William R. Wiley

EMSL

Environmental Molecular Sciences Laboratory

2006 Annual Report

A NATIONAL USER FACILITY FOR THE SCIENTIFIC COMMUNITY

Providing World-Class Research Capabilities
for Enabling Fundamental Research on
Physical, Chemical, and Biological Processes

PNNL-16489

Environmental Molecular Sciences Laboratory

2006 Annual Report

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Overview

This 2006 EMSL Annual Report describes the research and accomplishments of staff and users of the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), located in Richland, Washington.

Mission

> *EMSL, a national scientific user facility at Pacific Northwest National Laboratory (PNNL), provides integrated experimental and computational resources for discovery and technological innovation in the environmental molecular sciences to support the needs of DOE and the nation.*

EMSL strives for simultaneous excellence in 1) high-impact science and marquee capabilities, 2) outstanding management and operations, and 3) exceptional user outreach and services, and uses these tenets to deliver its mission and implement its strategy. The central focus of EMSL's strategy is delivery on the mission of the scientific user facility. In addition to its mission, EMSL has a vision and strategy that show where the user facility intends to be in the next 10 years and the progress that will be made during the next 5 years, respectively.

EMSL Resources and Facilities

EMSL is a national scientific user facility available to researchers worldwide from academia, industry, and national laboratories. EMSL users pursue the understanding of molecular systems essential to scientific breakthroughs and discoveries for a broad set of DOE missions in energy, environment, climate, and national security. Staff at EMSL develop and maintain extensive advanced research and development capabilities that are used to generate new scientific knowledge. EMSL delivers substantial value to its users by understanding their needs, creating responsive new ideas and capabilities, and delivering exceptional results—all achieved through the expertise of facility staff, demonstrated excellence in management and laboratory operations, and high-value partnerships with its users.

The operating budget for EMSL is provided by DOE Office of Biological and Environmental Research (BER), while the research conducted within the facility is beneficial to the DOE Office of Science and many funding agencies, including other offices within DOE, the National Institutes of Health, the National Science Foundation, and the Department of Defense.

Since beginning operations in October 1997, EMSL has provided advanced and one-of-a-kind experimental and computational resources to scientists engaged in fundamental research in the physical, chemical, and biological processes that underpin environmental remediation and other important scientific issues facing DOE and the nation. In addition to physical resources, EMSL provides unprecedented technical support and expertise, allowing its users a highly efficient and focused resource that enhances their work.

Cutting-edge resources available to EMSL users are available in the following six facilities:

- *Chemistry and Physics of Complex Systems Facility* for understanding and mitigating the environmental impacts of energy use and contaminant release, and fostering fundamental research in the natural sciences to provide the basis for new and improved energy technologies.

- *Environmental Spectroscopy and Biogeochemistry Facility* for studying complex chemical phenomena and mechanisms on mineral and microbe surfaces and on heterogeneous environmental materials.

- *High-Field Magnetic Resonance Facility* for determining and imaging molecular structures that impact environmental remediation and biological health effects.

- *High-Performance Mass Spectrometry Facility* for analyzing the response of biomolecules to environmental stimuli.

- *Interfacial and Nanoscale Science Facility* for studying chemical transformations at surfaces and for fabricating and characterizing materials with nanoscale features.

- *Molecular Science Computing Facility* for theory, modeling, and simulation of complex phenomena in chemistry, biology, climate science, and subsurface fate and transport.

Additionally, the following three organizations within EMSL provide services that enable effective computer, instrument, and user support:

- *User Services and Outreach* to facilitate and promote the effective use of EMSL resources by staff and users.

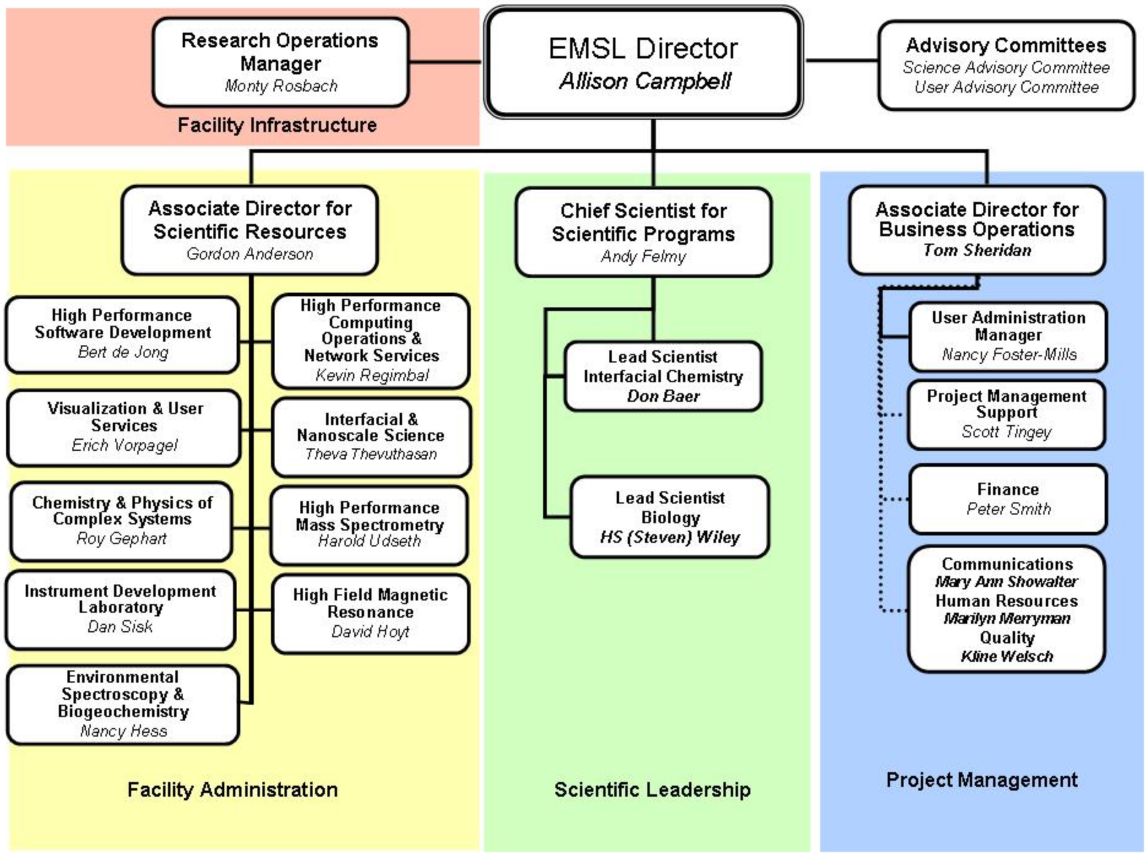
- *High-Performance Computing and Networking Service*s for operation and maintenance of EMSL's computing infrastructure.

- *Instrument Development Laboratory* for design, development, and deployment of advanced, state-of-the-art instruments, and custom-application software.

Organization

The EMSL project is managed by a Director, an Associate Director for Scientific Resources, an Associate Director for Business Operations, a Research Operations Manager, a Chief Scientist, and Scientific Facility Leads who are the front-line project managers responsible for user projects within their facilities. In addition, two advisory committees—the User Advisory Committee (UAC) and the Science Advisory Committee (SAC)—provide advice on short-term, user-related issues and longer-term scientific direction. EMSL's SAC was refreshed during Fiscal Year 2006, and the UAC is targeted to become a self-electing committee in Fiscal Year 2007.

As shown below, the EMSL project is organized into Scientific Resources, Scientific Programs, and Business Operations groups.



User Advisory Committee

The UAC is an independent body of experts from academia, industry, and the national laboratory system that is charged with providing objective, timely advice and recommendations to EMSL leadership. The Committee reports directly to the EMSL Director and serves as the official voice of EMSL's user community in its interactions with EMSL management.

The responsibilities of the User Advisory Committee include the following:

- Provide a clear channel for the exchange of information and advice between EMSL users and management.
- Provide a formal vehicle for EMSL users to transmit concerns and recommendations to the EMSL Director.
- Design and oversee the EMSL User Meetings.
- Provide advice and recommendations to the EMSL Director on how to facilitate the effective use of EMSL.
- Nominate active users for future membership to the committee.

In Fiscal Year 2006, the UAC charter was revised to call for a self-electing committee. Preparations were made for nomination and election processes that would take place for a refreshed UAC in Fiscal Year 2007.

Science Advisory Committee

The independent SAC provides objective advice on long-term science direction to the EMSL Director related to topics such as:

- EMSL's focus on national priorities and science challenges
- strategy for accomplishing EMSL's vision
- potential opportunities for transferring science to applications
- stewardship.

The SAC is comprised of distinguished scientists from academia, national laboratories, and research institutions across the United States who provide expertise in EMSL's major capability areas of biology, environmental science, molecular science, and theory. The committee reports to the Director, Pacific Northwest National Laboratory. Responsibilities and activities of the Science Advisory Committee include:

- providing advice on scientific direction for the EMSL user program
- recommending appropriate balance of instrument time for Grand Challenges, general users, and capability development activities

- assisting EMSL with formulating policies related to facility scientific output, scientific impact of the EMSL user program, user access, and other issues, as needed
- performing periodic reviews of scientific impact from the various elements of the EMSL user program.

In Fiscal Year 2006, the SAC membership was refreshed. The committee meets annually at EMSL and the 16 members serve staggered 4-year terms. The current members of the SAC are as follows:

- Len Spicer, Duke University (Chair)
- Mark A. Barteau, University of Delaware
- Gudmundur S. "Bo" Bodvarsson, Lawrence Berkeley National Laboratory
- Gordon E. Brown, Jr., Stanford Synchrotron Radiation Laboratory
- Charles T. Campbell, University of Washington
- Marvin Cassman, University of California
- Gregory Choppin, Florida State University
- Barbara J. Finlayson-Pitts, University of California
- George W. Flynn, Columbia University
- David J. Galas, Keck Graduate Institute
- Sam Kaplan, University of Texas-Houston Medical Center
- Mary P. Neu, Los Alamos National Laboratory
- Julia Rice, IBM Almaden Research Center
- Peter J. Rossky, University of Texas at Austin
- James M. Tiedje, University of Michigan
- Mary F. Wheeler, University of Texas at Austin.

Proposals and User Access Modes

EMSL users are encouraged to submit proposals in response to periodic or continuous calls for proposals. By responding to different calls for proposals, users have the opportunity to choose from different options regarding the speed of access and the length of time over which a proposal may remain active. Different options for the type of proposal, type of access, and proprietary status are available to optimize scientific impact and facilitate evolution of EMSL capabilities and science to address cutting-edge science questions.

Calls for Proposals

- **Science Theme Call.** Users are encouraged to submit proposals that fit into major areas of current and growing user activity associated with scientific challenges that address topics of societal importance. EMSL's four science themes are: Atmospheric Aerosol Chemistry, Biological Interactions and Interfaces, Geochemistry / Biogeochemistry and Subsurface Science, and Science of Interfacial Phenomena. To highlight these areas, theme-based calls for proposals occur at least once a year. Science Theme proposals are valid for one year and can be extended twice for a total period of three years. Some EMSL resources may be especially dedicated to science theme proposals. EMSL's first Science Theme call for proposals was sent out in April 2006.

- **Grand Challenge Computational Call.** EMSL's Molecular Science Computing Facility (MSCF) sends out a call for Computational Grand Challenges once a year, providing that computer time is available. The call includes research applications in biology, chemistry, climate, and subsurface science and is open to all research entities regardless of research funding source. Computer time for Computational Grand Challenges is allocated for up to three years, with the computer allocation appropriate for the scope of research to be performed.

- **Capabilities-based Call.** The EMSL Capabilities-based call for proposals is focused on new and extended use of EMSL capabilities. Proposals that use EMSL's unique and new or developing capabilities, that apply EMSL capabilities in specific developing areas, or that propose environmentally or other important work that may not fit within the EMSL four science themes will be encouraged. The EMSL Capabilities-based call replaced the previous semi-annual High-Field Nuclear Magnetic Resonance Facility call. Proposals in response to this call are valid for one year and can be extended only once for a total open period of two years.

- **Open Call.** EMSL users can continue to submit general-use proposals at any time. This type of proposal may not be extended and will be valid for only one year. A new proposal is required each year.

Types of Proposals

- **General.** Use of existing EMSL resources typically falls into this General use category. General use proposals may be submitted to EMSL at any given time throughout the year. General Use proposals are evaluated by peer review prior to work. Proposals may be from individuals or groups who need access to the facility to carry out their research, using existing equipment in the EMSL. The scope of a General Use proposal can vary from a single experiment proposal to full project proposal (valid for multiple visits and substantial access to a range of equipment extended over multiple years). Individual and group proposals, including collaborative proposals with EMSL staff, are encouraged.

- **Partner.** Partner proposals are individuals or groups who not only carry out research at EMSL but have developed an agreement to also enhance the capabilities. Typically they develop the facility instrumentation in some way, bringing outside financial and/or intellectual capital into the evolution of EMSL. These contributions must be made available to the general users and so benefit them as well as the facility. In recognition of their investment of either resources or intellectual capital and in order to facilitate and encourage their involvement, Partner proposals may allocate participants with limited access to one or more facilities over a period of several years, with the possibility of renewal. Partner user activities are negotiated among the teams involved. New Partner proposals can be submitted in response to Science Theme or other calls, but requires information and discussions beyond the two page proposal work description required for a general type of proposal. Partner proposals are subject to the same peer review process as general proposals. Teams planning a partner proposal should have discussions with EMSL team leads before this type of proposal is submitted.

Types of Access

EMSL users can access the capabilities of the user facility in two ways.

- **Standard Access.** Standard access to EMSL facilities can vary from a single visit, single experiment proposal to a full project proposal (valid for multiple visits and substantial access to a range of equipment extended over multiple years). Prior to any work, a proposal must pass peer review. This is the most common mode of access to EMSL capabilities.

- **Rapid Access.** In limited cases, users may need access to EMSL capabilities where rapid turnaround of data is required (e.g. thesis work, project progress, and paper publication or proposal preparation). If approved, a rapid access proposal will be valid for no more than one month of EMSL use. These proposals must clearly justify why Rapid Access is needed. Work on proposals can be started subject to instrument and resource availability and subject to approval of the Scientific Facility Lead. Proposals will undergo internal peer review that will be conducted as work is initiated. However, all other reviews, including ES&H and the business office, must be complete before usage can begin. If users need rapid access for research that they may want to continue, they may also submit (possibly at the same time) a standard access proposal.

Proprietary Status

- **Non-Proprietary Research.** Research and equipment usage conducted at EMSL where the results and information are fully disclosed and disseminated are considered non-proprietary. Authors of non-proprietary proposals may retain rights to intellectual property resulting from the use of EMSL, but the government is granted a nonexclusive license to use the intellectual property.

- **Proprietary Research.** EMSL facilities can be used for proprietary research. DOE requires that such work pay full-cost recovery of the facilities used which includes, but is not limited to, labor, equipment usage, consumables, materials, and EMSL staff travel.

Science Themes

EMSL established key science themes that focus the strengths of the facility and its user program on increased scientific impact. Science themes guide user outreach efforts, help prioritize investments in equipment and staff, and guide review of user proposals. The objective of science themes is to define and develop key collections of user projects that, taken together, can significantly and positively impact an important area of environmental molecular science.

EMSL's four science themes are:

- **Atmospheric Aerosol Chemistry.** Expanding a global- to molecular-scale understanding of aerosol processes and their impacts.
- **Biological Interactions and Interfaces.** Developing a molecular-scale understanding of cells and biomolecules to provide a scientific solutions approach to biological systems.
- **Geochemistry/Biogeochemistry and Subsurface Science.** Expanding a molecular-level understanding of subsurface fate and transport and biogeochemical cycling.
- **Science of Interfacial Phenomena.** Tailoring interfacial structures for dynamics, reactivity, and transport.

In April 2006, the first-ever EMSL Science Theme Call for Proposals was sent out to users. The inaugural call was a success, with 98 proposals received: 8 for Atmospheric Aerosol Chemistry, 13 for Biological Interactions and Interfaces, 21 for Geochemistry/Biogeochemistry and Subsurface Science, and 56 in Science of Interfacial Phenomena. Based on instrument availability and scientific merit, 90 of the proposals were selected and the principal investigators notified in July 2006. The next Science Theme Call for Proposals will be sent out in February 2007.

EMSL Scientific Grand Challenges

EMSL has been challenging the traditional approach to research with two Scientific Grand Challenges—complex, large-scale scientific and engineering problems with broad scientific and environmental or economic impacts whose solution can be advanced by applying high-performance scientific techniques and resources. EMSL Scientific Grand Challenges differ from typical research projects in that they are performed by multi-institution (universities, other federal laboratories, and industry), outcome-driven multidisciplinary teams that use EMSL's cutting-edge resources.

Progress in EMSL's two Scientific Grand Challenges can help DOE resolve the enormous problems associated with environmental contamination across the complex, saving DOE and the country hundreds of millions of dollars and reducing risk to humans and the environment. The Scientific Grand Challenges have brought together some of the world's best minds and engage scientists from more than 20 universities and research institutions worldwide.

Biogeochemistry Scientific Grand Challenge

A Scientific Grand Challenge in biogeochemistry, led by PNNL scientists John Zachara and Jim Fredrickson, is studying how organisms exchange energy and electron flux with mineral matter in soils, sediments, and subsurface materials. This exchange occurs across a mineral-microbe interface that is a minute, but chemically active domain whose molecular workings have perplexed scientists for decades. The Biogeochemistry Scientific Grand Challenge uses EMSL's advanced instrumental capabilities and high-performance computing capabilities to understand the biologic and physical architecture of this remarkably complex domain and the microbe-mediated chemical reactions that occur within it. The research allows scientists to understand this most basic earth-life interaction that is fundamental to the migration of environmental contaminants, to water quality, and to soil fertility and trace metal availability. Publications involving the Biogeochemistry Scientific Grand Challenge in Fiscal Year 2006 include the following:

- A manuscript detailing research performed under the Biogeochemistry Scientific Grand Challenge was published in the July 2006 issue of *Journal of Bacteriology*. The article describes work in which a protein complex implicated in the reduction of manganese and iron was purified and its subunits were identified. To clarify the roles of cytochromes OmcA and MtrC in the bacterium *Shewanella oneidensis* MR-1, the researchers—EMSL scientists, EMSL scientific consultants, and staff and users from PNNL—cloned, expressed, and purified the cytochromes, permitting for the first time direct measurements of their metal-reducing activity and functional association. The results of this study will help provide an important understanding of how metal reductase activities can function in the reductive immobilization of toxic metals at contaminated sites. Future experiments will measure the possible association and function of a reconstituted OmcA-MtrC complex against solid metals to determine whether binding and metal reduction involve a direct association with individual proteins.

- EMSL researchers, along with scientists from PNNL, Argonne National Laboratory, and the University of Wisconsin, Milwaukee, are studying the biomolecular mechanisms of the *S. oneidensis* and uranium interaction. Under anaerobic conditions, microbes like *S. oneidensis* can donate electrons to, or reduce, metals. Changing a metal's chemistry in this way affects its solubility. For example, *S. oneidensis* reduces very soluble hexavalent uranium, U(VI), to less soluble uranium oxide, UO_2, limiting its movement in groundwater. To study electron transfer at the microbe-mineral interface and how extracellular UO_2 is formed, the researchers used a novel combination of high-resolution electron microscopy analyses at EMSL and synchrotron-based X-ray fluorescence microscopy at Argonne's Advanced Photon Source. The team is the first to confirm that *c*-type cytochromes, which are proteins on the bacterial outer membrane, are essential for U(VI) reduction and UO_2 particle formation. Further, the cytochromes and biogenically reduced UO_2 particles are co-localized in the extracellular polymeric substance (EPS), a protective matrix on the outside of some bacteria. The association of cytochromes and UO_2 in the EPS may shed some light on the long-term fate of biogenically reduced UO_2 in the environment. The EPS may affect the fate of UO_2 by influencing its susceptibility to oxidation or its transport in soils and sediments. Results of this research were reported in the *Public Library of Science Biology*.

Membrane Biology Scientific Grand Challenge

Dr. Himadri Pakrasi from Washington University in St. Louis is leading a Scientific Grand Challenge in membrane biology that uses a systems approach to understand the network of genes and proteins that govern the structure and function of membranes and their components responsible for photosynthesis and nitrogen fixation in cyanobacteria (blue-green algae). A systems approach integrates all temporal information into a predictive, dynamic model to understand the function of a cell and the cellular membranes. These microorganisms make significant contributions to harvesting solar energy, planetary carbon sequestration, metal acquisition, and hydrogen production in marine and freshwater ecosystems. Cyanobacteria are also model microorganisms for studying the fixation of carbon dioxide through photosynthesis at the biomolecular level. The results of this Scientific Grand Challenge are providing the first comprehensive systems-level understanding of how environmental conditions influence key carbon fixation processes at the gene-protein-organism level. This topic was selected because it addresses critical DOE science needs, provides model microorganisms to apply high throughput biology and computational modeling, and because it takes advantage of EMSL's experimental and computational capabilities. Publications involving the Membrane Biology Scientific Grand Challenge in Fiscal Year 2006 include the following:

- In the June 2006 issue of *Proceedings of the National Academy of Sciences of the United States of America*, Nicole Koropatkin, Himadri Pakrasi, and Thomas Smith of EMSL's Membrane Biology Scientific Grand Challenge team describe the first structure determined for a nitrate receptor, that of NrtA in a species of cyanobacteria. Nitrate is the most important nutrient for photosynthesis and growth, and cyanobacteria are capable of both nitrogen fixation and photosynthesis. NrtA represents a previously uncharacterized class of transport proteins. The closest homologue of NrtA is CmpA, a bicarbonate-binding protein found in several species of cyanobacteria. The similarity of NrtA to other nitrate and bicarbonate receptors sheds light on the possible differences between nitrate and bicarbonate binding and reveals a previously unknown link between nitrate and bicarbonate uptake in cyanobacteria. Knowledge gained by studying photosynthesis and nitrogen fixation can be applied to issues of environmental sustainability, such as improvements in solar energy conversion and carbon sequestration.

EMSL Highlights

EMSL Science Highlights

In Fiscal Year 2006, staff and users from the six research facilities at EMSL performed leading-edge research in a variety of scientific disciplines. Below are brief research summaries for each research facility, with more in-depth highlights of research provided in subsequent sections of this annual report.

Air Campaign Studies Role of Hydrocarbons and Aerosols in Industrial Setting. Three portable mass spectrometers that are part of the Chemistry and Physics of Complex Systems Facility's suite of state-of-the-art research instruments played an important role in a study of hydrocarbons and aerosols in the atmosphere during a field campaign in Houston. The September 2006 campaign involved EMSL researchers and users as well as scientists from PNNL, who joined forces with colleagues from around the world to examine the distribution of ozone-damaging gas and particles in an industrialized environment within the greater Houston area. Measurements were taken using the mass spectrometry combination from three locations associated with elevated ozone levels: (1) in the southeast portion of the city near the largest complex of petrochemical and oil refineries in the world; (2) in southwest Houston, where nitrogen emissions from automobiles are prevalent; and (3) north of Houston, near natural sources of hydrocarbons. The combined use of the mass spectrometers—a Quadrupole Aerosol Mass Spectrometer, a Time-of-Flight Aerosol Mass Spectrometer, and a Proton Transfer Reaction-Mass Spectrometer—resulted in a unique data set that will help the researchers answer questions related to hydrocarbon/aerosol interactions. This recent study followed a campaign conducted in 2000 to provide an understanding of how ozone levels in Houston far exceeded those found elsewhere in the United States, and how they amassed in such a short time. Results from the 2006 study will help researchers now determine the effectiveness of emissions controls, implemented following the 2000 study, in reducing high ozone episodes.

Three portable mass spectrometers and EMSL research experts were instrumental in a September 2006 atmospheric field campaign in industrialized Houston.

Flow and Transport Capabilities Support Effort to Strengthen Permeable Reactive Barrier. A permeable reactive barrier installed in the late 1990s at the Hanford Site has been used to prevent chromate—used by early DOE agencies to prevent fuel element corrosion in nuclear reactors—from reaching the nearby Columbia River. However, the toxic material has been detected in several groundwater monitoring wells at the site, indicating premature loss of reductive capacity of the barrier. To inhibit chromate migration, the EMSL Environmental Spectroscopy and Biogeochemistry Facility's subsurface flow and transport capabilities were used to conduct column and flow cell experiments to assess the viability of adding zero valent iron enhanced with polymer solutions to portions of the barrier that have lost reductive capacity. The experiments effectively yielded the necessary polymer, polymer concentration, and injection parameters to considerably improve the effectiveness and longevity of the barrier. These results are now being used by Fluor Hanford—the prime Hanford Site contractor for environmental cleanup—for the design of a pilot test for the insertion of the zero valent iron and polymer solution to the barrier in Fiscal Year 2007.


EMSL's 900-MHz NMR spectrometer is helping users characterize strontium binding in various synthetic soils.

Using One of the Highest Available Fields to Characterize Hanford's Most Abundant Radionuclide. Strontium is the most abundant radionuclide found in tank waste at the Hanford Site in Richland, Washington. Using the marquee 900-MHz NMR spectrometer at EMSL's High-Field Magnetic Resonance Facility—one of the highest NMR fields available—and pulse sequence methods developed at EMSL, users from Pennsylvania State University and the University of Illinois, along with researchers from EMSL, are characterizing strontium binding in various synthetic clay soils. The molecular-level structure of strontium binding sites has rarely been explored in clay minerals by direct spectroscopic means and is not well understood, yet strontium binding directly affects the transport, sequestration, and remediation of the radionuclide released from high-level waste storage tanks. This research, outlined in the February 2006 issue of *Solid State Nuclear Magnetic Resonance* and the April 13, 2006, issue of *Journal of Physical Chemistry B,* has implications for understanding how strontium contaminants can be contained in clay soils.

Researchers Make Strides Toward Neurodegenerative Disease Studies. EMSL users from PNNL, in collaboration with scientists from UCLA's David Geffen School of Medicine, are researching the precise connection between oxidative stress—cell damage caused during metabolism when the oxygen in the body assumes ever more chemically reactive forms—and neurodegenerative diseases such as Parkinson's, Alzheimer's, and Lou Gehrig's. Through use of the EMSL High-Performance Mass Spectrometry Facility's state-of-the-art mass spectrometry capabilities that allow protein identification and separation with unprecedented precision, researchers were able to conduct this important study from the largest and most detailed proteomic analysis of a mammalian brain generated to date—nearly 8,000 different, detectable proteins in the brain of a mouse. Results of the study suggested that many neurodegenerative diseases leave the biomarker, nitrotyrosine, which could be used to predict the earliest stage of brain impairment and perhaps lead to detection of disease states before symptoms occur. The researchers will continue their study using tissues with neurodegenerative diseases. This research was described in detail in *Biochemistry*, while details of characterization of the mouse brain proteome were detailed in *Journal of Proteome Research*.

New Model System Offers Fundamental Insight into Catalyst Structure and Behavior. A new model system of tungsten nano-structures offers chemists a view into the structure and reaction mechanisms of metal oxides. Developed by users of EMSL's Interfacial and Nanoscale Science Facility from PNNL, the University of Texas-Austin, and Washington State University, formation of the model system was reported in the June 23, 2006, online issue of *Angewandte Chemie, International Edition*. The discovery may offer a platform for fundamental reactivity studies of metal oxides used as catalysts in converting hydrocarbons into fuels and value-added chemicals. The model system—where all the molecular clusters are the same size, are evenly dispersed, and are oriented in one of two directions on a single layer of titanium oxide crystals—holds promise as a platform for studying the behavior of early transition metal oxides.

Modeling of Water Cluster Results in a Sustained Peak Flop Efficiency of 63 Percent. High-level correlation modeling of water clusters has provided 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 PNNL used the highly scalable and parallel NWChem software 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. This huge NWChem CCSD(T) sustained an average of more than 63 percent of peak flops efficiency (6.99 teraflops) during the calculation, demonstrating the unique capabilities of the NWChem software and the supercomputer architecture and meeting a stretch goal of DOE's Office of Advanced Scientific Computing Resources outlined in PNNL's contract.

EMSL Staff Highlights

In 2006, EMSL staff received continued recognition for progress in development of state-of-the-art capabilities and expertise, and for their professional contributions.

EMSL Staff Member Receives a 2005 Presidential Early Career Award for Scientists and Engineers. In July 2006, Yanwen Zhang, an EMSL materials physicist in the Interfacial and Nanoscale Science Facility, was notified that she had been chosen to receive a 2005 Presidential Early Career Award for Scientists and Engineers (PECASE), the highest honor bestowed by the U.S. government on outstanding scientists and engineers who are beginning their independent careers. Zhang and 55 other recipients were honored by President Bush and received their awards from John Marburger, director of the White House Office of Science and Technology Policy. The award recognizes scientists and engineers who show exceptional potential for leadership in scholarship, service, and education.


EMSL staff member Yanwen Zhang shakes hands with Secretary of Energy Samuel Bodman during a ceremony to receive the prestigious PECASE Award.

To be eligible for the presidential award, Zhang first had to be selected by DOE for its Early Career Scientist and Engineer Award. As a Presidential Early Career Award recipient, Zhang receives a commitment from DOE's Office of Science to continue funding the research for which the award was given for 5 years.

Zhang's research focuses on interactions of energetic ions with solid materials and how those interactions can be applied to the analysis and study of those materials. Zhang developed a novel way of measuring the energy loss of atomic particles as they pass through materials. Accurate measurements of such energy loss were a long-standing problem until Zhang successfully used high-resolution, time-of-flight spectroscopy to determine energy loss over a continuous range of energies.

With more than 100 publications and several long-term international research collaborations, Zhang is recognized for her contributions in ion-solid interactions, irradiation effects, and ion-beam techniques. She also is active in several professional societies, has received many international scientific and academic awards, and is involved in educational activities and community service. She routinely hosts visiting scientists at EMSL's ion-beam user facility; lectures on topics related to ion-beam physics; mentors postdoctoral fellows, graduate students, summer undergraduates, and high school interns; serves on Ph.D. committees;

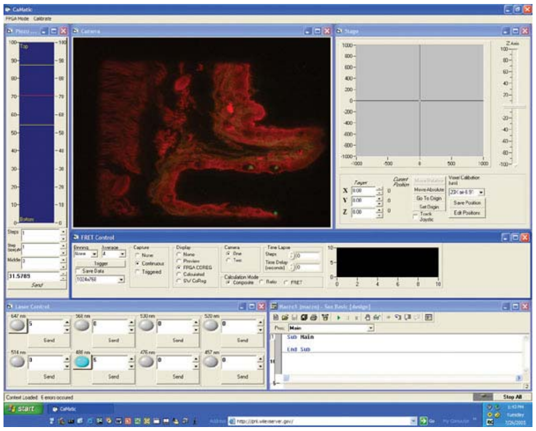
assists local middle schools with Chinese translations; and serves as a judge for local science fairs.

Zhang holds two doctorate degrees—one in engineering physics from Lund University in Sweden and another in science from Beijing Normal University in China.

EMSL Director's Research Earns Two Prestigious Awards. EMSL Director Allison Campbell received a 2006 Federal Laboratory Consortium Excellence in Technology Transfer Award and a 2006 R&D 100 Award for a novel water-based process for depositing bioactive calcium-phosphate coatings containing therapeutic agents on orthopedic implants and medical devices. The surface-induced mineralization process provides patients with a two-fold benefit: implants that are bacteria resistant and are easily assimilated into the body. The process involves unique calcium-phosphate coatings containing an antimicrobial agent that was proven in tests to kill infection-causing bacteria or greatly inhibit bacteria growth in the body, helping prevent dangerous and costly post-surgical infections. The water-based deposition process, coupled with the bioactive therapeutic agent, also provides an advanced method for applying pure calcium-phosphate coatings to artificial joints, allowing enhanced bone bonding.

EMSL Director Allison Campbell (back, center) shared R&D 100 Award honors with team members (from left) Barbara Tarasevich, Peter Rieke, and Shari Li.

Instrument Development Laboratory Staff Develop Remote Control Software for State-of-the-Art Confocal Microscope. EMSL Instrument Development Laboratory staff Derek Hopkins and Brian LaMarche, intern Anoop Mayampurath, and research staff from PNNL developed software to control a state-of-the-art confocal microscope in real time from a remote location. In a recent demonstration, live cell images were acquired and streamed across a 1-gigabit Ethernet connection at 15 and 30 frames per second. This capability will ultimately enable external researchers to use unique instruments found only at PNNL, as well as provide unique opportunities for real-time collaboration.



Confocal microscope software developed by EMSL Instrument Development Laboratory staff along with researchers from PNNL.

This development expands the potential reach of the EMSL user program by providing a framework for remote access of state-of-the-art instrumentation. The demonstration displayed the potential of remote control software tools to expand availability by enabling researchers around the world to remotely access instrumentation, limited only by the available bandwidth.

Current studies on cell physiology and reaction to stimuli usually are performed using cells cultured on two-dimensional surfaces. This geometry greatly simplifies the methodology used to observe and propagate cells; however, it places great constraints on how one can investigate intercellular communication and stress responses. The high-speed confocal microscope is a tool necessary to analyze cell signaling in a three-dimensional environment. It provides users the ability to look at cellular signaling, protein interactions, and cellular localization/translocation of signaling molecules, in real time and in living cells. These capabilities are being applied to research in cell, cancer, and radiation biology.

The microscope control software was based on the flexible Surf-O-Matic architecture developed initially at EMSL for surface science research. The application has controls for setting the laser wavelength and amplitude, three-axis stage positioning, and image capture settings, and allows the user to write Visual Basic-like scripts to automate all aspects of the application. This provides the unique capability to run highly configurable experiments unattended for long periods of time. The imaging portion of the software interfaces two Coreco PC-DIG capture cards capable of frame rates up to 30 frames per second. At full frame resolution, the software captures 15 frames per second—or 14.4-million pixels per second. Each frame captured is approximately 1.3 MB in size. Coupled with automated experiments running days on end while generating images at 15 fps, this system is capable of generating large amounts of data in a short time span. The software is also unique because it corrects for physical defects in the images (e.g. lens distortion) by using a distinctive image registration technique that allows a pixel-perfect match in real time.

EMSL Researcher Honored for Safety Role. Jim Follansbee, a staff member in EMSL's Instrument Development Laboratory, was honored by PNNL as the first-ever Cognizant Space Manager of the Year. Follansbee has been responsible for several laboratory areas in EMSL since the user facility opened in 1997. During this time, he has maintained an accident-free environment within these spaces—which are used frequently by PNNL staff, visiting users, and local students. He was honored on September 12, 2006, at a luncheon and awards ceremony.

Instrument Development Laboratory staff member Jim Follansbee (right) accepts the first-ever PNNL Cognizant Space Manager of the Year Award from Mike Schlender, Deputy Laboratory Director for Operations.

EMSL User Highlights

The following is a sampling of the many user highlights that occurred in Fiscal Year 2006 as a result of research conducted at EMSL.

Finlayson-Pitts Elected to Two Prestigious Academies. Within a week's time, Barbara Finlayson-Pitts was elected Fellow of the American Academy of Arts and Sciences and the National Academy of Sciences. Finlayson-Pitts is involved in the study of chemical reactions in the lower atmosphere to better understand air pollution in urban and remote areas and has studied the effects of sea salt on urban smog formation and on remote atmospheres, as well as how chemical reactions on the surfaces of buildings and roads affect urban air quality and models of air pollution.

Barbara Finlayson-Pitts

Bruce Kay

Kay Honored by American Association for the Advancement of Science. Bruce Kay was inducted as a Fellow in the American Association for the Advancement of Science, which cited his "meritorious efforts to advance science or its applications."

Julia Laskin

Laskin Appointed to American Society for Mass Spectrometry Board of Directors. Julia Laskin has been appointed to the American Society for Mass Spectrometry Board of Directors. Laskin will act as treasurer of the Board. In this role, she will make recommendations to the Board relevant to preserving the economic health of the Society and will present a financial report at each annual meeting.

Kerisit Receives 2005 M.T. Thomas Award. Sebastien Kerisit was selected as the 2005 recipient of the M.T. Thomas Award for Outstanding Postdoctoral Achievement in recognition of such accomplishments as seminal and novel theoretical advancements in understanding electron transfer reactions at environmental interfaces and the impact on the field of geochemistry. Use of his unique combination of molecular dynamics simulations, electronic structure calculations, and kinetic Monte Carlo simulations constitutes the first attempt to computationally model the bioreduction of iron at mineral surfaces at the atomic level. Kerisit has used these techniques to contribute significantly to the EMSL Biogeochemistry Scientific Grand Challenge, where he has computed rates of electron transfer in iron oxide lattices and from heme groups in outer-membrane cytochromes to various hematite (α-Fe_2O_3) surfaces. His work has been published in the

Sebastien Kerisit received the 2005 M.T. Thomas Award for Outstanding Postdoctoral Achievement.

Journal of Chemical Physics and *Geochimica et Cosmochemica Acta.*

Greg Kimmel

Kimmel Featured in *Chemical and Engineering News.* Greg Kimmel was featured in the September 26, 2006, issue of *Chemical and Engineering News*. Kimmel was one of 200 scientists from around the world who attended a Nuclear Energy Workshop held by the U.S. Department of Energy to identify key areas of science in which fundamental research has the potential to make a significant impact on the future of nuclear power.

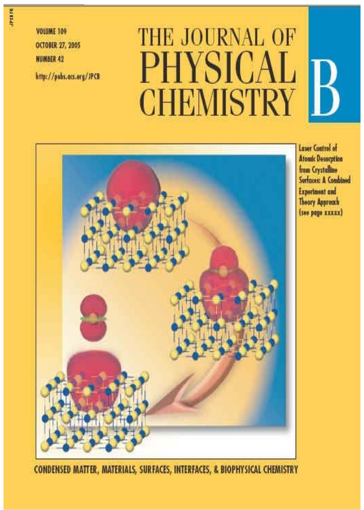
Yuehe Lin

Lin Receives Several Publishing Honors. Publications detailing research of carbon nanotube—materials 10,000 times smaller than a human hair that have potential application for the next generation of biosensors and for high-efficiency fuel cells—performed using the capabilities of EMSL's Interfacial and Nanoscale Science Facility have earned Yuehe Lin several prestigious citation honors. Among them, a paper by Lin and PNNL postdoctoral fellow Guodong Liu, "Carbon Nantotube-Templated Assembly of Protein," was featured on the April 2006 cover of the *Journal of Nanoscience and Nanotechnology*. A paper published in 2003 by Lin and his collaborators in *Advanced Materials* is featured on the Institute for Scientific Information's Essential Science Indicators as one of the highly cited papers in the field of materials science. Finally, a paper by Lin and his collaborators published in the *Journal of the American Chemical Society* was the most cited paper of nearly 10,000 papers published in that journal from January 2003 to December 2005, based on ISI's citation data.

Bowman Serves on Thesis Defense Committee. Mike Bowman traveled to Washington State University, Pullman Washington, to serve on a Thesis Defense Committee. He participated in the doctoral thesis defense of Dr. Jonathan Cape. Dr. Cape's thesis topic was "The Mechanism of Quinol Oxidation in the Cytochrome bc complex." This doctoral defense included work performed as a user in the EMSL High-Field Magnetic Resonance Facility.

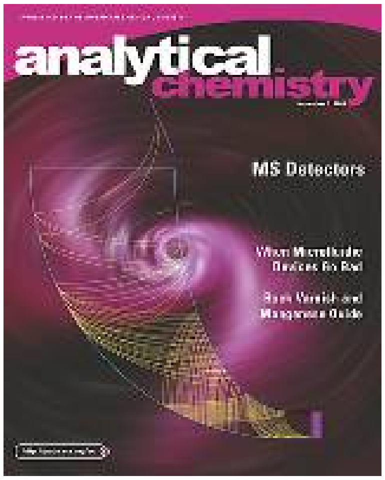
Journal Covers

During Fiscal Year 2006, research by EMSL users and staff was highlighted on six scientific journal covers. The following describe the research that led to these covers.



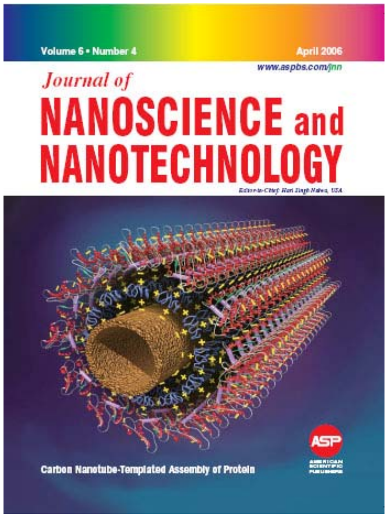
Wayne Hess, Alan Joly, Ken Beck, and Matthias Henyk, along with their collaborators at University College London, have focused on hyperthermal desorption of halogen atoms and show that yield, electronic state, and velocity distributions of desorbed atoms can be selected using tunable laser excitation. Results show that desorption of these materials leads to controlled modification of their surface geometric and electronic structures. This research was featured on the cover of the October 27, 2005, *Journal of Physical Chemistry B*.

Hess WP, AG Joly, KM Beck, M Henyk, PV Sushko, PE Trevisanutto, and AL Shluger. 2005. "Laser Control of Desorption through Selective Surface Excitation." *Journal of Physical Chemistry B* 109:19563-19578.



Dave Koppenaal and his collaborators provided expert commentary on the variety of types of mass spectrometer detectors and the consideration and needs related to various research areas. The commentary was featured on the cover of the November 1, 2005, issue of *Analytical Chemistry*.

Koppenaal DW, CJ Barinaga, MB Denton, RP Sperline, GM Hieftje, GD Schilling, FJ Andrade, and JH Barnes IV. 2005. "MS Detectors." Analytical Chemistry 77(21):418A-427A.

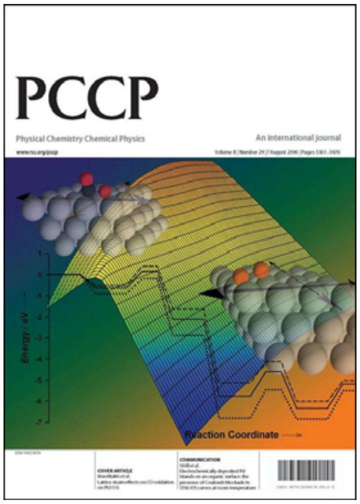


Guodong Liu and Yuehe Lin describe a novel general strategy for fabricating protein-polyion multilayers by electrostatic layer-by-layer self-assembly on carbon nanotube templates. Such a noncovalent functionalization method is important for preserving the activity of biomolecular, the mechanical, and electrical properties of carbon nanotubes. The research was featured on the April 2006 cover of the *Journal of Nanoscience and Nanotechnology*.

Liu G, and Y Lin. 2006. "Carbon Nanotube-Templated Assembly of Protein." *Journal of Nanosscience and Nanotechnology* 6(4):948-953.

LS Wang, EMSL user from PNNL, and collaborators from the University of Nebraska have uncovered a class of gold atom clusters that are the first known metallic hollow equivalents of the famous hollow carbon fullerenes known as buckyballs. This research has so far led to stories in several journals and websites, including *Chemical & Engineering News*; the *Seattle Post-Intelligencer*, *Chemistry World*, which is published by the Royal Society of Chemistry in the United Kingdom; and *Nanotechwire*. This work was also featured on the cover of the May 30, 2006, issue of the *Proceedings of the National Academy of Science*.

Bulusu S, X Li, LS Wang, and XC Zeng. 2006. "Evidence of Hollow Golden Cages." Proceedings of the National Academy of Science 103(22):8326-8330.



Lars Grabow, Ye Xu, and Manos Mavrikakis, University of Wisconsin-Madison, conducted research that discovered that surface strain plays a major role in determining the rate limiting step and catalytic activity of platinum for CO oxidation. This research was featured on the cover of the August 7, 2006, issue of *Physical Chemistry Chemical Physics (PCCP)*.

Grabow L, Y Xu, and M Mavrikakis. 2006. "Lattice Strain Effects on CO Oxidation on Pt(111)." *Physical Chemistry Chemical Physics* 8:3369-3374.

Hua-Jin Zhai and Lai-Sheng Wang (Washington State University, Tri-Cities), and Dmitry Zubarev and Alexander Boldyrev (Utah State University) have discovered a new class of endohedreal lead cage compounds that they have named "plumbaspherenes" (see research highlight entitled "Pb_{12}^{2-}: Plumbaspherene"). The existence of these new cage compounds may allow for the insertion of other atoms inside these cages to create new materials with unique properties for a wide range of applications. This research was featured on the cover of the August 31, 2006, issue of the *Journal of Physical Chemistry A*.

Zhai HJ, LS Wang, DY Zubarev, and AI Boldyrev. 2006. "Gold Apes Hydrogen. The Structure and Bonding in the Planar $B_7Au_2^-$ and B_7Au_2 Clusters." *Journal of Physical Chemistry A* 110:1689-1693.

Patents

EMSL staff and their collaborators received three patents in Fiscal Year 2006.

U.S. Patent 6,979,816 for the "Multi-source Ion Funnel" was issued in December 2005 to K Tang, MB Belov, AV Tolmachev, HR Udseth, and RD Smith.

U.S. Patent 6,989,674 for the "Advanced Slow-Magic Angle Spinning Probe for Magnetic Resonance Imaging and Spectroscopy" was issued in January 2006 to RA Wind, JZ Hu, KR Minard, and DN Rommereim.

U.S. Patent 6,999,174 for "Photoacoustic Spectroscopy Sample Array Vessels and Photoacoustic Spectroscopy Methods for Using the Same" was issued in February 2006 to JE Amonette, ST Autrey, and NS Foster-Mills.

Outreach Activities

Past and current EMSL users from 40 institutions gathered at a recapitalization workshop designed to investigate the future instrumentation needs of EMSL related to work in four science areas.

EMSL Hosts Recapitalization Workshop. On August 1 and 2, 2006, EMSL hosted 104 past and present users from 40 institutions at a recapitalization workshop that centered around EMSL's four science themes. The participants—hailing from academia, industry, and the national laboratory system—worked together in a collaborative mode to identify the technical and scientific challenges they expect to face, including:

- Identifying the molecular-level mechanisms by which microbes sense changes in environmental conditions.
- Identifying the mechanisms of nucleation and growth of cloud droplets.
- Unraveling the genesis, properties, and effects of nanominerals and nanostructured materials in the environment.
- Understanding and controlling structure-function relationships of surfaces and interfaces, including those relevant to catalysis and energy production.

The participants, once they identified the key challenges, worked together to identify the instrumentation needed to address the challenges. The results are being rolled up into a facility refreshment plan that will bring state-of-the-art equipment into EMSL during the next five to seven years.

EMSL hosted 40 users at a radiological NMR spectroscopy workshop in May 2006.

Radiological NMR Spectroscopy Meeting Held in May. On May 1-2, 2006, EMSL brought together 40 users from 11 institutions and 6 countries to discuss the future need for radiological NMR capabilities at EMSL. Many of the participants, representing the computational actinide chemistry community, identified the need to increase capabilities to calculate NMR spectra in agreement with experiment as well as capabilities to perform high-level relativistic calculations for heavy elements. Partially as a result of the workshop, EMSL is planning for construction of a 6700-square-foot annex to house radiological research work in the Fiscal Year 2009 or 2010 timeframe. The radiological annex will contain environmental and molecular sciences research equipment similar to that in the main EMSL facility, but will provide users with unique resources to study samples containing radiological materials.

EMSL Targets User Outreach at Two Large Professional Meetings. EMSL developed a booth presence and provided outreach to attendees at the American Association for the Advancement (AAAS) of Science meeting in St. Louis and the American Chemical Society (ACS) National Meeting in San Francisco in February 2006 and September 2006, respectively. At the AAAS meeting, EMSL led a symposium on its scientific grand challenge approach, and at both meetings booth staff made connections with participants who are potentially future users of EMSL. Investments in such events can help EMSL increase its pool of new users while also raising the visibility of EMSL as a national scientific user facility.

To connect with potential users, EMSL provided a booth presence at the AAAS and ACS meetings in 2006.

EMSL User Survey

The following are the responses to the EMSL April 2006 user survey submitted between April 8, 2006, and July 10, 2006.

- Survey Satisfaction: 92.1%
- Survey Responses: 231
- Surveys Sent: 461
- Survey Response Rate: 50.1%.

1. How satisfied were you with the availability of facilities and equipment?

- 132 Very Satisfied
- 83 Satisfied
- 9 Neither Satisfied nor Dissatisfied
- 3 Dissatisfied
- 3 Not Applicable.

2. How satisfied were you with performance of facilities and equipment (e.g., were they maintained to specifications for your intended use, ready when scheduled, etc.)?

- 130 Very Satisfied
- 85 Satisfied
- 7 Neither Satisfied nor Dissatisfied
- 3 Dissatisfied
- 1 Very Dissatisfied
- 5 Not Applicable.

3. List additional capabilities that you think EMSL should have.

User comments and EMSL responses to this question are grouped by facility and provided at http://www.emsl.pnl.gov/homes/survey.shtml.

4. With the new knowledge gained at EMSL, I expect to (check all that apply):

- 206 - Disseminate new knowledge via publication in peer-reviewed open literature.
- 172 - Disseminate new knowledge via presentations at professional society meetings.
- 16 - Acquire a patent.
- 94 - Further DOE's mission(s).
- 135 - Facilitate collaborative interactions (e.g., stimulated new ideas for future experiment; increased; work; etc.).
- 89 - Train students (undergraduate, graduate or postdoctoral associate).
- 129 - Use data for a future proposal.
- 83 - Establish or grow network and/or further collaboration.

5. How satisfied were you with the assistance provided by EMSL technical staff?

- 145 - Very Satisfied
- 68 - Satisfied
- 10 - Neither Satisfied nor Dissatisfied
- 2 - Dissatisfied
- 5 - Not Applicable.

6. How satisfied were you with the assistance provide by the EMSL administrative staff?

- 121 - Very Satisfied
- 75 - Satisfied
- 11 - Neither Satisfied nor Dissatisfied
- 1 - Very Dissatisfied
- 23 - Not Applicable

7. How appropriate and user friendly were the training and safety procedures?

- 76 - Very Satisfied
- 85 - Satisfied

- 21 - Neither Satisfied nor Dissatisfied
- 3 - Dissatisfied
- 42 - Not Applicable.

8. How satisfied were you with the proposal process (e.g. submission and review)?

- 61 - Very Satisfied
- 81 - Satisfied
- 20 - Neither Satisfied nor Dissatisfied
- 6 - Dissatisfied
- 1 - Very Dissatisfied
- 59 - Not Applicable.

9. How did you learn about the EMSL?

- 32 - Scientific meeting/conference
- 8 - Internet search
- 11 - Journal publication
- 58 - Previous EMSL use
- 82 - Colleague
- 106 - PNNL staff member
- 19 – Other.

10. Is there anything that would have improved your visit to EMSL, your experience using EMSL resources, or you interactions with EMSL Staff?

User comments included:

- I think the attitude in EMSL is one of commitment to improvement. There have been very positive improvements over the last few years and I expect they will keep moving in that direction.
- A great and very useful facility - nothing like it anywhere else.
- This is an easy to use and convenient facility.

- We are long-time collaborators on PNNL projects and we always appreciate the professional level of PNNL/EMSL staff.
- This is the best equipped lab I have ever worked in.
- I have always received EXCELLENT response from both scientific and EMSL staff.
- Staff are extremely knowledgeable and willing to assist in research endeavors.

User Administration

EMSL's User Administration group implements and manages policy and tools for various aspects of the user proposal and access process, as well as reporting statistics that support management and tracking of EMSL's impact. User Administration works with users and EMSL management to address users' issues and concerns in order increase user satisfaction. The group also leads outreach activities, working in conjunction with the EMSL Communications Manager (CM) and Scientific Facility Leads to promote public awareness and recognition of the research and unique integrated experimental and computational resources leading to advocacy for EMSL, as well as increased impact on the nation's largest challenges in the environmental sciences via such avenues as regional and national society meetings, visiting universities, workshops, and courses.

Since 2002, EMSL has developed electronic tools to automate management of user proposals [EMSL Usage System (EUS)], proposal review [EMSL Proposal Review System (EPRS)], and tracking use of EMSL resources [EMSL Resource System (ERS)].

EMSL Usage System

The EUS tracks the lifecycle of a proposal—from submittal, through review and acceptance, to closure. At various stages in this cycle and at completion, proposal authors are asked for updates of the progress of the research and copies of any publications resulting from the work. Highlights of some of the enhancements made to the EUS during Fiscal Year 2006 include:

- the ability to assign hazards to proposals
- revision of user survey logistics, questions, and emails
- electronic automation of the Appendix B of the Non-Proprietary Use Agreement
- installation of a new faster server, and relocation of the application and database.

EMSL Resource System

The ERS is a web-based tool that tracks the use of all significant resources in EMSL. EMSL's need to manage its assets and systematically track and report the use of EMSL resources resulted in development of the ERS to provide data needed to assure maximum efficiency, effectiveness, impact, and continued demand for installed resources. Highlights of improvements made to the ERS in Fiscal Year 2006 include:

- redesign of the system due to new user definition
- creation of a variety of reports for to incorporate strategic metrics
- archival of monthly data

- automatic import of MPP2 users (Gold data).

EMSL Proposal Review System

The EPRS was designed and implemented in Fiscal Year 2006 to automate, manage, and document the proposal review process throughout a proposal's life cycle, including calls for proposals, communications with internal and external reviewers, external access by reviewers where appropriate, documentation of all review results, and reports summarizing current and past review cycles. This system allows:

- a mechanism for communications with reviewers
- a mechanism for external access by reviewers
- the ability for proposal attachments to be reordered and the order of attachments reflected in the peer-review package
- generation of a single PDF of all attachments and the proposal summary so that the reviewer only has to handle one file per proposal
- creation of two reviewer status reports
- creation of reviewer comment reports for proposal authors
- the ability for a reviewer to monitor scores and submit all reviews at once.

Outreach

In addition to the above system enhancements, a variety of management and outreach activities took place in Fiscal Year 2006, including:

- serving as staff liaison to the UAC, including participating in development of the call for nominations and the resulting election website
- serving as staff liaison to the SAC, including coordinating off-cycle visits
- developing the EMSL Outreach Plan
- coordinating the EMSL Science Theme call for proposals
- updating the EMSL external website with new policies
- coordinating EMSL information booths at major scientific society meetings, including the American Chemical Society National Meeting in San Francisco in September 2006 and the American Association for the Advancement of Science Meeting in St. Louis in February 2006

- serving as chair of EMSL's M.T. Thomas Outstanding Post-doctoral Award Committee
- overseeing more than 130 tours of EMSL encompassing nearly 700 people
- revising the user survey (shortening content, reorganizing and rewording to provide clarity and content, refocusing to users within previous six-month period, and adding a reminder email) to serve EMSL users more effectively.

Communications

The EMSL CM manages and directs the development and implementation of communications critical to EMSL's business strategy and scientific user program, particularly in the areas of EMSL science themes, EMSL Scientific Grand Challenges, and refined business practices as they apply to EMSL staff and users. The CM achieves these objectives by employing diverse communications strategies and processes, and through development of multiple strategic products. These accomplishments are conducted through effective partnering and teaming with EMSL staff and users, as well as with peers and staff members in the PNNL Communications and External Relations Directorate to manage and deliver services for EMSL. The CM also provides counsel and information to the EMSL Director and management team and serves as a member of the EMSL management team, addressing a host of directorate issues and priorities.

Future Directions

In Fiscal Year 2007, the EMSL User Administration Manager (UAM) and EMSL CM will conduct strategic activities in user outreach and communications in an effort to meet EMSL's mission, goals, and science themes.

User Administration Manager

Deliverables of the EMSL UAM in Fiscal Year 2007 include:

- Serve as point of contact for EMSL systems (i.e., EUS, ERS, EMSL EPRS).
- Ensure a transparent proposal process, placing guidance and policy online.
- Enable and broadly distribute calls for proposals, and provide oversight of peer-review and approval processes.
- Increase EMSL name recognition and enhance reputation.
- Diversify portfolio of top universities and minority institutions.
- Increase presence at national professional society meetings.
- Attend/host workshops and symposia, and user meetings.
- Establish a relationship with other user facilities.
- Serve as EMSL's National User Facility Organization (NUFO) representative.
- Serve as liaison for EMSL's User and Science Advisory committees.
- As point of contact for EMSL's user survey, ensure responsiveness and satisfaction of users.
- Develop possible new user-friendly capabilities, such as a user portal, which will allow proposal participants to log in and view a list of their proposals and status, as well as allow them to submit summaries or publications; a staff portal, which will allow coordination among PNNL's electronic systems; and a centralized user administration office.
- Streamline training without affecting user safety.

EMSL Communications Manager

The following actions show the future direction that EMSL's CM support will take in Fiscal Year 2007 and beyond:

- Identify opportunities (press releases, articles) that will raise EMSL visibility nationally and internationally.

- Further develop targeted overview and facility-specific posters, brochures, and website highlights that market EMSL science, facilities, and capabilities.

- Coordinate activities that support EMSL's anniversary as a decade-old user facility.

- Begin a major effort to improve/revamp the EMSL external website, which will provide impactful, timely information to EMSL's client, users, and potential users.

- Work with PNNL's Science and Engineering External Recognition Awards Program and EMSL Scientific Facility Leads to identify staff who can be placed into PNNL awards development pipeline and targeted for external honors.

- Revive the EMSL News as a vehicle for informing past, current, and potential users of science and capabilities of EMSL.

- Provide updates to the EMSL internal website.

- Provide continued booth and symposium presence at major national meetings, and communications support to staff who attend such meetings.

- Provide further updates and improvements to relevant displays in the main EMSL hallway (e.g., posters, brochures) to support the high volume of tours hosted by EMSL. These tours range from high-level political visits to general staff tours. Potential specific posters include an EMSL timeline, overview, map, facility descriptions, mission statement, vision and value statements, supercomputer dynamic content displays, and EMSL Scientific Grand Challenges.

- Provide support as needed to various PNNL-level requests for EMSL information.

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Chemistry and Physics of Complex Systems Facility

The Chemistry and Physics of Complex Systems (CPCS) Facility supports the U.S. Department of Energy (DOE) mission of fostering fundamental research in the natural sciences to provide the basis for new and improved energy technologies and for understanding and mitigating the environmental impacts of energy use and contaminant releases. This research provides a foundation for understanding interactions of atoms, molecules, and ions with materials and with photons and electrons. Particular emphasis is on interfacial processes.

A distinguishing feature of research at national laboratories is their approach to problem solving. Significant scientific issues are addressed using focused and multidisciplinary investigative teams with each team member bringing a particular skill and capability to bear on the problem. This approach accelerates progress. The same approach—involving groups of scientists within the program as well as collaborators from throughout Pacific Northwest National Laboratory and the external scientific community—is inherent in how the CPCS Facility is managed.

The CPCS Facility and its staff have particular capabilities and expertise that support user research involving preparation and spectroscopic analysis of molecular clusters; high-resolution imaging of biological samples and studies of cellular processes, including DNA damage and repair and low-dose radiation processes; ultra-fast and non-linear optical spectroscopies; ultrahigh-resolution spectroscopy for measurements of electronic and geometric structures and dynamics; surface and interface structure; chemical reaction dynamics and kinetics; ion-molecule traps and storage technology; and specialized chambers, instruments, and models for studying chemical reactivity and analyzing atmospheric species including aerosols.

Our research underpins the fundamental understanding of chemical transport and reactivity in the condensed phase. It addresses the underlying uncertainties in thermal and non-thermal (i.e., radiation) chemistry, interfacial molecular and ionic transport, and other processes in complex natural and human-made systems related to energy use, environmental remediation, waste management, and understanding biological responses to environmental stresses. One focus is on structures and processes of molecular and nanoscale systems in complex environments such as condensed phases and interfaces. Research guides the development of new materials and approaches for clean and efficient energy use.

Instrumentation & Capabilities

- reaction mechanisms at solid, liquid, and gas interfaces
- high-energy processes at environmental interfaces
- cluster models of the condensed phase
- single-molecule spectroscopy and biomolecular sciences
- ultra-sensitive and environmental analysis.

Another central feature is the development of innovative experimental methods with broad applications to research in the natural sciences. Two examples of innovative methods developed in the CPCS Facility include 1) detecting and monitoring trace atmospheric species, including gaseous and particulate matter, and 2) studying biological processes important in the environment and health, including imaging of live cells to observe the reaction dynamics of functioning biological systems in real time, advancing our understanding of protein-protein interactions and DNA damage and repair using single-molecule spectroscopy, and studying cellular responses to low-dose radiation using novel instrumentation.

Capabilities

The capabilities of the CPCS Facility support research in five general areas, which are described below.

Reaction Mechanisms at Solid, Liquid, and Gas Interfaces. Research in this area focuses on developing fundamental molecular information about processes occurring at the interfaces between environmentally important liquids, solids, and gases. For example, a common element in environmental restoration is the need to understand molecular processes 1) in aqueous solutions and at the interface between aqueous and organic solutions and 2) at the interface between aqueous solutions and environmentally important solid materials. Examples of instruments that enable this research are shown in Figures 1 and 2.

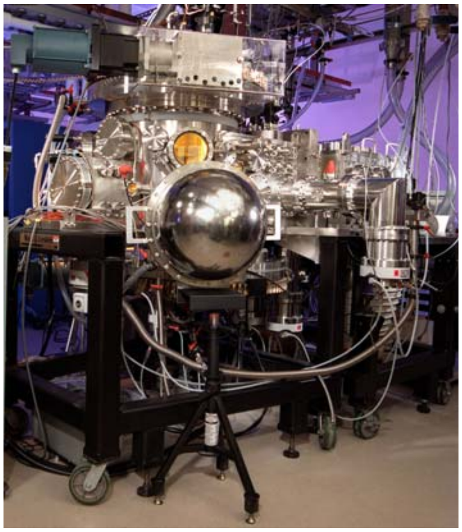

Figure 1. State-of-the-art molecular beam surface-scattering and kinetics instrument.

Figure 2. Combined instrument that allows fluorescent optical microscopes and magnetic resonance microscopes to focus on the same samples at the same time.

Molecular processes occurring at liquid-liquid interfaces also play an important role in the subsurface transport of contaminants such as organic solvents (e.g., chlorinated hydrocarbons) released into soil and groundwater. Processes at the gas-liquid interface are critical in atmospheric transport processes.

