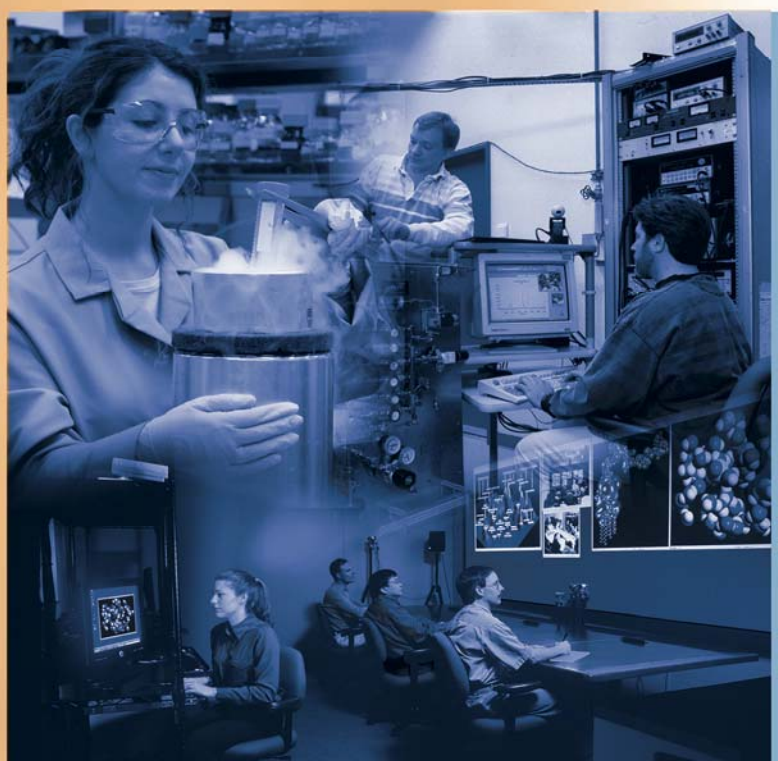
ENVIRONMENTAL MOLECULAR SCIENCES LABORATORY

EMSL

W.R. Wiley Environmental Molecular Sciences Refreshment Plan: Capital Equipment Section

2006



William R. Wiley
EMSL
Environmental Molecular Sciences Laboratory

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Capital Equipment Section

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Executive Summary

The William R. Wiley Environmental Molecular Science Laboratory (EMSL) is a National Scientific User facility operated for the DOE and located at Pacific Northwest National Laboratory. EMSL is currently in its tenth year of operation. The vision that directed the development of the EMSL has led to significant scientific progress and impact in several areas including: mass spectrometry for atmospheric and proteomics applications, nuclear magnetic resonance relative to biological and environmental applications, and understanding of oxide and mineral surfaces relevant to biogeochemistry, catalysis, and energy needs. Our scientific staff and users are recognized nationally and internationally for their significant contributions to challenging scientific problems. We have explored new scientific frontiers by organizing a vibrant and diverse user community in support of our mission as a scientific user facility that provides integrated experimental and computational resources in the environmental molecular sciences. Users from around the world—from academia to industry and national laboratories to international research organizations—use the resources of EMSL because of the quality of science that EMSL enables.

Enabling high impact science, a quality user program and safe and secure facilities requires continual planning and evaluation of instruments, staffing needs, and facilities. After nine years of operation, some EMSL instruments need to be replaced, infrastructure needs are increasing, and support to users has been stretched. Of even greater importance, through the efforts of many researchers including those using EMSL, the scientific forefronts have advanced and there are new research opportunities that require updated and advanced capabilities and/or an updated mix of tools and capabilities. The challenge is not simply to keep EMSL capabilities up to date, but to focus and equip EMSL to remain at the forefront of environmental molecular science research for the next decade. The increasing need for refreshment and revitalization of EMSL has been expressed by the EMSL User Advisory Committee as well as in a 2005 Committee of Visitor review of BER programs and a 2005 BERAC review of the EMSL User Program.

The EMSL capital equipment section of the refreshment plan is intended to be a blueprint guiding the refreshment EMSL's scientific capabilities and facility over a five-ten year period. The overall plan is based upon a series of planning activities that have taken place over the past year. Significant among these activities were two EMSL sponsored workshops related to developing new capabilities for the facility. The first workshop, "The Environmental Molecular Sciences Laboratory, Radiological NMR Spectroscopy Workshop" was held on May 1-2, 2006, and included 36 participants from 6 countries brought together to discuss the possibilities and value of a growth of radiological capabilities with an emphasis on NMR and EPR capabilities. The second workshop, "The Development of New User Research Capabilities in Environmental Molecular Science" was held on August 1 and 2, 2006 and included 104 workshop participants representing 40 institutions including 24 Universities and 5 National Laboratories. This workshop was

organized around EMSL's four science themes: Atmospheric Aerosol Chemistry, Biological Interactions and Interfaces, Science of Interfacial Phenomena, and Geochemistry/Biogeochemistry and Subsurface Science. These science themes are described in more detail in the EMSL Strategic Plan and the supporting science theme documents.

In each science theme area participants collective views were gathered in three areas:

1. Key scientific challenges in the area of environmental molecular sciences that should be addressed over the next ten years. *(i.e. What science challenges should EMSL capabilities be updated to address?)*

2. Important technical challenges and opportunities that if adequately addressed will provide the research tools to enable progress on the scientific challenges. *(i.e. What are the research techniques that will fuel cutting edge science and should be included in the EMSL?)*

3. Recommendations on specific capabilities where investments should be made to meet or address the technical challenges.

The workshop announcement was broadly distributed to National leaders in all four of the science theme areas in addition to the EMSL user community. The workshop summary was sent to participants for their comments and additions and to many invited participants who were unable to attend but wished to provide input.

Both workshop reports are included as appendices to this plan.

Other direct sources of input for this report included numerous recapitalization meetings and reviews involving both EMSL staff and users as well as recent reports from the National Research Council. In the latter regard, the most recent NRC report on "Visualizing Chemistry: The Progress and Promise of Advanced Chemical Imaging" was especially valuable as noted later in this plan.

This plan will be reviewed annually to take account of changing strategic circumstances, new technologies and updated priorities. The final version of this plan will describe planned investment in three Sections: 1) Capital equipment (CE), 2) programmatic General Plant Project (GPP) and line item requests and 3) Operations expense funding (expense). This version specifically addresses only capital equipment.

Capital Equipment (CE) Investments

EMSL plans to maintain its scientific impact by focusing attention, capability development and investments in specific areas identified as high-priority science themes. These science themes provide the basis for defining and developing key capabilities that can have significant impacts on important areas of environmental molecular science that are critical to DOE and the nation. The science themes provide the basis for decision making by EMSL management on future investments in staff expertise and capital equipment and the science themes formed the basis for the workshops and discussions held over the past year in formulating this refreshment plan and the CE investments described in this section. However, it also became clear during the workshops that many

of the CE investments would contribute significantly to more than one science theme. Hence the CE investments are organized into cross-cutting capability areas outlined in the most recent recapitalization workshop report. These cross-cutting capability areas are: Microbial Dynamics and Visualization Capabilities, Surface Dynamics and *In Situ* Capabilities, Multiscale structure synthesis and high resolution characterization, Enhanced NMR, EPR and Mass Spectrometry Capabilities, and Information Infrastructure and Storage. Information on how these capabilities address scientific challenges in the four EMSL science themes are given in the EMSL recapitalization workshop report.

We project that a capitalization investment of approximately $85M investment over the next 5-6 years will be required to move EMSL into its second decade of operation (Table 1). This represents an investment of approximately 55% of the original EMSL capitalization budget of approximately $120M and subsequent capitalization investments totaling $20M over the past 9 years. Investments of approximately $10-20M annually for the next five years will result in a substantial refreshment of EMSL's capabilities and enable EMSL to maintain outstanding capabilities to enable world class science.

Table 1 illustrates the total cost per investment category. In addition to the cross-cutting capability areas described above, we have also added a General Tactical Investment Category. This category is added to capture smaller investments such as equipment upgrades, repairs and replacements of existing equipment, and immediate tactical investments by the facility management (generally <$400K per item) that are necessary to respond to new advancements and opportunities. Details on each of these investment categories are provided in later sections.

Table 1: Planned Total CE cost by investment category (in thousands of dollars). The final tactical investment category was adjusted to the nearest thousand dollars to exactly match budget guidance for each year.

Investment Category	FY07	FY08	FY09	FY10	FY11	FY12	Total
Enhanced Mass Spectrometry/ Nuclear Magnetic Resonance / Electron Paramagnetic Resonance	$ 1,200	$ 1,000	$ 1,500	$ 4,500	$4,200	$3,000	$15,400
Microbial Dynamics and Visualization Capabilities	$ 1,900	$ 1,000	$ 1,000	$ 1,500	$ 1,900	$ 1,900	$ 9,200
Surface Dynamics and In Situ Capabilities	$ 700	$ 5,500	$ 2,600	$ 2,300	$ 3,000	$3,800	$17,300
Multiscale Structure Synthesis and High Resolution Characterization	$2,250	$ -	$ 1,900	$ 4,400	$ 3,900	$ 4,000	$16,450
Information Infrastructure and Storage	$ 500	$ 500	$ 900	$ 2,000	$ 2,000	$ 2,000	$ 7,900
General Tactical Investments and Replacements/Upgrades	$ 2,254	$ 804	$ 2,213	$ 2,800	$ 5,000	$ 5,300	$18,971
Total Investment	**$8,804**	**$8,804**	**$10,113**	**$17,500**	**$20,000**	**$20,000**	**$85,221**

It cannot be over emphasized that significant technological advances have been taking place in all areas since EMSL was established. Although many areas of importance (and related equipment) for environmental molecular science are readily identified now, it is also clear that significant scientific and technical advances will occur over the next five year period. We have, therefore, identified general needs and the technical approaches we would consider at this time. Focusing on need identification will also allow us to take advantage of technology advances as they occur. Therefore, although this plan forms the basis for the EMSL investment strategy, each FY EMSL management will evaluate the planned investments for the next FY and beyond, taking into account technological advances as well as input from the user community DOE and other stakeholders.

Enhanced Capabilities in NMR, EPR, and Mass Spectrometry

The EMSL has been one of the world's leaders in the development and application of mass spectrometry and NMR to issues in the environmental molecular sciences. In the EMSL recapitalization workshop these capabilities were viewed to be as important or more important in the future. Therefore, there was a strong recommendation that EMSL make certain critical investments in these areas. In particular, opportunities for new capabilities were identified in mass spectrometry and EPR and, in the case of NMR, major recommendations to invest in new unique probes (e.g. cryogenic or controlled environment) and other facility upgrades.

The MS investments include one major investment in a new "EMSL flagship capability" in high resolution MS analysis with the overall objective of obtaining entire proteome determination in a single LC-MS experiment. This investment is currently envisioned to be the 21 Tesla FTICR being considered for development at the National High Magnetic Field Laboratory at Florida State University (Table 2). Investments in two other critical areas of MS are also planned. One of these targets post-translational modifications of proteins and the other particle imaging and analysis. Investments in capabilities for determining post-translational modification of proteins are planned for FY07 and FY08 with an upgrade scheduled in the outyears (FY11). The imaging and analysis area impacts several different science theme areas including biogeochemistry, biological interactions, and aerosol chemistry in terms of the ability to analyze surfaces. Investments in this area are scheduled for FY08. Taken together these capability should keep the EMSL at the forefront of research in MS analysis in environmental molecular science.

Planned EPR investments include upgrading our current pulsed and continuous wave (CW) EPR systems to higher frequency capabilities (9.5 to 35GHz), the purchase of a new EPR instrument with higher magnetic fields and frequencies (95GHz) in FY09, and another longer term EPR upgrade in the outyears (FY12). These investments should allow the EMSL to meet the long term science challenges in the biological science and biogeochemistry areas related to characterization of metalloproteins and membrane proteins as well as allow transfer of an instrument to the proposed radiological annex (to be described in the GPP section of this refreshment plan). The need for EPR capabilities

in the area of actinide chemistry was a strong recommendation from the Radiological NMR Workshop report.

The investment in specialized NMR probes, including the development of cryogenic probes and controlled atmosphere probes, is scheduled early in this refreshment plan along with an upgrade in the outyears. Investments in NMR supercooled detector systems were also a general recommendation in the NRC report on Visualizing Chemistry. The EMSL also has an opportunity to acquire a 600 MHz shielded system from another program at reduced cost. Purchase of this instrumentation will allow expansion of the user program and reduce floor space needs relative to our current unshielded system. Hence, this investment is also planned for early in the refreshment plan.

Finally, there is a long term investment planned for the outyears in coupling NMR and MS methods with applications directed at the growing field of metabolomics. While details of such long term investments are yet to be determined, it is useful to note that the general area of multi-technique imaging was identified as the "Grand Challenge" in Chemical Imaging in the recent NRC report. This overall theme of development of multi-technique capabilities reoccurs throughout this refreshment plan.

Table 2. Planned investments in NMR, EPR, and mass spectrometry.

	FY07	FY08	FY09	FY10	FY11	FY12	Total
Enhanced Mass Spectrometry/ Nuclear Magnetic Resonance / Electron Paramagnetic Resonance							
High Performance Mass Spectrometry for Proteomics (e.g. Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometer 21 Tesla magnet)				$3,000	$3,000	$1,500	$7,500
Mass Spectrometry methods for determining post-translational modifications of proteins (e.g. electron transfer and capture dissociation).	$100	$300			$400		$800
Particle imaging and analysis using high-resolution mass spectrometry (e.g. Desorption electrospray ionization)		$500					$500
EPR upgrade to 35GHz	$300						$300
Characterization of large membrane proteins and metalloproteins (e.g. Electron Paramagnetic Resonance (EPR) system).			$1,500				$1,500
Enhanced capability for membrane analysis (e.g. updated EPR)						$1,500	$1,500
600 MHz NMR magnet and console	$400	$200					$600
Special NMR probes (cryo and controlled atmosphere)	$400				$400		$800
Development of next generation metabolomics capability (e.g. Coupled Mass Spectrometer (MS) and Nuclear Magnetic Resonance (NMR) separations systems).				$1,500	$400		$1,900
Total	**$1,200**	**$1,000**	**$1,500**	**$4,500**	**$4,200**	**$3,000**	**$15,400**

Microbial Dynamics and Visualization Capabilities

The EMSL recapitalization workshop report lists a great many capabilities to be included in this research area, which is focused on understanding the dynamics of living cells and microbial communities. Not all of the recommended capabilities can be accommodated by the projected budget, so priority was given to those items essential to establishing

EMSL as a unique and powerful resource for investigating biological interactions and interfaces.

To accomplish this goal, we propose to build an integrated capability for growing and analyzing both microbial monocultures and communities (see Table 3). This includes chemostat systems for continuous growth of microbes under controlled conditions and instruments for the growth of defined microbial biofilms. These systems will enable continuous monitoring, sampling, and analysis of microbes under a variety of different environmental conditions, thus creating an extremely rich dataset for understanding metabolic and gene regulatory networks. This will provide a fundamental basis for understanding microbial functions at a systems level, which is necessary for future efforts in re-engineering microbial systems for a variety of different uses.

Conceptually, the Microbial Dynamics and Visualization Facility (MDVF) can be divided into two areas: 1) chemostat-based instrumentation for analysis of individual cellular properties, and 2) biofilm-based instrumentation to understand both the interaction of cells as communities and their interaction with solid surfaces. Much of the proposed instrumentation will be devoted to continual live-cell monitoring of either the chemostat or biofilm systems, but we also propose a suite of instrumentation for analyzing samples collected from either system. Monitoring will include both molecular and cell-based measurements.

For the chemostat-based instrumentation, we envision a collection of bioreactors that have been modified to allow continuous sampling. Cell samples can be analyzed immediately using attached flow cytometers or microscope flow cells. Alternately, samples can be automatically concentrated and flash-frozen for later biochemical analysis (e.g., proteomic, genomic, and metabolite analysis). Headspace gas samples can also be continuously sampled and analyzed by mass spectrometry, and the medium can be analyzed by HPLC for metabolite production or depletion. Data and samples will be collected and logged automatically by an integrated data management system. Chemostats will also be combined with NMR instrumentation to allow continuous monitoring of cellular metabolism.

The biofilm-based instrumentation will be built on a custom multiphoton imaging platform that will allow visual monitoring of gene expression patterns and cellular properties. This platform will also support the use of multispectral approaches for analyzing protein interactions within living biofilms, such as fluorescence resonance energy transfer (FRET). It will also enable the use of fluorescence reporter probes for monitoring the cellular microenvironment. Other custom instrumentation will allow the direct measurement of electron transfer and ion distribution within the biofilms. A combined NMR/confocal instrument will permit the simultaneous monitoring of the spatial distribution of different cells, gene expression patterns, and metabolite profiles.

A suite of support instruments will be assembled to analyze the molecular properties of cells and samples that will be generated by the facility. In particular, a set of high-resolution, multiscale, multispectral microscopes will be obtained and modified for the

MDVF. These instruments will be capable of extremely high optical resolution using structured illumination or other innovative technologies. We will obtain instruments that are capable of simultaneous atomic force and single-molecule fluorescence imaging for correlating topographical properties with chemical information of cellular nanostructures and proteins. An enhanced Cryo-transmission electron microscope will be obtained for analysis of multiprotein complexes and cellular structures. Supporting the suite of analytical instruments will be equipment for biofilm dissection and cell isolation, such as a laser-capture microdissection apparatus as well as fractionation tools, such as zonal centrifuges and free-flow electrophoresis equipment.

