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Research Highlights

Studies of Damage Accumulation in 4H Silicon Carbide by Ion-Channeling Techniques

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The study non-equilibrium defects introduced by irradiation has broad impact by providing an understanding of equilibrium defect properties and materials performance for applications in environmental restoration, energy production, and national security.

Silicon carbide (SiC) is a wide-gap semiconductor material with superior electrical, thermal, and mechanical properties that can be used for high-power, high-frequency, and high-temperature or heterostructure applications. Doping in SiC is quite a challenge, since the thermal diffusion of dopants requires extremely high temperatures. Furthermore, epitaxial growth processes do not allow planar selective area doping, which is essential to fabricating devices. Ion implantation is a critical technique to selectively introduce dopants for production of SiC-based devices at low temperatures. However, ion implantation produces defects and even amorphization of the crystalline lattice. Therefore, one of the critical issues for SiC device fabrication is to understand defect production, accumulation, and damage annealing mechanisms, which are essential to implementing implantation doping techniques in SiC-based electronic device fabrication.

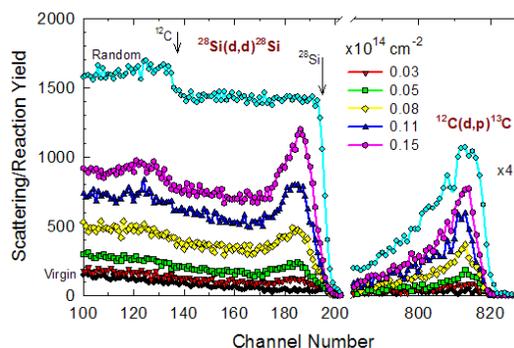


Figure 1. <0001>- aligned Rutherford backscattering and nuclear reaction analysis spectra for 4H-SiC irradiated with 2.0-MeV gold ions to different ion fluences at 165 K.

In this work, single crystal 4H-SiC was irradiated with 2-MeV gold ions at 165 K. Ion-induced defect configurations and damage accumulation were then studied by ion-channeling techniques along the $\langle 0001 \rangle$, $\langle \bar{4}40\bar{3} \rangle$, and $\langle \bar{2}20\bar{1} \rangle$ directions. The Rutherford backscattering and nuclear analysis reaction spectra along the $\langle 0001 \rangle$ direction shown in Figure 1 are representative of the other orientations. The increase in disorder on both the silicon and carbon sublattices with increasing ion fluences is clearly evident in Figure 1. The disorder profiles of silicon sublattice along the three orientations are shown in Figure 2 for the as-implanted sample to a fluence of $1.1 \times 10^{13} \text{ cm}^{-2}$, which represents the general behavior for other ion fluences. The results clearly show a higher degree of disorder along the $\langle \bar{4}40\bar{3} \rangle$ and $\langle \bar{2}20\bar{1} \rangle$ directions over the whole implantation range.

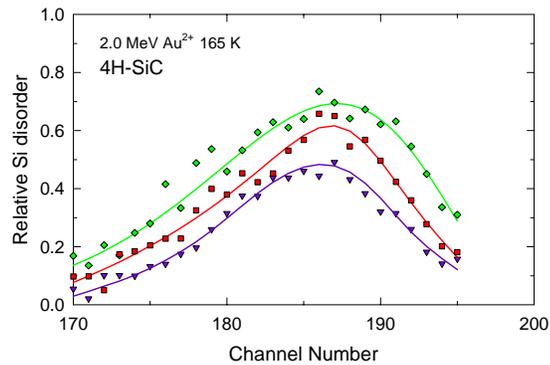


Figure 2. Relative silicon disorder along different orientations under 2-MeV Au^{2+} irradiation to a fluence of $1.1 \times 10^{13} \text{ cm}^{-2}$ at 165 K.

The relative disorder on the silicon and carbon sublattices at the damage peak for the as-implanted samples is shown in Figure 3 as a function of the local dose (dpa). A sigmoidal dependence of damage accumulation on dose is observed along all three directions and on both sublattices. A nonlinear dependence of damage accumulation is observed for both the silicon and carbon sublattices along all three directions, and the relative disorder observed along the $\langle \bar{4}40\bar{3} \rangle$ and $\langle \bar{2}20\bar{1} \rangle$ directions is much higher than that along the $\langle 0001 \rangle$ direction, as shown in Figure 3. The damage accumulation can be described by a disorder accumulation model, which indicates that defect-stimulated amorphization is the primary amorphization mechanism in SiC, and the high-disorder level for the large off-axis angles is attributed to particular defect configurations. Molecular dynamics simulations demonstrate that most single interstitial configurations are shielded by silicon and carbon atoms on the lattice sites along the $\langle 0001 \rangle$ direction, which significantly reduces their contribution to the backscattering/reaction yield along the $\langle 0001 \rangle$ direction.

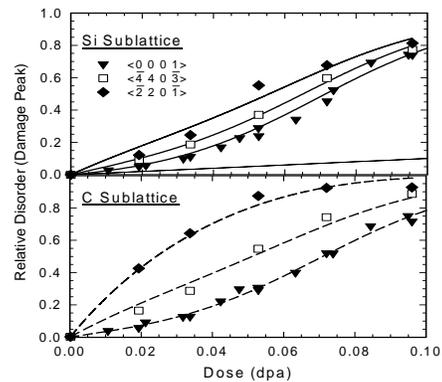


Figure 3. Relative disorder along the $\langle 0001 \rangle$, $\langle \bar{4}40\bar{3} \rangle$, and $\langle \bar{2}20\bar{1} \rangle$ directions on both the silicon and carbon sublattices as a function of local dose at the damage peak.

Computational Design of Catalysts: The Control of Chemical Transformation

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Catalysts are substances that speed up specific chemical reactions, and are widely used in chemical industry for the production or processing of materials. Plastics, fuel, and pesticides are just a few examples of materials that are processed, in part, using catalysts. Better catalyst design provides the opportunity for quicker and cleaner production of items that we need to live our everyday lives.

Historically, development and discovery of catalysts have been expensive processes of trial and error. For a given reaction type, hundreds or thousands of candidate catalysts must be painstakingly developed and tested before a suitable catalyst is identified. Designing a catalyst from first principles based on the details of a reaction, a process known as rational design, would dramatically impact the field of catalysis because it could help eliminate most of the candidates that are unlikely to succeed, thus providing a substantial reduction in the cost of developing a new catalyst. Rational design has been a long-standing goal of catalysis science, but realizing this vision has remained elusive. However, recent developments in the areas of pure and alloy metal catalysts have the potential to yield catalysts of greatly improved activity and selectivity. Using density functional theory (DFT) calculations, J. Greeley and M. Mavrikakis from the University of Wisconsin-Madison discovered a new class of near-surface alloys (NSAs) that can yield superior catalytic behavior for hydrogen-related reactions. Some of these NSAs bind atomic hydrogen (H) as weakly as the noble metals (copper, gold) while, at the same time, dissociating H₂ much more easily (Figure 4). This unique set of properties may permit these alloys to serve as low-temperature, highly selective catalysts for pharmaceuticals production and as robust fuel-cell anodes. This work represents an important progress in using fundamental first-principles and computational modeling to predict catalysis materials with unique properties. EMSL's MPP2 supercomputer, located within the MSCF, was partially used to perform these calculations. The results were published as a full paper in *Nature Materials* (Greeley and Mavrikakis 2004) and have been highlighted by the American Chemical Society news magazine *Chemical & Engineering News* (Jacoby 2004).

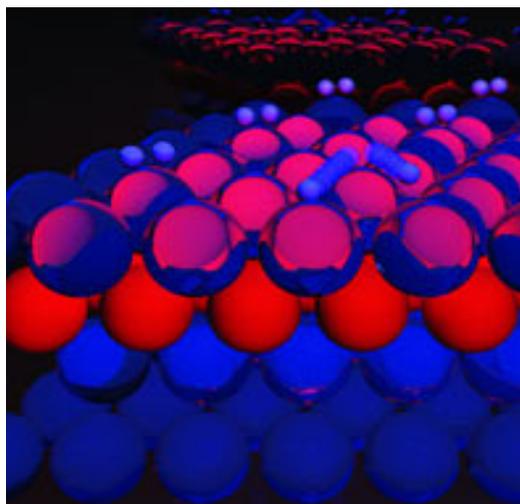


Figure 4. Theoretical studies predict that some alloys consisting of a host metal (large blue spheres) such as Pt or Pd and a subsurface solute (red) such as Ta or W will make excellent hydrogenation catalysts because of their unique ability to dissociate H₂ (small spheres) readily and bind atomic hydrogen weakly.

References

Greeley J and M Mavrikakis. 2004. "Alloy Catalysts Designed from First Principles." *Nature Materials* 3(11):810-815.

Jacoby M. 2004. "Catalysis by the Numbers, Advanced Computational Methods are Revealing Mechanistic Details and Guiding Catalyst Design." *Chemical & Engineering News* 82(48):25-28.

Hydrogen Storage Materials

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Hydrogen offers a potential clean energy source; however, new materials must be developed that provide high-volume storage capacity for hydrogen. This research aims to advance the fundamental understanding necessary for development of these materials.

