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Research Highlights

NMR Spectroscopic Investigation of Human Carbonic Anhydrase Points to Alternative Mechanism of Action

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Carbonic anhydrase (CA) catalyzes a deceptively simple chemical reaction—the hydration of CO_2 to yield bicarbonate and a proton: $\text{CO}_2 + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+$. Further, CA was the first enzyme recognized to have a biological function for Zn^{2+} , which was postulated as the activation of bound H_2O . Abundant in all mammalian tissues, plants, algae, and bacteria, CA is perhaps the most studied metalloprotein with more than 180 crystal structures in the protein database. Scientists at PNNL recently found evidence that a commonly held mechanism of action for human CA may not be correct. Instead, the new data are consistent with an alternative mechanism proposed in Merz et al. 1989 and were generated using novel low-temperature solid-state nuclear magnetic resonance (NMR) spectroscopy, which allowed direct observation of the Zn^{2+} in CA.

Originally, this research began as part of efforts to calibrate the spectroscopy developed in Ellis' EMSL laboratory; however, during the process, the scientists discovered that assumptions about how this enzyme works were incorrect. The spectroscopy data showed that more research is warranted to understand the

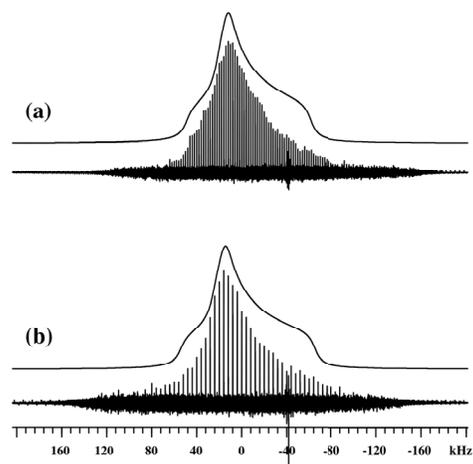


Figure 1. Low-temperature (10 K) solid-state ^{67}Zn NMR spectra of CA at (a) pH 5 and (b) pH 8.5. Above each experimental spectrum is a simulation of the spikelet envelope. At pH 5, the extracted value of C_q is 9.6 MHz, whereas at pH 8.5 the value is 10 MHz.

mechanisms of CA. In addition, PNNL now has a powerful tool to probe otherwise very difficult states in this class of metalloprotein.

The most active form of CA has very fast reaction rates approaching $\sim 10^6/8$. As a result, innumerable studies have been conducted directed at this protein's action mechanism. The accepted reaction mechanism holds that the water ionizes (rate-limiting step) to yield a bound hydroxide that then adds to the nearby CO_2 , resulting in a Zn^{2+} -bound bicarbonate. The presence of bound water and fast catalytic rates together presents a problem that up to now could not be explained. Simple arguments would predict that the fastest that CA could turn over would be at rates on the order of $10^4/8$.

The principal observable in a solid-state ^{67}Zn NMR experiment is the quadrupole coupling constant, C_q . The ^{67}Zn C_q values are sensitive to changes in structure and bonding associated with water or hydroxide. Figure 1 shows data collected using EMSL's 18.8-tesla NMR spectrometer, illustrating that the ^{67}Zn NMR measurement is independent of pH over the range of 5 to 8.5.

The two spectra are essentially the same. At pH 5, the Zn^{2+} should be coordinated by H_2O , and as a result, the ^{67}Zn NMR spectrum is expected to be three to five times broader than the spectrum at pH 8.5. This is clearly not the case; however, these data are consistent with OH^- being bound to Zn^{2+} , not H_2O over the entire pH range investigated and as modeled by molecular theory. This observation is contradictory to the accepted mechanism. However, it is consistent with an alternative mechanism proposed by Merz et al. Further, these data also provide an explanation for the issues associated with the turnover rates for CA. In addition, these results point to an important complementary aspect of NMR methods to X-ray diffraction, namely the sensitivity of the NMR parameters to the presence or absence of protons. Moreover, this work demonstrates the impact zinc spectroscopy can have with respect to delineating the structure and action mechanism of this important class of metalloproteins.

Reference

Merz KM, R Hoffmann, and MJS Dewar. 1989. "The Mode of Action of Carbonic Anhydrase." *Journal of the American Chemical Society* 111(15):5636-5649.

Toward the Solution Synthesis of the Tetrahedral Au₂₀ Cluster

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One of the long-standing objectives of cluster science is to discover highly stable clusters and use them as building blocks for bulk cluster-assembled materials. The discovery of C₆₀ in the gas phase and its subsequent bulk synthesis provide classical inspiration and a prototypical example. However, it is generally believed that few other stable gaseous clusters may be assembled into bulk materials because of cluster-cluster interactions leading to agglomeration. Indeed, no cluster-assembled materials have been synthesized on the basis of stable gaseous clusters other than the fullerenes, despite intensive experimental and theoretical efforts.

Recently, we reported that a 20-atom gold cluster possesses a tetrahedral (T_d) structure with a remarkably large highest occupied molecular orbital-lowest unoccupied molecular orbital energy gap, suggesting that it would be highly chemically inert and may have novel optical and catalytic properties (Li et al. 2003).

Here, we report the observation of the tetrahedral Au₂₀ cluster in solution, ligated with triphenyl phosphine (PPh₃) ligands, and its confirmation by theoretical calculations. The current work represents a successful synthetic effort directly guided and motivated by a gas-phase observation, validating the gas-phase-to-condensed-phase approach for the discovery of cluster-assembled nanomaterials.

Because of potential cluster-cluster agglomeration, Au₂₀ must also be protected by ligands in order to be used as a building block for cluster-assembled materials. To maintain the unique structural and electronic properties of the T_d Au₂₀, the ligands must be carefully chosen. Thiol ligands strongly interact chemically with gold and would alter the electronic structure of the T_d Au₂₀. Preliminary theoretical

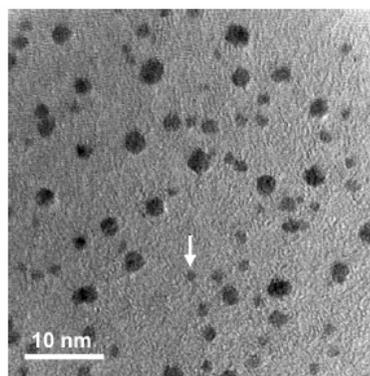


Figure 2. High-resolution transmission electron microscopy image of the synthesized Au-phosphine nanoparticles. The arrow points to one possible Au₂₀ cluster.

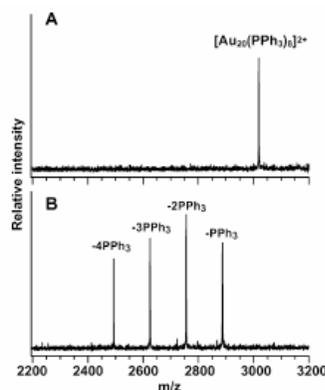


Figure 3. Collision-induced dissociation of Au₂₀(PPh₃)₈²⁺.

calculations revealed that the $\text{Au}_{20}(\text{PR}_3)_4$ ($\text{R} = \text{H}, \text{Ph}$) complexes indeed possess high stability. The high-resolution transmission electron microscopy image in Figure 2 shows that the soluble samples contained gold nanoparticles with diameters as large as 3 nm, but the majority of the particles have diameters of less than 1 nm. We further characterized the sample using a high-resolution Fourier transform ion cyclotron resonance (FTICR) mass spectrometer, which was accurately calibrated and equipped with an electrospray ionization source. A careful examination of the mass spectrum revealed doubly charged ions corresponding to Au_{20} clusters with eight and seven PPh_3 ligands. To obtain structural information for the $\text{Au}_{20}(\text{PPh}_3)_8^{2+}$ cluster, we conducted collision-induced dissociation experiments in the FTICR cell. These results, shown in Figure 3, suggest that the tetrahedral core of Au_{20} is intact in the PPh_3 -coordinated clusters. This is consistent with our initial expectation and calculation that the four apex sites of Au_{20} are the most reactive sites that bind strongly to the four PPh_3 ligands.

The current experimental and theoretical results suggest that $T_d \text{Au}_{20}$ clusters coordinated with phosphine ligands may be obtained in bulk quantity. It is expected that by increasing the size of the ligands, one can synthesize the $T_d \text{Au}_{20}$ clusters with only the four apex sites coordinated. These clusters may be promising catalysts with the highest surface area and well-defined surface sites.

These exciting results are featured in and on a recent cover of the *Journal of Physical Chemistry B* (Figure 4).

References

- Li J, X Li, HJ Zhai, and LS Wang. 2003. "Au₂₀: A Tetrahedral Cluster." *Science* 299(5608):864-867.
- Zhang HF, M Stender, R Zhang, C Wang, J Li, and LS Wang. 2004. "Toward the Solution Synthesis of the Tetrahedral Au₂₀ Cluster." *Journal of Physical Chemistry B* 108(33):12259-12263.



Figure 4. Tetrahedral Au_{20} cluster. Research carried out at Pacific Northwest National Laboratory.

