EMSL Report

November/December 2005

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Research Highlights

High-Field Magnetic Resonance Characterization of Titanate-Based Ceramics and Glasses for High-Level Waste Immobilization.

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Researchers have developed a technique that allows normal titanium samples, including materials simulated to study radioactive waste vitrification, to be studied for the first time by nuclear magnetic resonance spectrometry.

Characterization of the titanate phases of synroc and titanosilicate glasses is an important step to understanding the materials chosen to immobilize high-level waste streams generated by nuclear fuel reprocessing. However, the spectroscopy of titanium is complicated by several issues, such as titanium's low gyromagnetic ratio and the fact that the material is a quadrupolar nuclide with two active isotopes having nuclear magnetic resonance (NMR) frequencies nearly coincident. The NMR active isotopes for titanium are ^{47}Ti and ^{49}Ti, which are present at 7.44 percent and 5.41 percent natural abundance, respectively. On a 500-MHz NMR spectrometer, they differ in resonant frequency by only 6.25 kHz. As quadrupolar nuclei, their linewidths are much larger, so the two hopelessly overlap. The only previous solution was to isotopically enrich samples in one or the other of the two, but this severely limits the samples that can be studied. Using very high magnetic fields, such as the 21.1-tesla available on EMSL's 900-MHz NMR spectrometer, enhances the minimal frequency difference and reduces the quadrupolar broadening of the lines so that in some cases, they are barely resolvable.

By using a novel pulse program equipped with frequency selective excitation, this collaborative group has been able to produce spectra at 900 MHz from anatase containing a natural abundance of ^{47}Ti and ^{49}Ti,, where the complete spectrum of the isotopes are collected separately (Figure 1). This requires the highest magnetic field possible, as well as the new pulse program, and creates the opportunity to study titanium by NMR at natural abundance, which is crucial for structural studies on glasses used for immobilizing radioactive waste. This research is discussed further in Larsen et al. 2006 (in press).

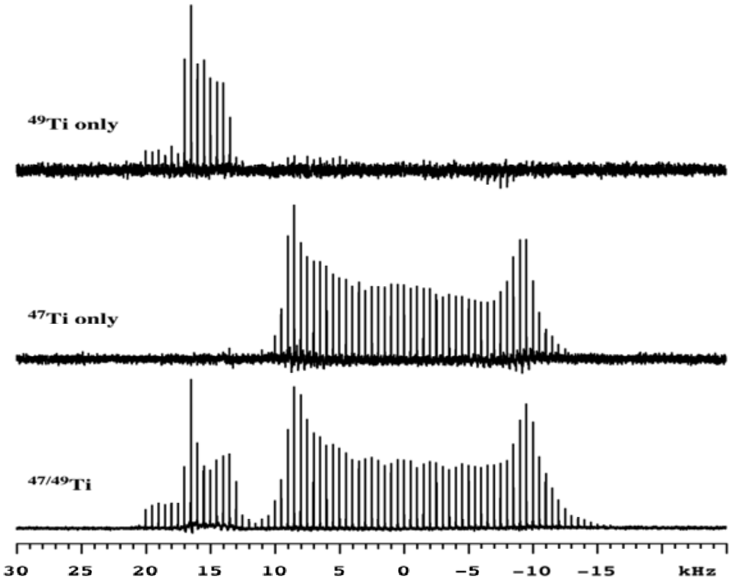

Figure 1. Experimental ^{47}Ti,^{49}Ti spectra of anatase acquired at 21.1 tesla (50.75 MHz) using the Quadrupole Carr-Purcell Meiboom Gill pulse sequence with ^{49}Ti-selective pulses. Top: The ^{49}Ti-selective pulse sequence. Middle: The ^{47}Ti-selective pulse sequence. Bottom: All experiments employed an radio frequency field strength of 12.5 kHz, s_1 = 50.0 ls, s_2 = s_4 = 76.0 ls, and s_3 = 24.0, M= 50, s_a = 2.0 ms, a dwell time of 2.0 ls, and 512 scans. All experiments were acquired using a recycle delay of 5 seconds and apodized by Lorentzian linebroadening of 10 Hz.

Citation

Larsen FH, I Farnan, and AS Lipton. 2006. "Separation of ^{47}Ti and ^{49}Ti Solid-State NMR Lineshapes by Static QCPMG Experiments at Multiple Fields." *Journal of Magnetic Resonance* (In Press).

Discovery of "Shrinking New Giant" Mechanism of Fullerene Formation by QM/MD Simulations

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Simulations conducted by EMSL users from Emory University provide a comprehensive understanding of the formation of carbon nanostructures, with the widest range of promising applications in materials science, molecular electronics, and molecular machinery.

Carbon nanostructures, such as fullerenes (buckyballs) and single- or multi-walled nanotubes, today are the most intensively researched species in the context of molecular engineering on the nanometer scale, with the widest range of promising applications in materials science, molecular electronics, and molecular machinery. Key to the development of highly efficient and commercially viable fullerene generation techniques is the search for the optimal reaction conditions, and development of these techniques requires a comprehensive understanding of the synthesis process.

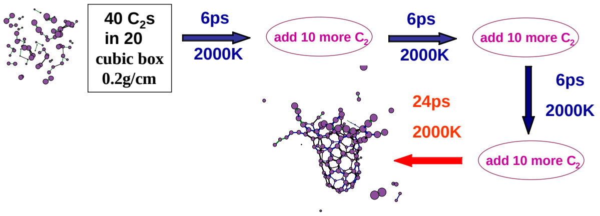

Figure 2. Simulations show that the high-density fullerene formation scheme leads to smaller fullerenes and fewer giant fullerenes.

Researchers at Emory University used the computing resources of EMSL's Molecular Science Computing Facility to gain a comprehensive understanding of the formation of carbon nanostructures from a flow of C_2 gas at high temperature (2000 K) and at various high concentrations. They discovered that fullerene formation follows a two-step mechanism. In the first "size-up" step, giant fullerenes with low curvature are readily formed by interaction of polyyne chains, formed from the C_2 molecules, with themselves and later attached to curved graphene sheets. This process is depicted in Figure 2. In the second "size-down" step, following Smalley's "shrink-wrap" mechanism, giant fullerenes are reduced in size until kinetically stable fullerenes remain. Smaller fullerenes are sometimes formed by losing carbon fragments in "fall-off" or "pop-out" annealing processes under prolonged heating of giant fullerenes. The latter step is found to have a strong dependence on influences such as time and temperature gradient.

The combination of subsequent "size-up" followed by "size-down" steps in the formation of fullerenes provides explanations for the appearance of C_{60} and larger fullerenes in combustion and carbon arc experiments and for the existence of readily formed endohedral metal carbide fullerene complexes. The researchers coined the name "shrinking new giant" mechanism of fullerene formation, and suggest that it is universally valid for both carbon plasma as well as polycyclic aromatic hydrocarbon combustion experiments. This research is described in more detail in Zheng et al. 2005a and b.

Citations

Zheng G, S Irle, and K Morokuma. 2005a. "Performance of the DFTB Method in Comparison to DFT and Semiempirical Methods for Geometries and Energies of C_{20}-C_{86} Fullerene Isomers." *Chemical Physics Letters* 412(1-3):210-216.

Zheng G, S Irle, and K Morokuma. 2005b. "Towards Formation of Buckminsterfullerene C_{60} in Quantum Chemical Molecular Dynamics." *Journal of Chemical Physics* 122(1):014708 (pages 1-7).

Crystalline Ice Growth on Pt(111): Observation of a Hydrophobic Water Monolayer

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Understanding the dynamics and morphology of crystalline ice formation is important in atmospheric science. In the seeding of clouds, for example, the water-particle interaction is a critical factor for the nucleation of ice crystals.

Water-surface interactions are ubiquitous in nature and play an important role in many technological applications such as catalysis and corrosion. To understand these interactions, numerous prior experiments have been done on thin water films grown on single crystal metals such as Ru(0001) and Pt(111), which are considered to be good templates for the epitaxial growth of crystalline ice (CI). However, despite years of effort, our understanding of fundamental aspects of water-surface interactions, and even the structure of bulk water, remains incomplete.

Water adsorbs molecularly on Pt(111). At temperatures above 60 K, the adsorbed water monomers become mobile and form hydrogen-bonded clusters as the coverage increases. For typical water fluxes, crystalline ice (CI) films result for growth temperatures above 125–135 K. For multilayers of CI, the equilibrium structure has the lattice constant of bulk ice and is incommensurate with the substrate. Multilayer CI films desorb with zero-order desorption kinetics. Based on these and other observations, the prevailing view has been that multilayer films of water wet Pt(111).

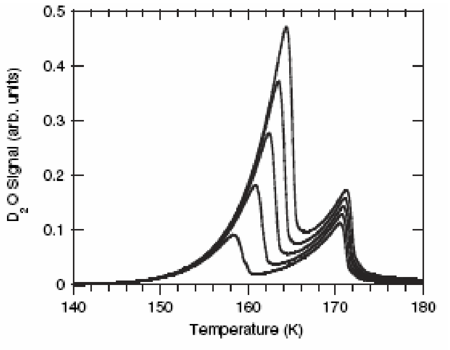

Figure 3. D_2O TPD spectra for 2, 3, 4, 5, and 6 ML CI films. The spectra exhibit zero-order desorption from the CI multilayers (i.e., the leading edges of the low-temperature peaks are aligned), and the monolayer desorbs at higher temperature. These characteristics are typically believed to indicate that the water films wet the substrate.

