control, and safety and health training, the conference provides networking and mentoring on the PNNL VPP program to other entities aspiring to VPP Star Status, the highest level of VPP recognition. PNNL's VPP continues to be a leader in excellent worker safety and health programs through rigorous self assessment and continual improvement, and was recertified for Star Status in 2004.

Major Facility Upgrades

None

News Coverage

None

Visitors and Users

Chemistry and Physics of Complex Systems Facility

- Ben Arthurs, Washington State University, Pullman, Washington, worked on microscopy automation of scoring low-dose radiation responses in a green fluorescent protein-based vector.
- Olexandr Bondarchuk, University of Texas at Austin, Texas, worked on the study “Atomically Resolved Studies of Transition Metal Oxides.”
- Paul Boynton, University of Washington, Seattle, Washington, and Riley Newman, University of California, Irvine, California, gave the seminar “Gravitational Physics Research on the Fitzner-Eberhardt Arid Lands Ecology Reserve.”
- Daniel Chiu, University of Washington, Seattle, Washington, gave the seminar “Dialogs with Single Cells.”
- Ivan Chu, University of Hong Kong, Pokfulam, Hong Kong, participated in the Interfacial and Condensed-Phase Chemical Physics Summer Research Institute and worked on the study “Energetics of Dissociation of Peptide Radical Cations.”
- Luis Cuadra-Rodriguez and Barney Ellison, University of Colorado at Boulder, Colorado, collaborated with EMSL researcher Steve Barlow and PNNL researchers Jim Cowin and Alla Zelenyuk on reactions of organics on aerosols.
- Bill Durham, University of Arkansas, Fayetteville, Arkansas, gave the seminar “Applications of Ruthenium Bipyridine Complexes to Kinetic Problems in Biochemistry.”
- Todd Engstrom, University of Texas at Austin, Texas, worked on the study “Condensed Phase Chemical Physics of Low Temperature Amorphous Solids and Gas Surface Interactions.”
- Shaun Garland, Shasta College, Redding, California, worked on the study “Characterization of Functional Nanoscale Materials for Vapor Sensing.”
- Jason Green, Purdue University, West Lafayette, Indiana, participated in the Interfacial and Condensed-Phase Chemical Physics Summer Research Institute and worked on the study “Soft-Landing of Peptide Ions on Surfaces.”

- Assa Lifshitz, Hebrew University of Jerusalem, Jerusalem, Israel, gave the seminar “Anatomy of Complex Reaction Systems. Combustion Reaction Mechanisms from Ignition Delay Times.”
- Anoop Mayampurath, Utah State University, Logan, Utah, participated in the Interfacial and Condensed-Phase Chemical Physics Summer Research Institute and worked on the study “Develop a Procedure for the Determination of the Calibration Parameters on the Host Side and Integrate Them into the Hardware to Facilitate Real Time Multiband Analysis.”
- Vladimir Mikheev, Innovatek, Inc., Richland, Washington, worked on the ongoing research collaboration “Ultra-Trace Molecular Detection Instrumentation Based on Aerosol Nucleation with Rapid Preconcentration and Separation.”
- Klaus Mueller, State University of New York at Stony Brook, Stony Brook, New York, worked on the study “Development of Data Analysis and Visualization Software – SpectraMiner.”
- Luis Rodriguez, National Cancer Institute, Bethesda, Maryland, worked on the study “Development of Multi-Functional Microscopy (MFM) for Cancer and AIDS Research.”
- Andy Shaller, Washington State University, Pullman, Washington, participated in the Interfacial and Condensed-Phase Chemical Physics Summer Research Institute and worked on the study “Single Molecule Dynamics of Protein DNA Interactions.”
- Wei (David) Wei, University of Texas at Austin, Texas, participated in the Interfacial and Condensed-Phase Chemical Physics Summer Research Institute and worked on the study “Photoelectron Emission Microscopy (PEEM) Study of Cu Nanoparticles on TiO₂(110).”
- Tieqiao Zhang, National Institutes of Health, Bethesda, Maryland, worked on the study “Analysis of Lipid Nanoparticle Interaction with Cell Membrane.”
- Zhenrong Zhang, University of Texas at Austin, Texas, participated in the Interfacial and Condensed-Phase Chemical Physics Summer Research Institute and worked on the study “Photochemistry of Halogenated Hydrocarbon on TiO₂(110) Surface.”