Growing demands for clean energy sources that do not add more carbon dioxide and other pollutants to the environment have resulted in increased attention worldwide to the possibilities of a "hydrogen economy" as a long-term solution for a secure energy future, based on potentially renewable resources. Some of the greatest challenges are the discovery and development of new on-board hydrogen storage materials and catalysts for fuel cell-powered vehicles. New materials that store both high-gravimetric, high-volumetric densities of hydrogen which release H₂ at temperatures < 100°C and uptake H₂ at pressures < 100 bar are highly desired. The volumetric constraints eliminate from consideration pressurized hydrogen systems and guide towards the development of solid storage materials. There are no currently known materials that meet these requirements. As such, there is a need for a fundamental understanding of the chemical and physical properties of hydrogen-rich materials. The following is a portion of our experimental analysis for researching the molecular attributes which facilitate the release and uptake of molecular hydrogen.

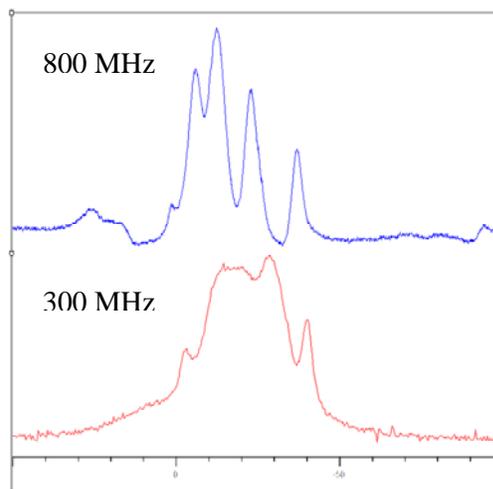


Figure 5. ¹¹B{¹H} SSNMR (spinning speed 10 kHz) of NH₃BH₃ reaction products as a function of field. The increased resolution at 800 MHz allowed identification of two new products.

We recently suggested that efficient storage of hydrogen might be accomplished in compounds that have alternating electron-rich and electron-deficient sites capable of covalently binding H^+ and H^- , respectively. There are two fundamental premises that will guide us towards the discovery of novel hydrogen-rich materials that are operational at temperatures between ambient and 100°C : (1) binding of hydrogen requires formation of chemical bonds, and (2) inherent polarity of low molecular weight species bearing electron-rich and electron-deficient sites will likely result in the formation of molecular solids.

These guidelines led us to initially consider ammonia borane ($AB = \text{NH}_3\text{BH}_3$). This inorganic analog of ethane yields far more favorable volumetric densities, as it is a solid (m.p. 115°C) rather than gas. The molecular crystalline solid is composed of a network of dihydrogen bonds formed between the protic H^+ attached to nitrogen and hydridic H^- attached to boron.

Preliminary results showed the rates of hydrogen release from the bulk phase solid ammonia borane follows an apparent nucleation and growth kinetic model. However, little is known about the nucleation events and the role of the intermolecular dihydrogen bonding in the formation of molecular hydrogen. Solid-state nuclear magnetic resonance (SSNMR) $^{11}\text{B}\{^1\text{H}\}$ spectra of these reactions taken at 300-MHz ^1H frequency aided in determining reaction mechanisms; however, some products remain unidentified due to spectral overlap. NMR experiments run using higher fields (500 MHz and 800 MHz) enhanced resolution and reduced the quadrupolar coupling, which simplified the distinction between quadrupolar coupling and multiple species reaction products formed as a result of hydrogen release (Figures 5 and 6). In some cases, 500 MHz was adequate to identify products, but 800 MHz was needed to clear ambiguities, as shown in Figure 6.

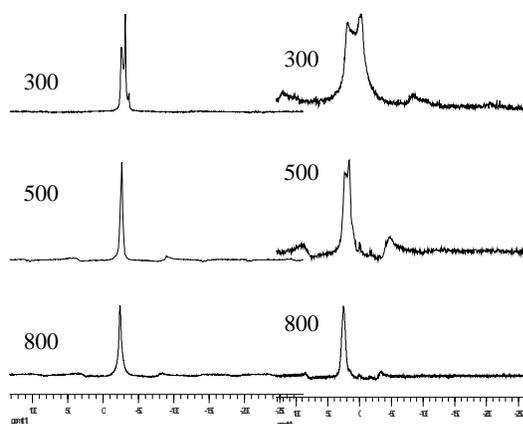


Figure 6. SSNMR $^{11}\text{B}\{^1\text{H}\}$ spectra as a function of field, spinning at 10 kHz. The starting material (left) and the final reaction products (after heating at 170°C --right) are shown at all three fields. For some compounds, such as NH_3BH_3 (left), 500 MHz provides maximum narrowing. For some of the products (right), 800 MHz is needed to sufficiently narrow the peaks. Investigating at all three fields provides important information about the coupling constant, the symmetry and the products.

In addition to the ^{11}B SSNMR experiments, ^1H SSNMR spectra were also attained at 800 MHz. Each of the starting materials and reaction products were studied. As expected, chemical shift differences were observed. These observations will be further quantified using heteronuclear correlation to correlate the ^1H and ^{11}B resonances to provide further product information. ^1H experiments are also being used to investigate scaffolding properties. We found that scaffolding the NH_3BH_3 into mesoporous silica reduces the temperature for hydrogen release. The chemistry and thermodynamics behind this observation are not understood; however, the extreme narrowing in the proton NMR would suggest either an increased ordering or a more liquid-like behavior in the scaffold (Figure 7). Further experiments such as rotational echo double resonance for the direct investigation of atomic distances are necessary to propose a mechanism, but the initial insight provides evidence of a fundamentally different organization within the scaffold.

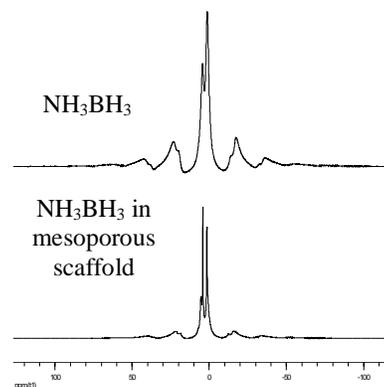


Figure 7. ^1H SSNMR (spinning speed 15 kHz) reveals a distinct narrowing of the two resonances as a function of scaffolding NH_3BH_3 into mesoporous silica.

Accurate Identification of Peptides Using Tandem Mass Spectrometry

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Genes are DNA segments which, when “turned on,” provide living cells with instructions on how to build proteins. Proteins are molecules which can be used as the cellular “skeleton,” allow some cells to move, process energy and waste products, and participate in virtually every function required for cells to live. Understanding how genes work requires us to obtain a detailed picture of how proteins work.

In recent years, gene sequences have been completed for a wide array of organism types—from single-cell bacteria to human. These genomes are the culmination of world-wide collaborative efforts among academic institutions, private industry, and government agencies. The net result has been the generation of a historically unparalleled amount of publicly available data for organism gene sequences. This information resource continues to grow as the sequences of new organisms are completed. Putting this huge information resource to practical use has brought the next layer of knowledge—proteomics—increasingly to the forefront of biology.

Proteomics is the study of proteins in a whole organism under a given set of conditions. Proteins—the molecular “building blocks” in biological systems—perform any number of special functions, allowing cells to live, grow, and react to their surroundings. Proteins are made by joining amino acid residues (smaller molecular units) end-to-end in a particular order that is determined by gene sequence. After proteins reach their final or functional form, they are ready to interact with other proteins, substances inside or outside cells, or genes. Because of their central role in almost all of the processes required to sustain life, understanding protein behavior is a key aspect of understanding any organism’s behavior.

To keep pace with the growing demand for proteomic data, high-throughput methodologies have been developed which provide a “snapshot” of all the protein contents of a biological sample. One such method is known as tandem mass spectrometry (MS/MS). Proteins from biological samples being analyzed by MS/MS are first digested with trypsin to produce smaller fragments (peptides), which are then sorted by liquid chromatography elution or some other method. These smaller fragments are then sent to the first stage of the tandem MS process, in which the charge-to-mass ratio of the fragment is determined. In the second phase of tandem MS, the population of identical peptides is broken with high-energy beams, resulting in collection of small fragments representing the various ways the peptide can be broken. These fragments are sent through a second MS stage, and all of their charge-to-mass ratios are obtained in one dataset. The collection of fragment masses can be thought of as a fingerprint—a profile of peak locations which is unique for each peptide. Developing methods for accurately identifying peptides from this fingerprint is the aim of this MSCF Computational Grand Challenge (Heredia-Langner et al. 2004).

Currently, peptides are identified by creating hypothetical fingerprints of known peptides. The list of known peptides can be any available set of protein sequences and identities. Then for a given spectrum (experimental fingerprint), the similarity to all known peptides of the correct mass-to-charge ratio is calculated, and statistical methods are used to assess the confidence in each similarity score.

This peptide identification scheme has been implemented in a software development project, called POLYGRAPH, on two high-performance environments: MPP2, MSCF's 1960-processor Linux cluster, and Altix1, the PACC's 128-processor SGI machine. In both environments, the independent nature of individual spectrum scoring has been exploited to achieve near-perfect speedup. On MPP2, early benchmarks of POLYGRAPH, shown in Figure 8, scaled well to thousands of processors using a protein database with 88,000 entries. Larger databases, such as the nonredundant protein database (nr), may contain millions of entries and must be distributed for POLYGRAPH to function.

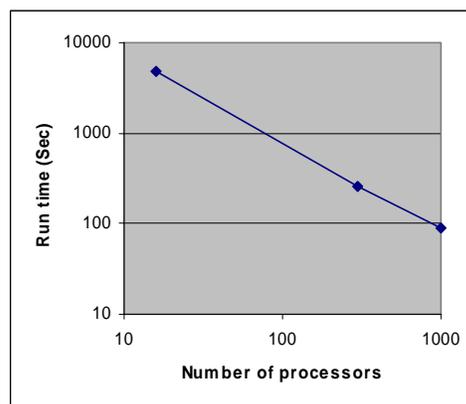


Figure 8. Run time of POLYGRAPH on MPP2.