In this work, we investigated the growth of crystalline ice films on Pt(111) using temperature-programmed desorption (TPD) of both water and krypton adsorbed on the water films. As expected, the water monolayer wets the Pt(111) surface. Figure 3 shows a typical series of TPD spectra for crystalline D_2O on Pt(111). The multilayer ice films desorb with zero-order kinetics, resulting in the low-temperature peak that shifts to higher temperature with increasing coverage. The water monolayer desorbs at higher temperature (about 170 K). Water TPD spectra similar to these have been obtained on a variety of metal surfaces and presented as evidence for the wetting growth of the multilayer water films on these metals.

Figure 4 displays the TPD of krypton layers deposited on top of various water films deposited at low temperatures. The krypton desorption temperature is sensitive to the height of the desorbing atom above a metal surface. This approach can also be used to determine the height distribution of a thin water film grown on a metal substrate: the solid blue, red, green, and black lines in Figure 4 with peaks labeled W0, W1, W2, and W3 show the TPD spectra of 1 ML of krypton adsorbed on clean Pt(111) and 1, 2, and 3 ML of water deposited at 100 K, respectively. Clearly, adsorption of krypton on 1 ML of water can be easily distinguished from 2 or more layers of water or from the bare Pt(111). Hence, as we show below, TPD of physisorbed krypton can be used to probe the growth of water films on Pt(111).

Using the above experimental techniques, we investigated the growth of crystalline water films on Pt(111). We find that the water monolayer wets Pt(111) at all temperatures investigated (20–155 K). At low temperatures (T < 120 K), additional water layers kinetically wet the monolayer surface. However, for coverages greater than 1 ML, the additional water molecules form ice crystallites that do not wet the water monolayer, which remains exposed even for total coverages as large as 45 ML.

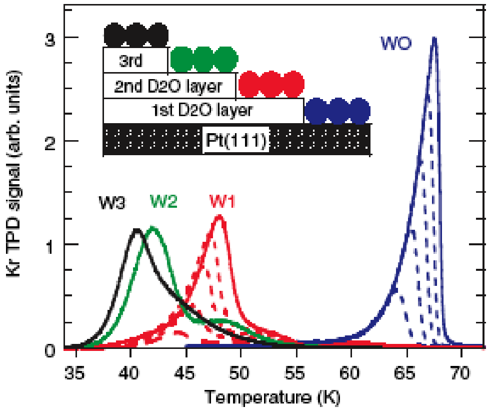

Figure 4. TPD spectra for 1 ML of krypton on various coverages of D_2O deposited on Pt(111) at 100 K where the films kinetically wet the surface. The solid blue, red, green, and black lines are the spectra for 0, 1, 2, and 3 ML of D_2O, respectively.

Crystalline ice films grown at higher temperatures (T >135 K) do not wet the water monolayer. The structure of the water monolayer on Pt(111), which has no dangling OH bonds or lone pair electrons, is key to understanding the nonwetting growth of CI films. The fully coordinated water monolayer results in a hydrophobic surface on which water diffusion is facile. At high temperatures where large-scale rearrangement of the films is kinetically accessible, the low surface energy of the hydrophobic water monolayer relative to the crystalline ice surface thermodynamically favors the formation of nonwetting, three-dimensional ice crystallites. The hydrophobic character of the water monolayer is further supported by the observation that kinetically wetted, amorphous films dewet upon heating, exposing the water monolayer. We have also obtained results similar to the D_2O data presented here for H_2O on two different Pt(111) crystals, and for H_2O films grown on a thin epitaxial Pd(111) film deposited on Pt(111).

These results help clarify several reports in the literature and increase our fundamental understanding of ice structure. The absence of layer-by-layer growth can be due to thermodynamics (i.e., nonwetting or incomplete wetting of the substrate) or can arise from kinetic limitations. It is now clear that the nonwetting growth of three-dimensional ice crystallites on the water monolyayer is thermodynamically favored. The Pacific Northwest National Laboratory researchers involved in this work are the first to observe this effect (Kimmel et al. 2005). For the novel hydrophobic property to show itself, the water-substrate bond has to be strong enough to form a stable monolayer. Weaker bonding results in a "classic" hydrophobic state, in which the water merely balls up immediately; in other words, not even a first monolayer of ice forms. This research should be of interest to those who, for example, study the seeding of clouds.

Citation

Kimmel GA, NG Petrik, Z Dohnalek and BD Kay. 2005. "Crystalline Ice Growth on Pt(111): Observation of a Hydrophobic Water Monolayer." *Physical Review Letters* 95(16):166102 (pages 1-4).

Initial Proteomic Profiling of Human T-Cell Populations Using High-Throughput Liquid Chromatography-Mass Spectrometry

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Proteomics analysis of specific blood cell populations, such as T-cells from human patients, provides the opportunity for comprehensive monitoring of the dynamic changes in gene products responding to diseases. The identification of novel regulatory genes/proteins may provide diagnostic or predictive values for diseases and disease outcomes.

Quantitative proteomic analysis of human blood leukocyte populations with specific functional perturbations from patients will lead to the identification of novel regulatory genes/proteins that may provide predictive values for clinical outcomes. To provide the basis for use of the PNNL-developed high-throughput accurate mass and time (AMT) tag-based proteomics strategy for quantitative analysis of trauma patient leukocyte populations, initial proteomic profiling was applied to enriched human T-cell populations with the combined purposes of providing an initial catalog of proteins present, evaluating the sample processing techniques for human blood cells, and establishing an initial AMT tag database specific to the human T-cell subpopulation to facilitate subsequent quantitative analysis.

Isolation of T-cell subpopulations was performed at the University of Florida, and three T-cell samples from normal subjects (Sample ID 170611, 170612, and 170616) were shipped to PNNL for proteomic profiling. All three samples were subjected to cell lysis in the presence of detergent, 0.1% RapiGest (Waters Corporation). Extracted proteins were denatured by boiling for 5 minutes, reduced with 5-mM dithiothreitol and digested by trypsin at 37^oC for 5 hours using a 1:50 enzyme/protein ratio. Approximately 20-μg aliquots of peptides from each sample were used for a comparison among the three samples by liquid chromatography-tandem mass spectrometry analysis. The remaining portions of the three samples were pooled and subsequently fractionated by strong cation exchange chromatography into 25 fractions, and each fraction was analyzed by liquid chromatography-tandem mass spectrometry (i.e., two-dimensional liquid chromatography-tandem mass spectrometry). Peptide tandem mass spectrometry fragmentation spectra were identified by database searching against the human International Protein Index database using the SEQUEST algorithm. The final list of peptide/protein identifications was obtained after applying stringent filtering criteria to ensure a high-confidence level for peptide identifications (Qian et al. 2005). Table 1 provides a summary of the peptide and protein identification results from single analyses of the three individual samples. Comparable numbers of peptide and protein identifications were obtained from all three samples with ~70 percent of proteins common to each sample. The results suggest overall good reproducibility for the analytical strategy.

Table 1. Summary of the Peptide and Protein Identification Results from Single Analyses of the Three Individual Samples

Sample ID	170611	170612	170616
Number of cells (millions)	16	8.4	6.9
Amount of peptide recovered (µg)	115	90	56
Quantity of peptide used for analysis (µg)	20	20	20
Peptides identified	3549	3325	3349
Proteins identified	1097	1036	1020
Common peptides and proteins in all three samples	1775 peptides and 705 proteins		

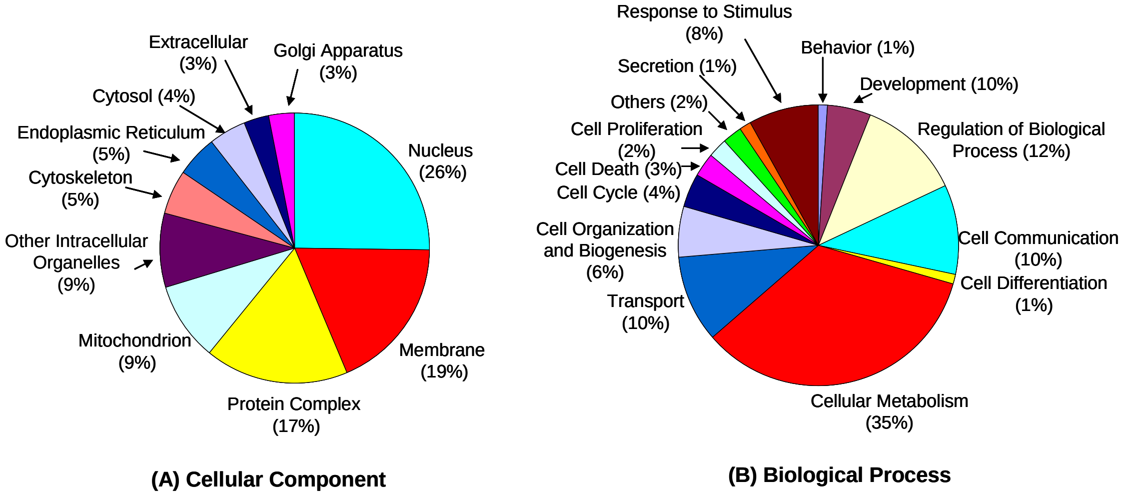

Figure 5. Categories of protein identifications based on GO analysis. (Note that GO categories overlap for some of the proteins.)