Uranium Immobilization by Sulfate-Reducing Biofilms

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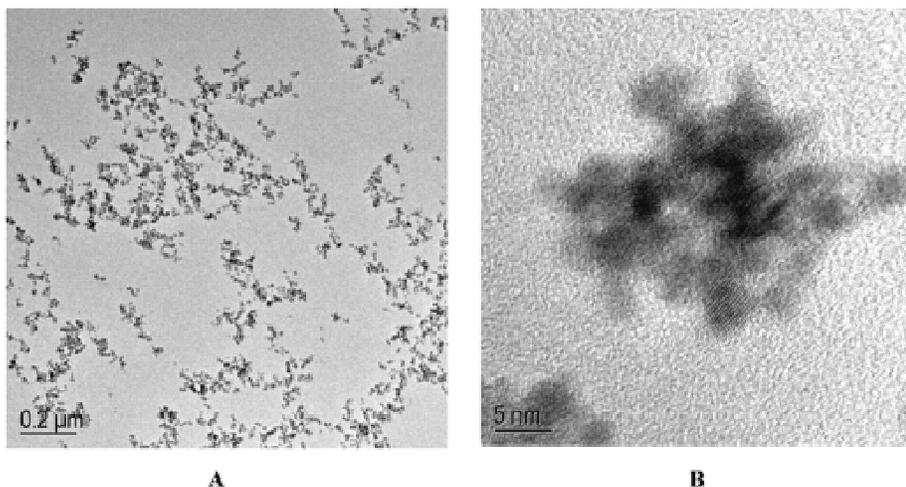


Figure 5. (A) TEM photomicrographs of unstained thin sections from U(VI) incubated with Na₂S, illustrating the production of reduced uranium. (B) High-resolution TEM micrograph of uranium precipitates. The average particle size of the newly formed biogenic uraninite was 4 nm.

In this research, hexavalent uranium [U(VI)] was immobilized using biofilms of the sulfate-reducing bacterium (SRB) *Desulfovibrio desulfuricans* G20. The dynamics of uranium immobilization in the SRB biofilms were quantified by estimating:

- microbial activity in the SRB biofilm, defined as the hydrogen sulfide (H₂S) production rate and estimated from the H₂S concentration profiles measured using microelectrodes across the biofilms
- the concentration of dissolved uranium in the solution
- the mass of uranium precipitated in the biofilm.

Results of this research suggest that uranium was immobilized in the biofilms enzymatically and chemically, the latter by reacting with microbially generated H₂S. Selected-area electron diffraction pattern and crystallographic analysis of transmission electron microscope (TEM) lattice-fringe images confirmed the structure of precipitated uranium as being that of uraninite.

TEM imaging and analysis (Figures 5 and 6, respectively) were used to investigate the reduced U(IV)-containing minerals associated with the bacterial cells. Cross-sectional TEM is the only method that provides a view of the inside of a bacterial cell and allows researchers to study the exact location of the newly formed biominerals. To assist with this research, PNNL provided a unique capability for examining these redox-sensitive systems following a protocol for anaerobic sample processing developed in EMSL's labs. In addition, EMSL's state-of-the-art high-resolution TEM coupled with an energy dispersive spectroscopy system provided atomic resolution imaging and elemental analysis of structures on a nanolevel critical for their identification.

This research allowed scientists from the Multiphase Environmental Research group at Washington State University in Pullman, Washington, to understand uranium precipitation and cycling by dissimilatory metal-reducing bacteria in their experimental setup.

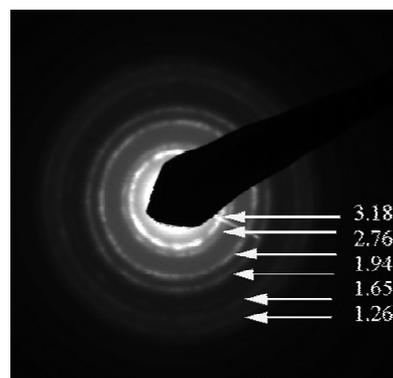


Figure 6. Electron diffraction pattern of the uranium particles precipitated by Na_2S . The electron diffraction pattern of uranium (reduced by sodium sulfide) shows rings characteristic for nanocrystalline material, with d spacing values in a good accordance with the listed nonbiogenic uraninite diffraction data.

F-Element Coordination by Kläui Ligands

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Understanding the fundamental coordination chemistry of actinide ions is critical to making further advances in the field of actinide separations. For example, exploiting differences in how ligating groups prefer to orient around tetravalent actinide ions may provide a basis for designing systems that separate these ions from hexavalent actinide ions. Existing processes (e.g., TRUEX and DIAMEX) co-extract tri-, tetra-, and hexavalent actinides. Based on its tripodal geometry, we found that compounds of the type depicted in Figure 7 offer the opportunity to extract Am(III), Cm(III), and Pu(IV) selectively over U(VI). We hereafter refer to these anionic cobalt(III) phosphito compounds as “Kläui ligands.” This work focuses on the fundamental chemistry of Kläui ligand systems. In particular, the effects of structural variation in the ligand on metal ion binding are being

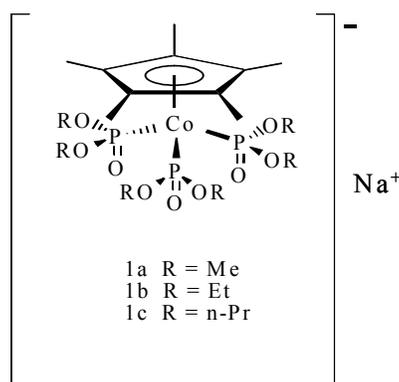


Figure 7. Structure of the Kläui Ligands.

investigated by PNNL and EMSL researchers both experimentally and through molecular modeling. In the following paragraphs, some of the coordinating processes followed by NMR spectroscopy are described.

In Fiscal Year 2002, we initiated investigations of the series of Kläui ligands depicted in Figure 7. Complexation of the Kläui ligands to trivalent (La^{3+} , Am^{3+}) and tetravalent (Pu^{4+} , Th^{4+}) f-block ions and even to the unusual Tc(VII) as TcO_3^+ was confirmed in the wet lab studies, and computational methods to predict the structures of these complexes were developed. Initial investigations using NMR spectrometry indicated that methyl and ethyl Kläui derivatives bound lanthanides too strongly to measure free energies of binding via this technique. As the ligand is substituted with larger alkyl groups, it appears that the binding is becoming something other than “tripodal.” Moreover, metals such as uranyl (UO_2^{2+}) tend to bind Kläui ligands, but apparently do so with an alternate mode. Fortunately, the 1:1 and 2:1 methyl and ethyl Kläui complexes were isolable for lanthanum, uranium (IV), thorium (IV), and plutonium (IV), and a substoichiometric ethyl-Kläui:uranyl (VI) complex was isolated as well. For several of these, we obtained crystal structures. The n-propyl Kläui ligand and higher alkyl substituted complexes tended to be reluctant to crystallize, and they displayed aforementioned alternate coordinative modes.

^1H , ^{13}C , and ^{31}P NMR spectra of several Kläui complexes were obtained. The ^{31}P NMR spectra shown in Figure 8 exemplify the transition from free methyl or ethyl Kläui to the 1:1 complex and then to the 2:1 ethyl Kläui complex that is observed for trivalent lanthanides and U(IV), Pu(IV) metal nitrates, chlorides, perchlorates, etc. In contrast, the behavior of the 1:1 n-propyl Kläui lanthanum complex was different in that the 2:1 complex would not form. The ^{31}P NMR spectra of the n-propyl Kläui lanthanum solutions showed only the 1:1 complex and free ligand even when a 10-fold excess of the ligand was present. Therefore, a new coordinative mode arises presumably due to steric crowding from the propyl ligand. However, the greater charge-to-size ratio of thorium apparently allowed 2:1 complex formation as followed in ^{31}P experiments and verified by X-ray crystal structure. We believe the coordination of both metals occurs in solution with a varying degree of fluxional behavior. Variable temperature experiments are planned to probe for fluxional behavior in the n-propyl Kläui complexes.

The trans-oxo moiety in the uranyl cation (UVI), and likely those of NpVI and PuVI, should prevent efficient 2:1 binding of these species. Indeed, the addition of an excess of ethyl Kläui to $\text{MO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, where $\text{M} = \text{U}$, Pu , and Np , gave rise to isolable solids that displayed complex ^{31}P NMR spectra. The spectra were consistent with the formation of dimeric or higher order polymeric species that typically show poor extraction behavior. Thus, the tetravalent actinides were extracted from the hexavalent actinides in high yield.

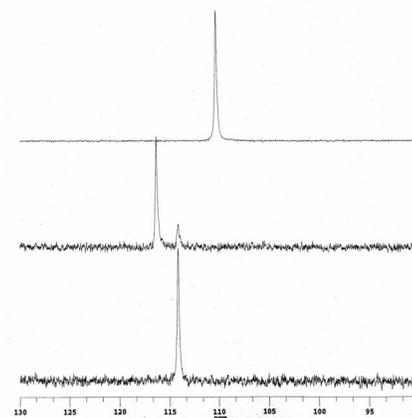


Figure 8. ^{31}P NMR of the 1:1 and 2:1 $\text{La}(\text{NO}_3)_3$ ethyl Kläui complexes. In solution, the ^{31}P NMR spectrum indicates a symmetric disposition of the Kläui ligand. All ^{31}P NMR were referenced to a 95% $\text{H}_3\text{PO}_4/\text{D}_2\text{O}$ standard.

Finally, the protonation of the ethyl Kläui ligand was followed by ^{31}P NMR and ^1H NMR to understand the binding of the ligand with the TcO_3^+ cation. This cation is bound as a 1:1 complex. Titration of the ligand with nitric acid resulted in discrete shifts in the ^{31}P resonance of the free ligand; the peak is located near 110 ppm at 0.1 M HNO_3 and shifts to 122.5 ppm at 2 M HNO_3 . Higher acid concentration produced no further changes in the spectrum. Metal extractions, which are typically carried out in nitrate or chloride media, compete with the proton interaction with the ligand. For the weakly bound TcO_3^+ cation, ligand binding was at a maximum near 0.5 M HNO_3 and the protonation reaction prohibited binding at acid concentrations greater than 2 M. The ^{99}Tc NMR of the complex is planned to measure the binding constant for the ethyl Kläui TcO_3^+ complex in competitive nitrate media.