Development of the distributed database version of POLYGRAPH has resulted in novel algorithms for managing this massive amount of data in both shared memory and distributed memory architectures. This represents a significant development for capabilities in the growing field of data-intensive computing, and allows for the solution of previously intractable problem sizes using high-performance machines.

Reference

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Mid-Infrared Versus Far-Infrared (THz) Relative Intensities of Room-Temperature *Bacillus* Spores

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This research evaluates potential spectroscopic techniques that may be used for rapid and accurate detection of biological spores and other possible bioterrorism agents.

Recently, interest surged in the far-infrared or terahertz (THz) spectral region. An advantage of working at these wavelengths, located between the infrared and millimeter-wave regions, is that many synthetic materials are transparent, and although there are interferences from rotational transitions of water vapor, the transitions are relatively few at the very long wavelengths (i.e., $<50\text{ cm}^{-1}$). Work in the THz domain recently warranted great interest with emphasis placed on both sensor development (such as those focusing primarily on technologies using pulsed laser sources and gated detectors) as well as signatures recognition—THz spectral signatures have been reported for explosives, nucleotides, DNA/RNA samples, organics, a few gas-phase samples, and pharmaceuticals whose coatings are transparent in the THz region, thus allowing for mapping within a tablet.

We recently reported identification and discrimination of bacterial spores using mid-infrared technologies. Certain gram-positive bacteria have the ability to form spores, a dormant state that is highly resistant to both chemical and thermal extremes. Using both transmissive and photoacoustic infrared methods, we extended the mid-infrared studies for identifying vegetative bacteria to include bacterial spores. Applying established chemometric methods to our spectra, the data could be reduced to distinguish spores from unknowns, and also distinguish between spores of similar *Bacillus* species and strains.

The present work compares the relative signal strengths of the mid-infrared to the far-infrared signatures of spores, thus probing the possibility of using THz signatures for clinical, analytical, or forensic applications (Johnson et al. 2005).

Typical results for bacterial spore absorbance spectra are shown in Figure 9 for *B. subtilis* 49760 and *B. thuringiensis subsp. kurstaki*. The data above 1900 cm^{-1} revealed little information other than the well-characterized C–H stretches, and are therefore not discussed here. The strongest bands are the protein Amide I and Amide II bands near 1657 and 1541 cm^{-1} , respectively, with nucleic acid and lipid skeletal modes seen at lower frequency. Of greater interest is the lack of spectral signatures seen in the long wavelength regions (wavenumbers $<600\text{ cm}^{-1}$). Each of the mid- and far-infrared spectra was recorded for the same sample on the same substrate. With the exception of a weak 431 cm^{-1} band, no far-infrared signatures were found that are clearly associated with the sample. Although an exact spore count for the sample is not easily ascertained, an estimated spore count was between 108 and 1010.

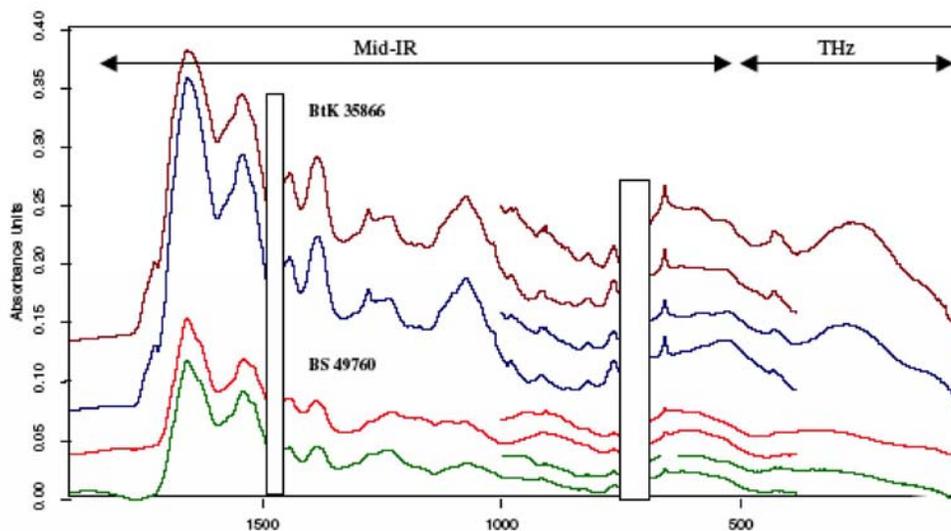


Figure 9. Composite mid-infrared and THz spectra of *B. thuringiensis ssp. kurstaki* and *B. subtilis* 49760 from 1800 to 30 cm^{-1} . Those regions where the polyethylene substrate does not transmit have been blocked out for clarity. Spectra were recorded at 2 cm^{-1} resolution. Spectra have been vertically offset for clarity with the THz 3 spectrum of a sample plotted directly atop the mid-infrared spectrum of the same sample.

The present data demonstrate that any THz signatures associated with the room-temperature spectra of bacterial spores are comparatively weak. Averaged over 30 spectra and comprising five *Bacillus* species, any THz signatures are 28.5 times weaker (based on p-p noise) than the 1657 cm^{-1} Amide I band. The lack of THz peaks makes conjecture as to their (non-) origin difficult. Others have reported DNA/RNA/nucleotide THz signals, but a spore is a complex containing thousands of chemical species. Smearing of large molecule signatures may play a role, as well as masking by spore-bound water molecules. It may be that the transition dipole moments for such large amplitude motions are fundamentally weak. We anticipate cooling the samples (e.g., 77 or 10 K) would increase the intensity by narrowing the linewidths of the THz bands as has been shown (10–110 cm^{-1}) not only for short peptides, but also long chain retinal and DNA nucleotides. However, for many applications (e.g., first responders), time is critical and precludes using cryogenic methods. Although other species may show stronger signatures, particularly at low temperatures, the present work may suggest a limited utility of the THz domain for the room temperature detection of spores.

Reference

Johnson TJ, NB Valentine, and SW Sharpe. 2005. "Mid-Infrared Versus Far-Infrared (THz) Relative Intensities of Room-Temperature *Bacillus* Spores." *Chemical Review Letters* 403(1-3):152-157.

Electron Microscopy Evaluation of the Role of Dissimilatory Metal-Reducing Bacteria in Biomineralization Pathways

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The interaction of metal-reducing microorganisms with mineral surfaces such as iron oxides is one of the most complex and important reactions in nature. Use of electron microscopies allows investigation of mineral association with bacterial cells, crystal size, morphology, and spatial relationships. Understanding these processes may lead to improvements in bioremediation processes.

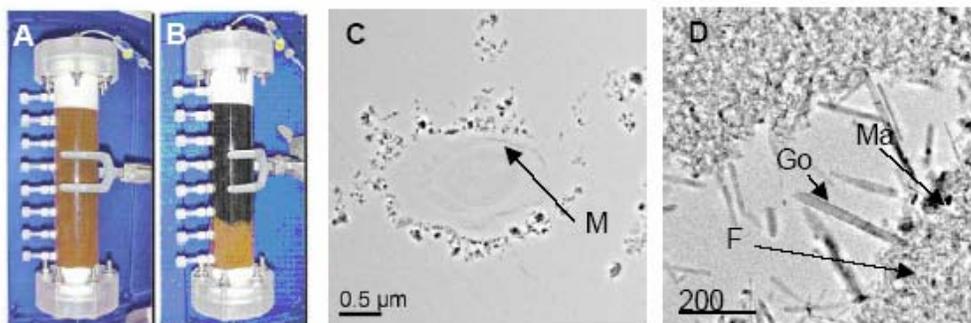


Figure 10. Bacterially assisted mineral transformation of ferrihydrite-coated sand in advective flow columns. (a) Ferrihydrite at the starting point. (b) After 16 days of reduction, magnetite was the dominant phase. (c) Unstained cross section of secondary minerals surrounding bacterial cell (the membrane is shown by an arrow). (d) Goethite needle-like crystals (Go), magnetite (Ma), nanocrystalline ferrihydrite (F). Scale bar is 200 nanometers.

The importance of microorganisms in the biogeochemical cycling of iron is well recognized. Dissimilatory metal-reducing bacteria, which are ubiquitous in soils and aquifers, couple the oxidation of organic matter or H₂ with the reduction of various Fe(III) oxide phases to obtain energy for growth and function. They can also catalyze Fe(III) reduction under anaerobic conditions, using crystalline and poorly crystalline iron oxides as a terminal electron acceptor.

Microbially induced iron mineral transformations were examined using *Shewanella putrefaciens*, strain CN32, in an artificial groundwater medium in columns under advective flow conditions (Hansel et al. 2003) (Figures 10a and 10b). In this experiment, columns were filled with ferrihydrite-coated quartz sand inoculated with *S. putrefaciens* (initial cell density 108/mL). Lactate was added as an electron donor. Changes in microbial metabolism, aqueous chemistry, and solid-phase distributions were then monitored at time points until termination of the column experiment at 16 days.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used for investigating mineral association with bacterial cells, crystal size, morphology, and spatial relationships. A special TEM sample preparation protocol developed at EMSL was used for the accurate preservation of both the biological and mineral portion of the sample. To eliminate exposure of the anaerobic sample to oxygen, the whole embedding procedure, as well as the thin sectioning on an ultramicrotome, was carried out in an anaerobic glove box (95 percent argon, 5 percent hydrogen). Ultrathin sections of the material were studied using a JEOL 2010 TEM operating at 200 kV coupled to an Oxford energy dispersive spectroscopy system. Images were collected and analyzed using a DigitalMicrograph™ (Gatan), with selected area diffraction patterns evaluated by Desktop Microscopist (Lacuna) software.