Improved proteome coverage was achieved when two-dimensional liquid chromatography-tandem mass spectrometry was applied to the pooled samples. A total of 3206 non-redundant proteins was identified with high confidence (>95 percent) from combined one-dimensional and two-dimensional liquid chromatography-tandem mass spectrometry analyses. Figure 5 graphically depicts the Gene Ontology (GO) analysis results based on cellular component and biological process using the GoMiner software tool (Zeeburg et al. 2003). 2344 out of 3206 non-redundant proteins (73 percent) have associated GO terms. Proteins from almost all cellular components were identified, with the majority of these proteins from the plasma membrane, nucleus, protein complex, mitochondria, and other intracellular organelles. Similarly, proteins identified cover a variety of different biological processes. While metabolism is the largest observed category, nearly 10 percent and 8 percent of these proteins were categorized as cell communication and response to stimulus, respectively.

Overall, these results indicate that the set of T-cell proteins identified using the present approach provide a substantially unbiased representation of the T-cell proteome with regard to cellular component and biological process. Interestingly, based on the GO analysis results, 6 out of 7 members of the T-cell receptor complex and 79 cell surface receptor proteins linked to signal transduction (listed in Table 2) were identified in this dataset, suggesting overall extensive coverage of the proteome, including low-abundance signaling membrane proteins.

Table 2. Gene Names for the 79 Identified Cell Surface Receptor Proteins Linked to Signal Transduction as Revealed by GO Analysis

CD2	CD3D	CD3E	CD3G	CD3Z	CD4	CD5
CD7	CD8A	CD8B1	CD47	CD59	CD97	CD99
IL7R	HPRP8BP	DGKA	GIT2	ITGAM	AZU1	MULK
DGKQ	LAT	CSNK2A2	GNA13	LCP2	PTPRJ	GOLGA5
ILK	BRD4	TBL3	GNAQ	MAPK14	PRKCA	TLE3
CBLB	EVL	HRMT1L2	PIP5K2B	CLC	GNG2	AXIN1
PHIP	AHSG	INS	CAP1	SLC9A3R1	FYN	ERBB2IP
RGS19	PIK3CG	RGS6	PLCB2	ADAM10	MIF	TGFB1
MYD88	IFITM1	LTB4R2	DGKB	GFRA1	GNAI3	ITGB3
CCNK	PGRMC2	MTSS1	NCSTN	PTK2B	CARKL	DOK1
NCK1	ITGA6	ILKAP	ARL3	ECGF1	12716	TRPV1
CSNK1A1	ITGB7					

To summarize, this T-cell proteomic profiling experiment established an initial AMT tag database with extensive proteome coverage, including low-abundance membrane and signaling proteins. This initial database provides a solid basis for subsequent quantitative proteomic analyses of T-cell samples from severe trauma and burn patients, applying the high-throughput AMT tag approach. The methodology exploited here will also be extended to other patient leukocyte subpopulations in the studies proposed.

Citations

Qian WJ; T Liu; ME Monroe, EF Strittmatter, JM Jacobs, LJ Kangas, K Petritis, DG Camp II, and RD Smith. 2005. "Probability-Based Evaluation of Peptide and Protein Identifications from Tandem Mass Spectrometry and SEQUEST Analysis: The Human Proteome." *Journal of Proteome Research* 4(1):53-62.

Zeeberg BR; W Feng, G Wang, MD Wang, AT Fojo, M Sunshine, S Narasimhan, DW Kane, WC Reinhold, S Lababidi, KJ Bussey, J Riss, JC Barrett, and JN Weinstein. 2003. "GoMiner: A Resource for Biological Interpretation of Genomic and Proteomic Data." *Genome Biology* 4(4):R28 (pages 1-8).

Observations of Void Formation during the Initial Oxidation of Iron Nanoparticles at Room Temperature and Their Implications

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The use of nano-sized particles of iron for cleaning up contaminants in groundwater, soil, and sediments is an exciting new technology contributing to general enthusiasm about nanotechnology. However, there are many unanswered questions about the appropriate and optimal implementation of the nano-iron technology. In this research, microstructure of iron nanoparticles passivated with an iron-oxide shell were studied using high-resolution transmission electron microscopy and high-angle annular dark-field imaging in aberration-corrected scanning transmission electron microcopy.

Phenomena related to iron oxidation are common in our daily lives. In nature, iron occurs in oxidation states that range from Fe^0 (for example, at the core-mantle boundary) to Fe^{3+} (at the Earth's surface). A pristine surface of Fe^0 exposed to air or oxygen-including atmosphere is oxidized instantly, a process normally called initial oxidation. On a very broad basis, oxidation behavior of iron is highly dependent on factors such as temperature, oxygen partial pressure, and time, all having an influence on the overall oxide layer thickness. High-temperature thickening of oxide layers on metal surfaces is very well understood based on intensive experimental work and thorough theoretical derivations. Microscopically, the phase and composition of the thick oxide layer depend on the distance of the layer to the iron/oxide interface. It is normally true that a thick oxide layer has the oxidation products $Fe:FeO:Fe_3O_4:Fe_2O_3$.

Contrasted with the understanding of high-temperature growth of thick oxide layers, less is known about the initial oxidation process of iron and the structural nature of their product. The initial oxidation process has two features: the formed oxide layer is normally just a few nanometers, and the growth rate is rapid. Depending on the type of migrating lattice defects, the reaction of oxide either can be at the metal-oxide interface (oxygen ions inward transport) or at the oxide-gas interface (metal ions outward transport). Under the framework of the Caberra-Mott theory of oxidation of metal, the initial oxidation process of iron can be described as the following: Upon initial attachment of oxygen onto the surface of metal and formation of a thin layer of oxide, electron tunnels through the thin oxide layer and ionizes the oxygen, leading to an electrical field between the metal and the surface of the oxide layer. The electrical field will subsequently drive the outwards diffusion of the ionized iron. With the Caberra-Mott model, estimation has given that at room temperature, it takes about 0.2 femto second to form an initial 1-nm thickness of oxide layer on a freshly exposed iron surface, and 40 seconds for a film of 2 nm, 40 weeks for a film of 3 nm, and 600 years for a film of 4 nm.

Two issues have to be addressed related to the initial oxidation: the phase formed and the transporting species during this process. Intensive research has been carried out to understand the nature of this oxidation process. This is most often accomplished by using single crystal Fe(100) at ultrahigh vacuum. Based on these research efforts, a common notion that has been reached is that the oxidation layer formed during the initial oxidation is composed of γ-Fe_2O_3/Fe_3O_4. On one occasion, it was reported that FeO was formed initially, and subsequent heating leads to the transformation of FeO to γ-Fe_2O_3/Fe_3O_4.

In this highlight, we report measurements on two types of iron nanoparticles using high-resolution transmission electron microscopy (HRTEM) (Figure 6), HRTEM image simulations, high-angle annular dark-field (HAADF) imaging in aberration corrected scanning transmission electron microscopy (STEM) (Figure 7), and nanometer-scale energy-dispersive spectroscopy analysis of initial oxidation products of these two types of iron particles. We found that the oxidized iron nanoparticles have a hollow core, as a result of fast cation diffusion.

Implications of this observation on application of nanoparticle were also discussed. For particles with a size of larger than ~ 10 nm, it shows a core-shell structure with a thickness of the oxidized layer being around 3.5 nm. Electron diffraction and HRTEM imaging have revealed that although the core iron is a single crystal, the oxide layer is not single crystal. It is composed of small crystallites that were oriented differently. Multidomain orientations of the oxide layer indicate that the nucleation and growth of the oxide shell on the single crystal surface of iron follow a homogenous nucleation process. The specific orientation relationship between the oxide shell and the iron core will be further investigated.

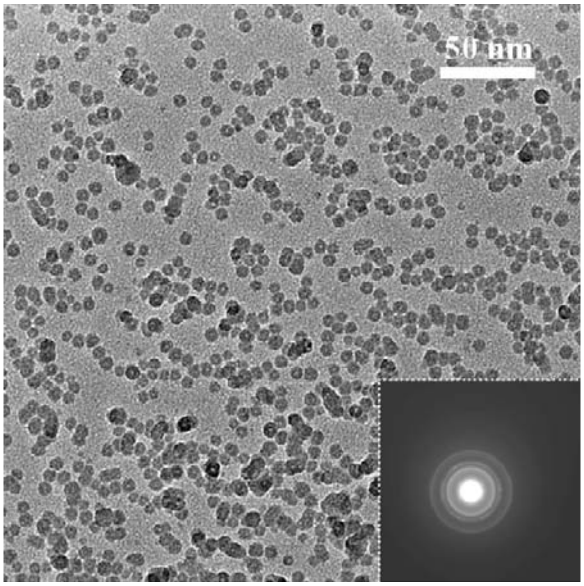

Figure 6. HRTEM images of the iron nanoparticles.

The average oxide layer thickness was around 3.5 nm and showed no significant dependence on particle size. It should be noted that the oxide layer thickness depends on the time of the particle exposed to air. Furthermore, the crystallite nature of the oxide grains makes any single measurement of oxide thickness just an approximation.