Model systems such as amorphous solid water permit detailed studies of solvation and the effects of solvation on chemical reactivity. These studies provide information about intermolecular interactions that lay the foundation for accurate modeling of solution processes. Studies provide information about factors that control the rates of reactions in solution. This information is essential to both predicting the fate of contaminants in aqueous environments and influencing the selectivity of ligands for specific ions important in developing separations agents for waste treatment processes.

It is also crucial to understand molecular processes at the interface between aqueous solutions and environmentally important materials, such as aerosol particles, minerals, and glasses. This addresses fundamental science questions about contaminant fate and transport and waste immobilization. Because most environmental materials are in an oxidized form, we emphasize the structure and chemistry of oxide materials, especially naturally occurring oxides of silicon, aluminum, and iron. The adsorption of species on and their incorporation in soil minerals affect their transport through soil. Mineral interfaces can enhance or retard reactivity as well as transform contaminants. Knowledge of molecular processes at solid-liquid interfaces is also important to understanding the stability of glasses proposed for encapsulating high-level radioactive wastes that must be stored for long periods of time. Over the long half-lives of radionuclides, water can degrade these waste-encapsulating glasses, thus leading to higher-than-expected releases of radionuclides.

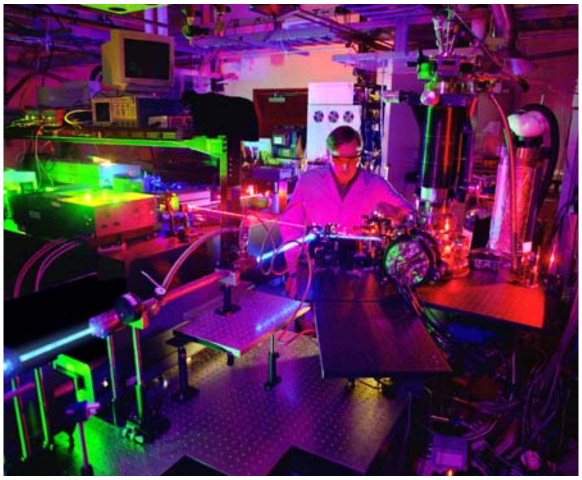

Figure 3. Laser desorption experiments investigate the effects of electronic excitation on crystalline materials.

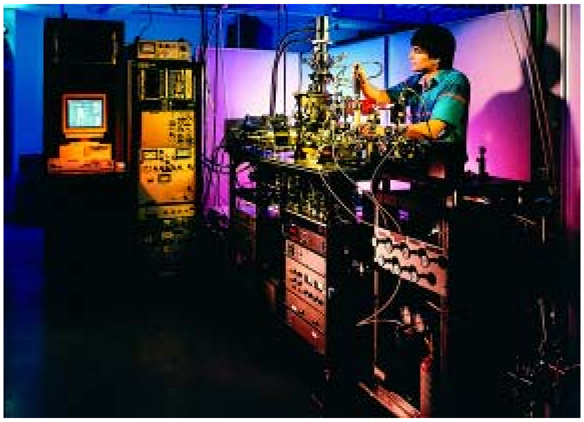

Figure 4. Electron-stimulated surface reaction apparatus is used to study non-thermal reactions that occur on surfaces or at interfaces.

High-Energy Processes at Environmental Interfaces. Research in this area focuses on obtaining a mechanistic understanding of chemical transformations resulting from electronic excitation in condensed-phase materials relevant to the DOE environmental cleanup mission. Examples of capabilities that enable this research are shown in Figures 3 and 4. Energetic processes are important in the degradation of mixed wastes because of the radiolytic decay-driven chemistry that occurs in the solid and liquid phases of stored radioactive waste and in final waste storage forms. Reactions occurring at interfaces are of particular interest for characterizing material composition and response to electronic excitation. We use pulsed femtosecond and nanosecond laser sources to study laser-solid interactions in a combined experimental and theoretical program. Our goal is to continue development of models for excited-state reactions by measuring ultra-fast dynamic processes and by demonstrating laser control of solid-state chemistry.

Cluster Models of the Condensed Phase. This research is aimed at providing a molecular-level understanding of solvation and subsequent reactions in simple and complex systems as they relate to the chemistry of complex wastes, contaminated solids and groundwater, and other systems found in nature. A major experimental and theoretical effort is devoted to understanding surface and interface properties using cluster models to study structure and bonding. Small and controllable cluster systems provide atomic-level models that enable us to understand bulk surfaces and defect sites. They are also an excellent testing ground to benchmark theories intended for large and real-world systems. A productive collaboration in this area is illustrated in Figure 5.

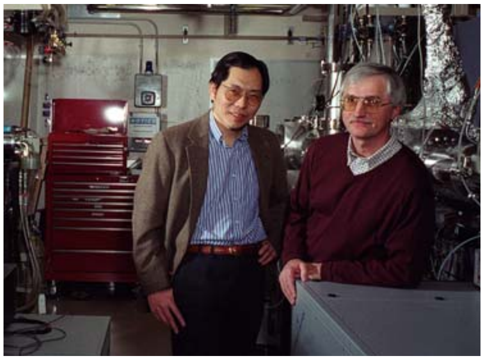

Figure 5. CPCS Facility users/collaborators L-S Wang, Washington State University Tri-Cities, Richland, Washington, and AA Boldyrev, Utah State University, Logan, Utah, are combining experimental and theoretical approaches to understand the unique properties and characteristics of metal clusters. Their research is at the forefront of cluster science.

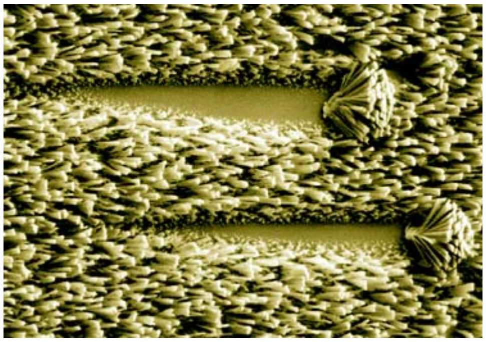

Figure 6. Nanostructures could be used to control and enhance chemical reactivity. Researchers at the CPCS Facility are trying to determine how molecules enter pores, are captured, and eventually released.

Single-Molecule Spectroscopy and Biomolecular Sciences. This research emphasizes single-molecule spectroscopy and high-resolution biological imaging techniques for studying biological systems. Recent advances in fluorescence microscopy, at both the EMSL and elsewhere, make it possible to detect single molecules at room temperature and to conduct spectroscopic measurements to monitor their dynamic processes. We have demonstrated fluorescence imaging of single molecules by two-photon excitation with a femtosecond laser. This approach has several advantages—the excitation volume is small, the penetration is deep, and photo-damage is reduced for biological samples—thus offering the opportunity of viewing chemical reactions in a living cell in real time. Structures are known for many proteins that perform vital cell functions, including DNA damage repair, reaction catalysis, and cell signaling. Nanoscale-structure materials will affect their properties; Figure 6 provides an example. However, how they perform these functions is generally not understood. Single-molecule and single-cell measurements provide real-time data on the molecular motions involved during these functions and how the timing of these reactions is correlated with other cellular biological activities. These data are likely to produce new information that is otherwise hidden, and will open up exciting possibilities for probing cellular processes.

Ultra-Sensitive Trace Gas Analysis. Research in this area focuses on developing a suite of instrumentation for fast, accurate, highly sensitive, and discriminatory real-time analyses of chemical and biological natural or human-made agents. Such instruments are ideally suited for identifying and quantifying many gases and pollutants, trace isotopic species, metabolic products in the breath, and chemical precursors and products from industrial processes. Some of these techniques can be developed for remote probing over long optical paths for remote interrogation of trace absorption features. Our infrared methods are supported by a state-of-the-art, high-resolution infrared spectroscopy laboratory that also is used for studies of the structures and dynamics of molecular species important in contaminant chemistry, photochemistry, and atmospheric processes. The high-resolution infrared spectroscopy laboratory is shown in Figure 7.

Figure 7. The high-resolution infrared spectroscopy laboratory is used by numerous users and U.S. government agencies to obtain high-resolution infrared spectra for applications in remote sensing, atmospheric science, space and planetary research, and infrared databases.

Analyses of Environmental Aerosols Characterization of particulate matter in the atmosphere represents a unique challenge. Several approaches for both bulk and single particle analyses are employed that, in combination, are designed to understand the evolving inventory of atmospheric particulate matter and how particulates are changed by reactions with gas-phase species, photochemistry, and condensation and evaporation processes.

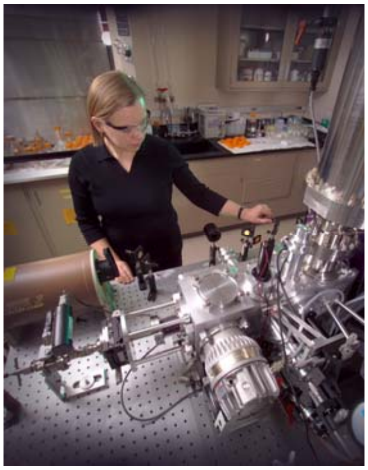

Figure 8. The second-generation single particle laser ablation time-of-flight mass spectrometer offers users the versatility of laboratory studies and field campaigns.

CPCS Facility capabilities relevant to aerosol characterization and aerosol chemistry research include single-particle mass spectrometry that provides real-time sampling and analysis of aerosol particles in laboratory and field studies, a variety of electron microscopy and microanalysis techniques for in-depth analysis of individual particles, and high resolution mass spectrometry for analysis of high molecular weight organic species (oligomers) in bulk aerosol samples. Figure 8 shows a unique, high-precision time-of-flight spectrometer used to study fundamental processes that govern the chemistry and physics of particles on the nano and micro scales.

In conjunction with these analytical techniques, an array of special devices is being developed and deployed to collect and preserve aerosol samples for later analysis of in the laboratory. For example, in 2006 CPCS Facility researchers took part in a four-week field study in Mexico City (Figure 9), with the goal to characterize aerosol formation and changes in aerosol composition, size distribution, light scattering coefficient, absorption coefficient, optical depth, soot-specific absorption, and radiative fluxes at selected vertical and horizontal locations in the outflow downwind of Mexico City.

Figure 9. EMSL staff have studied aerosols and aerosol transformations in many locations, such as Mexico City.

Together these analytical and sampling approaches and sampling techniques provide information over a broad range of particle types, chemistry, size, and morphology, leading to a more comprehensive understanding of the relationship between particles composition and their climate-related effects. In field studies, information is also correlated with meteorology data to understand possible sources and transport patterns of aerosols.

Instrument Upgrades

In 2006, the CPCS Facility made several upgrades and procurements:

- **Vacuum and turbo pump replacements.** Six systems were purchased and delivered, with four in use by September 2006.
- **Environmental scanning electron microscope.** Two systems were procured, with one received in September 2006.
- **Laser development and documentation.**
- **Fourier transform ion cyclotron resonance data acquisition system.** This new system was procured to replace an older system no longer serviced by its vendor. This instrument will support structural and thermodynamic studies of molecules. Full operation of this instrument is expected in early Fiscal Year 2007.
- **Zeiss Incubator and QuadView System.** This new system will be used for cell growth control and protein imaging. It is expected to be operational in early Fiscal Year 2007.
- **Photo-emission electron microscope cooling and sample transport mechanism.** This system will be used for studying catalytic and photocatalytic processes. It is expected to be operational in early Fiscal Year 2007.
- **High-sensitivity interface for proton transfer reaction mass spectrometer.** This system will extend detection limits for volatile organic compounds and allow real-time measurement of trace organic gases collected from atmospheric samples. It is expected to be operational in early Fiscal Year 2007.
- **High-resolution time-of-flight mass spectrometer and light-scattering module.** This system will be used for rapid single-particle measurements of complex organic species in particulates. It is expected to be delivered in mid-Fiscal Year 2007 and operational soon after.
- **High-resolution mass spectrometer LTQ-Orbitrap and support instrumentation.** This system will be used for chemical characterization of organic aerosols. This system is expected to be fully operational in mid-Fiscal Year 2007.

Future Directions

The CPCS Facility plans to support approximately 90 users and 8 distinctive users in Fiscal Year 2007. To provide the most effective support to projects and programs at EMSL, it is necessary to keep pace with state-of-the-art capabilities in characterizing the fundamental interactions among solids, liquids, and gases on a particle to the molecular level to understand the basic chemistry and physics of complex environmental and engineered systems. This will be done by:

- **Extending experimental characterization and description** of chemical reactions to encompass the effects of condensed media and interfaces.
- **Describing interfacial chemical processes** relevant to improved energy technologies, and understanding and mitigating the environmental impacts of energy use.
- **Creating state-of-the-art research and analytical methods** for characterizing complex materials of the types found in catalysts, natural and contaminated human-made systems.
- **Studying reaction mechanisms** at liquid interfaces, high-energy processes at interfaces, models of the condensed phase, and single molecule/particle kinetics and dynamics.

Gold Apes Hydrogen. The Structure and Bonding in the Planar $B_7Au_2^-$ and B_7Au_2 Clusters

HJ Zhai,[(a)] LS Wang,[(a)] DY Zubarev,[(b)] and AI Boldyrev[(b)]

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(b) Utah State University, Logan, Utah

Clusters are groups of a small number of atoms that often have chemical and physical properties that are different than the corresponding bulk materials. Understanding the underlying physical and structural reasons for these unique properties may allow for improved materials for electronics, sensors, and catalysis.

Pure boron clusters have received limited experimental attention in the literature during the past couple of decades. A major breakthrough has resulted from a series of recent joint experimental and theoretical studies that have established that all small boron clusters are planar or quasi-planar. These studies have shown that photoelectron spectroscopy in conjunction with accurate *ab initio* calculations is a powerful approach to elucidate the complex structures of atomic clusters. Furthermore, the theoretical analysis has yielded detailed information about the chemical bonding in the clusters and allowed the planarity of the boron clusters to be understood on the basis of π and σ aromaticity/antiaromaticity.

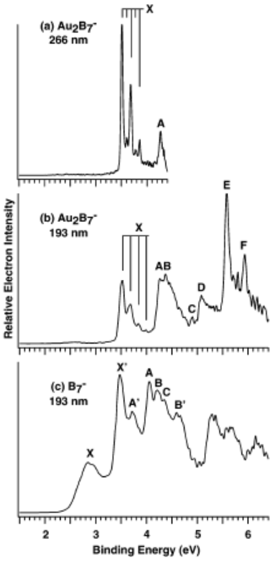

Figure 1. Photoelectron spectra of B_7Au_2 (a) 266 nm, (b) 193 nm, and of B_7^- (c).

The $B_7Au_2^-$ anions were produced using a laser vaporization cluster source and the photoelectron spectra obtained using a magnetic bottle-type photoelectron spectrometer. The photoelectron spectra of $B_7Au_2^-$ at 266- and 193-nm photon energies are shown in Figure 1 and are compared with that of B_7^-. The photoelectron spectra of $B_7Au_2^-$ are substantially simpler and better resolved than those of B_7^-, despite its larger size. Most surprisingly, despite the addition of two heavy atoms, the ground-state transition (X) of $B_7Au_2^-$ is completely vibrationally resolved at 266 nm (Figure 1a) with the excitation of two vibrational modes, a low-frequency mode of 790 cm^{-1}, and a high-frequency mode of 1380 cm^{-1}. The vibrationally resolved ground-state transition yielded an accurate electron affinity of 3.52 eV for B_7Au_2.

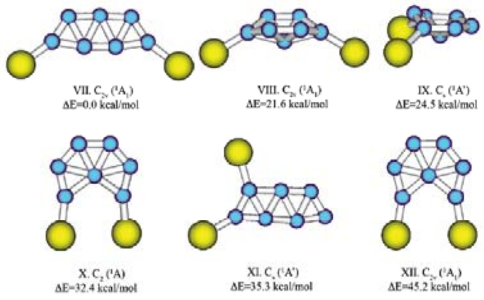

Figure 2. Global minima and low lying isomers of B_7Au_2.

Interestingly, the electron affinity of B_7Au_2 is very close to that of the elongated planar C_2V isomer for B_7 (3.44) corresponding to feature X′ in the spectrum of B_7^- (Figure 1c). Clearly, only one dominant isomer was present in the spectra of $B_7Au_2^-$. The observed $B_7Au_2^-$ cluster is likely to correspond to this isomer of B_7^- by adding two gold atoms to its two terminal B atoms similar to the ground-state structure of $B_7H_2^-$, as we expected.

To prove our hypothesis and confirm the observed $B_7Au_2^-$ structure, we performed quantum chemical calculations for a variety of $B_7Au_2^-$ structures. Figure 2 shows the global minimum and low-lying isomers of $B_7Au_2^-$. The good agreement between the experimental and theoretical vertical detachment energies confirmed the theoretical prediction of the global minimum structure VII for $B_7Au_2^-$, which is the same as that of $B_7H_2^-$.

The similarity in stability, structure, and bonding in the global minima of $B_7Au_2^-$ and $B_7H_2^-$ is analogous to the previous discovery of the gold/hydrogen analogy in silicon-gold clusters. Similar to the silicon-gold bond, which is highly covalent, we found that the boron-gold bonds in $B_7Au_2^-$ are also highly covalent with very little charge transfer from gold to boron. This is again due to the close electronegativity of boron and gold as a result of the strong relativistic effects in gold. This study demonstrates that the gold/hydrogen analogy may be a more general phenomenon and may exist in many species involving gold. The gold/hydrogen analogy will not only extend our understanding of the chemistry of gold, but will also be highly valuable in predicting the structures and bonding of many gold alloy clusters.

This exciting research appears in a recent issue of *The Journal of Chemistry A* and is featured on the cover (Figure 3).

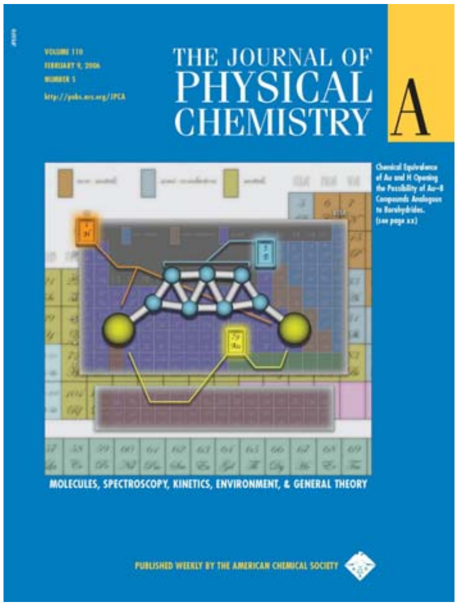

Figure 3. Cover of the February 9, 2006, issue of *The Journal of Physical Chemistry A*.

Citation

Zhai HJ, LS Wang, DY Zubarev, and AI Boldyrev. 2006. “Gold Apes Hydrogen. The Structure and Bonding in the Planar B_7Au_2- and B_7Au_2 Clusters.” *Journal of Physical Chemistry A* 110(5):1689-1693.

Evidence of Hollow Gold Cages

S Bulusu,[a] X Li,[b] LS Wang,[b] and XC Zeng[a]

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(b) Washington State University Tri-Cities, Richland, Washington

In this work, the researchers have found that some gold atom clusters form structures with hollow cages. The existence of these cages may allow for the insertion of other atoms to create new materials with unique properties for a wide range of applications.

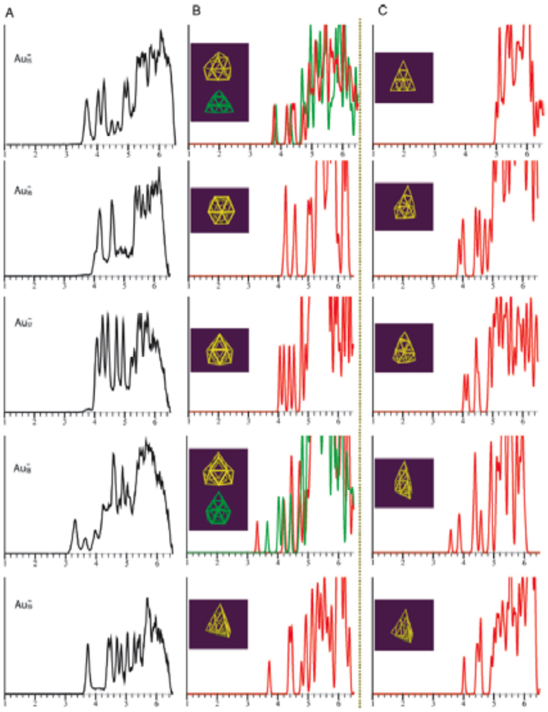

Figure 1. Experimental photoelectron spectra of Au_n^- (n = 15–19) compared with those simulated theoretically. (A) Experimental spectra measured at 193 nm (6.4 eV). (B) The simulated spectra for one (or two) lowest-lying isomer. (C) The simulated spectra for the non-hollow-cage candidate isomer.

The detection of carbon-free hollow cages has attracted much interest since the discovery and synthesis of the buckyball, C_{60}, and the higher fullerenes. Although “free-standing” inorganic cages have been synthesized, bare elemental metal cages have not been observed in nature or detected in the laboratory. Among metals, gold has unique properties, including strong relativistic effects and aurophilic attraction. Recently, a fullerene-like hollow cage with 32 gold atoms was predicted to be highly stable. However, photoelectron spectroscopy (PES) combined with theoretical calculations shows that at this relatively large size the overwhelming population of low-lying clusters for Au_{32} near room temperature appears to consist of only compact structures because of the entropic factor. Other, larger gold clusters with cage-like local minimum structures also have been suggested, but none have been observed experimentally. Conversely, it has been established from both ion-mobility and PES experiments that the most stable anion gold clusters (Au_n) in the size range n = 5–13 possess planar structures and that a structural transition from planar to three-dimensional structures occurs at n = 14. Beyond n = 14, previous global-minimum searches based on empirical potential functions of gold or semi-empirical tight-binding models of gold suggest that all low-lying isomers of gold clusters assume space-filling compact structures. Among the larger gold clusters, Au_{20} is the most interesting; it has been found to possess a pyramidal structure with tetrahedral symmetry just as carved out of the bulk face-centered cubic crystal.

To elucidate the structural transition from the planar Au at n = 13 to the pyramidal Au_{20}, we carried out a joint experimental PES and theoretical study on Au_n^- for n = 15–19. The measured spectra are shown in Figure 1A with numerous well-resolved features in the lower binding energy part, which are used to compare with theoretically simulated spectra (Figures 1B and 1C) with the candidate lowest-energy clusters.

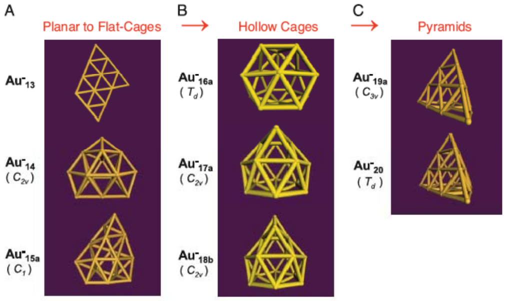

Figure 2. Structural evolution of mid-sized gold anion clusters from Au_{13} to Au_{20}. (A) The two-dimensional planar to three-dimensional flat-cage structural transitions (11). (B) The hollow gold cages with diameters 5.5 Å. (C) The pyramid-like clusters, which resemble bulk gold.

Remarkably, we observed that all but a total of three candidate lowest-energy isomers of Au_{16}^- , Au_{17}^-, and Au_{18}^- are "hollow cages" with an empty interior space. The interior space (typically with length scale 5.5 Å) of these hollow cages can easily host a foreign atom. Among the five candidate lowest-energy structures of Au_{15}^-, three are flat-cage structures, whereas the other two are pyramid-like structures. Previous studies have shown that in stable gold clusters, gold atoms tend to have a maximum coordination number of six (e.g., in the two-dimensional planar structures of Au_9 to Au_{13} and in the pyramidal structure of Au_{20}). Hence, it is understandable that both the flat-cage and pyramid-like structures are energetically competitive for the gold clusters within the size range Au_{14} to Au_{20}. Conversely, it is quite surprising that the hollow-cage structures dominate the low-lying population of Au_{16}^- to Au_{18}^- clusters. Specifically, at Au_{16}, only one of the five candidate lowest-energy structures has a flat-cage structure whose interior length scale can be 5 Å. The structural transition from hollow-cage to pyramid-like structure appears to occur at Au_{19}. To illustrate the structural evolution of gold clusters from two-dimensional planar to three-dimensional flat-cage, hollow-cage, and pyramid-like structures, we show in Figure 2 those candidate lowest-energy clusters that can provide a reasonable match to the experimental photoelectron spectra (Figures 1A and B). Our first-principles global search provides the electronic energy based evidence that the overwhelming majority of the low-lying clusters of Au_{16}^- to Au_{18}^- exhibit hollow-cage structures. These clusters and their larger neighbors are stable at room temperature; the size of the hollow should allow for other atoms to be trapped inside. The interior doping of these hollow clusters may dramatically change the cluster properties and thereby allow for the tailoring of the clusters for specific applications. This work was featured on the

Figure 3. May 23, 2006, issue of the *Proceedings of the National Academy of Science.*

cover of the May 23, 2006, issue of the *Proceedings of the National Academy of Science* (Figure 3) Bulusu et al. 2006).

Citation

Bulusu S, X Li, LS Wang, and XC Zeng. 2006. "Evidence of Hollow Golden Cages." *Proceedings of the National Academy of Science* 103(22):8326-8330.

Imaging Adsorbate O-H Bond Cleavage: Methanol on TiO_2(110)

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The wide-ranging importance of titanium oxide (TiO_2) in heterogeneous catalysis, photocatalysis, sensor applications, and hydrogen production using solar cells has made this surface one of the most extensively studied. Despite this extensive research attention, the interactions of well-characterized TiO_2 surfaces with simple molecules that participate in a number of catalytic reactions on TiO_2 are not well understood. This study focused on further developing our understanding these fundamental reaction mechanisms with the intent of further exploiting the properties of this technologically important material.

The thermal and photocatalytic oxidation of simple alcohols has been extensively studied on TiO_2 surfaces as a prototype for the catalytic oxidation of organic contaminants. Among them, methanol (CH_3OH), which is one of the simplest organic molecules, is often adopted as a probe. Experiments have shown that both molecular and dissociative adsorption take place on defective rutile TiO_2(110) surfaces. Methanol dissociation occurs primarily on bridge-bonded oxygen vacancy (BBOV) defect sites with some evidence for CH_3OH dissociation at non-defect sites as well. First-principle calculations show that on a stoichiometric surface, the dissociative adsorption of CH_3OH can occur via both O-H and C-O bond scission and that it is slightly favored over molecular adsorption. However, the atomic level understanding of these systems is still missing.

Scanning tunneling microcopy (STM) is an ideal analytical tool that allows researchers to track adsorbates on different surface sites. In this study, we employed *in situ* STM to follow the adsorption and dissociation of CH_3OH on BBOVs of TiO_2(110). Experiments were performed in an ultrahigh vacuum variable-temperature STM chamber. Figure 1 shows a set of STM images obtained from the same TiO_2(110) area before and after dosing with CH_3OH at 300 K. Figure 1a represents a clean surface before CH_3OH adsorption. The bright rows on Figure 1a are identified as the fivefold coordinated Ti^{4+} ions; the dark rows are the bridge-bonded oxygen (BBO) ions. The bright spots between the Ti^{4+} rows are assigned to BBOVs, believed to act as the primary dissociation centers for the alcohols. Statistically, the number density of BBOVs on this surface is about 8% with respect to the number of Ti^{4+}. The magnified images (insets in Figure 1) highlight the position of six BBOV sites (marked by yellow circles in Figure 1a) to illustrate the processes observed during CH_3OH adsorption.

The surface after an 80-s methanol dose is shown in Figure 1b. The CH_3OH adsorption-induced features appear as bright features on the BBOVs. The spatial location of adsorption sites becomes apparent from comparison of the magnified areas in the insets of panels “a” and “b” in Figure 1. The pattern of the bright features (marked with blue circles on the of panel b inset) is the same as the BBOV pattern on the clean surface (yellow circles on the panel a inset), indicating that CH_3OH preferentially adsorbed on the BBOVs. Comparing line profiles along the [001] direction shows that the bright features are 0.8 Å higher than BBOVs and that the CH_3OH-induced bright features have their maxima located on the original BBOV sites, but are asymmetric. This finding suggests that these features originate from two different chemical species present on neighboring BBO sites, in accord with the previously observed formation of hydroxyl and methoxy species resulting from the dissociative adsorption of CH_3OH. This process is shown schematically in Figure 1f.

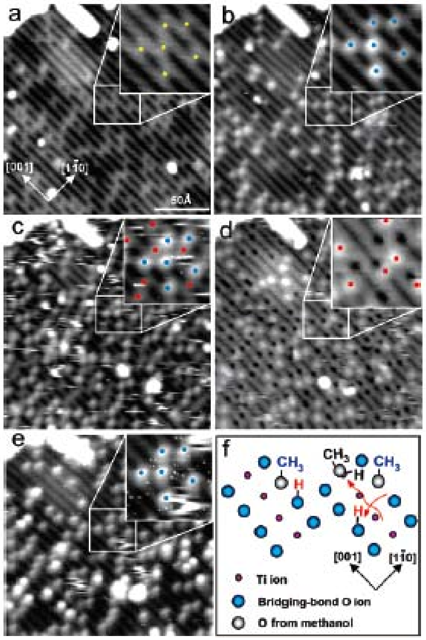

Figure 1. STM images of same area before and after adsorption of CH_3OH on $TiO_2(110)$ at 300 K: (a) bare surface; (b) after 80-s exposure to CH_3OH ; (c) after 110-s exposure to CH_3OH ; (d) taken on (c) after spontaneous tip change; (e) after high bias sweep of (c); (f) schematic of the adsorption process.

We conclude that CH_3OH dissociates on BBOVs via O-H bond scission. In the case of C-O bond scission, the hydroxyl rather than the methoxy group would appear on the original BBOV sites. At high coverage levels (Figure 1c), all the hydroxyl groups appear to be spatially separated from the methoxy groups (bright/gray; 1:1) as they migrated away from their original geminate sites. We propose that diffusing CH_3OH molecules assist hydroxyl migration, most likely through proton “hopping.” At CH_3OH coverage below the BBOV coverage, the CH_3OH molecules diffusing on Ti^{4+} rows dissociate after encountering an empty BBOV. At CH_3OH coverage exceeding the BBOV coverage, excess CH_3OH is mobile and leads to the observed dramatic increase in hydroxyl migration. Figure 2 shows a schematic model for CH_3OH-assisted hydroxyl migration on $TiO_2(110)$. Repeated imaging of the same area provides additional evidence for the high mobility of hydroxyls at high CH_3OH coverage. We believe this mobility is facilitated by molecular CH_3OH diffusing along the Ti^{4+} rows: as much as 40% of the hydroxyls changed position in two consecutive images (3 min).

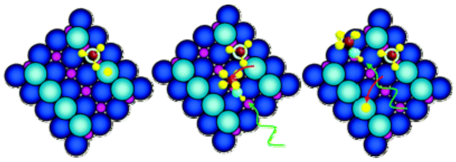

Figure 2. A schematic for methanol-assisted hydroxyl migration on $TiO_2(110)$.

In summary, we present the first atomically resolved images of dissociative methanol adsorption on BBO vacancies of $TiO_2(110)$. Imaging of the same area before and after adsorption allowed us to establish that the dissociation proceeds via O-H bond scission. At CH_3OH coverage below the BBO vacancy coverage, the methoxy and hydroxyls occupy primarily neighboring BBO sites. At higher levels of coverage, facile hydroxyl migration assisted by mobile, Ti^{4+}-bound CH_3OH molecules is observed.

This research is described in more detail in Zhang et al. 2006.

Citation

Zhang ZR, O Bondarchuk, JM White, BD Kay, and Z Dohnalek. 2006. "Imaging Adsorbate O-H Bond Cleavage: Methanol on $TiO_2(110)$." *Journal of the American Chemical Society* 128(13):4198-4199.

Pb_{12}^{2-}: Plumbaspherene

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(a) Washington State University Tri-Cities, Richland, Washington
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In this work, the research team discovered a new class of endohedreal lead-cage compounds that they have named "plumbaspherenes." The existence of these new cage compounds may allow for the insertion of other atoms inside of these cages to create new materials with unique properties for a wide range of applications.

During recent photoelectron spectroscopy (PES) experiments aimed at understanding the semiconductor-to-metal transition in tin clusters, we found the spectra of Sn_{12}^- to be remarkably simple and totally different from the corresponding Ge_{12}^- cluster. This observation led to the discovery of a C_{5V} cage structure for Sn_{12}^-, which is only slightly distorted from the icosahedral (Ih) symmetry as a result of the Jahn-Teller effect. However, adding an electron to Sn_{12}^- resulted in a highly stable and closed-shell I_h Sn_{12}^{2-} cage cluster. Because of the large 5p-5s energy separation, the I_h Sn_{12}^{2-} cage was found to be bound primarily by the $5p^2$ electrons, which form four radial π bonds and nine in-sphere σ bonds, with the $5s^2$ electrons behaving like lone pairs. The Sn_{12}^{2-} cage was shown to be iso-electronic to the well-known $B_{12}H_{12}^{2-}$ molecule with the $5s^2$ lone pairs replacing the localized B-H bonds, and was named "stannaspherene" for its π-bonding characteristics and high symmetry.

In this highlight, we report both experimental and theoretical evidence that the corresponding Pb_{12}^{2-} cluster also exists as a highly stable I_h cage that has an even larger interior volume than stannaspherene and can host most transition metal atoms in the periodic table to form a new class of endohedral cage clusters.

Experimental evidence was obtained with a PES apparatus consisting of a laser vaporization supersonic cluster beam source and a magnetic bottle electron analyzer. Figure 1 shows the

PES spectra of Pb_x^- (x = 11-13) at 193 nm. Clearly, the Pb_{12}^- spectrum is special relative to those of its neighbors, showing only four bands (i.e., the X, A, B, and C bands), whereas much more complex spectral features are observed for Pb_{11}^- and Pb_{13}^-. This observation suggests that Pb_{12}^- should possess a relatively high symmetry structure. The current experimental data are better resolved spectra, have more accurate electron binding energies, and have more spectral features to cover the valence spectral range. As such, useful insights into these experimental results can be obtained from high-quality *ab initio* quantum mechanical calculations.

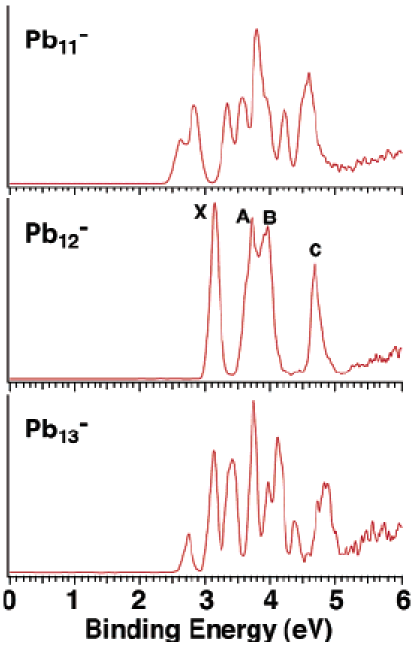

Figure 1. Photoelectron spectra of Pb_x^- (x = 11-13) at 193 nm. Note the relatively simple spectral pattern of Pb_{12}^- with respect to those of Pb_{11}^- and Pb_{13}^-.

Results of these calculations are shown in Figure 2. Geometry optimization for Pb_{12}^- from a high-symmetry icosahedral cage led to a Jahn-Teller distorted lower symmetry C_{5V} ($^2A_1$) species (Figure 2a) that is analogous to Sn_{12}^-. The computed first vertical detachment energy (3.08 eV) of the C_{5V} Pb_{12}^- is in excellent agreement with the experimental value of 3.14 eV. Whereas ion mobility experiments suggest that Pb_x^+ clusters possess compact near-spherical morphologies, several theoretical studies have given various structures for neutral Pb_{12}. However, we find that the doubly charged Pb_{12}^{2-} species is a highly stable and a perfect I_h cage with a closed electron shell (Figure 2b). Analogous to Sn_{12}^{2-}, which has been named stannaspherene for its π-bonding characteristics and its nearly spherical structure, we suggest the name "plumbaspherene" for the highly stable and robust Pb_{12}^{2-} cage. As such, we expect that the Pb_{12}^{2-} plumbaspherene should also be a stable species in solution and can be synthesized in the condensed phase. Plumbaspherene has a computed diameter of 6.29 Å, which is slightly larger than that of stannaspherene (6.07 Å). Thus, it is expected that Pb_{12}^{2-} can trap an atom inside its cage to form endohedral plumbaspherenes, M@Pb_{12}.

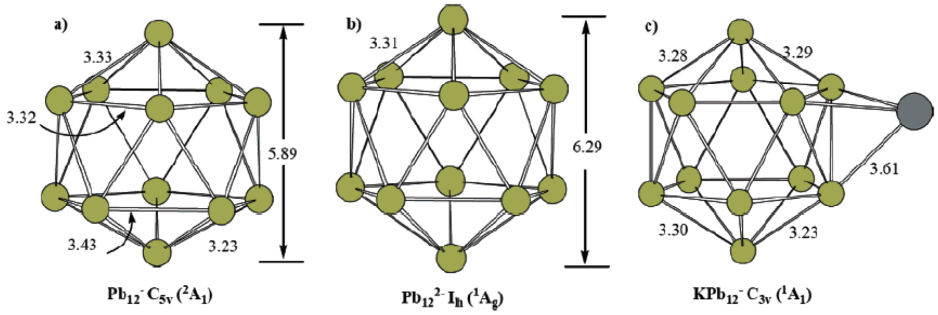

Figure 2. Optimized structures: (a) Pb_{12}^-, (b) Pb_{12}^{2-}, and (c) KPb_{12}^-. The bond distances and cage diameters are in Å.

We expect that a whole new family of stable M@Pb_{12} endohedral clusters may exist, analogous to the endohedral fullerenes. The plumbaspherene cages may be able to host a variety of transition metal atoms, thus creating a new class of endohedral cage clusters. Varying the host metal inside an M@Pb_{12} cage may dramatically change the properties of the cluster, thereby allowing the clusters to be tailored for specific applications. This exciting work was featured on the cover of the August 31, 2006, issue of *The Journal of Physical Chemistry A* (Figure 3).

Figure 3. Plumbaspherence shown on the cover of the *Journal of Physical Chemistry A.*

Citation

Cui LF, X Huang, LM Wang, J Li, and LS Wang. 2006. "Pb_{12}^{2-}: Plumbaspherene." *Journal of Physical Chemistry A* 110(34):10169-10172.

User Projects

Low-coordinated Oxygen Sites on MgO Surfaces

O Diwald, E Knozinger, Vienna University of Technology, Wien, Austria

High-resolution Gas-phase UV- and IR-absorption Cross-sections of Naphthalene to Calibrate the First DOAS Detection of Naphthalene in Mexico City

MJ Molina, Massachusetts Institute of Technology, Cambridge, Massachusetts

RM Volkamer, University of California, San Diego, La Jolla, California

Study of Martensitic Transformations in Shape Memory Alloys by Real-time Measurement of Surface Work Function Change

M Cai, JT Dickinson, Washington State University, Pullman, Washington

AG Joly, G Xiong, WP Hess, Pacific Northwest National Laboratory, Richland, Washington

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

Properties of Ice and Liquid Interfaces (Kay's BES-Surface Kinetics, PNNL Scope #16248)

JP Cowin, HM Ali, Pacific Northwest National Laboratory, Richland, Washington

MJ Iedema, Environmental Molecular Sciences Laboratory, Richland, Washington

Y Lilach, Unknown, Richland, Washington

Characterization of Quantum Cascade Lasers

J Kelly, Pacific Northwest National Laboratory, Richland, Washington

MA Mangan, Sandia National Laboratory, Albuquerque, New Mexico

Photoreflectivity in Ge/Si Thin Films

AG Joly, Pacific Northwest National Laboratory, Richland, Washington

D Brewe, Argonne National Laboratory, Argonne, Illinois

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

E Stern, University of Washington, Seattle, Washington

Energetic Processes: Reaction in Thin Organic Films

GB Ellison, University of Colorado, Boulder, Colorado

Mechanisms of Fragmentation of Post Translationally Modified Peptides

H Lioe, RA O'Hair, University of Melbourne, Melbourne, Victoria, Australia

J Laskin, Pacific Northwest National Laboratory, Richland, Washington

Theoretical Studies of Kinetic Processes in Nanoscale Ice Films

BD Kay, RS Smith, Z Dohnalek, Pacific Northwest National Laboratory, Richland, Washington

HN Jonsson, University of Iceland, Reykjavík, Iceland

Thrust 4: Surface Enhanced Raman-AFM and Antibody Force Microscopy (LDRD: Cytochrome and Whole Cell Ineteractions with Iron Oxides)

HP Lu, Bowling Green State University, Bowling Green, Ohio

Laser Ablation/Ionization Characterization of Solids

JT Dickinson, Washington State University, Pullman, Washington

Probing the Electronic Structure of Metal Clusters

X Li, Washington State University, Richland, Washington

L Cui, Ln Wang, L Wang, H Zhai, J Yang, W Huang, Washington State University Tri-Cities, Richland, Washington

Energetics of Dissociation of Peptide Radical Cations

J Laskin, JH Futrell, Z Yang, Pacific Northwest National Laboratory, Richland, Washington

IK Chu, N Lam, The University of Hong Kong, Pokfulam, Hong Kong

Photoelectron Emission Microscopy (PEEM) Study of Cu Nanoparticles on TiO2(110)

WP Hess, Pacific Northwest National Laboratory, Richland, Washington

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

JM White, W Wei, University of Texas at Austin, Austin, Texas

Atomically Resolved Studies of Adsorbates on TiO_2(110)

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O Bondarchuk, JM White, S Li, Y Kim, University of Texas at Austin, Austin, Texas

Develop a Procedure for the Determination of the Calibration Parameters on the Host Side and Integrate Them into the Hardware to Facilitate Real Time Multiband Analysis

MB Sowa, KA Perrine, Pacific Northwest National Laboratory, Richland, Washington

AM Mayampurath, Utah State University, Logan, Utah

Infrared and CARS Spectroscopy of Cyclopropane

JW Nibler, Oregon State University, Corvallis, Oregon

J Kelly, Pacific Northwest National Laboratory, Richland, Washington

A Masiello, National Institute of Standards and Technology, Gaithersburg, Maryland

Aerosol and Organic Precursor Measurements at Ground-Based Sites during the Megacity Aerosol Experiment in Mexico City 2006 (MAX-Mex 2006)

JS Gaffney, University of Arkansas, Little Rock, Little Rock, Arkansas

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V Shutthanandan, Environmental Molecular Sciences Laboratory, Richland, Washington

RJ Hopkins, Lawrence Berkeley National Laboratory, Berkeley, California

PW Lunn, RC Petty, DOE BER Climate Change Research ASP, Washington DC, Wash DC

R Gonzalez, Molina Center for Strategic Studies in Energy and the Environment, La Jolla, California

Aerosol Composition and Hydrocarbon Measurements from the DOE G-1 Aircraft during the Megacity Aerosol Experiment in Mexico City (Max-Mex)

Ln Kleinman, Brookhaven National Laboratory, Upton, New York

JV Ortega, Environmental Molecular Sciences Laboratory, Richland, Washington

High Resoulution Infrared Spectroscopy of Methyl Phosphonic Difluoride

J Kelly, Pacific Northwest National Laboratory, Richland, Washington

Chemical Ionization Mass Spectrometry of Organic Aerosols

PN Irving, Innovatek, Inc., Richland, Washington

VB Mikheev, Battelle Columbus, Columbus, Ohio

High Resolution Infrared Spectroscopy of Trans-Hexatriene

RL Sams, Pacific Northwest National Laboratory, Richland, Washington

A Masiello, National Institute of Standards and Technology, Gaithersburg, Maryland

NC Craig, Oberlin College, Oberlin, Ohio

High and Moderate Resolution Infrared Spectroscopy of Diiodomethane

TJ Johnson, Pacific Northwest National Laboratory, Richland, Washington

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Dynamic Changes in Molecular Interactions along the Circadian Rhythm

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HB Pakrasi, Washington University in St. Louis, St. Louis, Missouri

T Ogawa, Shanghai Institute of Plant Physiology and Ecology, Shanghai, China

AFM Imaging of Photo System Protein in Photosynthetic Membranes

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HP Lu, Bowling Green State University, Bowling Green, Ohio

Reactive and Non-Reactive Deposition of Hyperthermal (1-100 eV) Peptide Ions Surfaces

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PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

Mechanisms of Organic Ions Release from Water Droplets

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High Resolution Infrared Spectroscopy of cis-cis and trans-trans Difluorobutadiene

NC Craig, Oberlin College, Oberlin, Ohio

High Resolution Infrared Spectroscopy of the 360 cm^{-1} Band of Acetonitrile

L Brown, Jet Propulsion Laboratory, Pasadena, California

Comparative Analysis of Growth and Morphology among Citric Acid Producing and Non-Producing Strains of *Aspergillus niger*

KS Bruno, Z Dai, LL Lasure, Pacific Northwest National Laboratory, Richland, Washington

Morphology and Composition of Encoded Segmented Metal Oxide Nanowires

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Environmental Effects of Aircraft Engine Exhaust Particles

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CW Spicer, MW Holdren, Battelle Columbus, Columbus, Ohio

Oxidation of Atmospheric Organic Particulate Matter

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Visualization of Gamma H_2AX Foci

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WF Morgan, University of Maryland, Baltimore, Maryland

Chemical Characterization of Arrays of TiO_2 Nanocolumns

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B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

C Mullins, DW Flaherty, University of Texas at Austin, Austin, Texas

Measurement of Ambient Concentrations of Aerosols to Support the Analysis of MIRAGE Urban Plume Transport and Chemistry

BK Lamb, Washington State University, Pullman, Washington

Chemistry and Microphysics of the Small Particles

BJ Finlayson-Pitts, Y Yu, M Ezell, University of California, Irvine, Irvine, California

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JV Ortega, ML Alexander, MK Newburn, Environmental Molecular Sciences Laboratory, Richland, Washington

K Mueller, State University of New York at Stony Brook, Stony Brook, New York

Y Han, Y Cai, Unknown, Richland, Washington

Nanoscale Insight into the Living Cell Membrane Responses to Ultrafine PM

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C Rodriguez, Washington State University Tri-Cities, Richland, Washington

FRET Screening of Protein-Protein Interactions in *Shewanella*

GN Orr, MF Romine, DJ Panther, B Hooker, HS Wiley, Pacific Northwest National Laboratory, Richland, Washington

Regulation of Cell Surface Ligand Dynamics

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SPLAT: Real-Time Characterization of Individual Exhaust Particles

A Zelenyuk, Pacific Northwest National Laboratory, Richland, Washington

Y Cai, Unknown, Richland, Washington

Aerosol Aging and Climate Change

JP Cowin, Y Liu, Pacific Northwest National Laboratory, Richland, Washington

MJ Iedema, A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

X Yang, Fudan University, Shanghai, China

In situ Probe of Oxidation at Environmental Interfaces

JP Cowin, Y Liu, Pacific Northwest National Laboratory, Richland, Washington

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Optical and Hygroscopic Properties of Atmospheric Aerosols

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L Alvarez-Aviles, University of Alaska Fairbanks, Fairbanks, Alaska

Use of SEM/EDX Analysis to Study the Oxidation of Aerosol by Hydroxyl Radical

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Transition Metal Oxide Clusters - Electronic Structure and Chemical Bonding Using Photoelectron Spectroscopy

H Zhai, L Wang, Ln Wang, X Wang, Washington State University Tri-Cities, Richland, Washington

Spectral Library

SW Sharpe, TJ Johnson, RL Sams, DC Scott, RG Tonkyn, Pacific Northwest National Laboratory, Richland, Washington

TA Blake, Environmental Molecular Sciences Laboratory, Richland, Washington

Infrared Reflectance Spectroscopy of Soils

TA Blake, PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

Infrared Spectroscopy of Methyl Halides

TJ Johnson, Pacific Northwest National Laboratory, Richland, Washington

TA Blake, Environmental Molecular Sciences Laboratory, Richland, Washington

Personal Samplers for Traffic-Related Particle Exposures in NYC

SR Chillrud, Columbia University, palisades, New York

JP Cowin, Pacific Northwest National Laboratory, Richland, Washington

MJ Iedema, TA Seim, Environmental Molecular Sciences Laboratory, Richland, Washington

Electronic Properties of the Metal and Thin Film Oxide Insulator Junction

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

PTR-ITMS: Next Generation Aircraft Instrumentation

SP Garland, University of California, Davis, Redding, California

CM Berkowitz, Pacific Northwest National Laboratory, Richland, Washington

ML Alexander, MK Newburn, Environmental Molecular Sciences Laboratory, Richland, Washington

Innovative Aerosol Collector

ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

D Worsnop, J Jayne, Aerodyne Research Inc, Billarica, Massachusetts

Fundamental Investigations of Water Splitting on Model TiO_2

GA Kimmel, NG Petrik, Z Dohnalek, Pacific Northwest National Laboratory, Richland, Washington

CD Lane, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

The Non-Covalent Interaction of Some Aromatic Molecules with H_2O Studied with Photoelectron Energy Spectroscopy and Quantum Chemical Calculation

LN Wang, Washington State University Tri-Cities, Richland, Washington

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Development and Testing of a New Ion Trap Assembly

JA Lloyd, MV Johnston, University of Delaware, Newark, Delaware

ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

TA Smith, Genesee Community College, Arlington, Virginia

Laboratory Studies of Gas-Particle Reaction Kinetics of Particulates Emitted from Aircraft

JP Cain, H Wang, University of Southern California, Los Angeles, California

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Exploratory Synthesis of Novel Cluster-Based Nanomaterials

TL Hubler, Pacific Northwest National Laboratory, Richland, Washington

LN Wang, Z Sun, Washington State University Tri-Cities, Richland, Washington

MF Bertino, University of Missouri, Rolla, Rolla, Missouri

Infrared Spectra of HCN at Low Temperatures

MA Smith, NASA Langley Research Center, Hampton, Virginia

Infrared Spectral Library of Bacterial Spores

TJ Johnson, NB Valentine, Pacific Northwest National Laboratory, Richland, Washington

Vibration-Rotation Spectroscopy of Sulfur Trioxide

JW Nibler, Oregon State University, Corvallis, Oregon

J Kelly, Pacific Northwest National Laboratory, Richland, Washington

A Masiello, AN Webber, National Institute of Standards and Technology, Arlington, Virginia

AG Maki, Private, Mill Creek, Washington

Soft-Landing of Complex Ions on Surfaces

JR Green, RG Cooks, W Peng, MP Goodwin, Purdue University, West Lafayette, Indiana

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Z Zhu, PL Gassman, AS Lea, Environmental Molecular Sciences Laboratory, Richland, Washington

Chemistry of Aerosols in Mexico City: MILAGRO 2006 study.

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MK Gilles, RJ Hopkins, A Tivanski, Lawrence Berkeley National Laboratory, Berkeley, California

Chemical and Physical Properties of Biomass Burning Aerosol

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JL Hand, JL Collett, SM Kreidenweis, Colorado State University, Fort Collins, Colorado

A Laskin, CN Wang, Environmental Molecular Sciences Laboratory, Richland, Washington

Energy and Entropy Effects in Dissociation of Non-Covalent Complexes: A Combined Experimental and Theoretical Investigation

J Laskin, Z Yang, Pacific Northwest National Laboratory, Richland, Washington

Open Ocean Ship-Board Study of Atmospheric Aerosols at the Equatorial Pacific: Characterizing Iron in Marine Aerosol

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V Shutthanandan, Cn Wang, Z Zhu, A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

AM Johansen, LS Shank, Central Washington University, Ellensburg, Washington

JW Murray, University of Washington, Seattle, Washington

The Formation and Structure of Tropical Organic/Water Aerosols

GB Ellison, LA Cuadra-Rodriguez, University of Colorado, Boulder, Colorado

A Zelenyuk, J Laskin, Y Dessiaterik, Pacific Northwest National Laboratory, Richland, Washington

ML Alexander, A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

Development of Novel Microchip CE-MS Platform for Organic Aerosol Characterization

X Yu, Y Lin, Pacific Northwest National Laboratory, Richland, Washington

ML Alexander, L Saraf, Environmental Molecular Sciences Laboratory, Richland, Washington

Integrated Experimental and Modeling Studies on Secondary Organic Aerosol Formation

R Zaveri, SM Kathmann, A Zelenyuk, DA Maughan, JC Birnbaum, Pacific Northwest National Laboratory, Richland, Washington

SN Madronich, National Center for Atmospheric Research, boulder, Colorado

A Laskin, ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

JA Thornton, University of Washington, Seattle, Washington

Characterization of Organic Aerosols throughout the Depth of an Urban Planetary Boundary Layer: Proposed Field Deployment of EMSL Mass Spectrometers

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R Zhang, Texas A&M University, College Station, Texas

ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

D Worsnop, J Jayne, Aerodyne Research Inc, Billarica, Massachusetts

Secondary Organic Aerosol Formation

R Zaveri, X Yu, CM Berkowitz, C Song, Pacific Northwest National Laboratory, Richland, Washington

ML Alexander, MK Newburn, JV Ortega, Environmental Molecular Sciences Laboratory, Richland, Washington

High Resolution Infrared and Coherent Raman Studies of Propellane

RW Kirkpatrick, JW Nibler, Oregon State University, Corvallis, Oregon

A Masiello, A Weber, National Institute of Standards and Technology, Gaithersburg, Maryland

Infrared Spectra of the Fundamental Bands of $^{34}SO_2$

WJ Lafferty, National Institute of Standards and Technology, Gaithersburg, Maryland

JH Flaud, University of Paris-7, Creteil CEDEX, France

High Resolution Spectra of Phosphine in the 1370-800 Wavenumber Region

RL Sams, Pacific Northwest National Laboratory, Richland, Washington

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L Brown, Jet Propulsion Laboratory, Pasadena, California

Excitation of Surface Excitons in the Nanoscale Calcium Oxide Surface

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

O Diwald, Vienna University of Technology, Wien, Austria

Study of Martensitic Transformations in Shape Memory Alloys by Real-time Measurement of Surface Work Function Change

M Cai, JT Dickinson, Washington State University, Pullman, Washington

G Xiong, WP Hess, Pacific Northwest National Laboratory, Richland, Washington

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Laser Desorption from Metal Oxides

AL Shluger, PV Sushko, London, University College, London, United Kingdom

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Nanoparticle Fluorescence

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Investigation of Hydrogen Tunneling in Tropolone

RL Redington, Texas Technical University, Lubbock, Texas

Jet Spectrum of Nitromethane

DS Perry, University of Akron, Akron, Ohio

High Resolution Infrared Spectroscopy of Boron Trifluoride

AG Maki, Private, Mill Creek, Washington

High Resolution Infrared Spectroscopy of Metyl Nitrite

LM Goss, Idaho State University, Pocatello, Idaho

TA Blake, Environmental Molecular Sciences Laboratory, Richland, Washington

Pd Nanoclusters Supported on MgO(100): Effects of Cluster Size on Chemisorption Properties

RS Smith, Z Dohnalek, Pacific Northwest National Laboratory, Richland, Washington

SL Tait, S Fain, CT Campbell, University of Washington, Seattle, Washington

Laboratory Studies of Atmospheric Processing of Sea Salt

BJ Finlayson-Pitts, JN Pitts, RC Hoffman, WH Robertson, University of California, Irvine, Irvine, California

Development of an Electrospray Photoelectron Spectroscopy Apparatus with a Low Temperature Ion Trap

H Woo, Washington State University, Richland, Washington

LN Wang, X Wang, Washington State University Tri-Cities, Richland, Washington

Development of an Electrospray Photoelectron Spectroscopy Apparatus with a Low Temperature Ion Trap

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High Resolution Infrared Spectroscopy of Isotopically Substituted Butadienes

NC Craig, Oberlin College, Oberlin, Ohio

High Resolution Infrared Spectroscopy of Acetaldehyde

JT Hougen, National Institute of Standards and Technology, Gaithersburg, Maryland

Investigation of the Electronic Structure of Fe-S Clusters

T Ichiye, Y Fu, Washington State University, Richland, Washington

Ln Wang, X Wang, Washington State University Tri-Cities, Richland, Washington

X Yang, Fudan University, Shanghai, China

Investigation of Aromatic and Other Novel Gas Phase Atomic Clusters and Molecules

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Investigation of Aromatic and Other Novel Gas Phase Atomic Clusters and Molecules

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Computational Chemistry Modeling of Main-Group and Transition-Metal Cluster Systems

J Li, Environmental Molecular Sciences Laboratory, Richland, Washington

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S Li, Xinzhou Teachers University, Xinzhou, Shanxi, China

Adiabatic Following Spectroscopy Using Quantum Cascade Lasers

G Duxbury, University of Strathclyde, Glasgow, United Kingdom

Synthesis and Analysis of Organic Hydroperoxide by PTR-MS

BT Jobson, Washington State University, Pullman, Washington

TL Hubler, Pacific Northwest National Laboratory, Richland, Washington

ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

TG Karl, NCAR, Boulder, Colorado

Microscopic Studies of Hydration and Corrosion in Nuclear Materials Disposition

SA Joyce, Los Alamos National Laboratory, Los Alamos, New Mexico

Mexico City Municipal Area Air Pollution Study, 2003

BT Jobson, Washington State University, Pullman, Washington

JP Cowin, CE Seifert, Pacific Northwest National Laboratory, Richland, Washington

MJ Molina, LT Molina, KS Johnson, BM Zuberi, Massachusetts Institute of Technology, Cambridge, Massachusetts

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Surface Induced Dissociation of Peptides using FTICR Mass Spectrometry

J Laskin, JH Futrell, Pacific Northwest National Laboratory, Richland, Washington

FM Fernandez, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

K Kuppannan, VH Wysocki, KA Herrmann, University of Arizona, Tucson, Arizona

High-Resolution Infrared Spectroscopy of Nitrogen Dioxide and Water.

RL Sams, J Kelly, Pacific Northwest National Laboratory, Richland, Washington

MA Smith, NASA Langley Research Center, Hampton, Virginia

TA Blake, Environmental Molecular Sciences Laboratory, Richland, Washington

High Resolution Infrared Spectroscopy of Methane

J Kelly, RL Sams, Pacific Northwest National Laboratory, Richland, Washington

L Brown, Jet Propulsion Laboratory, Pasadena, California

Ultrasonic Catalysis of Chemical Reactions

KM Judd, Pacific Northwest National Laboratory, Richland, Washington

AM Williams, Gonzaga University, Spokane, Washington

Single Molecule Dymanics of Protein DNA Interactions

AD Shaller, AD Li, Washington State University, Pullman, Washington

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HP Lu, Bowling Green State University, Bowling Green, Ohio

Using the Environmental Scanning Electron Microscope for Studying the Atmospheric Transformations of Organic and Inorganic Particles

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Soft-landing of Peptide Ions on Surfaces

J Alvarez, RG Cooks, JR Green, Purdue University, West Lafayette, Indiana

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Real Time Trace Gas Measurements by Chemical Ionization Mass Spectrometry

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ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

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Inelastic Electron Scattering Cross Section Measurements in Liquid Water

RG Tonkyn, NG Petrik, Pacific Northwest National Laboratory, Richland, Washington

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Development of Data Analysis and Visualization Software - SpectraMiner

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Computer Programming of Data Acquisition Board for Single Particle Laser Ablation Time-of-flight Mass Spectrometer (SPLAT-MS)

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Determination of the Mo...OX Bond Strengths in Oxomolybdenum Model Complexes

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Laser-Materials Interactions: Theory and Experiment

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Single Particle Analysis of Smoke Aerosols During the Summer 2002 Yosemite Aerosol Characterization Study

JL Hand, Colorado State University, Fort Collins, Colorado

Second Harmonic Generation from Organic Water/Air Interfaces

AT Maccarone, GB Ellison, University of Colorado, Boulder, Colorado

Surface Induced Dissociation of Polyatomic Ions

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Single Molecule Approach for Understanding EGFR Molecular Interactions

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Electron Stimulated Reactions in Thin Water Films

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AG Kavetski, Khlopin Radium Institute, St. Petersburg, Russian Federation

Condensed Phase Chemical Physics of Low Temperature Amorphous Solids and Gas Surface Interactions

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Use of Fluorimeter in EMSL 1205 for Quantum Efficiency Studies on Semiconductor Quantum Dots

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Single Molecule Electron Transfer Dynamics

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Site-specific Spectroscopy and Optical Imaging

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AFM-enhanced FLIM and Raman Imaging

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Protein-protein Interaction Dynamics

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Microbial Cell Analysis and Imaging

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Ion Channel Protein Dynamics in Lipid Bilayer

PK Kienker, Yeshiva University, Albert Einstein College of Medicine, Bronx, New York

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Syntheses of Fe-S Cluster Complexes with Peptides as Terminal Ligands

Y Fu, Washington State University, Richland, Washington

L Wang, Washington State University Tri-Cities, Richland, Washington

Development of Multi-Functional Microscopy (MFM) for Cancer and AIDS Research

TJ Weber, L Rodriguez, Pacific Northwest National Laboratory, Richland, Washington

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Investigation of 4Fe-4S Cluster Complexes with Peptides as the Terminal Ligand

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L Wang, X Wang, Washington State University Tri-Cities, Richland, Washington

Atomically Resolved Studies of Transition Metal Oxides

RS Smith, Z Dohnalek, DJ Gaspar, Pacific Northwest National Laboratory, Richland, Washington

JM White, O Bondarchuk, University of Texas at Austin, Austin, Texas

Chemical Characterization of Heterogeneous Inclusions in Soot Particles

Z Yang, University of Delaware, Newark, Delaware

H Wang, University of Southern California, Los Angeles, California

Temperature-Dependent Yield of Frenkel Pairs Generated by Valence Excitation in NaCl

K Tanimura, Osaka University, Osaka, Japan

EMSL CAT in Analytical Mass Spectrometry

RG Cooks, JR Green, Purdue University, West Lafayette, Indiana

MV Johnston, University of Delaware, Newark, Delaware

H Woo, Washington State University, Richland, Washington

WL Hase, Texas Technical University, Lubbock, Texas

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FM Fernandez, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

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Early Transition Metal Oxides as Catalysts

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High Resolution Infrared Spectroscopy of BF_2OH

J Kelly, Pacific Northwest National Laboratory, Richland, Washington

JH Flaud, University of Paris-7, Creteil CEDEX, France

High Resolution Infrared Spectroscopy of Peroxynitric Acid

J Kelly, Pacific Northwest National Laboratory, Richland, Washington

WJ Lafferty, National Institute of Standards and Technology, Gaithersburg, Maryland

Metal Sulfide Clusters in the Environment

MV Johnston, JM Spraggins, University of Delaware, Newark, Delaware

J Laskin, Pacific Northwest National Laboratory, Richland, Washington

Photoelectron Spectroscopic Studies of Complex Anion Solvation in the Gas Phase

H Woo, Washington State University, Richland, Washington

Ln Wang, X Wang, W Huang, J Yang, Z Sun, Washington State University Tri-Cities, Richland, Washington

Phosphorous Poisoning of Automotive Catalysts

BG Bunting, Oak Ridge National Laboratory, Knoxville, Tennessee

Ultra-Trace Molecular Detection Instrumentation Based on Aerosol Nucleation with Rapid Preconcentration and Separation

H Woo, Washington State University, Richland, Washington

N Laulainen, O Egorov, Pacific Northwest National Laboratory, Richland, Washington

VB Mikheev, Battelle Columbus, Columbus, Ohio

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Environmental Spectroscopy and Biogeochemistry Facility

The Environmental Spectroscopy and Biogeochemistry (ES&B) Facility supports experimental and modeling studies of chemical phenomena and mechanisms on mineral and microbe surfaces and on complex heterogeneous environmental materials from soils, sediments, and groundwater zones. ES&B Facility staff members, along with other Pacific Northwest National Laboratory staff, form a multidisciplinary research team with expertise in chemistry, mineral physics, geochemistry, soil chemistry, microbiology, and hydrology and advanced computational methods.