We also propose to create a new instrument for a 2D biomolecular imaging system based upon a MALDI Q-TOF mass spectrometer that is modified by a PNNL-designed/developed ion mobility separation (IMS)/ion funnel front end. This system would build upon our proteomics capability to include ultra-sensitive imaging of biological surfaces (e.g., microbial biofilms) and be a major advance in the state of the art because of the incorporation of added information from the IMS. Importantly, the system will be ultra-sensitive because of the incorporation of PNNL ion funnel technology, and the MALDI stage will operate at 10 to 50 torr, thus allowing use of “wet” samples.

The timeline and prioritization of equipment acquisition is based on both a necessary sequence of events (i.e., samples must be generated before they can be analyzed) and a critical need to enhance some current EMSL capabilities. Thus, the initial purchases in FY07 will be to enhance our optical microscope capability and obtain fractionation equipment necessary to analyze current samples. This will be followed in FY08 by the acquisition of the chemostat-based instrumentation necessary to generate the next generation of biological samples.

During FY09, we will acquire the biofilm-generating and monitoring instrumentation (NMR:confocal-based) and the optical instruments necessary for biofilm analysis. We will then expand our ability to analyze biofilms and microbial communities in FY10 by constructing the 2D mass spectrometry-based analyzer and the enhanced, multispectral imaging microscope. We will also upgrade our chemostat-based instrumentation by adding continuous NMR-based monitoring. In the following year (FY11), we will use the experience gained with the first generation of chemostat and biofilms-based instrumentation to expand to a fully functional, state-of-the-art facility.

We believe that acquiring and modifying all the instrumentation planned for the MDVF in two phases is prudent because much of it will be unique. Experience gained during Phase 1 will usefully inform the decisions made in Phase 2. In FY11 we will also upgrade our capabilities for investigating cellular process at the molecular level (i.e., single-molecule microscopy). Finally, in FY12 we will upgrade our capabilities for cellular and subcellular imaging (e.g., Cryo-Transmission Electron Microscope (TEM) enhancements) and build a second-generation proteomics/biomolecular imaging system.

Table 3. Planned investments in microbial dynamics and visualization.

Microbial Dynamics and Visualization Capabilities	FY07	FY08	FY09	FY10	FY11	FY12	Total
Three Dimensional Laser confocal microscope	$1,200						$1,200
Microbial fractionation & characterization capabilities (e.g. laser microdissection, microtome).	$700						$700
In situ capability for the study of cell and microbe dynamics (e.g. growth chambers, coupled confocal and optical methods).		$1,000			$500		$1,500
High speed, multiscale, multispectral microscopes for imaging of biofilms and cellular communities			$500	$500			$1,000
Enhanced capabilities for cellular and sub-cellular imaging (e.g. Cryo-Transmission Electron Microscope (TEM) enhancements).						$1,400	$1,400
Capabilities for dynamical studies of living cells (e.g. Micro-Raman Atomic Force Microscope/Laser Confocal Microscope with wet cell capability).					$900		$900
Proteomics/biomolecular imaging system (2D scanning Q-tof mass spectrometer)				$500		$500	$1,000
In situ probes for bioreactors (e.g.NMR centric chemostats, combined NMR:confocal microscope).			$500	$500	$500		$1,500
Total	$1,900	$1,000	$1,000	$1,500	$1,900	$1,900	$9,200

Surface Dynamics and In Situ Capabilities

Although significant progress has been made (and will be made) using *ex situ* analysis which inherently involves removing specimens from the actual conditions of interest, techniques that facilitate analysis at the temperature and in environmental conditions of technological and scientific interest are both increasingly valuable to the developing science and increasingly possible as technology advances. Methods associated with surface dynamics and *in situ* capabilities were identified as highly important in the EMSL recapitalization workshop by the independent working groups in each of the four science theme areas.

To a large extent, the methods listed in this section involve three different categories of experimental approach (and combinations of them with other methods): those based on optical methods, vacuum based electron or ion techniques, and those associated with scanning probes (see Table 4). Optical (or photon based) methods are applicable in many transparent environments and are readily associated with dynamics and time dependence for time frames that vary from femto-seconds to hours or longer. Electron beam and electron spectroscopy techniques involve vacuum, and a special effort is required to use them in operando or nearly operando conditions. Fortunately, modern environmental cells and differential pumping methods enable electron beam methods to be used in increasingly realistic conditions and the ability to obtain physical (and sometimes chemical) information at very high resolution make them highly valuable for many types of studies. Scanning probe microscopy methods have been and will continue to be used to obtain many types of chemical and physical information in many different environments.

In the suite of equipment proposed in this area over a six year period, five are primarily optically based methods, two combine optical methods with scanning probe technologies, one combines optical and magnetic resonance techniques, and three are based on electron or ion beam methods.

The electron or ion beam methods include what we anticipate will be an "EMSL flagship capability", an aberration corrected transmission electron microscope (TEM) with environmental cells that will allow collection of structural and site specific chemical information in conditions relevant to many catalytic and geochemical studies (planned for FY08). A new generation scanning electron microscope (SEM), also equipped to operate in gaseous environments, will also be important for catalytic and fuel cell work. Because of the large working space around specimens in the SEM we will be able to incorporate optical spectroscopy into the SEM. This developmental investment is planned for the outyears (FY12). The development of a unique instrument that uses secondary ion mass spectrometry (SIMS) to examine the chemical structure of solid/liquid interfaces is proposed starting in FY10 to provide unique information about molecular interactions at at solid\liquid and liquid/liquid interfaces. This altered version of a time of flight SIMS would apply cooling and gas dosing technologies currently used in other areas of surface science to examine model liquid surfaces and interfaces.

Because optical methods are especially valuable in dynamical studies several investments are planned. First, a general capability (the integrated optical system for in situ studies) will enable studies in gaseous, liquid or vacuum environments relevant to catalysis, geochemical, atmospheric and other important materials and interfaces. Because of the need to generate and examine particles *in situ*, another system will be dedicated to examination of aerosol growth. Two investments in laser systems are also planned. The first system is a general upgrade to our ultrafast laser capability in the EMSL. This capability will enable study of excited state kinetics, charge transfer kinetics (relevant to photovoltaic cells) and other processes that occur on the scale of 10s of femto-seconds. The second system is dedicated to second harmonic and sum frequency (SHG and SFG) analysis of interfaces (solid-solid, solid-liquid, liquid-liquid) which have previously been primarily the domain of highly specialized research groups. Fortunately, technology advances now allow a much more user friendly application of these techniques which has been identified as important in atmospheric, biogeochemical and subsurface, and interfacial science theme areas. Therefore, an investment in this area is planned for FY07. As indicated above, there have been rapid advances in several technologies due to advances in materials associated with light sources and photon detectors. Near the end of the funding period a new generation system for real-time operando measurements taking advantage of the newest (at that time) photon generation and detector technologies is planned. The objective will be to speed data collection and enhance the types of chemical information that can be collected for real time experiments.

Optical and scanning probe methods will be combined in at least two different ways. The combination of scanning probes with optical probes allows the determination of both physical and chemical properties at high spatial resolution. An investment in this area is planned for FY10. In addition, the use of the electric field concentration around a metal

tip enables even higher resolution application of optical methods. However, the tip enhance methods are a rapidly advancing and challenging research area. Hence, the incorporation of these methods into the user program is planned for the outyears of the refreshment program. Another combined approach is linking NMR with optical methods. The development of probes that allow temperature and environmental control in NMR and the addition of optical measurements will further enhance a new approach to "operando" spectroscopy. This developmental investment is currently planned for FY11.

Finally, imaging and characterization of the 3D structure of soils and sediments at the micron scale is a key factor in unraveling the mechanisms of subsurface fate and transport of environmental contaminants. An investment in this capability is scheduled in FY10.

Table 4. Planned investments in surface dynamics and *in situ* capabilities.

	FY07	FY08	FY09	FY10	FY11	FY12	Total
Surface Dynamics and In Situ Capabilities							
Field Emission High Resolution Transmission Electron Microscope with Aberration Correction, Monochromator, and Environmental Cell		$4,500					$4,500
In situ measurements - combined microscopy and spectroscopy (e.g. environmental SEM other spectroscopies for high spatial resolution studies in realistic conditions)					$1,000	$900	$1,900
In situ measurements - for depth resolution in solid/liquid interface sytstems (e.g. Specially Designed Secondary Ion Mass Spectrometer (SIMS))				$1,000	$500		$1,500
Integrated Optical Spectroscopy for in situ (operando) analysis - (e. g. combined optical system with liquid, gas and vacuum environmental cells allowing FTIR, UV Vis, RamanOptical capabilities coupled to environmental cells for catalysis, solution (geochemistry), sensor and aerosol studies.)			$800	$500		$100	$1,400
Temperature controlled aerosol growth chamber interfaced with Fourier Transform Infrared (FTIR) spectrometer and related components		$1,000				$100	$1,100
Ultra fast spectroscopy and microscopy laser detection systems (e.g. femto second portable laser to combine with photoelectron emission microscopy (PEEM) for imaging of charge transfer movement on 10s nm resolution relevant to photocells and high speed variable frequency laser time resolved kinetics, adsorption, e-h pair formation etc.)			$1,000				$1,000
Optical probes for interfacial reactivity (e.g. Second Harmonic Generation and Sum Frequency Generation)	$700						$700
Next Generation System for Real-time Operando chemical structure determination (e.g. enhance photon based spectroscopy - advanced sources and detectors)						$1,600	$1,600
Combined scanning probe microscopy and spectroscopy system (combined scanning probe with optical microscopy capabilities, Raman, IR instrumentation)			$800				$800
User Optimized High Spatial resolution optical system (e.g. tip enhanced optical properties)					$400	$500	$900
Tools for examining the growth and reactions of minor components in particles in-situ (e.g.environmentally controlled NMR probe and ultrafast optical probes).				$200	$1,100	$600	$1,900
Imaging of sediment structure and reactivity (e.g. X-ray and NMR)				$600			$600
Total	**$700**	**$5,500**	**$2,600**	**$2,300**	**$3,000**	**$3,800**	**$17,900**

Multiscale Structure and High Resolution Characterization

Pioneering fundamental research usually involves differing levels of sample synthesis, preparation and/or characterization. The need for synthesis and characterization capabilities cuts across all four science themes from determining microbial cellular structures, to aerosol particle characterization, to subsurface systems. Increasingly research involves the examination of both fundamentally and practically important processes that occur at specific sites or involve biological and material structures involving hierarchical structures that vary from nanometers to millimeters in size. The capabilities proposed in this area include: a unique system for synthesis of complex oxide films and surfaces; tools to synthesize and use micro-systems for microfuidics and micro-sensor components, and a number of important characterization tools that can be applied to synthetic and natural materials.

The major equipment item proposed in this area is focused on the synthesis of well defined single crystal oxide films and surfaces with increasingly complex composition (Table 5). The application of oxygen plasma assisted molecular beam epitaxy (OPA-MBE) to the formation of oxide films has been a unique capability in EMSL that has received world wide attention (and received a Federal Laboratory Consortium Award for technology transfer). The next generation system will be designed for more precise simultaneous control of multiple metal fluxes to a substrate to enable the growth of relative complex oxides in a highly controlled fashion. This investment is planned for FY10. The OPA-MBE system is a sophisticated research tool that involves both the growth chamber and advanced analysis tools. Once the methods for producing a particular type of crystal film are established, it will be possible to use a somewhat simpler system to more routinely produce films for materials, fuel cell, and biogeochemical studies thus impacting a much broader user community. This investment is planned for the out years.

Micro-systems were an important part of the discussions at the EMSL recapitalization workshop since they are increasingly useful in various types of research. Custom microfluidic and microsensor based systems can be used as part of mass spectrometer related analytical separations, for the creation of sensor array systems and to assist in custom designed materials for reactive transport studies. Therefore the capability plans include both lithography capability that can assist development of special devices and support for development of microfluidics systems in the area of flow studies and separations. This investment spans the FY07-FY10 time frame.

In the area of characterization tools for synthetic and natural systems investments are planned in three areas: surface and interface characterization, single site chemistry, and buried interfaces/3D analysis. In the surface and interface category the first planned investment is a new XPS instrument with enhanced capability for depth resolution. XPS capabilities are one of the most oversubscribed capabilities in the EMSL, so an initial investment is planned for FY07 with a follow on investment with enhanced performance in 2011. A highly surface sensitive time of flight secondary ion mass spectrometer (TOF-SIMS) is a planned FY07 investment recommended in the atmospheric and

interfacial areas because of the abilities for biological imaging, organic analysis (primarily applied to atmospheric chemistry and nanoscience), and microbial forensics (biothreat attribution).The less surface sensitive but very small area nanoSIMS instrument was mentioned in each of the science theme areas during the recapitalization workshop because of the ability to detect trace components in a variety of materials with nanometer resolution. This nanoSIMS purchase is currently planned for FY09. Our current accelerator based ion beam analysis capability is also highly used for atmospheric particulate analysis, creation and detection of radiation damage relevant to nuclear systems and radiation detectors, the study of ion transport in fuel cells and creation of nanostructured materials, among other areas. The refurbishment of the accelerator and updating of the control system is also proposed. This refurbishment and instrument upgrade is planned for FY11. Finally, in this category we must plan for upgrading/replacing our current TEM which is a very important and highly subscribe EMSL capability. This is in addition too the highly specialized chemically oriented TEM described in the *in situ* section. This new TEM is planned for FY11.

Single site studies are critically important for understanding catalytic and other chemical processes. It is possible to conduct such studies using scanning probe microscopy tools, including STM and non-contact AFM. However, the samples must be exceptionally "clean" to allow such precise measurements. This requires such studies be conducted at low pressures (good vacuum) to obtain the needed resolution and low temperatures are needed to counteract the lower pressures. We therefore plan to develop the first ultraclean low pressure coupled STM/AFM for single site studies in the EMSL. This investment is planned for FY10.

Tools for high resolution three dimensional analyses and characterization of buried interfaces are scheduled in later years of the refreshment plan. Plans for these developmental investments will finalize as the technologies evolve. The extreme importance of high resolution analysis is leading to rapid advances in methods. As one example, a new instrument based on a high resolution ion beam has the potential to provide a spatial resolution comparable to that currently available only through electron microscopy, but which might offer additional surface chemical information at approximately the same spatial scale. This instrument is still in the development state, but it is a method that might provide a revolution in high resolution three dimensional chemical and microscopy analysis if the technology proves to have the long term stability required for a useful instrument. For analysis of buried interfaces, advances in the energy resolution available during medium energy ion scattering (MEIS) are helping to provide highly detailed information about interface structures for interfaces about 100 nm below the outer surfaces of single crystal films (such as grown by OPA-MBE). This is important information, but other more general approaches may be available within a couple of years.

Finally it is important to note that EMSL was able to obtain some of the capabilities recommended in the workshop report with currently available funds. Prominent among these capabilites was a focused ion beam (FIB). FIB technology is increasingly useful for the preparation of samples for analysis by TEM, SEM and Auger electron

spectroscopy. The type of sample preparation and analysis provided by a new generation FIB/SEM capability is critically important to EMSL, and was identified in atmospheric aerosol chemistry, biogeochemistry, and interfacial science theme areas.

Table 5. Planned investments in multiscale structure synthesis and high resolution characterization.

	FY07	FY08	FY09	FY10	FY11	FY12	Total
Multiscale Structure Synthesis and High Resolution Characterization							
Next generation complex oxide synthesis system (e.g. OPA MBE optimized for complex oxides)				$2,200			$2,200
Materials capabilities for high throughput production and analysis (e.g parallel materials production and optimized analysis methods)						$1,500	$1,500
Microfluidics and lithography capabilities	$300		$300	$500			$1,100
Scanning X-ray microscope (new XPS with enhanced depth resolution capability)	$750						$750
Instrument for rapid determination of surface chemistry and composition (e.g high resolution, high intensity X-ray Photoelectron Spectrometer (XPS)					$1,500		$1,500
Time of Flight Secondary Ion Mass Spectrometer for biological imaging, organic analysis (including atmospheric chemistry), and microbial forensics.	$1,200						$1,200
Capabilities for enhanced imaging and spectral resolution of cellular structures, aerosol particles, nanoparticles (e.g. Nano Secondary Ion Mass Spectrometer (NanoSIMS))			$1,400				$1,400
Next genertion high resolution "workhorse" Transmission Electron Microscopy					$1,500		$1,500
Accelerator refurbishment and instrumentation upgrades					$500		$500
System for chemical measurements at specific reaction sites, (e.g. variable temperature, cryo-shielded Ultra High Vacuum (UHV) Scanning Tunneling Microscope/Atomic Force Microscope (STM/AFM)).			$200	$1,700			$1,900
Buried Interface Analysis Techniques (e.g. Medium energy ion scattering or ultrasonic scanning probe instrument)					$400	$1,100	$1,500
Advanced 3D (e.g. Ion Microscope)						$1,400	$1,400
Total	**$2,250**	**$0**	**$1,900**	**$4,400**	**$3,900**	**$4,000**	**$16,450**

Information Infrastructure and Storage

Two general areas of investment are planned in this area, upgraded archive storage and general data management (Table 6). The EMSL data archive provides storage for scientific data generated by EMSL instruments. It consists of disk and tape data storage devices. Each year additional storage is acquired to provide room for the growth in storage requirements. The area of general data management was a major topic of discussion at the EMSL recapitalization workshop where it was agreed that defining the specific investments would require a follow-on workshop with different level of technical expertise. However, one of the clear needs was for the envisioned Microbial Dynamics and Visualization Facility which will enable the creation of large-scale data sets that are necessary for understanding organisms from the systems level. This will require the creation of a comprehensive data management system to link analytical data, such as proteomics and metabolomics measurements, to the metadata describing the physiological state of the cell and other important experimental details.