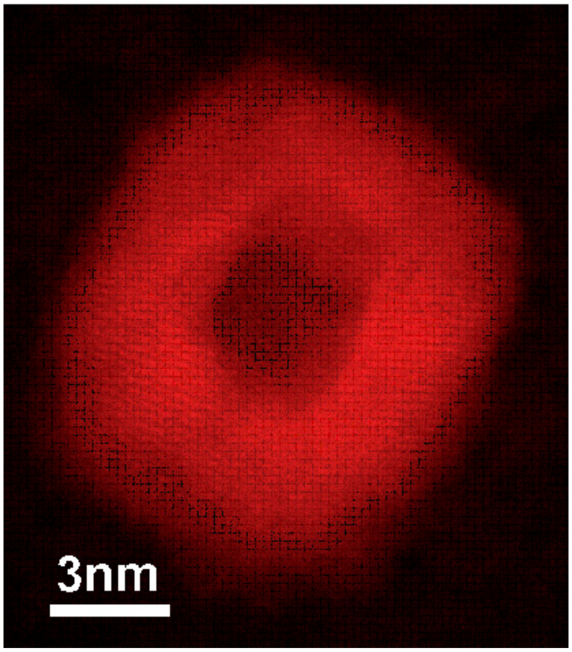

Figure 7. STEM-HAADF image of the iron nanoparticles.

We have observed that particles with a diameter of less than 8 nm are fully oxidized. A very common feature for the fully oxidized particles is the enclosure of a void at the center of the particle, as typically shown in the STEM-HAADF image. After further scrutiny of a large number of particles, we have found particles that were not fully oxidized frequently contain visible voids. For those core-shell structure particles, each particle includes several voids spatially located at the interface between the iron core and the oxide shell. This research work provides critical insights for pinpointing the physical and chemical processes that influence the behavior of iron nanoparticles for environmental remediation.

In-Situ TEM Study of Morphological Evolution of $Ba(NO_3)_2$ Supported on α-$Al_2O_3(0001)$

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Effective removal of pollutants such as NOx species is important to maintain and improve environmental quality. In this research, we explore the structural properties of the catalyst system based on BaO for removal of NOx species. In order to clarify the structural characteristics of this catalyst system during the uptake and release of NOx, instead of using traditional high-surface area γ-Al_2O_3 *powders as a supporting material, we chose to support the* $Ba(NO_3)_2$ *particles on a single crystal* α-Al_2O_3*. Based on this model system, the structural and morphological features of* $Ba(NO_3)_2$ *and the formation of BaO from* $Ba(NO_3)_2$ *during the release of NOx were systematically studied using ex-situ and in-situ transmission electron microscopy imaging, electron diffraction, energy dispersive spectroscopy, and Wulff shape construction.*

BaO supported on alumina has been extensively studied as a potential storage component of NOx storage/reduction catalysts. The mechanisms associated with the NOx uptake and release by this material have been examined in detail using temperature programmed desorption, vibrational spectroscopies (e.g., infrared spectroscopy), x-ray diffraction, electron microscopy [e.g., transmission electron microscopy (TEM)], and energy dispersive spectroscopy. We have proposed that the active NOx adsorption material consists of γ-Al_2O_3 surfaces covered by a monolayer BaO film, and with BaO nanoparticles sitting on top of this film when the BaO loading exceeds that required to form the monolayer coating (e.g., for a 20 wt.% BaO/Al_2O_3 sample). When the BaO/Al_2O_3 material is synthesized by the standard 'wet-impregnation' method using an aqueous solution containing dissolved $Ba(NO_3)_2$, initially large $Ba(NO_3)_2$ crystallites are formed on the alumina support after drying at low (<473 K) temperatures. A large fraction of the alumina surface remains barium-free after this procedure. Upon higher (~773 K) temperature thermal treatment required to prepare the active catalyst, these large $Ba(NO_3)_2$ crystallites decompose to form the nanosized BaO particles and monolayer BaO film. During room-temperature NO_2 uptake, both BaO-phases are transformed with the structure now consisting of nanosized (<5 nm) $Ba(NO_3)_2$ particles in addition to a monolayer nitrate phase. Heating the material to higher temperature (573 K) in the presence of NO_2 results in the sintering of the nanosized particles into larger $Ba(NO_3)_2$ crystals (<15 nm). At still higher temperatures, and even in the absence of NO_2, the average particle size of $Ba(NO_3)_2$ crystallites increases further (< 32 nm), and then, as $Ba(NO_3)_2$ decomposes between 500 and 900 K, the nanosized BaO particles reform on top of the interfacial (ML) BaO layer.

Direct and time-resolved TEM imaging to dynamically monitor the structural and morphological evolution of this material system would be very helpful to better understand the proposed morphology cycles. In order to address these issues and to understand the effects of crystal orientation, $Ba(NO_3)_2$ was supported on single crystal α-Al_2O_3(0001) instead of conventional γ-Al_2O_3 powder particles. The structural and morphological evolutions of this model system, as a function of calcination temperature, was studied in detail using a combination of *ex-situ* and *in-situ* TEM imaging, electron diffraction, energy dispersive spectroscopy, and Wulff shape construction.

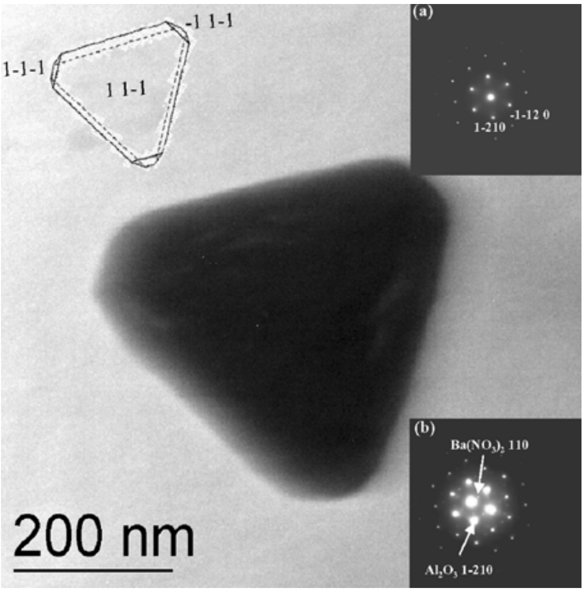

Figure 8. TEM image of the as-prepared $Ba(NO_3)_2$ particle supported on single crystal α-Al_2O_3.

The general morphology of $Ba(NO_3)_2$ supported on the single crystal α-Al_2O_3 is revealed by the TEM picture shown in Figure 8. $Ba(NO_3)_2$ possesses a well-defined morphology when imaged in TEM with the substrate oriented along the [0001] zone axis. Selected area electron diffraction indicates that the triangle-shaped $Ba(NO_3)_2$ particle is a single crystal. The crystallographic orientational relationship can be written as α-Al_2O_3[0001]//$Ba(NO_3)_2$[111] and α-Al_2O_3(1-210)//$Ba(NO_3)_2$ (110). Based on Wulff shape constructions, it is clear that the $Ba(NO_3)_2$ particles supported on a single crystal α-Al_2O_3 adopt a platelet morphology, with the surfaces and interfaces being invariably defined by 8 {111} type planes. Based on the Wulff shape constructions, we find that the thickness of the platelet is approximately ¼ that of the lateral dimensions, indicating that the interfacial free energy between $Ba(NO_3)_2$ and α-Al_2O_3 is approximately ¼ of the {111} surface free energy of $Ba(NO_3)_2$.

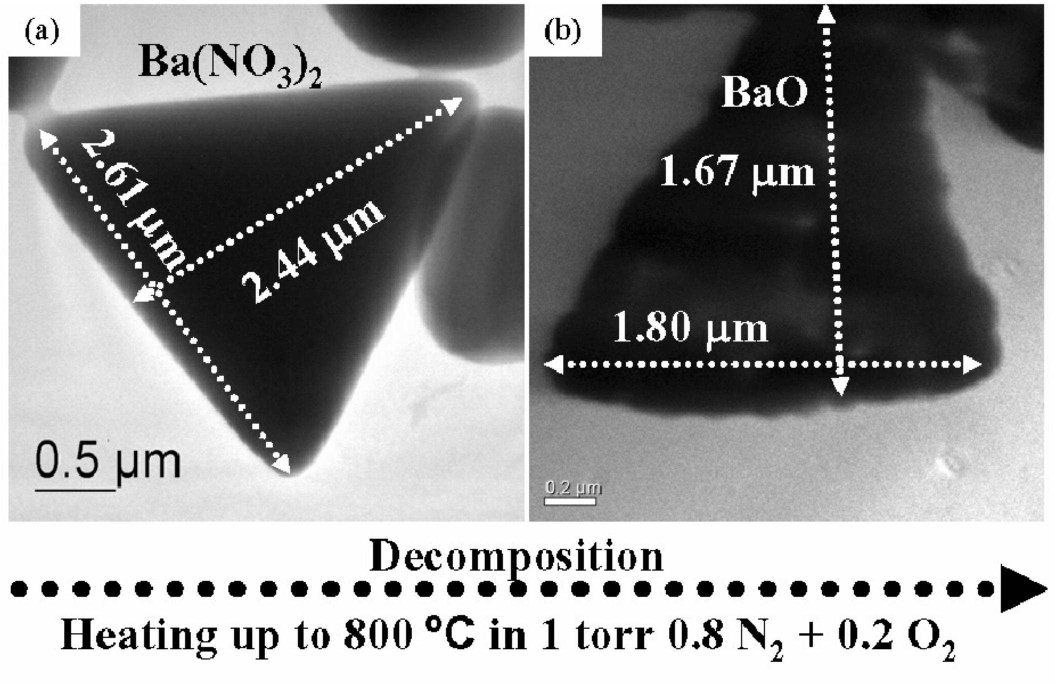

Figure 9. TEM images taken during the decomposition of the $Ba(NO_3)_2$ to form BaO particle

Decomposition of the single crystal $Ba(NO_3)_2$ particles supported on α-Al_2O_3 was monitored in real-time during the annealing of the specimen in an environmental TEM with a gas mixture of 0.8 N_2 + 0.2 O_2 at a total pressure of 1 torr. During high-temperature annealing up to 1075 K, $Ba(NO_3)_2$ decomposed to form BaO. Following the decomposition, BaO still retained a similar overall morphology as its parent single crystal $Ba(NO_3)_2$ particle, as shown in the TEM images Figure 9. The particle appears to go through a uniform shrinkage, therefore maintaining its original morphological shape. The measured linear shrinkage of the particle following decomposition is ~31 percent, which is approximately equal to the theoretically expected linear shrinkage of 32 percent, assuming that the newly formed BaO particles are single crystals or a fully dense polycrystalline compact. Detailed TEM imaging indicates that the BaO particles are not single crystals, instead being a collection of clusters of relatively small BaO particles. Furthermore, detailed electron diffraction analysis indicates that these BaO particles show neither orientational correlation among themselves nor specific orientational relationships with respect to the α-Al_2O_3 substrate.