Environmental Spectroscopy and Biogeochemistry Facility

- Baolin Deng, University of Missouri, Columbia, Missouri, continued his collaboration with Chongxuan Liu and Eugene Ilton, Pacific Northwest National Laboratory, Richland, Washington, on characterizing Cr(VI) removal from aqueous solutions using a commercial activated carbon that was coated with quaternized poly(4-vinylpyridine). The results suggest that this is a cost-effective method for removing chromate (a known carcinogen) from water. X-ray photoelectron spectral analyses indicated that chromate was partially reduced on the surface. This discovery suggests that better models describing chromium uptake by this type of material must be devised.
- Erica DiFilippo, University of Arizona, Tucson, Arizona, continued working with scientists Mart Oostrom, Pacific Northwest National Laboratory in Richland, Washington, and EMSL researcher Tom Wietsma. Her experimental flow and transport experiments were designed to investigate the

amount of dense nonaqueous phase liquid mass flux reduction as a function of source zone mass removal. This relationship will be useful in evaluating the benefit of partial source zone mass removal.

- Frannie Skomurski, University of Michigan, Ann Arbor, Michigan, continued working with Kevin Rosso, Eugene Ilton, and Sebastien Kerisit, Pacific Northwest National Laboratory, Richland, Washington, and EMSL researcher Mark Engelhard to investigate the role of electron transfer between hexavalent uranium in solution and the mineral magnetite (Fe_3O_4) using a combined experimental and modeling approach. Computer modeling is being used to simulate the adsorption of aqueous U(VI) onto different magnetite surfaces, and electron transfer calculations are performed to understand the process of reduction, and hence, immobilization, of U(VI) by Fe(II) in the magnetite lattice. Surface reaction experiments were performed using atomic force and scanning tunneling microscopy on natural magnetite samples, as well as on epitaxially grown magnetite thin films from PNNL. This is the first investigation to probe the reduction of U(VI) on magnetite at the molecular level. This process is important in understanding the capacity of mixed-valent iron-oxides for immobilizing uranium in the environment.
- Matthew Wander, Stony Brook University, Stony Brook, New York continued working with Kevin Rosso, Pacific Northwest National Laboratory, Richland, Washington, to study homogeneous and heterogeneous redox processes in aqueous systems including uranium and chromium with green rust.
- John H. Weare, University of California, San Diego, La Jolla, California, continued his collaboration with Eric J. Bylaska, Pacific Northwest National Laboratory, Richland, Washington, and EMSL researcher Marat Valiev. They are studying high-temperature (pressure) electrolyte solutions thought to facilitate metal ion transport in hydrothermal environments by using *ab initio* molecular dynamics methods, which require a parallel computational environment such as that provided by EMSL's supercomputer.
- Nicholas Wigginton and Mike Hochella, Virginia Polytechnic Institute, Blacksburg, Virginia, continued their collaboration with Kevin Rosso and Brian Lower, Pacific Northwest National Laboratory, Richland, Washington, to examine the electron-transfer properties of outer-membrane multi-heme cytochromes from the metal-reducing bacterium *Shewanella oneidensis*. Purified cytochromes (omcA, mtrC, mtrA) were imaged and characterized with current-sensing atomic force microscopy and scanning tunneling microscopy. The spectroscopic data will then be modeled/interpreted according to modern tunneling theories. As part of the Biogeochemistry Scientific Grand Challenge, the overall goal of this and other related studies is to verify and elucidate the mechanism of Fe(III)- and Mn(IV)-oxide reduction by these cytochromes and their associated complexes.

High-Field Magnetic Resonance Facility

- Myriam Cotten, Pacific Lutheran University, Tacoma, Washington, worked onsite using the 600-MHz spectrometer for the study "Investigating Molecular Recognition and Biological Function at Interfaces Using Antimicrobial Peptides."