Molecular Dynamics of a Naturally Occurring Sugar

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The molecular dynamics (MD) module in the NWChem software package is actively being used to study proteins, protein interactions with other biomolecules, and protein catalytic activity as exemplified by the research of various groups around the world.

Lins et al. used the NWChem MD module to study the interaction between trehalose and the hen egg-white protein lysozyme in solution (Lins et al. 2004). The naturally occurring sugar trehalose is known to protect biostructures, such as proteins, from damage due to dehydration, heat, or cold. Trehalose could be used to coat dried food, to slow down degradation and escape of flavors, to serve as a cryoprotectant, or to preserve delicate biological structures such as living cells in a dehydrated form. Although the effects of trehalose on biostructures has been studied extensively, the detailed mechanism remains unknown. Experiments aimed at understanding the protective mechanism have been inconclusive and have led to three different hypothesis. The MD studies by Lins et al. attempt to shed light on the mechanism at a molecular level. Their results, at low concentration and at room temperature, favor the so-called water-layer hypothesis in which water molecules get trapped close to the surface of the biostructure.

Reference

Lins RD, CS Pereira, and PH Hünenberger. 2004. "Trehalose-Protein Interaction in Aqueous Solution." *PROTEINS: Structure, Function, and Bioinformatics* 55(1):177-186.

Proteomic Approach to Characterize Protein Shedding

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Shedding (i.e., proteolysis of ectodomains of membrane proteins) plays an important pathophysiological role. Membrane proteins of different topologies [type I (extracellular N-terminal), type II (intracellular N-terminal), and type III (multiple membrane-spanning domains)] are released from the cell surface by shedding proteases (sheddases), whose substrates include receptors, cell adhesion proteins, and structural proteins. The main family of proteases involved in shedding is the ADAM (a desintegrin and metalloproteases); a notable example is tumor necrosis factor- α (TNF- α) converting enzyme, the first member of the ADAM family identified as a sheddase. Shedding occurs during normal development, but it is also known to contribute to human diseases, including cancer and rheumatoid arthritis, although the mechanism for these effects is incompletely understood. In addition, protein shedding can be up-regulated by certain agonists such as 4 β -phorbol 12-myristate 13-acetate (PMA). PMA stimulates the proteolysis of ectodomains of numerous membrane proteins, including pro-transforming growth factor- α , CD44, pro-epidermal growth factor receptor, interleukin-1 receptor, and pro-TNF- α , suggesting the existence of a common pathway.

Shed proteins are difficult to detect since they are present in low number and are found in the complex extracellular environment. Due to the biological significance of shed proteins, a need exists to improve their identification methods. In order to study the feasibility of identifying shed proteins, we analyzed serum-free media of human mammary epithelial cells by mass spectrometry both before and following induction of shedding by PMA. Different means of sample preparation, such as biotinylation of cell surface proteins, isolation of glycosylated proteins, and preparation of crude protein fraction, were carried out to determine the optimal method of sample processing. Mass spectrometry data from 10 sample preparations were evaluated, including three that represented biotinylated proteins, three that contained purified glycosylated protein, and four that represented total populations of proteins. In most cases, the samples were analyzed six times. In the case of biotinylated and glycosylated samples, insufficient material was available for multiple analyses, and most were evaluated twice. Resulting analyses identified 201 proteins distributed as follows: 24 originated from the biotinylated fraction, 16 were derived from the glycosylated fraction, and 180 were obtained from crude preparation (note that since some proteins were observed in more than one fraction, the total number of proteins identified is less than the sum of proteins in the fractions).

In order to identify proteins that are likely derived from the shedding process, we evaluated the extracellular nature of the identified proteins by predicting the presence of membrane helices using the transmembrane hidden Markov model (TMHMM). Proteins that did not contain transmembrane domains but are known to associate to the cell surface through a non-transmembrane domain manner, a receptor, or an adapter protein, were also included. Secreted proteins that are known to associate with membrane proteins were also considered.

Using these criteria, we identified 45 membrane-associated proteins from the three fractions. Of these, 22 proteins contained transmembrane domains. Moreover, 18 of these 22 proteins were identified by one or more extracellular peptides. Thus, these 18 proteins are strong candidates as shed proteins and likely enter the extracellular media through the process of regulated proteolysis. We also identified 23 proteins that associate to the cell surface indirectly and may be released into the media via shedding of membrane-integral proteins. Eight proteins of unknown localization were observed, including transketolase and heparin-binding growth factor binding protein.

Of the 45 membrane-associated proteins, 37 originated from crude preparation, whereas seven were detected in the biotinylated fraction and four from the glycosylated fraction. Three of the seven proteins found in the biotinylated fraction were also detected in the crude preparation. The four proteins identified from the glycosylated fraction were not detected in the other preparations and represented proteins identified by single peptide hits. These results indicate that even though the crude preparation contained a high proportion of non-membrane proteins, this preparation generated the largest number of membrane-associated proteins and likely shed.

The abundances of six proteins were measured as altered by PMA treatment. Two of these proteins were found in higher abundances in media of PMA-treated cells: syndecan-4 and HDGF. On the other hand, we concluded that the abundances of four proteins decreased, including enolase I, GRP78, lactate dehydrogenase A, and transketolase. With the exception of transketolase, whose cellular localization has not been reported, these proteins have been shown to be present on extracellular surfaces of cells. We validated protein abundance estimates using immunoblotting methods. Identical PVDF membranes containing total protein for the control- and PMA-treatment groups from two independent experiments were immunoblotted in duplicate with antibodies against syndecan-4, GRP78 or CD44. To ensure that we detected the shed portion of syndecan-4 and CD44E, we used monoclonal antibodies that specifically recognize the ectodomain of the corresponding proteins. The level of syndecan-4 protein increased in the PMA-treated samples by 2.3-fold relative to controls upon quantification of band intensities, whereas the abundance of GRP78 decreased by 2.0-fold. On the other hand, the level of CD44E was unaltered. These results were in good agreement with the abundance estimates from the mass spectrometry.

In summary, we used different methods to identify shed proteins by mass spectrometry and found the most protein identifications with the total protein preparation without chemical modification or affinity separation. We identified 18 proteins that are strong candidates as shed proteins in that they contained transmembrane domains and were identified by peptides derived from the extracellular portion of the protein. We also identified 23 proteins that associate to the plasma membrane via binding to integral membrane proteins and could be released as a result of shedding of these proteins. Upon estimating the abundance of proteins released in the media, we were able to identify six proteins whose abundances were altered by PMA treatment. The abundances of three proteins were validated by traditional immuno-detection methods.

Parallel Reactive Transport Modeling of Radioactive Waste Form Weathering Using the STORM Code

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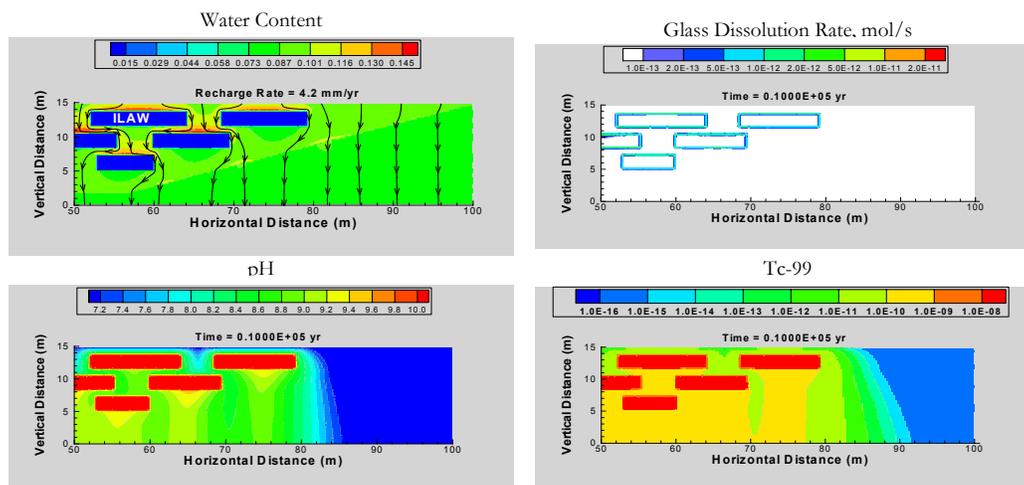


Figure 1. A few of the unknown factors [including distribution of a radioactive waste product (Tc-99)] solved during a typical simulation.

The STORM code, a parallel, coupled non-isothermal multiphase flow and reactive transport simulator, is used to calculate waste form release rates for immobilized low-activity waste (ILAW) created during processing of stored radioactive waste at the Hanford Site in southeastern Washington State. STORM stands for Subsurface Transport Over Reactive Multi-phases, the name given to the code by its developers, Diana Bacon, Pete McGrail, and Mark White at PNNL.

A large inventory of radioactive and mixed waste is stored in the Hanford Site's 177 underground single- and double-shell tanks. During cleanup activities, liquid waste recovered from these tanks will be pretreated to separate the low activity fraction from high-level and transuranic wastes. The low-activity waste—ILAW—will be immobilized in glass and placed in a near-surface disposal facility on the site. Before the ILAW can be disposed, however, a waste form that effectively protects both human health and the environment over the extremely long storage period must be selected. Thus, the STORM code is an effective tool for assessing performance of proposed waste forms.

The underlying mathematics in the STORM code is contained in a set of coupled, nonlinear, partial differential equations. These equations describe the rate of change of the solute concentrations of pore water in a variably saturated, non-isothermal porous medium, and the alteration of waste forms, packaging materials, backfill, and host rocks. The developers of STORM included a number of key features in the code:

- It can be used to calculate waste form release rates, a feature with direct application to the ILAW performance assessment.
- It simulates weathering of waste glass, packaging materials, backfill, and host rocks.
- It provides full coupling between unsaturated flow and reactive chemical transport.
- It performs global-implicit reactive transport for large time steps.
- It performs node-by-node iteration for a small Jacobian matrix and fast convergence.
- It is designed for parallel execution on multiple processors.
- It is capable of delivering solutions for extremely complex systems—for example, a typical simulation involves 4 million unknown factors and 100,000 time steps.

