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CMS Annual Report 2004

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Disclaimer

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Chemistry and Materials Science Directorate

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Chemistry and Materials Science DIRECTORATE

Annual Report 2004

chemistry & materials science

Lawrence Livermore National Laboratory

About the Cover

Formed in 2004 to exploit research opportunities in nanoscience and nanotechnology, the Nanoscale Synthesis and Characterization Laboratory is a new center of excellence for developing novel nanostructures that will enable many revolutionary applications.

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WHAT'S INSIDE CMS

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Materials properties and performance under extreme conditions

Chemistry under extreme conditions and chemical engineering in support of national-security programs

Applied nuclear science for human health and national security

Divisions, centers, and institutes

A message from Associate Director Tomás Díaz de la Rubia

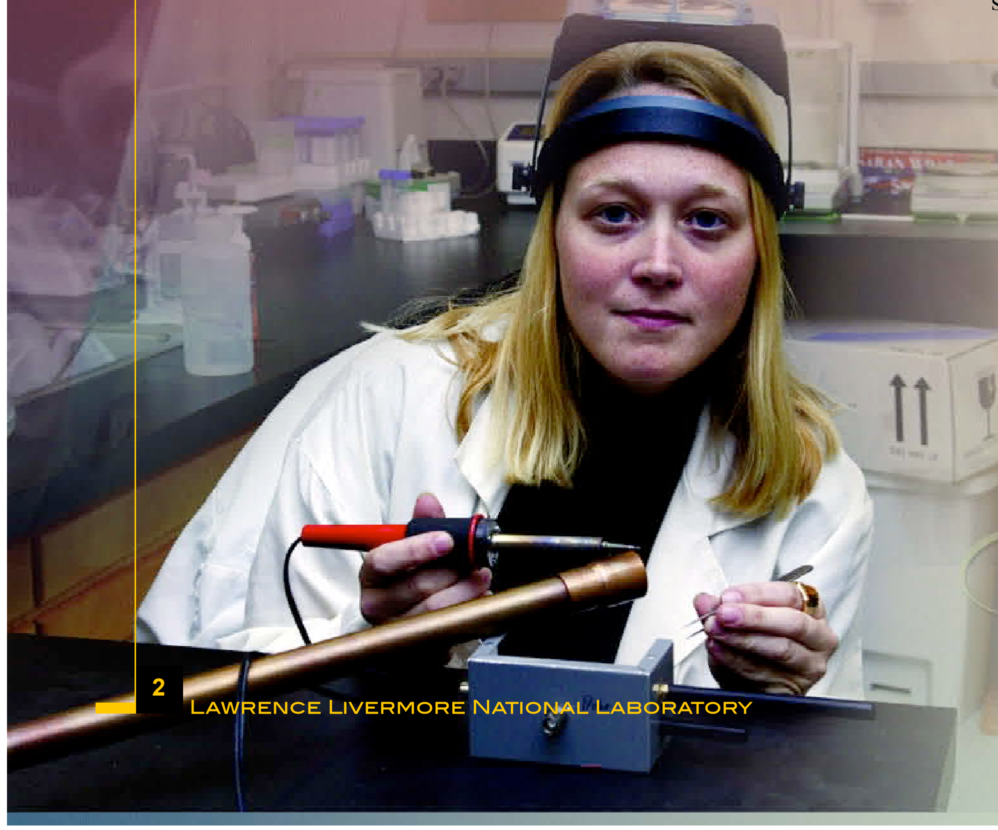
Glance at the articles in this report, and you will sense the transformation that is reshaping the landscape of materials science and chemistry. This transformation is bridging the gaps among chemistry, materials science, and biology—ushering in a wealth of innovative technologies with broad scientific impact.

The emergence of this intersection is reinvigorating our strategic investment into areas that build on our strength of interdisciplinary science. It is at the intersection that we position our strategic vision into a future where we will provide radical materials innovations and solutions to our national-security programs and other sponsors.

Our 2004 Annual Report describes how our successes and breakthroughs follow a path set forward by our strategic plan and four organizing research themes, each with key scientific accomplishments by our staff and collaborators.