Visual changes in the solid-phase within the column were evident: initial orange ferrihydrite started turning brown, and further darkened over the course of the experiment, as it was converted to predominantly goethite and magnetite (Figures 10c and 10d). In addition to spectroscopic methods, the presence of goethite and magnetite was further confirmed by TEM and SEM, and the spatial orientations and size of mineral particles were also determined. Typical needle-like structures of goethite crystals were predominantly associated with the surface of ferrihydrite, but were also found coupled with microbial cell surfaces. In fact, some bacterial cells appeared completely encrusted in goethite, most likely a result of electrostatic attraction between newly precipitated goethite and the microbial surface. Magnetite, on the other hand, was mainly associated with the ferrihydrite surface, and only rarely with the cell surface. Thus, the bacterial cell is only indirectly (by ferrous iron production) responsible for goethite and magnetite formation. Although intracellular precipitation of iron oxides in *S. putrefaciens* was recently reported (Glasauer et al. 2002), only extracellular precipitation was observed in this experimental setup. Bacteria have the ability to shed the mineral deposits from their outer membranes in order to prevent surface passivation caused by mineral sorption. Bacteria appeared to primarily serve as an Fe(II) source for the system; secondary mineralization was confirmed as a function of initial Fe(II) concentrations.

The mechanism of enzymatic reduction is not completely understood, and the accountable protein functions are being intensively investigated using several molecular biology techniques. Current and future studies will include immunogold labeling at the electron microscopy level as a method for determining localization of these proteins.

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Mechanism of Heteroepitaxial Growth at Initial Stages of Oxide Nanodot Formation: Cu_2O on $\text{SrTiO}_3(100)$

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The ability to synthesize copper (I) oxide quantum dots on strontium titanate surfaces is significant for exploring applications related to photocatalytic splitting of water into H_2 and O_2 or reduction of organic matter using sunlight. This work highlights the recent success of growth and characterization of copper (I) oxide quantum dots.

The initial stages of island growth and interface formation on strontium titanate surfaces have been examined by X-ray photoelectron spectroscopy (XPS). Spectra were acquired in situ at different stages of growth in a step-by-step mode, by temporarily interrupting growth at a particular thickness and quenching the sample to room temperature. A series of copper $2p_{3/2}$ spectra taken at the very initial stages of the growth at 760 K is presented in Figure 11(a). At the very initial stages of Cu_2O nanodot growth, a small spectral feature associated with the Cu(II) state appeared at ~ 934.5 eV and disappeared at $d > 0.8$ nm. This observation indicates some additional interaction between deposited copper atoms and oxygen of the SrTiO_3 substrate.

The intensity of the copper $2p_{3/2}$ signal as a function of the copper oxide effective thickness at the very initial stages of growth is shown in Figure 11(b), where there is an apparent deviation from linear rise of the signal. This finding suggests an absence of the continuous (wetting) layer formation, which otherwise would exhibit a linear increase during uniform growth of the first monolayer. Thus, Cu_2O on the $\text{SrTiO}_3(100)$ evidently grows via an island formation mechanism, with the metal oxide clusters starting to grow already at sub-monolayer coverages.

Atomic force microscope (AFM) images of surface morphologies, acquired ex situ at different stages of growth, are displayed in Figure 12. At very initial stages shown in Figure 12(a), AFM examination shows the formation of isolated square-based, truncated small nanodots with widths and heights in the range of ~ 8 -15 nm and of 0.8-2.0 nm, respectively. This is consistent with results from the XPS intensity analysis of the initial island formation at submonolayer

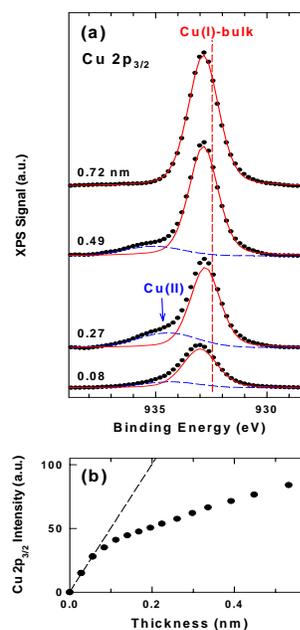


Figure 11. (a) Sequence of the copper $2p_{3/2}$ spectra, and (b) copper $2p_{3/2}$ intensity evolution for increasing effective thickness.

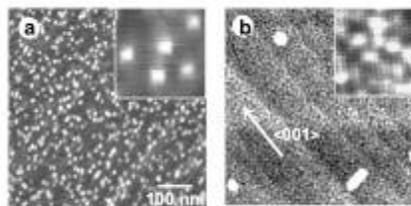


Figure 12. AFM images of the surface morphology evolution with thickness: (a) $d = 0.3$, (b) $d = 1.7$ nm. Inset: part of the image magnified \sim three times.

coverages, discussed above. Thus, the flat areas between nanodots are, apparently, the uncovered SrTiO₃(100) surface. Both the shape and orientation of nanodots, with edges mostly along the <011> direction, indicate a crystalline ordering and epitaxy. Further deposition results in an increase of nanodot density, as Figure 12(b) demonstrates for a 1.7-nm effective thickness. Comparison of the magnified image parts [inset of Figure 12(b)] reveals that lateral dimensions of nanodots do not change significantly in the process of initial quasi-planar growth. As a result, a dense layer of small, low aspect ratio nanodots forms at this stage of growth. In addition to the small nanodot layer, a subpopulation of considerably larger rectangular- and hexagonal-based clusters, with average lateral and vertical dimensions of 30-80 and 6-16 nm, respectively, also appear, as shown in Figure 12(b). Large nanodot density increases when growth proceeds to a larger thickness. It is remarkable that these large dots start to form only when the small nanodots reach some critical density of $\sim 10^{13}$ cm⁻², which occurs at $d \sim 1.5$ nm for a 760-K growth temperature.

In the studied system, the Cu₂O nanodot dimensions only weakly increase at the initial stages of growth, while continued deposition leads to an increase of dot density. A weak dependence of nanodot size on coverage indicates an existence of the optimal island size at initial stages of growth. The appearance of the larger-size dots beyond a certain density cannot be explained by a conventional ripening mechanism or by preferential direct growth of a subset of the small nanodots. If any of these mechanisms had been operable in the studied system, some more general transition would be expected in the size distribution from the small islands to the large ones. We propose that dot coalescence, driven by increasing dot density, decreasing separation, and fluctuations in dot size and separation during the growth/formation process, is the mechanism responsible for the sudden appearance of large dots superimposed on the distribution of small ones. In order to test this hypothesis, we used the kinetic model of the surface morphological evolution. It is based on surface diffusion driven by the elastic strain gradient and curvature of the surface, with or without interaction between neighboring dots. Figure 13 shows three snapshots of a distribution of dots, in which two dots are placed at a separation small enough to trigger interaction between the two dots. It is observed that when two dots are close enough, stress and diffusion cause the two dots to coalesce, leading to a larger dot that grows rapidly and adjusts to a different shape.

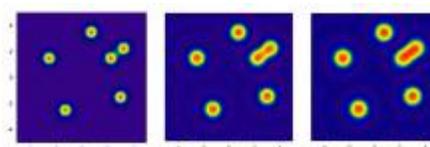


Figure 13. Simulated snapshots of evolution of the nanodot morphology.

In summary, the initial evolution of Cu₂O nanodot morphology may be described as progressing through several stages. Growth starts with formation of small well-ordered square planar nanodots at submonolayer coverages. At island densities less than critical, the optimal nanodot size only weakly changes with coverage. After reaching a critical dot density, formation of larger nanoclusters through coalescence begins. The coexistence of the different types of the nanodots results in a bi-modal distribution of their sizes and shapes.

Global Quantitative Proteome Analysis of HIV-1 Infection in CD4⁺-T-cells by ¹⁶O/¹⁸O Labeling and Accurate Mass and Time Tag Strategy

W Qian,^(a) T Liu,^(a) EY Chan,^(b) DL Diamond,^(b) DG Camp,^(a) MG Katze,^(b) and RD Smith^(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

(b) University of Washington, Seattle, Washington

This research represents the first large-scale quantitative proteome analysis of HIV-1 infection in human cell lines. The protein expression data obtained from this research is expected to provide new insights into the biological pathways regulated by HIV-1 infection.

Human immunodeficiency virus type 1 (HIV-1) is an enveloped retrovirus that causes severe depletion of the human immune system. The ~9-kb HIV-1 genome encodes nine open reading frames, consisting of fifteen distinct proteins that participate in different steps of the viral replication cycle. However, actions of these viral proteins alone cannot completely account for how HIV-1 efficiently replicates in a susceptible host. HIV-1 is expected to co-opt the host cell machinery to facilitate viral replication. In fact, many cellular proteins have been found to be incorporated into virions or otherwise interact with HIV-1. Although numerous interactions between HIV and host cell proteins have been described, the global effects of viral infection on the host cell proteome remains to be determined.

In this work, we demonstrate the first large-scale global quantitative proteome study of the primary effects of HIV-1 infection on host cellular protein expression by using ¹⁶O/¹⁸O stable isotope labeling, quantitative cysteinyl-peptide enrichment, and the accurate mass and time (AMT) tag strategy. The overall quantitation strategy is shown in Figure 14.