Modeling Highly Accurate Energetics of the $(H_2O)_8$ Cluster: NWChem Achieves Over 63% Sustained Efficiency on 1840 Processors

WA de Jong,[(a)] ***TL Windus,***[(a)] ***E Apra,***[(a)] ***and SS Xantheas***[(b)]
(a) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington
(b) Pacific Northwest National Laboratory, Richland, Washington

High-level correlation modeling of water clusters provides researchers with the most accurate interaction energies ever calculated, which will be used to gain insight into water's unique properties. These calculations also demonstrate the unique capabilities of NWChem and EMSL's supercomputer, located at the Molecular Science Computing Facility.

Researchers from EMSL and the Pacific Northwest National Laboratory used the highly scalable and parallel NWChem software, DOE's premier computational chemistry code that is part of the Molecular Science Software Suite developed at EMSL, to calculate accurate energetic information of a cluster of eight water molecules. The coupled cluster singles doubles with perturbative triples, or CCSD(T), calculation and an aug-cc-pVQZ basis set (1376 basis functions, 32 correlated orbitals) required 1840 processors, almost the entire machine, and 37 hours to complete.

For many years, scientists have attempted to construct simplified descriptions of the intermolecular interactions among water molecules in an effort to gain insight into water's unique properties from molecular simulations. One bottleneck in this effort is the lack of experimental energetic information regarding the interaction among water molecules that can be used to assess the accuracy of the proposed models. First principles electronic calculations, such as the calculation described here, offer the advantage of providing this essential energetic information that is the cornerstone in the benchmarking and parameterization of interaction potentials for water.

This huge NWChem CCSD(T) calculation on 1840 processors with a combined peak of 11.04 teraflops sustained an average of more than 63 percent of peak flops efficiency (6.99 teraflops) during the 37-hour calculation, demonstrating the unique capabilities of the NWChem software and the supercomputer architecture. About three-quarters of the time was spent in the triples correction part of the calculation, with a sustained performance of about 84 percent. This part of the calculation consists mainly of some network communication matrix-matrix multiplication operations, the latter of which is known to achieve more than 90 percent of peak performance on the Intel Itanium-II processor using the Hewlett Packard Mathematical Software Library. Figure 10 shows a 2-hour snapshot of the triples correction part of the performance run.

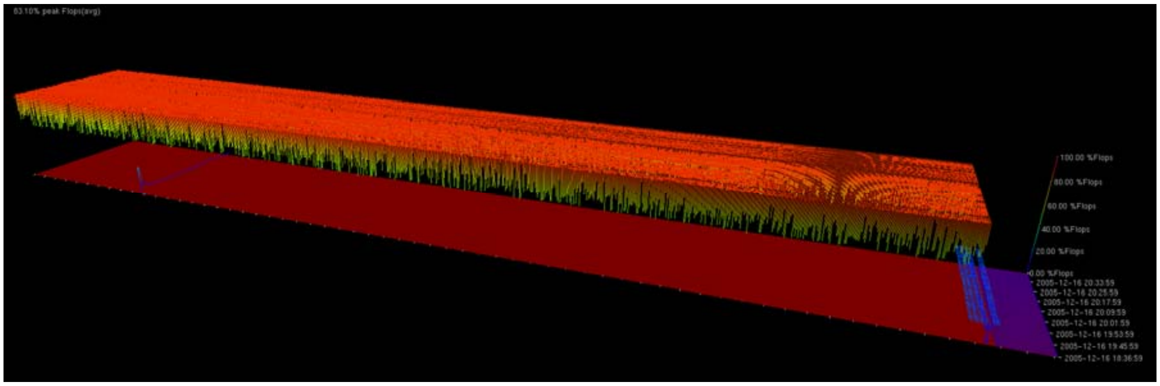

Figure 10. Snapshot of the Molecular Science Computing Facility system-wide monitoring tool. The vertical axis shows the percentage of peak flops (scale runs from 0-100 percent), the axis across the page represents all the processors in the cluster, and the axis perpendicular to the page shows a 2-hour window of time slices.

Electron Density Distributions Calculated for the Nickel Sulfides Millerite, Vaesite, and Heazlewoodite and Nickel Metal: A Case for the Importance of Ni-Ni Bond Paths for Electron Transport

GV Gibbs, [a] ***RT Downs,***[b] ***CT Prewitt,***[b] ***KM Rosso,***[c] ***NL Ross,***[a] ***and DF Cox***[a]
(a) Virginia Polytechnic Institute and State University, Blacksburg, Virginia
(b) University of Arizona, Tucson, Arizona
(c) Pacific Northwest National Laboratory, Richland Washington

Establishing the relationship between the crystal structure and physical properties of nickel sulfide ores leads towards a better understanding of acid mine drainage reactions that may occur in the environment.

Metal sulfides are an important class of ore minerals (Figure 11) that display a host of interesting bonded interactions and structure types in concert with an assortment of important electronic and magnetic properties. The properties have attracted the attention of solid-state physicists, material scientists, and mineralogists who have determined the crystal and electronic structures for a variety of sulfide minerals and representative clusters. Despite the important information provided by these studies, the understanding of the bond length and bond strength variations, bonded interactions, and the structures of a variety of sulfides is lacking, particularly when contrasted with that of the oxides. This shortcoming has been ascribed to the diversity of metal-metal (M-M) and sulfur-sulfur (S-S) bonded interactions displayed by a number of sulfides together with traditional metal-sulfur (M-S) bonded interactions displayed by these and by others. This is in contrast with the oxide minerals where only metal-oxygen (M-O) interactions are displayed.

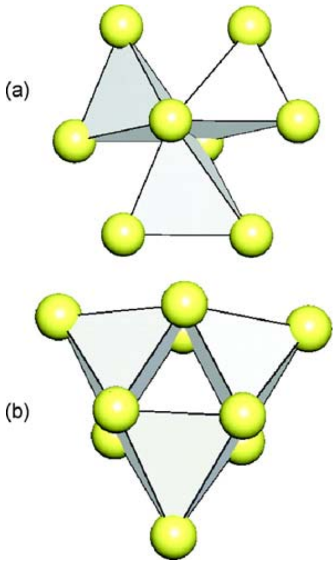

Figure 11. Polyhedral drawings of the (a) Ni_3S_8 cluster in heazlewoodite and the (b) Ni_3S_9 cluster in millerite. The large spheres represent sulfur. The nickel atoms are not displayed but are enclosed within the polyhedra. The nickel atoms are coordinated by four sulfur atoms disposed at the corners of a distorted tetrahedron in heazlewoodite and by five sulfur atoms disposed at the corners of a square pyramid in millerite.

This collaboration and resulting publication (Gibbs et al. 2005) focused on improving the understanding of how the electrical properties of nickel sulfide minerals arise from their structures. The strategy taken involves computation of the electron density along all possible interatomic paths in their crystal structures. Where the electron density is found to be locally maximal in two dimensions perpendicular to the interatomic path and locally minimal in the direction along the interatomic path, this is taken as direct evidence of a bonded interaction between the two atoms. By seeking bond paths and characterizing the electron density along the bond paths, we have categorized the bond types and numbers in each structure. Contiguous metal-metal bond paths are found in the structures that are electrical conductors, even if metal-metal distances are longer than in non-conducting structures. The calculations required treatment at the density functional level of theory and were performed on the EMSL supercomputer using the quantum mechanical codes Crystal98 and Topond98.

Citation

Gibbs GV, RT Downs, CT Prewitt, KM Rosso, N Ross, and DF Cox. 2005. "Electron Density Distributions Calculated for the Nickel Sulfides Millerite, Vaesite, and Heazlewoodite and Nickel Metal: A Case for the Importance of Ni-Ni Bond Paths for Electron Transport." *Journal of Physical Chemistry B* 109(46):21788-21795.

Awards and Recognition

PNNL Team Captures StorCloud Challenge, Finishes Second in Bandwidth Challenge. Image analysis algorithms designed for optimal segmentation, feature extraction, and object recognition in three-dimensional data have been developed for use with data captured by nuclear magnetic resonance and confocal microscopes at EMSL. For the Supercomputing 2005 (SC05) conference in Seattle, these algorithms were adapted to perform image recognition in video streams by treating the video stream as a three-dimensional volume.