STORM has been used to simulate the weathering of vitrified waste in the Hanford Site's Integrated Disposal Facility (IDF), and is currently being validated against a 14-year field experiment of vitrified waste corrosion at a site in Russia. In addition, STORM will be used to conduct waste form release calculations for the 2005 IDF Performance Assessment.

Figure 9 shows a few of the unknown factors [including distribution of a radioactive waste product (Tc-99)] solved for a typical simulation that involved 37 aqueous species, 19 equilibrium aqueous reactions, and 20 kinetic mineral reactions at 120,000 locations.

Performance assessment simulations must involve times of 10,000 years. Because time steps are usually limited to less than one month by either advection rates or mineral reaction rates, more than 100,000 time steps are required. Simulations may take weeks or even months when run in serial mode, and may be too large to run on a desktop workstation, so running simulations on parallel processor systems is highly desirable. Figure 10 shows how the run time of a test simulation decreases from 20 hours when run on nine processors to 1½ hours as the work is divided among 256 processors.

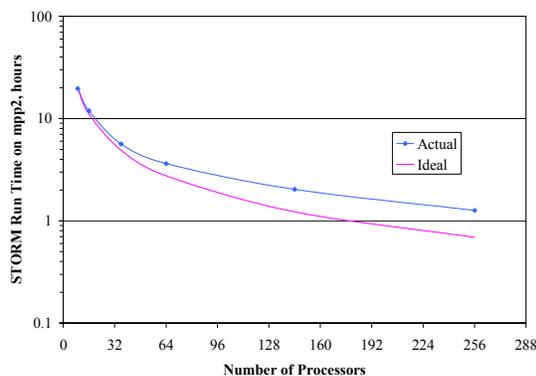


Figure 10. Run time of a test simulation decreases as the work is divided between 256 processors.

Nanoscale Effects on Ion Conductance of Layer-by-Layer Structures of Gadolinia-Doped Ceria and Zirconia

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Development of electrolyte materials that possess high oxygen ion conductance at relatively low temperatures is essential to increase the efficiency and lifetime of electrochemical devices such as solid-oxide fuel cells (SOFCs). The most advanced SOFCs employ oxide ion conducting zirconia-based electrolytes, specifically, yttria-stabilized zirconia (YSZ). The conductivity of the electrolyte determines the operating temperature of this device, which is currently around 1000 °C. Lower operating temperatures of ~500 °C would make SOFCs much more cost efficient and, most importantly, facilitate their practical use in electric vehicles. It is well established that ceria (CeO₂), doped with a divalent or trivalent cation, exhibits higher ion conductance at intermediate temperatures compared with YSZ, making ceria a promising material for SOFC applications.

Sata et al. 2000 found that an increase in the interface density in a two-phase multilayered calcium and barium fluoride structure drastically enhances the fluorine ion conductance of the material, particularly at film thicknesses in the range of 20-100 nm. Specifically, it was observed that this nanoscale lamellar structure exhibits higher ion conductance compared to either bulk calcium fluoride or barium fluoride along the interfacial directions at moderate temperatures when the number of heterojunctions is increased.

In this study, layer-by-layer structures of gadolinia (Gd₂O₃)-doped ceria and zirconia were synthesized on Al₂O₃(0001). The number of interfaces was varied by increasing the numbers of discrete layers, while the total film thickness was kept constant at ~155 nm. The films were grown in a dual-chamber ultrahigh vacuum system equipped with an electron cyclotron resonance oxygen plasma source. Cerium and zirconium sources (both 99.98% purity) were evaporated from separate electron beam sources, and gadolinium (99.98% purity) was evaporated from an effusion cell. The

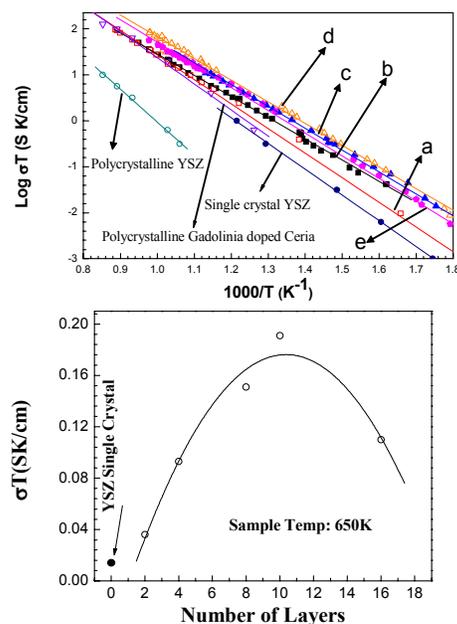


Figure 11. (Top) Arrhenius plots of oxygen ionic conductivity of two- (a) four-, (b) eight-, (c) ten-, (d) and sixteen-layer (e) gadolinia-doped ceria-zirconia thin films. (Bottom) Data from polycrystalline and single crystal YSZ. Conductivities of single crystal YSZ, two-, four-, eight-, ten-, and sixteen-layer films at 650 K.

growth rates of the films were monitored by quartz crystal oscillators. $\text{Al}_2\text{O}_3(0001)$ single crystal substrates were ultrasonically cleaned in acetone and methanol prior to insertion into the dual-chamber ultrahigh vacuum system through a load lock. Inside the molecular beam epitaxy chamber, the substrate surfaces were cleaned at 875 K for 10 minutes in activated oxygen from the electron cyclotron resonance plasma source at an oxygen partial pressure of $\sim 1.5 \times 10^{-5}$ Torr. The gadolinia-doped epitaxial structures of ceria and zirconia layers were grown on Al_2O_3 substrates by alternate evaporation of cerium and zirconium metals in the presence of low-pressure oxygen plasma.

Several in situ and ex situ techniques were used to characterize these films. These layered films are predominantly oriented along the (111) direction. The total thickness of each film was confirmed as ~ 155 nm. The gadolinium concentration in the ceria and zirconia layers was found to be 12 atomic percent. High-resolution transmission electron microscopy measurements showed that the layered structures contained structural domains within each layer as well as internal and interfacial dislocations between the layers.

Total conductivity, which consists of the sum of the electronic and oxygen ionic conductivity in these layered films, was measured as a function of temperature using a four probe van der Pauw technique. Since the electronic conductivity in these oxides is significantly less compared to ionic conductivity, especially at low temperatures, ionic conductivity dominates in these materials. As such, the total conductivity will be identified as oxygen ionic conductivity. Oxygen ionic conductivity results for two-, four-, eight-, ten-, and sixteen-layered Gd_2O_3 -doped CeO_2 and ZrO_2 films on $\text{Al}_2\text{O}_3(0001)$ substrates are displayed in Figure 11(top). The oxygen ionic conductivity data from polycrystalline (Nguyen and Takahashi 1995) and single crystal YSZ (Ikeda et al. 1985) are also shown for comparison. In general, these highly oriented films showed much higher conductivity compared to bulk polycrystalline YSZ. It is apparent from the impedance spectra that increasing the number of interfaces (i.e., the number of discrete layers) in the structure facilitates ion transport and leads to an increase in the oxygen ionic conductivity at low temperatures. The ionic conductivities for single crystal YSZ and the two-, four-, eight-, ten-, and sixteen-layered films, all at 650 K extracted from the Figure 11(top), are shown in Figure 11(bottom). At that temperature, increasing the number of layers resulted in higher oxygen ionic conductivity up to a thickness of 15 nm (for individual layers), beyond which conductivity decreases. The maximum value for the conductivity appears to be at least an order of magnitude higher than that from either polycrystalline gadolinia-doped bulk ceria or a single crystal, yttria-stabilized zirconia thin film.

References

- Ikeda S, O Sakurai, K Uematsu, N Mizutani, and M Kato. 1985. "Electrical-Conductivity of Yttria-Stabilized Zirconia Single-Crystal." *Journal of Materials Science* 20(12):4593-4600.
- Nguyen QM and T Takahashi. 1995. *Science and Technology of Ceramic Fuel Cells*. Elsevier, New York. 366 pp.
- Sata N, K Eberman, K Eberl, and J Maier. 2000. Mesoscopic Fast Ion Conduction in Nanometre-Scale Planar Heterostructures." *Nature* 408(6815):946-948.

Synthesis of Room-Temperature Ferromagnetic Cr doped TiO₂(110) Rutile Single Crystals Using Ion Implantation

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(b) Pacific Northwest National Laboratory, Richland, Washington

(c) Lawrence Berkeley National Laboratory, Berkeley, California

There is growing interest in synthesizing new diluted magnetic semiconductor materials because of their potential to efficiently inject spin-polarized carriers into nonmagnetic semiconductor heterostructures in spin-based devices. Recently, it was shown that certain oxide semiconductors doped with magnetic transition elements show room-temperature ferromagnetism. In particular, cobalt-doped titanium dioxide (TiO₂) appears to be the most promising candidate in terms of exhibiting a high-curie temperature. Several synthesis methods have been used to grow these materials in both anatase and rutile phases. However, care must be taken to avoid growth methods and conditions that promote the formation of cobalt nanoparticles.

We have recently shown that ferromagnetic chromium-doped TiO₂ anatase and rutile films can be synthesized using oxygen-plasma assisted molecular beam epitaxy. In this highlight, we show that ferromagnetic chromium-doped rutile TiO₂ single crystals can also be synthesized using Cr⁺ ion implantation at high substrate temperatures.

Single-crystal rutile TiO₂(110) substrates purchased from Princeton Scientific Corporation were implanted with 100 keV Cr⁺ ions at a substrate temperature of 975 K and an ion fluence of 1.25 x 10¹⁶ ions/cm².