Through this research, initial generations of AMT tag databases for cysteinyl-peptide and non-cysteinyl-peptides have resulted in identification of greater than 30,000 unique peptides covering ~6000 different proteins. Quantitative liquid chromatography-Fourier-transform ion cyclotron resonance mass spectrometry analyses has resulted in greater than 3000 proteins quantified with the relative abundance differences between the HIV-1 infected and mock infected cells accurately determined. More than 300 proteins exhibited significant

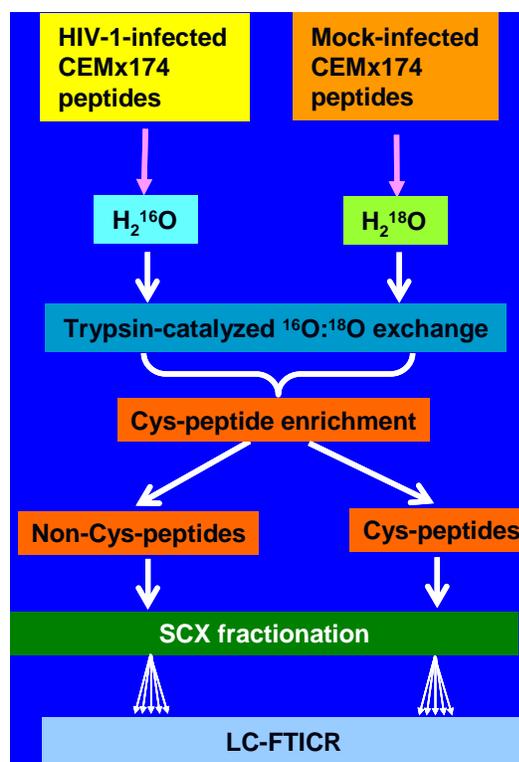


Figure 14. Quantitation strategy for studying HIV-1.

changes in protein abundance following HIV-1 infection, and many proteins have been previously shown to interact with HIV-1 viral proteins. Figure 15 shows an example of upregulated protein GTPase RAN, which has been shown to aid in the formation of HIV-1 protein Rev-associated complexes.

This work represents the most comprehensive global protein profiling study for an HIV-1 infection model system to date. We anticipate the large-scale protein expression data will provide new insights into the biological pathways regulated by HIV-1 infection.

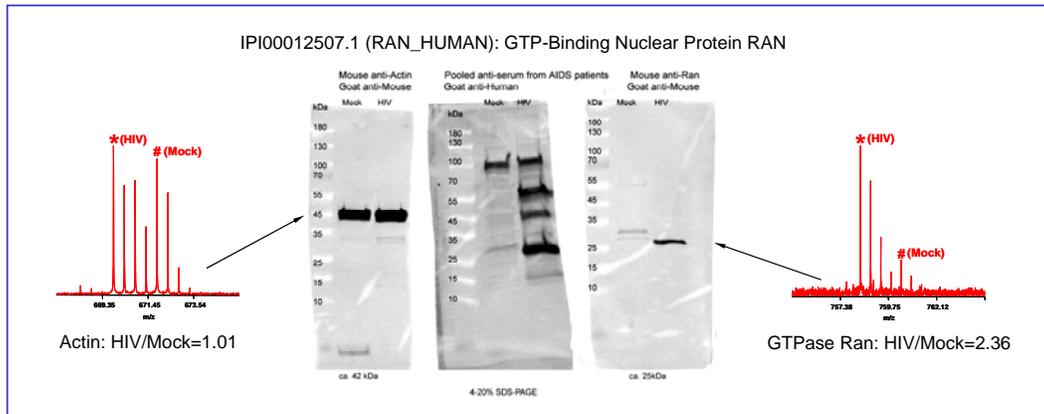


Figure 15. Many proteins with changes in abundance have been shown to interact with HIV-1 viral proteins, as annotated in the HIV-1 Human Protein Interactions Database. The GTPase RAN, which aids in the formation of Rev-associated complexes, was found up-regulated.

Awards and Recognition

U.S. Patent 6,808,694 “NO_x Reduction Methods and Apparatuses,” was issued on October 26, 2004, to PNNL researchers Russell G. Tonkyn and Gary Maupin, EMSL researcher Stephan E. Barlow, and former PNNL researcher M. Lou Balmer (now at Caterpillar, Inc.). One of the first steps in the catalytic conversion of NO_x back to N₂ is the oxidation of NO to NO₂. Researchers showed how this conversion could be accomplished in a cascaded system, resulting in overall high conversion (lower NO_x concentrations) and energy savings.

MSCF Makes a Splash in First Issue of New Computational Chemistry Journal. The very first issue of the new *Journal of Chemical Theory and Computation* (Jan/Feb 2005) includes three articles that contain acknowledgements of research use at EMSL and its Molecular Science Computing Facility (MSCF). These publications resulted from work performed in conjunction with three MSCF Computational Grand Challenges directed at understanding the synthesis and reactivity of nanoparticles for use in microfabrication and other processes (Barnard et al. 2005); rational design of catalysts (Harder et al. 2005), where one significant research effort in support of this Computational Grand Challenge is the development of new computational chemistry methods to address large systems; and properties of aluminum in nanoclusters (Schultz and Truhlar 2005).

Barnard AS, P Zapol, and LA Curtiss. 2005. “Modeling the Morphology and Phase Stability of TiO₂ Nanocrystals in Water.” *Journal of Chemical Theory and Computation* 1(1):107-116.

Harder E, B Kim, RA Friesner, and BJ Berne. 2005. “Efficient Simulation Method for Polarizable Protein Force Fields: Application to the Simulation of BPTI in Liquid Water.” *Journal of Chemical Theory and Computation* 1(1):169-180.

Schultz NE and DG Truhlar. 2005. “New Effective Core Method (Effective Core Potential and Valence Basis Set) for Al Clusters and Nanoparticles and Heteronuclear Al-Containing Molecules.” *Journal of Chemical Theory and Computation* 1(1):41-53.

Professional/Community Service

DOE Science Bowl. Theva Thevuthasan, Technical Group Leader of EMSL’s Interfacial and Nanoscale Science Facility, participated in DOE Science Bowl activities involving regional high school students. The DOE Science Bowl took place on February 26 at Washington State University, Tri-Cities in Richland, Washington.

Fabrication and Characterization of Nanomaterials Course. Twelve students (Figure 16) from the University of Washington, Oregon Health and Sciences University, Portland State University, and the South Dakota School of Mines and Technology participated in the 2005 Fabrication and Characterization of Nanomaterials course, developed through a National Science Foundation grant and held at EMSL. The course was coordinated by Fumio Ohuchi (University of Washington), Lai-Sheng Wang (Washington State University), and Don Baer (PNNL) and led by instructors from the coordinators’ institutions as well as

Stanford University, University of Idaho, and University of Alaska. The three-week course involved lectures on specific nanoscience and nanotechnology topics and small project activities in the laboratory, the latter which provided in-depth training of several EMSL capabilities and involved about 40 percent of the formal class hours. Coordinators view this course as not only a method for sharing the excitement of research at EMSL, but also as a way to grow and train highly qualified future users.



Figure 16. Students from the Fabrication and Characterization of Nanomaterials course held at EMSL.

Major Facility Upgrades

Flow Cell. A small (50-cm) chlorinated solvent resistant flow cell was designed and constructed (Figure 17) for use in the Subsurface Flow and Transport Laboratory within EMSL's Environmental Spectroscopy and Biogeochemistry Facility. Many of the experiments conducted in this laboratory do not require the use of the larger intermediate-scale flow cells (1 m). Thus, this smaller cell will allow multiple experiments to be conducted in the time it would take to pack a single large flow cell. It will also offer increased flexibility to run intermediate-scale experiments under multiple conditions more efficiently and allow testing—such as that performed in Figure 17—to determine experimental parameters prior to scaling up to larger flow cells.

After testing of the new flow cell is complete, facility researchers will examine the effect of modifying fluids with polymer to overcome flow bypassing due to heterogeneity.

The Digital Instruments BioScope atomic force microscope (AFM) has been upgraded. The older Nanoscope IIIa controller and related equipment were replaced by the Nanoscope IV version. The upgrade provides several new capabilities, including:

- the ability to collect images up to 4096 x 1024 pixels, which constitutes an improvement of 16 times the previous version
- the ability to control the quality factor for resonating cantilevers for intermittent and non-contact AFM measurements
- improved image processing capabilities

An ultraviolet-charge coupled diode camera and spectrograph were purchased in order to extend EMSL's time-resolved laser-induced fluorescence spectroscopy and imaging spectromicroscopy capabilities into the ultraviolet region. The camera will also be used to develop laser-induced breakdown spectroscopy/detection capabilities for the investigation, detection, and quantitative analysis of environmentally important toxic metals such as chromium, lead, arsenic, and sulfur as well as the detection of actinide-bearing aerosols and solid particles and nanocolloids in situ.

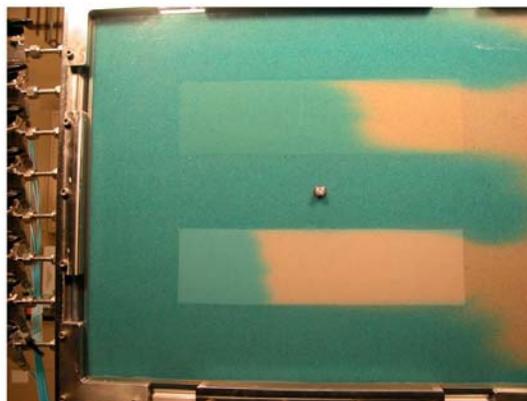


Figure 17. A water soluble dye (green) tracer test was conducted to evaluate the horizontal flow field of the newest flow cell in EMSL's Subsurface Flow and Transport Laboratory. The flow cell was packed with two zones that have lower hydraulic conductivities to demonstrate how the water will wrap around or bypass the regions of lower conductivity. As the solution flowed from left to right, the dye moved faster in coarser sand and slower in the two different finer sands.