Capabilities

Capabilities are available for materials characterization, aqueous- and solid-phase speciation and reaction/kinetic measurements, analytical environmental chemistry, molecular and thermodynamic geochemical process modeling, and intermediate-scale, reactive-transport studies. Research includes studies on:

- surface chemistry of Fe, Mn, and Al oxides; carbonates; and layer silicates
- redox reactions of organic and metal contaminants with Fe- and Mn-containing mineral solids
- biogeochemistry of Fe(III) and Mn(IV) oxide reduction by bacteria and associated bio-mineralization processes
- mineral surface structure and dynamics by modeling and microscopy
- sorbate surface structure and dynamics on mineral surfaces by spectroscopy
- reactivity and thermodynamics of contaminants at high ionic strengths
- intermediate scale subsurface flow and transport
- molecular, thermodynamic and kinetic modeling.

The ES&B Facility consists of seven laboratories that are proximally located to facilitate multi-technique studies. For example, environmental chambers are available with spectroscopic access to allow

Instrumentation & Capabilities

- Analytical chemistry instrumentation
- Scanning probe microscopy
- Spectrophotometers
- Laser fluorescence microscopy
- Laser spectroscopy and kinetic systems
- Scanning and transmission electronic microscopies
- Mössbauer spectroscopy
- Electron paramagnetic resonance spectroscopy
- Controlled atmosphere chambers
- Computational geochemical molecular modeling software and hardware
- Hydro- and biogeochemical modeling and software
- Subsurface flow and transport experimental laboratory
- Thermodynamics measurements of aqueous and adsorption reactions

controlled-atmosphere experiments. These laboratories are located near other instruments that are integral to environmental molecular science, including high-resolution scanning and transmission electron microscopies and a variety of ultrahigh vacuum microprobe techniques for surface analyses. The seven ES&B Facility laboratories are described below.

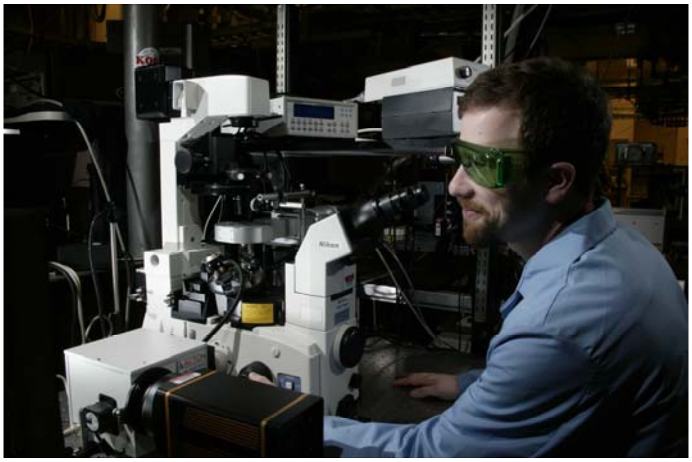
Figure 1. The ES&B Facility offers users an array of instruments, including fluorescence microscopies.

Optical Spectroscopy Laboratory. Laser-based-fluorescence, breakdown, nonlinear, and Raman spectroscopies and microscopies (Figure 1) are available to use in investigations of aqueous and interfacial reactions. Kinetic studies ranging from stopped-flow to ultra-fast optical pump-probe methods can be performed. Cryogenic capabilities and time-resolved detection methods from pico-second to millisecond for enhanced spectroscopic studies of solution and heterogeneous materials are available. State-of-science Fourier transform infrared (FTIR) spectrometers enable the study of various mineral-chemistry topics as well as sorbate binding mechanisms at mineral, biotic, and organic interfaces. The modular design of the spectrometers in this laboratory enables rapid changing of detector and beam-splitter combinations so researchers can readily change from the visible to the near-, mid-, or far-infrared wavelength ranges. A vacuum bench equipped with a helium-cooled bolometer and step-scanning capabilities is optimized for far-infrared measurements as well as time-resolved spectroscopy. A nitrogen-purged system equipped with a microscope and temperature-controlled mapping stage (-200 to 600°C) allows spatially resolved infrared measurements at the 60-µm level. A variety of cells are available for analyzing gas, liquid, solid, and slurry samples using a variety of techniques. Raman vibrational analyses can be obtained using the FT-Raman module and Raman confocal microscope.

Mössbauer Spectroscopy Laboratory. Four Mössbauer spectrometers with cryogenic capabilities allow studies of Fe structure and redox chemistry in oxides, clays, sediments and biogeochemical systems. Software incorporating Voigt-line fitting and quadrupole-splitting distributions enable state-of-science spectral deconvolution and fitting.

Electron Paramagnetic Resonance (EPR) Spectroscopy Laboratory. A continuous-wave, multi-frequency (S, X, and Q bands) EPR spectrometer equipped with helium-cooled cryostats and a stop-flow/freeze-quench system allows studies of free-radical reactions and electronic environments of paramagnetic species in solids, suspensions, and at surfaces.

Imaging Microscopy Laboratory. Optical and scanning-probe microscopies are available for particle imaging from millimeter to nanometer scales. An inverted optical microscope is available for time-resolved fluorescence imaging in a broad temperature range. Expertise is also available in the characterization of processes of microbial reduction and biogenic mineral formation by high-resolution transmission electron microscopy, involving lattice imaging, selected area diffraction, and energy dispersive spectrometer analysis. A state-of-science scanning-probe microscopy facility has been developed for imaging water-wet samples and microbe-water and mineral-microbe interfaces, and for characterizing a wide variety of environmental materials. A bio-atomic force microscope (AFM) scanning probe is available for protein imaging and force measurements. This new instrument will help researchers 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, and protein-protein interactions).

Environmental Analytical Chemistry Laboratory. A wide variety of instrumentation is available for quantification of inorganic and organic contaminants and their reaction, transformation, or degradation products. State-of-science separation instruments, including gas and high-performance liquid chromatographs coupled with mass spectrometry, are available to users engaged in diverse research activities. An inductively coupled plasma mass spectrometer with laser ablation for solids analysis and a collision cell for improved detection of oxide-interfering elements (e.g., Fe) is available for broad-spectrum, high-sensitivity inorganic analyses.

Computational Geochemistry. Multiple workstations linked to the computational infrastructure of the EMSL are available for molecular-level simulations and modeling to support research in the ES&B Facility. Experts are available to perform first-principles molecular dynamics calculations of molecular liquids and solid state systems as well as electronic structure calculations either as stand-alone activity or in support of experimental or spectroscopic measurements. Thermodynamic and kinetic geochemical codes also are available to users, as are multidimensional geochemical reaction/transport codes for numerical experiments or simulations of the intermediate-scale flow and transport experiments described below.

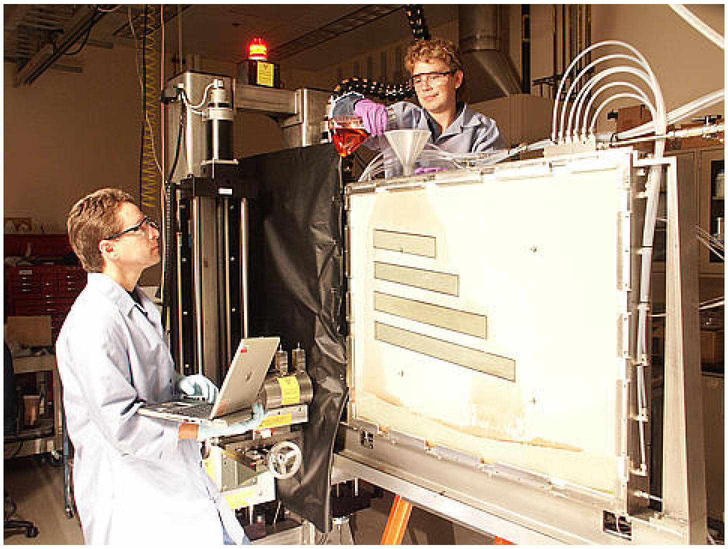

Figure 2. EMSL's Subsurface Flow and Transport Laboratory.

Subsurface Flow and Transport Experimental Laboratory (SFTEL). This laboratory (Figure 2) is uniquely equipped for intermediate-scale (i.e., meter-scale) experimentation in single-fluid and multifluid (air-water, air-nonaqueous-phase liquid [NAPL]-water, NAPL-water) porous media systems. These distinctive experimental systems allow testing of basic theories of flow and transport; studies of coupled processes involved with microbial, reactive chemical, or colloid transport; and experimental simulation of subsurface remediation scenarios. Close linkages exist between this center and the modeling facility, as both pre- and post-experiment modeling efforts are key to experimental design and interpretation. The main focus of the SFTEL is on intermediate-scale experimentation. The laboratory offers several meter-scale flow cells and columns for research in saturated and unsaturated porous media. Some of the flow cells and columns can be used in conjunction with a dual-energy gamma radiation system. The SFTEL also offers a fully automated saturation-pressure apparatus, as well as an automated system to measure fundamental hydraulic properties of soil.

Instrument Upgrades

In Fiscal Year 2006, the ES&B Facility made several upgrades and procurements. These capabilities are grouped by resource.

- **Spectroscopies.** The ES&B Facility demonstrated a laser-induced breakdown spectroscopy capability that will provide spatially resolved elemental analysis of geochemical samples at the micron scale. An infrared diode array detector became operational this past year and has been used to measure infrared fluorescence from technetium species and carbon nanotubes. A fluorescence spectrometer and an electronics upgrade for the confocal Raman spectrometer were procured to increase the efficiency of data collection. Continued investments have been made in an applied-field Mossbauer spectrometer, which is targeted for demonstration in Fiscal Year 2007.

  A confocal Raman microscope for the analysis of radiological samples was added to the facility. The research-grade Dilor XY 800 Raman spectrometer is a high-resolution, modular triple spectrometer that can be operated in high-resolution or high-throughput modes, with both bulk sample and confocal microscopic capability for spatially revolved analysis. In its current location at PNNL's 331 Building, significant quantities of radioactive materials and diverse radionuclides can be investigated. Research of this type has included the investigation of the effects of radiation damage in ^{238}P-substituted silicates as potential radioactive waste storage materials, characterization of novel uranium mineral phases, characterization of contaminated soils from the Hanford Site, and identification of technetium-carboxylate solution species.

- **Quantitative analysis capability.** A single-crystal x-ray diffraction capability, a joint venture with PNNL's Fundamental Science Directorate, became operational. The single crystal diffractometer is a Bruker Proteum rotating annode instrument that supplies brilliant copper radiation. Detection is by a large-format charged-coupled device. This combination of source and detector makes it ideal for determining the structure of very large biological molecules as part of PNNL's Structural Biology research program. Recently, the software was upgraded so that "small molecule" research such as inorganic compounds can be accommodated. For the "small molecule" application, in addition to *de novo* structural determinations, this instrument can provide extremely high-resolution measurements of defect structures and lattice strain as a function of composition that would not be possible on a diffractometer with molybdenum radiation. It also is equipped with a liquid nitrogen cooling stage for temperature-dependent measurements.

  Procurements were also made to upgrade and increase the efficiency of the atmospheric control of four anaerobic chambers. A new ion chromatography system was purchased to replace three older systems that required larger sample volumes and generated higher volumes of waste

- **Geochemical modeling.** The Spokane cluster, a replacement for the dated Seattle cluster, became operational. The system possesses a 32-node (64-processor) cluster, and each node consists of dual 3.0 GHz Intel EM64T Xeon processors, 4-Gb memory, and 73-Gb of disk storage. The system provides EMSL users with increased computational capacity and number of nodes, allowing more jobs to run simultaneously. This machine fills a critical computational need for the ES&B Facility because, historically, many of the projects involve small molecules where large-scale computing resources, such as MPP2, are not required. The scientific systems under study emphasize environmental remediation, including electron transfer involving metal oxides and metal complexes; reactions involving halogenated organic molecules; and reactions at mineral surfaces.

- **Subsurface flow and transport.** Low-flow pumps were procured for the SFTEL. These pumps will allow a better match between flow rates observed in the field and those attained at the laboratory scale.

Future Directions

The ES&B Facility will continue to solicit productive users who publish high-impact science in top-10 journals. The facility will encourage its scientific consultants to travel to either national meetings or to present seminars at universities not currently represented at EMSL. The facility will also coordinate efforts with EMSL User Administration to develop an electronic portfolio of facility research and capabilities to distribute to potential users. The facility will proactively notify users of upcoming national meetings and coordinate attendance so they can present EMSL research.

The ES&B Facility is targeting procurement of the following instruments for Fiscal Year 2007:

- **Applied-field Mossbauer.** Mossbauer spectroscopy is used to characterize both the oxidation state of iron and distribution of iron between different site symmetries in a material due to the electronic spins of the iron d-electrons. The effect of an applied magnetic field on iron in a sample depends on its intrinsic magnetic character (e.g., diamagnetic, paramagnetic, ferromagnetic). Because of this effect, it is possible to resolve peaks that otherwise overlie each other at zero-field. By adjusting the temperature of the sample and magnitude of the applied field, it is possible to completely characterize the iron chemistry of the sample. For example, using an applied field it is possible to distinguish between Fe(II) and Fe(III) in octahedral sites in magnetite. As a result, it is possible to characterize non-stoichiometric magnetite, as the result of incomplete reduction processes, and is difficult to characterize by other techniques. EMSL users have already inquired whether this capability is available.

- **Second harmonic generations (SHG).** With recent improvements in laser technology, stable powerful lasers necessary for SHG and sum frequency generation (SFG) are available and much easier to maintain and use. As a result, interest in SHG and SFG has resurfaced. SHG/SFG provides unparalleled sensitivity to *in-situ* surface speciation as a result of the symmetry relationships required for non-linear optical response.

- **Microfluidics capability**. A capability in microfluidics would serve to bridge the gap between the laboratory-scale flow capabilities currently available in the SFTEL and the spectroscopic and modeling efforts on the molecular scale at interfaces that dominate research in EMSL. Flow experiments in intricately patterned wafers were conducted using fluorescent imaging to monitor mixing of various chemical and biochemical reactants. These experiments involved use of two-dimensional flow cells less than 1 cm long and allowed researchers to investigate how mixing occurs with ion-milled pillars of different diameter, shape, and packing density. These experiments could be extended so that the silicon surface itself is functionalized.

Solution State Structure Determination of Silicate Oligomers by ^{29}Si NMR Spectroscopy and Molecular Modeling

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Silica solution species are an important complexant for many toxic contaminants in the environment, including radionuclides. Establishing a fundamental understanding of all silica solution species allows better prediction of the fate and transport of contaminants in the environment.

Evidence for nine new solution-state silicate oligomers was discovered at EMSL using ^{29}Si nuclear magnetic resonance (NMR) homonuclear correlation experiments of ^{29}Si-enriched samples. In addition to enhancing signal sensitivity, the isotopic enrichment increases the probability of the ^{29}Si-^{29}Si two-bond scalar couplings that are necessary for the observation of internuclear correlations in two-dimensional experiments. The proposed assignments are validated by comparisons of experimental and simulated cross-peaks obtained with high-digital resolution. The internuclear connectivity indicated by the NMR data suggests that several of these oligomers can have multiple stereoisomers, including conformers and/or diastereomers. The stabilities of these oligomers and their possible stereoisomers have been investigated by electronic structure calculations.

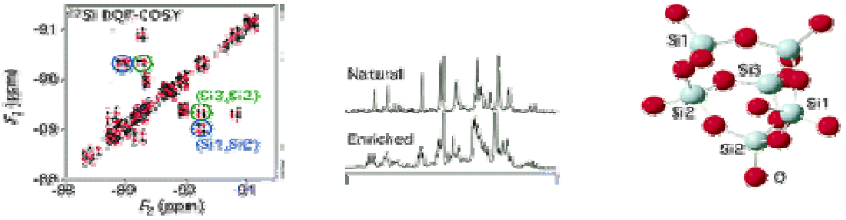

Figure 1. (Left) Two-dimensional ^{29}Si DQF-COSY spectrum of bicyclic hexamer, (center) comparison of one-dimensional ^{29}Si spectra natural and enriched abundance spectra, (right) energy-minimized trans bicyclic hexamer structure.

Experimentally, the significant advancement made in this study was the use of a double-quantum filter (DQF) in collection of the two-dimensional ^{29}Si COSY (COrrelation SpectroscopY) measurements of isotopically enriched silicate solutions. This was essential to suppress the intense dispersive diagonal peaks of singlet lines, which obscure several cross-peaks and autocorrelation multiplets near the diagonal in the nonfiltered experiment (Figure 1).

Computationally, analysis of the correlation experiments is that the newly detected oligomers contain only a small number of chemically inequivalent silicon sites, in most cases three or less. In addition, from the integrated one-dimensional peak intensities, it can be inferred that the new oligomers are comparable in concentration to the small oligomers discovered in the past. These observations imply that the new oligomers should have relatively simple, small, symmetric structures. From a survey of traditional ball-and-stick drawings of oligomer structures, it might appear that there are too few plausible candidate structures with NSi e 6 to support this conclusion, but such drawings fail to adequately represent the multiplicity of isomeric forms a silicate network can assume, especially when the potential chirality of Q3 and Q3t sites is considered. Computational models confirm that several oligomers have several stereoisomers that are stable energy minima, and thus are satisfactory structures. The chirality of certain silicon sites greatly expands the spectrum of geometries that a silicate network can have, both in solution-state species and in solid lattices. These diastereomers will have different NMR parameters, chemical properties, and structures, which suggest greater attention will be needed in future experimental and theoretical studies in the specification of silicate structures with the potential for configurational and conformational isomerism. This research is discussed in further detail in Cho et al. 2006.

Citation

Cho H, AR Felmy, R Craciun, JP Keenum, N Shah, and DA Dixon. 2006. "Solution State Structure Determination of Silicate Oligomers by ^{29}Si NMR Spectroscopy and Molecular Modeling." *Journal of the American Chemical Society* 128(7):2324-2335.

The Effect of Calcium on Aqueous Uranium(VI) Speciation and Adsorption to Ferrihydrite and Quartz

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This study demonstrated that the presence of calcium at environmentally relevant concentrations significantly reduces the amount of uranium adsorbed on ferrihydrate and quartz and increases the concentration of soluble and mobile uranium(VI) species.

Recent studies of uranium(VI) geochemistry have focused on the potentially important role of the aqueous species, $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3^0$(aq), on inhibition of microbial reduction and uranium(VI) aqueous speciation in contaminated groundwater. However, to our knowledge, there have been no direct studies of the effects of these species on uranium(VI) adsorption by mineral phases. The sorption of uranium(VI) on quartz and ferrihydrite was investigated in $NaNO_3$ solutions equilibrated with either ambient air (430 ppm CO_2) or 2% CO_2 in the presence of 0, 1.8, or 8.9 mM Ca^{2+}. Under conditions in which the $Ca_2UO_2(CO_3)_3^0$(aq) species predominates uranium(VI) aqueous speciation, the presence of calcium in solution lowered uranium(VI) adsorption on quartz from 77% in the absence of calcium to 42% and 10% at calcium concentrations of 1.8 and 8.9 mM, respectively. Uranium(VI) adsorption to ferrihydrite decreased from 83% in the absence of calcium to 57% in the presence of 1.8 mM calcium. Surface complexation model predictions that included the formation constant for aqueous $Ca_2UO_2(CO_3)_3^0$(aq) accurately simulated the effect of Ca^{2+} on uranium(VI) sorption onto quartz and ferrihydrite within the thermodynamic uncertainty of the stability constant value. This study confirms that Ca^{2+} can have a significant impact on the aqueous speciation of uranium(VI), and consequently, on the sorption and mobility of uranium(VI) in aquifers.

A Review of Multidimensional, Multifluid Intermediate-Scale Experiments: Nonaqueous Phase Liquid Dissolution and Enhanced Remediation

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Intermediate-scale flow cell experiments are used to simulate field-scale processes in the laboratory under controlled conditions.

An invited review of multidimensional, multifluid, intermediate-scale experiments involving nonaqueous phase liquids (NAPLs) was recently published in *Vadose Zone Journal* (Oostrom et al. 2006). These experiments were conducted at an intermediate scale between column studies and field trials (Figure 1). The primary advantage of intermediate-scale flow cell experiments is that field-scale processes can be simulated under controlled conditions. The experiments are frequently conducted to provide datasets to test and verify numerical and analytical flow and transport models. The controlled setting and laboratory instrumentation reduces the uncertainty in parameter estimation, allowing comparisons between simulation and experimental results to focus on flow and transport processes. A total of about 125 original contributions were identified and reviewed.

Research needs in NAPL dissolution include:

- Long-term dissolution studies of multicomponent NAPL in heterogeneous porous media

- Increased understanding of NAPL dissolution upscaling from the pore scale to the field scale
- New theoretical models for NAPL dissolution in mixed-wet porous media.

Research needs in NAPL remediation include:

- Development of multi-flood techniques that combine alcohol and surfactant flushing
- New dense-brine injection techniques
- Development of neutral buoyancy techniques for application in heterogeneous porous media
- Application of heat-based remediation techniques.

Figure 1. EMSL researchers test theories of flow and transport. The study coupled processes involved with microbial, reactive chemical, NAPLs, colloid transport, or test subsurface remediation scenarios using the Subsurface Flow and Transport Laboratory.

Citation

Oostrom M, JH Dane, and TW Wietsma. 2006. "A Review of Multidimensional, Multifluid Intermediate-Scale Experiments: Nonaqueous Phase Liquid Dissolution and Enhanced Remediation." *Vadose Zone Journal* 5:570-598.

Reductive Biotransformation of Iron in Shale-Limestone Saprolite Containing Fe(III) Oxides And Fe(II)/Fe(III) Phyllosilicates

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Iron reduction by dissimilatory metal-reducing bacteria is an important process in anoxic soils, sediments, and subsurface materials, particularly for bioremediation applications. However, the bioavailability of mineral Fe(III) to metal-reducing bacteria appears limited by numerous incompletely understood factors, such as crystal chemistry, solid-phase thermodynamics and surface area effects, and electron transfer efficiency at the mineral-microbe interface.

In this study, we used Mössbauer spectroscopy to determine 1) the distribution of Fe(III) and Fe(II) between mineral sites and between mineral phases prior to and following microbial reduction and 2) the fate of biogenic Fe(II). Mössbauer measurements on the bioreduced sediments indicated that both goethite and phyllosilicate Fe(III) were partially reduced. Biogenic Fe(II) resulting from phyllosilicate Fe(III) reduction remained in a layer-silicate environment that displayed enhanced solubility in weak acid (Figure 1). The mineralogic nature of the goethite biotransformation product could not be identified but was determined not to be siderite, green rust, magnetite, $Fe(OH)_2$, or Fe(II) adsorbed on phyllosilicate or bacterial surfaces. Several lines of evidence suggested that biogenic Fe(II) existed as surface-associated phase on the residual goethite, and/or as a Fe(II)-Al co-precipitate. The results of this work were published in the journal *Geochimica et Cosmochimica Acta* (Kukkapadu et al. 2006).

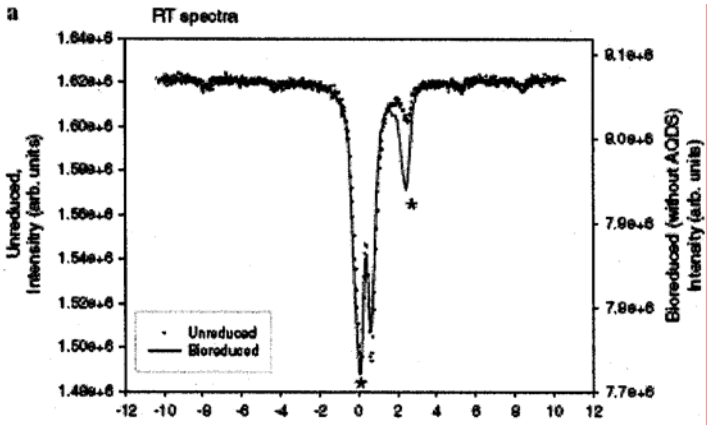

Figure 1. Mössbauer spectra of unreduced and bioreduced sediment.

Citation

Kukkadapu RK, JM Zachara, JK Fredrickson, JP McKinley, DW Kennedy, SC Smith, and HL Dong. 2006. “Reductive Biotransformation of Fe in Shale-Limestone Saprolite Containing Fe(III) Oxides and Fe(II)/Fe(III) Phyllosilicates.” *Geochimica et Cosmochimica Acta* 70(14):3662-3676.

User Projects

Lab Studies of Phytoremediation and Apatite Sequestration

JL Phillips, JE Szecsody, CA Burns, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

Formation of Iron(II) Secondary Minerals After Iron(III) Bioreduction in Humid Tropical Forest Soils

T Peretyazhko, G Sposito, University of California, Berkeley, Berkeley, California

Mossbauer Analysis for Goethite Reacted with Fe(II) and Membrane Fraction of *Shewanella oneidensis*

J Jang, Pennsylvania State University, University Park, Pennsylvania

Geochemical Testing and Model Development - Residual Tank Waste

KJ Cantrell, WJ Deutsch, Pacific Northwest National Laboratory, Richland, Washington

Novel Nanoporous Getters to Immobilize ^{99}Tc at the Yucca Mountain

HM Cho, OS Qafoku, S Mattigod, KM Rosso, Pacific Northwest National Laboratory, Richland, Washington

Environmental Sensing, Metabolic Response, Regulatory Network

JK Fredrickson, DW Kennedy, Pacific Northwest National Laboratory, Richland, Washington

Proteomics of Bioenergetics

JC Scholten, DW Kennedy, Pacific Northwest National Laboratory, Richland, Washington

Demonstration of the Capability of Mobility-Controlled-Flooding Technology to Overcome Heterogeneity Induced Bypassing in Subsurface Remediation

L Zhong, KJ Cantrell, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma. Environmental Molecular Sciences Laboratory, Richland, Washington

Low-Cost, Energy-Efficient Nitrogen Fertilizer 48291

JE Amonette, CC Bashore, Pacific Northwest National Laboratory, Richland, Washington

Mechanisms and Dynamics of Abiotic and Biotic Interactions at Environmental Interfaces

GE Brown, Stanford University, Stanford, California

KM Rosso, S Yanina, S Kerisit, Pacific Northwest National Laboratory, Richland, Washington

CS Lo, University of Alaska Fairbanks, Gaithersburg, Maryland

Lignin Content in Natural Fibers Utilizing Fluorescence Microscopy

JD Holbery, Pacific Northwest National Laboratory, Richland, Washington

Theoretical Treatment of the Kinetics of Uranium Reduction by Magnetite Surfaces

MC Wander, MA Schoonen, RJ Reeder, State University of New York at Stony Brook, Stony Brook, New York

JD Kubicki, Pennsylvania State University, University Park, Pennsylvania

The Reduction of Uranyl and Chromate to Insoluble Species by Green Rust and Other Ferrous Hydroxides Surfaces

MC Wander, MA Schoonen, RJ Reeder, State University of New York at Stony Brook, Stony Brook, New York

Scintillator Research

M Bliss, Z Wang, JE Amonette, SD Miller, Pacific Northwest National Laboratory, Richland, Washington

Thrust 3,4: Molecular Forces in Bacterial Adhesion at the Oxide-Water Interface

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Establish a Penn State Center for Environmental Kinetics - as part of the Environmental Molecular Science Institute (EMSI) Program (NSF/DOE-OBER)

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FTIR Characterization of Fe Films Formed on Ephemeral Pool

GH Grathoff, HR Easterly, Portland State University, Portland, Oregon

Characterization of Synthesized Mixed Valent Naturally Occurring Fe-Films

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Thrust 4: Whole Cell and Cytochrome Biological Force Microscopy

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Cr(VI) Removal from Aqueous Solution Using a Commercial Activated Carbon Coated with Quaternized Poly(4-vinylpyridine)

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Probing the Structural Network of Buried Water Molecules in the Hydrophobic Core of Staphylococcal Nuclease

RL Reynald, EE Lattman, Johns Hopkins University, Baltimore, Maryland

Thrust Area 4: How Redox Proteins on the Exterior of the Outer Membrane of *Shewanella* Accomplish Interfacial Electron Transfer to the Fe(III) Oxide Surface

CM Eggleston, University of Wyoming, Laramie, Wyoming

AM Spormann, JN Ha, Stanford University, Stanford, California

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Thrust Area 1: The Surface Structure of *Shewanella* and the Localization of Outer Membrane-associated Proteins Hypothesized to be Involved in Electron Transfer from Metal-reducing Bacteria to Metal Oxide Surfaces

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Thrust Area 3:Mutagenesis and Functional Characterization of *Shewanella oneidensis* Genes Involved in Fe(III) and Mn(IV) Oxide Reduction (LDRD #3)

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Simulating Mineral Interfaces

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The Interaction Between Uranium(VI) and Magnetite Surfaces: A Combined STM and Electron Transfer Calculation Approach

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Strait Science - Biosensor Task 1.1 of the Coastal and Environmental Effects Program

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FTIR and SEM Characterization of Desert Varnished Rocks

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Evaluate Injection of Zero Valent Iron (PNNL Scope# 488994: Oostrom, Fluor Daniel Hanford)

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Laser Fluorescence Analysis of Natural Isotopic Abundance Uranium Oxide Samples

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Time-Revolved Laser Spectroscopy of Europium Adsorbed on Gibbsite and Silica

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Foldable Polymers

JJ Han, AD Li, Washington State University, Pullman, Washington

Determination of DNAPL Mass Flux Reduction as a Function of Source Zone Mass Removal

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Characterization of Novel Arsenic-Iron Precipitates Formed during Biological Iron Reduction

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Determining the Effects of Gamma Irradiation on the Oxidation State of Iron using Mossbauer Spectroscopy

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Investigation of Metals Corrosion in SOFCs Using Raman Spectroscopy

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Mossbauer Effect of Organically Grown Plants

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Effect of NAPL Dissolution on NAPL-Water Interfacial Area

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Couple Proton-electon Dynamics in Iron-containing Phyllosilicates: Annite, $KFe_3AlSi_2O_{10}(OH)^{2}$ - Mössbauer Determination of Fe^{2+}/Fe^{3+} Ratio

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Transformations in Iron Mineralogy Induced by Microbial Processes in Natural Sediments

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Characterization of Synthetic Mixed Valence U Compounds

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Determination of Hydrolysis Rate for CCl_4 under Ambient Groundwater Conditions

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Zero Emission Research & Technology (ZERT) CO_2 Sequestration Leakage Evaluation Task: Parameterization of Leakage from Geologically Sequestered CO_2

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Microscopic Visualization of Membrane Pores and Bacterial Foulants

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Evaluation of Pore Scale Porous Media Effects on Reactive Transport in Groundwater

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Development of Microscopically-Based Models for Prediction of the Impact of Surface Grain Coating on Mineral Dissolution and Leaching Rates

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Multiscale Design of Advanced Materials based on Hybrid *ab-initio* and Quasicontinuum Methods

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Substrate-specific Binding of *Staphylococcus* Adhesins to Solid Surfaces

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Quorum Sensing in a Dissimilatory Metal Reducing Bacterium

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Raman Capability for EMSL Users

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Development of an Integrated Atomic Force/Fluorescence Microscope at EMSL

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Specificity of *Shewanella oneidensis* Outer Membrane Cytochromes OmcA and OmcB Towards Iron- and Manganese-oxide Surfaces

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Basis of Microbial Membrane Attachment to Mineral Surfaces and Ionic Contaminants Uptake

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Mössbauer Analysis of Microbial Redox Transformations of Naturally Occurring Fe(III)-bearing Phyllosilicates

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Determination of Hydraulic Conductivity and Soil Moisture Retention Relations with the EMSL Hydraulic Properties Apparatus

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IR and RAMAN Analysis of Water Diffusion in the Surface of Glasses for Nuclear Waste Immobilization

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Determination of Fluorescence Lifetime of Natural Organic Matter

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Enhancing C Sequestration in Terrestrial Ecosystems: Linking C and N Cycling in Soils (Part of Center for Research on Carbon Sequestration in the Terrestrial

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Mineralogical Analysis of Substrates and End-products of Microbial Fe Redox Transformations

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A Theoretical and Experimental Investigation of Multiplet Splitting for CR and U Spectra Generated by X-ray Photoelectron Spectroscopy

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Microbial Reduction of Iron in Sedimentary Clays: Implications for Subsurface Microbial Ecology and Bioremediation

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Nanoscale Investigation of Microbial Role in Promoting the Smectite to Illite Transformation

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Characterization of Biologically Reduced U Particles

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Formulating the CD-MUSIC Surface Complexation Model from First Principles Calculations for Phosphate Adsorption on Goethite

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Analyses of Electron Density Distributions in Earth Materials with Implications for Reactivity

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Surface Structure Effects on Direct Reduction of Iron Oxides by *Shewanella oneidensis*

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Structure and Reactivity of the Basal and Edge Surfaces of Gibbsite

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Critical Point Properties of Electron Density Distributions in High-pressure Mineral Phases

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Investigation into the Polarized Raman Spectra of Benzene, Benzene-d6 and Hexafluorobenzene

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The Aqueous Thermodynamics and Complexation Reactions of Anionic Silica and Uranium Species to High Concentration

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Multi-Resolution Structure and Reactivity of Kinetically Roughened Oxide Surfaces: Nanometric Scaling Behavior and Molecular-Scale Controls

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The Development of Thermodynamic Models for Actinide Species in Mixed Solvent Systems: Application to Binding in Microbial Membranes

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Model Porous Solids and Sediments

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Enhancing Carbon Sequestration and Reclamation of Degraded Lands and Sequester C in Soils

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Carbon Tetrachloride Degradation Reaction Mechanisms

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A Bioengineering Approach to the Production of Metal and Metal Oxide Nanoparticles

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Chemical Speciation of Americium, Curium, and Selected Tetravalent Actinides in High Level Waste

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Interactions Between Fe(III) - Reducing Bacteria and Fe Oxides: Microbial and Geochemical Dissolution Controls

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Coupling of Fe and Tc Speciation in Subsurface Sediments: Implications to Long-Term Tc Immobilization

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Mineralogic Residence and Desorption Rates of Sorbed ^{90}Sr in Contaminated Subsurface Sediments: Implications to Future Behavior and In-Ground Stability

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Characterization of U(VI) Sorption-Desorption Processes and Model Upscaling

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Remediation and Closure Science Project/Subsurface Science Tasks

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Influence of Mass Transfer on Bioavailablility and Kinetic Rate of U(VI) Biotransformation

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Reactions and Transport of Toxic Metals in Rock Forming Silicates at ^{25}C

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Actinide Interactions with Environmental Bacteria

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Characterization of U(VI) Speciation in Samples from Laboratory Batch and Column Experiments

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Liquid Infrared Spectroscopy and Spill Phenomenology

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Movement and Dissolution of a Viscous, Multicomponent Light Nonaqueous-Phase Liquid in a Fluctuating Water Table System

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Quantification and Chemical Analysis of Iron Oxidation in Microbially-Reduced Sediments

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Model Development on Using Clay Membranes for Arsenic Removal from Drinking Water

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Biogeochemical Heterogeneity in the Subsurface

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Intermediate Flow Cells

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Computational Investigation of Acid Base, Surface Complexation, and Oxidation/Reduction Reaction Mechanisms on Iron Oxide and Iron Silicate Surfaces

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Enhance Plutonium Mobility during Long-Term Transport through an Unsaturated Subsurface Environment: Iron and Manganese Oxide Characterization

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Uranium Immobilization by Sulfate-Reducing Biofilms

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Fate of Nitrogen Gas Produced by Denitrification during U and Tc Bioreduction

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Interfacial Reduction-Oxidation Mechanisms

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How Aluminum Substitution in Goethite Affects Iron Release

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Characterization of Coupled Hydrologic-Biogeochemical Processes Using Geophysical Data

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Separation of Corn Fiber and Conversion to Fuels and Chemicals - Pilot Operation

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Influence of Calcium on Aqueous U(VI) Speciation and U(VI) Sorption to the Hanford Sediments

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Photophysics of Organophosphorous Compounds

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Influence of Flow on Abiotic and Biotic Reactivity of CL--20 (hexaanitrohexaazaiso-wurtzitane)

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Conductivity of Bacterial Nanowires

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Transmission Electron Microscopy Analysis of a Novel Organo-Cr(III) Degrading Bacterium

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Mossbauer Spectroscopic Investigations of Fe Doped SnO_2 Powders

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Synthesis and Characterization of Limited Solubility U(VI) Bearing Compounds in Concrete

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High-Field Magnetic Resonance Facility

The High-Field Magnetic Resonance Facility (HFMRF) brings a powerful synergy of creative scientific staff and unique instrumentation to bear on complex scientific problems. HFMRF is equipped with state-of-the-art nuclear magnetic resonance (NMR) and pulsed electron paramagnetic resonance (EPR) instruments, all of which play a role in determining molecular structures that are relevant to environmental remediation efforts, materials development for national energy needs, and biological health effects.

HFMRF offers unique tools and techniques designed in-house to enable novel research, including 1) *in situ* catalysis probes, 2) radionuclide NMR capabilities, 3) solid-state NMR cryogenic probes for direct observation of metals in macromolecules, 4) high-temperature probe technology, 5) laser-polarized gas for visualizing gas-filled spaces using magnetic resonance imaging (MRI), and 6) pulsed EPR techniques designed to follow conformational changes in membrane protein complexes containing metal clusters. In collaborative partnership with world-class scientists around the globe, we forge innovative approaches to some of the most pressing research needs in environmental molecular science and other national research priorities.

Staff and science consultants within this facility offer expertise in the areas of structural biology, solid-state materials characterization, and MRI techniques. Research activities include structure determination of large molecular assemblies such as protein-DNA (normal and damaged DNA) and protein-RNA complexes that model assemblies that may form as a cellular response to chemical or radiological insults; examination of conformational changes in membrane protein complexes involving metal clusters using pulsed EPR; NMR-based structural and functional genomics; multi-nuclear detection and catalyst and materials characterization using solid-state techniques; and non-invasive biological imaging, integrated magnetic resonance and confocal microscopy, and slow-spinning NMR to study cell systems.

Instrumentation & Capabilities

NMR and EPR

- 900-MHz NMR
- 800-MHz NMR
- 750-MHz NMR
- 600-MHz NMR (two systems)
- 500-MHz (two wide-bore systems and one narrow-bore system)
- 300-MHz wide-bore NMR (two systems – one radionuclide capable)
- Horizontal-bore 2-tesla NMR
- EPR spectrometer with electron nuclear double resonance (ENDOR)/electron-electron double resonance (ELDOR) capability

Additional Capabilities

- Combined optical and magnetic resonance microscope
- Low-temperature probes for metallo-protein chemistry and structure
- Virtual NMR capability enabling use and collaboration with EMSL scientists for remote users via secure shell over the internet

Since EMSL opened in October 1997, HFMRF has been one of the highest-volume experimental user facilities in support of local and external user research programs. During Fiscal Year 2006, HFMRF supported several projects in which 80 external scientists used the NMR spectrometers.

The research interests of staff and users include some of the most exciting areas in modern molecular biology and biochemistry:

- **Structural/Functional Genomics**. Determination of three-dimensional structures of DNA, RNA, proteins, and enzymes and their intermolecular associations. Particular interests and collaborations exist relative to protein fold classification and sequence-structure-fold relationships.
- **Biomolecular Complexes**. Understanding the molecular interactions of larger complexes of biomolecules (proteins, DNA, RNA, and mimetic membranes) that are key regulators in cell signaling and growth (e.g., DNA damage recognition and repair processes).
- **Biological Imaging**. Acquisition of imaging and corresponding chemical information in biological samples, with particular interest in development of combined magnetic resonance and optical spectroscopy techniques to observe and elucidate biological processes.
- **Solid State**. Low-gamma nuclei detection, ultra-low-temperature NMR for sensitivity enhancement, and slow-magic-angle-spinning (MAS) methodologies for nondestructive research of cells, tissues, small animals, and bacterial colonies.
- **Measurement Science and Instrumentation Development**. Development and application of novel and unique NMR instrumentation techniques for biological and environmental problems.

Capabilities

Varian INOVA 900. The Varian 900 (Figure 1) is an INOVA-based spectrometer utilizing an Oxford 21.1-tesla (T) magnet with a 63-mm room-temperature bore. This system is capable of high-resolution liquid- and solid-state NMR. There are four radio frequency (RF) channels with waveform generators and triple-axis pulsed-field gradients. The wide-line analog digital converters (ADCs) run at 5 MHz and the narrow ADCs have a maximum rate of 500 kHz. This console also has a solids variable-temperature (VT) control capability. We currently have a 5-mm HCN probe with X, Y, and Z axis gradients for liquids, a 5-mm orthogonal HX powder probe optimized

Figure 1. 900-MHz NMR spectrometer.

for low-gamma nuclides, a 5-mm orthogonal H-N-Zn triple-tuned probe for powders, and a 3.2-mm low-gamma HX MAS probe (24 kHz spinning).

Figure 2. Varian INOVA 800-MHz NMR spectrometer.

Varian INOVA 800. The Varian 800 (Figure 2) is an INOVA-based spectrometer utilizing an Oxford 18.8-T magnet with a 63-mm, room-temperature bore. This system is capable of high-resolution liquid- and solid-state NMR. There are four RF channels with waveform generators and pulsed-field gradients. The wide-line ADCs run at 5 MHz, and the narrow-line ADCs run at a maximum rate of 500 kHz. This console also has a solids VT control capability. Available probes include a 5-mm HCN cryoprobe and two room-temperature 5-mm HCN probes with Z gradient for liquids, a 4-mm HXY MAS probe (25-kHz spinning, VT-capable), a 5-mm HX orthogonal powder probe optimized for low-gamma (38 to 65 MHz) nuclides, and a 5-mm HX static low-temperature probe (3.8 to 300 K). A 5-mm HX MAS probe (12-kHz spinning) is under construction.

Figure 3. Varian INOVA 750-MHz NMR spectrometer.

Varian INOVA 750. The Varian 750 (Figure 3) is an INOVA-based spectrometer utilizing an Oxford 17.6-T magnet with a 51-mm, room-temperature bore. This system is capable of high-resolution liquid- and solid-state NMR. There are four RF channels with waveform generators and pulsed-field gradients. The narrow ADCs have a maximum rate of 500 kHz. We currently have two 5-mm HCN probes (Z gradient), a 5-mm HCP probe (Z gradient), a 5-mm HX MAS probe (X tuning range is 321 to 130 MHz; the spinning speed is rated to 12 kHz), and two 5-mm HX MAS probes (15-kHz spinning) with X tuning ranges of 60 to 120 MHz and 30 to 50 MHz.

Figure 4. Varian INOVA 600-MHz NMR spectrometer with Cryoprobe.

Varian INOVA 600. The Varian 600 (Figure 4) is an INOVA-based spectrometer utilizing an Oxford 14.1-T magnet with a 51-mm, room-temperature bore. This system is capable of high-resolution liquid-state NMR. There are four RF channels with waveform generators and pulsed-field gradients. The narrow-line ADCs run at a maximum rate of

500 kHz. We currently have a cryogenically cooled and a room-temperature 5-mm HCN probe with Z gradient and a 5-mm HX probe (X tuning range is 242 to 60 MHz).

Figure 5. Varian INOVA 600- MHz NMR spectrometer.

Varian Unity 600. The Varian 600 (Figure 5) is an INOVA-based spectrometer utilizing an Oxford 14.1-T magnet with a 51-mm, room-temperature bore. This system is capable of high-resolution liquid-state NMR. There are three RF channels with waveform generators and pulsed-field gradients. The narrow-line ADCs run at a maximum rate of 500 kHz. We currently have a 5-mm pentaprobe (proton, phosphorus, carbon, nitrogen and deuterium) with Z-gradient, a 5-mm HCN probe with Z gradient and a 5-mm HX probe (X tuning range is 242 to 60 MHz).

Figure 6. Varian NMR System 500-MHz wide-bore NMR spectrometer.

Varian NMR System 500 Wide Bore. The Varian 500 Wide Bore (Figure 6) has a new VNS-based spectrometer console and utilizes an Oxford 11.7-T magnet with an 89-mm room-temperature bore. This system is capable of a full range of solid-state NMR, experiments, including windo-less sequences and PISEMA. There are three RF channels with waveform generators. The wide-line ADCs run at 5 MHz. We currently have a new 4-mm HXY MAS probe capable of bio-solids triple resonance experiments and a new 7.5-mm HX MAS probe (8-kHz spinning), an HX single-crystal probe, a ^{1}H CRAMPS probe, a micro-coil imaging probe, a 40-mm imaging probe, and a static HX low-temperature probe (2 to 300 K).

Figure 7. Bruker Avance 500-MHz NMR spectrometer.

Bruker Avance 500 Wide Bore. The Bruker Avance 500 Wide Bore (Figure 7) is a micro-imaging system using an 89-mm vertical room-temperature bore. The system is capable of imaging mice and also has high-resolution liquid magnetic resonance capabilities with a Bruker 10-mm QNP probe. This liquid probe has a ^{1}H outer coil and an inner coil that is switchable among ^{13}C, ^{31}P, and ^{19}F with no gradients. The system is equipped with a combined confocal and magnetic resonance microscope capable of monitoring single layers of eukaryotic cells in a perfusion system simultaneously with both modalities.

Varian/Chemagnetics Infinity 500. The Chemagnetics 500 (Figure 8) is an Infinity-based spectrometer utilizing an Oxford 11.7-T magnet with a 51-mm, room-temperature bore. This system is capable of high-resolution liquid- and solid-state NMR. It has three RF channels and is equipped with both 16- and 14-bit ADCs. The solution state probes for this instrument include a 5-mm HCN gradient probe, a 5-mm DB gradient probe (X tuning range is 208.1 to 49.5 MHz), and a 10-mm HX probe (X tuning range is 218.6 to 21.2 MHz). There are two solid-state probes, a 5-mm HX MAS probe (X tuning range is 206.6 to 47 MHz; the spinning speed is rated to 12 kHz) and a 6-mm HX MAS probe (X tuning range is 218.6 to 48.7 MHz, H/F tuning range is 510.6 to 459 MHz; the spinning speed is rated to 9 kHz).


Figure 8. Varian/Chemagnetics Infinity 500-MHz NMR spectrometer.

Varian/Chemagnetics Infinity 300. The Chemagnetics 300 (Figure 9) is an Infinity-based spectrometer utilizing an Oxford 7.02-T magnet with an 89-mm room-temperature bore. This system is capable of high-resolution liquid- and solid-state NMR. It has three RF channels and is equipped with both 16- and 14-bit ADCs. The solution-state probes for this instrument include a 5-mm HX probe and a 10-mm HX probe. The solids probes are a 7.5-mm HX MAS probe (X tuning range is 136.7 MHz to 29.5 MHz; H tuning range is 274.7 to 349.1 MHz; spin rate is rated to 7 kHz) and a 5-mm HXY MAS probe (X tuning range is 129 to 57.4 MHz; Y tuning range is 85.1 to 21.2 MHz; spin speed is rated to 12 kHz). Further probes available are a 7-mm HX MAS probe (10-kHz spinning), an HX single-crystal probe, a ^{1}H CRAMPS probe, a single-tuned HX 5-mm, low-temperature MAS probe (35 to 300K, 12-kHz spinning), a 7-mm HX high-temperature probe (-100 to 500°C, 7-kHz spinning)


Figure 9. Varian/Chemagnetics Infinity 300-MHz NMR spectrometer.


Figure 10. Horizontal-bore 2-T magnet.

Horizontal-Bore 2-T Magnet. The 2-T magnet (Figure 10) provides unique capabilities for the HFMRF. It is connected to a Varian Unity+ console with two RF channels and wideline 5-MHz

ADCs. It has a 30-cm, room-temperature bore and is equipped with an imaging gradient set capable of 50 gauss/cm. It is suitable for small animal or large sample imaging and *in vivo* spectroscopy. Three homemade birdcage coil probes are available: 8-cm and 5-cm imaging/spectroscopy probes and a 5-cm ^{3}He probe.

Bruker Pulsed EPR/ENDOR/ELDOR Spectrometer. This multi-functional pulsed EPR spectrometer (Figure 11), operating in the X-band near 9.5 GHz, permits application of modern pulsed magnetic resonance techniques to systems containing unpaired electron spins. The system is based on the Bruker EleXsys console and SuperX-FT microwave bridge, which allow both ELDOR (electron-electron double resonance) and ENDOR (electron nuclear double resonance) measurements. A number of probes for both continuous-wave and pulsed spectroscopy are included, with an operating temperature ranging from room temperature to below liquid helium. System capabilities include measurement of g-tensors; hyperfine and nuclear quadrupole-coupling tensors for the study of electronic wavefunction of free radicals and metallo-proteins; and determination of small dipolar interactions by pulsed ELDOR and double electron-electron resonance methods for the measurement of distances between radicals in solids or between spin labels in proteins.

Figure 11. Bruker pulsed EPR/ ENDOR/ ELDOR spectrometer.

Upgrades

In 2006, the HFMRF has improved research capabilities both by upgrading current instrumentation and acquiring/developing new instrumentation.

- **Dynamic magic-angle spinning probe.** Capability development funds supported completion of the first dynamic magic-angle spinning probe, which, with a unique hardware and pulse sequence design, enables *in-situ* chemistry studies for users. The probe allows the flow of gases or liquids under controlled pressures to flow over solid-state materials for reaction chemistry studies and provides an exit for the products. An invention report has been submitted and accepted.

- **900-MHz high-temperature probe.** A 900-MHz high-temperature probe arrived at the end of September 2006. This probe will feature magic-angle spinning capability at temperatures of more than 400ºC, which will be an invaluable capability enhancement for catalysis work. Component testing and integration with the magnet system is still needed.

- **800-MHz cold probe.** This probe provides the highest sensitivity of any probe at PNNL for the study of biological molecules in the liquid state. The sensitivity gained is about four times that of a comparable 800-MHz probe. This probe will be of great use in the structure and dynamics characterization of large biomolecular complexes.

Future Directions

The HFMRF will continue to support researchers by providing state-of-the-art magnetic resonance resources and scientific consulting to enable top-tier research and publication in respected journals. DOE has challenged the facility to focus the power of its marquee instrument, the 900-MHz medium-bore magnet, on high-impact research that may contribute to a major article in *Science*, *Nature*, or the *Proceedings of the National Academy of Sciences*, or that could possibly lead to a Nobel Prize. In Fiscal Year 2006, the facility published five papers using data from the marquee instrument; three of these are in top-10 ISI journals, and one is in a top-5 journal, *Molecular Cell.* In addition, research accomplished on the 800- and 750-MHz magnets contributed to an article in *Proceedings of the National Academy of Sciences* in 2006. Facility staff will seek to continue the record of high-quality publications and have set a goal of continuing to publish 50% of articles in top-10 journals in 2007.

- **Continue to provide NMR expertise.** All advanced scientific instrumentation requires continuous effort to maintain peak performance of both hardware and software, and the science knowledge base to effectively and efficiently use the resource to obtain publishable data. Scientific consultants provide the operational knowledge base for users to efficiently use facility resources. The High-Field Magnetic Resonance Facility will continue to optimize user support efforts and provide scientific expertise, as budget allows, by providing researchers access to NMR experts who can assist with experimental design and setup, data collection, processing, and analysis. The facility will require at least five individuals knowledgeable in solid-state NMR, liquid-state NMR, and imaging to provide the expertise needed for users to effectively use the facility's resources.

- **Obtain electronics experts.** Two trained electronics technicians are needed to provide instrumentation design and development for specific user needs, and to troubleshoot equipment failures and maintain equipment in optimum operating condition. These individuals are key to the creation of new probe designs for making innovative solutions to scientific problems addressed by magnetic resonance methods.

- **Provide support to calls and Scientific Grand Challenges**. EMSL management actively supported two High-Field Magnetic Resonance Facility-specific calls for proposals in 2006, but in 2007 this call will be transitioned to EMSL-wide science theme and capabilities-based calls. The facility will continue to support the EMSL Scientific Grand Challenges. In addition, as additional mission-critical projects are identified, appropriate staff must be added to address applicable research needs.

- **Add LC-NMR Spectrometry System.** The facility plans to add a 600-MHz LC-NMR spectrometry system dedicated to support the field of metabonomics, a rapidly growing area of research with much user interest. The system would enable accurate lineshape deconvolution and analysis of biomarkers in complex mixtures, supporting EMSL's Biological Interactions and Interfaces, Geochemistry/Biogeochemistry and Subsurface Science, and Science of Interfacial Phenomena science themes. User projects that address biological health effects, microbial production of alternative fuels, detection of biosecurity threats, and environmental remediation and protection are expected to benefit from use of this capability. The data generated would be complementary and integrated with other analytical techniques, especially LC-mass spectrometry.

- **Expand development of unique *in-situ* catalysis NMR probe designs.** The facility seeks to expand development of unique *in-situ* catalysis NMR probe designs developed at lower field and apply the technology to second-generation probes with variable temperature capabilities. Such a technology would be integrated with the 900-MHz NMR spectrometer to enable the study of catalytic reactions over solid-state transition metal-laden materials that benefit the most from study at the highest fields, such as titanium, molybdenum, strontium, and other important quadrupolar nuclei. These studies will have a major impact on the ability to follow reaction chemistries and lead to optimization of new materials for alternative fuel production and reduction of harmful emissions to the atmosphere.

NMR Structural Investigations of the Breast Cancer Susceptibility Protein, BRCA1

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BRCA1 is a complex protein that, when it malfunctions via mutations, can cause cancer. This research addresses how this protein interacts with other proteins in order to perform its various functions, including reducing the risk of breast and ovarian cancer.

Our work on the breast and ovarian cancer tumor suppressor protein, BRCA1, represents the convergence of two central research themes. The first relates to the importance of BRCA1 to a number of fundamental cellular processes, such as the cellular response to DNA damage, homologous recombination, and transcriptional regulation. Investigation of the function of BRCA1 in these pathways promises to yield insights into the role of BRCA1 in normal cellular development, and how loss of function results in the onset of breast and ovarian cancer. The second theme relates to mechanisms underlying ubiquitination. Protein ubiquitination provides a powerful regulatory mechanism for controlling pathways that include cell-cycle progression, transcriptional regulation, and responses to DNA damage. The importance of ubiquitin as a central biological process is underscored by the award of the 2004 Nobel Prize in Chemistry for research into the function of ubiquitination at the molecular level. It has recently been shown that BRCA1 can function as an E3-ubiquitin ligase. This activity is only observed when BRCA1 is complexed with a second protein called BARD1. Both BARD1 and BRCA1 have N-terminal RING-domains which mediate the interaction between the two proteins. Thus, work on BRCA1 allows us to integrate structural investigations on the role of BRCA1 in the development of breast and ovarian cancer as well as the study of the mechanisms of protein ubiquitination.

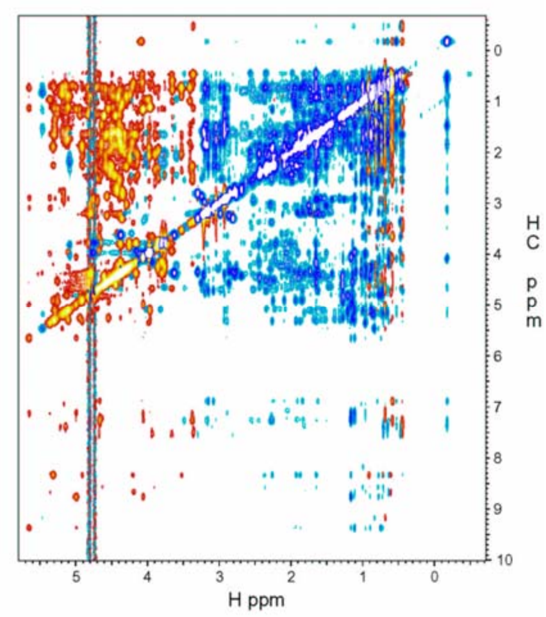

Figure 1. Two-dimensional projection of a three-dimensional Noesy-^{13}C-HSQC spectrum of unlabled ubiquitin bound to ^{15}N-^{13}C-labeled UbcH5c collected at 900 MHz.

BRCA1 is a large and complicated protein which is undoubtedly comprised of a multiplicity of functional domains. A growing body of literature suggests that BRCA1 interacts with at least 30 different macromolecules to accomplish its diverse functional roles. Our structural work involves characterization of macromolecular complexes involving the N-terminal RING domain and the C-terminal BRCT domain of BRCA1. Much of our recent work at EMSL has focused on understanding the ubiquitination activity mediated by the BRCA1 RING domain. As E3-ligases, RING domains are thought to facilitate the specificity of ubiquitination reactions by forming a multiprotein complex, binding both a ubiquitin conjugating enzyme (E2) covalently activated with ubiquitin and specific proteins targeted for ubiquitination. In addition, the BRCA1 RING domain mediates its interaction with BARD1. Cancer predisposing mutations found in the BRCA1 RING domain have been found to interfere with its ability to function as a ubiquitin ligase.

Figure 2. Structure of the noncovalent complex formed between UbcH5c and ubiquitin. Ubiquitin (red) binds to the exposed β–sheet region of UbcH5c (blue-green). The active site of UbcH5c is on the opposite side of the molecule.

This system provides a unique opportunity for studying protein-protein interactions by nuclear magnetic resonance (NMR). It involves characterizing the structures and interactions among at least four different protein components: BRCA1, BARD1, an E2 (UbcH5c or UbcH7), and ubiquitin (Ub). The molecular weight of the fully assembled complexes approaches 60 kD. In previous years, we have been able to collect a great deal of data on the individual components of this system. During the last year, data collected on EMSL's 600-, 800-, and 900-MHz NMR spectrometers have allowed us to develop a model of the complex series of protein-protein interactions that are required to assemble an active BRCA1-dependent ubiqutin-ligase complex.

Recent work at EMSL allowed us to determine the structure of the noncovalent complex between UbcH5c and Ub. The high-field 800- and 900-MHz NMR spectrometers were critical to this effort and provided the necessary sensitivity and resolution (Figure 1) required to determine the solution structure of the 25-kD complex (Figure 2). Though a host of other structurally similar E2 exists, the ability to form a noncovalent complex with ubiquitin is unique to the UbcH5 family of ubiquitin-conjugation enzymes. Our structural work provided a foundation for investigating the mechanistic importance of this interaction. We were able to design a mutation, Serine 22 to Arginine (S22R), in UbcH5c that selectively abrogates the noncovalent binding of ubiquitin, leaving all other functions of UbcH5c intact. The integrity of the noncovalent ubiquitin binding interface is critical for the function of UbcH5c in ubiquitin transfer reactions. Though S22R-UbcH5c is capable of transferring a single ubiquitin to a target protein, it can no longer form poly-ubiquitin chains in BRCA1-directed ubiquitination reactions.

Part of the answer to this riddle is provided by our work on the activated UbcH5c~Ub covalent complex. UbcH5c carries activated ubiquitin via formation of a covalent thiolester bond between the active site cysteine of UbcH5c and the C-terminus of ubiqiutin. Formation of the activated UbcH5c~Ub complex in the context of S22R-UbcH5c allows us to investigate in molecular detail the structural changes caused by activation. This work is presently ongoing at EMSL. However, when we use wild-type UbcH5c, we find the presence of the noncovalent ubiquitin-binding site allows activated UbcH5c~Ub to self-assemble into higher molecular weight complexes. This ability to self-assemble is critical for the formation of poly-ubiquitin chains. Much of this work will be detailed in an upcoming publication of *Molecular Cell*.

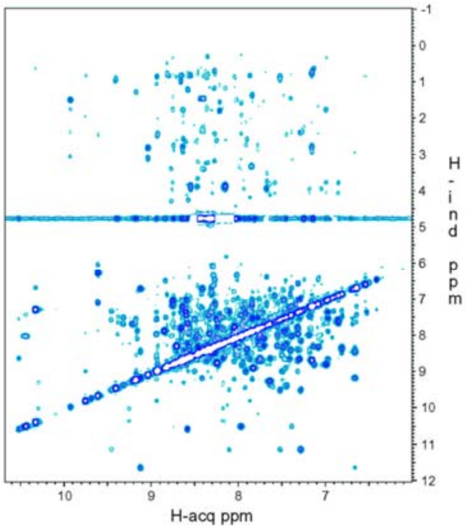

Figure 3. Two-dimensional projection of a three-dimensional Noesy-^{15}N HSQC spectrum of ^{2}H,^{13}C,^{15}N-labeled BRCT domain of BRCA1 in complex with an unlabeled domain of CtIP collected at 600 MHz. The molecular weight of the complex is ~35kD. Many of the peaks observed in the top half of the spectrum represent intermolecular interactions.

The recent installation of cold probes on 600- and 800-MHz NMR spectrometers has allowed us to investigate other BRCA1 protein-protein complexes. The C-terminus of BRCA1 contains an ~225 residue BRCT domain that also contains a number of cancer-predisposing mutations. This domain specifically binds a phosphopeptide motif found in a number of nuclear proteins. One of these, CtIP (CtBP Interacting Protein) is of particular interest as its association with both CtBP, a ubiquitous transcriptional repressor, and BRCA1, a transcriptional regulator, is believed to play a crucial role in the tumor suppressor function of BRCA1. As shown in Figure 3, we have been able to collect high-quality data on the BRCA1-CtIP complex, allowing investigation into the molecular details of this interaction.