Table 6. Planned investments in information infrastructure and storage.

Information Infrastructure and Storage	FY07	FY08	FY09	FY10	FY11	FY12	Total
Archive Storage for 2007	$500						$500
Archive Storage for 2008		$500					$500
Archive Storage for 2009			$500				$500
Data management capabilities for 2009			$400				$400
Archive Storage for 2010				$1,000			$1,000
Data management capabilities for 2010				$1,000			$1,000
Archive Storage for 2011					$1,000		$1,000
Data management capabilities for 2011					$1,000		$1,000
Archive Storage for 2012						$1,000	$1,000
Data management capabilities for 2012						$1,000	$1,000
Total	**$500**	**$500**	**$900**	**$2,000**	**$2,000**	**$2,000**	**$7,900**

General Tactical Investments and Replacements/Upgrades,

This category includes numerous instrument upgrades and replacements and small (<$400K) tactical investments as needed (Table 7). These could include: vacuum and turbo pumps, uninterruptable power sources (UPS's), lasers, liquid chromatography instruments, Ultramicrotomes, microscopes (e.g., infrared, confocal), mass spectrometers (e.g., Inductively Coupled Plasma, Proton-Transfer Reaction), small computer clusters (<100 nodes) for science theme areas, subsurface flow and transport intermediate scale cells, and miscellaneous equipment such as Mossbauer cryostats, solution synthesis capability, mobility particle sizer, infrared diode array detector, Total Nitrogen/Total Carbon analyzer, ion chromatograph, Contact Profilometer, Walk-in Fume Hood, Carbon Coater, Molecular Beam Epitaxy (MBE) Chamber upgrades, and Ultraviolet Light Source.

Table 7. Planned tactical investments and replacements/upgrades.

General Tactical Investments and Replacements/Upgrades	FY07	FY08	FY09	FY10	FY11	FY12	Total
Replacements/Upgrades	$2,254	$804	$2,213	$2,800	$5,000	$5,300	$18,371
Total	**$2,254**	**$804**	**$2,213**	**$2,800**	**$5,000**	**$5,300**	**$18,371**

The attachments contain the two EMSL workshop reports upon which much of this capital equipment section of the investment plan is based.

ENVIRONMENTAL MOLECULAR SCIENCES LABORATORY

EMSL

The Development of New User Research Capabilities in Environmental Molecular Science Workshop

August 1-2, 2006

William R. Wiley
EMSL
Environmental Molecular Sciences Laboratory

The Development of New User Research Capabilities in Environmental Molecular Science:

Workshop Report

Held August 1-2, 2006
W.R. Wiley Environmental Molecular Sciences Laboratory
Richland, WA

Executive Summary

On August 1, and 2, 2006, 104 scientists representing 40 institutions including 24 Universities and 5 National Laboratories gathered at the W.R. Wiley Environmental Molecular Sciences Laboratory, a National scientific user facility, to outline important science challenges for the next decade and identify major capabilities needed to pursue advanced research in the environmental molecular sciences. EMSL's four science themes served as the framework for the workshop. The four science themes are 1) Biological Interactions and Interfaces, 2) Geochemistry/Biogeochemistry and Surface Science, 3) Atmospheric Aerosol Chemistry, and 4) Science of Interfacial Phenomena.

Examples of key scientific challenges that were identified in the four science themes included: What are the molecular level mechanisms by which microbes sense changes in environmental conditions? What are the mechanisms of nucleation and growth of cloud droplets and ice crystals? How do we unravel the genesis, properties, and effects of nanominerals and nanostructured materials (anthropogenic and natural) in the environment? How do we understand and control structure-function relationships of surfaces and interfaces, including those relevant to catalysis and energy production.

Examples of key investment needs outlined in the workshop to address these scientific challenges included: system dynamics and in situ capabilities for probing interfacial reactions, nanoscale structure synthesis and characterization capabilities, development of a microbial dynamics and visualization laboratory, enhanced capabilities in mass spectrometry and electron paramagnetic resonance spectroscopy, and enhanced sample synthesis and preparation capabilities. Specific examples of needed capability development of capital equipment are given in each section.

These new investments can impact a wide range of National and Department of Energy needs related to global climate change, subsurface remediation, and development of new energy technologies.

Background

The W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL) was conceived by PNNL Director William R. Wiley and his leadership team some twenty years ago. An extensive set of workshops and reviews were organized involving experts in experimental and theoretical molecular sciences to define the rationale and scope of what is now the W. R. Wiley Environmental Molecular Sciences Laboratory. However, much has changed in the science and technology universe since EMSL was dedicated in 1997, and these changes in science and technology require that we re-examine our priorities and retool capabilities in the context of 21st Century challenges. It was therefore timely to organize a workshop that took both a snapshot of the environmental molecular sciences in 2006 and identified needs for user capabilities for research in environmental molecular sciences for the next decade.

Scope of the Workshop

The objectives of the workshop were to define important science challenges for the next decade, describe limitations in present approaches, and identify major tools and advances in the measurement sciences needed to pursue advanced research in the environmental molecular sciences. EMSL's four science themes served as the framework for the workshop. The four science themes are 1) Biological Interactions and Interfaces, 2) Atmospheric Aerosol Chemistry, 3) Geochemistry/Biogeochemistry and Surface Science, and 4) Science of Interfacial Phenomena. There were 104 workshop participants representing 40 institutions including 24 Universities and 5 National Laboratories.

During the workshop the insights of workshop participants were collected in written form and by taking notes during the discussions. This information was collected to assemble participants' collective views on:

1. Key scientific challenges in the area of environmental molecular sciences that should be addressed over the next ten years. *(i.e. What science challenges should EMSL capabilities be updated to address?)*

2. Important technical challenges and opportunities that if adequately addressed will provide the research tools to enable progress on the scientific challenges. *(i.e. What are the research techniques that will fuel cutting edge science and should be included in the EMSL?)*

3. Recommendations on specific capabilities where investments should be made to meet or address the technical challenges.[i]

[i] The major focus on the workshop was identification of key science and technical challenges and workshop participants were asked to prioritize topics in those areas. The listing of specific capabilities for investment helped clarify the how the technical challenges might be met, but these items were not systematically prioritized.

The workshop involved plenary sessions where experts explored both future issues in areas relevant to EMSL science themes and the frontiers of experimental methods development. Input was collected from participants both by written notes and recorded discussion comments. Four breakout groups worked to synthesize and prioritize the science issues, technological challenges and to identify, where possible, specific investment recommendations. The following sections summarize the outputs from the different breakout groups.

Although the scientific challenges are different in each area, there are several common themes in technical approach or capability needs. These will be summarized in the last section of this workshop report.

This workshop report provides essential information about scientific and potential EMSL user needs regarding equipment and facilities that will be incorporated into a Refreshment Plan for EMSL. The workshop and the report identify needs and the relevance of types and classes of capabilities for the next generation of environmental molecular science. Additional issues such as budget, scheduling, space and facilities as well as input from other workshops will be integrated into a final EMSL Refreshment Plan.

Biological Interactions and Interfaces

Understanding and optimizing the response of biological systems to interactions with their environment can have a significant impact on achieving viable solutions to several problems of national concern. For example, anaerobic microbial metabolism is of direct relevance to the Department of Energy (DOE) missions in environmental stewardship (contaminant bioremediation, microbial impacts on global warming through production and sequestration of methane and carbon dioxide), clean and secure energy (methane and H_2 from wastes as alternative energy sources), and basic science (cycling of carbon, nitrogen, metals, and radionuclides). As one example, molecular scale measurements, and the corresponding insight into biochemical processes, can lead us to new predictive computational models that will provide a solid basis for using microbes effectively and safely to mitigate the impacts of energy-production-related activities on the environment and human health.

Scientific Challenges

Biology is making a transition from a descriptive to a predictive science. This transition is being driven by exponentially increasing amounts of genomic, proteomic and metabolomic data. Fundamental to making sense of this flood of data is an appropriate computational infrastructure that can handle both the amount and complexity of biological data. This transition involves a combination of technical and scientific challenges. The science challenge of identifying molecular processes that control environmentally dependent behavior of cells will occur in the overall context of rapidly expanding creation, collection and integration of many types and scales of information.

The overall picture of the cell microenvironment and cellular response, illustrated in Figure 1, helps identify the molecular processes that control the context-dependent behavior of cells. Microorganisms must be able to sense changes in their surroundings and they must be able to respond to these changes by producing new proteins, or metabolites. This picture leads directly to the following key environmental molecular science challenges that need to be addressed.

- *What are the molecular level mechanisms by which microbes sense changes in environmental conditions?*

- *What are the molecular level responses to these changes in conditions in terms of production of specific proteins, multiprotein complexes, metalloproteins, cell surface molecules or metabolites?*

- *Where within (or possibly outside) of the organism are these specifically produced molecular complexes located and how do they catalyze the specific reactions for which they were intended?*

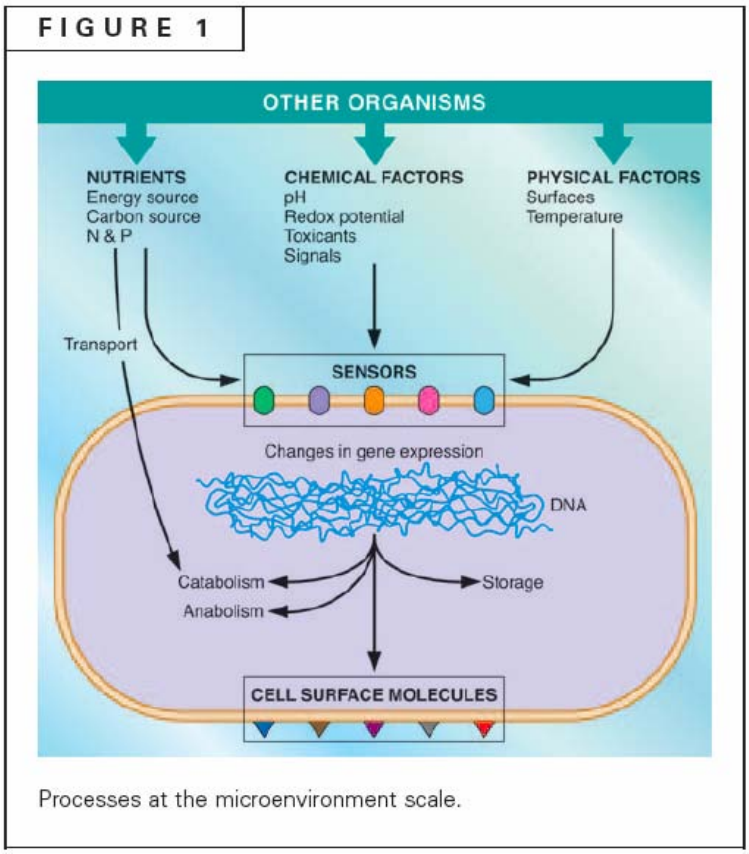
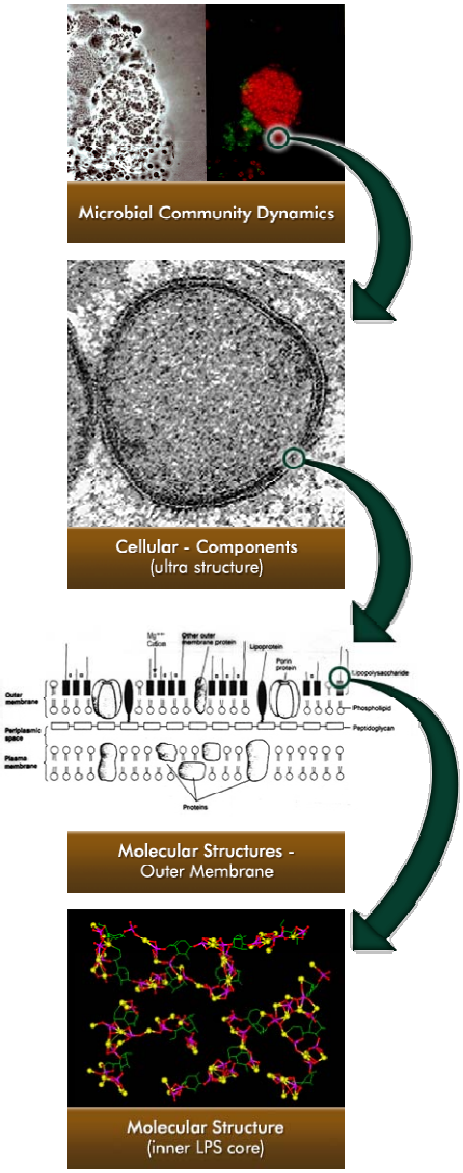


Figure 1. The microbial microenvironment and cellular responses (from presentation by Allan Konopka during this workshop, August 1, 2006).

Technical Challenges

The key technical challenges required to address these science challenges occur at different scales of measurement ranging from identifying the microbial community in which the organism exists down to the scale of nanometers in identifying the specific molecular level structures. *For maximum scientific impact EMSL must provide a range of capabilities to deal with scale dependence.* There must also be appropriate data management and analysis systems in place to both organize and understand complex, multi-scale information. The series of technical challenges and their inter-relationships are illustrated in Figure 2, and described in detail below.



(a) Image on the left is a black and white image of the microbial consortium using conventional light microscopy. In color on the right is a fluorescent in situ hybridization (FISH) image that shows ammonium oxidizing bacteria in red; the green cells are nitrite oxidizers that use nitrite produced by the ammonium oxidizers.

(b) Microbial ultrastructure of a gram-negative bacterium.

(c) Diagrammatic representation of the major components in the outer microbial membrane of a gram-negative bacterium.

(d) Molecular dynamic simulation of the inner core of the external lipopolysacchardides in the bacterium *Pseudomonas aeruginosa*

Figure 2. Scale dependence of technical challenges in the area of biological interactions and interfaces.

The first main technical challenge is at the level of the microbial community (see Figure 2a). *Capabilities should be developed to grow, identify and select individual organisms or subsets of organisms from a microbial consortium.* These facilities should be available within the EMSL and allow the ability to vary environmental conditions, observe the microbial community both spatially and temporally, and select specific members of the population for more detailed mesoscale or molecular level analysis. This capability is essential to meeting all three scientific challenges but especially challenges one and two.

A second main technical challenge is at the cellular and subcellular level (see Figure 2b,c). *Capabilities need to be developed to characterize the surfaces of living cells, determine the location of specific proteins or metalloproteins, and to subsection individual cellular structures for ex situ detailed molecular level analysis*. It was suggested that many of these capabilities could be co-located as part of an overall Microbial Cell Dynamics Laboratory for ease of user access (see below for details). This capability is critical for the last two scientific challenges.

The third main technical challenge is at the level of characterizing specific molecular level interactions that occur in biological systems. *Capabilities need to be developed to characterize specific posttranslational modifications of proteins, multiprotein complexes and metalloproteins, their 3-D structure, and where applicable their catalytic mechanisms.* The identification of catalytic mechanisms will require the ability to identify the reactant molecules in real-time along with the associated biological structures.

The information related technical challenge is the development of software systems that can facilitate the analysis of the large amount of data that can be collected and which support predictive modeling and exploit the computer resources at the EMSL. This software should exploit the sequence data that is being generated by other facilities, such as the JGI and broadly enable the understanding of complex, multicellular systems. Because interaction data is being gathered on multiple spatial and temporal scales, from the atomic to the community level, computational systems that can link these scale is essential. Data linking, integration, analysis and access are fundamental requirements for enabling the system-level approach to biology that promise to solve important problems in the next several decades.

Recommendations on Specific Investments

Numerous investment recommendations were offered during the workshop to address these technical challenges and these have been grouped into the following three areas: development of a microbial cell dynamics and visualization laboratory, enhanced capabilities in the areas of NMR/EPR/MS, and development of bioinformatics and data analysis capabilities. *The computational infrastructure needed for the next generation of biological studies was considered very important, but it was also generally agreed that*

this topic would require a separate workshop to develop specific implementation plans. Specific recommendations in the other two areas are described below.

Development of a Microbial Cell Dynamics and Visualization Laboratory

The technical challenges related to the need to grow and characterize living cells under specific growth conditions, determine the location of specific molecular structures within the cells, and subsectioning the cells or microbes for more detailed molecular level characterization requires an integrated suite of *in situ* microbial growth and characterization capabilities. Capabilities recommended to be located in such a facility include:

- Growth chambers for culturing microbes under specific environmental conditions and with *in situ* optical and fluorescence imaging capability.
- Analysis of gene expression profiles and molecular modification of cells to facilitate visualization of gene expression patterns.
- Sample preparation capabilities for proteomics and metabolomics studies.
- Development of NMR centric chemostats or bioreactors for studying cellular systems *in situ* and in real-time.
- Extended spectral range, high speed, high power, multiphoton confocal microscope for imaging living cells.
- Laser capture microdissection and other methods for subcellular fractionation.
- Cryo TEM for cellular and subcellular imaging and analysis.
- AFM for force measurements with whole cells or to use with specific antibody tags for cell surface imaging.
- NanoSIMS for enhanced imaging and spectral resolution of cellular structures.
- Coupled confocal microscopy and NMR analysis methods.
- Surface Plasmon Resonance (SPR) microscope for probing protein-protein, protein-DNA, and protein-ligand binding.

Taken together such a cell dynamics and visualization capability would represent an invaluable resource to the scientific user community.

Development of Enhanced Capabilities in NMR, EPR, and MS.