News Coverage

A portion of the iron particle research performed at EMSL by researchers from EMSL, PNNL, and the University of Minnesota was featured in the February 10, 2005, *USA Today* article "Nanotech shows promise for cheaper Superfund cleanup" (http://www.usatoday.com:80/tech/news/nano/2005-02-10-nano-iron-cleanup_x.htm).

An article about recent research of artificially petrified wood was featured in the January 28, 2005, *news@nature.com* article "Furnace Creates Instant Fossils" (<http://www.nature.com/news/2005/050124/full/050124-14.html> - subscription required) and the January 25, 2005, *USA Today* article "Topping Mother Nature, lab makes petrified wood in days." http://www.usatoday.com/tech/science/discoveries/2005-01-25-petrified_x.htm. Part of the characterization research was performed using EMSL resources.

New EMSL Staff

Tyson Tucker joined the CaNS group as a research scientist. In this role, he provides Unix and Linux support to EMSL researchers and users. Before officially joining the group, Tyson worked with CaNS for two years as a student while completing his Computer Science degree from Washington State University, Tri-Cities.

Bruce Arey joined the Interfacial and Nanoscale Science Facility as a technologist responsible for all user and program activities related to scanning electron microscopy in the electron microscopy suite.

Visiting Users

Chemistry and Physics of Complex Systems Facility

- Micha Asscher, The Hebrew University of Jerusalem, Jerusalem, Israel, gave the seminar "Layer Growth on Solid Surfaces: From Fundamental Science to Applications."
- Olexandr Bondarchuk, University of Texas, Austin, Texas, worked on the study "Atomically Resolved Studies of Transition Metal Oxides."
- Rob Crowell, Argonne National Laboratory, Argonne, Illinois, gave the seminar "Ultrafast Radiation Chemistry and the Development of Laser Based Electron Sources."
- Demetra Farley, Prairie View A&M University, Prairie View, Texas, worked on the study "Fluorescence Imaging of Cellular Protein Dynamics."
- Victor Klimov, Los Alamos National Laboratory, Los Alamos, New Mexico, gave the seminar "Functional Nanocrystal-Quantum-Dot Assemblies: From Light-Emitting Diodes and Multicolor Lasers to Carrier-Multiplication-Based Solar Cells."
- Han Myoung Lee, Washington State University Tri-Cities, Richland, Washington, worked on the study "Photoelectron Spectroscopic Studies of Complex Anion Solvation in the Gas Phase."

- Xiang Li, John Hopkins University, Baltimore, Maryland, collaborated on “Photochemistry of Biologically Important Molecules in Gas Phase as well as Femtochemistry of Negative Ion Clusters of Dioxygen.”
- 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.”
- Bill Morgan, University of Maryland, Baltimore, Maryland, worked on the study “Electron Induced Genomic Instability.”
- J. Patrick Pancras, University of Maryland, College Park, Maryland, gave the seminar “Highly Time-Resolved Metals Study for Unprecedented Source Attribution of Primary Atmospheric Aerosol.”
- Bill Robertson, University of California, Irvine, California, worked on the study “Laboratory Studies of Atmospheric Processing of Sea Salt.”
- Luis Rodriguez, National Cancer Institute, Bethesda, Maryland, worked on the study “Development of Multi-Functional Microscopy (MFM) for Cancer and AIDS Research.”
- Alex Shluger, University College London, London, United Kingdom, gave the seminar “Mechanisms of Laser-Induced Desorption of Oxide Surfaces: New Results and Insights.”
- Tieqiao Zhang, National Institutes of Health, Bethesda, Maryland, worked on the study “Analysis of Lipid Nanoparticle Interaction with Cell Membrane.”

Environmental Spectroscopy and Biogeochemistry Facility

- Paul Bagus, University of North Texas, Denton, Texas discussed progress with Eugene Ilton, Pacific Northwest National Laboratory, Richland, Washington, on relativistic ab initio cluster model calculations that have important ramifications for rigorously modeling the 2p X-ray photoelectron spectroscopy of open-shell metals that are in the condensed phase. Results for MnO indicate that the cluster model approach improves the match between theory and experiment relative to atomic calculations, without the ad hoc adjustments used in semi-empirical methods.
- William P. Ball, Johns Hopkins University, Baltimore, Maryland, along with Chongxuan Liu and Zheming Wang, Pacific Northwest National Laboratory, Richland, Washington, continued their collaboration characterizing aqueous uranyl carbonate species using laser-induced time-resolved fluorescence spectroscopy.
- Barry Bickmore, Brigham Young University, Provo, Utah, in collaboration with Kevin Rosso, Pacific Northwest National Laboratory, Richland, Washington, continued their density functional theory calculations of gibbsite edge surface structures.
- Yin-Chu Chen, Oregon Health Sciences University/Oregon Graduate Institute, Beaverton, Oregon, and Zheming Wang, Pacific Northwest National Laboratory, Richland, Washington, continued their studies of the steady-state fluorescence anisotropy of molecularly imprinted polymer sensors.
- Hailiang Dong, Miami University, Oxford, Ohio, and EMSL researcher Ravi Kukkadapu continued Mössbauer measurements of bioreduced nontronites.
- Gerald Gibbs, Virginia Polytechnic Institute, Blacksburg, Virginia, in collaboration with Kevin Rosso, Pacific Northwest National Laboratory, Richland, Washington, continued

electron density distribution calculations in silicates. Silicate minerals comprise more than 90 percent of the earth's crust. Electron density is one of the most important properties of earth materials, providing information about the bonded interactions and structure together with important information about chemical reactivity.

- Je-Hun Jang, Pennsylvania State University, University Park, Pennsylvania, and EMSL researcher Ravi Kukkadapu collaborated on the Mössbauer analysis of synthetic goethite reacted with Fe(II) and membrane fraction of *Shewanella oneidensis*.
- Dan Kaplan, Westinghouse Savannah River, Aiken, South Carolina, and EMSL researcher Ravi Kukkadapu continued Mössbauer measurements of Savannah River Site sediments. The mobility of plutonium in the subsurface environment is significantly influenced by its oxidation state: Pu(V/VI) is 500 times more mobile than Pu(III/IV). Plutonium (IV) and Pu(VI) were placed in Savannah River Site (SRS) lysimeters and exposed to natural weather conditions with the intent of measuring the influence of Pu oxidation state on Pu mobility through the SRS subsurface sediments. These tests also showed that Pu(IV) oxidation may also be occurring, which may lead to migration of the plutonium in the ground. Mössbauer spectroscopy is being used to characterize the sediment minerals and to identify the minerals capable of reducing and oxidizing plutonium.
- Postdoctoral research fellow Sebastien Kerisit (Figure 18) and researcher Kevin Rosso, Pacific Northwest National Laboratory, Richland, Washington, are performing molecular dynamics calculations of electron transfer in iron oxide minerals as part of EMSL's Biogeochemistry Scientific Grand Challenge. The final steps of the respiratory cycle in *Shewanella oneidensis* involve electron transfer to oxide minerals. However, reduction of the mineral surface has been shown to occur at locations which differ from the points of attachment of the bacteria. Therefore, the goal of these calculations is to evaluate the rate of charge migration through the mineral and to investigate whether electrons donated at the oxide surface are free to diffuse away from the initial acceptor site.
- Andy Neal, University of Georgia, Aiken, South Carolina, and Tracy Cail, Oak Ridge National Laboratory, Oak Ridge, Tennessee, in collaboration with Kevin Rosso, Pacific Northwest National Laboratory, Richland, Washington, continued their studies of the adhesion of the metal-reducing bacteria *Shewanella* onto various well-defined single crystalline iron oxide surfaces.
- Tanya Peretyazhko and Gary Sposito, University of California, Berkeley, California, and EMSL researcher Ravi Kukkadapu continued Mössbauer measurements on biostimulated soils from Puerto Rico.



Figure 18. Sebastien Kerisit.

- Leila Reynald, Johns Hopkins University, Baltimore, Maryland, worked with EMSL researcher Paul Gassman to evaluate the effect of mutation in *Staphylococcal* nuclease protein on water structure within the hydrophobic core using room-temperature and cryogenic Fourier-transform infrared microscopy (Figure 19). Proteins fold in order to carry out their function. Mutations may cause proteins to misfold, which in some proteins are believed to be responsible for diseases such as Alzheimer's disease, cystic fibrosis, BSE (Mad Cow disease), and even many cancers.



Figure 19. Paul Gassman and Leila Reynald.

- Jiamin Wan and Joern Larsen, Lawrence Berkeley National Laboratory, Berkeley, California, and Zheming Wang, Pacific Northwest National Laboratory, Richland, Washington, continued their collaboration characterizing uranium-contaminated sediments.

- John H. Weare (Figure 20), on sabbatical from the University of California, San Diego, La Jolla, California, and his graduate student Stuart Bagatko visited EMSL to continue their 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 the EMSL supercomputer.

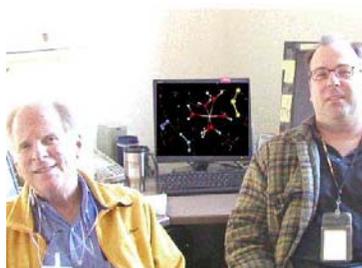


Figure 20. John Weare and Eric Bylaska.