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Brzovic PS, A Lissounov, DE Christensen, DW Hoyt, and RE Klevit. 2006 "A UbcH5/Ubiquitin Noncovalent Complex Is Required for Processive BRCA1-Directed Ubiquitination" *Molecular Cell* 21(6): 873-880

Microscopic View of Strontium Interactions in Minerals

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Characterization of strontium in phyllosilicate minerals with solid-state nuclear magnetic resonance spectrometry (NMR) will contribute to an understanding of strontium/mineral interactions in soils exposed to leaking waste tanks, thus enabling the design of better models for predicting the fate of strontium in the environment and better cleanup technologies.

The interactions of strontium with clay minerals and zeolites are not well understood and must be researched so accurate models for predicting the environmental fate of radioactive strontium-90 released from sites such as Hanford can be developed. Solid-state NMR spectrometry is a useful tool for probing the molecular structure of materials, including the interactions of cations sorbed by mineral systems. However, there is only one NMR active isotope of strontium (i.e., strontium-87) and the direct study of strontium with solid-state NMR is experimentally challenging. Strontium-87 has similar chemistry to strontium-90 and is a quadrupolar nucleus (I = -9/2) with a low natural abundance (~7%), a low gyromagnetic ratio ($\gamma = -1.163 \text{ x } 10^{7}\ 1^{-1}T^{-s}$), and large quadrupolar coupling constants (14-25 MHz) (Larsen et al. 2000; Bastow 2002; Bowers et al. 2006 a, b). These factors contribute to a lack of sensitivity that must be overcome to perform time-efficient studies of strontium in natural samples, such as environmentally relevant clay minerals and zeolites.

In our ongoing studies at PNNL on the 21.14-tesla (T) (^{1}H resonance frequency of 900 MHz) instrument, we are using sensitivity-enhancing techniques to characterize the local electromagnetic environment of strontium nuclei in mineral systems.

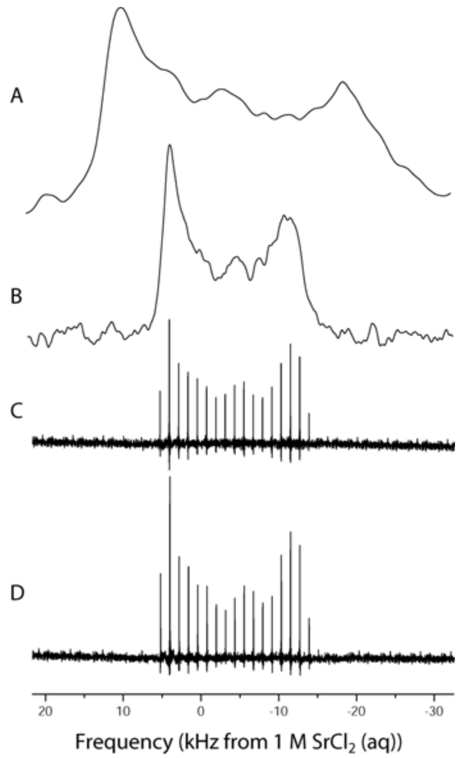

Figure 1. Strontium carbonate strontium-87 NMR spectra: (A) static echo at 11.74 T (800 MHz), (B) static echo at 21.14 T scaled by 1/37, (C) QCPMG at 21.14 T (900-MHz) scaled by 1/275, (D) DFS-QCPMG at 21.14 T scaled by 1/826.

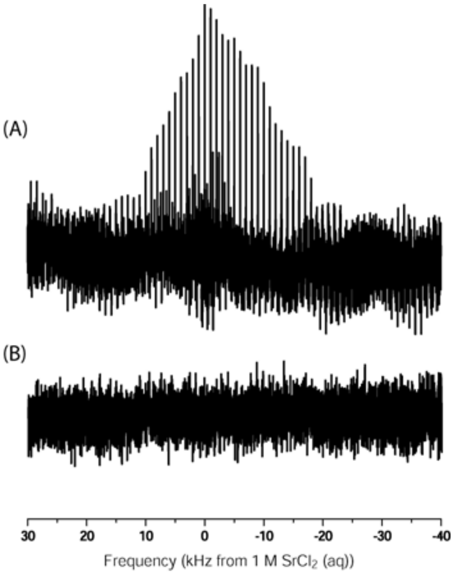

Figure 2. Strontium NMR spectra of Na-4 Mica after (A) and prior to (B) heat treatment at 500˚C for four hours. The heat-treated sample produces a single strontium resonance fit well by a quadrupolar line shape.

We have shown in recent work that the 21.14-T (900-MHz) field strength provides an order-of-magnitude enhancement to the signal-to-noise ratio for strontium-87 experiments and that quadrupolar Carr Purcell Meiboom Gill (QCPMG) analysis adds an additional order of magnitude (Bowers et al. 2006). Unfortunately, these enhancements were insufficient to observe strontium in complex minerals. In the past year, we were able to demonstrate that adding the double frequency sweep (DFS) preparatory scheme results in up to an additional fivefold enhancement to the signal-to-noise ratio (Figure 1), thereby permitting the detection of strontium resonances in soil minerals.

With DFS-QCPMG at 21.14 T (900 MHz), we were able to perform solid-state NMR studies of strontium in additional inorganic and organic systems, where these studies were impossible with QCPMG analysis alone. One important conclusion from our data is that water-strontium interactions have a profound effect on strontium-87 NMR spectra; in fact, we have been unable to observe strontium in any system where there is water in the strontium hydration sphere (Figure 2). The reasons for this are the subject of current investigations. DFS-QCPMG at 21.14 T has also been used to successfully examine the strontium-binding environment in a number of heat treated micas, montmorillonites, titanates, and titanosilicates. To perform such strontium-87 NMR analyses at more conventional fields (i.e., 11.74 T) would require on the order of 1800 days rather than the three days required to produce the spectrum shown in Figure 2. The library of quadrupolar parameters and their relationship to crystal structure prepared from our studies of simple systems now allows informed predictions of the strontium-binding environment based on strontium-87 NMR parameters and x-ray diffraction studies. This library could not have been developed over the past year without the use of DFS-QCPMG on the EMSL 21.14-T (900-MHz) NMR spectrometer. A detailed discussion of the strontium-binding environment in one of the mica samples mentioned earlier is the subject of a manuscript published in the *Journal of Physical Chemistry B* (Crosson et al. 2006). We also intend to publish the results of our mineral studies in a paper that will detail strontium binding in phyllosilicates and in another paper that will describe strontium binding in designer titanosilicate materials.

In the coming year, we intend to return to EMSL to study additional titanosilicate materials developed at Savannah River National Laboratory specifically to sequester strontium from Hanford-like wastes. Some of these materials have tunable selectivity for cesium and strontium, making this work highly important to the DOE mission. We will also continuing our investigations of mineral weathering under near-field exposure to simulated tank waste leachate (Chorover et al. 2003; Crosson et al. 2006) by monitoring the kinetics of mineral dissolution and re-precipitation in samples of natural Hanford sediments.

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Solution Structure of the Complex Between Poxvirus-Encoded CC Chemokine Inhibitor vCCI and Human MIP-1ß

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The chemokine system is critical for host defense in healthy individuals, but it also can lead to inflammatory diseases including asthma, arthritis, and atherosclerosis. This novel work used high-field nuclear magnetic resonance (NMR) spectroscopy to reveal the first known structure of a 35-kDa pox virus chemokine inhibitor:human chemokine complex, which is a stepping stone to future therapeutic drug design.

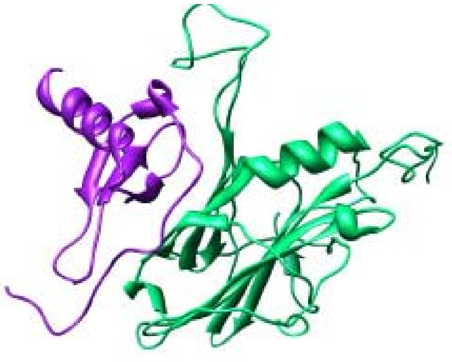

Figure 1. Solution structure of the vCCI:MIP-1β complex, with vCCI backbone in green and MIP-1β backbone in violet.

Chemokines (i.e., chemotactic cytokines) comprise a large family of proteins that recruit and activate leukocytes, giving chemokines a major role in both immune response and inflammation-related diseases. To date, about 50 chemokines have been identified, and these small proteins (7 to 14 kDa) are believed to function by binding with endothelial or matrix glycosaminoglycans (GaGs) to form a concentration gradient that is then sensed by high-affinity, 7-transmembrane domain G-protein coupled chemokine receptors on the surface of immune cells, leading to activation and chemotaxis. Chemokines play critical roles in the immune system, causing chemotaxis of a variety of cells to sites of infection and inflammation, as well as mediating cell homing and immune system development (Baggiolini 2001; Gerard and Rollins 2001). There are four subfamilies of chemokines, CC, CXC, C, and CX_3C, which are named for the position of conserved N-terminal cysteine residues; different subfamilies tend to function on different cell subsets (Baggiolini 2001).

All known pox and herpes viruses encode proteins that interfere with the host chemokine network, probably as part of a strategy to manipulate and subvert the immune system (Boomker et al. 2005). Such virally encoded proteins include chemokine mimics, chemokine receptor analogs, and a group of secreted, soluble chemokine binding proteins (CKBPs) that exhibit little similarity to any mammalian protein (Seet and McFadden 2002). CKBPs competitively bind to chemokines and disrupt chemokine interactions with the host cell surface receptors or GAGs. Although some CKBPs interact with a very broad spectrum of chemokines across several chemokine subfamilies, the poxvirus-encoded viral CC chemokine inhibitor (vCCI) proteins bind selectively to the CC family of pro-inflammatory chemokines (Seet and McFadden 2002; Lalani et al. 1998). The vCCI proteins have been shown to be potent inhibitors of chemokine action *in vitro* (Lalani et al. 1998) and effective anti-inflammatory agents in vivo (Dabbagh et al. 2000).

Although the structures of several chemokines (Clore et al. 1990; Mayer and Stone 2000; Crump et al. 1997; Fernandez and Lolis 2002), as well as the individual structure of vCCI (11) are known, no structure had previously been solved of a vCCI:chemokine complex, so the structural basis of vCCI's interaction with chemokines was not clear. We have used heteronuclear multidimensional NMR to determine the first structure of an orthopoxvirus vCCI in complex with a human CC chemokine MIP-1ß variant. Access to high-field spectrometers at the EMSL High-Field Magnetic Resonance Facility was critical to obtaining the spectral data that enabled structure determination work on this 35-kDa complex.

Our structural studies reveal that the vCCI and MIP-1ß form a complex in a 1:1 stoichiometry, and that vCCI occludes the regions in the chemokine that are important for chemokine homo-dimerization, receptor binding, and glycosaminoglycan interaction (Figure 1). The structure also defines key interactions that form the basis for the affinity and selectivity of vCCI towards certain CC chemokines. The insights gained from this groundbreaking work will be critical to development of therapeutic agents to modulate immune response. This work was published in *Proceedings of the National Academy of Sciences of the United States of America* 103(38):13985-13990.

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A Solid-State ^{95}Mo NMR and Computational Investigation of Dodecahedral and Square Antiprismatic Octacyanomolybdate(IV) Anions: Is the Point-Charge Approximation an Accurate Probe of Local Symmetry?

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Solid-state nuclear magnetic resonance (NMR) studies of low-gamma nuclei have been hampered in the past because of inherent difficulties associated with observing low-frequency quadrupolar nuclei. Such studies are becoming feasible and productive with the use of the highest possible magnetic field strengths coupled with sensitivity-enhancement experiments.

Because of the experimental challenges they present, solid-state NMR studies of quadrupolar nuclei with small magnetic moments represent a relatively undeveloped area of research. The inherently low NMR sensitivity of such nuclei means that considerable time is required to obtain NMR spectra of adequate signal-to-noise characteristics—a problem that is often compounded by the fact that solid-state NMR spectra, particularly of quadrupolar nuclei, may span several hundred kilohertz. Recent technological advances have enabled NMR data collection for challenging quadrupolar nuclei that have previously been refractory to observation. For example, the development of high-field magnets and new-and-improved pulse sequences facilitate data collection; high magnetic fields result in increased sensitivity and amplification of the magnetic shielding, σ, interaction and, in addition, substantially reduce probe ringing, which is often an experimental hindrance when observing low-frequency quadrupolar nuclei. New pulse sequences include a variety of sensitivity-enhancement techniques that further improve the quality of the NMR experiment and result in significant reductions in experimental time.

One important isotope that falls into the small magnetic moment category is ^{95}Mo. Despite the prevalence of molybdenum in modern chemistry, ^{95}Mo has received little attention from the solid-state NMR community, primarily because of its unfavorable properties: $\Xi = 6.547$ MHz, N.A. = 15.92 %, $Q = -0.022\times10^{-28}$ m^2. Unfortunately, the small quadrupole moment, Q, of ^{95}Mo creates an additional impediment for NMR studies in the solid state to long spin-lattice relaxation times. Nevertheless, by employing the highest possible magnetic field strengths and available sensitivity-enhancement techniques, we have been able to undertake ^{95}Mo NMR studies. Through determination of the molybdenum σ and electric field gradient (EFG) tensors, a wealth of information on molecular and electronic structure can be obtained.

In this study, we have demonstrated the efficiency and effectiveness of solid-state ^{95}Mo NMR spectroscopy as a tool for analyzing two symmetry forms of the diamagnetic octacyanomolybdate(IV) anion: 1) the approximate dodecahedral, D_{2d}, symmetry and 2) the approximate square antiprismatic, D_{4d}, symmetry. The success of this study is attributed to the use of the highest available magnetic field strengths, 21.15 tesla (T), which corresponds to 900-MHz proton frequency; 17.63 T (750 MHz); and 11.75 T (500 MHz), and the quadrupolar Carr-Purcell Meiboom-Gill (QCPMG) and double-frequency sweep (DFS)/QCPMG sensitivity-enhancement techniques. By examining the D_{2d} and D_{4d} $Mo(CN)_8^{4-}$ anions in the solid state, we have studied each structure independently and have characterized the molybdenum σ and EFG interactions, thereby avoiding problems associated with solution NMR studies, such as ligand exchange or interconversion between symmetry forms. The acute sensitivity of the molybdenum σ and EFG tensors to small changes in the local structure of these anions has allowed the approximate D_{2d} and D_{4d} $Mo(CN)_8^{4-}$ anions to be readily distinguished.

Our results indicate that the magnitudes of the molybdenum σ and EFG interactions are comparable for the D_{2d} and D_{4d} $Mo(CN)_8^{4-}$ anions; however, the relative values and orientations of the principal components of the molybdenum σ and EFG tensors for the two symmetry forms are different, resulting in ^{95}Mo NMR line shapes that are distinctly different at the fields employed here (Figure 1). Quantum chemical calculations of the molybdenum σ and EFG tensors, using zeroth-order regular approximation density functional theory (ZORA DFT) and restricted Hartree-Fock (RHF) methods, have also been carried out, and the results obtained are in good agreement with experimental results. The most significant and surprising result from the DFT and RHF calculations is a substantial EFG at molybdenum for an isolated $Mo(CN)_8^{4-}$ anion possessing an ideal square anti-prismatic structure; this is contrary to the point-charge approximation, which predicts a zero EFG at molybdenum for this structure.

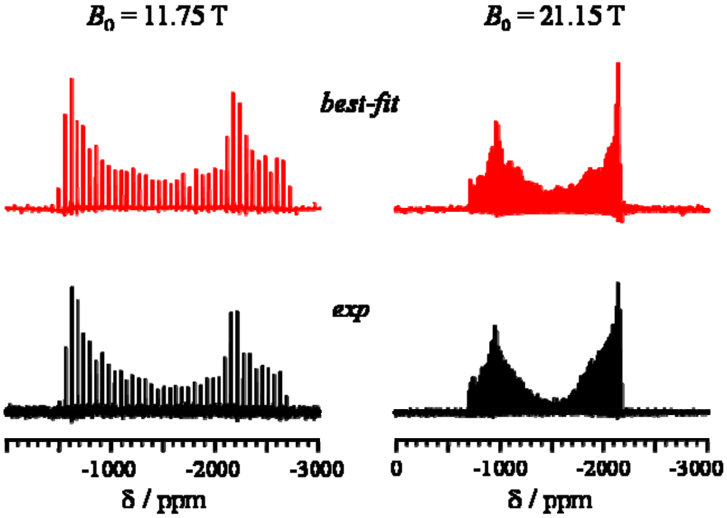

Figure 1. Experimental and best-fit simulated ^{95}Mo central-transition NMR spectra of a solid, stationary sample of $Tl_4Mo(CN)_8$ acquired using the QCPMG pulse sequence at 11.75 T (left) and the DFS/QCPMG pulse sequence at 21.15 T (right). A total of 31 760 transients were summed for $Tl_4Mo(CN)_8$ at 11.75 T and 8192 at 21.15 T.

Citation

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User Projects

Structural Studies of Riboswitches

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MA Kennedy, S Ni, Miami University, Oxford, Ohio

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Structure of Telomerase RNA and Telomeric Proteins

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Application for 800MHz NMR Spectrometer Time to Facilitate the Structural Study of the Complex Formed by Pox Virus Encoded Protein vCCI and Human CC Chemokine MIP-1beta

PJ LiWang, L Zhang, Texas A&M University, College Station, Texas

alphaB-crystallin - the Core and the Oligomer : A Structural Investigation

P Rajagopal, R Klevit, University of Washington, Seattle, Washington

Determination of the Three-dimensional Solution Structure of NosL, a Potentially Novel Copper(I) Metal Transporter

V Copie, LM Taubner, GA Jacobs, Montana State University, Bozeman, Montana

Structure and Interactions of a Domain of Dynein Intermediate Chain--Protein Folding Coupled to Binding

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Slow MAS of Lipids in Mouse Fast and Slow Skeletal Muscle

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Solid State MAS NMR of High-Valent Cation Exchanged H-MFI

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Study of the Network Structures of Polymer-Derived Amorphous SiAlCN Ceramics

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Hydrogen Storage Materials

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Hydrogen Storage Materials

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Structural Genomics of Eukaryotic Model Organisms

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Study of the Binding Mechanism of Mutant SN-15 to Hydroxyapatite using ^{15}N{^{31}P}REDOR

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Structure of PR Domain of RIZ1 Tumor Suppressor

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Routine $_1$H and $_{13}$C NMR Analysis of Functionalized Semiconductor and Metallic Nanoparticles Synthesized for Biodetection Studies

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Routine ^{1}H and ^{13}C NMR Analysis of Functionalized Semiconductor and Metallic Nanoparticles Synthesized for Biodetection Studies

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NMR Structural Studies of Clustered DNA Damage

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Structural Investigations of Solid Materials by High Resolution Solid State NMR at Very High Field

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NMR Structural Studies of a 180 kDa HDL Particle

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Structural Studies of Lipid-free Apolipoprotein A-I

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Investigating Molecular Recognition and Biological Function at Interfaces Using Antimicrobial Peptides

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Correlation of Structure and Function of Zinc Metalloproteins Via Solid-state NMR Methods

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Magnetic Resonance Microscopy of Environmental Lung Injury

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Investigation of the Role of Mg_2^+ in DNA Repair Proteins APE1, Pol, and FEN1

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Investigation of Catalyst Reaction Mechanisms by In-situ High Field, High Resolution NMR Spectroscopy

J Hu, Pacific Northwest National Laboratory, Richland, Washington

Development of a Novel Approach for Imaging Inhaled Particulates

KR Minard, Pacific Northwest National Laboratory, Richland, Washington

Slow-MAS NMR Methodology Developments

RA Wind, Pacific Northwest National Laboratory, Richland, Washington

HYSCORE Analysis of Protein Peroxyl Radicals in Myoglobin and Hemoglobin

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Deposition of Cobalt-doped Oxides for Spintronic Applications

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Grand Challenge in Biogeochemistry

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Structural Investigation of a Molecular Chaperone

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Pulsed EPR of Membrane Proteins

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Properties of Surface Functional Groups of Black Carbon from Historic Charcoal Blast Furnaces

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***In-situ* High Field, High Resolution NMR Spectroscopy**

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NMR Study of Effects and Mechanisms of Mechanical Activation on Hydrogen Sorption/Desorption of Nanoscale Lithium Nitrides

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NMR Study of Effects and Mechanisms of Mechanical Activation on Hydrogen Sorption/Desorption of Nanoscale Lithium Nitrides

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An Extended Study of the Molybdenum(IV) Octacyanide Anion: Comparison of Dodecahedral versus Square Antiprismatic Structural Forms via Solid-State ^{95}Mo Nuclear Magnetic Resonance Spectroscopy

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Thrust Area 1: Purification and Biophysical Characterization of MR-1 Redox Proteins
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Thrust Area 1: Metal-reducing *Shewanella* Believed to be Involved in the Dissimilatory Reduction of Solid Phase Iron (III)

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High-Resolution Imaging of the Passive Heart and Cardiac Valves for the Next Generation Cardiac Models

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Investigation of Biodegradable and Nonbiodegradable Thermalreversible Gelling Polymers Using Slow Magic Angle Spinning NMR Spectroscopy

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Grand Challenge in Membrane Biology

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Dissolution of Borosilicate Waste Glass: Effect of Al and B Coordination on Alkali Ion Exchange

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Structure and Function of the Membrane Protein OEP16

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Structure of Trityls

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Interrogation of Glucose Metabolism by Oral Biofilms Using Combined NMR/Optical Spectroscopy and Stable Isotope Labeling

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Combined NMR/Optical Microscopy for Oral Biofilm Physiology Studies

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PNNL Metabolomics Measurement and Validation Development for Renewable Energy Research

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MRI for Understanding Water Management in PEM Fuel Cells

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Sensitivity Enhancing NMR of Strontium-87 Nuclei in Clays, Zeolites, and Waste Cleanup Technologies

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In vivo and *ex vivo* High Resolution Slow-MAS MR Spectroscopy in Mice

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Characterization of *in vivo* ^{1}H-NMR Biomarkers for Pulmonary Phospholipidosis

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MR Imaging of Respiratory Structure and Function

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A Multinuclear MAS NMR Investigation of Environmentally Relevant Materials: Lanthanum Strontium Gallium Magnesium Oxide and Magnesium Aluminum Layered Double Hydroxides

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High-Field Solid-State Mn-55 NMR Spectroscopy of Manganese Pentacarbonyls

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Structural Investigation of alphaB-Crystallin Core Domains

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Structural Biology of the Human High Mobility Group A (HMGA) Proteins: Characterizing the Hub of Nuclear Function

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Structural Studies of Regulators of Histone Protein Synthesis

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Analysis of Nitrogen in Humic Substances and Photochemical Degradation of TNT

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Structural Studies of a Novel Family of Manganese Uptake Proteins in Cyanothece Containing a Repeated Five-Residues Domain (RFR).

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Structural Studies of a Family of Proteins from the Diurnal Cyanobacteria Cyanothece 51142 that Contain an Unusual Repeated Five-Residues Domain (RFR).

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Identify Biomarkers for COPD (Chronic Obstructive Pulmonary Disease) in Humans using Metabonomic Analysis of Serum and Urine by NMR.

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Investigation of Crystalline to Amorphous Phase of Cellulose by using Slow Magic Angle Spinning NMR Spectroscopy

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Identifying Value Added Products from Biomass Conversion Reactions by NMR

H Zhao, JE Holladay, Pacific Northwest National Laboratory, Richland, Washington

Mistranslation Fragment of an *in silico* Designed Novel-fold Protein Forms and Exceptionally Stable Symmetric Homodimer with a High-affinity Interface

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Structure of Designer Proteins

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Determining *in vivo* Concentrations of Bacterial Autoinducers

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High Resolution NMR Investigation of the Nano-materials

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Elucidation of the NAD Sensing Mechanism of Mitochondrial Apoptosis Inducing Factor

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Solid State NMR to Investigate Protein Interactions at Interfaces

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The Iron Binding Environment of the Cyanobacterial Ferric Ion Transporter, FutA1

TJ Smith, Donald Danforth Plant Science Center, Saint Louis, Missouri

Characterization of *in-vivo* ^{1}H-NMR Biomarkers for Pulmonary Phospholipidosis

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Pulsed EPR Studies of Nanocrystalline Zeolites and Hollow Zeolite Structures

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High-resolution ^{27}Al MAS NMR of Weathered Clays and Hanford Sediments

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Binding Environment of Strontium-87 Nuclei in DOE Waste Remediation Materials

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Solid-State NMR Characterization of the Surface Sites of Alumina Nanofibers

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The Mechanism of Action of Carbonic Anhydrase and LpxC

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Conformational Dynamics of Pin1 Regulation of APP Processing and Abeta Production

LK Nicholson, Cornell University, Ithaca, New York

Source Attribution of Biological Weapons (Ricin and Associated Metabolites) using NMR Spectroscopy

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Metabonomic Studies of Host Response to *Yersinia pestis* Exposure through Analysis of Plasma and Urine from Mice

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MA Kennedy, Miami University, Oxford, Ohio

NMR Assignment and Structure of the C-Terminal Domains of Human Villin

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Sintering of Hydroxyapatite for Advanced Orthopedic Applications

LL Shaw, University of Connecticut, Storrs, Connecticut

^{99}Tc NMR Study of Tc(V) Solids

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Magic Angle Spinning NMR Experiments on Radioactive Samples with a Microcoil Spinner

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Structure of Complex Proanthos\Cyanidins by High Field NMR Spectroscopy

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Solid State NMR Studies of Nano-materials

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NMR and Computational Studies of Chemical Transformations at Complex Interfaces

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Clusters of Damage in Irradiated DNA

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Free Radical Reactions in the Catalytic Cycle of Cytochrome bc Complexes

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Solution Structure of a 42 kDa "Metal Sensor" CzrA-DNA Complex

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Protein Interactions and Interfaces

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Solid-State NMR Spectroscopy on Radioactive Samples with Microcoils

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NMR Studies of Human Apolipoprotein-E

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Molecular Probes of Quinol Oxidation by the Cytochrome b6f complex

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Ultra-High Field NMR Studies of Stable Isotope Applications

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Structural Proteomics of Myobacterium Tuberculosis

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NMR Structural Investigations of BRCA1

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Solid-State ^{67}Zn NMR of Synthetic Metalloprotein Models

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NMR Microscopy of Diffusive Transport in Natural Porous Mineral Grains

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Free Radical Processes in g- and Heavy Ion Irradiated DNA

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Solid-State NMR Characterization of Metal Phosphines

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Probing the Mechanism of the Alkaline Phosphatase Reaction by ^{67}Zn and ^{25}Mg NMR

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NMR Structural Investigations of BRCA1

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Distance Measurements in RNA using DEER Spectroscopy with Site-directed Spin Labeling

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Structural Proteomics: Annotating the Genome using 3D Structure

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Defect Dynamics on Crystalline Quartz

JJ Weil, SM Botis, SM Nokhrin, University of Saskatchewan, Saskatoon, Saskatchewan, Canada

Microscopic Characterization of Porosity, Diffusivity, and Tortuosity in Single Particles of Hanford Sediments using Nuclear Magnetic Resonance (NMR) Technique

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Special Purpose Re-configurable ASIC Hardware for Accelerating Protein Structure Analysis Software

TJ Conroy, University of Regina, Regina, Saskatchewan, Canada

Studies of Ligand-Induced Conformational Change in CD44 receptor

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Solid State NMR Studies of Chloropropyl Silica Gels

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Composite Gadolinium Oxide and Yttrium Phosphate Nanoparticles for Managing Cancer Therapy with Magnetic Resonance Imaging

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Interaction of *Escherichia coli* Formamidopyrimidine-DNA Glycosylase (Fpg) with Damaged DNA Containing an 7,8-Dihydro-8-oxoguanine Lesion

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TRAPDOR Experiments on Siliceous Sinters from Thermal Springs

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Magnetic Resonance Microscopy of Water Dynamics at Hydrophilic Surfaces

GH Pollack, University of Washington, Seattle, Washington

Complexation of Th(IV) by Organic Acids in Aqueous Solution

HM Cho, Pacific Northwest National Laboratory, Richland, Washington

Kinetics of Polyphosphate Decomposition in Heterogeneous Environments

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Nuclear Magnetic Resonance Detection of Radiation Damage in Ceramics

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NMR Analysis of Synthesized Organic Compounds for Modification of Nanostructures

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Pulsed-EPR studies to Investigate a New Family of Free Radical Spin Traps

GM Rosen, University of Maryland, Baltimore, Maryland

Study of the Structures of Thermally Formed Oxides on Amorphous SiAlCN Ceramics

L An, Y Wang, University of Central Florida, Orlando, Florida

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

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Stabilization of Soil Organic Matter: Land Use, Erosion and Burial

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Structure of the PR Domain of RIZ1 Tumor Suppressor

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Separation of ^{47}Ti and ^{49}Ti Solid-State NMR Lineshapes by Static QCPMG Experiments

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PNNL/NESG Structural Genomics

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Structure and Dynamics of aB57

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Structural Studies of Lipid-free Apolipoprotein A-I

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Structural Studies of Apolipoprotein A-I/preb-HDL Particles

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Solid State ^{183}W MAS NMR at High and Ultra High Magnetic Fields

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Investigation of the Role of Mg_2^+ in DNA Repair Proteins

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Structural Genomics: Determining the Structure of Proteins from the Infectious Agent *Pseudomonas aeruginosa*

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Correlation of Structure and Function of Zinc Metalloproteins via Solid-state NMR Methods

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Drug Interactions of Human and Bacterial Cytochrome P450s Probed by Pulsed Electron Paramagnetic Spectroscopy

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Investigation of Soot Morphology and Microstructure with Respect to the Oxidation

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Development of Organophosphorus Compounds for Solid-state Lighting Applications

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High-Performance Mass Spectrometry Facility

The High-Performance Mass Spectrometry Facility (HPMSF) provides state-of-the-art mass spectrometry (MS) and separations instrumentation that has been refined for leading-edge analysis of biological problems with a primary emphasis on proteomics. Challenging research in proteomics, cell signaling, cellular molecular machines, and high-molecular weight systems receive the highest priority for access to the facility. Current research activities in the HPMSF include proteomic analyses of whole cell lysates, analyses of organic macro-molecules and protein complexes, quantification using isotopically labeled growth media, targeted proteomics analyses of subcellular fractions, and detection of post-translational modifications (PTM) such as phosphorylation and ubiquination. More than a dozen microbial systems are currently being studied in HPMSF by researchers from throughout the country. In addition, there are several ongoing projects in higher order systems (including mammalian systems) that are investigating a broad range of biological questions from cancer screening to infectious diseases to fundamental questions of post-translational modifications and protein-protein interactions.

Capabilities

The facility features state-of-the-art liquid chromatographic (LC) separations capabilities coupled to a complete suite of MSs for proteomics analysis. The available instruments range from a group of nine ion trap spectrometers for tandem mass spectrometry (MS/MS) work to very high-sensitivity and high-resolution Fourier transform ion cyclotron resonance (FTICR) spectrometers that offer 1 ppm mass measurement accuracy. Proteomics analysis on these FTICR spectrometers is complemented by a quadrupole time-of-flight (QTOF) spectrometer that combines MS/MS analysis with mass measurement accuracy. These spectrometers are coupled with very high-resolution separations (500 peak capacity) that are highly beneficial to these areas of research. Focused research projects into biomolecular complexes and macro-molecules are supported on the facility's 7-tesla FTICR spectrometer, a flexible instrument that can be configured in many different ways.

Instrumentation & Capabilities

Mass Spectrometers

- QTOF
- Five ion trap spectrometers
- Four linear ion trap mass spectrometers

FTICR

- 7, 9.4, 11.5 and 12-T FTICR spectrometers

FT Spectrometer

- Orbitrap™

Additional Capabilities

- Twelve custom high-performance liquid chromatography (HPLC) systems
- Agilent capillary HPLC system

The HPMSF is committed to maintaining state-of-the-art MS and separations capabilities. To this end, the facility's staff work to develop and implement new capabilities such as the ion funnel, dynamic range enhancements applied to MS (Dynamic Range Enhancement Applied to Mass Spectrometry [DREAMS]), and data analysis tools, which are incorporated into the capabilities of the facility as they become available. As part of this commitment the facility added a 12-T FTICR spectrometer that is being optimized for work on intact proteins for the identification of post-translational modifications and protein isoforms. In addition, an Orbitrap™ MS was added to the facility. This instrument provides performance similar to the FTICR spectrometers but without the need for a superconducting magnet. The members of the facility staff are highly skilled in all areas required for proteomics research, from sample preparation to analysis and data interpretation, and they are available to help develop methodologies to tackle these challenging problems. As needed, scientific staff not assigned to the facility can be accessed as matrixed members of the facility. Since its inception, more than 100 separate user projects have been undertaken in the facility, with some spanning over a year in duration.

The HPMSF has developed state-of-the-art software for the acquisition and analysis of FTICR mass spectra. This software package is called ICR-2LS. It is a Microsoft Windows-based application that enables many of the unique instrument control functions developed in the W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL). This same software allows automated spectral interpretation of raw FTICR data. The spectral interpretation features are integrated into our application and, thus, are not easily transferred. The data acquired in the facility is stored and managed in an in-house-developed relational database.

Mass Spectrometry Research Capabilities. Nine ion trap MSs from ThermoElectron are available in the facility: two Finnigan LCQ Classics, two Finnigan LCQ Duos, one Finnigan LCQ DECAXP, and four LTQs that provide greater than an order of magnitude improvement in dynamic range from Finnigan. An example of one of these instruments is shown in Figure 1.

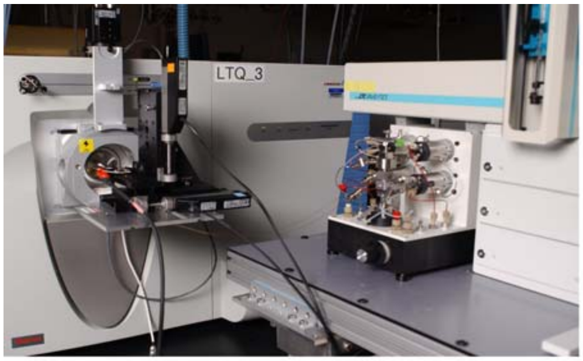


Figure 1. Ion trap MS in an HPMSF laboratory.

The ion trap instruments have either a three-dimensional quadrupole ion-trap or a two-dimensional elongated trap designed for use with electrospray ionization sources. These instruments are well-suited to MS/MS spectrometer experiments because of their very high collection efficiency for product ions. The mass range of this instrument is 150 to 2000 m/z, but the range can be extended to 4000 m/z for some applications. The ion trap instruments have a maximum resolution of 10,000 in the zoom-scan mode, and 4000 in full-scan mode. In addition, the system is easily operated in either positive or negative ion mode with the addition of SF_6 as a sheath gas.

Figure 2. Wide-bore, passively shielded 11.5-T FTICR MS.

Fourier Transform Ion Cyclotron Resonance Mass Spectrometers. This 11.5-T ultrahigh-performance MS uses a wide-bore (205 mm), passively shielded (Figure 2) superconducting magnet. The spectrometer is equipped with an electrospray ionization source and an ion funnel. The 11.5-T FTICR has a resolution of 150,000 at m/z 60,000 and a mass accuracy of 1 ppm for peptide samples with molecular weights ranging from 500 to 2000 Da. Ions are collected external to the magnet in a series of quadrupoles that allow the researcher to eliminate irrelevant ions before analysis in the FTICR spectrometer. DREAMS is a unique capability of this facility. The 11.5-T FTICR instrument can be fitted with an HPLC system and is equipped with an infrared laser for multiphoton dissociation of samples for MS/MS in the ion cyclotron resonance (ICR) cell.

Figure 3. 150-mm-bore, actively shielded 9.4-T FTICR instrument.

The 9.4-T FTICR spectrometer (Figure 3) is a 150-mm-bore, actively shielded Bruker Daltonics APEX III. The original ion source has been replaced with a custom source that incorporates a dual-channel ion funnel for simultaneous introduction of calibrant ions, DREAMS technology, and automatic gain control. These modifications permit maximum use of the spectrometer's capabilities by maintaining the optimum number of ions in the ICR cell throughout an LC separation. The outstanding resolution of over 60,000 is maintained throughout the separation with a sensitivity comparable to the other FTICR instruments in the facility. This system is seamlessly integrated with the facility's automated HPLC (5000 psi) system for unattended operation 24 hours a day, 7 days a week.

The Waters' Micromass Ultima application program interface (API) QTOF instrument is an orthogonal extraction-TOF MS that has enabled automated exact mass measurement with the ultimate performance (Figure 4) in MS and MS/MS. The instrument features optimized resolution, enhanced ion optics for enhanced sensitivity, a quadrupole mass filter, and a collision cell for MS/MS analyses. These features are also accessible over an enhanced linear dynamic range, enabling rapid and reliable quantification. This powerful combination of capabilities delivers simple exact mass measurement of precursor and fragment ions with maximum sensitivity to yield the highest confidence in structural elucidation and databank search results.

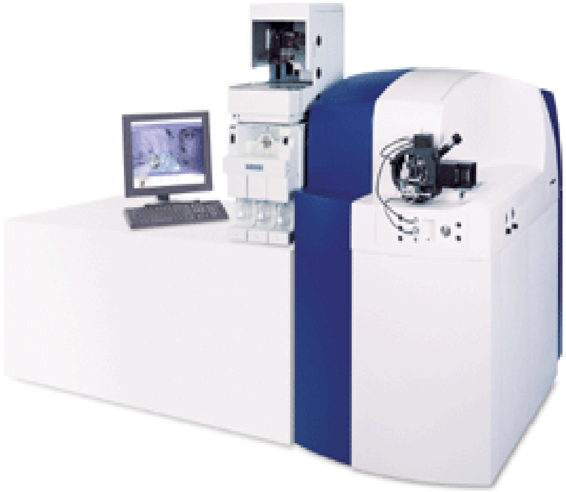


Figure 4. QTOF instrument in the HPMSF.

A signature capability of the facility is the efficient coupling of capillary separations (Figure 5) to our MSs. Instruments for both LC and capillary electrophoretic separations are available. Two ABI 270A electrophoresis systems are available along with one Agilent capillary LC and one Shimadzu capillary LC system. Unique to this facility are the in-house-developed LC systems. These systems deliver constant-pressure gradient separations at up to 5000 psi. Continuing developments of high-pressure versions of these LC systems feature a PAL autosampler with cooled sample holder, VALCO high-pressure valves, and ISCO syringe pumps. Computer software has been developed that allows the system to be configured with any of our spectrometers through DCOM communication protocols.

Figure 5. Capillary ultrahigh pressure separations capability.

Figure 6. 7-T FTICR spectrometer.

The 7-T FTICR spectrometer is based on a 160-mm-bore, superconducting magnet and is equipped with a custom electrospray ionization source (Figure 6). This instrument has high-mass-resolving power (e.g., a mass-resolution greater than 2,000,000 has been obtained for insulin), while unit resolution is routinely achievable during online capillary isoelectric focusing (CIEF) experiments for proteins with mass resolutions of less than 30,000 μ; mass accuracy less than 5 ppm is typical for peptide/protein samples with molecular masses ranging from 500 to 30,000 μ. A detection limit of approximately 10 attomoles has been obtained with online LC and CIEF separations.

Figure 7. 12-T FTICR spectrometer.

The 12-T FTICR (Figure 7) has a 100-mm-bore magnet that is actively shielded. The original ion optics have been upgraded to include an ion funnel and additional quadrupole stages for enhanced ion transmission and future implementation of data-directed ion selection for MS/MS studies. The system is being optimized for high-throughput, proteome-wide, high-accuracy measurements of the molecular weight of intact proteins. Additionally a "top-down" protein characterization using a variety of dissociation schemes, such as collisionally induced and electron capture dissociation, can be performed on this spectrometer. Protein-separation schemes based on reversed-phase capillary LC, CIEF, and high-field asymmetric ion mobility spectrometry are in use and under development with this system.

Instrument Upgrades

In Fiscal Year 2006, the following capability development and procurement activities occurred in the HPMSF:

- **Proteomics Research Information Storage and Management (PRISM) system.** This system has continued to increase in both size and capability to keep pace with EMSL's proteomics facility and the proteomics field itself. Storage servers were added to bring the online capacity of PRISM up to 20 terabytes. Several new analysis processing machines were added as well as a new SEQUEST cluster. This has brought the total number of computational processing units to more than 200.

- **X!Tandem and "theGPM."** The X!Tandem peptide identification program and "theGPM," an associated presentation web software, are both open source tools that are gaining broader acceptance in the proteomics community. X!Tandem uses a different algorithm than SEQUEST and provides both a complementary analysis capability and a welcome addition to the overall throughput of the proteomics facility. In addition, architectural changes to the Data Management System Analysis Manager program were made to allow the use of plug-in adapters to add new analysis tools to the pipeline as well as modules that pre-process the spectra collected from the mass spectrometry instruments.

- **Protein Sequences Database.** The Protein Sequences Database was implemented to solve the problem caused by an overwhelming proliferation of proteome description files (called "fasta" files, after their internal format). Research campaigns for more and more organisms have been added to PRISM, and each organism typically requires several different descriptions of its proteome. Different researchers want subtle variations on the basic versions that can be tailored to their specific experiment protocols. Additionally, there is a need to create reversed and scrambled versions of these files to support the assessment of false discovery statistics. This has led to a rapid proliferation of fasta files that were quickly becoming geometric in size. The Protein Sequences Database replaces these static fasta files with protein collections which are lightweight lists of references to protein definitions stored in a database. There is only one copy of any unique protein in the database, and protein collections simply reference them. Enhanced descriptive information is kept for each collection, making it easier to keep track of all the variations for each organism. Finally, reversed and scrambled sequences can be generated on demand by the Protein Sequences Database so that separate versions for these types of files do not need to be maintained.

- **OrbitrapTM spectrometers.** One system, acquired in September 2005, is now fully integrated into the facility. This instrument adds to the growing capability to acquire tandem mass spectrometry and accurate mass data more efficiently, providing additional capability for working on new biological systems. A second system was delivered and installed in September. These instruments are the first fundamentally new type of mass spectrometer to be developed in the last 20 years. They trap ions and detect their harmonic oscillations, similar to an FTICR mass spectrometer, but they do not require a magnet and use only electric fields.

- **12-tesla system.** A 12-tesla system is making significant contributions to three user projects. Development of electron capture dissociation for identifying post-translational modifications will continue.

- **Triple quadrupole mass spectrometer.** A new triple quadrupole mass spectrometer was delivered to EMSL in September 2006. This instrument provides greater dynamic range than ion trap mass spectrometers and will be essential in the validation of candidate biomarkers that are discovered with global proteomics analyses.

- **LC systems.** Two new LC systems were constructed in Fiscal Year 2006. Both are configured as dual-mixer systems and use 20,000 psi Teledyne/ISCO syringe pumps. These systems are the first that are configured to use the syringe pumps in a fully automated fashion on the proteomics production line.

Future Directions

The HPMSF expects to support at least 90 user projects in Fiscal Year 2007, made up of 80 distinct users of whom 6 would be distinguished users. Every effort will be made to encourage the submittal of Science Theme proposals from each of our active users during the February 2007 call. Other expected activities in Fiscal Year 2007 include:

- **Continue efforts to maintain the ability to support the ever-growing size of the PRISM system** with available resources. Whenever possible, the existing software source control and issues tracking infrastructure is replaced by open source products that offer improved performance and increased functionality without requiring licensing fees. A collaborative information website (or wiki) was also established as the primary platform for PRISM user documentation. Wiki functionality will allow any proteomics staff member, including developers, users, and collaborators, to incrementally improve and expand the documentation bit by bit.

- **Continue to refine and further develop DREAMS.** To further extend dynamic range and sensitivity in proteome studies, the facility developed and demonstrated the DREAMS approach for high-efficiency capillary LC separations with FTICR mass spectrometry. In an initial application, this approach approximately doubled the number of detected peptides from microbial proteomes for which quantitative information can be obtained. The results indicated that the overall dynamic range of measurements was increased by at least an order of magnitude (to ~10^5 or larger). For this demonstration, a 1:1 mixture of $^{14}N/^{15}N$ labeled *S. oneidensis* cells was analyzed. In the normal set of spectra, 2485 peptides pairs were identified, which corresponded to 1272 open reading frames (ORFs). The DREAMS approach allowed the identification of 1299 additional pairs (>50% increase), pointing to 481 new ORFs (~38% increase) not previously identified. Thus, using the Accurate Mass and Time tag approach, the researchers observed (and quantified) 1753 *S. oneidensis* proteins (>36% of the predicted *S. oneidensis* proteome) as peptide pairs in a single DREAMS analysis. This coverage compares favorably to typical coverage achievable using shotgun proteomics. Similarly, for *D. radiodurans*, a single DREAMS analysis identified 2244 peptides, covering 965 ORFs in the normal set of spectra and 2259 peptides, covering 1000 ORFs in the additional DREAMS set of spectra, for a total of 1244 non-redundant ORFs or 279 (30%) additional ORFs through the use of DREAMS

- **Use of automated gain control.** Another important improvement in FTICR performance is provided by automated gain control, a capability for data-dependent adjustment of ion accumulation time during an LC separation so as to maintain ion populations in the cell not exceeding a level that causes excessive space charge effects. The automated gain control also helps eliminate *m/z* discrimination in the external ion trap and improves the dynamic range of measurements and/or the mass measurement accuracy. The automated gain control capability is now commercially available and is included in the LTQ-FT purchased last year with program funds.

- **Continue development of the ability to detect post-translational modifications of proteins.** The ultimate goal will be to do this in a high-throughput fashion analogous to the existing capability for peptide detection. This will require the continued development of the new “top-down” proteomics capability that was demonstrated in Fiscal Year 2006 with the direct detection of intact protein isoforms and modified proteins from very limited amounts of user samples. Implementing the “top-down” approach on these limited samples will require nano-fractionation capabilities to be successful. This is the emerging method of choice for identifying post-translational modifications, which are very important in protein activation. This information complements the peptide-based “bottom-up” approach, which is superior for identifying the presence of protein families in a high-throughput fashion. Developing and implementing a protein fractionation protocol that can be used on eluting peaks from a separation will require substantial development and the use of infrared multiphoton heating of the ions coupled with either collision-induced dissociation or electron transfer dissociation. These efforts will be supplemented by the deployment of state-of-the-art ion trap mass spectrometer with electron transfer dissociation capability. This will allow us to effectively combine and compare analyses from the “bottom up” and “top down” approaches that use the same fundamental principles to identify the sites and nature of post-translational modifications.

Identification of Functional Pathways Associated with Clinical Tamoxifen-Resistance in Breast Cancer by Advanced Mass Spectrometry

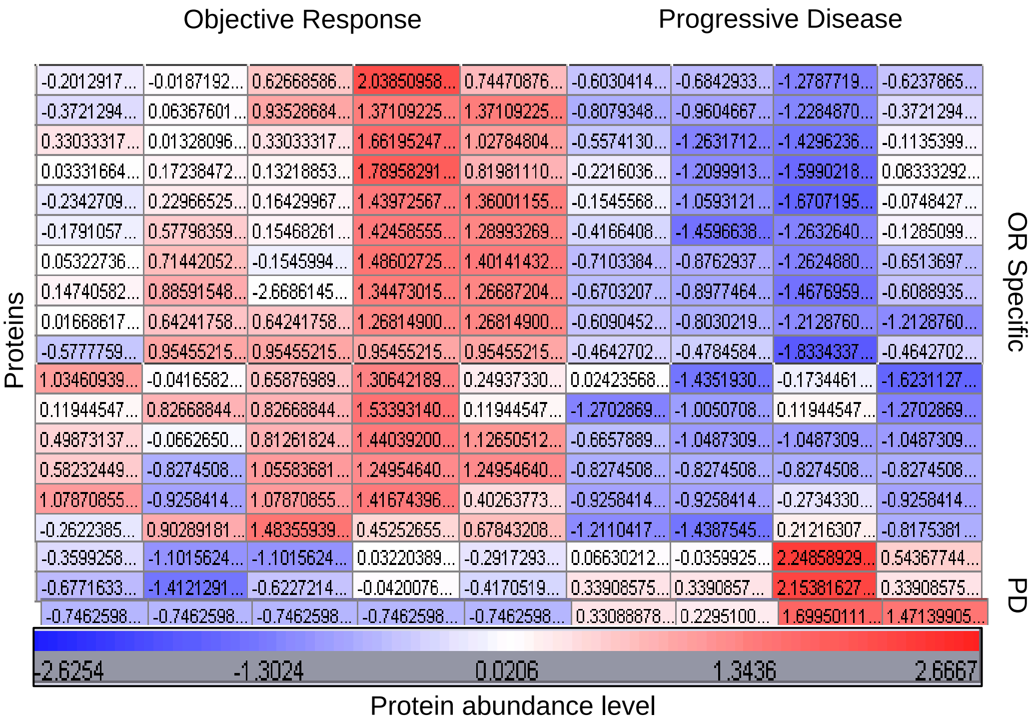
A Umar, [(a)] ***TM Luider,*** [(a)] ***JA Foekens,*** [(a)] ***and L Paša Tolić*** [(b)]

(a) Erasmus University Medical Center, Rotterdam, The Netherlands
(b) Pacific Northwest National Laboratory, Richland, Washington

Not all cancers respond equally to standard cancer drugs. If a doctor can determine how a cancer will respond to a drug before treatment begins, he will know if he has to prescribe an aggressive dose or a more modest one. By examining the proteins present in tumor samples from patients with a known response history, we can identify markers that will correlate with the response and aid doctors in prescribing the correct dose.

A Umar from the Erasmus University Medical Center in Rotterdam, The Netherlands, is visiting EMSL to characterize functional pathways that lead to clinical resistance to tamoxifen (anti-estrogen) treatment in breast cancer patients.

For this study, she has used laser microdissected tumor cells from patients that either were or were not responding to tamoxifen treatment. Protein profiles from these cells were generated by state-of-the-art nanoscale liquid chromatography Fourier transform infrared cyclotron resonance mass spectrometry (nLC-FTICR-MS), and the profiles were compared. Laser microdissection has the great advantage of enabling isolation of selected subpopulations of cells, such as tumor cells, and thus overcoming the issue of tissue heterogeneity. However, this process is very time consuming, so typically only a few thousand cells amounting to a few hundred nanograms of protein can be collected per tissue. Analysis of such minute amounts of sample by conventional proteomics tools is severely constrained by detection limits. As a consequence, ultra-sensitive nLC-FTICR technology developed at EMSL is the best choice for performing comprehensive proteome analyses. The nLC-FTICR-MS technique was applied to clinical samples and showed improved proteome coverage and good reproducibility attainable for ~3000 laser microdissected breast carcinoma cells as compared to what was previously described. As a next step, Umar used this approach to analyze 50 different tumor samples. She was able to detect protein profiles that were specifically expressed in either responding or nonresponding tumors (Figure 1). Validation of these protein profiles and further functional analysis of the proteins will eventually advance our understanding of breast cancer therapy-resistance and may lead the development of new and better therapies.



Objective Response					Progressive Disease			
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Figure 1. Detail of response-specific protein profile. Hierarchical clustering with z-scores was performed on 1999 proteins using protein abundance (obtained by averaging measured peptide abundances). The average protein abundance level (0.0206) is represented with a white background color, while the abundance levels above and below the average are represented by red and blue background colors,

Identification and Post-Translational Modification of Mitotic Regulatory Proteins

F Yang,(a) MA Gritsenko,(a) DG Camp,(a) RD Smith,(a) and DL. Stenoien(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

This highlight focuses on a class of proteins known as chromosomal passengers (CP) that, because of their complex localization patterns, are thought to play multiple roles in cell proliferation and cell cycle checkpoint signaling pathways. Therefore, the study of CPs represents an area of intense research because of their importance as mitotic regulators and their potential to be cancer targets. Transient protein modification by phosphorylation plays an essential role in regulating mitosis and preventing cancer. This research is designed to identify novel phosphoproteins and post-translational modifications that regulate mitotic progression.

Spatial and temporal changes in protein localization play important roles in regulating protein activity in many cellular processes. This is most evident during mitosis when cells undergo dramatic changes in their architecture. Phosphorylation of critical mitotic regulatory proteins is recognized as a key mechanism that controls the successful completion of mitosis with the high fidelity needed to prevent aneuploidy and possible cancer development. In our studies, we have chosen to perform targeted proteomic analyses on a subset of enriched mitotic regulatory proteins to increase the detection of very low abundance protein complexes and their post-translational modifications. We are using a phosphorylation site-specific antibody (P190) that recognizes several mitotic phosphoproteins that behave as CPs. CPs undergo dramatic changes in their localization as cells progress through mitosis, localizing on kinetochores during prophase and metaphase and at the mid-zone and mid-body at later stages of mitosis (Figure 1). Many of the known CPs, including aurora-B kinase, play critical regulatory roles during mitosis, and their functions are often compromised during cancer development.

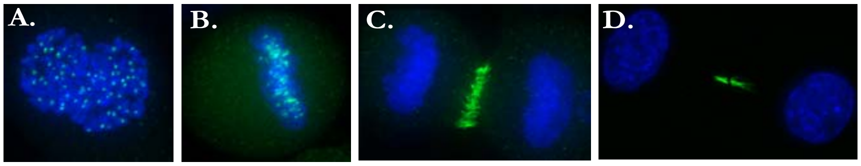

Figure 1. The P190 antibody recognizes chromosomal passenger proteins. Kinetochores are immunoreactive for the P190 antibody (green) in prophase (A) and remain labeled through metaphase (B). As the chromosomes (blue) separate, P190 labels the mid-zone during anaphase (C) and the mid-body after cell division (D).

To identify the phosphoproteins, protein complexes, and phosphorylation sites bound by the P190 antibody, we employed several mass spectrometry-based approaches to identify both peptides and phosphopeptides present in P190 immunoprecipitates (IP) (Figure 2). In one approach, we performed mass spectrometry on protein IPs from mitotic cell lysates to identify the protein complexes recognized by the P190 antibody. Using this approach, we were able to identify 298 unique proteins in the P190 IP versus 41 unique proteins in the control IP. Several known CPs were specifically present in the P190 IP, including Aurora-B, RCC1-like/TD-60, and INCENP, all of which are present in the same protein complex. We also identified other proteins that have known roles in mitosis and/or localize to the mitotic apparatus. These proteins include Aurora-A, ch-TOG, cyclin B, NuMA, cytoplasmic dynein, tubulins, actin, and actin-binding proteins. Other identified proteins include those involved in various signaling pathways that regulate mitosis such as SMAD2, Casein Kinase 1, serine/threonine protein phosphatase 2A, ALPHA-1 CATENIN, and 14-3-3 proteins. Many of the proteins specifically present in the P190 IP include those proteins present in ribosomes and spliceosomes, large protein structures that have known but poorly understood functions during mitosis. We also identified a large number of hypothetical proteins and proteins with no clearly defined cellular functions that represent candidates for novel CPs.

The P190 antibody was generated using a phosphopeptide (VLPRGL[pS]PARQLL) uniquely present in the progesterone receptor. Because the antibody cross-reacts with other phosphoproteins, we reason that the antibody only reacts with a subset of the amino acids present in the phosphopeptide that may also be present in other proteins. To determine the critical amino acid residues recognized by the antibody, we performed a tryptic digest of mitotic cell lysates followed by a phosphopeptide IP, IMAC enrichment, and identification of phosphopeptides. The most abundant peptide from this analysis was derived from ribosomal protein L12 and had the sequence, K.IGPLGL[pS]PK.K). Other proteins present in both the phosphopeptide and protein IPs include ch-TOG (KAPGL[pS][pS]KAK), Otthump22591 (QPPLSL[pS]PAP), and Ric 8/synembrin (IQPMGM[pS]PRG).

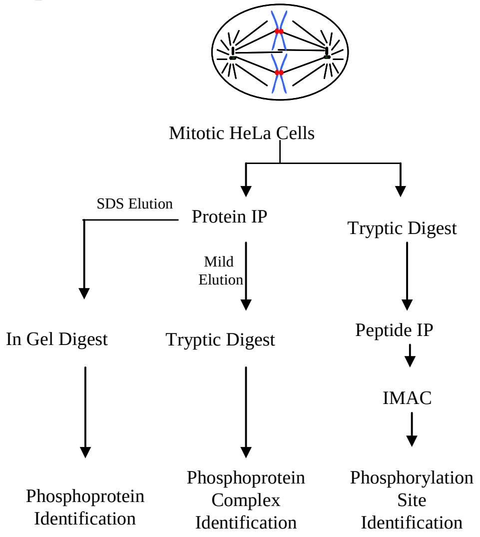

Figure 2. Strategy for identifying protein complexes and phosphorylation sites containing the P190 phosphoepitope.

From these peptides and the original starting peptide, we identified a motif of PXXLSP as the preferred binding motif of the P190 antibody. Interestingly, this motif is present in INCENP (PLPRTL[pS]PTP), the chromosomal passenger protein identified in the P190 protein IP. Other proteins in the protein IP containing this motif include SMAD2, stathmin 3, ABLIM1, Bcl9, Mystique, CAMTA1, Hira, and hypothetical protein DKFZP434K1815. Analysis of phosphorylation site databases showed that the motifs present in INCENP, SMAD2, stathmin 3, and ABLIM1 are phosphorylated *in vivo*. Functional assays are underway to address the significance of these specific phosphorylation events in regulating mitotic progression.

Proteomic Characterization of a Macaque Flu Infection Model System

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(b) University of Washington, Seattle, Washington

This research involves characterization of a non-human primate model system to gain more insight into the proteins that are important in the progression of flu infections.

Initial proteomic characterization of the macaque flu infection model system used a bottom-up proteomics approach with the isolation of proteins from macaque lung tissue either infected (influenza) or mock-infected, followed by tryptic digestion to peptide form for sequence identification and relative quantitation using liquid chromatography coupled to tandem mass spectrometry analysis. Additionally, a cysteinyl-peptide enrichment step was performed at the peptide level, providing enhanced coverage of the macaque model proteome. The resulting high-quality data set of 14,100 peptides and 3,548 proteins identified in this preliminary study of the macaque model system is, to our knowledge, the first comprehensive proteomic survey performed for this model. Among the proteins detected are many candidates of particular interest based on previous clinical, pathological, and gene expression data, demonstrating the suitability of the non-human primate model for studying influenza virus pathogenesis. These include several well-known interferon-induced proteins as well as other non-cellular mediators of the innate immune response. This new macaque lung protein database creates the foundation for future research efforts aimed at applying comparative quantitative proteomics measurements to longitudinal studies of non-human primate models of influenza virus infection.

When comparing the differentially identified proteins between uninfected and influenza virus-infected lung tissue samples, consistent with previous observations demonstrating the establishment of an antiviral state in the lungs of influenza virus-infected macaques, we observed an apparent up-regulation of many proteins involved in the innate immune response. These included both interferon-induced proteins and non-cellular mediators of the innate immune response. We believe the findings reported clearly demonstrate the potential of proteomics for assisting in the determination of protein players and pathways affected by influenza virus infection.

Proteomic Profiling of *Corynebacterium glutamicum* R Incubated at Very High Cellular Densities Under Oxygen-Deprivation Conditions

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The completion of the human genome dramatically showed that there are not enough genes available to account for the diversity and complexity that we have. Thus, it is the regulation of the translation of the genome into proteins that leads to this diversity and this regulation is one of the great unsolved problems in biology. Analysis of the proteins in simpler model systems like Corynebacterium glutamicum R *will give us insights into how this regulation is controlled.*

The recent completion of the genome sequence of *Corynebacterium glutamicum* R enables the implementation of post-genomic tools to define the physiological response exhibited by this microorganism when it is subjected to various environmental conditions. We have established and validated basic procedures for performing comparative proteomic profiles of *Corynebacterial* protein extracts. We observed a general agreement between proteomics and transcriptomics data. Further analyses could possibly reveal in this organism the presence of unknown regulatory mechanisms and global metabolic adaptations that occur when the culture is switched from the cell catalyst production phase to the product production phase.

In the quest for cost-effective production processes that would be suitable for producing a variety of commodity chemicals, such as ethanol or organic acids, the Research Institute of Innovative Technology for the Earth in Kyoto, Japan, has championed the development of novel processes that make use of very high cellular densities and oxygen-deprivation conditions. These conditions trigger the uncoupling of cell catalyst production and product production phases in anaero-tolerant and quorum-sensing sensitive organisms (Inui et al. 2004a, b; Inui et al. 2006). The complete genomic sequences of *C. glutamicum* R and *C. glutamicum* ATCC 13032 (Yukawa et al. 2006) enable us to use post-genomic tools for the global analysis of the cellular responses that *C. glutamicum* exhibits when subjected to various incubation conditions. Particularly, two-dimensional poly-acrylamide gel electrophoresis (2D-PAGE) combined to liquid chromatography/mass spectrometry (LC/MS) of *C. glutamicum* R protein extracts enabled to identify numerous enzymes of the central metabolism (Figure 1).

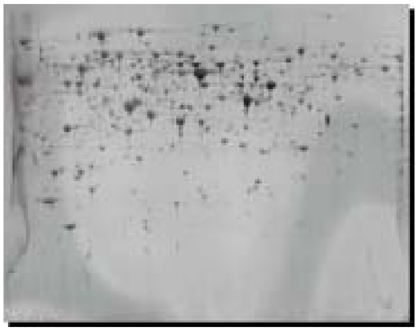

Figure 1. Two-dimensional poly-acrylamide gel electrophoresis imaging of *C. glutamicum* R protein extracts. Numerous proteins could be identified by LC/MS analysis, including key enzymes of the central metabolism (e.g., enolase, transketolase, fumarase, acetyl-CoA hydrolase, pyruvate kinase, malate dehydrogenase, glyceraldehyde-3-phosphate dehydrogenase, fructose-biphosphate aldolase, triosephosphate isomerase, and fructose-1,6-biphosphatase).

Moreover, global transcriptomics analyses unraveled the genetic expression patterns in *C. glutamicum* R incubated under very high cellular densities and then subjected to oxygen deprivation (Figure 2).