Video streams captured on the SC05 exhibitor floor were stored in a Hewlett Packard-provided Scalable File Share (SFS) storage solution, which is based on Hewlett Packard's open source Lustre file system. With contributions from Cisco and Federal Network Services, a layer 2 network over four bonded 10-Gigabit links to PNNL was used to mount the 32-node SFS filesystem on a 128-node Itanium 2 cluster. For PNNL's entry into the SC05 Bandwidth and StorCloud challenges, the Itanium cluster was used to deconstruct the video streams into the individual frames. After calculating RBG histograms and three Shannon entropy values, a summary of each frame was written back to the SFS file system.

PNNL took first place in the StorCloud challenge and finished second in the Bandwidth Challenge. The effort was led by EMSL researcher Tim Carlson and featured EMSL High-Performance Computing and Networking Services members Ryan Mooney, Evan Felix, and Ken Schmidt, as well numerous scientists from across the Laboratory.

EMSL User Featured in *Chemical and Engineering News.* Lai-Sheng Wang, Washington State University-Tri-Cities, Richland, Washington, was featured in the October 24, 2005, issue of *Chemical and Engineering News* for reporting the first experimental evidence for d-orbital aromaticity. This research was originally featured in the October 17 issue of *Angewandte Chemie International Edition.*

Top Physics Stories of 2005. *The Bulletin of Physics News*, No. 757, reports the American Institute of Physics selected "Hydrophobic Water Monolayer in Crystalline Ice Growth on Pt(111)" research as one of the top physics stories of 2005. Greg Kimmel, Nick Petrik, Zdenek Dohnalek and Bruce Kay, EMSL users from the Pacific Northwest National Laboratory, were the first to observe that when there is an amount of overlying water equivalent to about 40 or 50 layers does three-dimensional crystalline ice completely cover the hydrophobic monolayer.

Professional/Community Service

None

Major Facility Upgrades

Solid-State NMR. A new solid-state NMR probe purchased from Varian was installed on the 900-MHz magnet in December. This 3.2-mm HXY magic-angle spinning probe allows the study of membrane-bound biomolecules that previously could not be studied using the 900-MHz system.

Hydraulic Property Measurement Systems. EMSL capability funds were used to help construct an automated system to measure fundamental hydraulic properties of soil (Figure 12). This system is used for measuring capillary pressure–saturation relationships. It is constructed of inert materials and can be used with chlorinated solvents.

Figure 12. Hydraulic Property Measurement System.

Large Flow Cell Head Chamber. EMSL capability funds were used to construct an automated system to control flow by hydraulic head (Figure 13). This new capability enables more precise setup of flow fields via differences in hydraulic head, setup of both saturated and unsaturated (vadose zone) systems, and the ability to conduct experiments with a fluctuating water table. The new computer controlled system allows for the fluctuation of the water table in way that more closely mimics a natural system.

Figure 13. Large Flow Cell Head Chamber.

Scanning Probe Microscope. An Asylum Research MFP-3D Atomic Force Microscope situated on top of a Nikon 300TE inverted optical microscope has been purchased and installed (Figure 14). This scanning probe microscope will be used for protein imaging and force measurements, and it will help researchers to meet the special requirements of life sciences microscopy (e.g., studies of delicate biological samples under physiological conditions) and provide detailed observations of molecular structures with unprecedented resolution and without the need for rigorous sample preparation and labeling. The system can be used for studying cellular membrane structures, drug-receptor and virus-cell binding, as well as single-molecule recognition of molecular complexes (e.g., antibody-antigen, ligand-receptor, DNA-protein, DNA-DNA, protein-protein interactions). Presently, the system is being used by researchers on the EMSL Biogeochemistry Scientific Grand Challenge to examine whether the bacterium *Shewanella oneidensis* can generate energy for growth by using cell-surface proteins called cytochromes to transfer electrons generated inside the cell directly to Fe(III)-bearing minerals located outside the cell (Figure 15). This research is important in determining the effects that bacterial Fe(III) reduction has on the geochemistry of modern environments and how this can impact the bioremediation of subsurface environments contaminated with organic or metal contaminants.

Figure 14. Scanning Probe Microscope

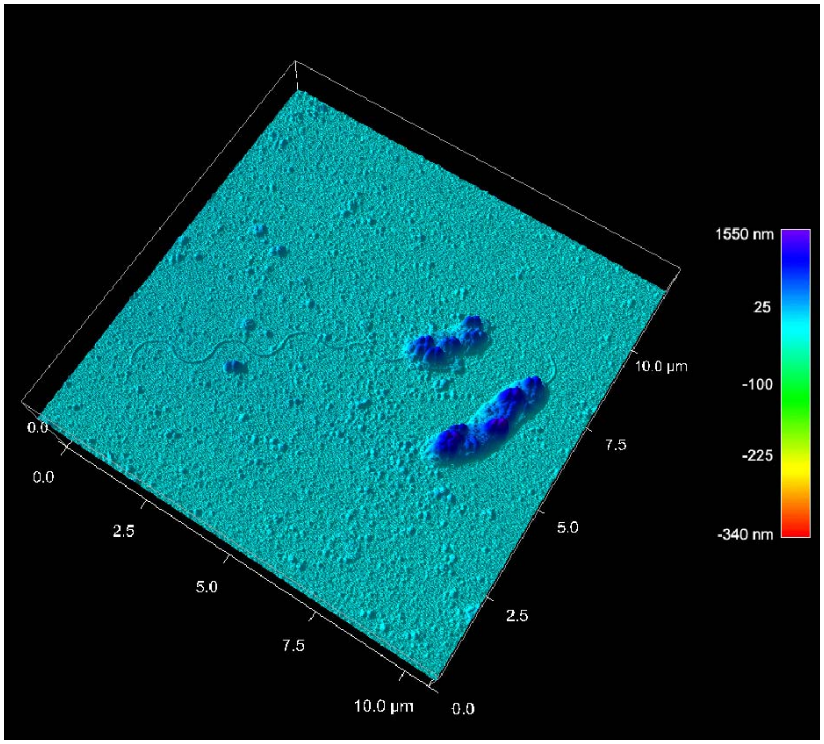

Figure 15. Three-dimensional image of *Shewanella* bacteria on hematite imaged with atomic force microscopy.

Stopped-Flow Absorbance Spectrometer System. A new BioLOGIC SFM-400 stopped-flow system was installed in EMSL's Environmental Spectroscopy Laboratory. The four-syringe system offers a minimum deadtime of 0.25 ms with a microcuvette. In our tests with regular cuvettes, an instrument deadtime of less than 1 ms with the FC08 (0.8-mm light pathlength) or ~ 2 ms with the FC10/100 (10-mm light pathlength) was easily achieved. The small sample volume of less that 0.03 ml makes the system ideal for experiments such as those involving biological reactants for which minimum consumption of reagents is desired. The availability of four syringes facilitates sophisticated experiments that require sample pre-mix and timed aging. The fast sampling rate of the MOS-250 spectrometer allowed us to record 8000 data points within a short time range of 0.16 seconds with excellent signal-to-noise ratio.

Gas Chromatograph-Mass Spectrometer. A new gas chromatograph-mass spectrometer system was purchased and installed. The system, which is used for the analysis of a wide range of volatile organic compounds and several inorganic permanent gases, is vital to the users of the Subsurface Flow & Transport Experimental Laboratory who are studying the different flow and transport aspects of various non-aqueous phase liquids in sediments.

News Coverage

None

Visitors and Users

Chemistry and Physics of Complex Systems Facility

- Ludwig Bartels, University of California, Riverside, California, gave the seminar "Adsorbate Dynamics at Copper Surfaces: A View at the Atomic Scale."

- Alexander I. Boldyrev, Utah State University, Logan, Utah, worked on the study "Investigation of Aromatic and Other Novel Gas Phase Atomic Clusters and Molecules."

- Olexandr Bondarchuk, University of Texas at Austin, Texas, worked on the study "Atomically Resolved Studies of Transition Metal Oxides."

- Barney Ellison and Luis Cuadra-Rodriguez, University of Colorado, Boulder, Colorado, worked on the study "Mechanisms of Organic Ions Released from Water Droplets."

- Weigang Lu, University of New Orleans, New Orleans, Louisiana, worked on the study "Early Transition Metal Oxides as Catalysts."

- 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."

- Luis Rodriguez, National Cancer Institute, Bethesda, Maryland, worked on the study "Development of Multi-Functional Microscopy (MFM) for Cancer and AIDS Research."

- Ebbe K. Vestergaard, University of Washington, Seattle, Washington, worked on the study "Photochemical Studies on N-Doped TiO_2 Single Crystals." Ebbe is also a participant in the Joint Institute for Nanoscience and Nanotechnology.

- Doug Worsnop, Aerodyne Research, Inc., Billerica, Massachusetts, gave the seminar "Aerosol Mass Spectrometry: What Have We Learned about Atmospheric Aerosol Chemistry?"

- Zhenrong Zhang, University of Texas at Austin, Texas, worked on the study "Photochemistry of Halogenated Hydrocarbon on TiO_2(110) Surface."

Environmental Spectroscopy and Biogeochemistry Facility

- Paul Bagus, University of North Texas, Denton, Texas, along with Eugene Ilton, Pacific Northwest National Laboratory, Richland, Washington, continued collaborations to study the effect of charge transfer configurations on the x-ray photoelectron spectroscopy of MnO.