- Nicholas Wigginton, Virginia Polytechnic Institute, Blacksburg, Virginia, working with Mike Hochella, in collaboration with Kevin Rosso and Brian Lower (Figure 21), Pacific Northwest National Laboratory, Richland, Washington, is currently examining the electron-transfer properties of outer-membrane multi-heme cytochromes from the metal-reducing bacterium *Shewanella oneidensis*. Purified cytochromes (omcA, mtrC, mtrA) will be 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 EMSL 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.



Figure 21. Brian Lower, Nick Wigginton, and Kevin Rosso.

- Postdoctoral research fellow Svetlana Yanina (Figure 22) and researcher Kevin Rosso, Pacific Northwest National Laboratory, Richland, Washington, are using AFM to quantitatively characterize the kinetics of dissolution on stable low-index surfaces of quartz. Naturally occurring quartz crystals exhibit large variations in the number and nature of extended defects, such as dislocations and grain boundaries. Surface retreat rate, as well as its dissolution morphology, shows strong dependence on defect distribution. In order to quantify the contribution of different types of defects to the dissolution process, the wavelet processing routines are being applied to the AFM images of the quartz surfaces undergoing dissolution. These data will be used to derive the dissolution rate laws that account for defect density variations in quartz crystals.



Figure 22. Svetlana Yanina.

High-Field Magnetic Resonance Facility

- James Aramini, Rutgers University, Piscataway, New Jersey, sent samples to be run on the 600-MHz spectrometer for the study “Structural Genomics of Eukaryotic Model Organisms.”
- Cheryl Arrowsmith, University of Toronto (University Health Network), Toronto, Ontario, Canada, sent samples to be run on the 600-MHz and 900-MHz spectrometers for the study “Structural Proteomics: Annotating the Genome Using 3D Structure.”
- Jordan Barton, University of California, Irvine, California, used the 500-MHz spectrometer for the study “The Structure and Dynamics of the Interaction of Membranes with Amyloid Oligomers.”
- Klara Briknarova, The Burnham Institute, La Jolla, California, sent samples to be run on the 600-MHz and 750-MHz spectrometers for the study “Structure of PR Domain of RIZ1 tumor Suppressor.”
- Peter Brzovic, University of Washington, Seattle, Washington, used the 600-MHz spectrometer to run samples for the study “NMR Structural Investigations of BRCA1.”
- Leonard Fifield, Pacific Northwest National Laboratory, Richland, Washington, used the 300-MHz spectrometer for the study “NMR Analysis of Synthesized Organic Compounds for Modification of Nanostructures.”
- Colin Fyfe, Celine Schneider, and Richard Darton, University of British Columbia, Vancouver, British Columbia, Canada, used the 500-MHz and 800-MHz spectrometers to run samples for the study “Structural Investigations of Solid Materials by High Resolution Solid State NMR at Very High Field.”
- Jian Zhi Hu, Pacific Northwest National Laboratory, Richland, Washington, used the 300-MHz and 800-MHz spectrometers for the study “Investigation of Catalyst Reaction Mechanisms by In-Situ High Field, High Resolution NMR Spectroscopy.”
- David Kramer, Washington State University, Pullman, Washington, used the electron paramagnetic resonance spectrometer for the study “Molecular Probes of Quinol Oxidation by the Cytochrome b6f Complex.”
- Do Heui Kim, Pacific Northwest National Laboratory, Richland, Washington, used the 300-MHz spectrometer for the study “Investigation of Soot Morphology and Microstructure with Respect to the Oxidation.”

- Howard Lacheen, University of California, Berkeley, California, used the 750-MHz spectrometer to run samples for the study “Solid State MAS NMR of High-Valent Cation Exchanged H-MFI.”
- Thomas Leeper, University of Washington, Seattle, Washington, sent samples to be run on the 600-MHz and 900-MHz spectrometers for the study “Structure of Telomerase RNA and Telomeric Proteins.”
- Jennifer Popham and James Gibson, University of Washington, Seattle, Washington, used the 300-MHz spectrometer for the “Study of the Binding Mechanism of Mutant SN-15 to Hydroxyapatite Using $^{15}\text{N}\{^{31}\text{P}\}$ REDOR.”
- Raymond Reeves, Washington State University, Pullman, Washington, sent samples to be run on the 600-MHz spectrometer for the study “Structural Biology of the Human High Mobility Group A (HMGA) Proteins: Characterizing the Hub of Nuclear Function.”
- Xuefeng Ren, Southern Illinois University, Carbondale, Illinois, used the 600-MHz, 800-MHz, and 900-MHz spectrometers for the study “Structural Studies of Lipid-free Apolipoprotein A-I.”

High-Performance Mass Spectrometry Facility

- Curt Scharfe and Peter Oefner, Stanford University, Stanford, California, worked on the study “Proteomics of Mitochondria.” In earlier work, mitochondrial organelles from yeast were purified using density gradient and free-flow electrophoresis, and the preparations were separated into mitochondrial membrane and matrix fractions. The fractions were then trypsin digested and analyzed by reversed-phase high-resolution liquid chromatography/tandem mass spectrometry and liquid chromatography/Fourier Transform-Ion Cyclotron Resonance mass spectrometry (FTICR). The earlier work also increased the coverage of the yeast mitochondrial proteome through the use of strong cation exchange fractionation followed by reversed-phase high-performance liquid chromatography and tandem mass spectrometry peptide sequencing. Work in progress includes the following:
 - Confirmation of yeast peptide sequences by liquid chromatography-FTICR, which will establish a comprehensive AMT tag database for the mitochondrial proteome in yeast.
 - Establishment of an AMT tag database for proteins of mitochondrial outer membrane vesicles (OMV) isolated from *Neurospora crassa*. Quantitative measurements on the mitochondrial proteome in *neurospora* and yeast under various conditions are planned. Using purified samples of the mitochondrial translocase of the outer membrane (TOM) of mitochondria complex from *neurospora*, for which the complex stoichiometry has been determined, the purified TOM complex subunits will be measured in comparison to proteins purified from OMV. Relative abundance changes can be determined by cross-labeling of the two samples using ^{16}O and ^{18}O stable isotope labeling. Absolute quantification will also be achieved by nano-high-performance liquid chromatography processing of both samples individually using liquid chromatography-FTICR.
 - Performance of quantitative measurements of yeast wildtype cells versus selected yeast deletion mutants involved in the mitochondrial quality control system located in the inner membrane. Protein abundances between

the wildtype and combinations of different yeast deletion mutants will be evaluated. The quantitative liquid chromatography-FTICR runs would include absolute protein quantification using nano-high-performance liquid chromatography in addition to stable isotope labeling experiments.

- Jon Jacobs and Dave Camp, Pacific Northwest National Laboratory, Richland Washington, worked on the study, “Proteomic Characterization of Cerebrospinal Fluid (CSF) by High-Resolution Liquid Chromatography/Tandem Mass Spectrometry.” In collaboration with Shaw Warren, Infectious Disease Unit of Massachusetts General Hospital, Boston, Massachusetts, the researchers are in the beginning stages of proteome analysis of human cerebral spinal fluid (CSF). CSF is routinely sampled in clinical medicine to help determine and monitor the presence of illness in the brain or spinal cord. Clinicians usually measure the total protein concentration for this purpose since very little is known about the protein composition, or proteome, of CSF in normal or disease states. Much of the current knowledge is based upon two-dimensional gel analysis techniques, which are severely limited in both sensitivity and throughput. The overall goals of the work proposed in this study are twofold: (1) determine, as possible, the content and distribution of proteins in “normal” human CSF for the creation of a mass and time tag database for future quantitative liquid chromatography-FTICR studies, and (2) evaluate how the content and abundance of proteins in CSF are altered in specific diseases of the brain and spinal cord.
- Initial work has proceeded rapidly with a series of experiments to optimize sample processing of CSF for the baseline studies. CSF proteins are highly glycosylated, which can present challenges for the separation and detection of peptides. Also, the overall protein content of CSF is relatively low when compared to human blood plasma, but this can be addressed by the high-sensitivity mass spectrometry instrumentation at EMSL. In approximately six weeks, the researchers received samples, performed mass spectrometry analyses, analyzed the data, and provided feedback and data to their collaborators. The researchers will soon begin to fractionate the CSF sample for optimization of protein coverage and dynamic range of detection. Once a baseline of proteins is established, comparative disease state samples will be provided for the eventual identification of potential biomarkers for application of clinical diagnosis

Interfacial and Nanoscale Science Facility

- Hye-Kyung Ahn, Chungbuk National University, Cheongju, Korea, and Man Bock Gu, Gwangju Institute of Science and Technology, Gwangju, South Korea, worked on the synthesis and characterization of single-enzyme nanoparticles and functionalized nanostructured matrices using the resources of the nanobiotechnology laboratory.
- Maxime J. Guinel, Washington State University, Pullman, Washington, used the high-resolution transmission electron microscope to study needle inclusions in a garnet matrix.
- Aaron David LaLonde, Washington State University, Pullman, Washington, characterized yttrium orthovanadate (synthesized at his university) using the high-resolution transmission electron microscope.
- Theresa McIntire and Barbara Finlayson-Pitts, University of California, Irvine, California, characterized ozone oxidized unsaturated self-assembled monolayers using time-of-flight secondary ion mass spectrometry and Auger electron spectroscopy.
- Joseph Megy, JDC Inc., New Cumberland, West Virginia, conducted research to determine the reaction and melting temperatures of phosphate ore mixture using X-ray diffraction and a thermogravimetric analyzer with a mass spectrometer.