Several key technical challenges associated with determining multiprotein complexes, posttranslational modifications to proteins, and the catalytic mechanisms of protein function can be addressed by mass spectrometry or magnetic resonance approaches, which are current strengths within the EMSL. Specific recommendations on how these capabilities should be enhanced in the future include:

- Electron transfer and electron capture dissociation mass spectrometry methods for determining posttranslational modifications of proteins.
- Development of a high field (as high as 21 Tesla) Fourier transform ion cyclotron resonance (FTICR) mass spectrometer for whole protein analysis and enhanced sensitivity and resolution in analysis of proteome complexity.

- High-field EPR (>10 Tesla) capabilities for electron and proton transfer reactions in biological systems.
- New high sensitivity cryogenically cooled NMR probes for examining metalloproteins, multiprotein complexes, and metabolites.

Atmospheric Aerosol Chemistry

Atmospheric aerosols (solid and liquid particles suspended in air) are produced by dozens of different processes that occur on land and water surfaces, as well as in the atmosphere itself. Aerosols occur in both the troposphere and the stratosphere, but there are considerable differences in the size ranges, chemical nature, and sources of the aerosols that occur in these two atmospheric layers. Many research efforts are under way to measure, characterize and model aerosols. This is because aerosols have important consequences for global climate, ecosystem processes, and human health.

Aerosols influence the Earth's radiation budget through *direct radiative forcing* by scattering and absorption of incoming solar radiation. They also affect climate *indirectly* by acting as cloud condensation nuclei (CCN) and ice nuclei (IN). The extent of *direct or indirect radiative* forcing by aerosols (see Figure 3) is an area of significant uncertainty in global and regional climate modeling. This uncertainty is inherent considering the variation of mass, composition and optical properties of tropospheric aerosols on local to regional scales.

Indirect radiative forcing by aerosols is of largest uncertainty. The efficiency of aerosols to act as CCN and IN depends critically on the hygroscopic properties of aerosols. It's generally believed that aerosols composed of highly soluble compounds enhance cloud formation while those composed of low-solubility constituents inhibit cloud formation. In addition, the chemical composition and physical properties of aerosols evolve during their lifetime as a result of photochemical processing and heterogeneous chemical interactions. Fundamental understanding of these dynamics is prerequisite for accurate atmospheric chemistry and climate modeling. Yet, the role of aerosols, especially organic aerosols, is one of the greatest sources of uncertainty in the interpretation of climate change over the last century and in the modeling of future climate changes.

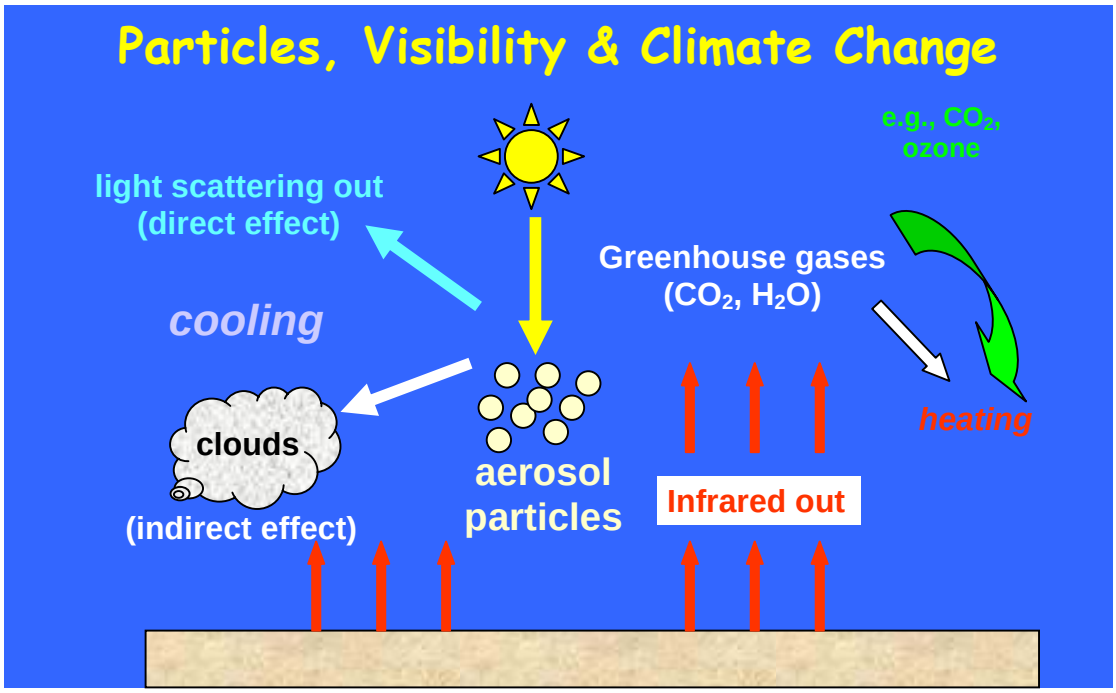


Figure 3. The impacts of aerosol formation on climate change (presentation by Barbara Finlayson-Pitts, UC Irvine, at this workshop August 1, 2006).

Scientific Challenges

The overall objective of this science theme area as articulated in the workshop was to *understand how physical properties and chemical composition of aerosols affect their interaction with radiation, water, and other gaseous species in the atmosphere and how these characteristics change during the aerosol life cycle*. As such, the key science challenges identified related to three processes in the aerosol life cycle: (1) aerosol sources, formation and growth, (2) aerosol transformation, and (3) aerosol impact on cloud formation and eventual deposition from the atmosphere.

Specific science challenges that workshop participants recommended for addressing in the EMSL user program included (Figure 4):

Aerosol Sources, Formation, and Growth: *Unravel the mechanisms of aerosol particle formation and growth.* This includes evaluating the processes leading to new particle formation, measuring the impacts of organics on aerosol particle formation and life-cycles, and deciphering the mechanisms of cloud droplet and ice crystal formation and growth in the atmosphere.

Aerosol Transformation (Evolution and Aging): *Understand the changes that occur inside and on the surfaces of aerosols during their atmospheric lifetime.* This includes unraveling the complexities of organic substances (including black carbon) in the atmospheric gas, particle, and droplet phases; their mixing and partitioning on the surface and in the bulk of the aerosols, and their evolution and transformations.

Cloud Processes, Scavenging and Deposition: *Evaluate how the changing chemical and physical properties of aerosols affect the formation and evolution of cloud droplets and ice crystals and subsequent aerosol deposition*. This includes understanding the impact of chemical and physical properties of aerosols on the formation and evolution of cloud droplets and the influence of solution non-ideality on warm cloud formation.

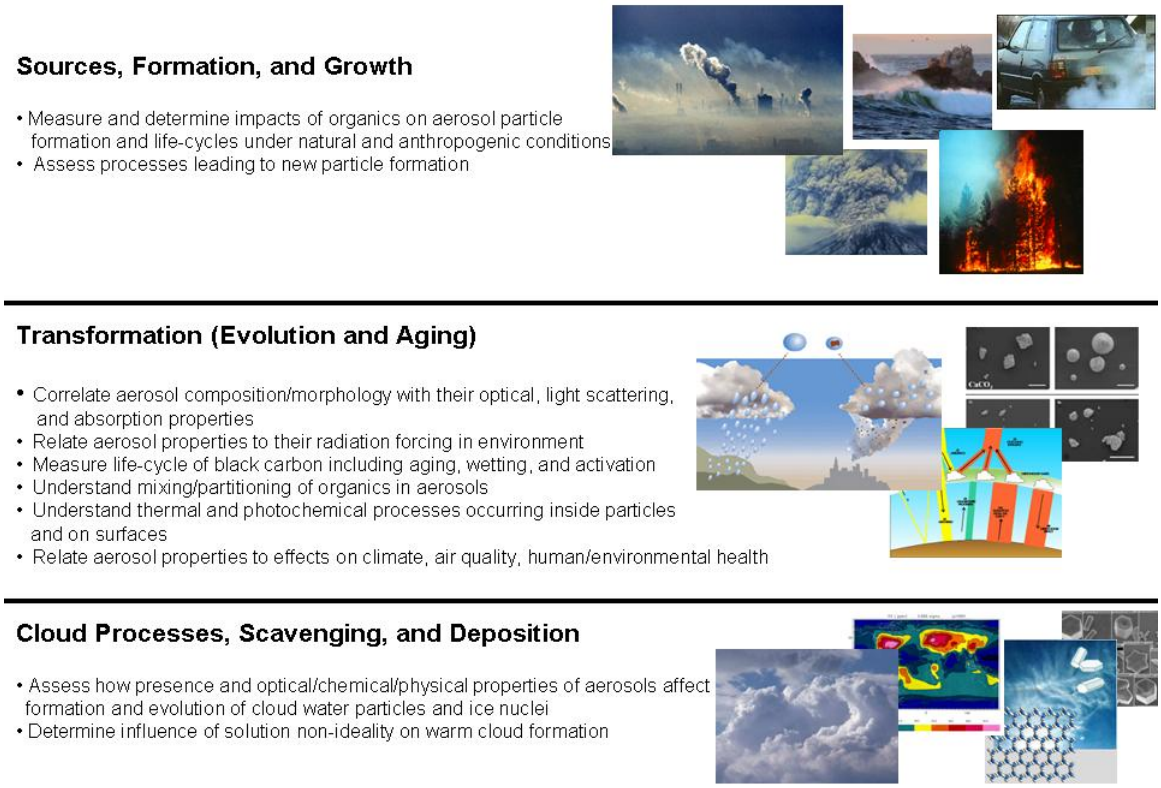


Figure 4. Scientific challenges identified in the area of atmospheric aerosol chemistry.

Technical Challenges

Workshop participants emphasized that the key technical challenges required to address these science challenges are related to characterization of chemical and physical properties of atmospheric aerosols and their evolution throughout their atmospheric life cycle. These include:

- Development of analytical techniques that operate under ambient conditions (1 atm, 0 – 100% RH, 230 – 320 K) for analysis of particles both suspended in air and collected on substrates.

- Chemical characterization of organic and inorganic aerosols and their transformations (aging, reactivity, condensation, etc.) using field deployable and laboratory techniques for both *in-situ* and *off-line* multidimensional, high-throughput analysis of atmospheric particles for both inorganic and speciated organics covering broad range of molecular weights (tens to10^4 amu) and particle sizes (~ 2 nm to 10 µm).
- Development of 3-D particle characterization techniques that provide information on heterogeneous properties of individual particles (particle morphology, bulk and surface composition, optical and hygroscopic properties, particle phases for solids and liquids, aerosol water content etc.) with respect to both inorganics and organics (not just elemental analysis) including speciated molecular information, oxidation states, etc., as a function of position in and coatings on particles.
- Development of sensitive techniques for trace isotope analysis (e.g. using carbon isotopes) of aerosol constituents to distinguish anthropogenic versus natural aerosol sources.

In the area of aerosol formation, the key technical challenges include development of improved *in-situ* chemistry probes for identification of gas-phase precursors and reaction intermediates relevant to formation of secondary organic aerosols; development of ultra-fast spectroscopic probes of non-equilibrium systems (super cooled water or water vapor) to illuminate the structure and dynamics of nucleation centers for both homogeneous and heterogeneous processes.

Other technical challenges include development of field techniques to ensure collection of representative samples (in composition, particle size, distribution, etc.) and development of large-scale data mining and analysis approaches, web based techniques for data sharing, storage and availability for scientific user community.

Recommendations on Specific Investments

Investment recommendations offered during the workshop related to the technical challenges described above included:

Advanced mass spectrometry instruments for analysis of aerosols using both in-situ and sample collection methods.

- New instrumentation for detailed real-time analysis of organic compounds in aerosols, including, but not limited to, mass spectrometry, ion and gas chromatography, and optical spectroscopic techniques.
- Particle imaging and analysis at atmospheric pressure using novel atmospheric pressure ionization techniques (DESI, DART, etc) combined with high-resolution mass spectrometry for chemical characterization of atmospheric aerosols collected on substrates and studying their transformations.
- New single-particle mass spectrometer for chemical characterization of ultra-fine (<100 nm) aerosol particles enabling simultaneous detection of particle size, shape and density.

- TOF-SIMS for submicron size single particle analysis.

Novel cutting-edge spectroscopy instruments for analysis of aerosols and their surfaces.

- XPS, SEM/EDX, TEM/EDX/EELS techniques for in-situ, real-time characterization of particle surfaces including black carbon during reactions with atmospheric oxidants and atmospherically relevant conditions (1 atm, 0 – 100% RH, 230 – 320 K, control of gas phase composition).
- Optical methods enabling real time, *in situ* and other types of analysis to be applied in a variety of ways. These should include Non-linear laser-based surface techniques (e.g., SFG, SHG) and improved capabilities for FTIR and Raman spectroscopy to study the special role that surfaces and interfaces play in atmospheric chemistry. <u>Specific applications and capabilities should include:</u>
    - temperature-controlled (down to 200 K) aerosol chambers with a suite of chemical instrumentation for real-time measurement of chemical composition and optical properties as a function of time, temperature, RH, and gas composition.
    - FTIR ellipsometry for measurements of optical constants for organics on surfaces, and
    - high spatial resolution FTIR and Raman microscopy capabilities for small area and single particle analysis.

It was also specifically noted that the development and use of many of these new capabilities will require developing the scientific expertise and personnel to operate such facilities.

Biogeochemistry and Subsurface Science

One of the most challenging and pressing issues confronting DOE and the nation is the safe and cost-effective management of environmental pollutants and the remediation of hazardous waste sites. The DOE is responsible for managing some 40 million cubic meters of contaminated soils and 1.7 trillion gallons of contaminated ground water. At Hanford alone, millions of gallons of highly radioactive and hazardous wastes in hundreds of underground tanks have leaked causing extensive contamination of the soil and groundwater. These issues are also national problems. For example, across the US, thousands of Superfund sites exist with various levels and types of contamination ranging from organics (PCBs, carbon tetrachloride, TCE), heavy metals (Hg, Cr, Pb, As), inorganics (phosphates, nitrates) to radionuclides (U, Tc, tritium, Pu, Sr, Cs, Am).

Molecular level processes, such as aqueous complexation, adsorption to different mineral phases, or microbial reduction of redox active metals, often control the transport and fate of contaminants in the environment. These processes occur in complicated subsurface environments that are chemically and physically heterogeneous. Understanding the structure, chemistry, and nano-scale geometric properties of the mineral/water and microbe/mineral interfaces are therefore key aspects of developing a mechanistic

understanding of contaminant transport. As a result molecular level studies of interfacial geochemistry and biogeochemical reactions have been an active area of research for more than a decade. Unraveling these phenomena at the molecular level and determining their impact on contaminant migration and transformation in the environment is a key objective of this science theme area.

Scientific Challenges

With this general understanding of subsurface systems, workshop participants outlined three key scientific challenges in the areas of nanobiogeoscience, system complexity, and bridging spatial and temporal scales. These challenges were identified in the context of where the EMSL could have a significant scientific impact on unraveling the mechanisms behind the fate and transport of contaminants and other constituents in subsurface systems.

- *Nanobiogeoscience: Unraveling the genesis, properties, and effects of nanominerals and nanostructured materials (anthropogenic and natural) in the environment.* This scientific challenge includes understanding mechanisms of biomineralization at the molecular-level (Bacteria express nanomaterial synthesis capabilities that offer exquisite control on product properties and morphology), elucidating the structure, unique properties, reactivity, and transport of nanostructured materials in the environment.

- *Natural Complexity and Molecular Resolution: Understanding the dynamics of reactions at complex interfaces with high temporal and spatial resolution.* This scientific challenge includes characterizing mineral surface structures including natural topographic heterogeneity and defects in different geochemical environments, determining the impacts of microbes, biofilms, and organics on mineral surface reactivity, and understanding coupled processes (e.g. diffusion/electron transport, surface proximity effects) with molecular resolution (see Figure 5).

- *Bridging Scales: Bridging the gap between molecular and continuum understanding*. This scientific challenge includes relating molecular properties to macroscopic properties such as solubility, dissolution, and adsorption; as well as investigating the effects of fluid flow from the microscale (confined spaces and fractures) to the continuum level.

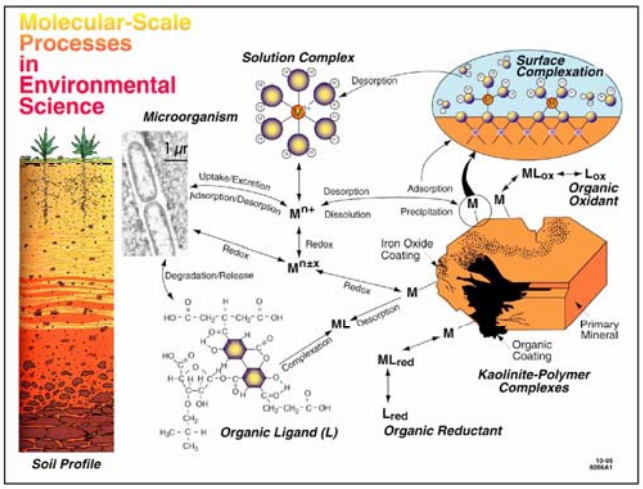


Figure 5. Molecular level complexity of biogeochemical systems (presentation by Gordon Brown, Stanford University, at this workshop August 1, 2006).

Technical Challenges

The technical challenges required to address these science challenges must therefore deal with the issues of characterizing the complexity of heterogeneous systems, evaluating coupled processes (dynamics), and linking molecular scale and macroscale reactivity (scaling).