Following implantation, the samples were characterized using vibrating sample magnetometry (VSM) to determine magnetic properties and a four-point probe to determine resistivity. Structural and compositional properties were determined using Rutherford backscattering spectrometry, proton induced X-ray emission, X-ray photoelectron spectroscopy depth profiling, and X-ray diffraction. Chromium and titanium L-edge and oxygen K-edge X-ray absorption near-edge spectroscopy (XANES) in total electron yield and total fluorescence yield were measured on beamline 9.3.2 at the Lawrence Berkeley National Laboratory

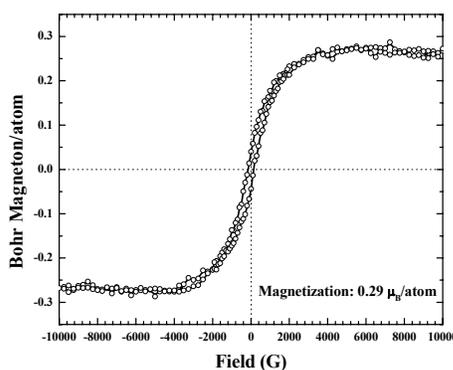


Figure 12. Room-temperature VSM hysteresis loop for ~1% chromium-implanted TiO₂ (110) rutile.

Advanced Light Source. In addition, chromium K-edge XANES measurements were made at Argonne National Laboratory's Advanced Photon Source using PNC-CAT beamline 20-ID.

A typical VSM hysteresis loop taken at room-temperature from a chromium-implanted $\text{TiO}_2(110)$ rutile sample is shown in Figure 12. The magnetic field was oriented perpendicular to the sample surface. However, there were no noticeable differences between in-plane and perpendicular magnetization loops. The sample shows clear ferromagnetic behavior with a saturation magnetization of $\sim 0.29 \mu\text{B}/\text{chromium atom}$, assuming that all chromium atoms contribute to magnetization. This value is less than that found for chromium-doped TiO_2 anatase grown by molecular beam epitaxy ($\sim 0.6 \mu\text{B}/\text{chromium atom}$). The coercive field was found to be $\sim 150 \text{ Oe}$ and the remanent magnetization on the order of $\sim 20\%$. This sample was also found to be semiconducting due to reduction associated with high-temperature implantation, with a resistivity of $360 \mu\Omega\text{-cm}$.

Chromium metal is antiferromagnetic, yet CrO_2 is a half metal. Therefore, its presence must be carefully monitored, lest the observed ferromagnetic response be due to this phase. We have employed chromium L-edge and K-edge XANES to determine the valence state of implanted chromium. Chromium K-edge XANES spectra from chromium-implanted rutile TiO_2 and various chromium-containing reference materials (chromium metal, Cr_2O_3 and CrO_2) are shown in Figure 13. It is clear that the spectrum for chromium-implanted TiO_2 strongly resembles that of Cr_2O_3 . Both spectra show the small pre-edge feature due to a dipole forbidden $1s-3d$ transition and an absorption edge at $E-E_0 = 12 \text{ eV}$. In addition, spectra obtained from chromium metal and CrO_2 are qualitatively different from that of chromium-implanted TiO_2 . Thus, no detectable $\text{Cr}(0)$ and/or $\text{Cr}(IV)$ were found in the implanted sample. Hence, the majority of the chromium atoms are in the +3 formal oxidation states. Substitution of $\text{Cr}(III)$ for $\text{Ti}(IV)$ requires one neutral oxygen vacancy (or doubly occupied fluorine center) for every two $\text{Cr}(III)$ ions in order to maintain charge neutrality.

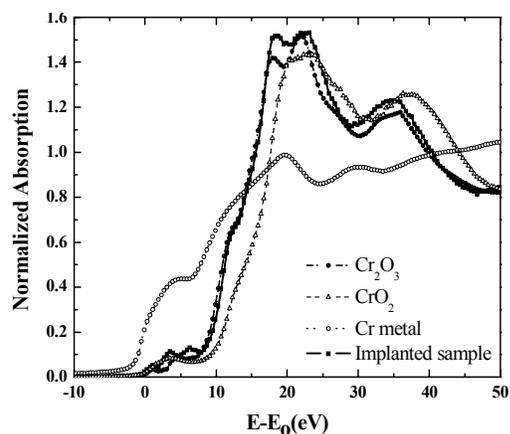


Figure 13. Chromium K-edge XANES spectra from chromium metal, CrO_2 , Cr_2O_3 , and Cr-implanted rutile TiO_2 .

Influence of Neurotoxin on Acetylcholinesterase

JM Bui,^(a) K Tai,^(b) JA McCammon^(a)

(a) University of California, San Diego, California

(b) University of Oxford, Oxford, England

Researchers at the University of California and Oxford studied the influence of the neurotoxin fasciculin-2 (Fas2) on mouse acetylcholinesterase (mAChE). Bui et al. used the molecular dynamics module of NWChem to examine the effect of the presence or absence of the peptide inhibitor Fas2 on the molecular motions and catalytic activity of mAChE (Bui et al. 2004). Experimental work has revealed a variety of molecular motions, but there is no clear understanding of the relationship between the motions of the protein and its functions. The simulations by Bui et al. show that Fas2 alters the activity of mAChE by changing the dynamics and structure of the enzyme. They observed enhanced fluctuations of molecular loop structures near the active site motions that might contribute to the residual activity of the Fas2-mAChE complex as the motions create alternative pathways to and from the active site for small molecules.

Reference

Bui JM, K Tai, and JA McCammon. 2004. "Acetylcholinesterase: Enhanced Fluctuations and Alternative Routes to the Active Site in the Complex with Fasciculin-2." *Journal of the American Chemical Society* 126(23):7198-7205.

Awards and Recognition

EMSL M.T. Thomas Award. Chemistry and Physics of Complex Systems Facility user Xin Yang was selected as the 2003 recipient of the M.T. Thomas Award for Outstanding Postdoctoral Achievement (Figure 14). He was selected for his contributions to the development of electrospray-photoelectron spectroscopy techniques and for leading its use in new research directions, including the investigation of complex anion solvations in the gas phase and the electronic structure of the active site of iron-sulfur proteins. His innovative studies on environmentally related solvated anions such as sulfate and nitrate and dicarboxylate dianions, which serve as models for peptide chains, have been published in *Science*, the *Journal of the American Chemical Society*, and the *Journal of Physical Chemistry*. His research has also included the discovery of Coulomb- and antiferromagnetic-induced fission in doubly charged cube-like [4Fe-4S] clusters. Such a process has never been observed before and may have important implications in understanding the functionality and transformations of iron-sulfur clusters in biological molecules such as proteins.



Figure 14. Left to right: EMSL Interim Director Allison Campbell, M.T. Thomas award recipient Xin Yang, Lai-Sheng Wang, and Tom Thomas.

Patent for Multi-Level RF Identification. Instrument Development Laboratory staff Kerry Steele and Gordon Anderson, along with Ronald W. Gilbert, were awarded U.S. Patent 6,765,476, "Multi-Level RF Identification." This newly patented technology is one part of PNNL's ongoing research to support the Defense Threat Reduction Agency in developing RF identification system technologies. It uses discrete frequencies to interrogate and obtain response from individual or groups of tags, versus using an embedded microprocessor to encode and decode messages.

Professional/Community Service

Molecular Modeling Workshop. Kevin Rosso, a scientific consultant for EMSL's Environmental Spectroscopy and Biogeochemistry Facility, helped design and instruct the workshop "Molecular Modeling Applied to Environmental Geochemistry." The workshop, held at Penn State University on August 15-20, 2004, was sponsored by a Summer School Grant from the American Chemical Society - Petroleum Research Fund. Topics of the workshop covered modeling techniques, molecular dynamics simulation, Monte Carlo simulation of solid surface growth/dissolution, ab initio molecular orbital theory, electron transfer calculations, solid surface chemistry with periodic models, and vibrational and transition-state calculations. Thirty graduate students, post-docs, and young faculty from chemistry, geoscience, physics, and engineering departments at national academic institutions were provided workstations for hands-on modeling exercises. As a direct result of this workshop, several new EMSL collaborations and user proposals are planned.

Molecular Science Computing Facility. The call for Computational Grand Challenge application proposals was successfully completed and is now closed. External scientific reviews have been completed for all 11 full proposals. Awards for proposals with the highest merit will be announced in September.

Major Facility Upgrades

Mössbauer Laboratory Cryostat. A liquid-cryogen-free, closed-cycle refrigerant (CCR) cryostat capable of cooling samples to liquid helium temperature (4.2 K) was installed in the Environmental Spectroscopy and Biogeochemistry Facility's Mössbauer laboratory. This CCR complements another unit in the laboratory that cools samples to ~10 K, and is a critical capability in characterizing speciation, mineralogy, and magnetic properties of iron-containing nanoparticles.

NWfs Hardware. In August 2004, the Molecular Science Computing Facility received new hardware for the second-generation NWfs archive storage system. This updated system will provide 380 terabytes (about 389,120 gigabytes) for storage of data primarily generated by the supercomputer and EMSL instruments. The new system will undergo configuration and testing and will be available for use in late calendar year 2004.

News Coverage

Computer Models of DNA. The news release "[Why damaged DNA gets a case of the bends - Study reveals how body's repair machinery recognizes altered DNA](#)" featured work discussed in a report given by PNNL researcher and EMSL user Maciej Haranczyk at the 228th American Chemical Society in Philadelphia, and mentioned that the nature of the work could not be performed without a large supercomputer such as EMSL's. The release was featured at a number of online news sites.