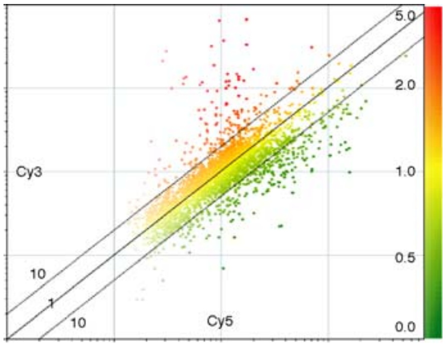

Figure 2. Scatter plot of log Cy3- and log Cy5-derived fluorescence. Each dot represents the average of six independent experiments. The RNA of *C. glutamicum* R cells grown under aerobic conditions and of similarly grown cells but reacted under process conditions was used for Cy3 and Cy5 labeling. The two outer dotted lines demarcate values for significant differences in gene expression levels (i.e., by factors of two and one-half).

While global transcriptional profiling constitutes an extremely useful technique for optimizing manufacturing strains by rational design, its main limitation is that it does not provide any relevant information regarding constitutively expressed genes or regarding those metabolic nodes that are regulated at the protein-modification level. In addition, transcriptome analysis cannot account for differential transcript stability, thus making the relationship between mRNA abundance and protein activity unclear for numerous enzymes (Yukawa et al. 2006). As a result, we applied mass spectroscopy techniques to trypsin-digested protein extracts of *C. glutamicum* R to attain both quantitative and qualitative data, in an effort to document the variations of the protein content of this organism. Specifically, we measured the relative abundance of several peptides per protein, thus uniquely characterizing that protein. This redundancy in data is important because it enables us to achieve higher data robustness. Beyond providing a complete list of such unique signature peptides, we compared the relative abundance of various proteins among samples including extracts representing protein soluble fractions, insoluble fractions, and total proteins. These fractions were isolated from both exponentially growing cells and from cells incubated under production conditions (very high cellular densities, oxygen-deprivation). As expected, a general tendency toward agreement between transcriptomic and proteomic data was observed (Figure 3).

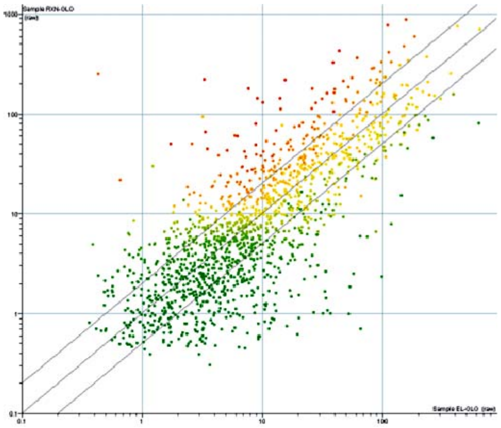

Figure 3. Scatter plot of relative protein abundance as measured by mass spectrometry of trypsin digests of total protein extracts recovered from exponentially growing cells (x axis), and from cells incubated under process conditions (y axis). The two outer dotted lines demarcate values for significant differences in protein levels (i.e., by factors of two and one-half).

This initial set of data demonstrates the robustness of the method employed, including the protein extract preparation method, and thus paves the way to detailed analyses of 1) the global metabolism of *C. glutamicum* and 2) the dynamic regulatory networks that regulate it. Furthermore, the various unique signature peptides identified in the course of these experiments will enable the study of very short proteins synthesized by *C. glutamicum*, and thus contribute significantly to enhancing the quality of the annotation of the *C. glutamicum* R and *C. glutamicum* ATCC 13032 genomes.

Citations

Inui M, H Kawaguchi, S Murakami, AA Vertès, and H Yukawa. 2004a. "Metabolic Engineering of *Corynebacterium glutamicum* for Fuel Ethanol Production Under Oxygen-Deprivation Conditions." *Journal of Molecular Microbiology and Biotechnology* 8(4):243-254.

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User Projects

Zangar NAF R33

RC Zangar, SM Varnum, Pacific Northwest National Laboratory, Richland, Washington

Identification of Post-translational Modifications and Protein Complexes under Conditions of Oxidative Stress

CA Sacksteder, TC Squier, Pacific Northwest National Laboratory, Richland, Washington

Proteomic Analysis of the HMEC Mitogenic Response

BD Thrall, T Liu, DG Camp, K Waters, Pacific Northwest National Laboratory, Richland, Washington

Proteomics of *Shewanella oneidensis* MR-1 Subjected to Solar UV Radiation Stress

JM Tiedje, Michigan State University, East Lansing, Michigan

Identification of Protein Components of Vaccinia Virus Particles

B Moss, W Resch, National Institute of Health, Bethesda,, Maryland

Identifying Targets for Therapeutic Interventions using Proteomic Technology

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HM Mottaz, Environmental Molecular Sciences Laboratory, Richland, Washington

F Heffron, S Wong, J Gustin, J Rue, R Estep, Oregon Health Sciences University/Oregon Graduate Institute, Portland, Oregon

Proteomic Characterization of Cerebrospinal Fluid (CSF) by High Resolution LC-MS/MS

S Warren, Massachusetts General Hospital East and Harvard University School of Medicine, Charlestown, Massachusetts

JM Jacobs, DG Camp, Pacific Northwest National Laboratory, Richland, Washington

Proteomic Analysis of the Cyanobacterium *Synechocystis* sp. PCC 6803

JM Jacobs, DG Camp, Pacific Northwest National Laboratory, Richland, Washington

HB Pakrasi, N Keren, Washington University in St. Louis, St. Louis, Missouri

Characterization of the Tumor Cell Lamellipodia Phosphoproteome

JM Jacobs, DG Camp, Pacific Northwest National Laboratory, Richland, Washington

RL Klemke, Y Wang, University of California, San Diego, La Jolla, California

Unraveling the Molecular Biology of Host-Pathogen Interactions

L Shi, Pacific Northwest National Laboratory, Richland, Washington

Peptide Observation Model

LJ Kangas, Pacific Northwest National Laboratory, Richland, Washington

L Wang, Washington State University Tri-Cities, Richland, Washington

Characterization of Neuropeptides Located in Neurosecretory Tissue of Cancer Borealis and Cancer Productus

KK Kutz, University of Wisconsin-Madison, Madison, Wisconsin

Protein Complex Identification using Novel Affinity Resins

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FedEx1

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Shew Strains

MS Lipton, Pacific Northwest National Laboratory, Richland, Washington

Reactive Oxygen and Nitrogen Species, Produce Dynamic Protein Modifications and Protein Complexes in RAW 264.7 Macrophage Cells

HS Smallwood, Pacific Northwest National Laboratory, Richland, Washington

Identification and Post-translational Modification of Mitotic Regulatory Proteins

DL Stenoien, Pacific Northwest National Laboratory, Richland, Washington

Proteomics of HCMV

SM Varnum, JM Jacobs, Pacific Northwest National Laboratory, Richland, Washington

J Dumortier, Oregon Health Sciences University/Oregon Graduate Institute, Beaverton, Oregon

Thrust Area 1: Characterization of Purified Proteins for Distribution to Grand Challenge Participants (EMSL User Support)

L Shi, Pacific Northwest National Laboratory, Richland, Washington

Development of High Throughput Global Metabolomics Approaches Based upon Mass Spectrometry

TO Metz, Pacific Northwest National Laboratory, Richland, Washington

Advanced Proteomics and Metabolomics Studies of Type 1 Diabetes

TO Metz, JS Zimmer, JM Jacobs, DG Camp, Pacific Northwest National Laboratory, Richland, Washington

Development of Metabolomics for Biomarker Discovery

TO Metz, JS Zimmer, Pacific Northwest National Laboratory, Richland, Washington

Proteomic Studies of Inflammation and the Host Response to Injury

LL Moldawer, University of Florida, Gainesville, Florida

W Qian, T Liu, Pacific Northwest National Laboratory, Richland, Washington

A Proteome for Specific Cell Types in *Caenorhabditis elegans*

DG Moerman, University of British Columbia, Vancouver, British Columbia, Canada

Proteomic Characterization of *in vivo* and *in vitro* Model Systems of Hepatitis C Virus Infection: Global Quantitative Proteome AMT Tag Measurements of Cellular Protein Expression

JM Jacobs, Pacific Northwest National Laboratory, Richland, Washington

MG Katze, DL Diamond, University of Washington, Seattle, Washington

Identification of Functional Pathways Associated with Clinical Tamoxifen-resistance in Breast Cancer by Advanced Mass Spectrometry

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Biomarker Development for Chronic Obstructive Pulmonary Disease

DL Springer, RE Johnson, JG Pounds, Pacific Northwest National Laboratory, Richland, Washington

Intra-species Proteome within a Natural Population of *Shewanella baltica*

JA Klappenbach, Rosetta Inpharmatics, LLC, Seattle, Washington

The Use of Novel Proteomics in the Plasma and Tumor Microenvironment for Class Prediction in Human Breast Cancer

LL Moldawer, SR Grobmyer, University of Florida, Gainesville, Florida

Molecular Mechanisms Underlying Cellular Adaptive Response to Low Dose Radiation

CA Sacksteder, TC Squier, MA Gritsenko, Pacific Northwest National Laboratory, Richland, Washington

Identify Biomarkers for COPD (Chronic Obstructive Pulmonary Disease) in Humans using Proteomic and Metabonomic Analysis of Serum and Urine.

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Plasma Proteomics Pilot Study to Identify Biomarkers of Stress and Nutritional Effects

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Comparative Proteomic Analysis of *Desulfovibrio vulgaris*

W Zhang, Pacific Northwest National Laboratory, Richland, Washington

Characterization of the Neurite Phosphoproteome

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Determining Proteins Expression is *Ralstonia* bacteria that Survive in Ultra Pure Water

KL Ogden, University of Arizona, Tucson, Arizona

Use of FTICR Mass Spectrometric Proteomics Analysis for the Identification of Novel Targets In Pain Research

M Yeo, W Liedtke, Duke University, Durham, North Carolina

Proteome Analysis of Members of the Family *Anaplasmataceae*

Y Rikihisa, T Kikuchi, Ohio State University, Columbus, Ohio

Fragmentation and Characteristic Study of Peptides Missed by SEQUEST

G Tan, VH Wysocki, University of Arizona, Tucson, Arizona

Proteome Analysis of Regulatory Gene Mutants in *Desulfovibrio desulfuricans* G20 and *Shewanella onedensis* MR-1

LR Krumholz, JL Groh, Q Luo, University of Oklahoma, Norman, Oklahoma

Proteomics of *Burkholderia mallei*

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The Schizophyllum Commune Proteome

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Advanced Proteomics and Metabolomics Studies of Type 2 Diabetes and Pre-Diabetes

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Proteomics of *in situ* Biostimulated Sediments

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Analysis of the Proteome and Transcriptome of In Vivo *Salmonella typhimurium* Infected Ileum

LG Adams, Texas A&M University, college station, Texas

Cellular Response to Virus Infection: Global Proteome Analysis of Macaque Models of HIV and Influenza Infection

MG Katze, DL Diamond, University of Washington, Seattle, Washington

Trauma-induced Reprogramming: Changes in Lipid Raft Protein Content

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Characterization of the SATB1 Phosphorylations

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Translation Repressor, 4E-BP2, is Covalently Modified in the Mammalian Brain

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Informatics Tool for Proteomic Biomarker Detection using Large-scale nanoLC-FT Mass Spectrometry Data

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Cyanobacteria Membrane Biology Grand Challenge: Systems Analysis of the Dynamics of Membrane Architecture, Composition, and Function- Proteomic, Metabolomic, and Metallomic Characterization

JM Jacobs, DW Koppenaal, TO Metz, Pacific Northwest National Laboratory, Richland, Washington

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Quantitative Characterization of Protein Post-translational Modifications using Mass Spectrometry

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Proteome Enabled Discovery of Growth and Survival Strategies of the High Level Nuclear Waste Actinomycete, *Kineococcus radiotolerans*

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Alpha Project Phosphoproteomics

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Pilot Study on Examination of LIRKO Islets and Serum Using Quantitative Proteomic Approaches

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Development of High Throughput Proteomic Production Operations

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Biomarkers for Early Detection and Other Stages

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High Throughput Proteomic and Metabolomic Early Biomarkers

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NBACC: Host/Pathogen Interactions

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Global and Targeted Proteomic Identification of Oxidative Modifications

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Control of Hydrogen Release and Uptake in Condensed Phases

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Cerebrospinal Fluid Proteome

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Platelet Secretome

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LC-MS-based Metabolomics for Computational Toxicology

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Identification of Metal Reductases

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Application of High-Throughput Proteomics

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Biomarker Discovery in Pathogens by Proteomics

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Secretome Analysis of Environmental Nanoparticle Induced Biomarkers

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LC-FTMS Analysis of Organophosphates

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Peptide Biomarker Analysis

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Environmental Proteomic Analysis of Anaerobic Methane Oxidizing Systems

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Proteome Analysis of *Anaeromyxobacter dehalogenans* Strain 2CP-C

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A Proteomic Dissection of the Hg(II) Toxicity Paradox

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Technology Development in Support of NCRR

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Low Dose

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Rhodobacter sphaerodies

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Regulated Proteolysis and Bystander Effects in Radiation

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Preliminary Work on the Proteomes of Brains and Dissected Brains Obtained from Control Mice and Treated Mice Simulating Parkinson's Disease

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Spatially Resolved Proteomic Studies of Brains Obtained from Control Mice and Treated Mice Simulating Parkinson's Disease

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Abundance of Protein Components in Photosystem II Protein Complex Purified from Mutant Cyanobacterial Cells Lacking Individual Subunit Protein

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Using Mass Spectrometry to Assist in Identifying Genes for Enzymes of Known Activity, Unknown OpenReadingFrame and Small Abundance

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Mass Spectrometric Analysis of Eukaryotic Proteosome

RA Maxwell, Pacific Northwest National Laboratory, Richland, Washington

Mass Spectrometry Analysis of Nucleotides/Nucleosides

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Protemic Analysis of Naturally Occurring Methane Oxidizing Archaeal Communities

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Proteomics of Membrane Protein Complexes

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Proteomic Analysis of *Deinococcus radiodurans* Under Oxidative Stress Irradiation

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Genomes-to-Life Protein Complex Isolation Capability

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Proteomics of Filamentous Fungi

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Sustrate Identification for Ser/Th Protein Phosphatase

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Identification of Functional Pathways Associated with Clinical Tamoxifen-resistance in Breast Cancer by Advanced Mass Spectrometry

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Cellular Response to Human Immunodeficiency Virus Type 1 Infection: Global Quantitative Proteome AMT Tag Measurements of Cellular Protein Expression

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Proteomic Analysis of *Shewanella oneidensis* Biofilms

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Membrane Proteins of Placental Parasites

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Combined Transcriptome and Proteome Analysis of *Shewanella oneidensis* MR-1 etrA and arcA Mutant Strains

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Proteomics of Mitochondria

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Proteomic Studies of Growth and Metabolism in *Corynebacterium glutamicum* R

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Interfacial and Nanoscale Science Facility

The Interfacial & Nanoscale Science Facility (INSF) is a world-class resource for scientific expertise and instrumentation focused on the study of interfacial phenomena and nanoscience and technology. This section summarizes the capabilities available in the INSF, along with research programs associated with facility users. Activities in the facility address national needs in environmental restoration, waste management, pollution prevention, energy production and storage, and national and homeland security through research that specializes in preparation, characterization, and reactivity of surfaces and interfaces. The range of scientific expertise and instrumentation within the facility provides a unique environment for research in areas such as nanoscience and nanotechnology; interfacial catalytic chemistry; designed oxide interfaces, including environmental aerosol and mineral interfaces; materials and chemoselective interfaces; and areas within microanalytical science, such as chemical sensing and nanobiotechnology.

The INSF and its scientific staff provide a broad range of instrumentation, laboratory capabilities, and expertise. Instrumentation is available for chemical synthesis, analytical chemistry, separations, electrochemistry, thin-film deposition, catalytic reactors, ion-beam processing, and microfabrication. Capabilities include an accelerator facility for material modification and analysis using ion beams along with interface characterization; scanning probe microscopies; electron microscopy and x-ray analysis; spectroelectrochemistry; high-spatial/energy resolution surface analysis; catalyst preparation, characterization, and reaction engineering; a fully equipped clean room for microfabrication, microanalytical systems development, and testing laboratories; inorganic, organic, polymer, and biochemical synthesis and characterization facilities; a full complement of thin-film deposition and characterization facilities; and fully equipped analytical support laboratories. The combination of surface and interface characterization techniques that provide high spatial, depth, and energy resolution for a broad array of methods is unmatched anywhere in the world. Many systems are coupled directly to film growth chambers, and samples can be moved among 16 different systems under controlled environments without exposure to air.

Instrumentation & Capabilities

- Thin-film deposition
- Surface analysis suite
- Electron microscopy suite
- Scanning probe microscopy
- Ion-beam processing and analysis
- Nanobiotechnology capabilities
- Surface Science and Catalysis Laboratory
- Catalytic reactors
- X-ray diffraction laboratory
- Microfabrication
- Chemical and biological sensing
- Other analytical and characterization laboratories

Staff assigned to the INSF perform innovative research in the areas of surface and interfacial chemistry, advanced materials synthesis and characterization, and microanalytical science. Our activities emphasize research relevant to the four U.S. Department of Energy (DOE) mission areas—science, energy resources, environmental quality, and national security—and to operation of a world-class user facility that supports the DOE science mission. Our staff also plays a major role in the continued success of the W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL) by providing support, training, and collaboration to onsite users. Over the past seven years, research activities in the INSF have focused on four major thrust areas: 1) films and interphases, 2) surface chemistry and catalysis, 3) material interfaces, and 4) microsensors, microfluidics, and new biotechnologies. Staff assigned to the INSF continue to focus their efforts in these four areas with research on the following topics:

- *Oxide and Mineral Films and Surfaces*. Structural and chemical properties of model single-crystal oxide and complex mineral surfaces.
- *Electronic and Catalytic Materials*. High dielectric materials, magnetic oxide semiconductors, and oxide catalysts.
- *Nanoscale Materials*. Oxide quantum dots and nanofilms of magnetic and oxygen ion-conducting oxides, buried nanoclusters in oxides.
- *Interfacial Properties and Reactivity*. Reactions at oxide and mineral interfaces and the structural and chemical properties.
- *Microanalytical Separations and Sensing*. Development of new microanalytical and sensing principles, tools, and testing.
- *Nanobiotechnology*. Single-enzyme nanoparticles, enzymes in nanostructured matrices; understanding the dynamics of these materials.
- *Environmental Studies*. Waste separations, structural and chemical stability of waste forms under different radiation and chemical environment, atmospheric aerosols.
- *Analysis and Characterization*. Fully equipped analytical laboratories and characterization facilities.

Films and Interphases. The physical and chemical properties of the region between single phases of a material (i.e., the interphase) have a major influence on many characteristics of the material, including stability, electronic properties, atomic and ionic transport, and chemical reactivity. Research programs include the synthesis of thin films and nanostructured materials, both of which contain a high concentration of interphase regions. Research activities also involve studies of solid/solid, solid/liquid, and solid/gas (or vacuum) interphase regions. Although most studies are focused on inorganic materials and interphases, organic and biological systems are becoming an increasingly large part of our work.

Surface Chemistry and Catalysis. Basic research is carried out with the most simple, well-defined, environmentally relevant crystallographic structures (e.g., mineral carbonates, metal oxides) for which molecular theory and spectroscopy are immediately applicable. The work then progresses to materials with more complex structures, such as iron and titanium oxides with substitutional impurities. For example, fundamental studies of the oxygen storage and release properties of pure and zirconium-doped ceria single-crystal thin films are aimed at understanding how these “oxygen storage materials” perform in an automobile exhaust system catalytic converter. In addition to fundamental surface chemistry research, we are developing materials and reactor designs for a number of heterogeneous catalytic processes. One study involves synthesizing, characterizing, and testing a group of novel, mesoporous, silica-supported, solid-acid catalysts for use in petroleum-refining processes.

Material Interfaces. Studies are being conducted in several areas: solid/solid interfaces in a wide variety of materials, radiation effects in materials, fundamental defect properties and interactions, atomic and ionic transport, and aerosol characterization. Many of the studies on solid/solid interfaces involve 1) characterization of interfaces between thin films and substrates, between ion-beam-modified surfaces and the original substrate, or between nanoclusters and host matrices; 2) segregation or diffusion of point defects, impurities, dopants, or gas atoms to or from such interfaces; 3) transport of hydrogen, oxygen, or other gases across such interfaces; 4) formation or destruction of such interfaces from radiation damage processes; and 5) stability of interfaces under a wide range of environmental conditions. Studies on radiation effects include experimental research on materials for immobilization of nuclear waste and plutonium, as well as materials for next-generation nuclear power production, wide-band-gap semiconductors, and multiscale computer simulations of damage production processes, defect diffusion, and microstructure evolution. Studies on atomic and ionic transport include ion exchange processes in nuclear waste glasses, hydrogen storage and transport in materials, and oxygen transport in fast ion conductors.

Microsensors, Microfluids, and Nanobiotechnology. This research includes four primary thrust areas: 1) array-based vapor sensors, 2) nanoscience, 3) bioanalytical microfluidics, and 4) radioanalytical microfluidics. Key areas of science in array-based vapor-sensing include rational design, development, and synthesis of polymeric-sensing materials, linear free-energy models for vapor/polymer interactions, organic thin films, photo-patterning methods for sensor materials, integrated sensor systems, and multivariate data analyses. The nanoscience area includes development of monolayer-protected gold nanoparticles for use on sorptive sensing films, single-enzyme nanoparticles as a new nanostructure for enzyme stabilization, and multi-functional nanoparticle assemblies for biodetection. The latter two areas represent a new thrust in nanobiotechnology, and a laboratory within EMSL has been established for synthesizing enzyme nanostructures and studying enzyme kinetics and enzymes in nanostructured matrices. Experimental research in bioanalytical microfluidics and radioanalytical microfluidics is now located primarily in other facilities, but close scientific ties with EMSL are maintained.

Capabilities

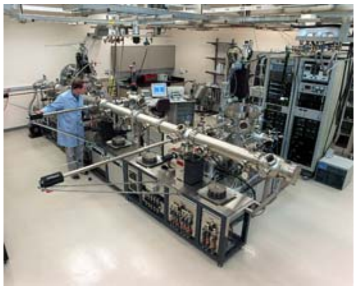

Figure 1. Oxygen plasma-assisted MBE system.

Thin-Film Deposition. Thin-film deposition capabilities include oxygen plasma-assisted molecular beam epitaxy (MBE) systems (Figure 1), a metal organic chemical vapor deposition system (MOCVD), and a sputter deposition system. The MBE systems consist of growth chambers connected to surface characterization chambers through sample transfer lines. The growth chambers have various electron beam and effusion cell sources along with reflection high-energy electron diffraction and quartz crystal oscillators to monitor the growth. The surface characterization chambers are equipped with several surface-science capabilities including x-ray photoelectron spectroscopy (XPS)/diffraction, Auger electron spectroscopy (AES) low-energy electron diffraction (LEED), and atomic force microscopy/ scanning tunneling microscopy (AFM/STM). The MOCVD system is specially designed for epitaxial growth of oxide thin films. The system comprises a rotating disk reactor, two metal organic source delivery systems (bubbler vapor-phase and direct liquid source-injection), an oxygen microwave plasma unit, a spectroscopic ellipsometer, and a Fourier transform infrared (FTIR) spectrometer. The system is capable of growing uniform (in both thickness and composition) oxide thin films with abrupt interfaces. The sputter deposition system consists of radio frequency and direct current sputtering sources.

Figure 2. X-ray photoelectron spectrometer.

Surface Analysis Suite. The surface analysis suite consists of a Physical Electronics Instruments (PHI) Quantum 2000 high-resolution, x-ray photoelectron spectrometer (Figure 2), a Kratos Axis multi-technique surface analysis system (SAS), a PHI Model T2100 time-of-flight secondary ion mass spectrometer (TOF-SIMS), and a PHI Model 680 AES/scanning Auger microprobe. The Quantum 2000 XPS system is unique in that it uses a focused monochromatic Al K α x-ray beam that can be varied in size from as small as 10 μm in diameter to approximately 200 μm. The TOF-SIMS system uses a pulsed and focused ion source and TOF analyzer to obtain high spatial- and mass-resolution data from a specimen surface. The multi-technique SAS enables surfaces to be probed with a variety of complementary analysis methods, and contains electron imaging, electron spectroscopy, and both primary and secondary ion-scattering capabilities. The Model 680 auger electron spectrometer (AES)/scanning Auger microprobe is based on a field-emission electron source and a cylindrical mirror analyzer. The electron beam size can be focused as low as 10 nm at 20 kV, although somewhat larger beams are typically used to collect AES data. Instrument features and capabilities include beam rastering, scanning electron microscope (SEM) imaging, mapping, specimen cleaning and depth profiling using a sputter gun, and sample rotation to allow “Zalar” rotation during sputtering. The system also is configured with an x-ray detector for near-surface analysis in combination with AES surface analysis.

Figure 3. High-resolution TEM.

Electron Microscopy Suite. The electron microscopy suite consists of a LEO 982 field-emission scanning electron microscope (FESEM), a high-resolution transmission electron microscope (TEM) (Figure 3), and another cryo-TEM dedicated for biological work (Cryo TEM). The FESEM is an ultrahigh-performance SEM with a resolution of 1 nm at 30 kV and 4 nm at 1.0 kV. It has a large specimen chamber equipped with multiple detectors, a below-lens secondary electron detector, an in-lens secondary electron detector, a backscatter electron detector, an energy-dispersive x-ray detector, and an electron backscatter diffraction detector. The JEOL 2010 is a high-resolution TEM with a spatial resolution of 0.194 nm. This instrument has a medium acceleration voltage of 200 kV, a high-brightness electron source, digital image recording, a computer-controlled sample goniometer, and a geometrically optimized x-ray detector. It has a wide range of illumination lens conditions:

TEM mode, energy-dispersive spectroscopy mode, nanometer beam electron diffraction, and convergent beam electron diffraction. The TEM is post-column attached with a Gatan image filter, giving an optimized energy resolution of approximately 1.2 eV, which allows analysis of light elements by electron energy-loss spectroscopy and elemental mapping in the electron spectroscopic imaging. The Cryo TEM is primarily used for biological imaging and tomography. The spatial resolution of the instrument is about 0.45 nm, and it has an accelerator voltage in the range of 80 to 120 kV.

Scanning Probe Microscopy. The scanning probe microscopy laboratory has a Digital Instrument Nanoscope IIIa AFM, a Topometrix TMX 1000 Explorer SPM, and an Omicron variable non-contact ultrahigh vacuum (UHV) AFM/STM system with surface-science capabilities including XPS, Auger electron microscopy, plasma cleaning, and deposition. The instrument is capable of operating in both air and liquid environments and in several modes that include contact, tapping, frictional force, phase/frequency, capacitance, and magnetic/electrostatic force. As a real space probe, the instrument can be used to probe surface morphology, defects, and electrostatic, magnetic, dopant concentration, and mechanical properties of conducting and non-conducting materials. The Topometrix TMX 1000 Explorer SPM can be used for both AFM and STM in air and in liquid and is particularly useful for larger samples. This instrument includes both contact and non-contact AFM modes. STM requires an electrically conductive sample and produces images based on the topography and electronic structure of the sample. AFM samples may be insulating or conducting; the image is based on the force between the AFM probe and the sample and is primarily a map of the surface topography. The Omicron variable scanning probe microscope can be used for both STM and AFM under UHV conditions. As a real space probe, this instrument is designed to probe surface structure, defects, and morphology of conducting and non-conducting materials. In addition to STM/AFM, the vacuum system also is equipped with other surface-science capabilities that include LEED, XPS, AES, and oxygen plasma cleaning.

Figure 4. Accelerator facility.

Ion-Beam Processing and Analysis. The accelerator facility (Figure 4) is equipped with capabilities to perform material modification and analysis using high-energy ion beams. The facility has two ion sources, a 3-MeV tandem ion accelerator, injector and analyzing magnets, beam lines, and four end stations. The end station on the +30° beam line is equipped with LEED, AES, XPS, oxygen plasma, and sputter cleaning sources and effusion cells in addition to the conventional ion-beam capabilities. Ion-beam capabilities include fixed and movable detectors for Rutherford backscattering spectrometry/channeling, nuclear reaction analysis (NRA), and elastic recoil detection analysis (ERDA). This beam line extends through the end station to another end station where experiments can be performed with the beam size of 20 microns or greater. The micro-beam end station is also equipped with capabilities for conventional ion-beam techniques including RBS, NRA, and proton-induced x-ray emission (PIXE). The +15° beam line is equipped with a raster scanner for ion implantation and ion-beam modification of materials, and the end station is equipped with all the conventional ion-beam capabilities. In addition, this beam line is equipped with heavy ion elastic recoil detection analysis capability for material characterization. The −15° end station is designed to carry out routine analytical work. The NEC RC 43 end station attached to this beam line is equipped with most of the standard ion-beam analytical capabilities including RBS, NRA, PIXE, particle-induced gamma emission, proton elastic scattering analysis, scanning transmission ion microscopy, and ERDA.

Surface Science and Catalysis Laboratory. Three UHV surface chemistry systems designed for studies of the molecular-level chemistry of adsorbates on metal oxide surfaces are available in the Surface Science and Catalysis Laboratory. These systems are equipped with a number of spectroscopic tools to follow changes in adsorbate chemistry, including high-resolution electron energy-loss spectroscopy, SIMS, ultraviolet photoemission, XPS, AES, and LEED. In addition, both electron-stimulated desorption and temperature-programmed desorption (TPD) studies are routinely performed in some systems. Typical information obtainable in TPD experiments includes the quantity and nature (intact or dissociated molecule) of an adsorbed gas. In addition, estimates of the sticking coefficient and the activation energy for desorption and/or reaction of the adsorbed molecule can be made. One of these systems has a combination of surface-science and high-pressure catalysis capabilities and is capable of measuring gas/solid reaction rates under realistic, high-pressure (approximately 1 atm) conditions using model, low-surface-area solid samples. Reaction rates as a function of temperature and varying reagent partial pressures also can be measured in this system.

Catalytic Reactors. The Reaction Engineering Laboratories are equipped with a variety of analytical capabilities and catalytic reactors including an Advanced Scientific Designs, Inc. RXM-100 catalyst testing and characterization instrument and a Zeton Altamira reactor test stand. The RXM-100, a multi-functional instrument used for catalyst studies, combines UHV and high-pressure capabilities in a single instrument without compromising specifications or ease of use. A number of measurements can be made using this instrument including chemical adsorption, physical adsorption, surface area, pore size, pore distribution, and temperature programmed characterization (desorption, reduction, and oxidation). An online mass spectrometer, gas chromatograph, FTIR, and thermal conductivity detector can be used to analyze effluent gases. The instrument has the capability of running up to 10 different gases simultaneously. In addition, high-pressure reactions (up to 1000 psi) can be run within a few minutes of each other on the same system, with little change in system configuration. This system offers extensive flexibility in catalyst testing and decreases inefficiency and contamination problems that arise from transferring materials between systems and waiting for data from other sources. The Zeton Altamira reactor test stand comprises three types of reactors generally used in bench-scale testing of catalysts: a fixed bed reactor, a Rotoberty reactor, and a continuous stirred tank reactor. This design allows users to evaluate catalyst performance and study chemical reactions in various reactor configurations.

X-Ray Diffraction. The suite of x-ray diffraction (XRD) equipment in EMSL consists of four instruments: a general-purpose XRD system for studying polycrystalline samples under ambient conditions, a special applications XRD system with low- and high-temperature sample stages covering the range of −193°C to +1000°C, and a four-circle XRD system. The general-purpose system is most often used to examine powder samples (x-ray powder diffraction), but it also can be used to study certain types of thin films. In addition to its non-ambient capabilities, the special applications system is equipped to examine thin-film samples in more detail, including grazing-incidence XRD (GIXRD) and x-ray reflectivity (XRR) measurements. The four-circle system is typically configured for high-resolution x-ray diffraction studies of epitaxial thin films. Additional applications of the four-circle system include stress measurements, texture analysis, GIXRD, and XRR.

Chemically Selective Materials and Sensors. Development and evaluation of sensor materials and chemical microsensors are supported by a wet chemistry laboratory for organic, polymer, and nanomaterial synthesis; a laboratory for evaluation of chemical sensor and sensor materials using automated vapor generation and blending systems; and a clean room with selected microfabrication capabilities. A variety of techniques for applying sensing materials to sensor devices are available, and numerous electronic test instruments are available in the sensing laboratories and the EMSL Instrument Development Laboratory. These capabilities are complemented by a range of surface analysis and characterization instruments as well as conventional analytical instrumentation in EMSL. Users may wish to bring new sensing materials to EMSL for application to sensing devices and evaluation, while others may bring complete sensor systems with data collection capabilities to couple to EMSL automated vapor generation systems. Research areas include sensor arrays, sensor materials design and synthesis, sensing material/analyte interactions, and chemometric methods.

Microfabrication. Microfabrication equipment provides a significant research and development capability in the areas of microstructures, microsensors, and microanalytical systems. Unlike highly automated industrial production equipment, the microfabrication equipment in EMSL has multipurpose functionality. The equipment supports a variety of microprocessing activities that include thin-film deposition, various thermal treatments, microphotolithography, chemical etching, inspection and characterization, bonding and packaging, and testing and measurement.

Nanobiotechnology Laboratory. The Nanobiotechnology Laboratory is equipped with capabilities to synthesize single-enzyme nanoparticles, functionalize nanostructured matrices, and analyze the activity and stability of enzymes and single-enzyme nanoparticles. This new laboratory consists of various small instruments (such as a black box, a glove box, a Dean Stark system, and shakers), a spectrophotometer, and a spectrofluorometer. A variety of basic enzyme work can be performed in this laboratory, including enzyme modification, enzyme immobilization, and enzyme-activity and stability measurements.

Instrument Upgrades

Several instrument developments are being implemented or planned to enhance capabilities and support our major research areas or areas selected for EMSL development. In Fiscal Year 2006, the following capability developments and procurements occurred in the INSF.

- **Cryo-transmission electron microscope (TEM).** This new EMSL capability (Figure 5) adds major TEM capabilities for life sciences; three-dimensional reconstruction by TEM tomography will literally bring a new dimension into all structural analyses. This state-of-the-art technology is based on acquirement of tilt series of a specimen and its software reconstruction and rendering. The TEM cryo stage will allow visualization of cells and macromolecules in their native hydrated state by physical fixation within ultra-thin, vitrified ice layers. Gaining these capabilities leads to a whole new area of structural biology investigations at PNNL that has been so far limited to the conventional TEM imaging. This new instrument provides a vital tool for morphological and functional studies in the area of cell biology and proteomics.

Figure 5. Cryo-TEM.

- **Ultrahigh Vacuum Scanning Probe Microscopy.** A great need exists to establish experimental tools to obtain single-site chemical information that will lead to new knowledge important in several areas, such as heterogeneous catalysis and for important catalytic materials such as metal oxides. Ideally, one would like to obtain chemically specific information on the sub-nanometer scale. The INSF has developed an ultra-high vacuum system with non-contact atomic force microscope/scanning tunneling microscope capability along with several surface science techniques to obtain single-site chemical information. When the development effort first began, atomic force microscopy/scanning tunneling microscopy technologies readily allowed the variation of sample temperature, which EMSL instrumentation allowed. However, this instrumentation has a rather limited capability at low temperatures, because of issues with sample contamination. Only truly low-temperature ultra-high vacuum scanning probe microscopy where the entire microscope head is kept at low temperature would allow this problem to be overcome.

- **Elastic recoil detection analysis (ERDA) development.** Light element analysis is critical in several EMSL associated research areas, including oxide thin films for optical, magnetic, and catalytic materials and characterization of environmental and biological samples. The time-of-flight ERDA technique will provide simultaneous detection and absolute quantification of hydrogen, carbon, nitrogen, oxygen, and other light elements as a function of depth in complex matrices containing heavy elements, and, as a result, considerable attention is being devoted in developing this capability in ion beam facilities. Since this is a powerful method to investigate elemental concentrations in the surface regions, this capability can be effectively applied to many different areas. This activity is almost complete, with a program associated with radiation detection materials development being worked and ready for users in Fiscal Year 2007.

- **Energy filtered imaging.** Electron energy loss spectroscopy for identification of light elements was developed, along with energy-filtered imaging with energy-specified electrons and electron diffraction capabilities. This capability development activity has been completed, and the capabilities are available for users.

- **Expert system for characterization of nanomaterials by x-ray photoelectron spectroscopy.** Development of this capability involved collaboration between the INSF and EMSL's Instrument Development Laboratory, and involves developing a software tool for faster and quantitative analysis of data from nanomaterials. This capability is not complete, and the facility is hoping to complete development by end of Fiscal Year 2007.

Future Directions

The overall objectives of the INSF are to support current highly productive users and user base and to expand outreach and capabilities related to developing areas associated with EMSL science themes and grand challenges. Accomplishments expected for Fiscal Year 2007 by this facility are as follows.

- **User support.** The facility's current user base is strong and productive. One objective is to maintain that base and the high level of user-produced output. The facility will also continue to make an impact in science themes and science theme-related calls, with significant contribution to the science theme call advertised in Fiscal Year 2006. The facility will work hard to obtain more than 20 science theme proposals during Fiscal Year 2007. The facility will also continue to work hard to update the user proposal database and convert most of the facility proposals to science theme proposals. The facility will continue to work to maintain/increase the total number of publications (110-120) with its distinguished and prominent user base. The long-term goal of the facility is to increase publications, especially in high-profile journals, and to increase the number of high-profile users.

- **Capability development.** As described below, significant new efforts are currently undertaken to enhance the support to all four EMSL science themes:
    - **Dual focused ion beam/scanning electron microscopy.** This new capability is crucial for the facility. Focused ion beams and two-beam focused ion beam/scanning electron microscopy systems are innovative instruments for nanoscience and engineering research that perform versatile tasks from prototyping novel architectures to materials analysis. The focused ion beam has revolutionized micromachining for the semiconductor device industry and is becoming a powerful tool in precise, cost-effective sample preparation of materials for transmission electron microscopy characterization. The facility will use the system's full capability

for nanomaterials synthesis and modification. This capability will include a cryo-stage so that biological samples can be successfully handled. In addition, the sample transfer system will help interface this capability with several other capabilities, including high resolution transmission electron microscopy, x-ray photon spectroscopy, and secondary ion mass spectrometry.

- **Time-of-flight secondary ion mass spectrometry.** Both biological systems and atmospheric chemistry research will be enhanced by a new generation of this capability, which will allow better depth resolution and extraction of information from environmentally unstable materials (biological and aerosol samples). Advances in the ion beam analysis capability will allow increased time resolution for atmospheric chemical analysis.

- **Catalytic reaction chamber for the quantum system.** This system will be connected to the existing Quantum x-ray photo spectroscopy system. It adds a new capability to Quantum and the planned capability will allow powder catalysis samples to be processed (heated in vacuum or in atmospheric pressure gas) before analysis by x-ray photon spectroscopy. This allows catalysts to be processed and analyzed without destroying information and minimizing changes to oxidation state. The same system will also have a higher-pressure reaction chamber where test catalytic reactions can be conducted and samples entered into the x-ray photon spectroscopy system, again without air exposure.

- **Hemispherical electron energy analyzer.** The ultrahigh vacuum scanning tunneling microscopy system will be upgraded with the high spatial and energy resolution hemispherical electron energy analyzer for examination of site specific chemical reactions. In general, the older analyzer analyzes a larger sample area. Experience has shown that the smaller sample size required compared to the sizes that could be analyzed by older analyzer. The new analyzer will be installed to do the smaller area analysis.

- **Ultra high vacuum processing chamber for Kratos AXIS system.** This capability will be crucial to process single crystals under ultra-high vacuum conditions for catalysis and photocatalysis studies. Sample quality and removal of contamination is a critical part of single crystal surface studies, including catalysis and photocatalysis. High-temperature sample heating, exposure to gases and sometimes plasmas are useful to accomplish this process. To heat samples to temperatures higher than allowed in the analysis chamber and allow exposure to higher gas pressures than desirable for the system, a modified existing chamber with sample manipulation capabilities would be connected to the Kratos AXIS system using the EMSL platen transfer approach.

- **Auger electron spectroscopy upgrade.** Two main instruments will be purchased and incorporated into a scanning Auger microscope. The first will involve an ion gun update to the Physical Electronics 680 Auger nanoprobe system, which will require a floating column design that generates high current densities at low beam energies and the ability to create low energy ion flood for use in sample neutralization. The second will involve a data acquisition system update to the Physical Electronics 680 Auger nanoprobe system.

- **Scanning multi-probe surface analysis system.** Very high demand exists for x-ray photoelectron spectroscopy analysis at EMSL. In addition, there are additional needs for state-of-the-art sputter depth profiling, in particular on biological samples and ultraviolet photoemission capability in conjunction with the x-ray photoelectron spectroscopy and depth profiling capability for organic samples. State-of-the-art sputter depth profiling of organic molecules, self assembled monolayers, and biological samples can be achieved by a new ion gun system based on ^{60}C. As such, a system will be developed in Fiscal Year 2007 that consists of ^{60}C ion gun sputter depth profiling capability and ultraviolet photoemission capability in addition to the small-spot x-ray photoelectron spectroscopy capability with high sensitivity.

Synthesis of Organically Templated Nanoporous Tin (II/IV) Phosphate for Radionuclide and Metal Sequestration

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Effective removal of heavy metals and pollutants from the environment will lead to a clean living environment. Nanoporous materials offer an efficient way of selectively sequestering many types of metals and radionuclides in a very small volume. The high-surface area of a nanoporous structure enhances mass transfer in sequestration applications and enables ions to be highly concentrated in a very small volume of material. Operations related to nuclear energy and weapons production have produced significant quantities of radioactive waste during the last half century that will be processed and buried in a deep geological repository at Yucca Mountain in Nevada. The current proposal is to include "getter materials" with this waste to sequester any radionuclides that might leach from the waste forms. Of particular interest are the long-lived actinide species (e.g., plutonium, americium, neptunium) and the anions (e.g., pertechnetate, iodide). Getter materials must be able to survive long-term exposure to elevated temperatures (>150°C) and moderately high radiation fluxes. The frailty of organic components towards radiolytic degradation precludes their use for either structure or function in the final getter material.

During the last decade, metal phosphates have been extensively studied for their potential use in catalysis, ion exchange, and phase separation. Since the first open-framework tin phosphates were prepared nearly 15 years ago, there has been interest in the structural flexibility of tin phosphates crystallizing in one-dimensional, three-dimensional, or layered structures. Open-framework tin phosphates have been prepared by direct precipitation and by incorporating organic amines into the crystal lattice. Surfactant-templated, open-framework tin phosphates have been reported using structure directing amine compounds including ethylenediamine, 1,6-diaminohexane, 1,2-diaminopropane, 1,8-diaminooctane, and 1,4-diaminobutane. Only recently, however, has a nanoporous tin (IV) phosphate been reported, and, to date, this is the only known report of a nanoporous tin phosphate. The cationic quaternary ammonium salt $CH_3(CH_2)_{15}N(CH_3)_3Br$ was used as the surfactant. The use of cetyltrimethylammonium bromide as surfactant resulted in surface areas of 230 m^2/g and pore sizes of 35-38 Å. Although the pore size was reduced from 39 to 35 Å, the structure was stable following calcination.

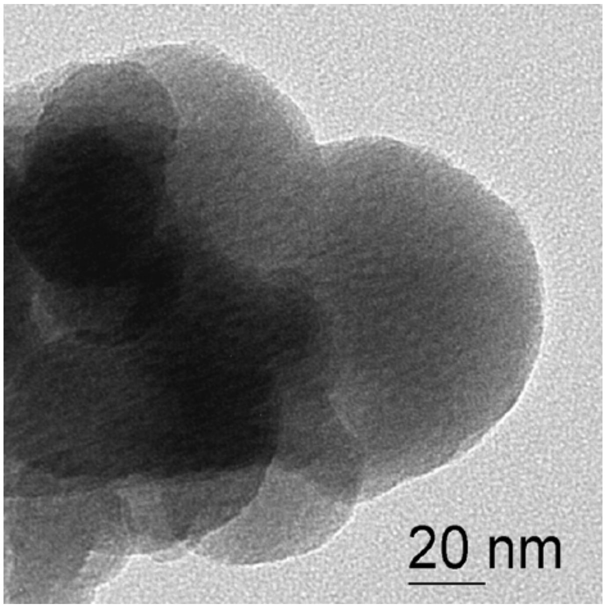

Figure 1. Calcination of the as-synthesized material at 500°C produced a material with a surface area of 262 m^2/g. The x-ray diffraction pattern of the surfactant-$SnPO_4$ and calcined $SnPO_4$ are shown above. The d spacing of the 100 plane in surfactant-$SnPO_4$ is 5.01 nm, whereas after calcination it was reduced to 4.62 nm. Subjecting the nanoporous $SnPO_4$ (NP-SnPO) to high temperatures during calcination has little impact on pore size.

The goal of this study was to produce a similarly stable, mesoporous solid using tin (II) as the starting material to produce a material capable of sequestering redox-sensitive species, such as pertechnetate, neptunium, chromium, and iodide. The large pores afforded with quaternary ammonium surfactants and the high-surface area of nanoporous structures are valuable features for enhanced mass transfer in sequestration applications. This work summarizes efforts to make a nanoporous tin(II) phosphate phase. The synthesis method consists of preparing 200 mL of 6.87 mmol cetyltrimethylammonium chloride $CH_3(CH_2)^{15}N(CH_3)^3Cl$, in deionized water. The solution is acidified with 0.626 mL of concentrated phosphoric acid. A concentrated solution of 15.22-g stannous chloride was dissolved in 100-mL hydrochloric acid. 2.5 mL of SnC^{l2}/HCl solution was added with stirring at room temperature to the acidified surfactant. The solution stirred for 30 minutes at room temperature and was placed in an oven at 65°C for 48 to 72 hours. The synthetic material was collected via vacuum filtration using a 0.45-μm filter, washed with deionized water, and dried under ambient conditions. Chemical analysis of the synthetic material indicates the structure is composed of Sn:P:O with a ratio of 1:1:5.

Selected-area electron diffraction analysis of a typical tin phosphate (NP-SNPO) illustrates a completely amorphous structure. Analyses with high-resolution transmission-electron microscopy revealed a spherical particle morphology approximately 150 nm across, with uniform pore distribution narrowly distributed around 2 nm. It was also observed that directly precipitated NP-SNPO materials, in addition to being thermally stable (500°C), are chemically stable over the entire pH range (pH = 0 to 14); therefore, tin will not leach into water during remediation operations (Figure 1).

Preliminary batch contact studies have been conducted to assess the effectiveness of NP-SnPO in sequestering redox-sensitive metals and radionuclides, technetium(VII), neptunium(V), thorium(IV), and a toxic metal, chromium(VI), from aqueous matrices. Equilibrium was achieved in less than an hour at a solution-to-solids ratio of 100, therefore a batch contact time of 2 hours was used to ensure that these values represent true equilibrium conditions. Under these conditions, the nanoporous, calcined tin (II) phosphate removed >95% of all contaminants investigated from solution. Distribution coefficients, Kd, are defined as a mass-weighted partition coefficient. Kd values were typically >10,000 in groundwater for the nanoporous tin (II) phosphate; whereas, Kd values for non-porous tin (II) phosphate was ~100. At a solution-to-solids ratio of 100, a Kd value of 10,000 indicates that at equilibrium there was 100 times as much contaminant in the nanoporous metal-phosphate phase as there was remaining in the supernantant solution.

Data obtained via x-ray absorption near edge spectra/extended x-ray absorption fine structure analysis clearly illustrate the sequestration of Tc(VII), Np(V), and Cr(VI) with NP-SNPO occurs through redox-coupled reactions with the target metals being reduced to their least soluble valence states, namely, Tc(IV), Np(IV), and Cr (III), with oxidation of tin in NP-SnPO. Although lacking spectroscopic data, we surmise that Th(IV) adsorption on NP-SnPO is due to Lewis acid-base interaction with PO_4 groups.

These nanoporous tin (II) phosphates exhibited significant promise as sorbent materials for anionic and redox-sensitive metals and actinides. The detailed kinetic studies of these materials are planned for publication.

A Soft X-ray Absorption Spectroscopy Study of Ceria Grown on $Al_2O_3(0001)$

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Both O 1s and Ce 3d x-ray absorption spectra show that ceria films with particle sizes of 3 nm and 7 nm are largely oxygen deficient. As a result, a significant amount of trivalent cerium ions are present in the ceria films, whereas the ceria film with a particle size of 38 nm is fairly stoichiometric CeO_2. *Furthermore, the* ^{18}O *intake measurements of ceria films show that the redox potential of* Ce^{3+}/Ce^{4+} *ions is flexible enough such that the nanocrystalline ceria is stable at room temperature and can be manipulated for specific applications, such as catalysis.*

Ceria-based oxides are being used as catalysts in many technological applications because of their unique redox properties. The overall performance of these oxides depends on particle size, structural characteristics, and chemical nonstoichiometry. Most applications for the ceria-based oxides are surface sensitive, and recent advances in nanotechnology enable fabrication of these oxides as nanostructures. These nanostructures can be used to reach a high surface-to-volume ratio, in addition to improved redox properties, related to oxygen vacancy generation. Therefore, a detailed scientific understanding of the growth and characterization of ceria nanostructures becomes necessary to determine viability of these materials for various applications. In this study, we investigated the oxidation state and local structure of ceria grown on $Al_2O_3(0001)$ single crystal surfaces with different particle sizes prior to and following oxygen intake using soft x-ray absorption spectroscopy.

The O 1s and Ce 3d x-ray absorption spectra of ceria films measured at Beamline 6.3.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory are shown in Figure 1. The prominent features in the O 1s spectra are a sharp pre-edge transition at 530 eV and an intense transition at 532.5 eV, which is superimposed on the edge jump, and a broad band centered at 536.9eV. The sharp pre-edge transition at 530 eV arises from the excitation of O 1s core electrons to 2p hole-states in the narrow 4f dominated bands resulting from strong Ce 4f and O 2p hybridization in the ground states of CeO_2. Similarly, the intense transition at 532.5 eV and the broad band at 536.9 eV are assigned to the transitions from O 1s to Ce $5d(e_g)$ and $5d(t_{2g})$ states, respectively, while the edge jump corresponds to transitions to empty continuum states. It can be noted from Figure 1a that the intensities of the transitions at 530 eV, 532.5 eV, and 536.9 eV in the O 1s spectra collected at both $\theta=0^o$ and $\theta=82.5^o$ increase with increasing the particle size of ceria films from 3 nm to 38 nm. This intensity increase for the transition at 530 eV amounts to ~19% and ~17% for the spectra recorded at $\theta=0^o$ and 82.5^o, respectively. For transitions at 532.5 eV and 536.9 eV, the intensity increase is 7% each for the spectra recorded at both $\theta=0^o$ and 82.5^o. In general, the electronic transitions in the x-ray absorption spectra occur from a selected atomic core

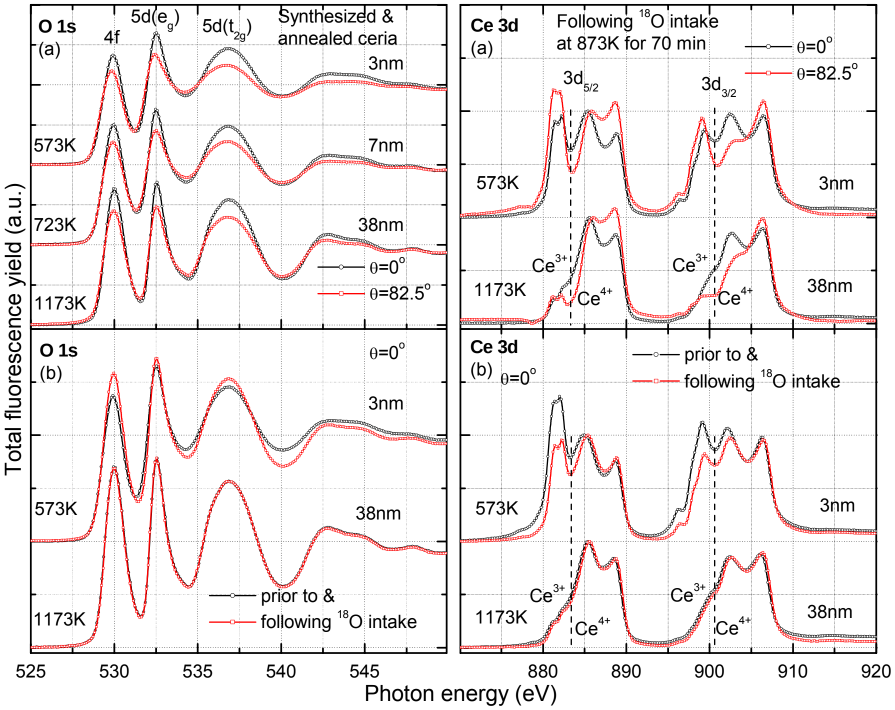

Figure 1. (a) Comparison of the normal ($\theta=0^o$) and grazing incidence ($\theta=82.5^o$) x-ray absorption spectra at O 1s and Ce 3d edges from ceria films on $Al_2O_3(0001)$ with particle sizes of 3 nm, 7 nm, and 38 nm. (b) The normal incidence ($\theta=0^o$) x-ray absorption spectra at O 1s and Ce 3d edges from ceria films on $Al_2O_3(0001)$ with particle sizes of 3 nm and 38 nm prior to and following ^{18}O intake by annealing the films in 4.0 x 10^{-6} Torr of $^{18}O_2$ at 873 K for 70 min.

level to unoccupied states and intensities of these transitions are directly related to the unoccupied density of states, which results from the chemical and electronic structures of a given chemical composition.

The x-ray diffraction and high-resolution transmission electron microscopy results show that the ceria annealed at 573 K and 723 K retain nanocrystalline phases, while the ceria annealed at 1173 K reveal characteristics of polycrystalline CeO_2. The intensity increase in the O 1s spectra suggests that the nanocrystalline ceria films with lower particle sizes are oxygen deficient, which leads to the formation of Ce^{3+} in the ceria films. With increasing annealing temperature, the oxygen-deficient nanocrystalline ceria films absorb oxygen from air, which facilitates the oxidation of Ce^{3+} to Ce^{4+} with increased bond formation leading to increased particle size and long-range ordering. Comparison of these O 1s spectra with the spectra from reference materials suggests that the pre-edge transition at 530 eV is originated from CeO_2, whereas the transitions at 532.5 eV and 536.9 eV can originate from oxide ions coordinated to both Ce^{3+} and Ce^{4+}. A moderate increase in intensity (~7%) for the transitions at 532.5 eV and 536.9 eV with increasing particle size of ceria films only suggests an increase of long-range ordering of the ceria film with annealing temperature, assuming that the fluorescence cross sections of oxide ions coordinated to Ce^{3+} and Ce^{4+} are the same. A drastic increase in intensity (19%) for the pre-edge transition at 530 eV shows the presence of Ce^{3+} in ceria film with lower particle size and it is being oxidized to Ce^{4+} in addition to increase of long-range ordering with increasing particle size of ceria films.

Furthermore, the intensities for all transitions in the O 1s spectra collected at $\theta=82.5^{o}$ are significantly reduced (14%) compared to the spectra at $\theta=0^{o,}$ regardless of ceria particle size (Figure 1b). These ceria films do not show polarization dependence because of the lack of specific orientation; however, the probing depth at $\theta=0^{o}$ is up to 300 nm, and it is restricted to only the near-surface region at $\theta=82.5^{o}$. Therefore, the difference between the spectra collected at $\theta=0^{o}$ and $\theta=82.5^{o}$ results from the variation of ceria surface from its bulk. A reduction in intensity for grazing incidence spectra suggests more oxygen deficiency and a lack of long-range ordering in the near-surface region compared to the bulk ceria film.

The O 1s x-ray absorption spectra collected at $\theta=0^{o}$ from ceria films with a particle size of 3 nm show an increase in intensity for all transitions following ^{18}O intake. However, the increase in intensity for the transition at 530 eV is significant as this transition is characteristic of CeO_2 and is sensitive to oxygen deficiency. These results suggest that the ceria film with a particle size of 3 nm is oxygen deficient and takes more oxygen when subjected to annealing at high temperature in an oxygen atmosphere. In contrast, the spectra for the ceria film with a particle size of 38 nm prior to and following annealing the films in 4.0×10^{-6} Torr of $^{18}O_2$ at 873K for 70 minutes show no changes, suggesting that this ceria film is stoichiometric CeO_2.

In the Ce 3d x-ray absorption spectra collected at $\theta=0$ and $\theta=82.5$ from ceria films grown on $Al_2O_3(0001)$ with particle sizes of 3 nm, 7 nm, and 38nm, the transitions occur from the initial $3d^{10}4f^{n}$ state to the final states of the form $3d^{9}4f^{n+1}$. Spin-orbit interaction splits the Ce 3d into $3d_{5/2}$ and $3d_{3/2}$ states separated by ~17.6 eV. The spectra reflect the oxidation states of Ce in ceria films with different particle size. Based on the spectra from reference materials, the transitions originating from Ce^{3+} and Ce^{4+} are separated with dashed lines in both the $3d_{5/2}$ and $3d_{3/2}$ edges of Ce. The energy separation between Ce^{3+} and Ce^{4+} in ceria films corresponds to ~3.0eV. The intensities of the transitions originating from Ce^{3+} relative to the intensities of the transitions originating from Ce^{4+} decrease for the spectra recorded at both $\theta=0^{o}$ and $\theta=82.5^{o}$ from ceria films with increasing particle size, suggesting that the relative concentrations of Ce^{3+} ions decrease. Furthermore, the relative intensities of the transitions originating from Ce^{3+} is larger for the spectra recorded at $\theta=82.5^{o}$ compared to the spectra recorded at $\theta=0,^{o}$ regardless of the particle size of the ceria film, suggesting that the relative concentrations of Ce^{3+} on the surface is larger than in the bulk of the ceria film with a specific particle size. Ceria on the surface is also more susceptible to reduction by x-ray, especially when the particle sizes are smaller, because of their larger surface area with no or reduced long-range ordering. These results are in good agreement with those obtained from O 1s spectra.

The intensities of the transitions originating from Ce^{3+} relative to the intensities of the transitions originating from Ce^{4+} are significantly reduced for the spectra recorded from ceria film with particle sizes of 3 nm following ^{18}O intake, compared to the spectra recorded prior to ^{18}O intake. These results suggest that the Ce^{3+} present in the ceria film with particle sizes of 3 nm prior to ^{18}O intake is oxidized to Ce^{4+} following ^{18}O intake. However, the spectra recorded from ceria film with particle sizes of 38 nm prior to and following ^{18}O intake show no changes, suggesting that this ceria film does not have significant concentrations of Ce^{3+}. These results are also consistent with those obtained from O 1s spectra.

Geophysical Imaging of Stimulated Microbial Biomineralization

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Understanding how microorganisms influence the physical and chemical properties of the subsurface is hindered by our inability to observe microbial dynamics in real time and with high spatial resolution. Here, we investigate the use of noninvasive geophysical methods to monitor biomineralization at the laboratory scale during stimulated sulfate reduction under dynamic flow conditions. Geophysical data reflected the distribution of mineral precipitates and biomass over space and time, with temporal variations in the signals corresponding to changes in the aggregation state of the nanocrystalline sulfides. These results were correlated with data obtained by transmission and scanning electron microcopy. The results suggest the potential for using geophysical techniques to image certain subsurface biogeochemical processes, such as those accompanying the bioremediation of metal-contaminated aquifers.

The problem of groundwater contamination by acid-mine drainage, industrial sources, and government nuclear weapons programs has spawned interest in the ability of microorganisms to facilitate remediation through sequestration of metals in insoluble precipitates. High-resolution geophysical techniques have proven extremely useful at the field scale for estimating hydrogeological properties, providing information about subsurface environments. In this study, the sensitivity of two geophysical techniques, complex resistivity and acoustic wave propagation, is tested to the products of microbial biomineralization. The primary objective was to follow the reaction dynamics of a column-scale biostimulation experiment using conventional biogeochemical and mineralogical measurements, as well as noninvasive geophysical techniques. We tested the hypothesis that metal sequestration via microbe-induced sulfide precipitation creates physical property changes that directly alter the response of geophysical signals. We compared the temporal response of such signals against concomitant changes in fluid chemistry and microbial biomass to investigate if the geophysical responses are sensitive to the products of biomineralization. Finally, we validated our interpretation of the geophysical responses using electron microscopy techniques.

Sulfate-reducing bacterium *Desulfovibrio vulgaris* was used for monitoring of microbe-induced ZnS and FeS precipitation within saturated sand-packed columns. Acoustic wave measurements and saturated hydraulic conductivity measurement were done during the duration of the experiment. Columns were terminated after 78 days and analyzed for concentration of sediment-affixed metal sulfides and microbial biomass. Solution samples from the influent, effluent, and multiport samplers were analyzed for major dissolved components at 3- to 5-day intervals. Total dissolved zinc and iron was determined by inductively coupled plasma atomic emission spectroscopy. Lactate, acetate, and sulfate concentrations were determined by gradient elution ion chromatography. Solution pH was measured using a sulfide-tolerant electrode. Transmission and scanning electron microscopy were used for characterizing microbe-mineral associations and the crystal size and aggregation state, and they documented significant spatial variability in the abundance and distribution of cells and their associated mineral products. Transmission electron microscopy-based analysis of the precipitates revealed them to be a mixture of sphalerite (ZnS) and mackinawite (FeS), with an average crystal size of 3 nm (Figure 1). Scanning electron microscopy revealed grain coatings consisting of dense accumulations of sulfide-encrusted microbes.

We have shown that the stimulation of sulfate-reducing microorganisms and the associated formation of insoluble metal sulfides create physical property changes that are directly detectable using geophysical techniques. We have resolved spatiotemporal changes in complex resistivity and acoustic wave propagation resulting from variations in the electric charge-carrying capacity and elastic moduli of precipitates and pore fluids. The changes persisted over time and were confined exclusively to those regions where metals were sequestered in insoluble precipitates. Temporal changes in the geophysical signals appear to offer insight into the aggregation state of the sulfides and may be indicative of pore-scale crystal growth and aging, with such a result having implications for the fate and transport of microbe-induced precipitates. Our laboratory results are relevant to the larger spatial scales of the natural environment where methods currently used for field-scale geophysical monitoring may be used in an analogous fashion. These results show the potential of using complex resistivity and acoustic wave techniques for remotely monitoring regions of contaminant sequestration via biomineralization and for evaluating the overall long-term stability of such precipitates.