- *Imaging of complex heterogeneous systems.* In working with complex heterogeneous materials the ability to image the system at different scales and selectively isolate fragments or parts of the system for further characterization until ultimately the molecular scale is obtained is of prime importance (see Figure 6).

- *In-situ characterization of biomineralization and mineral surface reaction dynamics.* Microbial processes, and many geochemically driven processes occur across a wide range of time scales. Furthermore, many of these processes are strongly influenced by the chemical and physical conditions of the system in its natural state. In order to evaluate such processes requires real-time, *in-situ* imaging and spectroscopic capabilities.

- *Development of techniques for microscale reactive transport studies.* The EMSL has and will continue to focus on molecular biogeochemistry. However, fluid flow and transport phenomena are also often important in the environment and in laboratory based systems in the near surface region or in confined spaces. Capabilities need to be developed in microscale reactive transport, adding chemistry on top of microfluidics, to better understand geochemical and biogeochemical reactivity as well as to help bridge the gap between molecular and continuum scales.

Recommendations on Specific Investments

Investment recommendations offered during the workshop related to these three technical challenges include:

Imaging of complex heterogeneous systems

- An aberration-corrected cryo-TEM for detailed high-resolution imaging of delicate samples such as cell structures in contact with mineral surfaces.
- Advanced capabilities in NanoSIMS for simultaneous imaging of elements/isotopes on minerals and soft surfaces at the nanoscale.
- MicroRaman/AFM/laser confocal microscope with wet cell capability for dynamic studies of living cells.

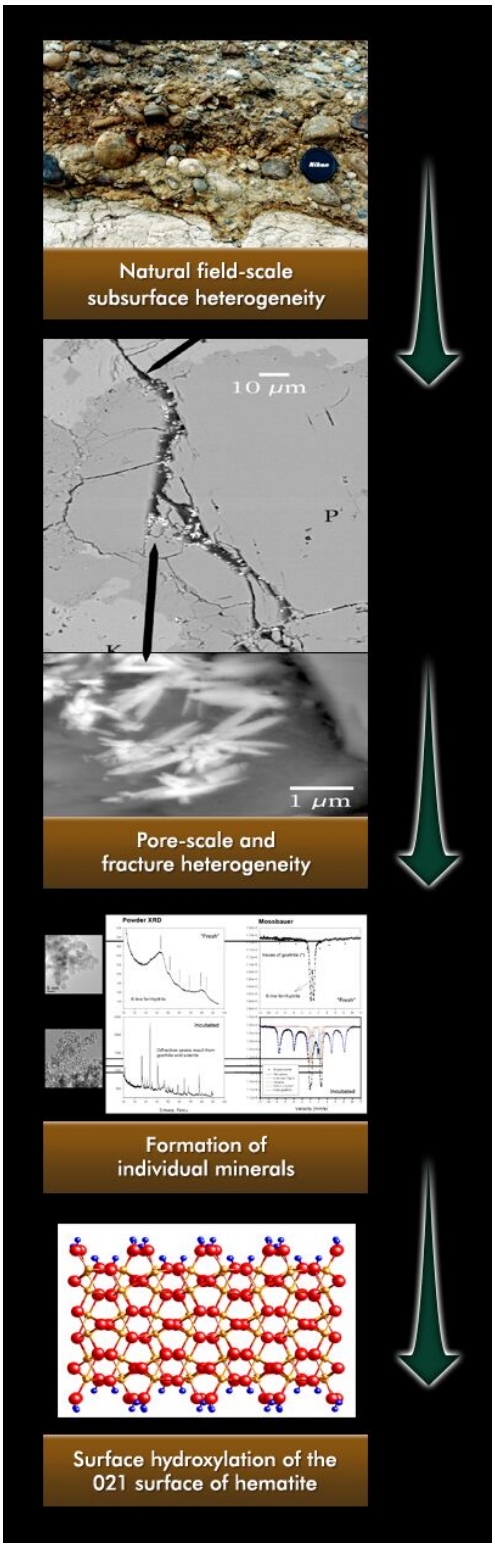
In-situ characterization of biomineralization and mineral surface reaction dynamics

- Development of Second Harmonic Generation (SHG) and Sum Frequency Generation (SFG) capabilities for probing interfacial reactions in in-situ.
- High resolution, high brightness, micro XRD for determining the mineral phases in micromineral assemblages.
- Focused ion beam (FIB) capability for partitioning and characterizing heterogeneous samples with high spatial resolution.
- Higher brightness (10x) monochromatic XPS for enhanced determination of surface phase composition and oxidation state information.

Development of techniques for microscale reactive transport studies

- Establish a Microfluidics Laboratory for studying reactive chemical transport in micron or smaller confined spaces. This facility should include capabilities for device fabrication.
- Enhanced NMR capabilities for imaging fluid flow in subsurface materials, a cryo-solids probe for analysis of low-abundance nuclei, and a MAS NMR flow-through (wet) cell.

In addition to these capabilities, there was strong support for enhanced capabilities to handle radionuclides and for the development of flexible and universal mechanisms for transferring samples between instruments under controlled atmosphere (anoxic) conditions.



(a) Soils and concretions present in the Ringold Formation (Vadose Zone) at the Hanford Site showing the intrinsically high degree of physical, spatial, and chemical heterogeneity at the field scale.

(b) Backscattered electron images of uranyl silicates within microfractures of a single granitic clast at the micron observation scale.

(c) Powder XRD and Mossbauer spectra of nanoparticulate ferrihydrite before and after microbial incubation.

(d) Molecular dynamics based prediction of the molecular-level structure and surface protonation of the hematite 021 surface.

Figure 6. Scale dependence of technical challenges in the area of biogeochemistry and subsurface science.

Science of Interfacial Phenomena:
Tailored Interfacial Structures for Dynamics, Reactivity, and Transport

Material systems with interfaces designed (tailored) and optimized to have specific properties are essential to many technologies needed to maintain a secure environment and obtain a stable energy future for the nation. Hydrogen production and storage, solid-oxide fuel cell research and development, materials for next-generation nuclear reactors, thin-film solar cells, radiation detectors and chemical sensors, the creation of a new generation of selective efficient and stable catalysts, environmental photocatalysis, and the development of solid-state lighting are all examples of technical areas that rely on improved understanding and control of molecular-level structural, dynamic, and transport properties of interfaces. As indicated in Figure 7, sensors, catalysts, photocells and other environmentally important systems usually involve solid-solid, solid-liquid, or solid-gas/vacuum interfaces of a variety of physical structures from which we need to extract chemical and functional information at the atomic or molecular scale. This science theme focuses on developing an understanding and gaining control of structure-function relationships at the atomic level that will allow, for example, the design of catalytic activity and selectivity. The science and technological issues identified highly link to those in the atmospheric, geological and biological areas.

Scientific Challenges

- *Expanding our understanding and ability to rationally design, synthesize and characterize complex surfaces, films and interfaces.* One focus of this area is enhancing our ability to deal with complex materials, complex structures and complex environments some of which are illustrated in Figure 7. These materials and the related interfaces are relevant to geochemical and biogeochemical processes and to the creation of films/materials with designed chemical, electronic, magnetic and optical properties related to sensor, detector, catalysis, and energy needs. Extension of the level of experimental and theoretical understanding available for metal and semiconductor surfaces to metal oxide, hydroxide, layered silicate and other insulating systems was a scientific challenge undertaken by EMSL at the inception. Success in addressing this challenge for relatively simple oxides provides capabilities and resources that will help fuel progress in many of the current science theme areas and leads naturally to facing the challenge of growing, characterizing and designing more complex oxides for a variety of applications.

- *Understanding or controlling structure-function relationships of surfaces and interfaces.* We are just beginning to understand the truly dynamic (time and environmental dependent) nature of surface and interface structures that will have major impacts on the nature and presence of defects and reaction sites. These dynamic effects may be more apparent for organic or biomaterials, but also apply to what has been commonly viewed as “static” inorganic surfaces and interfaces. This time and environment dependent nature adds new challenges and opportunities for understanding and controlling structure-function relationships at

surfaces and interfaces of many types. These dynamic effects will influence our understanding of chemical reactivity (catalysis, photocatalysis, and bioactive materials) and have significant implications for processes involving mass and charge transport (detectors, sensors, fuel cells, photovoltaics) and may offer new approaches to control reaction processes. Water at surfaces and buried interfaces (including solid/solid and solid/liquid) are particularly important interfaces to understand and very challenging to probe experimentally.

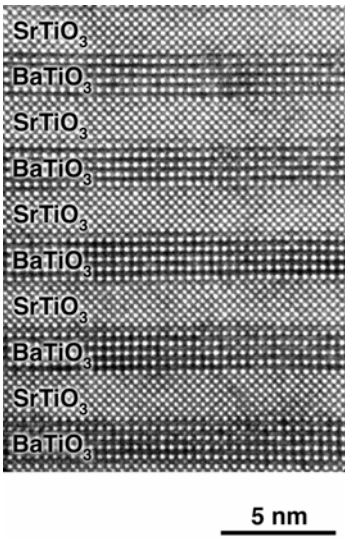
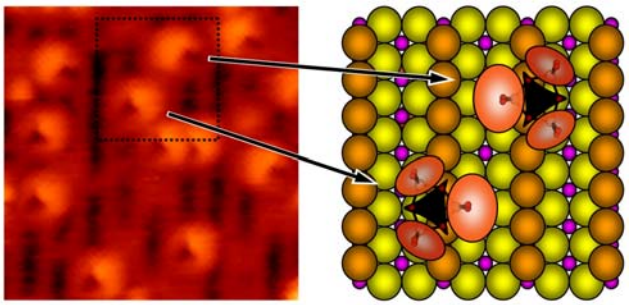
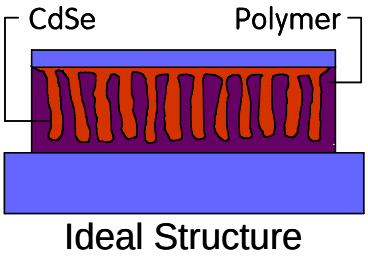


Figure 7 Examples of a variety of interfaces relevant to energy, environmental or sensor technologies

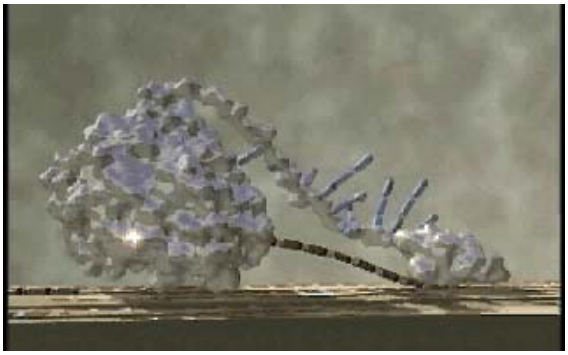
a) TEM image of multi-layer oxide structure grown by MBE. Such structures are relevant to ferroelectric materials, magnetic components or sensors and provide one example of buried solid-solid interfaces for which atomic level order (and deviation from that order) is significant. From Y. Suzuki presentation.



b) Scanning Tunneling Microscope image of catalytically nanometer sized active sites on an oxide surface. Specific reactive sites and sometimes defects play a major role in defining the chemical properties of surfaces and interfaces. From J. M. White presentation.



c) Model of future solar cell involving organic and inorganic materials and a complex geometrical structure. The ability to adequately characterize such complex mixed phase system is an important challenge. From M. Al-Jassime presentation.



d) Drawing of endoglucanase on a cellulose surface. Biological surfaces and interfaces are a challenge to fully characterize, but play a major role biomass conversion. From M. Davis presentation.

Technical Challenges

Several important general instrumental needs that involved a variety of technical challenges were identified in this area. It was clear that a wide range of different capabilities was necessary for Users to have access to the set of tools needed to make important scientific contributions. Specific areas included material synthesis, capabilities for probing single sites on surfaces, *in situ*/operado/real-time capabilities, surface and buried Interface capabilities. Participants especially noted that in a few areas US researchers do not have access to current state of the art instrumentation.

- *In situ/Operando/Real Time Probes.* The ability to measure chemical and structural characteristics of surfaces and nanostructured materials as a function of environment and time is critical for understanding the dynamical and transient behaviors of materials and interfaces relevant for a more advanced understanding of structure-property relationships. Capability developments that facilitate i*n situ* capabilities should be emphasized.

- *High Resolution and Interfacial Analysis Tools.* It is increasingly important to obtain information about the structure, composition and chemical properties of specific (single) sites and small areas. High resolution tools are also important for engineering and natural materials. The ability to probe atomic and molecular structure and composition of solid/solid (including organic/inorganic, inorganic/inorganic and organic/organic), solid/liquid, solid/gas interfaces is critically important and should include chemical imaging to the extent possible. It is increasingly important to combine spectroscopy (physical and chemical information) and microscopy (spatial information).

- *Sample synthesis and preparation are enabling capabilities for much important science and technology.* Important aspects in this area include the synthesis of complex (composition and morphology) oxide interfaces, films and surfaces as well as developing methods to observe and control growth processes real time (including in solution). The ability to prepare and handle samples to retain desired properties is a special and increasingly important challenge. The integration of precision calorimetric tools with nanostructure synthesis can provide the experimental basis for testing in detail theoretical model accuracy.

- *High throughput capabilities.* In some areas (including catalysis), high throughput synthesis and analysis are important enabling capabilities that have a qualitative impact on the level of science that can be accomplished.

It is apparent that an increasing number of tools need to be applied to adequately characterize many new materials. A specific challenge to a user facility is associated with letting people know what is available and supplying the information and expertise needed to apply the tools to specific problems or materials. Among the general challenges many of the above methods introduce is the ability to process and manage large amounts of

data. Transparent ability to store, share and mine large amounts of data is a general issue important in many areas of science.

Another important issue that was specifically noted in the workshop was in the area of developing a new level of verified theory especially relevant for interfaces and nanostructures. Although fundamental theoretical tools have developed such that theory can contribute to understanding molecular structures with increasing numbers of atoms and complexity, it remains difficult and important to validate theory applied to nanostructures and interfaces by comparison with critical experiments. Although it is possible to verify calculated structures, kinetic and energetics provide a more critical tests or accuracy. The objective is to achieve the ability to calculate energetics with the accuracy needed for chemical predictions.

Recommendations for Specific Investments

A wide range of recommendations for specific instruments or capabilities were made during the workshop. The items identified have been are grouped by the technology challenge areas where they apply. Some instrumental recommendations apply to more than one area.

In situ/Operando/Real Time Probes

- Chemically focused high resolution TEM to structure and single site behaviors of catalysis and structures on geochemical surfaces
- Optical methods (SHG, SFG, Raman) real time analysis of particles and interfaces and ultrafast spectroscopy and microscopy laser and detection systems for dynamical studies
- NMR/EPR with appropriate environmental controls and sample capabilities for real time in situ structure and chemistry measurements
- Ultrafast spectroscopy and microscopy laser and detection systems for dynamical studies

High Spatial Resolution and Interfacial Analysis Tools

- NanoSIMS for imaging of elements and isotopes and soft materials at the nanoscale and TOF-SIMS for molecular analysis of organic and inorganic surfaces
- FIB/SEM for three dimensional analysis and selection of specific sample areas TEM analysis
- Variable temperature UHV (cryo-shielded) STM/AFM surface analysis system for study of single site chemistry
- X-ray photoelectron capabilities including high spatial resolution, rapid data acquisition (x10 faster than current) and cryo-XPS for surface and interface analysis including solid-solution interfaces

- Near-Field Scanning Optical Microscopy and single molecule and tip enhanced optical microscopy (will require development to enhance usability) for single site and molecule measurement

Sample synthesis and preparation

- A new generation OPA MBE (with in situ structural characterization) will enable growth of complex materials and the ability to "scale-up" production.
- Anaerobic sample handling capabilities and advance sample preparation methods (FIB and advanced ion milling) to enhance ability to prepare and analyze samples without preparation or atmospheric alteration.
- The ability to synthesize complex structures, channels, and components relevant to micro-fluidic and sensor work is needed.
- Preparation of novel catalyst using soft-landing of mass-selected ions.

High throughput capabilities

- Purchase or develop advanced multiple sample catalysis testing capability for rapid property analysis
- Develop or purchase rapid testing capabilities (e.g. micro XRD) to enhance sample throughput

Cross Cutting Themes and Recommendations

Many of the suggested investments that were offered during the workshop overlapped the different science theme areas. This was natural and expected since many capabilities in environmental molecular science broadly underpin different science challenge areas from subsurface fate and transport to development of new energy systems. This section highlights several of these general areas and points out some of the interrelationships to help further refine the true science impacts of different investment recommendations related to technical challenges and specific instrument suggestions.

System Dynamics and In Situ Capabilities. Capabilities for studying dynamic properties and systems *in situ* was also a cross cutting theme of all four science theme areas. The dynamic properties of living cells have been addressed in the development of a microbial dynamics and visualization laboratory. New technologies allow an increasing range of capabilities to be applied or adapted for *in situ* and real-time measurements.

Candidates specifically mentioned at the workshop include:

- Operando TEM equipped with an environmental cell optimized for high resolution microscopy and chemical measurements.
- Development of Second Harmonic Generation (SHG) and Sum Frequency Generation (SFG) capabilities for probing interfacial reactions in in-situ.
- Development of a low temperature (down to 200K) stabilized growth chamber that is equipped with ultrafast optical probes, FTIR, and XPS for examining the growth and reactions of aerosol particles *in-situ*.