Visiting Users

Chemistry and Physics of Complex Systems Facility

- Anastassia Alexandrova, Utah State University, Logan, Utah, participated in the Interfacial and Condensed Phase Chemical Physics Summer Research Institute and worked on the study "Boron Clusters as Potential Compounds for the Storage of Hydrogen."
- Jormarie Alvarez, Purdue University, West Lafayette, Indiana, participated in the Interfacial and Condensed Phase Chemical Physics Summer Research Institute and worked on the study "Dissociative Charge Inversion of Peptides by Surface-Induced Dissociation."
- Benjamin Arthurs, Washington State University, Pullman, Washington, worked on the study "Image Acquisition and Analysis of Fluorescent Biological Samples."
- Emily Ashjian, Young Women in Science Program, Southridge High School, Kennewick, Washington; Brian Estes, Gonzaga University, Spokane, Washington; Brooke Holben, Washington State University, Pullman, Washington; and Bill Morgan, University of Maryland, Baltimore, Maryland, worked on the study "Electron Induced Genomic Instability."
- Olexandr Bondarchuk, University of Texas, Austin, Texas, worked on the study, "Atomically Resolved Studies of Transition Metal Oxides."
- Ben Elliott, Utah State University, Logan, Utah, participated in the Interfacial and Condensed Phase Chemical Physics Summer Research Institute and worked on the study "Determination of the Electronic Structure of Iron-Sulfur Clusters."

- Lisa Goss, Idaho State University, Pocatello, Idaho, in collaboration with EMSL scientist Tom Blake, synthesized methyl nitrite and recorded its fundamental vibrational bands using the high-resolution infrared spectrometer.
- Jason Han, 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.”
- Yufan He, University of Pittsburgh, Pittsburgh, Pennsylvania, gave the seminar “Nanoscale Dynamics of Molecular Self-Assembly at Solid-Liquid Interfaces.”
- Alexandre Kavetski, Khlopin Radium Institute, St. Petersburg, Russia, worked on the study “Electron Stimulated Reactions in Thin Water Films.”
- Paul Kienker, Albert Einstein College of Medicine, Bronx, New York, set up experiments with colicin channels in planar bilayer membranes.
- David Laman, Central Washington University, Ellensburg, Washington, participated in the Interfacial and Condensed Phase Chemical Physics Summer Research Institute and worked on the study “Charge Separation Kinetics in the α -Cr₂O₃/ α -Fe₂O₃ System.”
- 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.”
- Dmytro Nykypanchuk, University of Massachusetts, Amherst, Massachusetts, gave the seminar “A Single Molecule Study of DNA Dynamics and Partitioning in Module Porous Materials.”
- David Panther, George Fox University, Newburg, Oregon, worked on the study “Single Molecule Approach for Understanding EGFR Molecular Interactions.”
- Luis Rodriguez, National Cancer Institute, Bethesda, Maryland, worked on the study “Development of Multi-Functional Microscopy (MFM) for Cancer and AIDS Research.”
- Oscar Sanz, Consejo Superior de Investigaciones Cientificas, Madrid, Spain, conducted a study to probe the oxygen desorption process via resonance-enhanced multiphoton ionization and irradiation-mediated X-ray photoelectron spectroscopy of one type of thin film glass.
- Jeffrey Spraggins, University of Delaware, Newark, Delaware, participated in the Interfacial and Condensed Phase Chemical Physics Summer Research Institute and worked on the study “Large Molecule Characterization via Fourier Transform Ion Cyclotron Resonance.”
- Steven Tait, University of Washington, Seattle, Washington, participated in the Interfacial and Condensed Phase Chemical Physics Summer Research Institute and worked on the study “Pd Nanoclusters Supported on MgO(100): Effects of Cluster Size on Chemisorption Properties.”

- Gang Xiong, Wake Forest University, Winston-Salem, North Carolina, gave the seminar “Time-Resolved Photoluminescence of ZnO: Giant Oscillator Strength, Polariton Propagation and Donor-Acceptor Pair Recombination.”
- Zhiwei Yang, University of Delaware, Newark, Delaware, participated in the Interfacial and Condensed Phase Chemical Physics Summer Research Institute and worked on the study “Chemical Characterization of Heterogeneous Inclusions in Soot Particles.”

Environmental Spectroscopy and Biogeochemistry Facility

- Paul Bagus, University of North Texas, Denton, Texas, discussed with Eugene Ilton results and future direction of collaboration on theoretical predictions of X-ray photoelectron spectroscopy spectra for transition metals and actinides.
- Stephen Bialkowski, Utah State University, Logan Utah, began new project collaborations with Nancy Foster-Mills of EMSL and PNNL researchers Jim Amonette and Tom Autrey to examine spectroscopic techniques for detecting chemical weapons.
- Stuart Bogatko (Figure 15), University of California, San Diego, La Jolla, California, worked with Eric Bylaska, PNNL to study high-temperature and pressure electrolyte solutions thought to facilitate metal ion transport in hydrothermal environments using ab initio molecular dynamics methods (AIMD). All simulations performed in this work have extremely large computational and memory needs, requiring the use of massively parallel computing environments. However, performance on a parallel computer is dependent on the scaling of the required algorithms. As part of this collaboration, a new generation of parallel algorithms is being developed to both improve the performance and generality of algorithms used in AIMD calculations.
- Je-Hun Jang, Pennsylvania State University, University Park, Pennsylvania, visited EMSL to discuss becoming a user—most specifically using the Mössbauer spectroscopy—to help characterize iron oxides reduced with and without bacteria. The project is sponsored by the National Science Foundation to study iron isotopic fractionation during abiotic and biotic mineral dissolution of iron oxides. Jang met with EMSL researcher Ravi Kukkadapu and PNNL researcher John Zachara to discuss details.



Figure 15. Stuart Bogatko, University of California and Eric Bylaska, PNNL.

High-Field Magnetic Resonance Facility

- Linan An, University of Central Florida, Orlando, Florida, used the 300-MHz and 500-MHz spectrometers for “Study of the Structures of Thermally Formed Oxides on Amorphous SiAlCN Ceramics.”
- James Aramini, Rutgers University, Piscataway, New Jersey, sent samples to be run on the 750-MHz spectrometer for the study “Structural Genomics of Model Eukaryotic Organisms.”
- Cheryl Arrowsmith, University of Toronto (University Health Network), Toronto, Ontario, Canada, sent samples to be run on the 500-MHz and 750-MHz spectrometers for the study “Structural Proteomics: Annotating the Genome Using 3D Structure.”
- Elisar Barbar, Oregon State University, Corvallis, Oregon, sent samples to be run on the 600-MHz spectrometer for the study “Structure and Interactions of a Domain of Dynein Intermediate Chain—Protein Folding Coupled to Binding.”
- Peter Brzovic, University of Washington, Seattle, Washington, used the 600-MHz spectrometer to run samples for the study “NMR Structural Investigations of BRCA1.”
- Myriam Cotten, Pacific Lutheran University, Tacoma, Washington, used the 500-MHz spectrometer to run samples for the study “Investigating Molecular Recognition and Biological Function at Interfaces Using Antimicrobial Peptides.”
- 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.”
- Alfred Fuciarelli, Colorado State University, Fort Collins, Colorado, sent samples to be run on the 600-MHz spectrometer for the study “Metabonomics Assessment Following ANIT or Acetaminophen Administration to Male Fischer 344 Rats.”
- Evan Kantrowitz, Boston College, Chestnut Hill, Massachusetts, sent samples to be run on the 500-MHz spectrometer for the study “Probing the Mechanism of the Alkaline Phosphatase Reaction by ^{67}Zn and ^{25}Mg NMR.”
- Thomas Leeper, University of Washington, Seattle, Washington, sent samples to be run on the 600-MHz and 800-MHz spectrometers for the study “Structure of Telomerase RNA and Telomeric Proteins.”
- Bruce McNamara, Pacific Northwest National Laboratory, Richland, Washington, used the 300-MHz and 500-MHz spectrometers for the study “Kinetics of Polyphosphate Decomposition in Heterogeneous Environments.”
- Kristopher Ooms, Kirk Feindel, and Mathew Willans, University of Alberta, Edmonton, Alberta, Canada, used the 750-MHz spectrometer to run samples for the study “Lanthanum-139 Nuclear Magnetic Resonance Studies of Solid Oxo-Coordinate Compounds.”

- Raymond Reeves, Washington State University, Pullman, Washington, sent samples to be run on the 500-MHz and 600-MHz spectrometers for the study “Structural Biology of the Human High Mobility Group A (HMGA) Proteins: Characterizing the Hub of Nuclear Function.”
- Celine Schneider, University of British Columbia, Vancouver, British Columbia, Canada, used the 750-MHz spectrometer to run samples for the study “Structural Investigations of Solid Materials by High Resolution Solid State NMR at Very High Field.”
- Frank Soennichsen and Jeffrey Mills, Case Western Reserve University, Cleveland, Ohio, used the 800-MHz and 900-MHz spectrometers to run samples for the study “Structure Determination of Membrane Proteins from Mycobacterium Tuberculosis.”
- Thomas Squier, Pacific Northwest National Laboratory, Richland, Washington, used the 500-MHz and 600-MHz spectrometers to run samples for the study “Development of Multipurpose Tags and Affinity Reagents for Rapid Isolation and Visualization of Protein Complexes.”
- Suzana Straus and Pareshkumar Dave, University of British Columbia, Vancouver, British Columbia, Canada, used the 800-MHz spectrometer to run samples for the study “Investigation of Lineshapes in Fully $^{13}\text{C}/^{15}\text{N}$ -Labelled S1 Domain from RNaseE Using Solid State NMR.”
- Thomas Terwilliger, Los Alamos National Laboratory, Los Alamos, New Mexico, sent samples to be run on the 600-MHz spectrometer for the study “Structural Proteomics of Mycobacterium Tuberculosis.”
- Jianjun Wang (Figure 16) and Xuefeng Ren, Southern Illinois University, Carbondale, Illinois, used the 600-MHz, 800-MHz, and 900-MHz spectrometers to run samples for “Structural Studies of Apolipoprotein A-I/preb-HDL Particles.”