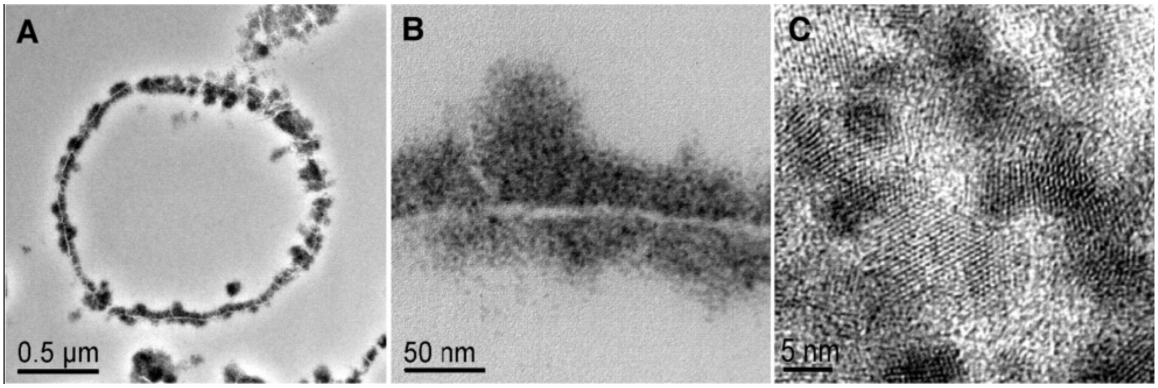

Figure 1. (A and B) Cross-sectional transmission electron microscopy images of a single *D. vulgaris* cell with membrane-bound ZnS and FeS precipitates. (C) High-resolution transmission electron microscopy revealed the nanocrystalline character of the precipitates with a typical particle size of 3 to 5 nm.

Kinetics of Electron-Beam-Enhanced Recrystallization of Amorphous Strontium Titanate

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Single crystal strontium titanate ($SrTiO_3$) is of technological interest in microelectronics industries because of its high dielectric constant, good insulating properties, outstanding wear resistance, high oxidation resistance, and chemical and thermal stability. Strontium titanate thin films are used as insulating layers in dynamic random access memories, ferroelectric thin-film structures, and high-T_c superconductor devices, as well as potential gate oxide candidates. Strontium titanate and other titanate ceramics have also been proposed as phases for immobilization of nuclear waste. In many of these applications, knowledge of dynamic recovery and nanostructure evolution is critical.

Irradiation of $SrTiO_3$ with 1.0 MeV Au at 400 K leads to formation of an amorphous surface layer. In this research, the damage and microstructural features in the samples were investigated by Rutherford back-scattering spectroscopy and high-resolution transmission electron microscopy (TEM) images, and the results show amorphous regions of ~10.6 nm and ~330 nm for sample A, as shown in Figure 1(a), and sample B, respectively. Following exposure of the amorphous layers to TEM electron-beam (*e*-beam), the amorphous thickness decreases with exposure time, and *in situ* epitaxial recrystalli-zation at the amorphous/ crystalline (a/c) interface is observed, as shown in Figures 1(b) and 2. In the central area of the cross-sectional TEM image of sample A in Figure 1(b) where the *e*-beam is the most intense, more amorphous material recrystallizes, and the a/c interface moves toward the surface. At both edges of the cross-sectional image where the *e*-beam density is lower, recrystallization is not as significant. This indicates a strong dependence of the recrystallization process on *e*-beam flux. The *e*-beam-induced recrystallization of the amorphous layer in sample B is shown in Figure 2, where rapid *in situ* recrystallization at the a/c interface is evident.

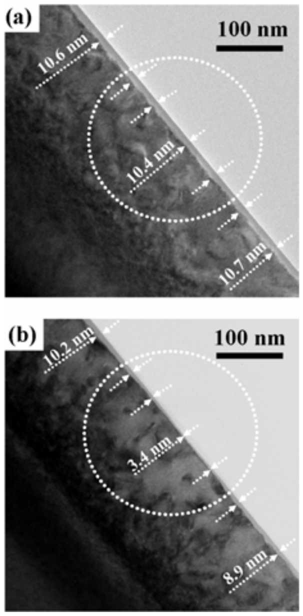

Figure 1. TEM images of sample A: (a) the amorphous layer. (b) recrystallization of amorphous layer following the *e*-beam irradiation.

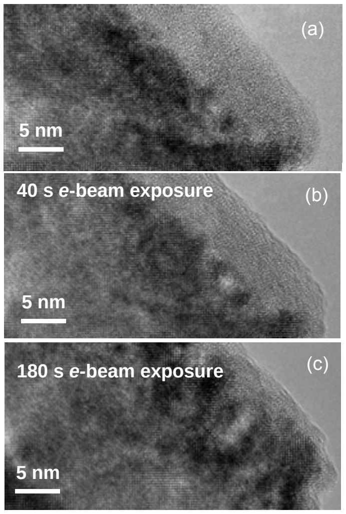

Figure 2. The a/c interface motion under *e*-beam exposure with flux of 5.0 ×10^{20} cm^{-2}s^{-1}.

The *in situ* recrystallization of the amorphous layer at room temperature under different beam flux is summarized in Figure 3. The solid phase regrowth appears as a series of linear stages with decreasing slopes as exposure time increases, resembling a sublinear-like regrowth behavior. In general, the recrystallization rate resulting from *e*-beam irradiation can be separated into three stages. During the initial stage (i.e., up to ~100 s), there exist many ion-induced defects near the a/c interface. Rapid motion at the a/c interface is observed, and the recrystallization processes proceed at a high rate. This fast recrystallization may be attributed to *e*-beam-enhanced defect annihilation at the a/c interface. Under the high *e*-beam flux (5.0 and 7.8 ×10^{20} cm^{-2}s^{-1}), the recrystallization processes during the initial stage occur very quickly, and no data were obtained during the very short durations. After the initial stage, during which most ion-induced defects were annealed out, the recrystallization rates become constant, and the recrystallization processes occur in a second stage. A well-defined linear relationship is observed for different fluxes at this stage. As the exposure time increases, little motion is observed at the a/c interface, and the recrystallization processes reach a saturation stage. The TEM observations indicate that the saturation stage occurs when the thickness of the amorphous layer is ~3 nm, which suggests that the surface may play an important role in stabilizing this final stage. It is evident in Figure 3 that the regrowth rate during the second stage increases with increasing beam flux from 1.2 to 5.0 ×10^{20} cm^{-2}s^{-1}, and shows no further increase with the increasing flux.

The regrowth rates in the second linear stage under *e*-beam irradiation were investigated as a function of flux and temperature. The *e*-beam enhanced recrystallization rates are orders of magnitude higher than those expected from thermal epitaxial recrystallization. Based on the temperature dependence of the recrystallization rates, an activation energy of 0.1±0.05 eV was determined for the *e*-beam-enhanced recrystallization processes. A sublinear-like regrowth dependence on exposure time may be used as a fingerprint for the *e*-beam enhanced recrystallization, as opposed to the superlinear-like behavior normally observed in thermal recrystallization.

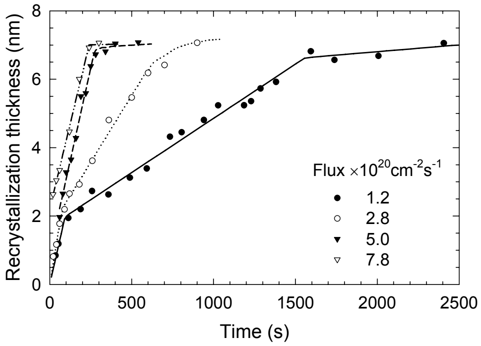

Figure 3. Solid phase regrowth of a/c transition as a function of exposure time to the *e*-beam under different fluxes.

During *e*-beam irradiation, the incident electrons primarily transfer energy by ionization processes that produce localized electronic excitations. The localized electronic excitations affect local atomic bonds and may effectively lower the energy barriers to recrystallization processes, which may involve local atomic hopping or rotation of atomic polyhedra.

Room-Temperature, Solvent-Free Synthesis of Monodisperse Magnetite Nanocrystals

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Magnetic nanoparticles are useful for a variety of scientific and technological applications such as magnetic storage media, ferrofluids, magnetic refrigeration, magnetic resonance imaging, hyperthermic cancer treatment, cell sorting, and targeted drug delivery. Iron oxides constitute one of the most fascinating classes of magnetic materials and have been extensively investigated. Based on chemical reactions in liquid or aerosol/vapor phases, different approaches such as coprecipitation, sol-gel, aging, ultrasound irradiation, and laser pyrolysis, have been established for preparing super-paramagnetic iron oxide nanoparticles typically smaller than 20 nm that are adaptable to variable applications. However, the relatively poor size uniformity and crystallinity of the nanoparticles obtained strongly affect their magnetic properties.

In this highlight, we report, for the first time, a novel, facile, and solvent-free synthetic method that allows the use of inorganic ferrous and ferric solids, along with surfactants, to produce monodisperse magnetite nanocrystals. The reaction is advantageous in that it is induced at room temperature rather than at the refluxing temperatures of ~265 to 350^{o}C used in the typical organic-solution phase decomposition method in which organic iron is dissolved in organic solvents. Highly crystalline and monodispersed Fe_3O_4 nanocrystalline particles are obtained by the new process despite the fact that the reaction occurs at room temperature. Such a solvent-free reaction provides a substantial environmental advantage in that it eliminates the need for disposing of or recycling toxic chemicals. A solvent-free approach based on solid-state reactions was previously used for simple synthesis of unassembled nanoparticles; however, no surfactant was used for particle size control.

Solvent-free synthesis of magnetite nanocrystals can be considered as a hybrid of solid-state reaction, co-precipitation, and organic solution-phase decomposition processes that take advantage of only the beneficial parts of these processes. In this approach, the following modifications were made: 1) inorganic ferrous, ferric, and base solids were used directly for the synthesis rather than aqueous or organic solutions; 2) an oleic acid-oleylamine adduct solid was used as the surfactant stabilizer rather than oleic acid and oleylamine liquids; 3) after the reaction, the Fe_3O_4 nanoparticles were extracted directly into hexane, and the unreacted materials and the byproducts were separated conveniently since they are insoluble in hexane; and 4) mono-dispersed, uniform Fe_3O_4 nanoparticles that can be assembled into ordered arrays were obtained. In addition, this method requires no complex apparatus and techniques, and enables one to synthesize Fe_3O_4 nanocrystals with almost uniform size in high yields and at a large scale. The reaction, if carried out in the presence of a surfactant such as oleic acid-oleylamine adduct, generated monodisperse Fe_3O_4 nanocrystals extractable directly from the reaction mixture. The extracted nanoparticles were capable of forming a self-assembled, two-dimensional, and uniform periodic array. The new process uses inexpensive and nontoxic starting materials, and does not require a use of high-boiling-point toxic solvents, so it is amenable to an environmentally desirable, large-scale synthesis of nanocrystals.

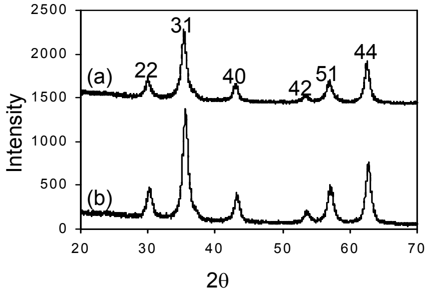

Figure 1. X-ray diffraction patterns of the nanoparticles.

X-ray diffraction patterns of the nanoparticles synthesized by the solvent-free reactions with and without the addition of oleic acid-oleylamine adduct are compared in Figure 1. Both patterns indicate the crystalline nature of the products, and the positions and relative intensities of all diffraction peaks coincide with those of the Joint Committee for Powder Diffraction Studies card (19-0629) for Fe_3O_4. No characteristic peaks of reactants and byproducts (mostly NaCl) were observed. The general transmission electron micrograph of the nanoparticles synthesized by the solvent-free reaction in the presence of surfactant is shown in Figure 2 (left image). The nanoparticles appear almost spherical and monodispersed with an average diameter of 5 nm, and self assemble into a two-dimensional array. A high-resolution transmission electron micrograph of the patterned nanoparticles is shown in Figure 2 (right image). The lattice spacing seen in the lattice fringe of the particles revealed the satisfactory crystallinity and structural uniformity of the sample.

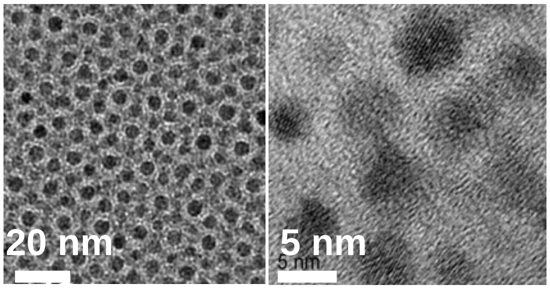

Figure 2. Transmission electron micrographs

We have successfully demonstrated and documented the synthesis of monodisperse Fe_3O_4 nanocrystals using a novel and easy one-step, solvent-free reaction (Ye et al. 2006). The reaction of the solvent-free synthesis in the presence of a surfactant is believed to precede a similar intermediate process via the formation of Fe(III) and Fe(II)-surfactant complexes. The reaction can be conveniently carried out at ambient temperature, thereby avoiding the use of toxic solvents with high boiling points. This technique, which uses inexpensive and nontoxic inorganic ferrous and ferric salts that are reacted at ambient temperature, is amenable to convenient, large-scale synthesis. With proper choices of inorganic metal salts and surfactants, this method may be extended to environmentally desirable preparation of a wide variety of monodisperse nanocrystals.

This research is described in more detail in Ye et al. 2006.

Citation

Ye X, C Daraio, C Wang, JB Talbot, and S Jin. 2006. "Room Temperature Solvent-Free Synthesis of Monodisperse Magnetite Nanocrystals." *Journal of Nanoscience and Nanotechnology* 6(3):852-856.

Identification of Isotopically Primitive Interplanetary Dust Particles

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Interplanetary dust particles (IDPs), which originate largely from comets and asteroids, are complex assemblages of various primitive solar system materials. Chondritic porous IDPs are dominated by anhydrous minerals, in contrast to chondritic smooth IDPs that are composed predominantly of hydrated layer lattice silicates. While specific parent bodies are not known, hydrated IDPs have been linked to asteroidal origins, whereas anhydrous IDPs may be more likely to have cometary origins.

Isotopic measurements of IDPs show the presence of abundant extra-solar phases. Significant depletions and enrichments in hydrogen isotopic compositions have been found in IDPs and almost certainly have an interstellar origin. The origin of nitrogen isotopic anomalies is more complicated than that of hydrogen, because nitrogen isotopic fractionation has not been observed in the interstellar medium and anomalous nitrogen can also have a nucleo-synthetic origin. However, recent theoretical work shows that chemical reactions in dense molecular clouds can produce elevated $^{15}N/^{14}N$ ratios.

High spatial resolution surface analytical instrumentation such as NanoSIMS and scanning auger microscopy have the ability to make isotopic measurements and identify mineralogical phases at the sub-micron scale, providing renewed opportunities to investigate the compositions of IDPs. Our goal has been to gain a better understanding of the abundance, nature, and distribution of isotopically anomalous phases in IDPs and, thereby, constrain both the nature of these phases and the parent bodies from which IDPs originate.

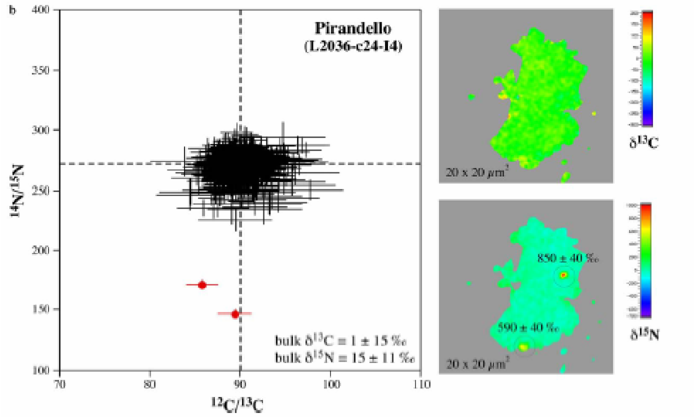

Figure 1. Carbon and nitrogen isotopic compositions of Pirandello from NanoSIMS analysis. Shown are isotope plots of the $^{12}C/^{13}C$ and $^{14}N/^{15}N$ ratios of 500 nm-sized subregions of the IDPs and false color images of the $\delta^{13}C$ and $\delta^{15}N$ compositions of the particles. Pirandello has isotopically normal bulk compositions in carbon and nitrogen, but contains two hot spots enriched in ^{15}N. Dashed lines show terrestrial carbon and nitrogen ratios.

Carbon and nitrogen isotopic compositions were measured in 39 IDPs from NASA collector flags L2009, L2011, and L2036. Hydrogen isotopic compositions were measured in a subset of these 39 IDPs. Typical data collected from these 39 IDPs, using NanoSIMs imaging and scanning Auger microscopy, are shown in Figure 1.

Auger elemental maps of pre-solar grain D1 from the IDP Deledda show that it is an iron-rich silicate (Figure 2). Iron-magnesium silicates, such as olivine and pyroxene, are expected to have magnesium-rich compositions under conditions of equilibrium condensation in the stellar winds of oxygen-rich RGB and AGB stars. Deledda appears to be an anhydrous IDP, which is unlikely to have experienced significant secondary processing. Thus, the pre-solar grain D1 may represent a primary iron-rich silicate condensate that formed under nonequilibrium conditions.

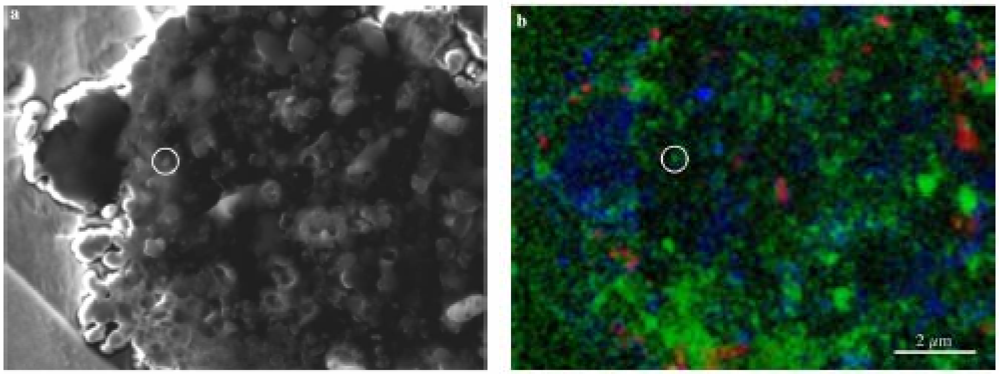

Figure 2. Auger elemental maps of presolar grain D1 from the IDP Deledda.

Isotopic imaging of a suite of IDPs shows that nitrogen isotopic compositions can be used to characterize IDPs and identify those that share a variety of primitive isotopic compositions, including the presence of abundant pre-solar silicate grains (Floss et al. 2006). Hydrogen and nitrogen isotopic compositions in these IDPs show similar distributions; fractionations are present both as small D-rich or ^{15}N-rich hot spots and as larger more diffuse anomalous regions. However, hydrogen and nitrogen anomalies are not correlated and D enrichments are not preferentially associated with isotopically primitive IDPs. Pre-solar silicate grains in the IDPs show a variety of isotopic compositions that are similar to the oxygen isotopic compositions of pre-solar silicate and oxide grains from primitive meteorites. Most of the grains have isotopic ratios consistent with origins from red giant or asymptotic giant branch stars. Pre-solar silicate abundances in the isotopically primitive IDPs are significantly higher than in most primitive meteorites, a characteristic that emphasizes the primitive nature of IDPs.

Citation

Floss C, FJ Stadermann, JP Bradley, ZR Dai, S Bajt, G Graham, and AS Lea. 2006. "Identification of Isotopically Primitive Interplanetary Dust Particles: A NanoSIMS Isotopic Imaging Study." *Geochimica et Cosmochimica Acta* 70:2371-2399.

Optimum Conductivity in Oriented $[Ce_{0.89}Sm_{0.11}]O_{2-x}$ Thin Films Grown by Oxygen-Plasma-Assisted Molecular Beam Epitaxy

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Investigations in alternative and clean energy technology have become essential to reduce the dependence on more traditional energy resources. Solid oxide fuel cells (SOFC) provide such clean energy without hazardous by-products. The research described in this highlight is motivated by the use of epitaxial Sm:CeO_2 *as a potential electrolyte material in SOFC. In this study, we have observed high conductivity values in epitaxial Sm:*CeO_2 *films.*

Development of electrolyte materials that possess high oxygen ion conductance at relatively low temperatures is essential to increase the efficiency and lifetime of SOFC. Lower operating temperatures would make SOFCs more cost efficient and could facilitate their use in broader applications. At lower operating temperatures, SOFCs could also avoid many undesirable interfacial reactions between electrodes and electrolyte materials. In this study, we used molecular-beam epitaxy, which enables precise growth control, to grow SOFC electrolyte layers. Oriented electrolyte layers, such as Sm:CeO_2, can potentially provide higher conductivity through a reduction in grain-boundary density, thus avoiding the unnecessary scattering across a layer. Sm:CeO_2 films were grown on single crystal c-Al_2O_3 in a dual-chamber, ultrahigh-vacuum system equipped with an electron cyclotron resonance oxygen plasma source.

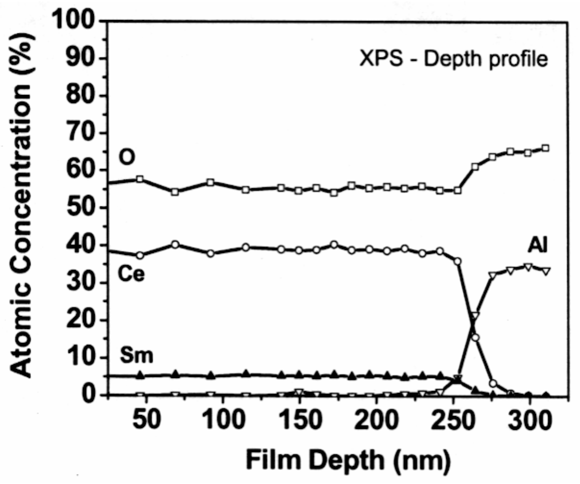

Figure 1. The XPS depth profile of 5 atom% Sm:CeO_2 film on c-Al_2O_3. A uniform samarium concentration throughout the film with surface oxygen enhancement can also be seen in the data.

After the surface plasma cleaning at 600°C, films were grown at simultaneous growth rates of 0.2 and 0.01 nm/s for cesium and samarium, respectively, in an oxygen partial pressure of $\sim 2.0\times10^{5}$ Torr and at a substrate temperature of 650°C. Cesium (99.98 percent purity) and samarium (99.98 percent purity) were evaporated from an e-bam source and an effusion cell, respectively. The growth rates of the films were monitored by quartz crystal oscillators (QCOs). The *in situ* film growth was monitored using reflection high-energy electron diffraction.

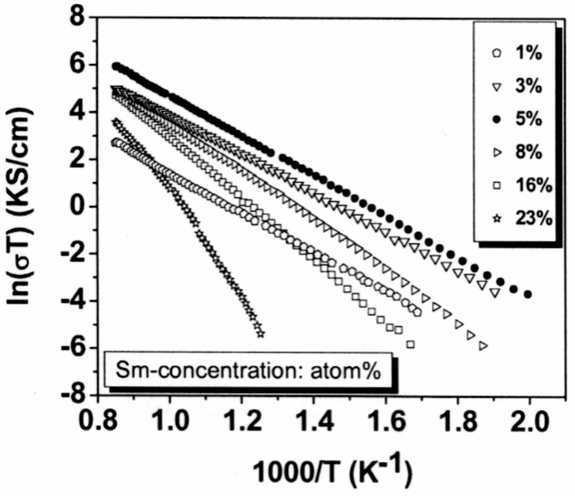

Figure 2. Arrhenius plots of Sm:CeO_2 films with various samarium atomic concentrations in the measurement temperature range of 500 to 900°C.

X-ray photoelectron spectroscopy (XPS) depth profiles give excellent overviews of the atomic elemental concentrations of cesium, samarium, oxygen, and aluminum as a function of film depth. Figure 1 shows the XPS depth profile in the case of 5 atom% Sm:CeO_2 film. A uniform samarium concentration as a function of film depth was noted, and $Ce_{0.89}Sm_{0.11}O_{2-x}$ was determined to be the stoichiometry of the film. In addition, a fairly sharp interface between Sm:CeO_2 and Al_2O_3 was also realized from the spectra. Four-probe conductivity measurements were done on Sm:CeO_2 films with samarium concentration in the range of 1 to 23 atom%. Figure 2 shows Arrhenius plots of Sm:CeO_2 films with various samarium atomic concentrations in the measurement temperature range of 500 to 900°C. The figure shows that film with a 5 atom% samarium concentration shows maximum conductivity compared to other doping concentrations. We concluded that a loss of (111) orientation enhances the grain boundary scattering, thereby reducing the conductivity. However, our observed conductivity of 0.04 S.cm^{-1} at 600°C is one of the highest conductivities observed in these materials. The activation energy E_a, derived from the slope of the Arrhenius plot, is observed at 0.86 eV for the as-grown films. Typically lower activation energy refers to lower barrier for the oxygen transport throughout the Sm:CeO$_2$ crystal.

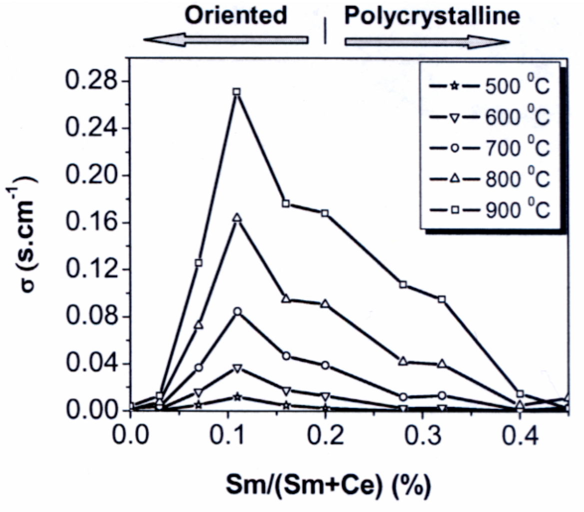

Figure 3. The conductivity of Sm:CeO$_2$ as a function of samarium concentration in the range of 1-23 atom% at measurement temperatures from 500 to 900°C. At all measurement temperatures, highest conductivity is seen at 5 atom% samarium concentration.

Figure 3 shows the conductivity of Sm:CeO$_2$ as a function of Sm/ (Sm+Ce) for the samarium concentration range of 1 to 23 atom%. The variation in conductivity as a function of temperature with different samarium concentrations is seen to get narrower at lower and higher samarium concentrations. The dopant saturation is likely to cause narrower conductivity variation at the higher samarium concentrations end, whereas limited dopant incorporation is primarily responsible for narrower variation at lower samarium concentrations.

Thermal Oxidation of Aluminum Nitride Powder

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The goal of this study was to determine and compare the oxidation behavior of two types of aluminum nitride (AlN) powder with different morphology and particle sizes. The kinetics of oxidation, the properties of the formed aluminum oxide layer, and the morphology change before and after oxidation were studied in detail using a combination of x-ray diffraction analysis and tunneling electron microscopy.

Aluminum nitride has a good thermal stability (melting point >2750°C), high thermal conductivity (3.2 W/cm·K) and electrical resistivity (>4 × 10^8 ohm·cm), and a low dielectric constant (9 at 1 MHz) and coefficient of thermal expansion (4.03-6.09 × 10^{-6}/K). Therefore, AlN has been widely used in the electronic and optoelectronic areas. Oxygen, a common impurity in AlN, has a detrimental effect on its properties: it reduces the lattice parameters of AlN and remarkably decreases its thermal conductivity. Therefore, understanding how oxygen enters the AlN lattice constitutes an important step for understanding the oxidation process. For example, a native oxide film of 5 to

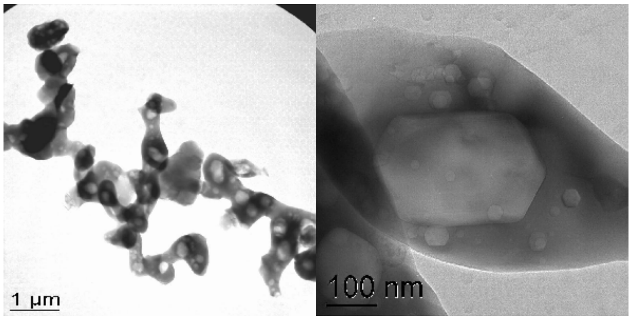

Figure 1. Transmission electron microscopy images of oxidized AlN particles, revealing a pore trapped in a particle.

10 nm in thickness is obtained following exposing AlN in air for 24 hours at room temperature. This initial oxide layer is protective and prevents further oxidation.

In general, three sequential steps occur during the thermal oxidation of most materials, one of which may be the rate-limiting step. First, the oxidant (typically oxygen or water vapor) transports in the gas phase to the oxide surface. Second, the oxidant diffuses through the oxide layer to the substrate/oxide interface. Third, and finally, the oxidation reaction occurs at the interface. The diffusion process in the gas phase is usually very fast compared to the other two steps, thus it is insignificant in determining the overall growth kinetics. Initially, when the oxide layer is thin, the oxidant quickly transports through the oxide to the interface to sustain the chemical reaction, hence the whole process is controlled by the interfacial reaction. As the oxide layer thickness increases, the diffusion of the oxidant through the oxide layer slows and becomes the rate-limiting step in the overall process. The thermal oxidation of silicon is a typical example of the three-step process. However, in the thermal oxidation of AlN, which is governed by the overall reaction $2AlN + 1.5O_2 \leftrightarrow Al_2O_3 + N_2$, the out-diffusion of product gas nitrogen through the oxide film and the removal of nitrogen away from the oxide surface are two additional steps that are not involved in the oxidation of silicon. The latter step is usually rapid and is not a rate-controlling step.

Two types of AlN powder were oxidized in flowing oxygen over the temperature range from 800 to 1150°C. For a Type-A AlN powder (average agglomerated particle size 1.8 µm), oxidation began above 900°C after 6 hours and was almost complete at 1050°C, but only for 30 minutes. Crystalline Al_2O_3 formed above 1050°C, while amorphous Al_2O_3 or oxynitrides formed at lower temperatures. The oxidation of Type-A AlN powder was a linear reaction over time between 800 and 1000°C, and the activation energy was 157.2 kJ/mol. These conditions indicated that an interfacial reaction governed the process. At temperatures higher than 1000°C (1050, 1100, and 1150°C), approximately 95 percent of the AlN was oxidized after only 30 minutes, and the conversion barely changed with further increases in the oxidation temperature or time. For a Type-B AlN powder (particle size 14.0 to 23 µm), oxidation became observable at 800°C after 6 hours, and the oxidation extent was higher than that of Type-A AlN powder at temperatures ranging from 800 to 1000°C. The oxidation kinetics changed from linear in the 800 to 900°C temperature range to parabolic in the 1000 to 1150°C range, suggesting that control of the process changed from interfacial reaction control to oxidant diffusion control. The complex oxidation difference observed between the two AlN powder types was probably caused by the different morphologies of the powders, and by their different particle sizes, particle-size distributions, and impurities. Figure 1 shows transmission electron microscopy images of oxidized AlN particles, revealing a pore trapped in a particle.

Oxidation of AlN powders, sintered polycrystalline substrates, and thin films has been extensively investigated. Abid et al. (1986) found that AlN powder was resistant to oxidation in air up to ~1000°C. For AlN powder heated to 1000°C, an unidentified phase was detected by reflection high-energy electron diffraction, possibly an oxide or oxynitride. At 1200°C, the AlN was completely transformed to α-Al_2O_3. However, no differences were reported for the oxidation of AlN powders with different particle sizes. Brown et al. (1998) observed a linear weight increase of AlN powder over time when heated in air at 850°C. The activation energy was calculated to be 271 kJ/mol. At temperatures above 850°C, the weight change increased parabolically, and the activation energy was 423 kJ/mol, which agreed well with the 459 kJ/mol experimental value for the diffusion of oxygen through polycrystalline Al_2O_3. X-ray diffraction, scanning electron microscopy, and infrared spectroscopy were employed by Ramanthan et al. (1995) to study the oxidation behavior of AlN powder at temperatures in the 900 to 1150°C range. An initial linear kinetic regime with activation energies of 197 and 270 kJ/mol was observed. A poorly crystalline spinel-type aluminum oxynitride formed at 900°C. This phase was transformed into α-alumina crystallites at higher temperatures. The oxide morphology changed from a fine-grained and coherent structure at 950°C to a porous fissured structure at 1150°C.

In addition to oxidation temperature and time, the condition of the original AlN powder is crucial in determining the thermal oxidation behavior. Particle size and impurity concentration are two important parameters in describing AlN powder. The surface-area-to-volume ratio of small particles is typically much higher than that of large particles, leaving more surface area exposed per mass. Thus, small particles are expected to oxidize faster than larger particles. The effect of particle size on the AlN oxidation rate was examined by Suryanarayana (1990). The initially rapid oxidation rate decreased over time for a fine AlN powder with a mean particle radius and standard deviation of 0.5 µm and 1.6, respectively. In contrast, the oxidation rate was almost constant with time for a coarse powder with a mean particle radius and a standard deviation of 3.1 µm and 2.1, respectively. Highly doped silicon substrates oxidize more rapidly than lightly doped silicon wafers, and the difference in reaction rates is greater at lower temperatures or for thinner oxides. One possible explanation is that oxidation requires volume expansion that can be provided by the consumption of vacancies at the silicon/silicon dioxide interface.

An article describing this research was published in the July 2006 edition the *Journal of the American Ceramic Society* (Gu et al. 2006).

Citations

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Study of Hydrogen Stability in Low-K Dielectric Films by Ion Beam Techniques

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With shrinking device geometries into the 65-nm technology node, a transition to low-k dielectrics becomes increasingly attractive. Negative bias temperature instability, which is associated with hydrogen migration at elevated temperatures, becomes the main degradation mechanism of concern for conductivity breakdown in semiconductor devices. The possibility of hydrogen release during each stage of the fabrication process is, therefore, of great interest to the understanding of device reliability. In this study, various low-k dielectric films were subjected to thermal annealing in a nitrogen atmosphere at temperatures that are generally used when fabricating devices. Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA) were used to investigate composition changes and hydrogen redistribution of the dielectric films.

In interlayer dielectric (ILD) applications, plasma-enhanced tetraethylorthosilicate (PETEOS) films have been used to achieve better step coverage, especially for submicron gap spaces. With addition of phosphorus dopants during the deposition, phosphorus-doped silicon glass (PSG) films become viscous at elevated temperatures and respond to surface tension forces and the rounding of sharp corners, which is extremely useful in forming uniform doping inside gaps with high aspect ratios.

Furthermore, PSG films have an alkali ion-gettering capability, which makes it well suited for use as a passivation layer. In this project, the composition changes of the PETEOS and PSG films before and after annealing at 400°C for 2 hours were studied by RBS. The RBS spectra along with the simulated spectra are presented in Figures 1(a) and 2(a). In addition, hydrogen stability was

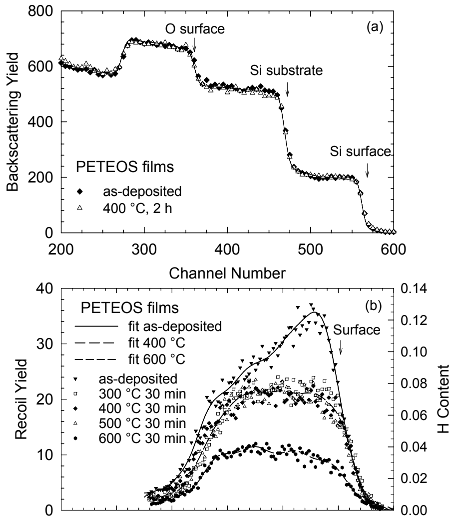

Figure 1. (a) RBS spectra of PETEOS films before and after 400°C for 2 hours; (b) ERDA spectra of the as-deposited PETEOS film and the films that are subjected to thermal treatments.

investigated by measuring the total hydrogen in the films using conventional ERDA after the heat treatments up to 600°C, as shown in Figures 1(b) and 2(b). In the figures, higher hydrogen concentrations are observed in the surface regions of as-deposited PETEOS and PSG films. In the as-deposited films, the hydrogen concen-tration in the surface region consists of hydrogen from the films and from the hydrocarbon contamination on the film surfaces. After heat treatment up to 400°C for 2 hours, the main structures of both films are preserved. Significant hydrogen reductions at both the PETEOS and the PSG sample surfaces are observed after annealing at 300°C. Although the PETEOS films show some hydrogen reduction in the bulk of the film after this annealing, reduction of hydrogen is less significant in the bulk of the PSG films, indicating the existence of weakly bound hydrogen compounds in the bulk of the PETEOS films. After annealing at 400 and 500°C, no significant hydrogen reduction is observed in both films, and hydrogen is more uniformly distributed in the films, approximately 7.5 percent in the PETEOS films and 2.5 percent in the PSG films. As the annealing temperature increases to 600°C, both the PETEOS and PSG films decompose with significant hydrogen releases, and a SiO_2 film begins to form.

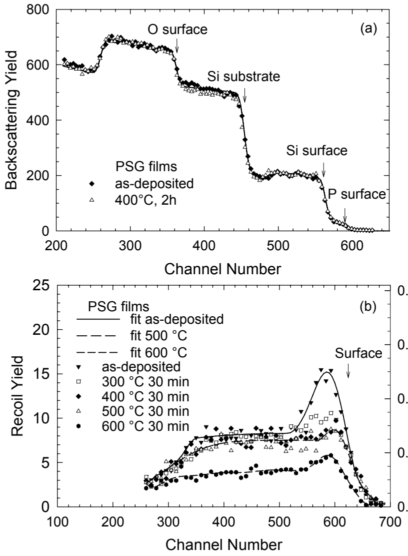

Figure 2. (a) RBS spectra of PSG films before and after 400°C for 2h. (b) ERDA spectra of the as-deposited and annealed PSG films.

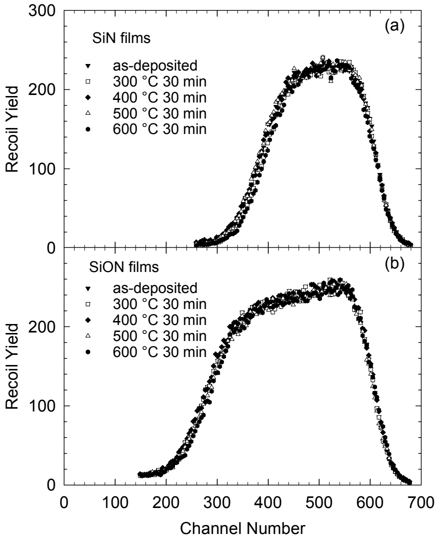

Figure 3. ERDA spectra of the as-deposited film and annealed (a) SiN films and (b) SiON films.

Silicon nitride (SiN) is a widely used dielectric material in very large-scale integration fabrication because of its impermeability to most impurities, such as a diffusion barrier to moisture, or as a selective oxidation mask to prevent oxygen from penetrating into the silicon underlayer. Silicon oxynitride (SiON) films, in which the composition changes continuously from oxide to nitride by varying gas flow during plasma-enhanced chemical vapor deposition, demonstrate improved stability and better cracking resistance with low film stress. Thus, SiON films are considered to be unique materials for intermetal-level dielectric and final passivation layers. The SiN and SiON films are thermally stable up to 600°C annealing, (Figure 3). No hydrogen redistribution or structural changes are observed within the measurement uncertainties.

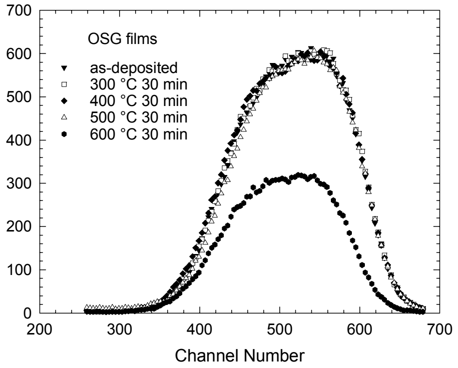

Figure 4. ERDA spectra of the as-deposited and thermally treated OSG films.

To further decrease the dielectric constant of the ILD layers as the device dimension decreases to sub-100-nm fields, introducing nanoscale pores into the dielectrics is an effective approach for meeting ultra-low-k demand. Among various porous low-k materials, organosilicate glass (OSG) films are promising candidates as ILD materials for high-performance interconnects. The OSG films used in this study were carbon-doped, low-k material with incorporated organic groups (e.g., -CH_3). No change was observed after heat treatment up to 400°C for 2 hours. ERDA results indicate that hydrogen bonds are stable up to 500°C for 30 minutes, as shown in Figure 4. However, release of hydrogen from the film during 600°C annealing is evident.

In this project, we investigated the stability of low-k dielectric films subjected to heat treatment up to 600°C. The results indicate that there is a significant hydrogen release from the surface region of the PETEOS and PSG films at 300°C and insignificant hydrogen releases in the temperature range from above 300°C to 500°C. The films start to decompose by releasing hydrogen at 600°C and form SiO_2. The SiN and SiON films are stable after heat treatment at 600°C for 30 minutes. Similar to the PETEOS and PSG films, the OSG films are stable up to 500°C and then break down at 600°C.

User Projects

Field Emission SEM of Anode Supported YSZ Fuel Cells Poisoned by Cr

SP Simner, J Kim, Pacific Northwest National Laboratory, Richland, Washington

MH Engelhard, Environmental Molecular Sciences Laboratory, Richland, Washington

Surface and Interface Study of Contacts to Carbon-based Films

TC Droubay, Pacific Northwest National Laboratory, Richland, Washington

LM Porter, PB Kulkarni, Carnegie Mellon University, Pittsburgh, Pennsylvania

Determination of the Catalytic Properties of Metal Coated Nanowires

AD Lalonde, MG Norton, Washington State University, Pullman, Washington

Novel Electrochemical Process for Treatment of Perchlorate

G Liu, Pacific Northwest National Laboratory, Richland, Washington

The Study of Atomic Gold Clusters in Polyaniline

AH Saheb, M Josowicz, JA Janata, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

Surface Characterization of Ambient Ultrafine Particles

EL Bullock, AM Johansen, C Thomas-Bradley, Central Washington University, Ellensburg, Washington

Stability of H Species in Various Dielectric Films used in Advanced Microelectronic Fabrication

YR Kuan, Texas Instruments Incorporated, Dallas, Texas

Routine SEM Analysis of Lysed *Bacillus* Spores

CL Warner, CJ Bruckner-Lea, Pacific Northwest National Laboratory, Richland, Washington

B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

Microscopy of Hanford Tank Sludge

EC Buck, Pacific Northwest National Laboratory, Richland, Washington

Electron Microscopy Investigation of Bacterial Outer Membrane Vesicles

MJ Kuehn, Duke University, Durham, North Carolina

Surface Area and Porosity Analyses of Mesoporous Thin Films and Powders

RD Champion, S Li, AR Courtney, Pacific Northwest National Laboratory, Richland, Washington

SEM Investigation of Thermal Barrier Coatings and ODS Alloys

GJ Grant, Pacific Northwest National Laboratory, Richland, Washington

B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

TEM Study on SOFC Interconnects

Z Yang, Pacific Northwest National Laboratory, Richland, Washington

An Experimental and Data Analysis Investigation into the Trapped Gases and Non-ice Material in the Surfaces of the Outer Planets Icy Satellites

CA Hibbitts, Johns Hopkins University, Laurel, Maryland

Physical Characterization of Defects in ZnO Diluted Magnetic Semiconductors

KR Kittilstved, DR Gamelin, University of Washington, Seattle, Washington

Investigation of Oxygen Diffusion in Single Crystal STO Films Grown on Si

ZJ Yu, Freescale Semiconductor Inc., Tempe, Maryland

Characterization of Mesoporous SiO_2 Particles for the Characterization of Non-ideal Sorption Behavior

DR Yonge, DL Washington, Washington State University, Pullman, Washington

Electrochemical Sensors and Biosensors for Environmental and Health Monitoring

J Xu, Nanjing University, Nanjing, China

Electrochemical Detection of Lead in Saliva

W Yantasee, A Cinson, D Choi, Pacific Northwest National Laboratory, Richland, Washington

Kn Hongsirikarn, Tn Sangvanich, K Pattamakomsan, Chulalongkorn University, Bangkok, Thailand

Molecular Beam Epitaxy Growth of Strontium Cobaltite

AJ Anderson, South Dakota School of Mines and Technology, Rapid City, South Dakota

Trace Metal Composition of Cobalt

JB Cliff, Pacific Northwest National Laboratory, Richland, Washington

A Combinatorial Sputtering Approach to Magnetic Properties Modification of FeCoB

DP Pappas, National Institute of Standards and Technology, Boulder, Colorado

RR Owings, Applied Materials, Boise, Idaho

Controlling the Thermal and Non-Thermal Reactivities of Metal Oxide Structures Through Nanoscaling - Controlling Reactivities of Metal Oxide Structures

MA Henderson, KM Rosso, NI Iordanova, SA Chambers, M Dupuis, AG Joly, JE Jaffe, G Xiong, Rn Shao, Pacific Northwest National Laboratory, Richland, Washington

IV Lyubinetsky, KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

MS Gutowski, Heriot-Watt University, Edinburgh, United Kingdom

X-ray Photoelectron Diffraction of MgO(111)-(1x1)

RA Plass, Sandia National Laboratory, Milwaukee, Wisconsin

M Gajdardziska-Josifovska, University of Wisconsin, Milwaukee, Milwaukee, Wisconsin

Electrochemical and TEM Characterization of Metal Nanoparticles Deposited in Carbon Nanotubes

CM Wai, Y Lin, University of Idaho, Moscow, Idaho

Chemical Characterization of Sub-micrometer Mineral Phases in Extraterrestrial Materials that have Previously been Characterized by NanoSIMS Isotope Imaging

FJ Stadermann, C Floss, Washington University in St. Louis, St. Louis, Missouri

T Yada, Institute of Astronomy and Astrophysics, Academia Sinica, Taipei, Taiwan, Province Of China

Chemically-selective Sensor Film Characterization

Z Wang, Pacific Northwest National Laboratory, Richland, Washington

WR Heineman, N Pantelic, University of Cincinnati, Cincinnati, Ohio

Advanced Electrode Concepts for CdZnTe Radiation Detectors

CE Seifert, G Dunham, Pacific Northwest National Laboratory, Richland, Washington

Advanced Electrode Concepts for CdZnTe Radiation Detectors

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MH Engelhard, Environmental Molecular Sciences Laboratory, Richland, Washington

Energetic Ion Studies of Key Future Technological Materials

MI Laitinen, University of Jyvaskyla, Jyvaskyla, Finland

HJ Whitlow, V Touboltsev, University of Jyväskylä, Jyväskylä, Finland

Investigation of the Surface Characteristics of Chemically Modified Natural Fibers

LS Fifield, JD Holbery, Pacific Northwest National Laboratory, Richland, Washington

X-ray Powder Diffraction Study of Fe_2O_3-Mn_2O_3 Phase Diagram

JV Crum, Pacific Northwest National Laboratory, Richland, Washington

Mesopore Uniformity and Hydrothermal Stability of Silica Thin Films for High Permeabilty Applications

RE Williford, Pacific Northwest National Laboratory, Richland, Washington

Stability of Ceria and Other Nanoparticles

Sn Kuchibhatla, S Seal, D Bera, University of Central Florida, Orlando, Florida

KH Pecher, Pacific Northwest National Laboratory, Richland, Washington

DR Baer, Environmental Molecular Sciences Laboratory, Richland, Washington

Nano-porous TiO_2 Ceramics

A Bandyopadhyay, Washington State University, Pullman, Washington

Novel Micro-manipulation Methods for Radioactive Particle Isolation and Characterization with Energy-filtered Electron Microscopy

EC Buck, BK McNamara, Pacific Northwest National Laboratory, Richland, Washington

A Dohnalkova, Environmental Molecular Sciences Laboratory, Richland, Washington

SEM/EDS of Solid Oxide Fuel Cell Seal Materials

JS Vetrano, Pacific Northwest National Laboratory, Richland, Washington

B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

Thermogravimetric Analysis of Organometallic Compounds and Semiconductor/Metal Nanoparticles

MG Warner, Pacific Northwest National Laboratory, Richland, Washington

XPS Studies of Self-Assembling Monolayers

BJ Tarasevich, Pacific Northwest National Laboratory, Richland, Washington

Understanding the Properties of Oxide and Metal Nanostructures

S Sivarajah, K Ahilan, University of Jaffna, Jaffna, Sri Lanka

Electroactive Materials for Anion Separation -- Technetium from Nitrate

TL Hubler, SD Rassat, Pacific Northwest National Laboratory, Richland, Washington

Spectroelectrochemical Sensor for Technetium Applicable to the Vadose Zone (PNNL Scope # 30948 Bryan/Hubler EMSP)

AS Del Negro, TL Hubler, SA Bryan, Z Wang, Pacific Northwest National Laboratory, Richland, Washington

WR Heineman, CJ Seliskar, University of Cincinnati, Cincinnati, Ohio

Surface Migration of Additives in Polymers

LA Archer, VS Minnikanti, Cornell University, Ithaca, New York

Characterization of Functional Nanoscale Materials for Vapor Sensing

SP Garland, University of California, Davis, Redding, California

CL Aardahl, RS Addleman, LS Fifield, F Zheng, DL Baldwin, On Reid, Pacific Northwest National Laboratory, Richland, Washington

B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

Oxidation State of Technetium Electrodeposited on Platinum

MD Engelmann, Pacific Northwest National Laboratory, Richland, Washington

AR Coatings

WD Bennett, DC Stewart, CC Bonham, DW Matson, Pacific Northwest National Laboratory, Richland, Washington

Characterization of Oxide Nanoparticles

L Wang, Pacific Northwest National Laboratory, Richland, Washington

XPS Study of CeO_2 and $CeZrO_2$

L Wang, Pacific Northwest National Laboratory, Richland, Washington

S Azad, UCAR Carbon Company Inc., Parma, Ohio

Novel Biosensor Based on Nanomaterials

G Liu, Y Lin, Pacific Northwest National Laboratory, Richland, Washington

B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

Surface Analysis of Functional Carbons

Y Shin, Pacific Northwest National Laboratory, Richland, Washington

Ion-Beam Synthesis of Materials for Hydrogen Storage

W Jiang, Pacific Northwest National Laboratory, Richland, Washington

***In situ* FTIR Studies of Alumina in a Hydrogen Environment: a Study of Hydrogen Chemistry within Ceramics**

AC Stowe, RH Jones, CH Henager, J Szanyi, Pacific Northwest National Laboratory, Richland, Washington

Steam Reforming of Bio-mass

H Roh, Pacific Northwest National Laboratory, Richland, Washington

Homogeneous Precipitation of Cerium Dioxide Nanoparticles

C Tseng, Oregon State University, Corvallis, Oregon

EC Buck, Pacific Northwest National Laboratory, Richland, Washington

Nanocrystalline MoS_2 Catalysts

WJ Shaw, J Franz, Pacific Northwest National Laboratory, Richland, Washington

Determination of Nanoporous Material Oxidation States

DM Wellman, AJ Karkamkar, Zn Hontz, En Richards, Pacific Northwest National Laboratory, Richland, Washington

Characterization of Pure and Doped ZnO Nanoclusters

J Antony, Y Qiang, University of Idaho, Moscow, Idaho

Z Wang, Pacific Northwest National Laboratory, Richland, Washington

Study of Some Specific Inclusions in a Garnet Matrix Using High Resolution Transmission Electron Microscopy (HRTEM)

MJ Guinel, MG Norton, Washington State University, Pullman, Washington

TOF-SIMS and Auger Studies of Ozone Oxidation of Unsaturated Self Assembled Monolayers on Silicon Surfaces

BJ Finlayson-Pitts, TM McIntire, University of California, Irvine, Irvine, California

PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

Preparation, Characterization and Application of Chemical Modified Electrodes

X Cui, Fudan University, Shanghai, China

XPS Analysis of Fabric Chars to Determine the Phosphorous - Nitrogen Synergism in Flame Retardants

S Gaan, S Gang, University of California, Davis, Davis, California

Image Iron Oxide Nanoparticles

GR Holtom, Environmental Molecular Sciences Laboratory, Richland, Washington

Stabilization of Polar Oxide Interfaces: Integrated Experimental and Theoretical Studies of Atomic Structure and Electronic Properties

S Cheung, Pacific Northwest National Laboratory, Richland, Washington

M Gajdardziska-Josifovska, University of Wisconsin, Milwaukee, Milwaukee, Wisconsin

Ion Beam Characterization of Nanocomposite Tribological Coatings

RJ Smith, PE Gannon, Montana State University, Bozeman, Montana

Surface Texture of Zircon Grains from the Sierra Madera Impact Structure, West Texas

SA Huson, MC Pope, Washington State University, Pullman, Washington

Thrust 4: Model Hematite Thin Films and Bacterial Iron Reduction

TC Droubay, Z Wang, L Shi, BH Lower, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

Characterization of Manganese Cobalt Oxides Using XPS

G Xia, Pacific Northwest National Laboratory, Richland, Washington

Molecularly Organized Nanostructural Materials

Y Shin, Gn Exarhos, CF Windisch, AR Teodoro-Dier, Pacific Northwest National Laboratory, Richland, Washington

B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

Measurements of Aerosol Composition by Aircraft during the 2005 Marine Stratus Experiment

PH Daum, Brookhaven National Laboratory, Upton, New York

Nuclear Reaction Analysis of Biotite Minerals

CV Ramana, En Essene, University of Michigan, Ann Arbor, Michigan

Determination of Cause of Bloating in Ti Pellets

NL Canfield

Pacific Northwest National Laboratory, Richland, Washington

Preparation of ZnO Thin Films by MOCVD

KR Kittilstved, DR Gamelin, University of Washington, Seattle, Washington

Investigation of Structural Properties of Oxide and Nitride Nanowires

MC Johnson, Lawrence Berkeley National Laboratory, University of California, Berkeley, Berkeley, California

Characterization of GaN/InGaN/GaN Thin Film Structures

F Ohuchi, E Venkatasubramanian, K Poochinda, University of Washington, Seattle, Washington

Compositionally Graded Co and Cr Doped TiO_2 Rutile for Optimum Thermoelectric Power

L Saraf, V Shutthanandan, Environmental Molecular Sciences Laboratory, Richland, Washington

A Yamamoto, AIST, Ibaraki, Japan

F Ohuchi, S Iwanaga, University of Washington, Seattle, Washington

Electron Microscopy of Single-walled Carbon Nanotubes during Growth on CoMo Bimetallic Catalysts

N Sakulchaicharoen, DE Resasco, University of Oklahoma, Norman, Oklahoma

Aerosol Sampling

PC Gray, Los Alamos National Laboratory, los alamos, New Mexico

Catalytic Ammonia Oxidation

GE Fryxell, Pacific Northwest National Laboratory, Richland, Washington

Structural Analysis of Kinetically Stabilized Core-Shell Nanoparticles

B Eichhorn, University of Maryland, College Park, Maryland

Analysis of Nanoparticulates

EW Hoppe, Pacific Northwest National Laboratory, Richland, Washington

SEM Analysis of Rotating Drum Impactor Filter Strips for Biological Species

ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

Adhesion of Polymer Sphere to Modified Natural Fiber via AFM

JD Holbery, Pacific Northwest National Laboratory, Richland, Washington

Collaborative Water Initiative Project on Stabilization of Water Treatment Residuals

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Systematical Study of Novel Nano-magnetic Materials

D Li, Y Liu, X Wang, Alfred University, Alfred, New York

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Functionally Graded Brake Materials

EV Stephens, Pacific Northwest National Laboratory, Richland, Washington

Determination P-dopant Concentration in Wide Band Gap SnO_2 Semiconductor, using RBS technique

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Fabrication of Microconduits

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Low Temperature Si Device Fabrication

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The Microstructural Influence on Fatigue Crack Growth in Rene 88DT

E Sackmann, KO Findley, Washington State University, Pullman, Washington

Characterizing Size, Morphology, and Mechanical Properties of Superalloy Carbides

J Hutchinson, KO Findley, JD Yeager, Washington State University, Pullman, Washington

Analysis of the Composition of Cu Films

R Johnson, DP Field, Washington State University, Pullman, Washington

Design and Synthesis of Tailored Band-Gap SiGe(C) Detectors

CH Henager, Pacific Northwest National Laboratory, Richland, Washington

M Elfman, Lund Institute of Technology, Lund, Sweden

Depth Profiles of Isotopic Oxygen in Cerium Oxide Catalysts

DA Berry, National Energy Technology - Laboratory, Morgantown, West Virginia

Surface Characterization of Granular Iron from Cores of an In Situ Permeable Reactive Barrier

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PIXE Elements Analysis of Carbon Nanosheets

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Norovirus TEM Proposal, Straub

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Rhenium and Technetium Uptake by Iron-Based Materials

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Friction stir processing TiB_2 into the Surface of Class 40 Grey Cast Iron to Improve the Wear Resistance

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GJ Grant, Pacific Northwest National Laboratory, Richland, Washington

Profilometry Studies of Printed Electrode Films for Fuel Cell Applications

CF Windisch, Pacific Northwest National Laboratory, Richland, Washington

Cost Effective Ultra-thin Palladium Based Membrane for Hydrogen Separation and Purification

Y Peng, Innovatek, Inc., Richland, Washington

High Resolution TEM Images and Electron Diffractions for Gold Nanotubes/Nanorods and Metal Vanadate Nanotubes/Nanorods

Y Wang, G Cao, University of Washington, Seattle, Washington

Nickel Coating of Polymer Microbeads

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Electron Microscopy Imaging of Cyanobacteria *Synechcystis sp*

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Electron Energy Loss in Radiation Detection

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Electron Microscopy of Novel Metal-Transforming Bacteria from Extreme Environments

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Characterization of Tungsten Carbide Synthesized by Controlled Template Method

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Investigation Cellulose Phase Change and Interaction with Other Molecules by DSC

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Determination of the Silica Polymorphs Thermally Grown on Silicon Carbide as a Function of Temperature and Time using X-ray Photoelectron Spectroscopy (XPS)

MJ Guinel, MG Norton, Washington State University, Pullman, Washington

Study of the Ferromagnetic Activation in ZnO Diluted Magnetic Semiconductors

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Transient Kinetics Experiments for Studying Catalytic Reactions for H_2 Production

Y Yang, RS Disselkamp, Pacific Northwest National Laboratory, Richland, Washington

CT Campbell, RJ Chimentao, L Cameron, IM Jensen, University of Washington, Seattle, Washington

Scanning Electron Microscopy of *Corynebacterium glutamicum*

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Ecophysiological Investigation of Cyanobacteria using Controlled Cultivation

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Optical Properties of Ag Nanoparticles Embedded in Polymer Matrices

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Controlling Field Emission from HV Structures

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Structural Characterization of Complex Electrodes

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Characterization of Oxide Based Diodes

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SEM-EDS Elemental Mapping of Weymouth Soils

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Segregation on Annealed R-Cut Sapphire Surfaces

SB Rivers, RJ Lad, University of Maine, Orono, Maine

Nanoengineered Electrochemical Sensor for Mixed Wastes

J Wang, Pacific Northwest National Laboratory, Richland, Washington

Structure of the *Shewanella* Cell Surface

AL Neal, University of Georgia, Aiken, South Carolina

Epitaxial Growth and Properties of Candidate Diluted Magnetic Oxide Semiconductors - Chemistry and Physics of Ceramic Surfaces

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Evaporative Co-deposition of Fluoride Materials

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Microscopic Analysis of Carbon-based Nanomaterials

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Measurement of Band Gap, Band Offset, and Thickness for Ultra-thin SiO_2, SiON and High-k Films on Si

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High-resolution Ion Scattering Studies of Nano-scale Oxide Films and Thermal Stability of Oxide-semiconductor Interfaces

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Evaluation of SIMS for Location of Bacterial Spores and to Source Growth Media and Geographic Location

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Test Mass Characterization for Precision Gravitational Tests

CD Hoyle, TS Cook, EG Adelberger, University of Washington, Seattle, Washington

Synthesis of Sub-micron Cuprous Oxide Films on a Silicon Nitride Membrane for Study using Time-resolved X-ray Techniques

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Investigation of Electron Emission from Nano-structures

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Molecular Beam Scattering Measurements on Anatase $TiO_2(001)$ and Rutile $TiO_2(110)$

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Fabrication of Si Templates for the Construction of Monolithic Multi-Electrospray Emitters

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Olefins by High-Intensity Oxidation

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Hydrogen Production

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Integrated Automated Analyzer for Groundwater Monitoring

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Klin Phosphoric Acid Process

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Mechanisms of Sulfur Poisoning of NOx Adsorber Materials

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Microstructural Examination of SOFC Materials Development

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Trace Impurities in Graphite Crucible used for Advanced Detector Materials Synthesis

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High Resolution TEM Analysis of $CuInS_2$ Nanoparticles and XRD analysis of $CuInS_2$ Thin Films

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Site Specific Valence Above and Below the Verwey Transition in Magnetite

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X-ray Analysis of Quantum Well Films

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TGA Analysis of Synthesized Organic Components of Self-assembled Monolayers on Mesoporous Silica

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The Use of FESEM

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Ion Beam Modification of Advanced Titanium Alloys

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Center of Excellence for Chemical Hydrogen Storage

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Technetium (Tc) Reduction by Chemically and Biologically Reduced Smectite Clay

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Applications of Nanostructured Materials and Electrodes in Electrochemical Sensors and Fuel Cell

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Computational and Experimental Nanoparticle Dosimetry for Nanomaterial Safety

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Micro-fabrication of Miniaturized Solid Oxide Fuel Cell (SOFC) on Silicon Chip

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Development of Wet Chemical Etching Methods to Create Chalcogenide Glass Film Structures

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Trace Signatures in Particles

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High Surface Area Nanocrystalline SiC Material Analysis

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Characterization of Microstructure and Composition of Magnetostrictive Nanobars for Bio-sensor Application

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Fundamental Investigations of Heterogeneous Catalysis Using Isotopic Transient Kinetic Analysis -(Scope 90001)