- Ultrafast spectroscopy and microscopy laser and detection systems for dynamical studies.
- Development of special purpose NMR probes for environmentally controlled studies.
- High-resolution mass spectrometry for *in situ* chemical analysis of catalyst surfaces and particle imaging using novel atmospheric pressure surface ionization techniques (DESI, DART, etc.).
- Metabolomics dedicated LC/NMR, LC/MS/NMR system for complementary mass spectrometry and NMR identification/quantification of metabolites in complex mixtures.

Multiscale Structure Synthesis and High Resolution Characterization Capabilities. Many fundamentally and practically important processes occur at specific sites or involve biological or material structures nanometers in size. The need for synthesis and characterization capabilities in this area cross cut all four science themes from determining microbial cellular structures, to aerosol particle characterization, to subsurface systems. Some synthesis capabilities are especially relevant in the interfacial sciences area but enable many types of research in other areas especially in the area of microfluidics.

Workshop participants suggested many capabilities that should be considered for inclusion in this area including:

- NanoSIMS for enhanced imaging and spectral resolution of cellular structures, aerosol particles, nanoparticles in the subsurface and Submicron size, high-energy ion beam capability for single particle analysis (TOF-SIMS).
- Focus ion beam (FIB) capability for partitioning and characterizing heterogeneous samples.
- High resolution, high brightness, micro XRD for determining the mineral phases in micromineral assemblages.
- Higher Brightness (10x) monochromatic XPS for enhanced determination of surface phase composition and cryo-XPS for surface and interface analysis including solid-solution interfaces.
- Near-Field Scanning Optical Microscopy and single molecule and tip enhanced optical microscopy (will require development to enhance usability) for single site and molecule measurements.
- Variable temperature UHV (cryo-shielded) STM/AFM surface analysis system for study of single site chemistry.
- Capabilities for highly specific preparation of novel catalysts using soft-landing of mass-selected ions.
- A new generation OPA MBE (with in situ structural characterization) will enable growth complex materials and the ability to “scale-up” production.
- Development of a Microfluidics Laboratory that includes device fabrication capabilities. The ability to synthesize complex structures, channels, and components impacts the interfacial sciences area (sensor development), biogeochemistry (flow in confined spaces and fractures) and in the biological sciences area (analytical separations). Microfluidics capabilities have been rapidly expanding throughout the world over the past two decades. The EMSL needs to take advantage of these capabilities.

Microbial Dynamics and Visualization Laboratory. This was one of the key new technical developments recommended for the biological interactions and interfaces areas but many of the capabilities also overlap with biogeochemistry and interfacial science areas.

Needed capabilities in such a facility include:

- MicroRaman/AFM/Laser Confocal Microscope with wet cell capability for dynamic studies of living cells.

- Growth chambers for culturing microbes under specific environmental conditions and with *in situ* optical and fluorescence imaging capability.
- Development of NMR centric chemostats or bioreactors for studying cellular systems *in situ* and in real-time.
- Extended spectral range, high speed, high power, multiphoton confocal microscope for imaging living cells.
- Laser capture microdissection and other methods for subcellular fractionation.
- Cryo TEM for cellular and subcellular imaging and analysis.
- AFM for force measurements with whole cells or to use with specific antibody tags for cell surface imaging.
- Coupled confocal microscopy and NMR analysis methods.
- Surface Plasmon Resonance (SPR) microscope for probing protein-protein, protein-DNA, and protein-ligand binding.

Enhanced Capabilities in Mass Spectrometry and EPR. The EMSL has been one of the world's leaders in the development and application of mass spectrometry and NMR to issues in the environmental molecular sciences. These capabilities are viewed to be just as important if not more important in the future. Therefore, it is strongly recommended that the EMSL maintain strong investments in those areas. In particular, good opportunities exist to advance the EMSL capabilities in mass spectrometry and EPR. These should be pursued if possible as described below. In the case of NMR, the EMSL has one of the largest, if not the largest, suite of NMR instruments in the world including a wide bore 900MHz capability. These capabilities should be upgraded as appropriate by investing in selected unique probes (cryogenic etc.). Although there was no clear consensus at the workshop that the time was right for large investments in significant new instrumentation a need for development of special purpose probes for environmentally controlled (*in situ*) measurements was noted, as listed above.

The recommended investments in mass spectrometry and EPR include:

- Electron transfer and electron capture dissociation mass spectrometry methods for determining posttranslational modifications of proteins.
- Development of a high field (as high as 21 Tesla) Fourier transform ion cyclotron resonance (FTICR) mass spectrometer for whole protein analysis and enhanced sensitivity and resolution in analysis of proteome complexity.
- Development of high-resolution mass spectrometer for accurate determination of binding energies for biomolecules.
- High-field EPR (>10 Tesla) capabilities for electron and proton transfer reactions in biological systems.
- Metabolomics dedicated LC/NMR/MS system for complementary mass spectrometry and NMR identification of metabolites in complex mixtures.
- Development of high-resolution mass spectrometry for accurate determination of binding energies for biomolecules.

Information infrastructure and storage. The ability to transfer, store, integrate, process and mine data from a variety of sources was a comment need identified by most breakout groups. This is an important, but universal, challenge in many areas of science and for many institutions. It is clear that EMSL needs to be near the forefront in this area, but there are both scientific and technical challenges and a universal solution is not likely to be possible in the near future.

Appendix: Comments from Reviewers

It is very important for the future of the EMSL that future decisions on the recapitalization of the facility be made with as broad a range of views from the scientific community as possible. Therefore, copies of this draft workshop were sent to invited participants who were unable to attend the workshop owing to schedule conflicts and others with expertise in the science theme areas who agreed to review the report. This section contains a brief summary of the specific recommendations received. The comments are summarized/paraphrased with a view toward their possible impact on EMSL recapitalization. These recommendations are being integrated into the development of the EMSL Refreshment plan in both short term tactical investments and longer term investment strategies.

Summary of Specific Recommendations

- Expand the scientific challenges considered by the EMSL to include issues associated with biofuels. Specifically, the sustainability of continuous cropping of biomass where the soil carbon can be reduced and nutrient cycling and soil structure altered. Capabilities in the EMSL might be well qualified to help understanding these issues.
- The EMSL is ideally poised for building and maintaining a state-of-the-art smog chamber to support DOE's needs in aerosol research. Such a chamber would be extremely useful to the DOE research community in addressing many of the objectives of the atmospheric science program.
- There is a need for more instrumentation in the biogeochemistry area that addresses the 10's to 100's of nanometers scale. Suggestions for such investments might include a UV resonance Raman Spectrometer and a Quartz Crystal Microbalance with Dissipation monitoring and Optical Waveguide Light Spectroscopy.
- Access to an EMSL Aerosol Mobile Laboratory designed to make basic measurements (an aerosol MS, PTR-MS, …) would be a terrific bonus to those of us concerned with indirect aerosol affects in real environments.
- I did not see a discussion of the compact X-Ray source presented at the workshop. It's the sort of capability that really belongs in a National Lab. There should be major value in having one's own 24 hour access to such a source, even if the brightness is somewhat lower than available at dedicated major synchrotrons.
- There maybe the potential to integrate biology into the atmospheric chemistry program. We have recently done some analysis that showed that indeed there are bacterial populations in cloud water and that they are potentially metabolically active.

Agenda

William R. Wiley EMSL Environmental Molecular Sciences Laboratory

A NATIONAL USER FACILITY FOR THE SCIENTIFIC COMMUNITY

The Development of New User Research Capabilities in Environmental Molecular Science

August 1-2, 2006
Richland, WA
EMSL Auditorium

Tuesday, August 1, 2006

TIME	TOPIC	SPEAKER
7:00-7:30	Registration	
7:30-7:45	Introduction and Welcome to EMSL	Allison Campbell - EMSL
7:45-7:55	Perspective from the Office of Biological and Environmental Research	Mike Kuperberg/Paul Bayer - Office of Biological & Environmental Research
7:55-8:20	Introduction and Expected Outcomes	Andrew Felmy - EMSL
8:20-8:50	Stanford EMSI - Current and Future Research Efforts	Gordon Brown - Stanford University
8:50-9:20	Electron Transfer at the Microbe-Mineral Interface	John Zachara - PNNL/FSD
9:20-9:40	Discussions	
9:40-10:10	Research Needs Related to the Center for Environmental Kinetics Analysis	James Kubicki - Penn State
10:10-10:40	Catalysis at Pacific Northwest National Laboratory	Mike White - University of Texas
10:40-11:10	Photovoltaics from the Laboratory to the Marketplace	Mowafak Al-Jassim - NREL
11:10-11:40	Challenges in Atmospheric Chemistry and Why We Should Care	Barbara Finlayson-Pitts - UC Irvine
11:40-12:10	NSF Workshop on Sustainability and Chemistry	Vicki Grassian - University of Iowa
12:10-1:30	Working Lunch	Morning presentations will be reviewed and discussed
1:30-2:00	EMSL Biology Grand Challenge	Dave Koppenaal - PNNL/Chief Research Office
2:00-2:30	How do Ecological Principles Limit and Inform the Molecular Analysis of Microbial Communities?	Allan Konopka - Purdue University
2:30-3:00	2005 DOE Biomass Energy Workshop	Mark Davis - NREL

3:00-3:20	Discussions	
3:20-3:45	Ideas Received from the Workshop Announcement and Group Instructions	Andrew Felmy - EMSL
3:45-5:00	Participant Discussions of Science Theme Challenges and Investment Ideas - Post Ideas on White Boards - Tour Facility	All
6:00-8:00	Dinner at Terra Blanca	Out of Town Guests or By Special Invitation

Wednesday, August 2, 2006

TIME	TOPIC	SPEAKER
7:30-8:00	Late Registration and Assignment Check-In	
8:00-8:30	Mass Spectrometry & Proteomics	Dick Smith - PNNL/FSD
8:30-9:00	National High Magnetic Field Laboratory at Florida State University	Alan Marshall - Florida State
9:00-9:30	Compact X-ray Sources	Steve Heald - PNNL/APS
9:30-10:00	Complex Oxide Heteroepitaxy	Yuri Suzuki - UC Berkeley
10:00-10:15	Discussions	
10:15-10:45	Ultrafast Laser Spectroscopy for Materials and Interface Research: A Unique Tool for Probing Dynamics	Jin Zhang - UC Santa Cruz
10:45-11:15	MRFM and Quantum Science: from Apollo-Style Science and Engineering to Federative Innovation and Enterprise	John Sidles - University of Washington
11:15-12:30	Working Lunch	Morning presentations will be reviewed and discussed in preparation for afternoon breakout session
12:30-1:00	Report on Day 1 Discussions; Charge to Breakout Groups	Andrew Felmy - EMSL
1:00-4:00	Breakout Group Discussions on Investment Options in Context of Science Challenges - Investment Prioritization	
4:00-5:30	Reports of Breakout Groups	
5:30	Adjourn	

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Security & Privacy
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ENVIRONMENTAL MOLECULAR SCIENCES LABORATORY

EMSL

Radiological NMR Spectroscopy Meeting

May 1-2, 2006

William R. Wiley
EMSL
Environmental Molecular Sciences Laboratory

Meeting Participants

Left to right: Lou Vance, David Koppenaal, David Clark, Georg Schreckenbach, Allison Campbell, David Hoyt, Kathleen McAteer, John Cort, Michael Bowman, Theresa Ramelot, Gordon Anderson, Felicia Taw, Paul Kanyha, John Hanna, Wolfgang Runde, Michael Janicke, Bruce McNamara, Jochen Autschbach, Julie Herberg, Wibe de Jong, Thibault Charpentier, Ian Farnan, Garry Buchko, Dimitris Sakellariou, Joseph Ford, Amber Wright, Cynthia Gong, David Dixon, Andrew Felmy, Nicholas Curro, Sarah Burton, Jun Li, Herman Cho.

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Summary

The Environmental Molecular Sciences Laboratory (EMSL) Meeting on Radiological NMR Spectroscopy was held in Richland, Washington, USA on May 1-2, 2006. Magnetic resonance spectroscopy is a popular and powerful method that is clearly not being used to full advantage in the radiological sciences, due mainly to the dearth of advanced instruments in radiological facilities. The purpose of this meeting was to survey recent activity in magnetic resonance studies of samples containing radioisotopes, and to stimulate interest and thinking in the promise of magnetic resonance spectroscopy for radiological science. A list of future directions and priorities was discussed and compiled with the participation of all of the attendees.

Introduction

In the U.S. and throughout the world, research activities in radiological laboratories are severely constrained by a shortage -- or in some cases complete absence -- of key instruments and capabilities, with the consequence that only a limited array of techniques are being brought to bear on complex problems and systems most in need of sophisticated methods of analysis.

One of the most important examples of a valuable and popular experimental technique that is falling far short of its potential in the radiological sciences is magnetic resonance spectroscopy, both nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR). With this in mind, on May 1-2, 2006, 36 scientists from six countries gathered at the William R. Wiley Environmental Molecular Sciences Laboratory in Richland, Washington to discuss the possibilities and value of a growth of radiological magnetic resonance capabilities.

The planning of the meeting was guided by three objectives: (1) to survey recent work on magnetic resonance spectroscopy of radiological samples; (2) to determine what facilities, instruments, and experiments are of the highest priority for the future; and (3) to organize an international network of scientists to promote growth and cooperation in this field of limited resources and complex, highly-specialized techniques.

Review of Current and Potential Research

A major reason for magnetic resonance spectroscopy's importance is its versatility, exemplified by the diversity of interests represented by the attendees of the meeting. As is the case for non-radioactive samples, magnetic resonance spectroscopy can be used for many different purposes in radiological contexts. In the invited talks and organized discussions, a wide variety of applications and new concepts were presented and proposed, including;

- *Fundamental studies of solution-state complexes amd interfacial reactions.* NMR spectroscopy is indispensable to chemists as a method for determining identities, structures, and stoichiometries and elucidating reactions and dynamics of solution-state molecules. While NMR will be of equal benefit to studies of complexes containing such radioisotopes as technetium and the actinides, the greatest need is for facilities and instruments that can handle samples with more highly active, fissile radioisotopes, particularly the transuranics. The workshop presentations of David Clark (Los Alamos National Laboratory) and Bruce McNamara (Pacific Northwest National Laboratory) provided examples of the contributions NMR spectroscopy can make in this area.

- *Advancement of* ab initio *theories of electronic structure.* In the development of theoretical treatments of electronic structure and bonding, NMR and EPR measurements have historically served a central role as rigorous experimental benchmarks. As computational and theoretical methods improve to meet the challenges of the heaviest and most complex elements in the Periodic Table, magnetic resonance measurements will be invaluable in evaluating and guiding progress towards accurate *ab initio* descriptions. The benefits flow in the other direction as well, from theoreticians to experimentalists. From the unusual magnetic parameters of heavy element isotopes, it can be predicted that their NMR and EPR spectra will be considerably more complex than those of lighter elements, and theoretical calculations will be a crucial aid in the acquisition and interpretation of experimental data. These ideas were the focus of presentations by Bert de Jong (Pacific Northwest National Laboratory), Georg Schreckenbach (University of Manitoba), David Dixon (University of Alabama), and Jochen Autschbach (University of Buffalo).

- *Structure in disordered and polycrystalline solids.* For solids that are incompatible with diffraction methods, NMR and EPR experiments are among the most effective and general ways to obtain detailed information on structure and bonding. It is natural to suppose that such an approach could be crucial in elucidating fundamental aspects of structure in highly radioactive, non-crystalline solids, including waste forms (both glasses and ceramics), advanced nuclear fuels, and certain high-temperature superconductors. The promise of NMR spectroscopy in investigations of radioactive solids was discussed by Ian Farnan (Cambridge University), Nicholas Curro (Los Alamos National Laboratory), Lou Vance (Australian Nuclear Science and Technology Organization), Thibault Charpentier (Commissariat à l'Energie Atomique), and John Hanna (Australian Nuclear Science and Technology Organization).

- *Customized magnetic resonance instrumentation for radioactive samples.* Novel technical and methodological developments will be essential to address the extreme and unique hazards of experimentation on radioactive samples, especially those containing transuranic isotopes.

Utterly safe, reliable operations are the paramount objective. Some nascent technological developments with applications for radiological magnetic resonance spectroscopy were introduced in the presentations by Dimitris Sakellariou (Commissariat à l'Energie Atomique) and Paul Kanyha (Tecmag, Inc.).

In addition to these areas, expanded radiological magnetic resonance spectroscopy capabilities would create extraordinary opportunities for other research of topical interest, including:

- *Tritium measurements.* ^{1}H is the best stable isotope for NMR detection, and at first glance the value of ^{3}H NMR measurements is not obvious. The record of the National Tritium Labeling Facility at the Lawrence Berkeley National Laboratory demonstrates, however, that ^{3}H-NMR studies of labeled organic molecules is a superb method for solution-state structure determinations. Tritium labeling can also be an attractive experimental strategy for observing trace-level amounts of a hydrogenated compound in the presence of a ubiquitous ^{1}H background, such as in metabolomics studies or a hydrated solid.

- *Determinations of fundamental nuclear parameters of radionuclides.* The current best values of fundamental nuclear parameters, such as magnetic moments and quadrupolar moments, of most radioisotopes have large reported uncertainties. NMR and EPR experiments, corrected for susceptibility effects, would be a comparatively safe and clean method for measuring these quantities with potentially orders of magnitude improvements in accuracy.

- *Analysis of process wastes from radioisotope production.* Although magnetic resonance spectroscopy is not usually considered an analytical technique, it has several virtues that make it appealing for analysis of radioactive samples, especially heterogeneous radioactive wastes: it is non-destructive, usually requires little sample processing, and generates little waste. NMR measurements are also inherently isotope-specific, and thus there is no beta-background interference problem when low-activity radioisotopes are analyzed in the presence of stronger emitters. Recently, promising applications of this approach have been demonstrated for ^{99}Tc in Hanford tank wastes.