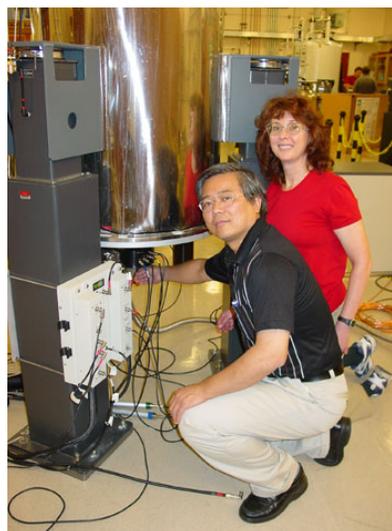


Figure 16. Jianjun Wang, Southern Illinois University and Nancy Isern, EMSL.

High Performance Mass Spectrometry Facility

- Diana Bigelow, Pacific Northwest National Laboratory, Richland, Washington, worked on the study “Proteomics of Membrane Protein Complexes.” The latest calcium channel rabbit samples were prepared and analyzed by liquid chromatography tandem mass spectrometry (LC-MS/MS).
- Steven Brown, Oak Ridge National Laboratory, Oak Ridge Tennessee, and Yuri Gorby, Pacific Northwest National Laboratory, Richland Washington, conducted combined transcriptome and proteome analyses of *Shewanella oneidensis* MR-1 *etrA* and *arcA* mutant

strains. The first sample set is being analyzed by LC-MS/MS. Once a preliminary mass tag database is built from these runs, the LC-FTICR-MS analyses will be compared against the database to provide accurate protein identifications.

- Mary Lipton, Pacific Northwest National Laboratory, Richland Washington, used the 9-tesla FTICR to analyze proteomic samples for the Shewanella federation, focusing on the characterization of proteins from cells grown in the presence and absence of oxygen. Under certain conditions, cells produced microfibers and these fibers were also subjected to proteomic analysis.
- Sandra McCutchen-Maloney, Lawrence Livermore National Laboratory, and Mary Lipton, Pacific Northwest National Laboratory, Richland, Washington, completed qualitative and quantitative analysis for the whole proteome of *Y. pestis*.
- Curt Scharfe, Stanford University, Palo Alto, California, worked on the study "Proteomics of Mitochondria." Approximately half of the 490 analyses generated by fractionating seven samples through a strong cation exchange column have been analyzed by LC-MS/MS. The data from these runs will be used to populate a preliminary mass tag database for future LC-FTICR-MS analyses.
- Alfred M. Spormann, Stanford University, Palo Alto, California, received data from the original set of samples for the study of proteomic analysis on *Shewanella oneidensis* biofilms. A second, larger set of samples has been sent and is currently being prepared for mass spectrometry analysis.
- Richard Zangar, Pacific Northwest National Laboratory, Richland, Washington, carried out research on biomarker-containing fluid with potential application to early breast-cancer detection. The O^{16}/O^{18} labeled samples were analyzed by LC-MS/MS and it was determined that only one was fit to be analyzed by LC-FTICR-MS. There are plans for strong cation exchange separations of the samples to generate a preliminary mass tag database for the study.

Interfacial and Nanoscale Science Facility

- Chundi Cao, University of Washington, Seattle, Washington, characterized the Pt/ Al_2O_3 catalyst.
- Xiaoli Cui, Eastern Michigan University, Ypsilanti, Michigan, worked on the study "Nanoengineered Electrochemical Sensors for Mixed Wastes" in the electrochemical laboratory.
- Aaron Feaver, University of Washington, Seattle, Washington, studied hydrogen storage materials in the catalysis laboratory.
- Karl Hibbitts, University of Washington, Seattle, Washington, investigated acid vapor weathering of Mars analog surface materials in the surface chemistry laboratory.

- Byoung Chan Kim, Gwangju Institute of Science and Technology, Gwangju, South Korea, worked on immobilized enzymes for bioremediation and biosensing in the nanobiotechnology laboratory.
- Meindert Kleecstra, AirAdvice Incorporated, Portland, Oregon, characterized indoor air quality volatile organic compound sensors in the surface analysis laboratory.

Molecular Sciences Software - New User Agreements with NWChem/Ecce

- Air Force Institute of Technology, Wright Patterson Air Force Base, Ohio
- Aristotle University of Thessaloniki, Thessaloniki, Greece
- Budapest University of Technology and Economics, Budapest, Hungary
- City College of New York, New York City, New York
- Colby College, Waterville, Maine
- Fudan University, Shanghai, China
- George Mason University, Fairfax, Virginia
- Illinois Institute of Technology, Chicago, Illinois
- Indiana University Bloomington, Bloomington, Indiana
- INFN National Research Center S3, Modena, Italy
- Institute of Chemical Materials, Mianyang, China
- Institute of Nuclear Chemistry and Technology, Warsaw, Poland
- Johannes Gutenberg University, Mainz, Germany
- Korea Institute for Advanced Study, Seoul, Korea
- LG Chemical, Ltd., Daejeon, Korea
- National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca, Romania
- National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan
- National Institute of Health, Bethesda, Maryland
- North Carolina Agricultural and Technical State University, Greensboro, North Carolina
- Norwegian University of Science and Technology, Trondheim, Norway
- Ohio State University, Springfield, Ohio
- Pliva Research Institute, Zagreb, Croatia
- Quadrics Supercomputers World Ltd., Bristol, United Kingdom
- Russian Academy of Sciences, Novosibirsk, Russia
- Saint Louis University, Saint Louis, Missouri
- Sandia National Laboratory, Albuquerque, New Mexico
- Savannah River Technology Center, Aiken, South Carolina
- Shenyang Pharmaceutical University, Shenyang, China
- Sichuan University, Chengdu, China
- Southeastern Louisiana University, Hammond, Louisiana
- Temple University, Philadelphia, Pennsylvania
- Texas Technical University, Lubbock, Texas
- The University of Queensland, Brisbane, Australia
- Universidade de Lisboa, Lisboa, Portugal
- Università degli Studi di Torino, Torino, Italy

- University of Ulster, Belfast, Great Britain
- Universitat Konstanz, Konstanz, Germany
- University of Alicante, Alicante, Spain
- University of California, Irvine, Irvine, California
- University of Cambridge, Cambridge, Great Britain
- University of Chile, Newark, Delaware
- University of Colorado, at Denver, Denver, Colorado
- University of Georgia, Athens, Georgia
- University of Hamburg, Hamburg, Germany
- University of Louisville, Louisville, Kentucky
- University of Newcastle, Newcastle upon Tyne, Great Britain
- University of North Carolina Charlotte, Charlotte, North Carolina
- University of Notre Dame, Notre Dame, Indiana
- University of Ontario Institute of Technology, Oshawa, Ontario, Canada
- University of Siena, Siena, Italy
- University of the Sciences in Philadelphia, Philadelphia, Pennsylvania
- University of Zaragoza, Zaragoza, Spain
- Vrije Universiteit/Scientific Computing and Modeling, Amsterdam, The Netherlands
- Weber State University, Ogden, Utah

Publications

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

Alexandrova AN, HJ Zhai, LS Wang, and AI Boldyrev. 2004. "Molecular Wheel B_8^{2-} as a New Inorganic Ligand. Photoelectron Spectroscopy and ab Initio Characterization of LiB_8 ." *Inorganic Chemistry* 43(12):3552-3554.

Bacon DH and BP McGrail. 2003. "Lessons Learned from Reactive Transport Modeling of a Low-Activity Waste Glass Disposal System." *Computers & Geosciences* 29(3):361-370.

Bacon DH and BP McGrail. 2003. "Waste Form Release Calculations for Performance Assessment of the Hanford Immobilized Low-Activity Waste Disposal Facility Using a Parallel, Coupled Unsaturated Flow and Reactive Transport Simulator." In 26th Materials Research Society Symposium Proceedings, Vol. 757, ed. Robert J. Finch and Daniel B. Bullen, pp. 43-48. Materials Research Society, Warrendale, Pennsylvania.

Beyenal H, RK Sani, BM Peyton, AC Dohnalkova, JE Amonette, and Z Lewandowski. 2004. "Uranium Immobilization by Sulfate-Reducing Biofilms." *Environmental Science and Technology* 38(7):2067-2074.

Biju V, M Micic, DH Hu, and HP Lu. 2004. "Intermittent Single-Molecule Interfacial Electron Transfer Dynamics." *Journal of the American Chemical Society* 126(30):9374-9381.

Brown LR, A Nikitin, DC Benner, VM Devi, MAH Smith, L Fejard, JP Champion, VG Tyuterev, and RL Sams. 2004. "Line Intensities of CH_3D in the Triad Region: 6-10 μm ." *Journal of Molecular Structure* 695-696:181-188.

Devi VM, DC Benner, MAH Smith, CP Rinsland, SW Sharpe, and RL Sams. 2004. "A Multispectrum Analysis of the $2\nu_2$ Spectral Region of $H^{12}CN-C^{14}N$: Intensities, Broadening and Pressure-Shift Coefficients." *Journal of Quantitative Spectroscopy and Radiative Transfer* 87(3-4):339-366.

Elliott DC, GG Neuenschwander, TR Hart, RS Butner, AH Zacher, MH Engelhard, JS Young, and DE McCready. 2004. "Chemical Processing in High-Pressure Aqueous Environments. 7. Process Development for Catalytic Gasification of Wet Biomass Feedstocks." *Industrial and Engineering Chemistry Research* 43(9):1999-2004.