- Leonard Fifield and Christopher Aardahl, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 500- and 300-MHz spectrometers for the study “NMR Analysis of Synthesized Organic Compounds for Modification of Nanostructures.”
- Michelle Forgeron, University of Alberta, Edmonton, Alberta, Canada, worked onsite using the 750-MHz spectrometer for “An Extended Study of the Molybdenum(IV) Octacyanide Anion: Comparison of Dodecahedral Versus Square Antiprismatic Structural Forms via Solid-State ⁹⁵Mo Nuclear Magnetic Resonance Spectroscopy.”
- Jian Zhi Hu, Charles Peden, and Yong Wang, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 750-MHz spectrometer for the study “*In-situ* High Field, High Resolution NMR Spectroscopy.”
- Michael Kennedy, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 800-, 750-, 600-, and 500-MHz spectrometers for the study “Structural Genomics Collaborative Access Team (CAT).”
- Rachel Kleivit and Peter Brzovic, University of Washington, Seattle, Washington, worked onsite and remotely using the 900-, 800-, and Cryoprobe 600-MHz spectrometers for the study “NMR Structural Investigations of BRCA1.”
- Andrew Lipton, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 900- and 800-MHz spectrometers for the studies “Correlation of Structure and Function of Zinc Metalloproteins via Solid-State NMR Methods” and “Investigation of the Role of Mg²⁺ in DNA Repair Proteins APE1, Pol, and FEN1.”
- Karl Mueller and Geoffrey Bowers, Pennsylvania State University, University Park, Pennsylvania, worked onsite using the 900-MHz spectrometer for the study “Sensitivity Enhancing NMR of Strontium-87 Nuclei in Environmental Samples.”
- Ronald Nieman and Douglas Klewer, Arizona State University, Tempe, Arizona, worked remotely using the 800-MHz spectrometer for the study “Structure and Function of the Membrane Protein OEP16.”
- Ponni Rajagopal, University of Washington, Seattle, Washington, worked remotely using the 900- and 750-MHz spectrometers for the study “Structural Investigation of a Molecular Chaperone.”
- Raymond Reeves, Washington State University, Pullman, Washington, worked remotely using the 900-, 800-, 750-, Cryoprobe 600-, and 600-MHz spectrometers for the study “Structural Biology of the Human High Mobility Group A (HMGA) Proteins: Characterizing the Hub of Nuclear Function.”
- Linda Sapochak, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 300- and 500-MHz spectrometers for the study “Development of Organophosphorus Compounds for Solid-State Lighting Applications.”

- Celine Schneider, and Richard Darton, University of British Columbia, Vancouver, British Columbia, Canada, worked onsite using the 900- and 800-MHz spectrometers for the study “Structural Investigations of Solid Materials by High Resolution Solid-State NMR at Very High Field.”
- Wendy Shaw, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 500-MHz spectrometer for the study “Hydrogen Storage Materials.”
- Gabriele Varani, University of Washington, Seattle, Washington, worked remotely using the 800-MHz spectrometer for the study “Structure of Telomerase RNA and Telomeric Proteins.”
- Jianjun Wang and Xuefeng Ren, Wayne State University, Detroit, Michigan, worked onsite and remotely using the 900-, 800-, 750-, and Cryoprobe 600-MHz spectrometers for the study “Structural Studies of Lipid-free Apolipoprotein A-1.”
- Marvin Warner, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 500- and 300-MHz spectrometers for the study “Routine ^1H and ^{13}C NMR Analysis of Functionalized Semiconductor and Metallic Nanoparticles Synthesized for Biodetection Studies.”
- Weixing Xu, University of Central Florida, Orlando, Florida, worked onsite using the 300-MHz spectrometer for “Study of the Network Structures of Polymer-Derived Amorphous SiAlCN Ceramics.”
- Ping Yan and Haishi Cao, Pacific Northwest National Laboratory, Richland, Washington, worked onsite and remotely using the 500- and 600-MHz spectrometers for the study “Development of Multipurpose Tags and Affinity Reagents for Rapid Isolation and Visualization of Protein Complexes.”
- Z. Gary Yang, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 300-MHz spectrometer for “NMR Study of Effects and Mechanisms of Mechanical Activation on Hydrogen Sorption/Desorption of Nanoscale Lithium Nitrides.”
- Aleksey Yezerets, Cummins, Inc., Columbus, Indiana, worked onsite using the 300-MHz spectrometer for the study “Investigation of Soot Morphology and Microstructure with Respect to the Oxidation.”