- *Analysis of radioisotope contamination in the environment.* Similar considerations that make magnetic resonance spectroscopy attractive for analyzing radioactive process wastes apply to the problem of analyzing for radioactive contamination in the environment, especially the troublesome ^{99}Tc isotope.

Priorities

In justifying the buildup of radiological magnetic resonance capabilities, an important distinction must be recognized between low activity radioisotopes, e.g., ^{238}U or ^{232}Th, and highly radioactive, fissile nuclides, such as most transuranic isotopes. The former can be currently accommodated in a large number of institutions, including many universities, while the latter are tightly controlled and require a combination of resources that few institutions in the U.S. or elsewhere are able to offer. Mandatory resources include a comprehensive infrastructure to provide support in radiation safety, sample preparation, and radioisotope procurement and handling, in addition to instrumentation and laboratories dedicated more or less exclusively to radiological work. Ideas for how such a magnetic resonance facility, specializing in highly radioactive samples, should be organized and equipped were compiled in the meeting's organized discussion periods and are presented in the subsections below.

Facility

For the immediate future, it appears the number of institutions, not to mention countries, that could sustain a radiological magnetic resonance facility will be extremely small. In view of this practical limitation, two attributes were emphasized as being of utmost importance for such a facility. First, allowable radioisotope limits must be high enough to ensure meaningful quantities would be allowed inside for magnetic resonance experiments. For example, maximum volumes of 3 mL or less for solution-state NMR samples, and maximum masses of 200 mg for solid-state samples would be required. Second, the facility should have the ability and commitment to accommodate outside researchers and the hazardous samples they would bring with them.

The facility need not have an all-inclusive sample preparation capability. Indeed, ample expertise already exists at other laboratories to create interesting samples. However, a magnetic resonance facility should have the non-trivial ability to receive radioactive specimens prepared elsewhere, package them for measurements, and dispose of samples upon completion of experiments. The ability to perform these functions rapidly could be crucial in cases where internal radiation damage of the sample needs to be minimized.

It is expected that most potential samples will be analyzed and screened by other relevant techniques in order to maximize the usefulness and effectiveness of the magnetic resonance resources. For solid samples, this might entail prior characterization by x-ray diffraction, electron microscopy, or magnetic susceptibility measurements. As with sample synthesis, interlaboratory collaborations will be essential in ensuring that a comprehensive spectrum of analytical and spectroscopic methods are available to complement magnetic resonance spectroscopy in the study of radioactive samples.

Magnetic resonance laboratories in the U.S. that have recently conducted experiments on highly radioactive specimens have maintained their workspaces in a contamination-free state through leakproof containment of samples. This has allowed the laboratories to operate as temporary Radioactive Materials Areas, instead of the more restrictive Contamination Areas. While this is clearly the preferred and safest mode of operation, it is nevertheless highly desirable that radiological NMR and EPR laboratories be designed with protective engineering controls, such as radiation monitors, negative pressure rooms, separated air spaces for magnets and consoles, etc., as insurance against releases of contamination.

Instruments
In NMR spectroscopy, increasing magnetic field brings the dual benefits of higher sensitivity and greater spectral dispersion. Insofar as small samples are preferred, especially with highly hazardous materials, instruments with the highest possible sensitivity are a clear priority.

Measurements over a range of magnetic field strengths from low to high can be very valuable nonetheless. Most elements of the actinide series have multiple stable oxidation states, with formal charges that imply the metal will have unpaired electrons. An example of the harmful effects of paramagnetism was found in NMR measurements of solution state complexes containing actinide centers performed at the Los Alamos National Laboratory. NMR spectra of the complexes that were investigated exhibited large paramagnetic shifts that can be problematic to capture within the spectral window of a liquid state NMR spectrometer and probe. For these complexes, low magnetic fields, perhaps down to 100 MHz (2.35 Tesla), would clearly be preferable to higher fields for NMR measurements.

Magnets with different field strengths also provide important opportunities for studies of solid samples. Whereas the chemical shift interaction is proportional to magnetic field strength, the second-order quadrupolar coupling is inversely proportional to the field. Access to lower field magnets thus allows one to increase the energy of the latter interaction, which would be useful in single-crystal rotation pattern experiments, or to observe the effects on the spectrum of varying the size of the quadrupolar coupling, which can be an aid in the interpretation of powder spectra. With one exception (^{239}Pu), all actinide isotopes with magnetic moments are quadrupolar, and therefore the availability of an array of field strengths would be extremely advantageous.

The prevalence of potentially paramagnetic metals among interesting radionuclides implies that EPR instruments and SQUID magnetic susceptometers would be valuable complements to NMR spectrometers in a radiological magnetic resonance facility. Similarly, the prevalence of quadrupolar nuclides with large quadrupolar moments among actinide isotopes suggests that a nuclear quadrupole resonance (NQR) instrument would bring a much-needed capability to magnetic resonance studies of radionuclides.

Based on these considerations, an ideally-equipped facility would have four or more NMR systems with superconducting magnets spanning field strengths from 100 MHz to 800 MHz, and perhaps a variable-field electromagnet. To accommodate radiation shielding and other safety measures unique to radiological NMR, magnets with wide or ultra-wide bores are desirable. Safety and a minimized magnet footprint would also be facilitated if self-shielded magnets were selected. The instruments should be equipped for both solution- and solid-state experiments. In addition to the NMR instruments, an X-band FT-EPR spectrometer can be justified, as well as a SQUID magnetic susceptometer, and an NQR console with a bandwidth up to 2 GHz.

Other capabilities
Interaction with theorists and computational chemists will be essential in the endeavor to study radioisotopes by magnetic resonance spectroscopy. Relatively little is known about chemical shifts, electric field gradients, and other NMR parameters, and indeed NMR signals have never been detected for many radioisotopes; the guidance of theory will be vital in locating and interpreting NMR and EPR signals. Even when it is not the radioisotope that is being detected but stable nuclides around the radioisotope, the commonly-encountered paramagnetic shifts will lead to complications that can only be resolved by detailed theoretical analysis. Thus, mechanisms for

encouraging the involvement of theoreticians, either locally or at other locations, must be in place to ensure success.

Computational resources will also be needed at the local level for the more mundane but essential purpose of signal processing and data analysis. The computational requirements of modern NMR experiments are fairly demanding, and usually require advanced resources such as large Linux clusters.

Commercial NMR instruments and accessories will not meet many of the special demands of experiments with radioactive samples. These include dangers to personnel and equipment that commercial products are not designed to protect against, radioisotopes with nuclear parameters that put their NMR energies outside the normal operating ranges of commercial probes and consoles, and exotic, non-standard experimental schemes, such as optically detected magnetic resonance (ODMR), that cannot be performed with commercially available equipment. A radiological magnetic resonance facility must therefore be prepared for these circumstances with a sophisticated instrument development capability that can construct equipment custom-designed for the rigors of radioactive samples.

Immediate Actions

To overcome the neglect of magnetic resonance spectroscopy in the radiological sciences, there must be close cooperation among interested radiological researchers to (a) develop a compelling case for increased support from funding agencies; and (b) share specialized information and resources, especially equipment where there is limited availability. Participants at the EMSL Radiological NMR Meeting offered the following recommendations to advance these goals:

- More vigorously advertise the benefits of this capability for high priority areas such as advanced nuclear fuels development, radioactive waste management, environmental chemistry, national security applications, and fundamental research in heavy element chemistry

- Support efforts of agencies, such as the DOE Office of Science's Heavy Element Chemistry program in the U.S. and Actinet in Europe, that fund basic research in radiological science

- Publish a periodic review article that surveys the progress in magnetic resonance experiments on radioactive materials

- Form an organization, with a central website or newsletter, for the purpose of unifying researchers in the field and disseminating practical information that is not necessarily suitable for publication in peer-reviewed journals

Radiological capabilities at the Environmental Molecular Science Laboratory and the Pacific Northwest National Laboratory as a whole are currently being expanded as part of the Research Campus of the Future construction project. With new facilities and a growth in capabilities, many of these activities could conceivably be centralized at PNNL for the near term.

Meeting Schedule

EMSL Radiological NMR Spectroscopy Meeting

Richland, WA USA (May 1 & 2, 2006)

Agenda – May 1, 2006

7:30 am – 8:45 am	Registration and Breakfast	EMSL Lobby
8:45 am – 9:00 am	Welcome – **Allison Campbell, Director** **Environmental Molecular Sciences Laboratory**	EMSL Auditorium
9:00 am – 9:15 am	Greeting – **Andy Felmy, Pacific Northwest National Laboratory**	EMSL Auditorium
9:15 am – 9:30 am	Meeting Agenda	EMSL Auditorium
9:30 am – 10:15 am	**David Clark** – Los Alamos National Laboratory "Comparative Studies of Transuranic Ions and Molecules: Applications of Solution NMR Spectroscopy"	EMSL Auditorium
10:15 am – 11:00 am	**Ian Farnan** – University of Cambridge "Identifying and quantifying actinide radiation damage in ceramics with radiological magic-angle spinning nuclear magnetic resonance"	EMSL Auditorium
11:00 am – 11:15 am	***BREAK***	
11:15 am – 12:00 pm	**Nicholas Curro** – Los Alamos National Laboratory "NMR Studies of Actinide Compounds"	EMSL Auditorium
12:00 pm – 1:00 pm	***Lunch***	EMSL 1077
1:00 pm – 1:45 pm	***Environmental Molecular Sciences Laboratory Tour***	EMSL
2:00 pm – 2:45 pm	**Georg Schreckenbach** – University of Manitoba "Actinide Molecular Science with Density Functional Theory: Theoretical Studies of Actinyl Complexes and of NMR Parameters of Uranium (VI) Complexes"	EMSL Auditorium
2:45 pm – 3:30 pm	**Bert de Jong** – Pacific Northwest National Laboratory "Heavy Element Chemistry: Combining Computational Modeling and Experiment"	EMSL Auditorium
3:30 pm – 3:45 pm	***BREAK***	
3:45 pm – 4:30 pm	**Lou Vance** – Australian Nuclear Science & Technology Organisation "NMR of Nuclear Waste Forms"	EMSL Auditorium
4:30 pm – 5:15 pm	**Thibault Charpentier** – Saclay "Contribution of solid state NMR to the study of nuclear waste material"	EMSL Auditorium
5:15 pm – 5:30 pm	Adjourn	EMSL Auditorium

Pacific Northwest National Laboratory
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William R. Wiley EMSL
Environmental Molecular Sciences Laboratory

EMSL Radiological NMR Spectroscopy Meeting

Richland, WA USA (May 1 & 2, 2006)

Agenda – May 2, 2006

7:30 am – 8:00 am	Breakfast	EMSL Lobby
8:00 am – 8:45 am	**David Dixon** – University of Alabama "TBD"	EMSL Auditorium
8:45 am – 9:30 am	**Jochen Autschbach** – SUNY Buffalo "Computation of NMR parameters for heavy nuclei: Theory and applications to solvent effects on NMR parameters of heavy metal complexes"	EMSL Auditorium
9:30 am – 9:45 am	***BREAK***	
9:45 am – 10:30 am	**Dimitris Sakellariou** – Saclay "Rotating microcoils in Nuclear Magnetic Resonance of Radioactive Solids"	EMSL Auditorium
10:30 am – 11:15 am	**Bruce McNamara** – Pacific Northwest National Laboratory "Radiolytic Field Alteration of Actinide Speciation in the Solution State as Followed by ^{13}C and ^{17}O NMR"	EMSL Auditorium
11:15 am – 11:45 pm	**Paul Kanyha** – Tecmag, Inc. "Single Board NMR Spectrometer"	EMSL Auditorium
11:45 am – 1:15 pm	***Lunch*** – Networking (Notes for afternoon discussion)	EMSL 1077
1:15 pm – 2:00 pm	**John Hanna** – Australian Nuclear Science & Technology Organisation "A ^{23}Na and ^{133}Cs MAS NMR Study of the Thermal Properties and Transformations of Microcrystalline $M_xWO_{3+x/2}ZH_2O$ Hexagonal Tungsten Bronze Compounds"	EMSL Auditorium
2:15 pm – 4:15 pm	Hanford Site Road Tour – **Richard Romanelli** ***Note: Cameras, Laptops, Cell Phones, etc. are NOT allowed on this tour**	EMSL Lobby
4:30 pm – 5:30 pm	Discussion Continuation and Meeting Summary	EMSL Auditorium
5:30 pm	Adjourn	EMSL Auditorium

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Speaker Presentation Abstracts

David L. Clark
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"Comparative Studies of Transuranic Ions and Molecules: Applications of Solution NMR Spectroscopy"

As one transcends the actinide series, each additional 5f electron is poorly screened from the increasing nuclear charge, resulting in a contraction of the 5f orbitals, and resulting in a decrease in covalency and more lanthanide-like behavior. The comparative behavior of light actinide ions with a common ligand provides a unique opportunity to assess the relative importance of the variations in size and electronic configuration on structural, spectroscopic, kinetic and thermodynamic variables. This presentation discusses a series of studies using the linear actinyl ions AnO_2^{2+} (An = U, Np, Pu, and Am) to probe such changes using carbonate ligation, and with an emphasis on the role of multinuclear NMR spectroscopy.

David ClarK

Ian Farnan
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"Identifying and quantifying actinide radiation damage in ceramics with radiological magic-angle spinning nuclear magnetic resonance"

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High-resolution NMR can be used to determine the 'number fraction' of amorphous material present in a radiation damaged sample through spin-counting techniques. In samples with a known alpha dose, the number of atoms displaced per alpha decay may be determined from an integration of the spectrum. We have developed a protocol for performing magic-angle spinning on α-emitting ceramic samples with an activity of > 5 GBq. We will discuss some of the precautions and limitations associated with the method. Results obtained have allowed data from ancient, radiation damaged mineral samples of $ZrSiO_4$ ($^{238}U/^{232}Th$) to be compared with modern $^{238/239}Pu$ doped ceramic $ZrSiO_4$ samples. The number of atomic displacements per alpha particle from ^{239}Pu is similar to that for ^{238}U ($4980 \pm 300/\alpha$). There are significant differences in the amorphous volume fraction (observed by density and x-ray diffraction) and the number fraction of displaced atoms (as measured by NMR) as a function of cumulative dose. These differences arise from local density considerations that manifest themselves in the local structure of the amorphous and crystalline phases. Using ab initio simulations of the damaged crystalline and amorphous regions, the magnetic response of these

structures and hence the NMR shifts can be compared with experiment to reveal the nature of radiation induced changes occurring at the local scale.

Ian Farnan

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"NMR Studies of Actinide Compounds"

I will discuss NMR experiments on two plutonium based compounds: Ga stabilized delta-Pu, and the superconductor $PuCoGa_5$. The NMR data in the delta-Pu do not reveal any evidence for local moment magnetism, but do suggest the presence of local disorder around the Ga_5 sites. The data in the $PuCoGa_5$ reveal an unconventional superconducting order parameter, as well as fluctuating magnetic moments in the normal state. Measurements of the electric field gradient suggest that the lattice suffers age-dependent radioactive damage, and offers a quantitative measure of aging phenomena.

Nicholas Curro

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"Actinide Molecular Science with Density Functional Theory: Theoretical Studies of Actinyl Complexes and of NMR Parameters of Uranium (VI) Complexes"

Georg Schreckenbach and Grigory A. Shamov , University of Manitoba

In this presentation, we will present results of theoretical studies on actinide species. The talk consists of three parts.

First, we will briefly introduce and evaluate the methods and approximations that are necessary in the theoretical study of actinide chemistry. Despite considerable recent progress, theoretical actinide molecular science remains a "grand challenge area" for computational chemistry. The critical evaluation of various quantum chemical methods is therefore an ongoing effort.

Second, we will discuss actinyl complexes, and use these to illustrate the type of questions that can be addressed by current theoretical methods. We will present results for actinyl-water complexes $[AnO_2(H_2O)_n]^{1+/2+}$, n = 4, 5, 6, and actinyl inclusion complexes with expanded porphyrins (N-donor pyrrol based macrocycles).

Third, we shall present calculated NMR shieldings and chemical shifts for a variety of diamagnetic uranium (VI) complexes. Both, ligand and ^{235}U chemical shifts have been calculated. We will

illustrate the unique ability of theory to relate trends in calculated chemical shifts to the electronic structure.

For our theoretical studies, we have employed density functional theory (DFT) and different relativistic approximations including the zeroth order regular approximation for relativistic effects (ZORA), relativistic effective core potentials (ECP) and a scalar four-component relativistic method. Effects of the solvent environment are modeled by continuum solvation models or by explicitly including solvent molecules. NMR chemical shifts and shieldings are calculated using the "gauge including atomic orbitals" (GIAO) approach.

H Georg Schreckenbach

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"Heavy Element Chemistry: Combining Computational Modeling and Experiment"

W.A. de Jong and H.M. Cho, Pacific Northwest National Laboratory

Computational chemistry has reached the point where it can make significant contributions to heavy-element chemistry, to the understanding and interpretation of experimental data, the prediction of chemical and physical properties of heavy transition metal, lanthanide and actinide complexes. The results of combined experimental and computational chemistry research in the Environmental Molecular Sciences Laboratory will be presented. Sensitive experimental NMR measurements are combined with the interpretative power of *ab initio* theory to measure and understand structural and bonding parameters in heavy element complexes, and to test the accuracy of the available computational methodologies.