Fu YJ, X Yang, XB Wang, and LS Wang. 2004. "Terminal Ligand Influence on the Electronic Structure and Intrinsic Redox Properties of the $Fe_4S_4^{2+}$ Cubane Clusters." *Inorganic Chemistry* 43(12):3647-3655.

- Gaspar DJ, A Laskin, W Wang, SW Hunt, and BJ Finlayson-Pitts. 2004. "TOF-SIMS Analysis of Sea Salt Particles: Imaging and Depth Profiling in the Discovery of an Unrecognized Mechanism for pH Buffering." *Applied Surface Science* 231-232:520-523.
- Han L, W Wu, FL Kirk, J Luo, MM Maye, NN Kariuki, Y Lin, C Wang, and CJ Zhong. 2004. "A Direct Route Toward Assembly of Nanoparticle-Carbon Nanotube Composite Materials." *Langmuir* 20(14):6019-6025.
- Hoffman RC, A Laskin, and BJ Finlayson-Pitts. 2004. "Sodium Nitrate Particles: Physical and Chemical Properties during Hydration and Dehydration, and Implications for Aged Sea Salt Aerosols." *Journal of Aerosol Science* 35(7):869-887.
- Hu DH and HP Lu. 2004. "Placing Single-Molecule T4 Lysozyme Enzymes on a Bacterial Cell Surface: Toward Probing Single-Molecule Enzymatic Reaction in Living Cells." *Biophysical Journal* 87(1):656-661.
- Jiang W, V Shutthanandan, S Thevuthasan, DE McCready, and WJ Weber. 2004. "Carbon Analysis Using Energetic Ion Beams." *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 222(3-4):538-546.
- Johnson MC, ED Bourret-Courchesne, J Wu, Z Liliental-Weber, DN Zakharov, RJ Jorgenson, TB Ng, DE McCready, and JR Williams. 2004. "Effect of Gallium Nitride Template Layer Strain on the Growth of $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ Multiple Quantum Well Light Emitting Diodes." *Journal of Applied Physics* 96(3):1381-1386.
- Nemykin VN, J Laskin, and P Basu. 2004. "Isolation, Characterization of an Intermediate in an Oxygen Atom-Transfer Reaction, and the Determination of the Bond Dissociation Energy." *Journal of the American Chemical Society* 126(28):8604-8605.
- Roberts AG, MK Bowman, and DM Kramer. 2004. "The Inhibitor DBMIB Provides Insight into the Functional Architecture of the Q_o Site in the Cytochrome *b_6/f* Complex." *Biochemistry* 43(24):7707-7716.
- Rosso KM, DMA Smith, and M Dupuis. 2004. "Aspects of Aqueous Iron and Manganese (II/III) Self-Exchange Electron Transfer Reactions." *Journal of Physical Chemistry A* 108(24):5242-5248.
- Zhai HJ, X Yang, YJ Fu, XB Wang, and LS Wang. 2004. "Sequential Oxidation of the Cubane 4Fe-4S Cluster from $[\text{4Fe-4S}]^-$ to $[\text{4Fe-4S}]^{3+}$ in $\text{Fe}_4\text{S}_4\text{L}_m^-$ Complexes." *Journal of the American Chemical Society* 126(27):8413-8420.
- Zhang H-F, M Stender, R Zhang, C Wang, J Li, and L-S Wang. 2004. "Toward the Solution Synthesis of the Tetrahedral Au_{20} Cluster." *The Journal of Physical Chemistry B* 108(33):12259-12263.

Presentations

Although not an inclusive list, the following illustrates the variety of topics presented by staff members and users at meetings and events. EMSL does not typically collect presentation information from users external to the laboratory.

Alexeev Y, TL Windus, M Valiev, and DA Dixon. 2004. "New Mechanism of Catalytic GTP Hydrolysis: Quantum and Molecular Dynamics Simulations." Presented by Yuri Alexeev (Invited Speaker) at the 228th American Chemical Society National Meeting, Philadelphia, Pennsylvania on August 25, 2004.

Ayotte P, RS Smith, GR Teeter, Z Dohnalek, GA Kimmel, and BD Kay. 2004. "Creating Beakers without Walls: Formation of Deeply-Supercooled Binary Liquid Solutions from Nanoscale Amorphous Solid Films." Presented by Bruce D. Kay (Invited Speaker) at the 228th American Chemical Society, Philadelphia, Pennsylvania, on August 22, 2004.

Cowin JP and MJ Iedema. 2004. "Buried Liquid-Liquid Interfaces." Presented by James P. Cowin (Invited Speaker) at the 228th American Chemical Society, Philadelphia, Pennsylvania, on August 24, 2004.

Cowin JP. 2004. "Proton-Oriented Ice at Low Temperature: Disequilibria, Pyroelectricity, and Planetesimals." Presented by James P. Cowin (Invited Speaker) at the Workshop on Studies of Ice, Icy Particles, Ice Surfaces, and Ice Adsorbate Interactions: A Molecular View, Telluride, Colorado, on July 26, 2004.

Daschbach JL, GK Schenter, P Ayotte, and BD Kay. 2004. "Diffusion of He in Amorphous Solid Water: Observation of an Inverse H/D Lattice Isotope Effect." Presented by Bruce D. Kay (Invited Speaker) at the Gordon Conference, Andover, New Hampshire, on August 3, 2004.

Felmy AR, JR Rustad, and DA Dixon. 2004. "Molecular Simulation of Clusters and Surfaces in Contact with Solution: Applications in Geosciences and High Level Waste Processing." Presented by Andrew R. Felmy (Invited Speaker) at the 2004 Gordon Research Conference on Computational Chemistry, Plymouth, New Hampshire, on July 6, 2004.

Henyk M, KM Beck, AG Joly, and WP Hess. 2004. "Surface Spectroscopic Properties and UV Laser-Induced Morphological Changes Studied on Nanoporous MgO Thin Films." Presented by Matthias Henyk (Invited Speaker) at the Gordon Research Conference, Andover, New Hampshire, on August 3, 2004.

Hess WP, AG Joly, KM Beck, JT Dickinson, PV Sushko, and AL Shluger. 2004. "Laser Controlled Desorption from Ionic Crystals." Presented by Wayne P. Hess (Invited Speaker) at the Gordon Research Conference, Andover, New Hampshire, on August 3, 2004.

Joly AG, WP Hess, DM Laman, JR Williams, and SA Chambers. 2004. "Carrier Lifetimes and Dynamics in Epitaxial Grown Fe₂O₃/Cr₂O₃ Thin Films Measured by Femosecond Transient Reflectivity and Absorption." Presented by Alan G. Joly (Invited Speaker) at the Gordon Research Conference, Andover, New Hampshire, on August 2, 2004.

Kay BD. 2004. "Kinetics of Diffusion, Crystallization, and Reactions in Amorphous Solid Water." Presented by Bruce D. Kay (Invited Speaker) at the Workshop on Studies of Ice, Icy Particles, Ice Surfaces, and Ice Adsorbate Interaction: A Molecular View, Telluride, Utah, on July 27, 2004.

Kenny JP, S Benson, Y Alexeev, JJ Sarich, C Janssen, LC McInnes, M Krishnan, J Nieplocha, ER Jurrus, C Fahlstrom, TL Windus, and DE Bernholdt. 2004. "Component-Based Integration of Chemistry and Optimization Software." Presented by Yuri Alexeev (Invited Speaker) at the 228th American Chemistry Society National Meeting, Philadelphia, Pennsylvania on August 24, 2004.

Lu HP. 2004. "Single-Molecule Protein Conformational Dynamics in Cell Signaling." Presented by H. Peter Lu (Invited Speaker) at the 228th American Chemical Society Meeting, Philadelphia, Pennsylvania, on August 25, 2004.

Rosso KM, S Yanina, JR Rustad, and P Meakin. 2004. "Addressing Complexity at Rough Mineral Surfaces." Presented by Kevin Rosso (Invited Speaker) at the 228th National American Chemical Society Conference, Philadelphia, Pennsylvania, on August 26, 2004.

Subramani V, X Ma, C Song, MH Engelhard, and Y Chin. 2004. "Promotional Effect of Potassium on the Adsorptive Desulfurization of Transportation Fuels over K-Exchanged NiY-Zeolites." Presented by Velu Subramani at the American Chemical Society Philadelphia National Meeting, Division of Petroleum Chemistry, Philadelphia, Pennsylvania, on August 23, 2004.

Tenney ND. 2004. "Installing, Configuring and Maintaining Large Clusters: A Case Study of the HP-Built PNNL Supercomputer." Presented by Nathan Tenney (Invited Speaker) at HP World 2004, Chicago, Illinois, on August 17, 2004.

Wang Z, CC Ainsworth, KM Rosso, and JK Fredrickson. 2004. "The Kinetics of the Reduction of Uranium(VI) Complexes by Microbially-Reduced Anthraquinone-1,6-Disulfonate." Presented by Zheming Wang at the 228th National American Chemical Society Meeting, Philadelphia, Pennsylvania, on August 24, 2004.

Wang Z, JM Zachara, JP McKinley, SC Smith, TT Resch, and O Qafoku. 2004. "A Cryogenic Fluorescence Spectroscopic and Microscopic Investigation of Sorbed Uranium in the Hanford Vadose Zone Sediments." Presented by Zheming Wang at the 228th National American Chemical Society Conference, Philadelphia, Pennsylvania, on August 24, 2004.

Xia Y, AR Felmy, NJ Hess, and Z Wang. 2004. "Thermodynamic Model for the Solubility of NaUO₂PO₄·3H₂O(c) in the Aqueous Na⁺-H⁺-H₂PO₄⁻-HPO₄²⁻-OH—NO₃⁻- H₂O System." Presented by Yuanxian Xia at the 228th National American Chemical Society Meeting, Philadelphia, Pennsylvania, on August 23, 2004.