- Chih-Heng Tseng, Oregon State University, Corvallis, Oregon, used the electron microscopy suite to investigate homogeneous precipitation of cerium dioxide nanoparticles.
- Diana Washington, Washington State University, Pullman, Washington, characterized mesoporous SiO₂ particles using X-ray diffraction, nuclear magnetic resonance, and high-resolution transmission electron microscopy.

Molecular Sciences Software – New User Agreements with NWChem/Ecce

- Academy of Sciences of the Czech Republic, Prague, Czech Republic
- Beijing Normal University, Beijing, Peoples Republic of China
- Fujitsu Kyushu System Engineering Ltd., Japan, Chiba, Japan
- Indian Institute of Technology Bombay, Bombay, India
- Lawrence Berkeley National Laboratory, Berkeley, California
- NCE Discovery, Cambridge, Great Britain
- Pittsburgh Supercomputing Center, Pittsburgh, Pennsylvania
- Seoul National University, Seoul, Korea
- Tartu University, Tartu, Estonia
- The University of Western Ontario, London, Ontario, Canada
- University of California, Berkeley, Berkeley, California
- University of Cincinnati, Cincinnati, Ohio
- University of Girona, Girona, Spain
- University of Missouri - St. Louis, St. Louis, Missouri
- University of North Texas, Denton, Texas
- University of Oregon, Eugene, Oregon
- University of Paul Sabatier/Laboratoire de Physique Quantique, Toulouse, France
- Vanderbilt University, Nashville, Tennessee
- Virginia Polytechnic Institute, Blacksburg, Virginia
- Western Kentucky University, Bowling Green, Kentucky

Publications

The following list represents publications by EMSL staff members and users where the publication resulted from research carried out at EMSL.

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Presentations

The following list represents presentation by EMSL staff members and users where the presentations resulted from research carried out at EMSL.

Alexander ML, BT Jobson, GD Maupin, and GG Muntean. 2005. "On-Line Analysis of Organic Compounds in Diesel Exhaust Using Proton Transfer Reaction Mass Spectrometry." Presented by Mike Alexander (Invited Speaker) at the 2nd International Conference on Proton Transfer Reaction, Obergurgl, Austria, on February 4, 2005.

Alexander ML. 2005. "Proton Transfer Reaction Ion Trap Mass Spectrometer (PTR-ITMS): Next Generation Aircraft Instrumentation for Gas Phase Organic Analysis." Presented by Michael Alexander (Invited Speaker) at the DOE Atmospheric Science Program Meeting, Charleston, South Carolina, on January 25, 2005.

Autrey T, A Gutowska, L Li, JC Linehan, RS Smith, BD Kay, and MS Gutowski. 2005. "Controlled Hydrogen Release from Ammonia Borane Using Mesoporous Scaffolds." Presented by Tom Autrey (Invited Speaker) at the University of Washington Inorganic Chemistry Seminar, Seattle, Washington, on January 31, 2005.

Ayotte P, JL Daschbach, Z Dohnalek, GA Kimmel, KP Stevenson, GR Teeter, RS Smith, and BD Kay. 2005. "Beakers Without Walls: Using Nanoscale Amorphous Films to Study Supercooled Water and Liquid Solutions." Presented by Bruce Kay (Invited Speaker) at the University of Utah, Salt Lake City, Utah, on January 31, 2005.

Baer DR. 2005. "What Do We Mean by Nanoscience or Nanotechnology Education?" Presented by Don Baer (Invited Speaker) at the US-Korea Nano Forum, Los Angeles, California, on February 17, 2005.

Blake TA and NB Gallagher. 2005. "Infrared Reflectance Spectroscopy: Spectral Signatures of Chemicals on Soils." Presented by Tom Blake at the Desert Trafficability Workshop, Winthrop, Washington, on January 22, 2005.

Briknarova K, F Nasertorabi, ML Havert, E Eggleston, DW Hoyt, K Vuori, and KR Ely. 2005. "Solution Structure of the Serine-Rich Domain from Crk-Associated Substrate (p130Cas)." Presented by Klara Briknarova at the Frontiers of NMR in Molecular Biology IX (A8), Banff, Alberta, Canada, on January 29, 2005.

- Dohnalek Z, J Kim, and BD Kay. 2005. "Growth and Catalytic Activity of Epitaxial Palladium (111) Films." Presented by Zdenek Dohnalek (Invited Speaker) at the Gordon Research Conference, Ventura, California, on February 14, 2005.
- Gao F, WJ Weber, R Devanathan, and Y Zhang. 2005. "Multi-Scale Computer Simulations of Radiation Damage in Ceramics." Presented by Fei Gao (Invited Speaker) at the Seminar for Michigan University, Ann Arbor, Michigan, on January 14, 2005.
- Henderson MA. 2005. "Heterogeneous Photocatalysis on Single Crystal Oxides." Presented by Mike A. Henderson (Invited Speaker) at the Gordon Research Conference, Ventura, California, on February 14, 2005.
- Henderson MA. 2005. "Photochemistry on Single Crystal Oxide Surfaces." Presented by Michael A. Henderson (Invited Speaker) at the 4th International Workshop on Oxide Surfaces, Aussois, France, on January 5, 2005.
- Henyk M, KM Beck, MH Engelhard, AG Joly, AL Shluger, PV Shusko and WP Hess. 2005. "Surface Electronic Properties and Site-Specific Desorption Processes Studied at Highly Structured Nanoporous MgO Thin Films." Presented by Ken Beck (Invited Speaker) at the Fourth International Workshop on Oxide Surfaces, Aussois, France, on January 6, 2005.
- Hoyt DW, P Brzovic, D Christensen, J Keefe, AV Lissounov, and RE Klevit. 2005. "NMR Investigations of BRCA1-Directed Ubiquitination: Assembly and Structure of a Multi-Protein Ubiquitin Ligase Complex." Presented by David W. Hoyt at the Frontiers of NMR in Molecular Biology IX (A8), Banff, Alberta, Canada, on January 31, 2005.
- Hu D and HP Lu. 2005. "Single-Molecule Enzymatic Reaction on a Bacterial Cell Surface." Presented by Dehong Hu (Invited Speaker) at the Biophysical Meeting, Long Beach, California, on February 13, 2005.
- Iordanova NI, KM Rosso, and M Dupuis. 2005. "Charge Transport in Metal Oxides." Presented by Michel Dupuis (Invited Speaker) at the University of Tokyo, Tokyo, Japan, on January 31, 2005.
- Kim J, Z Dohnalek, and BD Kay. 2005. "Structural and Catalytic Properties of Nanoporous Pd Films Grown Via Ballistic Deposition." Presented by JooHo Kim at the 2005 Gordon Research Conference on Chemical Reactions at Surfaces, Ventura, California, on February 14, 2005.
- Laskin A. 2005. "Applications of Advanced Analytical Techniques for Analysis of Laboratory and Field Collected Aerosols." Presented by Alex Laskin (Invited Speaker) at Duke University, Durham, North Carolina, on January 28, 2005.
- Laskin A. 2005. "Laboratory Studies of Optical and Hygroscopic Properties of Field Collected Atmospheric Aerosols." Presented by Alex Laskin (Invited Speaker) at the First Annual Science Team Meeting, Charleston, South Carolina, on January 25, 2005.

Laskin J. 2005. "Energetics of Gas Phase Dissociation of Large Molecules." Presented by Julia Laskin (Invited Speaker) at the Gordon Research Conference, Ventura, California, on February 28, 2005.

Lu HP. 2005. "Single-Molecule and Site-Specific Spectroscopy Studies of Interfacial Electron Transfer Dynamics." Presented by H. Peter Lu (Invited Speaker) at the University of Notre Dame, South Bend, Indiana, on January 20, 2005.

Lu HP. 2005. "Single-Molecule Protein "Fly Fishing" in Cell Signaling." Presented by H. Peter Lu (Invited Speaker) at the Biophysical Society Meeting, Long Beach, California, on February 14, 2005.

Maheswaran S, S Thevuthasan, F Gao, V Shutthanandan, and CM Wang. 2005. "Ion Scattering Simulations of Misfit Dislocations at the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$." Presented by S. Maheswaran at the 16th National Congress at the Australian Institute of Physics in Sydney, Australia, on January 1, 2005.

Pawley NH, MD Clark, and R Michalczyk. 2005. "Improving Accuracy and Precision in NMR Relaxation Measurements." Presented by Norma Pawley at Keystone Symposia Frontiers of NMR in Molecular Biology IX, Banff, Alberta, Canada on January 29, 2005.

Resat MS, WB Chrisler, and L Opresko. 2005. "Intercellular Signaling in Mammary Epithelial Cells: Implications for the Radiation-Induced Bystander Effect." Presented by Marianne Sowa Resat (Invited Speaker) at the Gordon Research Conference, Ventura, California, on February 4, 2005.

Shutthanandan V, S Thevuthasan, RS Disselkamp, Y Xie, E. Smith, and BD Milbrath. 2004. "A Unique Capability to Measure Size and Time Resolved Atmospheric and Radionuclide Aerosols." Presented by S. Thevuthasan (Invited Speaker) at the 5th International Symposium on BIOPIXE, Wellington, New Zealand, on January 19, 2005.

Wellman DM, BK McNamara, SD Burton, and JP Icenhower. 2005. "Polyphosphate Amendments for In-Situ Immobilization of Uranium Plumes." Presented by Dawn Wellman at the 3rd International Conference on Remediation of Contaminated Sediments, New Orleans, Louisiana, on January 25, 2005.