The following individuals sent samples to be run on the 900-, 750-, 600-, and 500-MHz Cryoprobe NMR spectrometers in support of EMSL's Structural Genomics Collaborative Access Team, led by Michael Kennedy, Pacific Northwest National Laboratory, Richland, Washington:

- Cheryl Arrowsmith, University of Toronto, Toronto, Ontario, Canada
- Guy Montelione, Rutgers University, Piscataway, New Jersey.

High-Performance Mass Spectrometry Facility

- Josh Adkins, Pacific Northwest National Laboratory, Richland, Washington, worked on the study “Identifying Targets for Therapeutic Interventions using Proteomic Technology.” Progress is being made towards several manuscripts using the data and results from the analysis of the samples for this project. The annual report will also go out at the end of this month to the administrative center for the project.
- Edward DeLong, Massachusetts Institute of Technology, Cambridge, Massachusetts, worked on the study “Proteomic Analysis of Naturally Occurring Methane Oxidizing Archaeal Communities.” The original samples were analyzed against two different databases supplied by the collaborators. The data have been sent for their analysis.
- Jon Jacobs, Pacific Northwest National Laboratory, Richland, Washington, worked on the study “Proteomic Characterization of Cerebrospinal Fluid (CSF) by High Resolution LC-MS/MS.” Recent collaborative work between researchers from PNNL and Massachusetts General Hospital has resulted in an in-depth proteomic characterization of human cerebral spinal fluid. More than 1,000 proteins have been detected and identified in human cerebral spinal fluid by using advanced mass spectrometry proteomic techniques, resulting in the most comprehensive coverage to date and providing a database for future comparative studies of disease model systems.
- Richard Klemke, Scripps Research Institute, La Jolla, California, worked on the study “Characterization of the Tumor Cell Lamellipodia Phosphoproteome.” Klemke, along with researchers at PNNL, have continued to make progress in characterizing the important cellular signaling pathways described in the phosphoproteome of tumor cell lamellipodia (the mechanism by which cancer cells metastasize). Using unique phosphopeptide isolation and quantitation techniques in conjunction with high mass accuracy mass spectrometry, researchers have detected, identified, and quantified more than 100 phosphorylated proteins, many of which were observed to have altered phosphorylation patterns between the normal cell and the lamellipodia cell extensions used for metastasis.
- Liang Shi, Pacific Northwest National Laboratory, Richland, Washington, worked on the study “Unraveling the Molecular Biology of Host-Pathogen Interactions.” Shi submitted several large batches of samples that were obtained from various *Salmonella*-containing vacuole purification schemes. The samples have been prepared and are currently being analyzed by mass spectrometry.
- Alexander Vasilenko, Uniformed Services University of the Health Sciences, Bethesda, Maryland, was given an overview of the proteomic pipeline used to conduct high-throughput proteomic research at EMSL. Previous to his visit, he participated in important research evaluating manganese and its role in the radiation resistance of *Deinococcus radiodurans*. During his visit, he was given a tour of the laboratory, a hands-on demonstration in procedures used for extracting proteins from bacterial samples, and instruction on bioinformatics tools used to process and organize proteomic data for analysis. While visiting, he used these tools to evaluate stored proteomic data obtained from earlier *D. radiodurans* studies in preparation for the future proteome comparison of two *D. radiodurans* mutants to wild-type *D. radiodurans*.

Interfacial and Nanoscale Science Facility

- Jiji Antony, University of Idaho, Moscow, Idaho, performed fundamental basic science studies that will benefit a whole range of applications involving nanoparticles in solution, including environmental remediation, corrosion, magnetic storage media, and heterogeneous catalysis.