We have organized this report into two major sections: *research themes* and our *dynamic teams*. The research-theme sections focus on achievements arising from earlier investments while addressing future challenges. The dynamic-teams section illustrates the directorate's organizational structure of divisions, centers, and institutes that support a team environment across disciplinary and institutional boundaries.

The research presented in this annual report gives substantive examples of how we are proceeding in each of these four theme areas and how they are aligned with our national-security mission. By maintaining an organizational structure that offers an environment of collaborative problem-solving opportunities, we are able to nurture the discoveries and breakthroughs required for future successes.



Science Supporting National Objectives at the Intersection of Chemistry, Materials Science, and Biology

Many applications in nano- and biotechnology readily build on our unique mixture of disciplines, specifically at the intersection of chemistry, materials science, and biology. We are conducting research that will enable new technologies and tools to combat chemical and biological terrorism and enhance fundamental human-health research.

By manipulating materials through laboratory-synthesized functionalized membranes, chemically engineered proteins, and carbon nanotubes, we continue to develop new materials systems for advanced nanoscale sensors and detectors. Our studies on the molecular mechanisms of tissue mineralization may allow us to better define strategies for designing therapeutic drugs to treat diseases such as kidney stones. The discoveries also help us predict molecular interactions in complex environments, support Livermore's mission in sensing, and sustain a strong life-science effort.

Materials Properties and Performance under Extreme Conditions

Our emerging ability to control matter on the nanometer scale is leading to many revolutionary applications. Successful synthesis of nanoporus materials with engineered properties is the first step toward entirely new types of novel materials that will find applications as critical components of future targets for the National Ignition Facility and other high-energy-density-science platforms.

Unparalleled resources—both in computation and experiments—are required in order to observe the ultrafast dynamics of materials at the same scales of the underlying physics. Fundamental understanding of dislocation, metal deformation, electronic structural changes, and quantum criticality offers insight into materials performance and, more importantly, their failure mechanisms.

Chemistry under Extreme Conditions and Chemical Engineering to Support National-Security Programs

Taking advantage of the immense computing resources at Lawrence Livermore, our scientists have unique tools to not only study extreme phenomena of chemical detonation, but also to decipher the chemistry of planetary interiors and other extreme environments. Our ability to approach multiscale modeling of extreme chemistry is best illustrated in our latest simulation-based discoveries of superionic and polymeric phases of water and the origin of methane at extreme geophysical pressures.

A new generation of experimental techniques enables us to probe materials under previously inaccessible conditions, allowing us to validate our simulations and discover new chemical and physical phenomena. Our scientists also continue to improve the structural control in the synthesis of nanoscale sol-gel materials with desired composition and morphology.

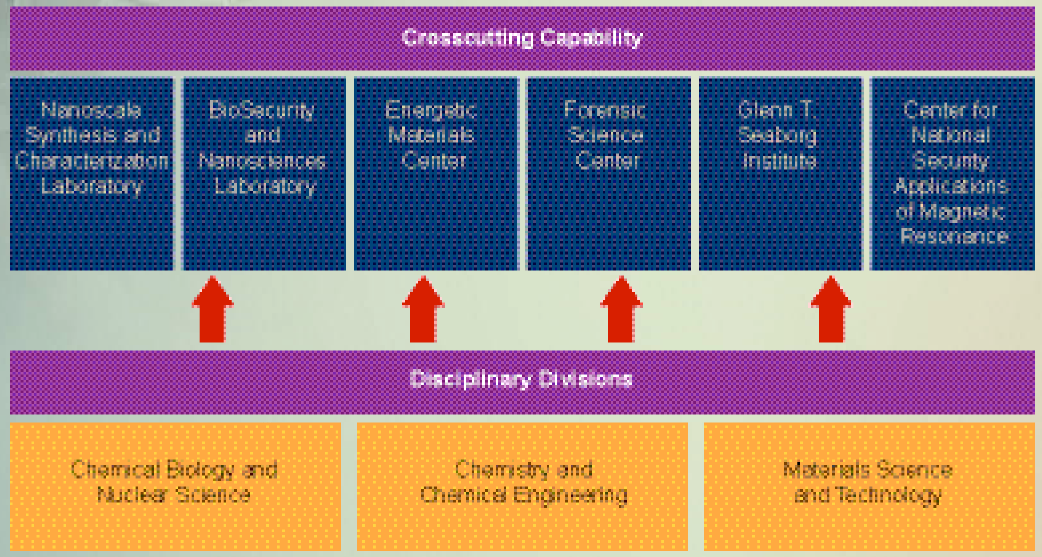
Applied Nuclear Science for Human Health and National Security