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Surface-Modified Iron Oxide Nanoparticle Characterization by Transmission Electron Microscopy

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Development of a Catalyst for the Steam Reformation of JP-10

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Spectroscopic Study of the Bioactivity of Nanoparticles by Exposure to Human Lung Cells

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X-ray Photoelectron Spectroscopy and Expert Consulting on Thermal Stabilization of Multi-component Inorganic Oxide Materials

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Examine the Compositions of the Black Sands in Northern Oregon

JS Young, David Heil Associates Corporation, Portland, Oregon

Equilibrium-induced Decomposition of Nitrates on a NOx Storage/Reduction Catalyst

WS Epling, University of Waterloo, Waterloo, Ontario, Canada

X-ray Photoemission Study of Graphite

S Azad, UCAR Carbon Company Inc., Parma, Ohio

The *in vivo* Localization and Interactions between Structural Components of the *Shewanella oneidensis* MR-1 Metal Reducing System by High Resolution Transmission Electron Microscopy

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The Biogeochemical Mechanisms Controlling Reduced Radionuclide Particle Formation Properties and Stability

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Radionuclide Reduction by *Anaeromyxabacter dehalogenans*

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Chromium Diffusion Kinetics in Nano-ceria and Doped Ceria Coatings: An UCF-PNNL Collaboration

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Spectroscopic and Microscopic Characterization of Graphite

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Non-destructive SEM-based Analysis of Complex Functional Structures in Insects: Development of Tools for Rapid Species Diagnosis in Tropical Biodiversity Surveys

NO Pellmyr, University of Idaho, Moscow, Idaho

High-resolution Interfacial Studies of Nano-scale Oxide Films

S Ramanathan, Harvard University, Cambridge, Massachusetts

Effects of Temperature and Time (130 Years) on Surface Charges and Chemical Properties of Black Carbon

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Molecular Beam Scattering Measurements on Anatase TiO_2(001) and Rutile TiO_2(110)

U Burghaus, North Dakota State University, Fargo, North Dakota

Characterization of Novel DNA/Semiconductor Nanoconjugates

F Zhou, Dn Jiang, California State University, Los Angeles, Los Angeles, California

Fundamental Investigations of Heterogeneous Catalysis Using Isotopic Transient Kinetic Analysis

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Characterization of High Surface Area Tungsten Carbide Synthesized by Templated Synthesis Methods Electrocalytic Applications

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Post Growth Analysis of Compositionally Graded InGaN Grown with MOCVD

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Compositionally Graded V_2O_5 for Improved Thermoelectric Power

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Novel Catalytic Materials for the Hydrodesulfurization and Water-Gas Shift Processes

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Amorphous Semiconductor Analysis using Ion Beam Tools

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Fundamental Studies of Nitrogen Oxide Surface Chemistry: A Model System Approach

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Post Growth Analysis of GaN and InGaN Grown with MOCVD

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Hydrogen Materials Compatibility Studies

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Model Oxide Defects with Vicinally Stepped NiO(100) Substrates

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MBE Growth and Properties of Model TiO_2 Surfaces for Fundamental Studies of Heterogeneous Photocatalysis

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MBE Growth and Properties of N-doped TiO_2 for Enhanced Visible Light Absorption and Water Splitting

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Epitaxial Growth and Properties of Magnetically Doped ZnO Prepared by Pulsed Laser Deposition of Nanoparticle Targets

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Real-time FTIR Measurements of Fe-oxide Transformation in Presence of Dissimilatory Fe-reducing Bacteria

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Visualization of a Pd-Au{100} Catalyst: a Scanning Tunneling Microscopy Study

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Directed Self-assembly of Metal Oxide Island Nanostructures

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Structure-Property Relationships in Thin Film Energy Conversion Materials and Coatings

DW Matson, PE Burrows, LC Olsen, PM Martin, ME Gross, WD Bennett, CC Bonham, G Graff, ES Mast, SN Kundu, AB Padmaperuma, LS Sapochak, Pacific Northwest National Laboratory, Richland, Washington

Nerve Agent Detection Using Enzyme-Coated Nanowires

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Elemental Characterization of Ionizer Filaments for Thermal Ionization Mass Spectrometry (TIMS)

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Molecular-level Understanding of Transport and Optic Properties of Doped Oxide Nanoclusters

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Molecular Level Construction of Functional Surfaces

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Selective Heterogeneous Catalysis

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Early Transition Metal Oxides as Catalysts: Crossing Scales from Clusters to Single Crystals to Functioning Materials

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NOx Adsorber Materials: Fundamental Studies, and Investigations of Sulfur Poisoning and Thermal Deactivation

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Metal-induced Crystallization via Sputtering Deposition on Flexible Substrates and its Applications

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Development of Room Temperature Ferromagnetism in Wide-band-gap Oxide Semiconductor Nanostructures

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Chemistry of Outer Solar System Materials

TB McCord, GB Hansen, University of Washington, Seattle, Washington

An Experimental and Data Analysis Investigation into the Trapped Gases and Non-ice Material in the Surfaces of the Outer Planets Icy Satellites and Our Moon

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Crystal Perfection in Cadmium Zinc Telluride Radiation Detectors

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Photochemical Studies on N-doped TiO_2 Single Crystals - Fundamental Investigations of Water Splitting on Model TiO_2

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Biomineralology and Ultrastructure of Neutrophilic Iron-oxidizing Bacteria

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Study of Thermal Decomposition of Polyester Fibers Treated with Phosphorus Flame Retardants

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Enhanced Ionic Conductivity of Samaria Doped Ceria Thin Films through Tailoring the Dopant Concentration and Microstructures

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Cryo-EM Investigations of Interfacial Bacterial Extracellular Polymeric Substance (EPS) in Vanadium Interactions

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The Role of PdZn Alloy Formation and Particle Size on the Selectivity for Steam Reforming of Methanol

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Characterization of Chemistry and Physics at Metal-Polythiophene and Metal-Carbon Interfaces

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Model System Surface Science Approach to Study Photochemistry at Adsorbate-substrate Interfaces: The Trimethyl Acetate, Silver, Titania System

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Bone Growth on Tailored Biomimetic Surfaces

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Defects and Defect Processes in Ceramics

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Catalytic and Optical Properties of Surface Attached and Matrix Embedded Quantum Dots

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Electron Energy Loss in Radiation Detection Materials

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Thin Film Electrolyte/Electrode Development and Enhanced Ionic Transport in Miniaturized Solid Oxide Fuel Cells on Silicon Chips

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Surface and Bulk Characterization of Ambient Ultrafine Particles

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Surface Characterization of Calcium Phosphates

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Mixed Oxide Films for Gas Sensing and Photo-catalytic Applications

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Spin Electronic Phenomena in Magnetically Doped Perovskites and Complex Oxide Interfaces

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Materials for Automotive Sensor Development

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Toward Preparation and Operando Characterization of Nanostructured Heterogeneous Photocatalysts

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Near Real-time Alkene Sensor for Atmospheric Aerosol Chemistry Monitoring

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Design of Micro-cantilever Actuators for Measuring Surface Tension of Sub Microliter Volumes Applied Towards Monitoring Interfacial Processes

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Characterization of Mixed Monolayers with X-ray Photoelectron Spectroscopy (XPS)

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The Thickness Measurement of Electrolyte Cast on Mylar Film

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Thin Film X-ray Diffraction Studies of Calcium Phosphate Films and XPS Studies of Self-Assembling Monolayers

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Reforming of Hydrocarbons on Solid Oxide Fuel Cell Anodes

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Structural and Chemical Properties of Catalysts

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Characterizations of NiAu Bimetallic Butane Steam Reforming Catalyst

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Structure and Composition of Electrochemically Active Mixed Metal Oxides

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Response of Radiation Detector Materials to Ions

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Low Angle X-ray Characterization of Catalyst Porosity

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Mechanisms of Environment-Assisted Degradation in Reactor Materials

JS Vetrano, S Bruemmer, Pacific Northwest National Laboratory, Richland, Washington

Gold Hollow Nanostructures: Synthesis and Optical Properties

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Characterization of Metal Nanoparticles for Optimization of Process Parameters to Support Synthesis of Well-defined Carbon Nanotubes

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Cellular Internalization Studies of Semiconductor Nanoparticles in Bacteria

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Understanding Particle Generation and the Risk of Occupational Exposure and Environmental Release of Nanoparticles During Processing of Nanocomposite Materials

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Evaluation of Multicomponent Porous Oxide Films

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Spectroscopy and Microscopy of Doped TiO_2 Nanocrystalline Materials

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Investigation of Oxidation State of Elements in Natural Brannerites

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Nondestructive Carbon Nanotube Modification of Tailored Functionality

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Investigating Electrochemical Properties, Composition and Oxidation States of Nanoparticles and Catalysts Using Electrochemistry and XPS

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Use of EMSL Scanning Microscopy Capabilities to Study Soil Mineral Weathering

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SEM of Life Stages of Gall Wasps of the Family *Cynipidae*

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SEM Image Acquisition, X-ray Elemental Analysis

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Reaction Specificity of Nanoparticles in Solution

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Experimental and Theoretical Studies of Reaction Pathways for the Breakdown of Chlorinated Hydrocarbon Molecules by Metal and Metal Oxide Nanoparticles

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Experimental Measurements of the Band Offsets of Epitaxial Silicon on $LaAlO_3$ Single Crystals

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Using Ni-ion Irradiation for the Development of Advanced Materials for the Next Generation Nuclear Reactor

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Characterization of Mn Oxidation State with Electron Energy Loss Spectroscopy

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Characterization and Method Development for Back-end of the Line Wafer Processing Concepts

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Oxidation Studies of Coatings for Interconnect Plates in Solid Oxide Fuel Cells

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Metallurgical Characterization of Coatings Deposited by Electrospark Deposition

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Solid Phase Transformations in the Hanford Sediments Treated with Al-rich, Hyperalkaline and Saline Solutions

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Immobilized Enzymes for Bioremediation and Biosensing - Armored Enzyme Nanoparticles for Remediation of Subsurface Contaminants

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Immobilized Enzymes for Bioremediation and Biosensing

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Environmental Scanning Electron Microscopic Analysis of Gas Hydrate and Hydrate-Bearing Sediments

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SEM on Electrode Surface/Electrode Preparation and Testing

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The Measurements for Nano-tip'ID

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Modified Carbon Supports for Aqueous Phase Catalysis--Applications for the Conversion of Glucose and Fermentation Products to Value-Added Chemicals

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SEM and SIMS Analysis of Organic Semiconductor Films Grown using Liquid Crystal Solvents

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Characterization of Heat Treated Silicon Carbide Specimens using Scanning Electron Microscopy

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High-resolution Transmission Electron Microscopic Evidences of Stacking Faults in Zeolitic Minerals Formed in Hanford Sediments Reacted with Simulated Tank Waste Solutions

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On-Line Determination of Selected Vapor-Phase Hoffmann List Compounds by PTR-MS

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DC-1 Molecular & Bio Imprinting

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Silicon Carbide Nanowires and Nanospings: Processing, Self-assembly, Characterization, and Properties

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2-D Photonic Crystals Grown by Atomic Layer Deposition for Near IR and Visible Optoelectronics Applications

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Mechanisms of Sulfur Poisoning of NOx Adsorber Materials

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Ion-Solid Interactions in Ceramics

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Monolayer Protected Gold Nanoparticle Investigation and Characterization

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Synthesis and Characterization of Novel Nanocrystalline Oxide Film Structures

Interface Controlled, Self-Assembled Oxide Quantum

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TEM Study of Carbon Nanotube Reinforced Polymer-Derived Ceramic Composites

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PTR-MS Characterization of Carbon Nanotube Preconcentrators for Trace Chemical Signature Detection

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Characterization of Noble Metal Catalysts for Hydrogen Production and Purification in Fuel Cell Applications

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Characterization Polymer Thin Films and Arrays

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Field Effect Studies of CoxTi1-xO_2 Thin Films

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Elemental Analysis of Bulk Aerosol Samples Collected with Drum Impactor during MCMA 2003 Field Study

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Continuous Isosorbide Production

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New Technologies for Reduction of Automobile Exhaust Emissions

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Bioavailability of Arsenic in Dislodgeable Residue from Pressure-Treated Wood

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XPS Characterization of Diesel Soot Materials

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Characterization of Regenerable CO_2 Sorbents

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Europium Uptake in Various SAM Coated Mesoporous Silica

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TEM and XPS Analysis of Ligand-functionalized Semiconductor Quantum Dots used in Biodetection Studies

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Phenotypic Characterization of TCE and PCE Degrading *Dehalococcoides*

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Investigation of Strain in InGaN MQW Structures

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Oxidation of Lead Sulfide Surfaces in the Presence of Phosphate: Nanoparticle Formation

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TEM and SEM Investigation of Non-pathogenic Bacterial Cultures

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Observations of Scytonema-colonized and Non-colonized Fiber Cement Roofing Shingles

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Magnetic and Transport Studies of Co Doped TiO_2 Thin Films

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Composition Characterization of ZnO:Cr and ZnO:Co

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MBE Growth of Epitaxial Anatase TiO_2 (001) on STO(001) on Si(001) and Characterization of TiO_2 Films

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Fabrication and Characterization of Functional Nanostructured Materials

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Synthesis and Characterization at Atomic Level of Novel Nanocrystalline Metal Oxide Structures

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Surface Analysis of Metal Carbides

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Analysis of Catalysts and Microchannel Components

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STM Tip Analysis by TEM

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Sulfur Absorbents for Emission Control

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Development of a Soldier-Portable Power System

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Characterization of Surface and Materials

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SEM Characterization of Proposed Hydrogen Storage Materials

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XPS Analysis of Fuel Cell Components

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Investigation of Elemental Contamination in Solid Oxide Fuel Cell Materials

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Investigation of the Stability of Secondary Precipitates Incorporated with Contaminants

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Analysis of Catalysts

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Chalcogenide Surface Science

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Hydrogenation of Pyrolysis Oils to Create Gasoline

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Characterization of Lithium Aluminate Powders

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Deposition of Metal-Doped Oxides for Spintronic Applications

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Study of Compositional Variations in Combinatorially-sputtered Transparent Conductive Oxides

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Probing Cation Disordering in $Gd_2Ti_2O_7$ Pyrochlore by X-ray Photoelectron Spectroscopy

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In situ XPS Measurements of Reforming Catalysts

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Studies of Corrosion of Materials by Lead Alloys for Advanced Reactor and Nuclear Waste Amelioration Applications

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Influence of Gd and Sm Doping on Atomic and Ionic Transport Properties of Novel Nanostructured Ceria-Zirconia Multilayers

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Fundamental Studies of Oxygen Storage Materials

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Fundamental Studies of NOx Adsorber Materials

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Early Transition Metal Oxides as Catalysts: Crossing Scales from Clusters to Single Crystals to Functioning Materials - Catalysis Science

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Nanotemplated Electrodeposition

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Conductivity of Functionalized Carbon Nanotube Films

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Irradiation Induced 3-D Ordered Arrays of Nanostructure

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Nanoengineered Electrochemical Sensors for Mixed Wastes

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Develop Stable Bipolar Membranes

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Characterization of Sputter Deposited Co Doped TiO_2 Films

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Hydrogen Storage of Chemical Hydrides

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Crystallization Behavior of Bulk Amorphous Alloy

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Structural Characterization of Nanoporous Thin Films

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Measurements of Aerosol and Aerosol Precursors during the Summer 2004 Northeast Aerosol Experiment (NEAX)

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Microcharacterization of Engineered Mono-Sodium Titanate

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Characterization of Nanostructured Ceramics

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X-ray Photoelectron Spectroscopy of Materials for Hydrogen Storage

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Synthesis of Cu_2O under Protein Control

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Deposition of Fuel Cell Materials

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Deposition of Fuel Cell Materials

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Yttrium Phosphate/Gadolinum Phosphate Particles for Cancer Imaging and Treatment

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Microstructural Investigations of Novel Magnetic Oxide Semiconductors

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ATM, ISO and Other Standard and Metrology Measurements for Surface Analysis

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Ion Channeling Studies of Epitaxial Oxide Films and Gas-Solid Interfaces

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Soft Lithography for Optics

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Nanomaterial Toxicology

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Aging of Lean NOX Traps

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Characterization of Cr(III) Solid Phases

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XPS Studies of Coablt Phthalocyanine Thin Films

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Surface Characterization of Calcium Phosphates

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Origin of the Face Dependent Photocatalytic Activity of TiO_2:Probing Surface Chemistry with Molecular Adsorption

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Photochemical Studies on N-doped TiO_2 Single Crystals - Fundamental Investigations of Water Splitting on Model TiO_2 (Mike Henderson's BES Project - 48526)

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Size Selected Gas-phase Soot Aerosol Oxidation

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SEM Image of Microparticles

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Structure and Property Tailoring of Metal Nanoparticles Dispersed in Dielectrics by High Energy Ion Implantation

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New Materials as Sulfur Absorbents

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Surface Analysis of IAQ VOC Sensors

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The Characterization of Aluminum Nitride-silicon Carbide Alloy Crystals on Silicon Carbide Substrates

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Surface State Characterization of Pt/Al_2O_3 Catalyst for the CPO Reaction

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Gas Cell Metalization

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Chemical Analysis of Nano-structures for Toxic Gas Detection

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Synthesis and Characterization of Enzyme Nanoparticles

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Mesopore Uniformity and Hydrothermal Stability of Silica Thin Films for High Permeabilty Applications

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Determination of Pore Structure in Highly Porous Silica Oxide Powders

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Characterization of Corrosion Products on Iron Aluminide Coated Alloys

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XPS Investigations of Transition Metal Doped Oxide Semiconductors

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Molecular Science Computing Facility

The Molecular Science Computing Facility (MSCF) supports a wide range of computational activities in environmental molecular research, from benchmark calculations on small molecules to reliable calculations on large molecules, from solids to simulations of large biomolecules, and from reactive chemical transport modeling to regional cloud climate modeling. MSCF provides an integrated production computing environment with links to external facilities and laboratories within the U.S. Department of Energy (DOE) system, collaborating universities, and industry.

Capabilities

Instrumentation & Capabilities

- **MPP2**. Production cluster of 980 HP rx2600 nodes, 1960 1.5-gigahertz IA64 processors, 450-terabytes local disk, 6.8-terabytes memory, and 11.8-teraflops theoretical peak performance
- **Dtemp**. Shared parallel high-performance filesystem on MPP2, 53 terabytes
- **NWfs**. EMSL long-term data store, 300 terabytes
- **Network**. OC196 (10 GBit/sec) internet connection, 10 Gigabit Ethernet MSCF backbone
- **NWVisus**. Visualization server, SGI Onyx 3400Graphics, 8 processors, 8-GB RAM, two Infinite Reality3 pipes, 144-GB disk, with a PanoramTech 3-screen monitor Digital video editing suite
- **Molecular Science Software Suite**. NWChem, Ecce, GA Tools

MSCF provides computational resources for Computational Grand Challenges in environmental molecular science and basic and applied research areas that address the environmental problems and research needs facing DOE and the nation. Computational grand challenge projects typically involve multiple investigators from universities, national laboratories, and industry working collaboratively as teams. These projects are usually granted computer time allocations for three years. MSCF supported 16 three-year grand challenge projects during 2006. The average annual computer time allocation for grand challenge projects in 2006 was 872,929 central processor unit (CPU) hours, down slightly from the previous year. The decrease is attributed to time allocations for EMSL Science Theme projects.

MSCF also supports smaller, shorter-term projects called MSCF Pilot Projects. Pilot Projects are limited to a maximum of 75,000 processor hours and a one-year duration, with short extensions occasionally granted for project completion. MSCF supported 35 Pilot Projects during 2006, with an average allocation of 70,914 CPU hours. Pilot Projects are typically directed at developing the capability to submit a Computational Grand Challenge proposal in the future (e.g., a combination of theory/method or code development activities, or calculations that provide the initial scientific basis of a Computational Grand Challenge proposal). Pilot Projects are also awarded for computer support of experimental research taking place within other W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL) facilities.

A third category of MSCF computer projects are provided to the Office of Science. In 2006 there were four such projects for a total of 750,000 CPU hours.

A new category of MSCF computer project was initiated in 2006, that of the EMSL Science Themes. These projects center around four science themes and encourage users to allocate time in multiple EMSL facilities. In 2006, there were 10 such projects that were awarded an average allocation of 75,500 CPU hours.

User Computing in MSCF. To optimally address the complex environmental problems facing DOE and the nation and to best use limited staff resources, EMSL follows the recommendation of the EMSL Science Advisory Committee to use a Computational Grand Challenge approach to providing large blocks of resources to the user community. A call for proposals is issued annually, and teams of computational scientists respond with peer-reviewable proposals for system time allocations. Access for the grand challenge teams is granted for periods of one to three years. The following criteria are used when reviewing proposals:

- scientific merit
- appropriateness of the proposed method or approach
- relevance to the environmental problems and research needs of DOE and the nation
- technical competence of the investigators, potential for high visibility journal articles
- reasonableness and appropriateness of the proposed computer resources.

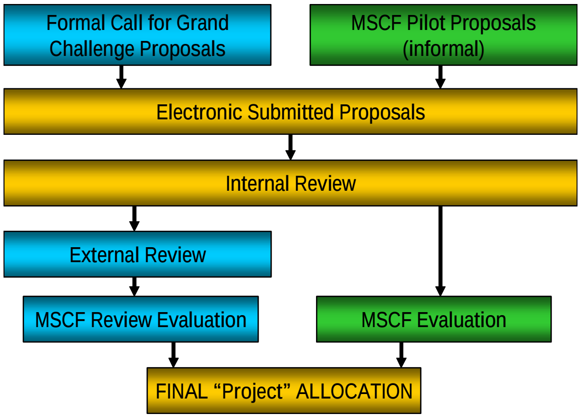

Figure 1. Review process and allocation proposal flow chart.

The process used to review proposals and allocate MSCF computing resources is shown in Figure 1. The request for proposals is open to all researchers, regardless of their institution or source of funding. A call for Computational Grand Challenge applications was made April 1, 2006. The facility received 21 letters-of-intent requesting over 20 million CPU hours. Thirty seven external scientific reviewers from leading universities and research institutions from around the world reviewed the 18 full proposals. Each proposal received three reviews on average and was awarded time according to how well they rated and their allocation request. The average time awarded was 547,000 CPU hours.

MSCF Resources

MSCF provides a combination of production computing hardware and software resources and visualization tools to support the scientific research activities of the Computational Grand Challenge and EMSL Pilot Projects. The hardware and visualization resources are the High-Performance Computing System-2 (MPP2), NWfs, the Graphics and Visualization Laboratory (GVL), and the Molecular Science Software Suite (MS^3). These resources are discussed below.

MPP2. MPP2 provides a balanced supercomputer. Since becoming operational in July 2003 with a theoretical peak performance of 11.8 teraflops, 6.8 terabytes of RAM, and 450 terabytes of disk, the Hewlett-Packard supercomputer (Figure 2) has been tailored to meet the operational needs of EMSL users.

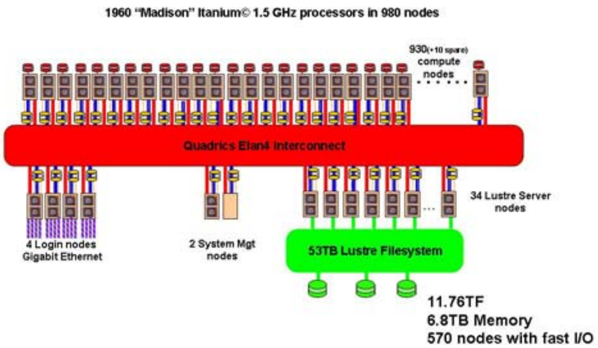

Figure 2. MPP2 Configuration.

NWfs. NWfs, which is the EMSL archive system located in MSCF, uses a groundbreaking approach to disk storage that clusters many low-cost commodity disks to provide fault-tolerant, scalable, long-term storage. Such large-capacity archive systems usually rely on tape for mass storage, but NWfs distinguishes itself by having all its data instantly accessible on disk-based storage. NWfs currently has a capacity of 300 terabytes and the ability to grow as needed to over a petabyte.

GVL. GVL provides production graphics and visualization facilities for the display and analysis of complex datasets from both experiments and simulations. GVL contains four high-performance graphics stations based on Silicon Graphics Incorporated (SGI) technologies with high-speed Gigabit Ethernet connections to the production supercomputers and to NWfs, a digital video system integrated with the workstations to facilitate the display and capture of scientific data, and digital video editing equipment for the preparation of scientific presentations. The video system also is connected to the EMSL auditorium and to the World Wide Web to facilitate internet conferencing. An IBM Scalable Graphics Engine is connected to the MSCF Dell Linux Cluster to provide the highest performance visualization capabilities.

MS^3. Software resources include MS^3, which is a comprehensive, integrated set of tools that enables scientists to understand complex chemical systems at the molecular level. MS^3 couples the power of advanced computational chemistry techniques with existing and rapidly evolving high-performance massively parallel computing systems with extensible problem-solving capabilities. The suite consists of three components: 1) the Northwest Computational Chemistry Software (NWChem), 2) the Extensible Computational Chemistry

Environment (Ecce), and 3) the Global Array Tools (GA Tools). These three components are briefly described below.

- ***NWChem***. Version 5.0 of NWChem was released in September 2006. Documentation and information are available on the NWChem Website (http://www.emsl.pnl.gov/docs/nwchem). NWChem provides many methods for computing the properties of molecular and periodic systems using standard Gaussian and planewave-based quantum mechanical descriptions of the electronic wave function or density. In addition, NWChem can perform classical molecular-dynamics and free-energy simulations. These approaches may be combined to perform mixed quantum-mechanics and molecular-mechanics simulations.

  NWChem is available on almost all high-performance computing platforms, workstations, PCs, and clusters of desktop or workgroup servers. NWChem development provides maximum efficiency on massively parallel processors. Among the new features available in the 5.0 version, the following are worth mentioning:
  - A completely new quantum mechanical/molecular modeling module that interfaces between classical molecular mechanics and quantum mechanical modules
  - Several new response properties of the density functional theory and Hartree-Fock wavefunctions.

- ***Ecce***. Ecce, which is composed of a suite of client/server Unix-based applications, is a domain-encompassing, problem-solving environment for computational chemistry. Applications for setting up, running, and analyzing the results of computational chemistry studies are built on top of a Web-based data management and inter-application messaging server framework. A computational code registration capability supports several underlying chemistry codes and the ability to integrate new ones without reworking core Ecce applications. Running jobs through industry standard remote communications, like secure shell, and a batch queue management system registration capability allows transparent access to high-performance compute resources from users' desktop workstations. A simple installation procedure and extensive online help combine to make Ecce a preeminent user environment for computational chemistry. The current production release of Ecce is version 4.0, released in September 2006. There are six major application components:
  1. Calculation Manager aids in the organization and manipulation of computational chemistry studies. This tool allows an at-a-glance overview of the status of every calculation and easy access to key setup parameters and run statistics.
  2. Molecule Builder is an intuitive point-and-click tool that enables the building, visualization, modification, and manipulation of three-dimensional representations of chemical systems.
  3. Basis Set Tool enables users to select from nearly 300 predefined Gaussian basis sets or the ability to create new ones for use in *ab initio* electronic structure calculations.
  4. Calculation Editor allows the user to choose input options using point-and-click interfaces for different chemistry codes, and then generates the code-specific input.

5. Job Launcher is used for submitting a calculation to a computer for processing. The user may submit a calculation to any computer that has been registered within Ecce and for which the user has an account.
6. Calculation Viewer provides convenient access to current information for a single calculation during execution or after completion. It has many features for viewing and visualizing chemical system properties.

- ***GA Tools***. GA Tools (also known as ParSoft) includes high-performance computing libraries and tools for applied parallel computing focused on inter-processor communications through the aggregate remote memory copy interface, high-performance input/output through the Parallel I/O tools, and programming models for hierarchical memory systems through the Global Arrays and Memory Allocator libraries. The development of these tools is driven by needs of real scientific application codes on the high-end parallel systems. Development of Aggregate Remote Memory Copy has been supported by EMSL operations and by the DOE Center for Programming Models for Scalable Parallel Computing. The most recent version of GA Tools, Version 4.0, was released in April 2006.

MSCF Organization

MSCF is organized into three project groups: 1) the Visualization and User Services Group, 2) the High-Performance Software Development Group, and 3) the Computer Operations Group.

Visualization and User Services Group (VisUS). This group provides an extremely diverse set of services for all users of the MSCF high-performance computers and GVL. Scientists who need access to high-end computing equipment frequently have difficulty getting started. The difficulties encountered range from logging in to getting user codes to run efficiently. VisUS handles user proposal applications, follows user progress during computational projects, manages proposal reviews for both Computational Grand Challenge projects and Pilot Projects, helps with user accounts, provides general consulting support for MSCF software packages, supports and maintains software, manages the GVL, conducts training and user workshops, develops visualization software and high-quality visualizations, and maintains Websites.

The group manages the Computational Grand Challenge and Pilot Project proposal process for the MSCF. This activity includes receiving proposals, providing preliminary review for EMSL missions, assigning external peer reviewers, evaluating peer reviews, granting project allocation, and managing the allocations by using GOLD, a dynamic-reservation-based allocations management system originally developed at PNNL.

Consultants have various roles, including those of administrator, scientific point of contact, tutor, programmer, or research scientist, and field a variety of requests for support. During 2006, five scientific consultants responded to more than 585 e-mail requests, and about 500 additional requests were handled over the telephone or during office visits. Consultants also work directly with MS^3 development teams to give customer feedback and to test functionality.

Information about the use and configuration of the MSCF computational resources is critical to the user base and is provided efficiently to users via the Internet through the MSCF home page. The MSCF Website contains all necessary information about how to establish accounts and get started, and about computer configurations as well as documentation and Web-based tutorials for MS^3. Scientists generate enormous amounts of data either from computational resources or from EMSL instruments. These data are usually complex and difficult to understand. The capabilities and expertise available in the GVL, including its high-performance graphics compute servers and state-of-the-art multimedia equipment, help scientists visualize these complex data. The real-time digital video capture capability from the graphics compute servers allows fast, yet high-quality, video production. Users can generate presentation media in any form—from video (including all international video standards) to Web-based animations. The group also provides basic video production services.

High-Performance Software Development Group. This group has the primary responsibility for developing and supporting MS^3. This effort includes:

- developing high-performance versions of the software and new high-performance algorithms
- continually refreshing the underlying software architecture to stay current with new hardware and software technology and standards
- responding to user requests for additional features
- supporting and maintaining the software
- diagnosing MS^3 problems associated with computer vendor hardware and software
- consulting on specific MS^3 problems
- distributing MS^3 to remote sites
- porting software to new architectures
- conducting training and user workshops.

The MS^3 project group focuses on developing next-generation molecular modeling software for newly evolving computer technologies, especially massively parallel computers. The project group is composed of computational chemists and computer scientists (with external collaborations to mathematicians) who work together to develop the MS^3 software. This software is used by many of the MSCF Grand Challenge projects and has been distributed to almost 1600 sites worldwide. In addition to the development activities, this group is also responsible for training software users, conducting tutorial workshops, and providing user support. Several resources have been developed to facilitate user support and training. These resources include MS^3 Websites with user and reference manuals, download information, release notes, FAQs, a list of known bugs, tutorials, and benchmark information, Web-based context-sensitive help available from within the software, as well as a mailing list where users can post support-related questions and get answers either from experienced users or from the NWChem developers.

Computer Operations Group. This group operates, maintains, and advances the capabilities of the MSCF scientific computing systems. The group is responsible for the operation and implementation of the various production supercomputers in the MSCF and has developed unique system management, monitoring, allocation management, and scheduling capabilities. The primary focus is on providing high-quality, reliable production computing cycles and storage capabilities in the MSCF to support very large parallel calculations for Computational Grand Challenge projects.

Upgrades

In Fiscal Year 2006, the following capability development occurred in the MSCF:

- **NWChem, Version 5.0.** NWChem, Version 5.0 was released in September 2006. Some of the important new capabilities in this release include new and improved high-accuracy methods; a new quantum mechanical/molecular mechanical module with functionality essential for studies of large biological systems and for understanding reaction pathways, kinetics, and equilibriums in complex chemical systems; improved parallelization of plane wave code; and improvements to the molecular dynamics module.

- **Ecce, Version 4.0.** Ecce, Version 4.0 was released in September 2006. In addition to the version 4.0 release, Ecce also had two minor 3.2.x production releases. The minor releases (Ecce 3.2.4 and Ecce 3.2.5) contained updated basis sets, enhancements to molecular orbital visualization and POV-Ray publication quality output, GAMESS-UK (see http://cfs.dl.ac.uk) code registration developed in collaboration with Daresbury Laboratory, and fixes resulting from user feedback. The major new capability in Ecce 4.0 is the end-to-end support for the NWChem molecular dynamics module. User interfaces were developed in tight collaboration with the NWChem developers and represent very close to a full mapping of the options available to NWChem molecular dynamics users who manually create input files.

- **Global Arrays, Version 4.0.** Global Arrays, Version 4.0 was released in April 2006. New features include processor group awareness and support for multilevel parallelism, support for very large arrays, optimized nonblocking one-sided operations and matrix multiply with SRUMMA, and port to the Cray X1 and SGI Altix. The first three features directly affect the capability of NWChem to perform cutting-edge scientific computations, enabling scalability to thousands and possibly tens of thousands of processors, and studies on problem sizes with correlated methods larger than for any other software suite.

- **Gaussian Basis Set Library.** EMSL's Gaussian Basis Set Library was released in September 2006. One of the most widely used databases associated with EMSL (http://www.emsl.pnl.gov/forms/basisform.html), the Gaussian Basis Set Library is a very important chemistry community resource reaching nearly 3000 unique visitors each month, but for the last two years, this database has received very little attention. Through SciDAC-I funding, a much improved version now enables efficient management of the database and underlying programs, provides a greatly improved web interface for browsing and downloading data, and allows basis set developers to directly contribute new data sets to the database. Some EMSL Operations funding was used to make this new resource production ready. This improved capability provides new basis sets for NWChem.

- **2-petabyte tape library**. A new 2-petabyte tape library will be used to make backup copies of MSCF data, particularly those from NWfs and MPP2. The library is expected to have a useful lifetime of at least five years.

- **Raised floor.** Nearly 4,000 square feet of raised floor was added in EMSL's supercomputing operations center, where the next-generation supercomputer will be housed.

- **Data storage capability.** A new method was developed for performing backups of NWfs data. This new capability will substantially decrease recovery time in the event of catastrophic failure of one or more NWfs nodes.

- **Development of a shared spreadsheet for tracking foreign national.** Many limits exist as to how long foreign national accounts can be active. When passports, visas, or work permits expire, so do their holders' computer accounts. Renewing an account requires the same amount of work as the original account. Multiple email messages arrive over the weeks alerting the facility host and Scientific Facility Lead of accounts nearing termination. This new spreadsheet allows the Visualization and User Services Group to track whether to extend an account or allow it to expire and has saved much time by avoiding double, triple and quadruple checking each time an email message arrives.

- **Improvement of scalability and efficiency of several codes.** Visualization and User Services consultants working with software developers, using EMSL's supercomputer, to suggest modifications to their code in order to improve efficiency and scalability.

- **A new script for gleaning CPU time used per project for the GOLD Allocation manager** saves two to four hours per month with increased accuracy. This script creates a file that is used to populate a master spreadsheet developed last fiscal year for monitoring computer use by each of the projects that have time allocated.

- **Video editing and computer visualization upgrade.** Equipment in the GVL has passed useful life and must be replaced to meet current and future needs of EMSL users. This equipment has been delivered and is being set up, with the old equipment excessed.

Future Directions

In Fiscal Year 2007, the MSCF will continue to support researchers by providing state-of-the-art computational resources. All advanced computing systems require continued effort in maintaining the system at peak performance as well as implementing the appropriate software and science knowledge base to effectively and efficiently use the technology. To address these needs, MSCF Operations will continue to operate facility systems, including MPP2 and NWfs. The facility will continue to provide support for computing installations and upgrades, operating systems support, improvements to the quality of the system software to improve the user environment, allocation tracking, direct interfacing with the vendor, system security, and system-level support to users.

The HPCS-3 project to procure and implement the next generation of computational resources will be a primary focus for the Operations team. The project will be compliant with DOE O413.3 (the DOE Critical Decision process).

Planned activities under Molecular Science Computing Facility Operations for Fiscal Year 2007 include:

- **Procurement of HPCS-3**, the next-generation marquee supercomputer for EMSL.
- **Continued operation of facility systems**, especially of MPP2 and NWfs.
- **Expansion of NWfs** disk storage capacity (currently estimated to be 450 additional terabytes).
- **Benchmarking of facility power consumption and efficiency** in order to gain a better understanding of how power is consumed in the facility. This will help facility staff learn to reduce the quantity of power consumed by power distribution and cooling, and to supply more power to systems within existing facility constraints.

In Fiscal Year 2007, MSCF High-Performance Software Development will continue to support users by providing state-of-the-art computational chemistry software. By providing cutting-edge capabilities and a fast time-to-solution, the goal is to increase the number of publications citing NWChem and Ecce to more than 110, with 70 in top-10 journals and 50 in top-5 journals.

Most of the EMSL user proposals using resources of this facility require NWChem. Proposed performance improvements, developments, and support are aligned with the needs of those proposals. Development of new methods and capabilities is essential for the long-term success of NWChem. Without the new methods and software development, NWChem will fall behind in providing solutions to scientists' challenges.

In Fiscal Year 2007, a NWChem Developers Meeting, "NWChem – Future Developments, Science Driven Petascale Computing and Capability Development," will be held. This meeting, featuring leading computational chemists, will lead to a report on the science needs within the DOE Office of Biological and Environmental Research and within the computational chemistry community that will drive new capability and petascale development in NWChem.

- **NWChem core and user support.** Improvements that will be made in Fiscal Year 2007 include:
    - Further improvements in time-to-solution, memory and disk needs, and the handling of even larger problem sizes for high-accuracy methods.
    - Further developments in efficiency and functionality of quantum mechanics/molecular mechanics methodologies to enable more realistic descriptions of dynamical (reaction) processes.

  - Extension of the Molecular Dynamics module to include general task-level parallelism using the Global Arrays processor group functionality. This will allow methods such as Replica Exchange to be easily implemented and will provide enhanced sampling for Free Energy calculations,
  - A major rewrite of the Molecular Dynamics module documentation. This documentation has not been updated for several years and requires major revisions. As molecular dynamics codes in general are hard to use, and to increase the ease-of-use for the users of the Molecular Science Computing Facility computing resources a new tutorial will be developed.
  - Further improvements in parallelization and efficiency of the plane wave and band structure code, with a focus on large numbers of processors to enable users to study larger systems at longer time-scales

- **Global Arrays Toolkit.** The Global Array Toolkit provides a high-performance programming interface for the scientific programmer by exploiting low-level network protocols and operating system-dependent interfaces. A significant component is maintenance and optimizations of software to keep it robust given the ongoing evolution of the compiler and operating systems. In Fiscal Year 2007, a new release (version 4.1) is planned that will include support for block cyclic distribution to allow better integration with Scalapack. In addition, this release will provide improved support for the Infiniband OpenIB standard, IBM LAPI and BlueGene/L, and Cray XT3 architectures. Each new capability was developed using other funding sources and EMSL core funding is used to make them production ready. These new architectures prepare the Global Arrays Toolkit and NWChem for EMSL's next-generation supercomputer and allow NWChem to run on the first-generation petascale platforms.

- **Ecce core and user support.** Improvements that will be made in Fiscal Year 2007 include:
  - Support for EMSL one-time login policy for MPP2 access to enable external users of the facility to use Ecce as a front end to submit calculations and to analyze results.
  - Enhancements to create full end-to-end NWChem Molecular Dynamics support, such as supporting the free energy task, essential dynamics in the analysis module, extended trajectory analysis/visualization.
  - Ecce user support, outreach, and education for the new molecular dynamics capability, which gives users an easy way to set up, run, and analyze calculations.
  - NWfs archival file support for large output files. This development is critical given the huge size of trajectory files for molecular dynamics, and the need to store this data in an archive.
  - Improving support for minor new NWChem features in Ecce.

- Continued porting of Ecce Basis Set Tool and Builder modules to the wxWidgets cross-platform user interface to allow users to run Ecce from any of their home platforms, including Windows machines.

- **NWChem and Ecce user support for user agreements.** In Fiscal Year 2007, approximately $100K will be spent on administering the user agreements for NWChem and Ecce. The distribution of NWChem and Ecce is getting more difficult every year due to addition distribution constraints and an ever-increasing number of new and returning sites. In Fiscal Year 2007, an additional 10% full-time equivalent has been allocated to develop a strategy, and to switch to an Open Source distribution model. There are three reasons to pursue the Open Source model:

    1. The approximately $100K can be used for the development of new science capabilities requested by the users of NWChem and the Molecular Science Computing Facility.

    2. Many developers interested in improving NWChem and Ecce, or adding new functionality, are reluctant to do so because of the user agreement restrictions. Moving NWChem and Ecce to Open Source will increase participation of external developers, and can lead to a reduction of core costs.

    3. One major target for NWChem development is the ability to run efficiently on petaflop platforms. The appropriate funding agency, DOE Office of Advanced Scientific Computing Resources, is mainly interested in supporting Open Source software.

- **EMSL Basis Set Support.** Funding is required to maintain the servers.

Molecular Science Computing Facility's VisUS will work with the rest of the facility and EMSL to provide the necessary services in computer operations, software development, and scientific consulting.

One of the goals is to focus research on challenging scientific problems in the environmental molecular sciences in support of the needs of DOE and the nation by providing unique computational capabilities that are likely to result in or contribute to a Nobel Prize, major articles in *Science*, *Nature*, or the *Proceedings of the National Academy of Science*, or Hot Papers as defined by ISI, or covers in ISI top-5 journals. With two-thirds of the Computational Grand Challenge projects (10) ending and 18 Computational Grand Challenge Applications accepted, the group expects a large turnover in user accounts. Some of the projects will be continuations of previous projects but even so, twice as many computer accounts are expected to be processed. Twice as much user support work is also expected this next fiscal year, which requires either additional personnel or decreased user support.

- **Increased publications.** With so many Grand Challenge projects coming to an end, the group expects to have an increased number of publications, with more of them in top-10 journals.

- **Support selection of computing resources.** The VisUS group will work with the Molecular Science Computing Facility team on the Request for Proposal and vendor selection for major computing resources. The group also expects to spend time testing the Phase I version of HPCS-3.

- **Provide consulting and other services.** The VisUS group will continue to provide users with access to consulting services, visualization, advanced data analysis and tutorials. The group will need to have at least one individual knowledgeable in each of the EMSL science themes and be able to provide the expertise necessary for all users to effectively use the facility's computational resources. With additional compute power available in the near future, the group needs to start training new scientific consultants so they are ready when the number of users increases dramatically.

- **Obtain additional staff.** Additional trained personnel are needed to provide visualization and advanced data analysis support as well as outreach efforts to expand the number of first-time users of the facility. Animations and user highlights can be produced to emphasize the computational science accomplished in EMSL as well as presentations given at conferences and workshops that display both exceptional science and eye-catching, content rich graphics, and animations.

- **Encouraging multi-facility use.** Annual calls for participation will be modified so that EMSL science theme calls that encourage multi-facility utilization will have increased priority. Separate Computational Grand Challenge calls will be issued later in the year as computer time is available. There will be continued support for the EMSL Scientific Grand Challenge Projects.

Estimated IR and Phosphorescence Emission Fluxes for Specific Polycyclic Aromatic Hydrocarbons in the Red Rectangle

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Calculated infrared spectra of polycyclic aromatic hydrocarbons were compared with available experimental infrared data to correctly identify spectroscopic components of the Red Rectangle Nebula (considered to be a Rosetta Stone for astrophysical processes).

Following tentative identification of the blue luminescence in the Red Rectangle Nebula by Vijh et al. 2004, Mulas and collaborators used EMSL's computational chemistry software, NWChem, to compute absolute fluxes for the vibrational infrared emission of three small polycyclic aromatic hydrocarbons (Vijh et al. 2005). The calculated infrared spectra were compared with available observational data from the Infrared Space Observatory (see Figure 1 for spatial distribution). A subset of the emission bands are predicted to be observable using presently available facilities and can be used for an immediate, independent, discriminating test of their alleged presence in this well-known astronomical object.

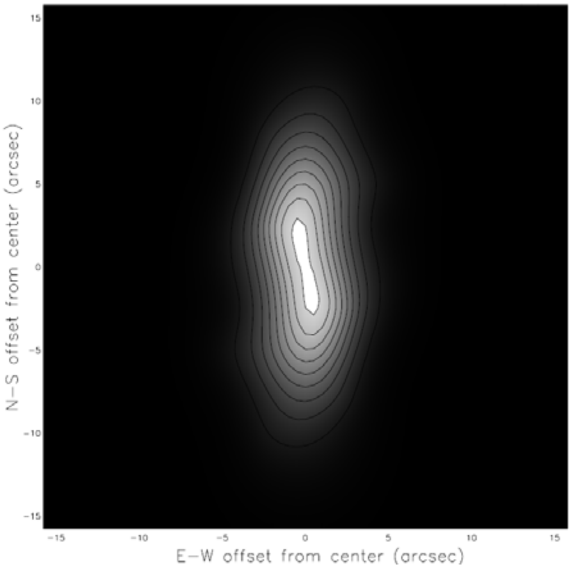

Figure 1. Spatial distribution of the blue luminescence surface brightness of the Red Rectangle Nebula, interpolated from the values given by Vijh et al. 2005. East is left, north is up, and contour lines are in 5% intervals.

Simulations of the photophysics of the candidate molecules were carried out using a Monte Carlo code, together with quantum-chemical calculations (NWChem and Octopus computer codes) for the relevant molecular parameters, and available laboratory measurements for the photoabsorption spectra and for the visible and infrared fluorescence quantum yields. This produced a quantitative prediction of the infrared and phosphorescence emission spectra for each given molecule, which must be related to the integrated blue luminescence attributed to this same molecule.

Citations

Mulas G, G Malloci, C Joblin, and D Toublanc. 2006. "Estimated IR and Phosphorescence Emission Fluxes for Specific Polycyclic Aromatic Hydrocarbons in the Red Rectangle." *Astronomy & Astrophysics* 446(2):537-549.

Vijh UP, AN Witt, and KD Gordon. 2004. "Discovery of Blue Luminescence in the Red Rectangle: Possible Fluorescence from Neutral Polycyclic Aromatic Hydrocarbon Molecules." *The Astrophysical Journal* 606:L65-L68.

Vijh UP, and AN Witt. 2005. "Small Polycyclic Aromatic Hydrocarbons in the Red Rectangle." *The Astrophysical Journal* 619:368-378.

Effect of Pore Scale Heterogeneity in Transport

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While there is general agreement that pore-scale heterogeneity plays an important role in subsurface reaction and flow/transport processes, characterization efforts have typically focused on sediment properties on the scale of architectural elements while essentially neglecting fine-scale heterogeneity. Consequently, there is a lack of consensus on which microscopic geometrical properties are needed to predict the macroscopic transport properties required for field-scale model predictions.

This project has been focused on 1) identifying which microscopic geometrical properties are needed to predict direction-dependent macroscopic properties, 2) quantifying the effects of pore-scale heterogeneity on macroscopic transport properties, and 3) comparing the relative contributions of physical and geochemical heterogeneities to field-scale reactive transport. Resolution of the effects of multiscale heterogeneity on subsurface transport requires large simulations, typically $\sim 10^5$-10^7 grid cells. Progress in this research is dependent on a variety of computer simulation tools, most of which have been developed for use on massively parallel computers, such as EMSL's supercomputer.

Ward and coworkers made use of a Lattice-Boltzmann model (Stewart et al. 2006, in press) and digital representations of porous media with different degrees of heterogeneity and particle aspect ratios (see Figure 1). The Lattice-Boltzmann flow simulation method can efficiently use massively parallel computers to resolve the effects of complex boundaries.

This work has led to the development of new constitutive theory for describing saturation-dependent anisotropy for porous media (Ward et al. 2006). The new theory has been incorporated into the PNNL STOMP (Subsurface Transport Over Multiple Phases) computer model and is already being used for the evaluation of remedial options for a variety of waste management areas at the Hanford Site and within the DOE complex.

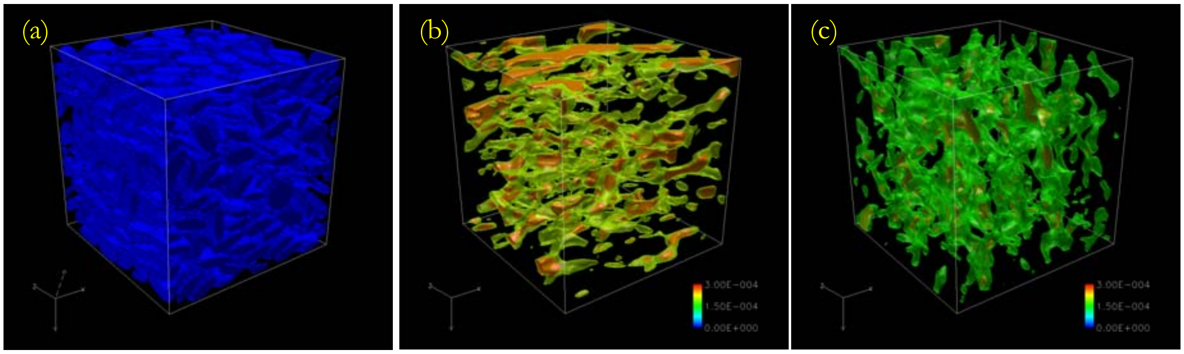

Figure 1. (a) Random particle pack with 3:1 aspect ratio and 0.58 porosity, (b) velocity distribution imposed by horizontal gradient, and (c) velocity distribution imposed by vertical gradient. Note the higher velocities in the horizontal flow case, indicated by yellow and red versus the green in the vertical flow case.

Citations

Stewart ML, AL Ward, and DR Rector. "A Study of Pore Geometry Effects on Anisotropy in Hydraulic Permeability Using the Lattice-Boltzmann Method." *Advances in Water Resources*, 29 (In Press).

Ward AL., ZF. Zhang, and GW Gee. 2006. "Upscaling Unsaturated Hydraulic Parameters for Flow Through Heterogeneous Anisotropic Sediments." *Advances in Water Resources* 29(2):268-280.

MSCF Users Leading the Way to Zero Emission Transportation

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Hydrogen fuel cells are an environmentally friendly way to power vehicles. Recent years have seen increasing interest for research on efficient hydrogen fuel cells from the federal government and the transportation industry. The main challenge today for energy industries is how to make hydrogen fuel cells economically competitive with their conventional fuel counterparts. A key issue that must be addressed is the efficient storage of hydrogen, which would allow hydrogen-powered cars to cover longer distances on a single "tank" and fuel distributors to efficiently deliver hydrogen to consumers.

The idea of "zero-emission" transportation has long been a dream for protecting the environment. Hydrogen-powered cars would bring that dream a step closer to becoming an economically viable alternative to conventional transportation fuels. Many research efforts focus on hydrogen fuel cells; however, hydrogen storage is a key bottleneck to implementing this approach. While highly compressed hydrogen gas and liquefied hydrogen are unlikely to be of sufficient volumetric density, the use of chemical hydrogen storage materials based on light elements is possibly a feasible approach. Recently a joint computational and experimental research project, led by PNNL scientists M Gutowski and T Autrey, has made important progress on ammonia borane (BH_3NH_3)-based materials, which hold great promise for hydrogen storage (Gutowski and Autrey 2006). The computational research of this project is part of the Molecular Science Computing Facility Computational Grand-Challenge 9601 (Computational Design of Materials for Hydrogen Storage, PI: Jonnson), which is one of the computational projects supported by the EMSL.

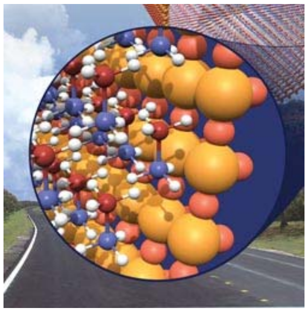

Figure 1. Ammonia borane materials consist of interlocking networks of ammonia and borane units, which form a structural and electrical scaffolding that can hold hydrogen.

The main challenges for making hydrogen fuel cells competitive with conventional fuel involve scale. A viable hydrogen storage medium would have to optimize the density of hydrogen while maintaining favorable electrical and thermodynamic properties. For ammonia borane compounds, the density of hydrogen storage is between 19% and 24%, which make these materials excellent study candidates for hydrogen storage. The computational simulation work has demonstrated that for a variety of ammonia borane materials, the release of hydrogen is for the most part thermodynamically neutral (i.e., the release and uptake of hydrogen from the material is nearly reversible at equilibrium). Currently, removing hydrogen from ammonia borane materials has been shown to be feasible at relatively low temperatures, which is an important characteristic for making hydrogen fuel cells practical in vehicles. However, a significant challenge still exists in that there is a large energy barrier associated with "filling" ammonia borane materials with hydrogen. This energy barrier represents a practical limitation in that to be competitive, distribution of alternative fuels to consumers must be easy. Future work from this Grand Challenge will focus, in part, on searching for a solution to this limitation for ammonia borane materials. If successful, this project could help pave the way to zero-emission transportation fuels that would revolutionize the automobile industry and have a significant impact on providing a solution for achieving and sustaining a clean environment.

Citation

Gutowski MS and T Autrey. 2006. "Hydrogen Gets Onboard." *Chemistry World* 3(3):44-48.

Using Advanced Statistical Models to Improve High-Throughput Proteomics

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(b) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington

Genes are DNA segments that when "turned on" provide living cells with instructions on how to build proteins, which are molecules that can be used as the cellular "skeleton," allow some cells to move, process energy and waste products, and participate in virtually every function required for cells to live. Understanding how organisms work requires us to get a detailed picture of the proteins inside them. High-throughput proteomics is a rapid way to measure the protein content of biological samples, but the veracity of those measurements is, in part, determined by the rate of correctly identifying proteins or protein pieces.

Detecting bioterrorism threats, ensuring a safe food supply, and using microbes to clean up the environment or as a "clean" energy source are just some of the areas of biology where rapidly analyzing very large collections of proteins, or working molecules is a key technology. High-throughput proteomics is a signature capability at PNNL, where the capability is made available to a worldwide community of users to rapidly identify all the proteins in a biological sample. Reliably identifying the protein content of a cell gives important information about its function, making it possible to develop new ways in which cells can easily be identified, which is important in detecting bio-threats.

The main computational challenge associated with high-throughput proteomics is the task of identifying protein fragments (peptides) from measurements of the mass-to-charge ratio (m/z) of small pieces of the peptides. In a high-throughput method known as tandem mass spectrometry (MS/MS), this collection of m/z values can be used as a mass fingerprint to identify the correct peptide sequence from a large list of candidate peptides. *Polygraph*, a high-performance application designed to perform this peptide identification task, has been demonstrated to improve the identification rate of peptides measured by MS/MS. This performance improvement is achieved, in part, by using an advanced statistical model to better understand and identify the fingerprint associated with each peptide. Previous methods generally worked under the assumption that peptides are equally likely to fragment anywhere along their length. However, measurements of the probability of fragmentation along the peptide have shown that there is a strong position-dependence to the likelihood of fragmentation (Figure 1). Including this additional information into *Polygraph* has resulted in a substantial improvement in the ability to correctly identify peptides.

Future directions of this Computational Grand-Challenge 9603 research include development of a data-intensive version of *Polygraph* that would reduce by a factor of one-third the time required to accurately identify peptides from MS/MS data.

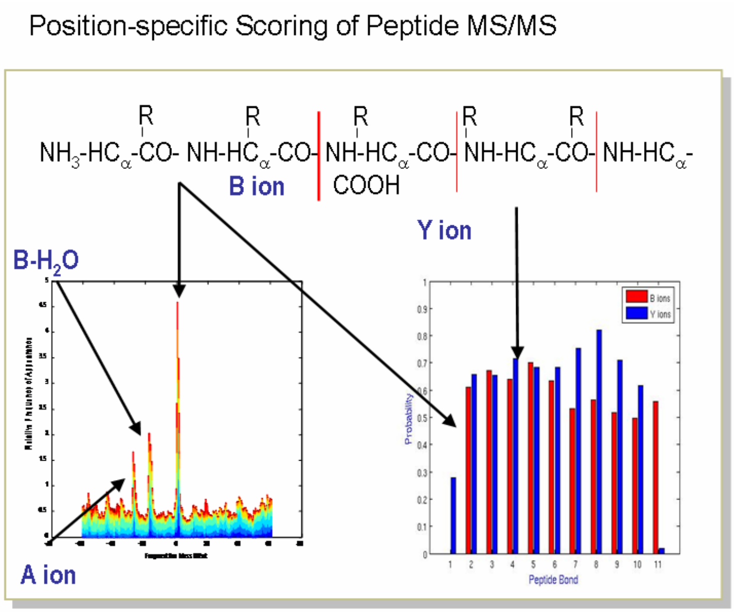

Figure 1. Using a position-dependent description of likelihood of peptide fragmentation has resulted in a fourfold reduction in the false positive identification rate.

Publications Resulting From This Grand Challenge and Pilot Project

Cannon WR and KD Jarman. 2003. “Improved Peptide Sequencing Using Isotope Information Inherent in Tandem Mass Spectra.” *Rapid Communications in Mass Spectrom*etry 17(15)1793-1801.

Cannon WR, KH Jarman, BM Webb-Robertson, DJ Baxter, CS Oehmen, KD Jarman, A Heredia-Langner, KJ Auberry, and GA Anderson. 2005. “A Comparison of Probability and Likelihood Models for Peptide Identification from Tandem Mass Spectrometry Data.” *Journal of Proteome Research* 4(5):1687-1698.

Heredia-Langner A, WR Cannon, KD Jarman, and KH Jarman. 2004. “Sequence Optimization as an Alternative to *De Novo* Analysis of Tandem Mass Spectrometry Data.” *Bioinformatics*. 20(14):2296-2304.

Jarman KD, WR Cannon, KH Jarman, and A Heredia-Langner. 2003. "A Model of Random Sequences for *De Novo* Peptide Sequencing." In *Proceedings of the 3rd IEEE International Symposium on Bioinformatics and Bioengineering*, pp. 206-213, IEEE Computer Society, Los Alamitos, California.

Malard JM, A Heredia-Langner, DJ Baxter, KH Jarman, and WR Cannon. 2004. "Constrained *De Novo* Peptide Identification via Multi-Objective Optimization." In *Proceedings of the 18th International Parallel and Distributed Processing Symposium*, pp. 191-199, IEEE Computer Society, Los Alamitos, California.

Malard JM., A Heredia-Langner, WR Cannon, RW Mooney, and DJ Baxter. 2005. "Peptide Identification via Constrained Multi-Objective Optimization: Pareto-Based Genetic Algorithms." *Concurrency and Computation: Practice and Experience* 17(14)1687-1704.

Full Collection of More Than 1.6 Million Proteins Analyzed Using ScalaBLAST

***CS Oehmen*[a] *and P Hugenholtz*[b]**

(a) Pacific Northwest National Laboratory, Richland, Washington

(b) Lawrence Berkeley National Laboratory, Berkeley, California

ScalaBLAST is a high-throughput sequence analysis engine based on the National Center for Biotechnology Information BLAST distribution. It allows users to harness the power of supercomputers or commodity clusters to accelerate the rate of performing normal BLAST searches against a target database.

One of the key limitations in any sequence analysis pipeline is the need to compare a large collection of proteins from many organisms against itself to detect commonalities between the proteins of different species and within a species. In conjunction with the Joint Genome Institute, current steward of a large collection of microbial genomes, CS Oehmen of Pacific Northwest National Laboratory and P Hugenholtz of Lawrence Berkeley National Laboratory used ScalaBLAST to analyze the full collection of more than 1.6 million proteins against itself in less than 13 hours using 1000 processors of the MPP2 supercomputer in the EMSL Molecular Science Computing Facility (MSCF).

An additional large search was performed in which each of the 1.6 million microbial protein sequences was compared to the nonredundant list of more than 3 million proteins distributed by the National Center for Biotechnology Information. This step is often performed on genomes as part of a quality control process. For a dataset of this size, it is not possible for most BLAST users to analyze the full dataset in a tractible time, because for most standalone BLAST installations, a single genome of a few thousand proteins takes many days to process.

Oehmen and Hugenholtz were able to use ScalaBLAST on MPP2 to process the entire list of 1.6 million proteins against the nonredundant database using 1500 processors in fewer than 20 hours. This collection of results will be shared with the Joint Genome Institute to be used in conjunction with the microbial genome data as a significant information resource for the worldwide community of biological researchers.

Full Stannaspherene: A Highly Symmetric Cage of Sn_{12}^{2-} Dianion

L-F Cui,[a,b] X Huang,[a,b] LM Wang,[a,b] DY Zubarev,[d] AI Boldyrev,[d] J Li,[c] and LS Wang[a,b]

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(c) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington
(d) Utah State University, Logan, Utah

In an effort to understand the semiconductor-to-metal transition in main-group elemental clusters, photoelectron spectroscopy (PES) was used to observe a remarkably stable tin cluster. The spectrum of Sn_{12}^- is remarkably simple and totally different from the corresponding Ge_{12}^- cluster, suggesting that Sn_{12}^- is a unique and highly symmetric cluster.

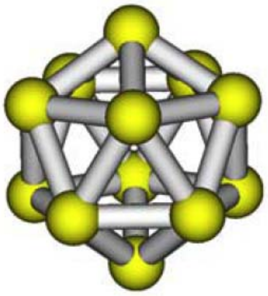

Figure 1. Computationally optimized structures of icosahedral Sn_{12}^- cluster.

Theoretical analysis and computational calculations show that the neutral Sn_{12}^- monoanion cluster has a slightly distorted icosahedral cage with C_{5v} symmetry (Figure 1). Adding an electron to Sn_{12}^- results in a stable closed-shell icosahedral I_h-Sn_{12}^{2-} cluster, which was synthesized in the form of KSn_{12-} ($K+[Sn_{12}^{2-}]$) with a similar PES spectrum as Sn_{12}^-. The calculated energy gap between the highest occupied and lowest unoccupied orbitals in the I_h-Sn_{12}^{2-} is 1.9 eV, which is even larger than that in C_{60} (1.62 eV), providing further evidence for its high stability. The theoretically calculated energy levels, including spin-orbit coupling effects, are in good agreement with the experimentally observed spectra. The I_h-Sn_{12}^{2-} cage is shown to be bonded by four delocalized radial π bonds and nine delocalized on-sphere tangential σ bonds from the 5p orbitals of the tin atoms, whereas the $5s^2$ electrons remain largely localized and nonbonding. The bonding pattern in Sn_{12}^{2-} is similar to the well-known aromatic $B_{12}H_{12}^{2-}$ cage, with the 12 $5s^2$ localized electron pairs replacing the 12 B-H bonds. Because of the delocalized π bonding in Sn_{12}^{2-} and its spherical symmetry, the name "stannaspherene" is suggested for this highly stable species.