- Chih-Hsin Cheng, Cornell University, Ithaca, New York, used x-ray photoelectron spectroscopy to measure the properties of surface functional groups of black carbon from historic charcoal blast furnaces.
- Yunchul Chung and Byoung In Sang, Korea Institute of Science and Technology, Seoul, South Korea, discussed enzyme stabilization for applications in bioremediation and biodetection.
- Anthony Cinson, Wheeling Jesuit University, Wheeling, West Virginia, visited EMSL as part of a Department of Homeland Security Fellowship to study the influence of gadolinium and samarium doping on atomic and ionic transport properties of novel nanostructured ceria-zirconia multilayers.
- Hsiu-wu Guo and Chen-Luen Shih, University of Washington, Seattle, Washington, studied the properties of polysilicon grown on silicon substrate with nickel metal as a buffer layer. There are various applications in the semiconductor industry related to the growth of polysilicon. These users are mainly using EMSL thin film sputter deposition capabilities to grow these films. They are also using EMSL x-ray diffraction, transmission electron microscopy, atomic force microscopy, and clean room capabilities that are directly associated with their research work.
- Shiho Iwanaga, University of Washington, Seattle, Washington, carried out fundamental research in synthesis and characterization of thermoelectric materials.
- Satyanarayana Kuchibhatla, University of Central Florida, Orlando, Florida, visited EMSL as a part of the Interfacial and Condensed-Phase Chemical Physics Summer Research Institute to investigate the properties of freestanding ceria nanoparticles and ceria nanodomains in thin films.
- Fung Suong Ou, Rensselaer Polytechnic Institute, Troy, New York, visited EMSL as part of the Interfacial and Condensed-Phase Chemical Physics Summer Research Institute to conduct research on controlled defect generation in porous silicon.
- Lea Ream, Yakima Valley Community College, Yakima, Washington, visited EMSL as a part of the community college initiative to investigate surface modification by high-energy ion beams.
- Nataphan Sakulchaichoen, University of Oklahoma, Norman, Oklahoma, investigated the growth mechanism of single-wall carbon nanotubes over a cobalt molybdate (CoMo) bimetallic catalyst using a model system: CoMo supported on a lacey silicon monoxide grid.
- Yiguang Wang, University of Central Florida, Orlando, Florida, visited EMSL as a part of the Interfacial and Condensed-Phase Chemical Physics Summer Research Institute to synthesize oxide electrolyte layer-by-layer structures using sputter deposition capabilities and characterize these films using various capabilities.
- Atsushi Yamamoto, Energy Technology Research Institute, Ibaraki, Japan, carried out fundamental research in synthesis and characterization of thermoelectric materials.

Molecular Science Computing Facility

- J. David Hobbs, Montana Tech of the University of Montana, Butte, Montana, learned firsthand how to use Ecce and NWChem while visiting EMSL. He will be using this software for student

instruction and for the study “NMR Chemical Shift Calculations for Novel Bioactive Metabolites from an Acid Mine Waste Organism.”

- Heather Netzloff, Australian National University, Canberra, Australia, met with the NWChem development team to learn more about the software development and to describe her recent research.
- Fang Peng, Ames Laboratory, Ames, Iowa, learned firsthand how to use NWChem and the Common Component Architecture (CCA) so that she could incorporate the computational chemistry code GAMESS into CCA components.
- Hubertus Johannes Jacobus Van Dam and Paul Sherwood, Council for the Central Laboratory of the Research Councils, Daresbury, Warrington, Cheshire, United Kingdom, discussed collaborations on NWChem software development for density functional theory calculations (e.g., automatic generation of Fortran code for density functionals, second derivatives of the quadrature weights) and for incorporating GAMESS UK into Ecce.

Molecular Science Computing Facility—New User Agreements with NWChem/Ecce

- Calvin College, Grand Rapids, Michigan
- Colorado School of Mines, Golden, Colorado
- Deakin University, Geelong, Australia
- Ecole Nationale Supérieure d'Ingenieurs de Caen & Centre de Recherche, Caen, France
- General Electric, Bangalore, India
- Institute of Chemical Research of Catalonia, Tarragona, Spain
- PJ Safarik University, Kosice, Slovak Republic
- Sandia National Laboratories, Livermore, California
- Tsinghua University, Beijing, China
- Univerista' di Bari, Bari, Italy
- University of Cologne, Cologne, Germany
- University of Versailles, Versailles, France

New EMSL Staff

None

Publications

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