- Barry Bickmore, Brigham Young University, Provo, Utah, in collaboration with Kevin Rosso and Eric Bylaska, Pacific Northwest National Laboratory, Richland, Washington, performed Car-Parrinello molecular dynamics simulations on pure water. The team is seeking proof that I.D. Brown's bond valence model relating the degree of oxygen valence saturation to coordination numbers and bond distances works for describing hydrogen bonding in water. Trajectories computed on a simulation cell of 64 water molecules using various exchange-correlation functionals are being used to test the hypothesis.

- Thomas Borch and Scott Fendorf, Stanford University, Stanford, California, and EMSL researcher Ravi Kukkadapu carried out Mossbauer studies of ferrihydrite that was adsorbed with phosphate, before and after bioreduction, at various temperatures. The iron-oxides are derived from a column study. In addition, Borch worked with EMSL researcher Alice Dohnalkova on transmission electron microscopy imaging and energy dispersive spectroscopy analyses of transformed nanoparticulate iron material adsorbed on quartz sand grains to obtain information for modeling of biogenic processes in soils.

- Bill Burgos, Pennsylvania State University, University Park, Pennsylvania, visited EMSL with a group of his graduate students to meet numerous Pacific Northwest National Laboratory scientists, tour the facilities, and identify how EMSL capabilities might be used in their own research. In addition, several students participated in experimental/analytical research activities including nuclear magnetic resonance spectrometry, electron microscopy, and enzyme kinetics. Hui Tan (Figure 16) and Daniel Hummer (Figure 17) worked with EMSL researcher Alice Dohnalkova on transmission electron microscopy characterization of natural manganese oxides collected from a limestone treatment bed designed for the remediation of acid mine drainage. These natural field-scale materials will be compared with biogenic oxides produced in subsequent lab-scale experiments. Dan Ross (Figure 18) attended a half-day demonstration of the newly installed Biologic SFM-400 four syringe stopped-flow system offered by Zheming Wang and Liang Shi, where they discussed their current research activities and discussed how to use the state-of-the-art stopped-flow system for future research in the areas of biology and mechanistic studies of microbial reduction of radioactive contaminants. In addition, Pennsylvania State University graduate students Geoffery Bowers and Mike Davis worked with EMSL researcher Joe Ford to collect data using the 900-MHz nuclear magnetic spectrometer as part of a project to study the chemistry of strontium in soil. This project has obvious applications for studying the chemistry and behavior of strontium in soil contaminated by leakage from the tank farms at the Hanford Site and other nuclear

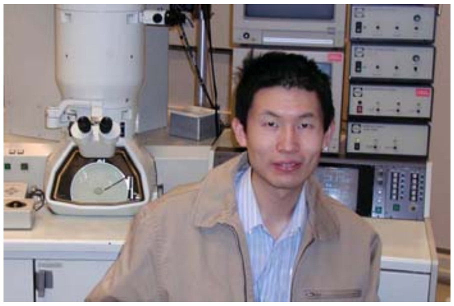

Figure 16. Hui Tan.

Figure 17. Dan Hummer.

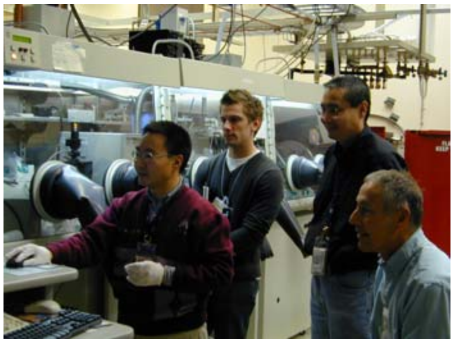

Figure 18. From left to right: Zheming Wang, Dan Ross, Liang Shi, and John Zachara.

sites. Burgos also presented the scientific seminar "Biological Reduction of Nano-Engineered Iron(III) Oxide Sculptured Thin Films."

- Baolin Deng, University of Missouri, Columbia, Missouri, along with Chongxuan Liu, Pacific Northwest National Laboratory, Richland, Washington, continued their collaboration to investigate arsenic removal from waste waters by clay or geotechnical membranes. Deng's research group is designing and synthesizing the clay membranes and performing experiments to assess membrane filtration properties and membrane behavior mechanisms. Liu is developing a coupled model of electrodynamics and irreversible thermodynamics for simulation.

- Carrick Eggleston, University of Wyoming, Laramie, Wyoming, on sabbatical at the Swiss Federal Institute of Technology, Lausanne, Switzerland, and Janos Vörös, ETH Zurich, Switzerland, continued collaborations with Brian H. Lower and Liang Shi, Pacific Northwest National Laboratory, Richland, Washington. They are studying the adsorption properties of *Shewanella oneidensis* cytochromes, OmcA and MtrC, with metal-oxide surfaces using optical waveguide lightmode spectroscopy. This research is part of the EMSL Biogeochemistry Scientific Grand Challenge, which is aimed at elucidating the mechanism of Fe(III)- and Mn(IV)-oxide reduction by bacterial cytochromes and their associated complexes.

- Gerald Gibbs, Virginia Polytechnic Institute, Blacksburg, Virginia, in collaboration with Kevin Rosso, Pacific Northwest National Laboratory, Richland, Washington, performed electronic structure calculations on a series of iron/copper sulfide minerals to seek relationships among bond distances, crystal structure, and the electron density at bond critical points. Metal-metal bond paths were also sought, in part to establish whether metal-metal bonding underlies the electrical conductivity behavior of the various phases.

- Kerstin Hoener zu Bentrup (Figure 19), Tulane University, New Orleans, Louisiana, worked with EMSL researcher Alice Dohnalkova to investigate the mechanism of cell infection with norovirus using transmission electron microscopy. She also helped establish a novel cell culture methodology with Pacific Northwest National Laboratory researcher Tim Straub. Her travel and living expenses were funded by EMSL as a relief effort when her laboratory at Tulane was damaged by Hurricane Katrina.

Figure 19. Kerstin Hoener zu Bentrup, a researcher from Tulane University, New Orleans, Louisiana.

- Martin Schroth (Figure 20), Swiss Federal Institute of Technology, Zurich, Switzerland, collaborated with Mart Oostrom, Pacific Northwest National Laboratory, Richland, Washington, and EMSL researcher Tom Wietsma to develop experimental procedures to determine interfacial areas between water and nonaqueous phase liquids, such as carbon tetrachloride and trichloroethene. The novel procedures led to interfacial areas estimates at various stages during dissolution of entrapped nonaqueous phase liquids in the subsurface. The new method produces interfacial area-saturation relationships needed in numerical subsurface flow and transport modeling.

Figure 20. Martin Schroth, Swiss Federal Institute of Technology, Zurich, Switzerland, visited EMSL for 1 week.

- Frannie Skomurski, University of Michigan, Ann Arbor, Michigan, in collaboration with Kevin Rosso and Sebastien Kerisit, Pacific Northwest National Laboratory, Richland, Washington, continued investigation of the reduction of uranyl by magnetite surfaces. *Ab initio* calculations were used to predict stable hydrated surface structures for the (100) and (111) surfaces of magnetite.

- 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.

- Matthew Wander, Stony Brook University, Stony Brook, New York, continued working with Kevin Rosso and Sebastien Kerisit, Pacific Northwest National Laboratory, Richland, Washington, to model the electron transfer kinetics for uranyl and chromate reduction by ferrous iron in homogeneous aqueous solution, and by Fe(OH)2 via a heterogeneous electron transfer process. The team is using a combination of density functional theory calculations and Marcus electron transfer theory to predict mechanisms and kinetics of reduction for these systems.

- Nicholas Wigginton and Mike Hochella, Virginia Polytechnic Institute, Blacksburg, Virginia, continued their collaboration with Kevin Rosso and Brian Lower, Pacific Northwest National Laboratory, Richland, Washington, to examine the electron-transfer properties of outer-membrane multi-heme cytochromes from the metal-reducing bacterium *Shewanella oneidensis*. They modeled experimental tunneling spectra collected over individual bacterial outer-membrane cytochromes using incoherent multi-step ET theory. The team is finishing a study defining the electron transfer quantities that underpin the tunneling behavior of OmcA and MtrC cytochromes. This research is part of the EMSL Scientific Biogeochemistry Grand Challenge, which is aimed at elucidating the mechanism of Fe(III)- and Mn(IV)-oxide reduction by bacterial cytochromes and their associated complexes.

High-Field Magnetic Resonance Facility

- Geoffrey Bowers and Michael Davis, Pennsylvania State University, University Park, Pennsylvania, worked onsite and remotely using the 900-MHz NMR spectrometer for the study "Sensitivity Enhancing NMR of Strontium-87 Nuclei in Clays, Zeolites, and Waste Cleanup Technologies."

- Garry Buchko, Michael Kennedy, and Shuisong Ni, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 600-MHz Cryoprobe spectrometer for the study "Structural Studies of a Novel Family of Manganese Uptake Proteins in Cyanothece Containing a Repeated Five-residues Domain." This study is part of EMSL' Membrane Biology Scientific Grand Challenge

- Myriam Cotten, Pacific Lutheran University, Tacoma, Washington, worked remotely using the 500-MHz NMR spectrometer for the study "Investigating Molecular Recognition and Biological Function at Interfaces Using Antimicrobial Peptides."