We will present results of measurements and calculations on the ^{17}O NMR nuclear quadrupole and chemical shift tensors in rutherfordine and other complexes. For rutherfordine the NMR tensor has exceptionally large chemical shift anisotropy for the uranyl bound oxygen. We have performed NMR measurements on both ^{17}O and ^{99}Tc in technetium complexes. The results of temperature dependent measurements on pertechnetate in solution, and interpretation of the results based on all-electron calculations of the various NMR tensors will be discussed. In addition we will discuss measured oxygen isotope effects on the NMR properties of ^{99}Tc in solutions.

This work was supported through the U.S. Department of Energy by the MSCF in EMSL at the Pacific Northwest National Laboratory. The MSCF and EMSL are funded by OBER in the U.S. Department of Energy. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

Bert De Jong

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"NMR of Nuclear Waste Forms"

E. R. Vance, [1*] J. V. Hanna,[1*] K. J. Pike,[1] I. Farnan,[2] M. E. Smith[3]
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At ANSTO, we have programs in the design of ceramics and glass-ceramics for high-level nuclear waste, geopolymers for low-level waste and mesoporous ion exchangers. Important features of the experimental design of the ceramic, glass-ceramic and geopolymer materials include their long-term dissolution behaviour in groundwater repository fluids and their response to radiation from the incorporation of radioactive waste. Solid-state nuclear magnetic resonance is a valuable tool in the design and understanding at the atomic level of these materials.

For low-level waste (LLW), radiation damage is not a problem as such but the presence of water in cementitious materials incorporating LLW or as repository barriers can lead to water radiolysis and consequent hydrogen production. Cements are fairly well crystallized and understood, apart from the C-S-H phase which governs a large component of the structural strength characteristics. However the geopolymer field is less mature and many structure/function elements are yet to be studied and understood. Geopolymers are synthesized from the action of alkali on reactive aluminosilicate precursors such as fly ash and metakaolinite, and are essentially amorphous apart from any unreacted fly ash component. We will some present a brief overview of some ^{29}Si, ^{27}Al, ^{133}Cs and ^{23}Na MAS NMR investigations, and some ^{23}Na MQMAS NMR investigations, into geopolymer systems suitable for low-level waste immobilization. In addition, very preliminary ^{43}Ca MAS NMR results will be discussed from studies that incorporated ^{43}Ca isotopic labelling into a cement preparation that was nominally pure C-S-H, and a standard fly ash based geopolymer with Si:Al = 2.0:1.0. At this early stage of investigation, it appears that C-S-H type phases are not formed in the disordered geopolymer matrix.

Radiation damage in water-free refractory waste form solids mostly derives from alpha-recoil and alpha particles arising from the decay of waste actinides. Such damage can be studied by many techniques, including heavy-ion/fast neutron irradiation, incorporation of short-lived ^{238}Pu or ^{244}Cm alpha-emitters (halflives of 87 and 18 yr respectively), fast electrons or neutrons etc. For NMR, sample radioactivity is a problem and this cannot be readily circumvented by the use of heavy ions as the range of such particles is very short and the use of mm-sized samples provides difficulties. One approach is to incorporate small quantities of ^{10}B in the solid followed by slow neutron irradiation to produce ^{7}Li and ^{4}He together with 2.79 MeV of energy/capture which is partly manifested in displacing atoms in the solid. We will discuss this proposed methodology that forms the basis of a collaboration with Cambridge University. Samples have been produced to study radiation damage in zircon ($ZrSiO_4$) and the structurally related xenotime (YPO_4) systems, with preliminary irradiations already completed. We will also discuss further new and emerging projects on 139La broadline NMR studies on lanthanum based materials focussing on Gen IV inert matrix fuels for actinide burning, and other proposed actinide immobilization phases such as $LaZr_2O_7$,$LaTi_2O7$and$LaPO_4$.

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"Contribution of solid state NMR to the study of nuclear waste materials"

T. Charpentier, M. Gaillard, D. Sakellariou, CEA Saclay

Since 1978, borosilicate glass has been considered in France as the reference industrial matrix for conditioning solutions of fission products (comprising more than thirty chemical elements) resulting from spent-fuel reprocessing operations. Research programs on the long-term behavior studies of glass package are currently conducted: the glass properties must be guaranteed to ensure chemical durability and good alteration resistance to self irradiation and lixiviation. The knowledge of glass structure and its modifications under different processes is thus of major importance for a better understanding of macroscopic properties. Solid state NMR is particularly powerful in providing structural information at the atomic level of amorphous solids. This will be illustrated with results from our studies performed on simplified inactive borosilicate glasses modeling the French Nuclear glass. Questions concerning the glass structure and its alteration induced by external beta irradiations and water leaching have been addressed. Similar experiments conducted on materials currently investigated for a specific conditioning of elements such as cesium or minor actinides will also be described. Underlying methodological developments of these studies (data processing and *ab initio* calculations) will also be discussed.

Thibault Charpentier

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"Computational Studies of NMR Chemical Shifts for Environmental Science and Catalysis"

Modern computational chemistry coupled with advanced computer architectures can now be used to predict salvation energeteics of heavy metal systems and nmr chemical shifts of ligands attached to a variety of heavy atoms. We have predicted the equilibrium for the water exchange reaction, $UO_2(H_2O)^{42+} + H_2O \leftrightarrow UO_2(H_2O)^{52+}$ using molecular orbital theory and density functional theory in combination with self-consistent reaction field approaches. The calculated free energies of reaction are very sensitive to the size of the cavity used in the PCM and SCIPCM models. Results consistent with the experimental HEXS value of -1.19 ± 0.42 kcal/mol (within 1 to 3 kcal/mol) are obtained with small cavities. Inclusion of a second solvation shell led to better agreement with experiment. The MP2 reaction energies for water exchange gave gas-phase results that agreed with experiment in the range -5.5 to +3.3 kcal/mol. The results were improved by inclusion of a standard PCM model with differences of -1.2 to +2.7 kcal/mol. Rearrangement reactions provide good values in comparison to experiment with values of ΔGexchange from -2.2 to -0.5 kcal/mol. The

inclusion of a second hydration sphere accounts for most solvation effects. Calculation of the free energy of solvation of the uranyl cation yielded an upper bound to the solvation energy of -410 ± 5 kcal/mol, consistent with the best experimental value of -421 ± 15 kcal/mol.

Our predicted 29Si NMR chemical shifts showed that lines in the spectra of complex silicate solutions not accounted for by the eighteen known species can be assigned to a number of new proposed oligomers having different isomeric forms. Studies on proton NMR chemical shifts of WxOyHz and $WOx(OH)y(OCH_3)z$ compounds showed a significant deshielding of the tungsten hydroxyl protons and were used in interpreting atomic layer deposition experiments. Prediction of 51V NMR chemical shifts for a series of clusters containing different substituents helped discriminate between the monomeric and dimeric form of V5+ -oxo structures on ZSM-5. Predicted shifts have also been used to assign nmr peaks in the process of acetylene trimerization on Rh in a zeolite.

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"Computation of NMR parameters for heavy nuclei: Theory, and applications to solvent effects on NMR parameters of heavy metal complexes"

First-principles theoretical approaches for the calculation of NMR parameters (nuclear magnetic shielding and nuclear spin-spin coupling) in the framework of relativistic quantum chemistry will be outlined. The use of a relativistic theory is imperative for heavier nuclei, as will be demonstrated with a simple model as well as by comparisons between density functional theory (DFT) and experiment. In some cases, relativistic "corrections" to NMR parameters can amount to between 100 or even 1000 per cent of a nonrelativistic result. Different relativistic computational strategies will be discussed, with a focus on the simple but accurate zeroth--order regular approximation (ZORA). DFT calculations have been performed by us to study the influence of solvation on the NMR parameters of heavy nuclei. It will be demonstrated that solvent coordination can have a huge effect on spin--spin coupling constants in heavy metal complexes. Chemical shifts can also be severely affected. It will be shown that in some cases relativistic effects can act as a "magnifying glass" for both solvent effects and chemical influences from different ligands. A recent study of ^{195}Pt chemical shifts highlights the inherent difficulties of such computational modelling but also shows in which way the computational model has to be improved. If time permits, we will briefly discuss vibrational averaging of NMR parameters in metal complexes.

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"Rotating microcoils in Nuclear Magnetic Resonance of Radioactive Solids"

Microcoils have been introduced in high-resolution NMR in 1995 [1]. In 2004 Yamauchi et al. have used microcoils to study static solids [2]. The main advantages from size reduction are optimal filling factor and large radio-frequency field amplitude. This last feature can have large impact in the development of new pulse sequences from quadrupolar nuclei, and in decoupling. On the other hand high-resolution NMR spectroscopy of anisotropic samples can be greatly enhanced using Magic-Angle Sample Spinning. It seems that combining microcoils with MAS would have tremendous impact in solids, but constructing microsize rotors seems technologically challenging, and difficult to implement in everyday studies.

We have introduced at the 1st EUROMAR conference [3] the concept of rotating microcoils placed inside the rotor. The sample is placed inside a capillary and is surrounded by a tightly wound microcoil tuned close to the Larmor frequency of the nucleus of interest. The microcoil is then inductively coupled with the coil of the MAS probe. The ensemble of the two resonant circuits is tuned and matched to 50 Ohms using the variable tuning and matching of the probe. The tuning of the probe and the coupling constant is not changing during rotation. We have developed our Magic Angle Spinning Coil (MACS) insert hardware for commercial rotors and probes.

The theory of inductive coupling is described and the conditions used in experimental conditions are simulated. We will be presenting experimental results proving that our invention allows for large signal enhancements in the case of mass limited samples and large radio-frequency field amplitudes (of the order of MHz). Examples of applications in the areas of liquids, HRMAS and solids will be presented. Nuclear waste samples can be efficiently studied using MACS, since they are confined inside triple barrier rotors [4] having an intrinsically low filling factor. Similar situations are common in small volume multiply labeled samples, biopsies, air sensitive samples and in general volume limited samples, where our technique can enhance dramatically the signal to noise.

References:
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"Radiolytic Field Alteration of Actinide Speciation in the Solution State as Followed by ^{13}C and ^{17}O NMR"

B.K. McNamara, L.A. Snow, H.M. Cho, C.Z. Soderquist, J.I. Friese, Pacific Northwest National Laboratory

It is well known that highly reactive species are produced during water radiolysis; however, little work has been reported that demonstrates the physiochemical impacts of such species on the resident actinides in spent nuclear fuel. The results discussed in this report demonstrate a real time, radiation-field dependent, chemical alteration of a uranyl system under conditions relevant to storage of spent nuclear fuels. We have followed by ^{13}C, ^{17}O NMR changes in the solution state speciation of several uranyl peroxy carbonates that exhibit general mononuclear structures as ($^{238}U^{17}O2(^{13}CO_3)_{3-x}(O_2)x^{4-}$) and/or multinuclear peroxo-bridged structures. These signatures are used to identify the major species produced by auto-radiolysis of alkaline carbonate solutions (pH=7.9-9.5) using the alpha decay from the uranyl tris carbonate ($^{233}U^{17}O_2(^{13}CO_3)_3^{4-}$). Under some conditions the uranyl trans oxo ^{17}O labeled oxygen has been noted to scramble in the presence of hydrogen peroxide. The thermodynamics of major solution state products will also be discussed.

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"Single Board NMR Spectrometer"

The single-board NMR spectrometer represents a new step in miniaturizing a complex technology. The current product is 11.5x8.5" and less than one inch high. It contains a single-channel, broadband spectrometer capable of operating at any frequency from 40 kHz to 120 MHz with a bandwidth up to 12.5 MHz. The transmitter provides RF pulses as short as 160 ns, with phase shifting in 90 degree increments in under 100 ns. A single-conversion RF receiver provides variable gain and a fixed IF frequency output to a 14-bit ADC with a 50MHz sampling clock. Critical components in the receiver are fully shielded. Digital quadrature detection and filtering is used, with bandwidths from less than 50 Hz to 12.5 MHz. Depending on the bandwidth, up to 16000 complex points can be acquired. The pulse programmer, with 20ns resolution, allows single scans with up to 1024 events. Each event can be between 160ns and 85s, and implicit and explicit loops and tables allow complex 2- 3- and 4-D experiments to be performed. Data set size is limited only by host computer memory. Synchronization and control for interfacing with other instruments are provided by user-programmable pulse sequence outputs and an external trigger input, and an optional external clock input. An expansion port provides for the addition of "daughter" or "mezzanine" boards for future options. A switching power supply with 12v input provides for battery operation, with a current drain of less than 2.5A. The spectrometer is controlled through USB interfaces from any Windows PC, including laptops, and uses standard software common to "full-size" instruments. A graphical sequence editor, data processing / analysis tools, and a pulse sequence library are standard features.

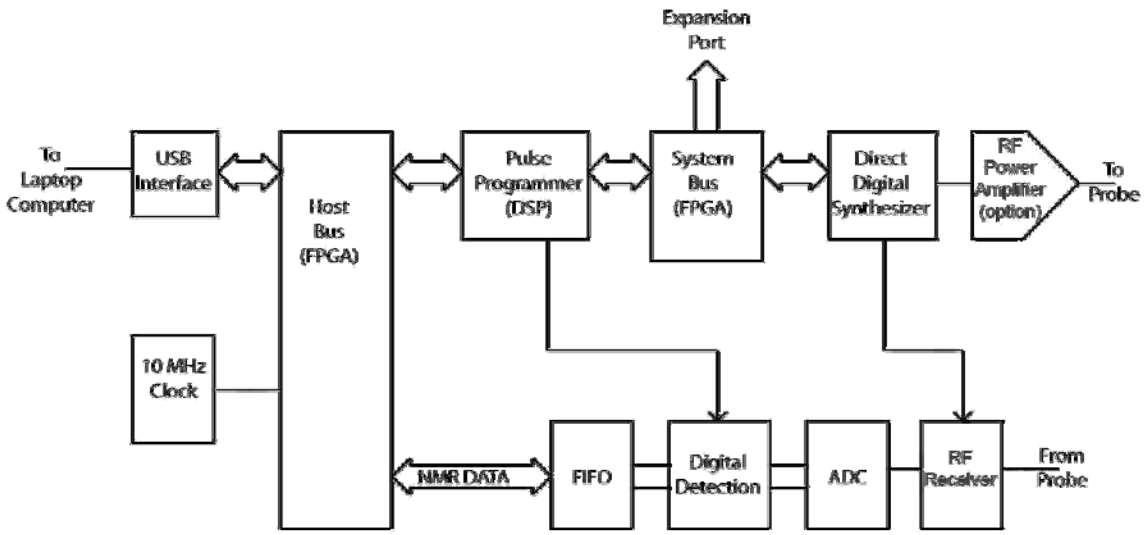

Figure 1. System architecture of the broadband single board NMR spectrometer.

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"A ^{23}Na and ^{133}Cs MAS NMR Study of the Thermal Properties and Transformations of Microcrystalline $MxWO_{3+x/2}ZH_2O$ Hexagonal Tungsten Bronze Compounds"

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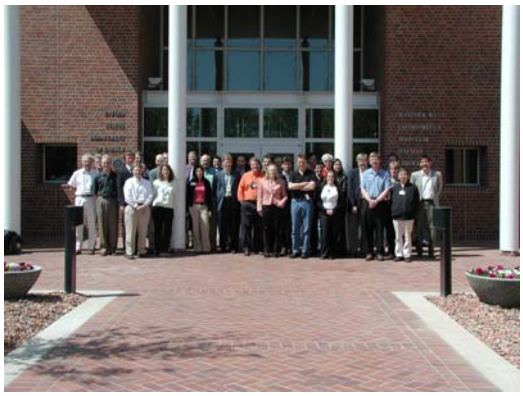
Low temperature (25-600 °C) thermal transformation in microcrystalline hydrothermally-prepared hexagonal tungsten bronze compounds ($A_xWO_3.2H_2O$ where A is an exchangeable cation located in hexagonal channels of the structure) are studied as a function the exchangeable tunnel cation composition. Thermal treatments in air were studied using conventional laboratory-based X-ray diffraction while vacuum heating was studied by synchrotron X-ray diffraction and neutron diffraction. For the sodium form of the bronze, cell volume contraction occurs from room temperature to about 350 °C; this is the regime in which water is squeezed out of tunnel sites. This is followed by a cell volume expansion throughout the 350–600 °C temperature range. Over this entire temperature range studied a net thermal contraction in cell volume is observed due to anisotropic variations in the cell dimensions in which the c-dimension contracts more than the concomitant expansion in the a-direction. These changes explain why Cs+ ions are locked into tunnel positions at temperatures as low as 400 °C resulting in a significant reduction in extractability in nitric acid. While similar effects are observed for the as-prepared Na^+- exchanged sample, the smaller radius of this cation causes it to be relatively easily removed under corresponding acidic conditions. ^{23}Na MAS and MQMAS NMR have been used to investigate the sodium speciation and

local order/disorder phenomena induced in the channel sites of the unsubstituted Na-tungsten bronze via a continuous and dynamic equilibrium with the intercalated H_2O. The speciation changes with thermal transformation and eventual phase transition over the 25-600 ^{o}C temperature range reported. Similarly, ^{23}Na and ^{133}Cs MAS NMR have been used to investigate the same phenomena in the Cs-substituted Na-tungsten bronze. These results corroborate the observations from quantitative Cs uptake measurements that the theoretical maximum Cs uptake in these systems is never achieved, and that the residual Na speciation after Cs incorporation demonstrates increased short-range positional order.

John Hanna

Photographs from the Meeting

Spin-spin coupling in heavy element compounds
Chemical shifts in heavy element compounds
Vibrational corrections