While cage structures involving tin were known in inorganic complexes and the Zintl phases, the I_h-Sn_{12}^{2-} cage was unknown. The high stability of this cluster suggests that it may be synthesized in the solid state using suitable ligands or counter ions. More interestingly, the Sn_{12}^{2-} cage has a diameter of ~6.1 Å, which is only slightly smaller than that of C_{60}, and it can host an atom inside much like the endohedral fullerenes. Preliminary experimental and theoretical results suggest that most transition metal atoms can be hosted inside the Sn_{12}^{2-} cage, yielding a large class of novel endohedral stannaspherene. These metal-encapsulated stannaspherene clusters give rise to a large family of endohedral chemical building blocks for cluster-assembled nanomaterials. This work is published in the Journal *of the American Chemical Society* (Cui et al. 2006).

Citation

Cui L-F, X Huang, LM Wang, DY Zubarev, AI Boldyrev, J Li, and LS Wang. 2006. "Sn_{12}^{2-}: Stannaspherene." *Journal of the American Chemical Society* 128(26):8390-8391.

Computer Simulation of Radiation Effects in Zircon

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(b) INSTN/UEPEM CEA-Saclay, Gif-Sur-Yvette, France

Using the computational resources of the MSCF MPP2 supercomputer and the NWfs (Northwest file system), massively parallel molecular dynamics simulations of uranium recoil damage in zircon were performed. Zircon is a durable ceramic that is a promising candidate for the safe immobilization of excess weapons-grade plutonium and high-level nuclear waste.

When doped with actinides, zircon undergoes α-decay that produces 70- to 100-keV heavy ion recoil. The recoil dissipates its energy by a cascade of atomic collisions, leading to defect production at the atomic-level, loss of crystalline structure, significant increase in leach rate of actinides, and degradation of mechanical properties. Because of the short time (ps) and length (nm) scales over which these processes take place, they are not easily accessed by experiments. To understand the fundamentals of radiation damage in ceramics and to design better nuclear waste forms, realistic computer simulations are needed in conjunction with experiments to shed light on the dynamics of collision cascades.

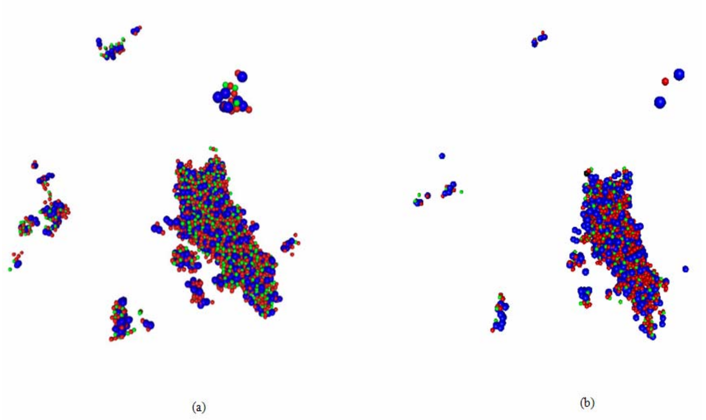

Figure 1. 30-keV uranium cascade in zircon showing (a) defects and (b) amorphous regions. The elements zirconium, silicon, and oxygen are represented by green, blue, and red, respectively.

In this project, the researchers simulated 10- and 30-keV uranium recoils in zircon, and developed new algorithms to distinguish between perfect crystalline, defective crystalline, and amorphous regions in the resulting collision cascade. The simulation cell contained more than one million atoms, which is remarkable in view of the long range of the Coulombic potential. Figure 1 shows the defects (a) and the amorphous regions produced by a 30-keV uranium recoil in zircon (b). The figure shows the formation of small amorphous clusters around the central amorphous core and nanoscale phase separation into zirconium- and silicon-rich regions. The observation of small nanosized amorphous clusters and segregation at the nanoscale enhances our under-standing of defect production in collision cascades in ceramics and provides useful information to guide the design of ceramic waste forms for nuclear waste disposal.

ScalaBLAST: A Scalable Implementation of BLAST for High-Performance, Data-Intensive Bioinformatics Analysis

CS Oehmen[a] and J Nieplocha[a]

(a) Pacific Northwest National Laboratory, Richland, Washington

Developers at PNNL have developed ScalaBLAST, a high-performance, sequence-alignment application that accommodates very large databases and scales linearly to hundreds of processors on both distributed memory and shared memory architectures. This new software represents a substantial improvement over the current state of the art in high-performance sequence alignment with scaling and portability and should have wide-ranging application to other informatics-driven sciences.

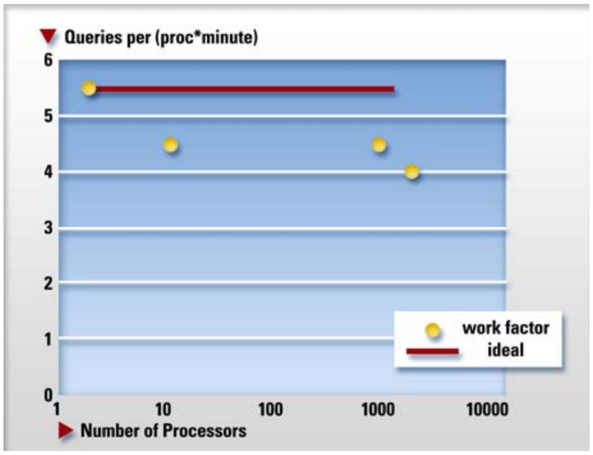

Figure 1. ScalaBLAST scalability

Genes in an organism's DNA (genome) have embedded in them information about proteins, which are the molecules that do most of a cell's work. A typical bacterial genome contains on the order of 5000 genes. Mammalian genomes can contain hundreds of thousands of genes. For each genome sequenced, the challenge is to identify protein components (i.e., proteomes) being actively used for a given set of conditions. Fundamentally, sequence alignment is a sequence-matching problem that focuses on unlocking protein information embedded in the genetic code, making it possible to assemble a "tree of life" by comparing new sequences against all sequences from known organisms. However, the memory footprint of sequence data is growing more rapidly than per-node core memory. Despite years of research and development, high- performance, sequence-alignment applications do not scale well, cannot accommodate very large databases, or require special hardware. To solve these propblems PNNL researchers developed ScalaBLAST, a high-performance, sequence-alignment application that accommodates very large databases and scales linearly to hundreds of processors on both distributed memory and shared memory architectures (see Figure 1). ScalaBlast represents a substantial improvement over the current state of the art in high-performance sequence alignment with scaling and portability. It relies on a collection of innovative techniques (e.g., target database distribution over available memory, multi-level parallelism to exploit concurrency, parallel input/output, and latency hiding through data pre-fetching) to achieve high performance and scalability. This demonstrated approach of database sharing combined with effective task scheduling should have wide-ranging application to other informatics-driven sciences.

Citation

Oehmen CS and J Nieplocha. 2006. "ScalaBLAST: A Scalable Implementation of BLAST for High-Performance, Data-Intensive Bioinformatics Analysis." *IEEE Transactions on Parallel and Distributed Systems* 17(8):740-749.

High-Throughput Visual Analytics for Biological Sciences: Turning Data into Knowledge

CS Oehmen,[a] LA McCue,[a] JN Adkins,[a] KM Waters,[a] T Carlson,[b] WR Cannon,[a] BJ Webb-Robertson,[a] DJ Baxter,[b] ES Peterson,[a] M Singhal,[a] A Shah,[a] and KR Klicker [a]

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A diverse team of researchers collaborated on an entry for the International Conference for High-Performance Computing, Networking, Storage, and Analysis (SC 06) Analytics Challenge and was named one of the top three finalists. The final competition will take place in November at the SC 06 meeting in Tampa, Florida.

For the SC 06 Analytics Challenge, we have demonstrated an end-to-end solution for processing data produced by high-throughput, mass spectrometry (MS)-based proteomics. This approach, which allows biological hypotheses to be explored, is based on a tool called the Bioinformatics Resource Manager (BRM). BRM will interact with high-performance architectures and experimental data sources to provide high-throughput analytics to specific experimental datasets. Peptide identification is achieved by a specially developed, data-intensive version of Polygraph, which has been shown to scale well beyond 1000 processors. Visual analytics applications, such as PQuad or Cytoscape, may be used to visualize protein identities in the context of pathways using data from public repositories such as the Kyoto Encyclopedia of Genes and Genomes. The end result is that a user can go from experimental spectra to pathway data in a single workflow, thereby reducing the time-to-solution for analyzing biological data from weeks to minutes. To view the video included with the PNNL/EMSL entry go to mms://ims4.pnl.gov/winmedia/2006/BRM/brm.wmv.

User Projects

Collaborative Development of Software for Electronic Structure Calculations

MF Guest, CCLRC Daresbury Laboratory, Warrington, United Kingdom

Calculated Rates of Water-Exchange on Large Aqueous Aluminum Nanoclusters

AG Stack, WH Casey, University of California, Davis, Davis, California

Coupled Quantum Simulation Techniques for Studying Nanostructured Materials

AJ Williamson, F Gygi, Lawrence Livermore - National Laboratory, Livermore, California

Correlation of Structure and Function of Zinc Metalloproteins Via Solid-state NMR Methods

G Parkin, Columbia University, New York, New York

ER Kantrowitz, Boston College, Chestnut Hill, Massachusetts

AS Lipton, PD Ellis, R Heck, Pacific Northwest National Laboratory, Richland, Washington

Single Enzyme Nanoparticle Crosslinking Polymerzation

MC Perkins, Pacific Northwest National Laboratory, Richland, Washington

Sub-Grid Modeling of Diesel Particulate Filtration Using the Lattice-Boltzmann Method

ML Stewart, Pacific Northwest National Laboratory, Richland, Washington

Computer Simulation of Optical Spectroscopy

D Pan, Pacific Northwest National Laboratory, Richland, Washington

HP Lu, Bowling Green State University, Bowling Green, Ohio

Integrated Multiscale Modeling of Molecular Computing Devices

L Tsetseris, Vanderbilt University, Nashville, Tennessee

RJ Harrison, Oak Ridge National Laboratory, Oak Ridge, Tennessee

Molecular Modeling

NU Mayer-Cumblidge, P Yan, H Cao, Pacific Northwest National Laboratory, Richland, Washington

Animation for Morphing Catalysis

MC Perkins, Pacific Northwest National Laboratory, Richland, Washington

MP2/CBS Pair Corrrelation Function of Liquid Water

RH Wood, University of Delaware, Newark, Delaware

HPC Challenge Benchmark

KM Fox, Environmental Molecular Sciences Laboratory, Richland, Washington

Simulation of HVDC Converter Valve Control and Protection Algorithms

JM Johnson, Pacific Northwest National Laboratory, Richland, Washington

Quantification of the Ligand Effects in Transition Metal Coordination Compounds using Electronic Structure Calculation Methods

CA Tsipis, C Kefalidis, Aristotle University of Thessaloniki, Greece, Thessaloniki, Greece

Establishing Benchmarks for Stability Testing of Future Intermediate Range Compute Server

V Glezakou, Pacific Northwest National Laboratory, Richland, Washington

LR Corrales, University of Arizona, Tucson, Arizona

Fluorescent Labeling of Proteins Based on Known Crystal Structures

L Rodriguez, Pacific Northwest National Laboratory, Richland, Washington

First-Principles Catalyst Design for Environmentally Benign Energy Production

E Mavrikakis, PA Ferrin, LC Grabow, S Kandoi, AA Gokhale, AU Nilekar, RP Nabar, University of Wisconsin-Madison, Madison, Wisconsin

Real-Time Atomistic Simulation Studies of Light Harvesting and Charge Transport for Hydrogen Production in Solar Cells

EJ Bylaska, Pacific Northwest National Laboratory, Richland, Washington

DS Kilin, SV Kilina, K Tsemekhman, O Prezhdo, WR Duncan, BF Habenicht, University of Washington, Seattle, Washington

Comparative Protein Structure Modeling: From Protein Sequence to High-accuracy Protein Structure

Y Xu, Jn Guo, University of Georgia, Athens, Georgia

TP Straatsma, Pacific Northwest National Laboratory, Richland, Washington

Comparative Molecular Trajectory Analysis

SK Wurstner, TP Straatsma, M Singhal, Pacific Northwest National Laboratory, Richland, Washington

DOE Matrix

KJ Roche, Oak Ridge National Laboratory, Oak Ridge, Tennessee

High-Fidelity Direct Numerical Simulations of Turbulent Combustion - Compression Ignition under HCCI Conditions and NOx Formation in Turbulent Jet Flames

JH Chen, Sandia National Laboratory, Livermore, California

HG Im, Cn Yoo, University of Michigan, Ann Arbor, Michigan

Y Wang, University of Wisconsin-Madison, Madison, Wisconsin

Y Wang, AC Trouve, University of Maryland, College Park, Maryland

Wet Electrons at Metal Oxide Surfaces

H Petek, J Zhao, University of Pittsburgh, Pittsburgh, Pennsylvania

Snow Pack Predictions for Next 50 Years in the Pacific Northwest

MC Perkins, Pacific Northwest National Laboratory, Richland, Washington

Thrust Area #2: Molecular Modeling of Electron Transfer in Fe(III) Oxides

KM Rosso, SN Kerisit, X Wang, Pacific Northwest National Laboratory, Richland, Washington

FN Skomurski, University of Michigan, Ann Arbor, Michigan

M Valiev, Environmental Molecular Sciences Laboratory, Richland, Washington

MC Wander, State University of New York at Stony Brook, Stony Brook, New York

JD Kubicki, Pennsylvania State University, University Park, Pennsylvania

Joint Application of Theory and Experiment to the Chemistry of Environmentally Important Organic Peroxides

GB Ellison, University of Colorado, Boulder, Colorado

BK Carpenter, A Litovitz, Cornell University, Ithaca, New York

JF Stanton, University of Texas at Austin, Austin, Texas

High Performance Sequence Analysis for Data-intensive Bioinformatics

CS Oehmen, L Mccue, HJ Sofia, Pacific Northwest National Laboratory, Richland, Washington

EA Welsh, Washington University in St. Louis, St. Louis, Missouri

DJ Baxter, Environmental Molecular Sciences Laboratory, Richland, Washington

Megaports Training Video Development

RA Pappas, BA Mcquerry, Pacific Northwest National Laboratory, Richland, Washington

Proton Transport in Polymer Electrolyte Membranes

R Devanathan, M Dupuis, A Venkatnathan, Pacific Northwest National Laboratory, Richland, Washington

***De Novo* Structure-Based Molecular Design**

V Bryantsev, California Institute of Technology, Pasadena, California

BP Hay, Oak Ridge National Laboratory, Oak Ridge, Tennessee

Compare Thermal Signature of Air-cooled RX2600 Node with SprayCool FX2600 Node

KM Regimbal, RW Mooney, Environmental Molecular Sciences Laboratory, Richland, Washington

Nanostructured Catalysts for Fuel Cells

CH Turner, CK Acharya, University of Alabama, Tuscaloosa, Tuscaloosa, Alabama

DFT Studies of Size and Structure Effects of Ir Nanoparticles on Their Catalytic Activities for Methane Dissociation

L Wang, Southern Illinois University, Carbondale, Illinois

Computational Study of Oxygen Reduction on SOFC Cathode Surfaces

M Liu, J Wang, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

Architectural Rendering of EMSL Office Expansion

MC Perkins, Pacific Northwest National Laboratory, Richland, Washington

Defect Processes, Phase Transformations, and Nanoscale Phenomena in Complex Ceramics

R Devanathan, F Gao, WJ Weber, Pacific Northwest National Laboratory, Richland, Washington

Cover Graphic for Nanoscience and Nanotechnology Trade Journal

MC Perkins, Pacific Northwest National Laboratory, Richland, Washington

Energy and Entropy Effects in Dissociation of Non-Covalent Complexes: Experimental and Theoretical Investigation of the Structures and Interactions of Glycopeptide Antibiotics-Cell Wall

Z Yang, J Laskin, Pacific Northwest National Laboratory, Richland, Washington

Investigation of DNA Structural Perturbations Induced by the Guanine Oxidation Products Spiroiminohydantoin and Guanidinohydantoin

ND Priestley, KD Sugden, University of Montana, Missoula, Montana

Asynchronous File System Experiments

MI Seltzer, CA Stein, Harvard University, Cambridge, Massachusetts

Computational Atomic and Molecular Physics for Advances in Astrophysics, Chemical Sciences, and Fusion Energy Sciences

JP Colgan, Los Alamos National Laboratory, Los Alamos, New Mexico

Pn Krstic, T Minami, CO Reinhold, Oak Ridge National Laboratory, Oak Ridge, Tennessee

MS Pindzola, SD Loch, FJ Robicheaux, Auburn University, Auburn, Alabama

NR Badnell, University of Strathclyde, Glasgow, Scotland, United Kingdom

DC Griffin, CP Balance, Rollins College, Winter Park, Florida

Theoretical Investigations of Chiral Self-Assembly at Solid Surfaces

I Paci, M Ratner, Northwestern University, Evanston, Illinois

Virtual Tools for Cardiac Remodeling

JM Guccione, University of California, San Francisco, San Francisco, California

DR Einstein, Pacific Northwest National Laboratory, Richland, Washington

Molecular Dynamics of Aqueous $NaNO_3$ and NaCl Solutions: The Surface Propensity and Thermodynamic Properties of Aqueous Anions

JL Thomas, BJ Finlayson-pitts, DJ Tobias, University of California, Irvine, Irvine, California

LX Dang, Pacific Northwest National Laboratory, Richland, Washington

First-Principles Calculations of La(1-x)Sr(x)Fe(1-y)Co(y)O_3 Solids and Surfaces

C Lee, SB Sinnott, University of Florida, Gainesville, Florida

R Devanathan, Pacific Northwest National Laboratory, Richland, Washington

Theoretical Characterization of H_3O^+ on the Water - Vapor Interface

LX Dang, Pacific Northwest National Laboratory, Richland, Washington

J Cui, KD Jordan, University of Pittsburgh, Pittsburgh, Pennsylvania

Molecular Recognition at the Electronic Level

JJ Stezowski, University of Nebraska, Lincoln, Nebraska

PA Karr, Wayne State College, Wayne, Nebraska

High Performance Sequence Alignment: OMB Software Effectiveness Metric Studies for FY06

CS Oehmen, Pacific Northwest National Laboratory, Richland, Washington

KJ Roche, Oak Ridge National Laboratory, Oak Ridge, Tennessee

Investigations into Sulfur Poisoning Mechanisms in Solid-State Oxide Fuel Cells Using Quantum-Chemical Computations

M Liu, Jn Wang, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

Molecular Dynamics Study of an Actin Septamer: Testing the Holmes Model and the Hydrophobic Plug Loop Hypothesis

GC Schatz, KM Barrett, MJ McCullagh, JT Paci, Northwestern University, Evanston, Illinois

KC Holmes, Max Planck Institut fur medizinische Forschung, Heidelberg, Germany

Exploratory High-throughput Sequence Analysis on Microbial Genomes

CS Oehmen, Pacific Northwest National Laboratory, Richland, Washington

E Szeto, Lawrence Berkeley National Laboratory, Berkeley, California

P Hugenholtz, Joint Genome Institute, Walnut Creek, California

Design Criteria for Organic Charge Transporting Materials through Computational Modeling

LS Sapochak, AB Padmaperuma, PE Burrows, Pacific Northwest National Laboratory, Richland, Washington

M Valiev, Environmental Molecular Sciences Laboratory, Richland, Washington

Oxide Surface Structure and Acidity

KM Rosso, SN Kerisit, Pacific Northwest National Laboratory, Richland, Washington

BR Bickmore, Brigham Young University, Provo, Utah

Lustre Scalability Research

EJ Felix, Environmental Molecular Sciences Laboratory, Richland, Washington

SGI Altix Allocation for Advanced Computing Technology Lab

J Nieplocha, AS Lipton, EJ Bylaska, CL Rakowski, JA Fort, BJ Palmer, MD Williams, SS Xantheas, PA Medvick, M Ovtchinnikov, Y Fang, M Singhal, ML Stewart, SM Robinson, AM Tartakovsky, Z Yang, DG Chavarria, DH Bacon, VL Freedman, GS Fanorrgakis, D Huang, LL Nuffer, M Krishnan, A Marquez, CS Oehmen, PD Ellis, WA Perkins, TR Shippert, S Kabilan, T Fu, V Tipparaju, Pacific Northwest National Laboratory, Richland, Washington

D Wang, J Li, Environmental Molecular Sciences Laboratory, Richland, Washington

EA Butterworth, University of Washington, Seattle, Washington

Chemical Fate of Contaminants in the Environment: Chlorinated Hydrocarbons in the Groundwater

DG Truhlar, JI Siepmann, CJ Cramer, JD Thompson, AW Jasper, BJ Lynch, NE Schultz, C Zhu, Y Zhao, BA Ellingson, S Nangia, EE Dahlke, EA Amin, University of Minnesota, Minneapolis, Minnesota

YA Borisov, Russian Academy of Science, GSP-1, Moscow V-334, Russian Federation

K Morokuma, IV Khavrutskii, SJ Mo, S Irle, Q Wang, G Zheng, HA Witek, J Liu, A Dutta, P Zhang, D Quinonero, K Omiya, DG Musaev, Emory University, Atlanta, Georgia

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A Chakraborty, Pennsylvania State University, University Park, Pennsylvania

Local Motions in Protein Structures

HL Selzle, Institut fur Physikalische and Theoretische Chemie of the Technische Universitat Muechen, Garching, Germany

EW Schlag, Technical University Munich, Garching, Germany

A Grid-Based Exact or High-Accuracy Solution of the Electronic Schrdinger Equation

S Hirata, Pn Fan, Mn Kamiya, University of Florida, Gainsville, Florida

RJ Harrison, GI Fann, Oak Ridge National Laboratory, Oak Ridge, Tennessee

T Yanai, Cornell University, Ithaca, New York

Computer Simulation of Radiation Effects in Zircon

R Devanathan, Pacific Northwest National Laboratory, Richland, Washington

CD Van Siclen, Idaho National Engineering and Environmental Laboratory (INEEL), Idaho Falls, Idaho

Complex Enzymatic Reactions Studied by Molecular Modeling and Electronic Structure Calculations.

MA Osman, Washington State University, Pullman, Washington

TP Straatsma, M Dupuis, RD Lins, B Gopalan, X Wang, TA Da Silva, WR Cannon, Pacific Northwest National Laboratory, Richland, Washington

H Michel, E Herzog, E Olkhova, CD Lancaster, T Frigato, Max Planck Institute of Biophysics, Frankfurt am Main, Germany

PM Kozlowski, University of Louisville Research Foundation, Inc., Louisville, Kentucky

L Adamowicz, S Bubin, University of Arizona, Tucson, Arizona

DM Smith, Whitman College, Walla Walla, Washington

ER Vorpagel, M Valiev, Environmental Molecular Sciences Laboratory, Richland, Washington

SK Shakya, VH Helms, W Gu, Universitat des Saarlandes, Saarbrucken, Germany

DE Gomes, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

Superparameterization: A New Paradigm for Climate Modeling

TP Ackerman, AS Koontz, L Leung, RT Marchand, M Ovtchinnikov, JW Voyles, LK Berg, TR Shippert, SA Mcfarlane, Pacific Northwest National Laboratory, Richland, Washington

DA Randall, MF Khairoutdinov, Colorado State University, Ft. Collins, Colorado

JG Michalakes, National Center for Atmospheric Research, Boulder, Colorado

RM Pincus, National Oceanic and Atmospheric Administration, Boulder, Colorado

EE Clothiaux, JN Cole, Pennsylvania State University, University Park, Pennsylvania

Molecular Computational Studies in Environmental Chemistry, Geochemistry, and Biogeochemistry

J Banfield, H Zhang, University of California, Berkeley, Berkeley, California

JW Halley, University of Minnesota, Minneapolis, Minnesota

JR Rustad, WH Casey, University of California, Davis, Davis, California

GE Brown, T Yoon, Stanford University, Stanford, California

EJ Bylaska, HM Cho, KM Rosso, TP Straatsma, JE Amonette, M Dupuis, JM Zachara, Pacific Northwest National Laboratory, Richland, Washington

G Waychunas, Lawrence Berkeley National Laboratory, University of California, Berkeley, Berkeley, California

GR Choppin, Florida State University, Tallahassee, Florida

BM Elsasser, University of Paderborn, Paderborn, Germany

DM Smith, Whitman College, Walla Walla, Washington

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DA Dixon, Rn Craciun, SA Dickinson, JP Keenum, TG Kelly, DJ Grant, WA Shaffer, LH Haselmaier, University of Alabama, Tuscaloosa, Tuscaloosa, Alabama

JH Weare, SA Bogatko, University of California, San Diego, La Jolla, California

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Nanostructure Formation, Aggregation, and Reactivity

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NMR Chemical Shift Calculations for Novel Bioactive Metabolites from an Acid Mine Waste Organism

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Computed Frequencies to Support Experimental Quests for Novel Molecules

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***Ab initio* Calculations on a Proposed Gating Mechanism for the KcsA Channel**

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Computational Study of Protein-protein Interaction Dynamics

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Computational study of protein-protein interaction dynamics

Multi-Region Reactive Transport Due to Strong Anisotropy in Unsaturated Soils with Evolving Scales of Heterogeneity

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EGFR Dimerization

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***Ab-initio* Simulations of the Catalytic Mechanism in Protein Kinases**

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Direct Numerical Simulations of Turbulent Combustion- Temperature Inhomogeneity Effects on the Autoignition of H_2/Air Mixtures in the Sponteneous Ignition Regime

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Quantum and Classical Simulations of Clusters, Self-assembly, Nano-scale Manipulations, Nanotribology, and Biological Processes

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Computing and Networking Services

The primary mission of Computing and Networking Services (CaNS) is to provide the infrastructure and computing services within the W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL) for an advanced computing environment that enables staff, visitors, and collaborators to effectively use computer and network resources for their scientific and business requirements. In supporting growing business and research needs of EMSL in the area of information sciences, CaNS secures global information access to our facilities by providing online remote access to both computing resources and scientific equipment. A large portion of the efforts undertaken by CaNS staff members involves providing customer support to EMSL researchers and offsite users. For offsite users, CaNS provides secure information access and dissemination among EMSL researchers and a global scientific user community.

Capabilities

One of the primary roles of CaNS is to provide computer support to all EMSL users and visitors, including scientists, technicians, and support staff. Computing support includes computer procurement assistance, setup, delivery, connection, and upgrade installation. System administration services include configuration management, software upgrades, security standards, account setup, and automated backup. CaNS is responsible for the design and implementation of EMSL's computing infrastructure, software, and Internet application development and support; conference room support; and management of computer maintenance contracts.

Expert Support and Services

- Security
- Desktop computing
- Scientific computing
- Instrument control systems
- Compute clusters and servers
- Infrastructure design and upgrade
- Web hosting and services
- Software application development and deployment
- Auditorium and conference room support

In Fiscal Year 2006, CaNS staff responded to approximately 6,600 formal requests for assistance (an increase of 20.6 percent over the 5,469 requests made in 2005) and 1500 informal requests. Demonstrating consistency and responsiveness, CaNS staff members resolve 50 percent of support requests within a day and 90

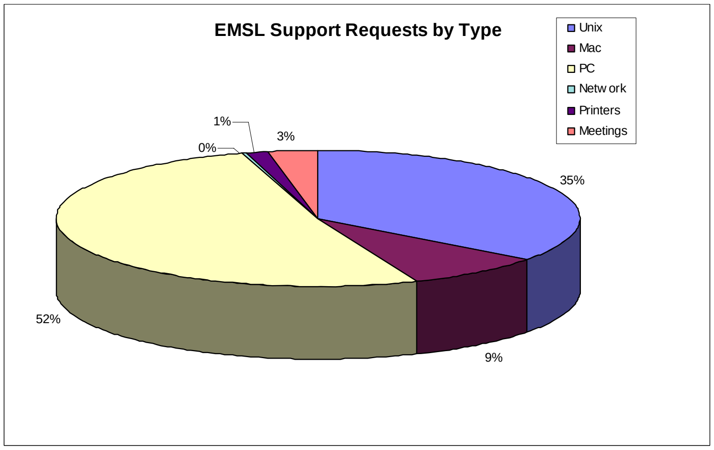

Figure 1. EMSL Support Requests by Type

percent within a week, giving priority to visiting scientists. Figure 1 shows a breakdown of computer support requests in 2006.

EMSL has a history of growth in the number and variety of computer systems used by its staff members (Figure 2). In Fiscal Year 2006, 361 systems were added to the support scope, and 177 systems were released, yielding a net increase of 184 systems (7.4%) and a total of 2023 systems in use in EMSL.

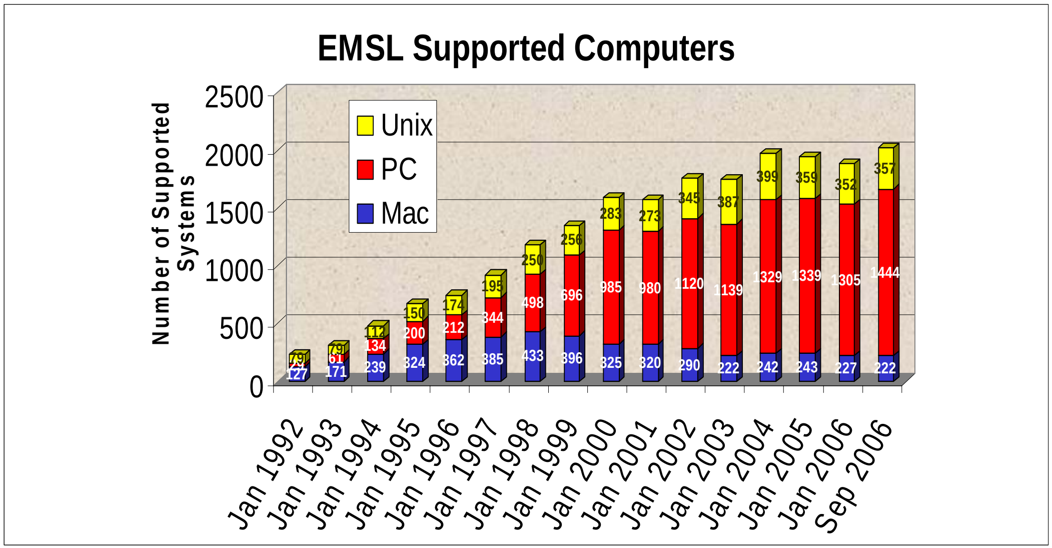

Figure 2. EMSL computer use trends.

In Fiscal Year 2006, CaNS added 163 new scientific users, increasing its support scope to 1043 active users. Of this total number of users, 564 use EMSL capabilities from offsite.

Support Queues. CaNS uses a web-based software-support request application (Footprints) to store and reply to submitted requests, and to record all dialogue surrounding problems. Users benefit by receiving a more thorough response, faster service, and an improved tracking system to ensure their problems are solved expeditiously. CaNS staff members benefit from the ability to better organize their work and identify chronic problems. CaNS also provides its support-request system to other projects in EMSL, such as NWChem and Ecce developers (see Molecular Science Computing Facility Overview section).

Data from Fiscal Year 2006 show that the 30 help queues were staffed by 116 administrators and experts, who together handled 15,000 support requests. Figure 3 shows historical use of the primary EMSL support queue, support@emsl.pnl.gov.

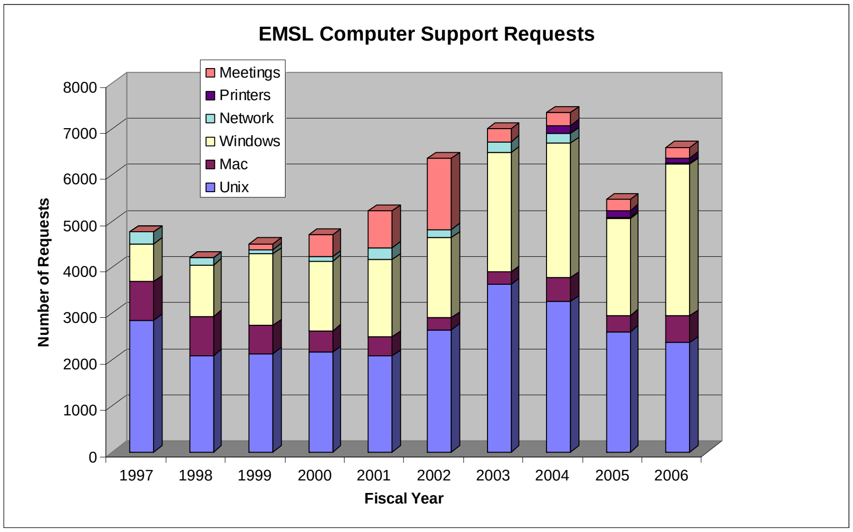

Figure 3. Computer support request history.

In 2005, an automatic support request satisfaction survey was implemented. Approximately one third of completed requests generate a survey query to the item's requestor. The requestor completes a simple survey rating our response and performance. The results are automatically recorded in a database and reviewed to identify areas for improvement. In Fiscal Year 2006, 308 customers replied. Average satisfaction with the service performed was 4.81 out of 5.0; average satisfaction with our response time was 4.81 out of 5.0. Six responses reported unsatisfactory service or response. These have been followed up on and corrective actions taken where necessary.

Security

A major CaNS focus involves infrastructure and application upgrades designed to increase the security of EMSL's computing resources while continuing to provide open access for visitors and collaborators. This is an increasingly difficult task as new and more sophisticated security threats arise. Major project areas focused on the formation of the CaNS Cyber Security team. The focus of this team is to unify the efforts of the CaNS and MSCF cyber security teams, reduce redundancy, increase collaboration, and build greater trust and peer interaction between the projects. This team spans both server and client along with UNIX, Linux, PC and Macintosh platforms. Some of the security tasks that have come out of the formation of this team include development of a management network in the form of the Secure Collaborative Zone (SCZ), CaNS brown bags, expanded scanning for vulnerabilities, unified UNIX sign-on, and PointSec deployment.

Secure Collaborative Zone (SCZ). The SCZ is an internet accessible network for the purpose of allowing external collaborators access and storage of raw data files for experiments and analysis via web applications.

Center for Internet Security Benchmarks. Expansion of the Center for Internet Security (CIS) benchmarks was carried out for EMSL server infrastructure. CIS benchmarks enumerate security configuration settings and actions that "harden" systems. They are unique, not because the settings and actions are unknown to any security specialist, but because consensus among hundreds of security professionals worldwide has defined these particular configurations. See http://www.cisecurity.org/ for further detail. When vulnerabilities are detected from the scans, corrections are made in a timely manner due to the use of the EMSL support queue, to track and triage service requests. This expanded scanning assisted in EMSL's "outstanding" rating from the DOE Site Assist Visit auditors on network and system security.

Unified UNIX sign-on. In Fiscal Year 2006, work began to create a unified UNIX sign-on, providing users of PNNL resources the need to remember just a single user ID and password pair. Integrating UNIX authentications with PNNL Active Directory, thereby reducing UNIX password maintenance and auditing to that of the central AD service the lab already uses for Microsoft Windows based systems. Initial analysis has been completed, and several issues were identified.

Tracking of security bulletins. To better reduce duplication of effort, a CaNS Security Bulletin queue was established. This support queue is shared by all CaNS security task leads. Currently, the MSCF security task lead is responsible for triaging all incoming vendor and government (i.e., CIAC) cyber security bulletins and then determining to which platforms the notice applies, who is responsible for responding to the notice, and what action is needed. Previously, each security function within EMSL managed security bulletins autonomously. This centralized system greatly reduces and concentrates effort.

Oracle upgrade. EMSL-managed UNIX systems were patched for Oracle vulnerabilities. A primary application server was patched along with two other managed PNNL infrastructure systems.

EMSL support queue server upgrade. The EMSL support queue utilizing the Footprints software was upgraded. This migration entailed upgrading the physical server, the web server, the database engine, and the Footprints software. This web-based software is EMSL's primary mechanism for tracking, managing, and resolving all incidents and problems for both internal and external users. The upgrade was seamless to users and to the six support queues that rely on the software application to track issues.

PointSec deployment. CaNS Linux staff were instrumental in developing a Linux standard configuration. PointSec combines a required log in along with strong encryption (AES) to create an advanced security solution. When the user logs in, the laptop is unlocked and the single log in can also unlock the other tasks (e.g., operating systems, networks, PKI, or digital signing). PointSec:

- allows only authorized users to access information stored on mobile computing devices
- enforces automatic mobile security practices (i.e., transparent encryption)
- allows mobility without compromising security
- minimizes financial losses and mitigates legal and regulatory risks associated with exposing sensitive information.

CaNS Brown Bags. In Fiscal Year 2006, “CaNS Presents” was established as a monthly mechanism to share technical capabilities with EMSL users. The primary presenters are CaNS staff, though the presenters have come from across PNNL in an effort to exchange ideas, raise awareness and create a more secure computing infrastructure. Twelve presentations were given during Fiscal Year 2006 on topics ranging from configuring system administration tools such as kickstart to current trends in spam. All presentations were very well received, often standing room only. A complete listing can be found at http://emslweb.emsl.pnl.gov/ops/comphelp/web/html/presentations.html.

Desktop Computing

Windows/Macintosh Desktop Support. The EMSL Office Computer Support team provided primary computer support services to more than 1300 Windows and 220 Macintosh computer systems. While the majority of these systems reside on user desktops, some systems are connected to specialized electronic instruments and devices that support the EMSL research mission. Most of the older Windows operating systems have been replaced with Windows XP and the Office 2003 suite, which provide EMSL users with increased reliability and capabilities, such as the ability to connect remotely to a desktop computer located in EMSL. Windows XP systems were upgraded to Service Pack 2 to implement needed security enhancements, and Software Update Service was implemented across the EMSL. Macintosh systems in EMSL are primarily G3, G4, and G5 models running OS X 10.4 and the Office 2004 suite.

Along with numerous support requests from PC and Macintosh users for personal digital assistant support, wireless configurations, and remote access, the team responded to increased requests related to the EMSL enclave, including administration of SecurID tokens and EMSL domain accounts for non-staff members.

Unix Desktop Support. Linux continues to grow in popularity and is now the dominant Unix desktop operating system, increasing from a 47 percent share in 2005 to a 53 percent share in 2006 (Figure 4). We anticipate that Linux will continue to dominate the Unix desktop environment in the future.

With the increase in the use of Linux, an effort was made to standardize a Linux version, and 400 licenses were purchased for Red Hat Enterprise Linux (RHEL). CaNS played a major role in the

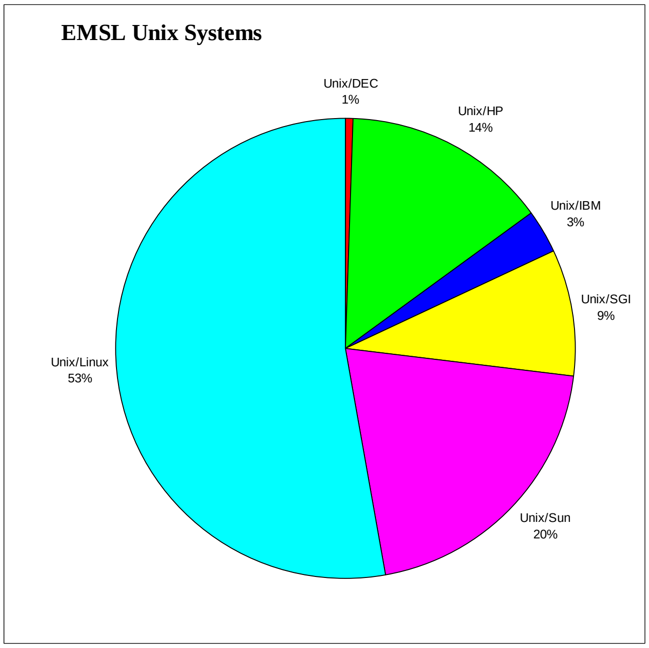

Figure 4. Distribution of Unix operating systems.

testing and deployment of RHEL Linux, with team members maintaining the central Linux installation server. This new server allows EMSL staff members to easily install Linux and subscribe their system to an update service that automatically updates their computer when new operating system patches are released. The RHEL update service is analogous to the Microsoft Windows Update service.

Scientific Computing

Windows Scientific Computing Support. CaNS supports computers used to control scientific instruments during experiments or to collect data from experiments. A variety of Windows, Macintosh, and other operating systems are installed on these computers. The estimated distribution is detailed in Figure 5.

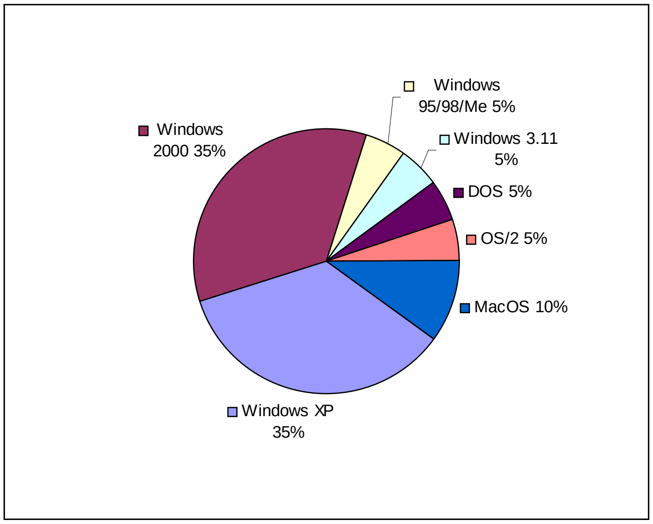

Figure 5. Distribution of Windows/Macintosh operating systems installed on computers used to control research instruments or collect data (excluding office systems).

Bionet is the CaNS-created private instrumentation network that provides computer network connectivity between laboratories and storage resources. This network is isolated from the PNNL network connectivity that is available in every office and laboratory, and it allows instrument control and data acquisition equipment to be connected to a network and available from specific gateways while protecting the equipment from all of the systems on the PNNL network. The number of machines on this network grew by 40 systems in Fiscal Year 2006 to a total of 125.

Cluster Support. A number of CaNS-supported Linux clusters experienced growth in both central processing unit (CPU) power and disk storage this year. The aging Weahltheow and Seattle clusters (64 CPUs total) were replaced by the Spokane cluster (with 74 new generation CPUS). In total, more than 20 terabytes of disk space and 64 CPUs were added to three Linux clusters. The number of supported Linux clusters is now 18, and they range in size from 8 to 200 CPUs. Customers continue to make extensive use of our test cluster, which now has both Gigabit Ethernet and Infiniband networking. Our test cluster also has the ability to run in either 32- or 64-bit modes, offering customers more options to test before deciding on a purchase.

The Math 1427 and ETB 104 computer rooms at PNNL were vacated this year. All cluster systems were relocated to the newly provisioned LSB 1C04 computer room.

In 2006, we added four new clusters and one high-performance symmetric multi-processing system (SMP):

- Cam is a 16-node, 64-core cluster with 256 gigabytes of shared storage, a Myrinet high performance interconnect, and 32 gigabytes of total system memory (2 gigabyte per node).

- Spokane is an 18-node, 72-core cluster with 600 gigabytes of shared storage, a gigabit network interconnect, and 108 gigabytes of total system memory (6 gigabytes per node).

- Underlord is an 8 node, 32 core cluster with 900 gigabytes of shared storage, an Infiniband high performance interconnect, and 128 gigabytes of total system memory (16 gigabytes per node).

- Nwvisus (an existing 8 processor SGI system with 8 gigabytes of memory and a high performance video display subsystem) was replaced by a new 16 processor SGI with 32 gigabytes of system memory.

All of these clusters were procured the PNNL Managed Hardware Program (MHP) where CaNS staff work with the MHP vendor to ensure availability of available components. The SGI system was procured with CaNS engineering/configuration participation.

CaNS continues to be the leader in cluster-computing solutions at PNNL.

Supercomputing '05. Tim Carlson managed the PNNL team that received the StorCloud challenge award at the Super Computing conference in Seattle in November 2005. The team consisted of scientists from EMSL and PNNL's Computational and Information Sciences Directorate, and corporate partners from HP, Cisco, and Federal Network Services. In addition to winning the StorCloud challenge, the team placed second in the Bandwidth challenge.

Infrastructure Design and Upgrades

Unix Infrastructure Backup System. The EMSL disk-based infrastructure backup system continues to perform well. Its disk arrays were upgraded in capacity to 20 terabytes, and it provides for recovery of infrastructure and shared file system files for a one year window.

Windows Server Backup Services. The Windows Infrastructure Team replaced subscription backup services for its 40 Windows Servers with a Symantic BackupExec infrastructure. The PNNL subscription service moved to a model where cost varied with storage capacity, and a cost analysis indicated that it would be less expensive to provide a more robust system owned by the EMSL service center. All 40 of the managed servers were moved to this new model in Fiscal Year 2006.

Unix/Linux Backup Services. The desktop Unix/Linux team similarly began to replace subscription backup service for over 200 CaNS-managed Unix/Linux systems for the same reasons. A third of these systems have been relocated to a disk-based backup system built around the Amanda open-source backup software.

Remote Installation Services (RIS). The Windows Infrastructure Team deployed a Microsoft RIS server on the EMSL network that provides the ability to boot directly from the network and install an OS on systems that support pixie network boots. This is a core capability to enable the use of thin clients.

Thin Client project: CaNS funded a capability enhancement project to deploy thin client systems to utilize a Citrix-based Terminal Server to support 25 EMSL users or staff for their daily computing needs, thus eliminating their need for a full-sized, stand-alone desktop computer. There are several benefits to using this approach for desktop computing, the most visible being the reduced cost of hardware and maintenance. This project will continue into 2007.

Distributed file services. The CaNS strategy for high availability in its distributed file services (Andrew File System or AFS) configuration paid off several times in Fiscal Year 2006 as hardware component failures were repaired without disruption of service to users. Besides high availability, the EMSL distributed file system provides uniform access for users to their personal and project areas from any Windows, Macintosh, or Unix system; enhanced and secure file-sharing capability; consistent file backups; access to shared software; access to Website content; and consistent tools across platforms. Of the 3.5 terabytes of available space, 1.3 terabytes are in use, which leaves plenty of space for both transient files and long-term storage. Figure 6 shows the historical usage versus capacity.

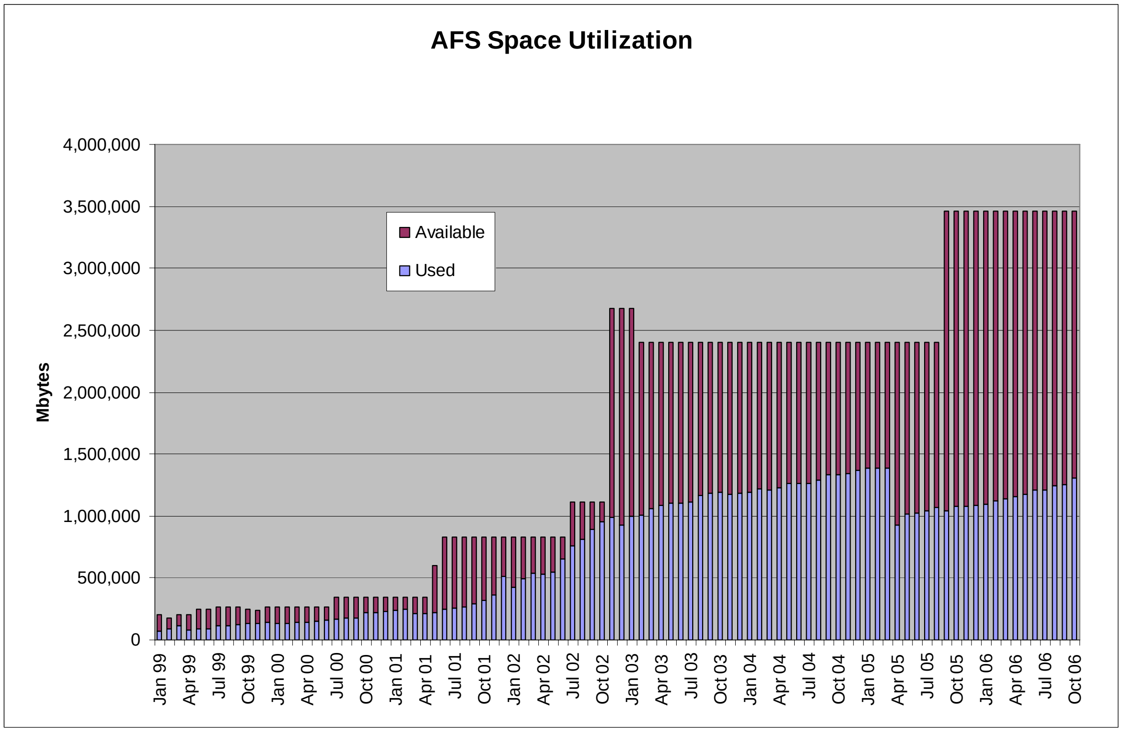

Figure 6. AFS capacity utilization.

Web Hosting and Services

EMSL Web Services. Increased security concerns required EMSL to split its web server and move the server with external access to a more secure configuration. To accomplish this upgrade, the layout of the server configurations was redesigned, and the redesigned layout was implemented. A new server was purchased and deployed to house the external server, and the internal web server was moved to its own system. The external server was put behind proxy servers in 2005 to manage secure internal and external access. In Fiscal Year 2006, a second web server, linux based, was also deployed behind the proxy servers.

The EMSL Website continues to be moderately busy with about 1,109,000 visits in 2006. The Website absorbed almost 10 million hits during the year. Figure 7 shows the history of user visits.

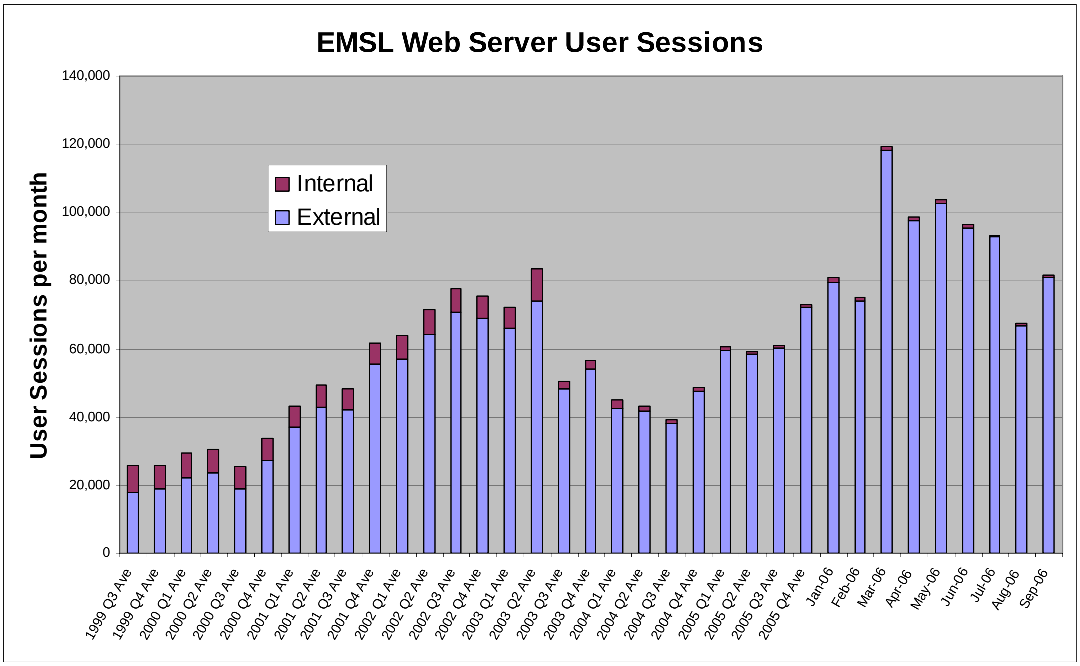

Figure 7. History of user visits.

Software Application Development and Deployment

Unix Software Repositories. Software repositories provide shared access to frequently used software including freeware and floating license managers for commercial scientific applications. Applications in the repository include computer languages and interpreters; editors and debuggers; configuration management tools; documentation tools and pre-viewers; communication and collaborative tools; visualization, plotting, and graphing tools; numerical tools and libraries; data acquisition tools; and data management, structure, and format conversion. More than 150 applications available via this repository have been built and compiled to operate over the various operating systems that CaNS supports. The repository is made available via the AFS distributed file system and provides the benefit of consistent applications that users do not have to build themselves.

Auditorium and Conference Room Support

CaNS supported approximately 300 symposia, conferences, and meetings throughout the year. CaNS also worked in conjunction with Streaming Video Services to provide Internet Streaming for several meetings through the year, the "Director Lecture Series Seminars" being an example. These seminars put on by the PNNL Director's Office host both PNNL and some external lecturers. The recorded meeting is hosted on the Director's website for on-demand viewing.

CaNS staff are also working to upgrade equipment in the Battelle Auditorium. A new projector is on order along with some camera equipment. This will aid in video taping and live streaming from the Battelle Auditorium.

CaNS supported the following major events in Fiscal Year 2006:

- New Zealand visit
- Staff seminars and group meetings
- DOE Basic Energy Sciences Catalysis Initiative
- National Center for Research Resources Advisory Committee
- NMR Conference
- CH2M Hill Technical Exchange
- Actinide Conference
- PNNL Fundamental Science Directorate Review (Battelle Auditorium)
- Washington Round Table Board Meeting

Future Directions

Funding was requested to support the Fiscal Year 2007 activities of CaNS.

- **Facility management**. Oversight, planning and management of the group.

- **Remote user support.** Direct support for users' Unix accounts, including account creation and closure, password management, and file disposition.

- **Auditorium operations.** Technical support, supplies, and equipment for the EMSL auditorium and open conference rooms.

- **Expanded office support.** Expanded support for users and scientific instrument systems and EMSL staff directly supporting those users and systems. Deliverables, in addition to those previously described, include delivery of network passwords to EMSL, support for the EMSL enclave, operating system and application software upgrades and security enhancements for Windows and MacOS, and access to mail and ETR without using SecurID.

- **Unix-based distributed file service.** Operation and management of EMSL's AFS distributed file system, which provides an independent platform, secure access to users' personal file space, shared project file space, and common applications. It also holds EMSL's web areas.
- **Windows based DFS and servers.** Windows user infrastructure including DFS space, user and project directories, some internal web space, mail and print servers, and terminal servers. It holds home directories for thin client users. Includes implementation and rollout of the EMSL thin client prototype, and, based on its acceptance, procurement of more clients.
- **Authentication services.** Operation and management of EMSL's authentication service providers. This includes completion of projects to consolidate authentication under PNNL's Active Directory service, development and implementation of account management policies and scripts, and background activities.
- **Email services.** Operation of EMSL's Unix email server, which provides routing of internal EMSL SMTP mail (generated on EMSL's Unix systems), routing of generic user mail from Unix to Exchange, and EMSL's mail list server.
- **Web application database services.** Operation of EMSL's database and application server, which provides back-end service for EMSL tours and user systems.
- **Security services.** Oversight of computer security issues for EMSL computing. This includes writing security plans, monitoring and responding to security bulletins, scanning EMSL systems, security training, configuration management, watching computer logs and responding to security situations, operating EMSL's Big Brother server, and other related activities.
- **Collaboratory service.** Support for EMSL-developed and -hosted Electronic Lab Notebook System, the virtual NMR, and other collaboratory services. The EMSL Collaboratory Support team assists in creating and supporting collaboration tools with EMSL that allow scientists the ability to access scientific instruments remotely and collaborate with others in a secure and effective manner.
- **Web-based help desk.** Operation of EMSL's web-based help desk system (Footprints), which currently hosts 30 support queues.
- **Web hosting services.** Support and operation of EMSL's web servers (internal and external), which host 11 external EMSL web sites including www.emsl.pnl.gov, mscf.emsl.pnl.gov and six internal sites.

- **Core infrastructure operations.** This encompasses all activities that cannot be described in terms of services a user sees, but are required to make everything work. These include network management and operations, backup services, console server operation, license server operation, building and operating a test environment so things can be tested before they are put in service, implementation of maintenance contracts, computer facility management, and life cycle management. Approximately one quarter to one third of the infrastructure equipment should be replaced each year to keep the infrastructure operating efficiently and securely.

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Instrument Development Laboratory

The Instrument Development Laboratory (IDL) designs, builds, and deploys advanced state-of-the-art instrument systems and custom application software in support of the ongoing experimental research efforts in the W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL). As depicted in Figure 1, IDL staff members support EMSL researchers and users by providing a wide variety of design and fabrication services for hardware and software, custom engineered solutions to research problems, and experience in the interface and control of commercial instrumentation. Most EMSL user projects have unique needs; IDL staff members are especially skilled in the integration of commercial and custom hardware/software packages to suit the exact specifications of specific research projects.

Capabilities

Some of the IDL's most recognizable expertise and capabilities fall into the following areas:

- high-voltage expertise
- radio frequency expertise
- high-speed analog and digital systems
- digital signal-processing and field-programmable gate array technologies
- databases
- laboratory automation
- data acquisition
- instrument control
- common communications methodologies
- software design and implementation (C, C++, Visual Basic, .NET, JAVA)
- embedded systems

Figure 1. IDL and its staff members provide a wide variety of technical support to EMSL staff and users.

The IDL Design Laboratory offers a staffed electronics and fabrication shop for EMSL research staff and facility users. IDL customers will find a fully stocked parts supply, electronic components and small hardware, test, and measurement equipment available for checkout, and ready assistance during business hours. For immediate hardware assistance, customers may access the IDL electronics laboratory and receive assistance from any IDL staff member. For work that is limited in scope and not time-consuming, there usually is no charge to EMSL staff for services. For larger projects, staff may also access the IDL electronics laboratory and speak with an IDL staff member, who will happily assist the customer in defining the work to be done and begin the process of designing solutions.

Custom Software Design, Development, and Support are critical services offered to IDL customers. IDL staff members specialize in several key services related to research: data acquisition, instrument control, laboratory automation, systems integration, data analysis and visualization, data management and archiving, and handheld and embedded systems. Using a modular code design model as their basis, IDL software developers can efficiently develop software in a number of languages, tools, and scripts (e.g., Visual Basic, Java, C, C++, .NET, Labview, Assembly, Access, and SQL Server). In addition, software developers are skilled in a number of instrument control strategies, including General Purpose Interface Bus, Serial (RS-232), infrared, Transmission Control Protocol/Internet Protocol, Analog and Digital I/O, and high-speed event counting and timing.

The IDL Support Queue is accessible by customers via e-mail (idl-support@emsl.pnl.gov). The queue is monitored daily, and customers are encouraged to submit their requests for any type of service offered by IDL.

The IDL Website at http://idl.emsl.pnl.gov provides a full description of IDL capabilities, access to the support queue, team highlights, recent projects, statement-of-work access, and a downloadable business plan.

IDL Technical Support is readily available to assist research by providing software modifications, troubleshooting, equipment fabrication, and research instrumentation support.

Future Directions

The IDL must play an integral role in the EMSL recapitalization effort. EMSL users and resident scientists will drive the selection and development of new instruments and methods; the role for this group must be to work with the scientists to provide insights into what is possible from a technology standpoint and expert opinions on the best and most efficient means of accomplishing the task. Past instances where research staff have, for instance, purchased $10K digital to analog converter boards that were not optimal for their needs points to the necessity of constant and facile communication between IDL engineers and scientific staff and users.

Some of the technologies that have the potential to “change the game” in environmental molecular science capabilities are detailed below. These technologies may offer the possibility of ten times the increase in speed or signal to noise, or they may make new measurements feasible. Continuing communication of these capabilities to EMSL staff and users must be an important component of the group’s strategy to maximize impact on the EMSL recapitalization effort.

- **Instrument automation and remote control** continue to evolve as software tools improve and network bandwidth increases. Automated instrument control can provide huge efficiency increases, freeing up EMSL staff and user time to analyze data, write up results or perform other research activities. New capabilities are currently being developed in Microsoft Visual Basic .NET, while old applications in Microsoft Visual Basic 6 will need to be ported to .NET.

- **Remote instrument control** offers the possibility of making EMSL capabilities available to users remotely, minimizing travel cost and time, and maximizing impact to the user community. The group proposes to develop a project plan, including timeline, cost, technical approach and milestones, to implementing remote control of heavily used instruments that can accommodate such a capability. Technologies such as these are essential to maximizing the IDL's impact in support of the user community.

- **Field programmable gate array (FPGA) technology** is being exploited in a new field known as reconfigurable computing. Programmable logic implements algorithms instead of sequential stored instructions. Performance gains of several orders of magnitude are possible with select algorithms. This dramatic improvement is clearly applicable to supercomputers and needs to be fully exploited if EMSL is going to remain on the leading edge of computational sciences. This effort must include FPGA architecture investigation, inter-FPGA communication, algorithm design and implementation, and testing and validation.

- **Digital signal processing** needs to be more extensively exploited to improve the performance of existing instruments. Doubling the signal-noise ratio of a given instrument is equivalent to acquiring a second instrument without the cost, support, and floor space.

- **Information management (informatics)** has become both a challenging problem and an area where the IDL has had a large impact. Proteomics research results in large datasets requiring information management systems that enable high throughput. The data production from imaging research can easily exceed the data volume produced by proteomics. These two emerging areas have highlighted the importance of information management. Facility staff have developed several man-years of experience with the PRISM system, and this technology is readily transferred to the imaging domain. As more and more projects and users rely on data management, an obvious need for a common platform emerges. It is essential to build this capability in EMSL. The development to date has been completed on projects specific to proteomics and imaging. The value of this system is seen in all aspects of the mass spectrometry research and in the proteomics capability utilized by many user projects, as well as to the Genomes to Life protein complex project, and a number of DOE Office of Biological and Environmental Research- and National Institutes of Health-funded projects. Continued development of the informatics capability will allow EMSL to support more users and increase the amount of research that can be accomplished with limited resources.

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Publications

Publications by EMSL staff members and from users where the publication resulted from research carried out at EMSL are listed below.

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