- Joan Frye, National Science Foundation, Arlington, Virginia, toured EMSL and met with several staff members to better familiarize herself with what EMSL has to offer users onsite as well as remotely.

- Jian Zhi Hu, Charles Peden, and Yong Wang, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 500-MHz NMR spectrometer for the study "*In-situ* High Field, High Resolution NMR Spectroscopy."

- Michael Kennedy, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 900-MHz, 800-MHz, 750-MHz, 600-MHz, and 500-MHz NMR spectrometers for the study "Structural Genomics Collaborative Access Team (CAT)."

- Rachel Klevit and Peter Brzovic, University of Washington, Seattle, Washington, worked remotely using the 600-MHz Cryoprobe spectrometer for the study "NMR Structural Investigations of BRCA1."

- Andrew Lipton, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 800-MHz NMR spectrometer for the study "Correlation of Structure and Function of Zinc Metalloproteins via Solid-State NMR Methods."

- Paul Majors, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 500-MHz NMR spectrometer for the study "Interrogation of Glucose Metabolism by Oral Biofilms Using Combined NMR/Optical Spectroscopy and Stable Isotope Labeling."

- Ronald Nieman, Arizona State University, Tempe, Arizona, worked remotely using the 800-MHz and 600-MHz Cryoprobe spectrometers for the study “Structure and Function of the Membrane Protein OEP16.”

- Ponni Rajagopal, University of Washington, Seattle, Washington, worked remotely using the 600-MHz NMR spectrometer for the study “Structural Investigation of alphaB-Crystallin Core Domains.”

- Raymond Reeves, Washington State University, Pullman, Washington, worked remotely using the 900-MHz, 800 MHz, 750 MHz, and 600 MHz NMR spectrometers for the study “Structural Biology of the Human High Mobility Group A (HMGA) Proteins: Characterizing the Hub of Nuclear Function.”

- Wendy Shaw, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 750-MHz and 300-MHz NMR spectrometers for the study “Draws Implementation.”

- Thomas Squier, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 500-MHz NMR spectrometer for the study “Development of Multipurpose Tags and Affinity Reagents for Rapid Isolation and Visualization of Protein Complexes.”

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

- Cheryl Arrowsmith, University of Toronto, Toronto, Ontario, Canada

- Guy Montelione, Rutgers University, Piscataway, New Jersey.

High-Performance Mass Spectrometry Facility

- Josh Adkins, Pacific Northwest National Laboratory, Richland, Washington, collaborated with researchers from Oregon Health and Science University (OHSU) for the study “Identifying Targets for Therapeutic Interventions using Proteomic Technology.” Databases have been built for two *Salmonella* species being investigated, and databases for the two viral species (*Vaccinia* and Monkeypox) are in the process of being built. Genetic mutants for *Salmonella typhimurium* are being generated by OHSU, and the appropriate growth conditions are being investigated. Collaborative work with OHSU involving the isolation of various viral enveloping components is in progress.

- Timothy Donohue, University of Wisconsin-Madison, Madison, Wisconsin, who is studying *Rhodobacter sphaerodies*, has generated two manuscripts related to his research. One is currently in review with *Molecular and Cellular Proteomics*, while the other is in draft for *Proteins and Peptides*. He continues to investigate the temporal changes in protein expression patterns of the organism as it transitions from the photosynthetic lifestyle to the aerobic lifestyle.

- Allan Konopka, Purdue University, West Lafayette, Indiana, provided samples of A*rthrobacter* for the mass tag creation process. All samples are currently processing through the system. Once completed, Konopka will be contacted to discuss specific experiments.

- Mary Lipton, Pacific Northwest National Laboratory, Richland, Washington, continues her study of *Shewanella oneidensis*. The mass tag database has been researched to confirm the annotation of many of the N-terminal peptides as well as other aspects of the annotation. Interpretation of data concerning the changes in protein expression patterns between aerobic and anaerobic lifestyles also continues.

- A new sample preparation method has been optimized and was successfully analyzed by mass spectrometry for Colette Sacksteder, Pacific Northwest National Laboratory, Richland, Washington. The data that was generated is currently being analyzed and will determine the future experimental path for the study of "Molecular Mechanisms Underlying Cellular Adaptive Response to Low Dose Radiation."

Interfacial and Nanoscale Science Facility

- Zsuzsanna Balogh, Washington State University, Pullman, Washington, used the electron microscopy suite to characterize mineral nanostructures in order to understand issues associated with soil mineral weathering.

- Sauha Cheung, University of Wisconsin, Milwaukee, Milwaukee, Wisconsin, studied the stabilization of polar oxide interfaces and integrated experimental and theoretical studies of atomic structure and electronic properties.

- Ricardo Chimentao, University of Washington, Seattle, Washington, worked on understanding the mechanisms associated with the catalytic properties of $Ba(NO_3)_2$ support on gamma alumina.

- Cynthia Dutton, University of Oregon, Eugene, Oregon, used EMSL capabilities to study the nanoscience of organomatellic chemistry.

- Michael Fischback, Washington State University, Pullman, Washington, worked on the study "Immobilized Enzymes for Bioremediation and Biosensing."

- Hsiu-wu Guo, University of Washington, Seattle, Washington, studied the properties of polysilicon grown on silicon substrate with nickel metal as a buffer layer. There are various applications in the semiconductor industry related to the growth of polysilicon. He is mainly using EMSL thin-film sputter deposition capabilities to grow these films. He is also using EMSL x-ray diffraction, transmission electron microscopy, atomic force microscopy, and clean room capabilities that are directly associated with their research work.

- Gregory Herman and William Stickle, Hewlett-Packard Company, Corvallis, Oregon, studied characterization of oxide based diodes.

- Kerstin Honer Zu Bentrup, Tulane University, New Orleans, Louisiana, used EMSL's electron microscopy suite to observe infection of the intestinal cells with norovirus.

- Jung Heon Lee, Chosun University, Gwangju, South Korea, worked on the study "Immobilized Enzymes for Bioremediation and Biosensing."

- Frank Stadermann, Washington University, St. Louis, Missouri, studied the chemical characterization of sub-micrometer mineral phases in extraterrestrial materials that have previously been characterized by NanoSIMS isotope imaging.

- Eswaranand Venkatasubramanian, University of Washington, Seattle, Washington, studied the post-growth analysis of GaN and InGaN grown with oxide metalorganic chemical vapor deposition.

- John Yeager and Kip Findley, Washington State University, Pullman, Washington, visited EMSL to use Auger electron spectroscopy to identify the composition, and morphology of carbides in nickel-based superalloys and relate these to the mechanical properties of these superalloys.

- Jongkyu Young, Korea Advanced Institute of Science and Technology, Daejeon, South Korea, worked on the study "Immobilized Enzymes for Bioremediation and Biosensing."

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

- A.M. Prokhorov General Physics Institute, Moscow, Russia
- Aristotle University of Thessaloniki Greece, Thessaloniki, Greece
- CFD Research Corporation, Huntsville, Alabama
- Dartmouth College, Hanover, New Hampshire
- Fudan University, Shanghai, China
- George Mason University, Fairfax, Virginia
- Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia
- Grupo de Fisica Matematica, Lisboa, Portugal
- Hewlett-Packard Company, Grenoble, France

- Indian Institute of Science, Bangalore, India
- Innovations for High Performance Microelectronics, Frankfurt, Germany
- Iowa State University, Ames, Iowa
- J.W.Goethe-Universitat Frankfurt Main, Frankfurt am Main, Germany
- Juntendo University, Inba-Gun, Japan
- Kazan State University, Kazan, Russia
- Kyoto University, Kyoto, Japan
- Linux Networx, Inc., Bluffdale, Utah
- Los Alamos National Laboratory, Los Alamos, New Mexico
- Max Planck Institute for Coal Research, Muelheim an der Ruhr, Germany
- National Energy Technology Laboratory, Pittsburgh, Pennsylvania
- National Research Council of Canada, Ottawa, Ontario, Canada
- Northeast Normal University, Changchun, China
- South China University of Technology, Guangzhou, China
- Universida Nacional Autonoma de Mexico, Mexico City, Mexico
- Universidad Autonoma del Estado de Hidalgo, Hildago, Mexico
- Universidad de Los Andes, Merida, Venezuela
- Universitaet Tuebingen, Tuebingen, Germany
- Universitat Autonoma Barcelona, Cerdanyola del Valles, Spain
- Universite di Palermo, Palermo, Italy
- Universite Montpellier 2-CNRS, Montpellier, France
- University of Alberta, Edmonton, Alberta, Canada
- University of Caen, Caen, France
- University of Cantabria, Santander, Spain
- University of Helsinki, Helsinki, Finland
- University of Kentucky, Lexington, Kentucky
- University of Poitiers. Poitiers, France
- University of Strathclyde, Glasgow, Scotland
- University of Western Australia, Nedlands, Australia
- University of Wisconsin-Madison, Madison, Wisconsin
- University of York, York, Great Britain

New EMSL Staff

None

Publications

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Anheier NC, Jr., CR Batishko, DR Bottenus, CJ Bruckner-Lea, BP Dockendorff, HC Edberg, JW Grate, MA Lind, JD Marks, GP Morgen, RM Ozanich, LA Smith, and MG Warner. 2005. "Sensor System for the Rapid, Sensitive Detection of Toxins." Presented by Marvin Warner (Invited Speaker) at the Interagency Botulism Research Coordinating Committee Meeting, Baltimore, Maryland, on December 5, 2005.

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