With tools such as the high-spatial-resolution NanoSIMS, our scientists are making dramatic advances in the science of isotope identification and nuclear chemistry. Their work is finding direct application to the investigation of interplanetary dust particles, as well as to human-health. Additionally, nuclear science and isotopic techniques are proving critically important in defining and solving national and international problems related to the environment and global security. From isotope tracers from reprocessed nuclear fuel to groundwater contamination, the broad applications in science, health, and national security reinforce the importance of our enduring capability in nuclear science and contribute to the success of our core mission.

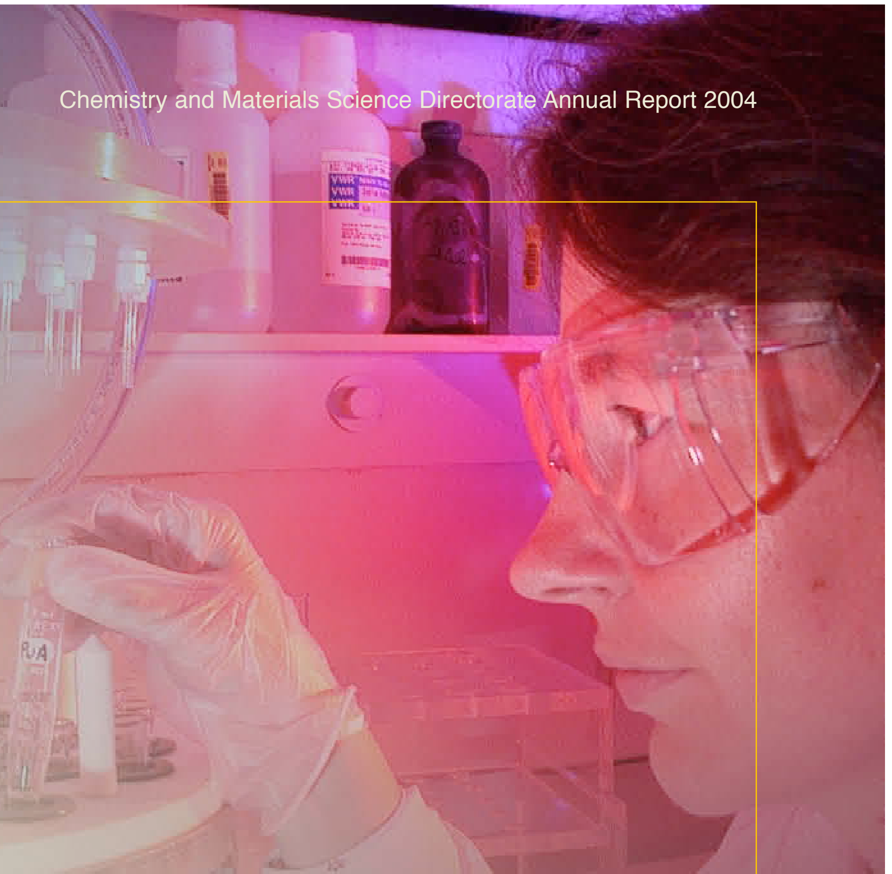
Dynamic Teams

The Chemistry and Materials Science (CMS) Directorate at Lawrence Livermore National Laboratory is arranged to represent the culture of our directorate—discovery-class science and a dynamic organizational structure. We have six crosscutting scientific centers that are staffed by personnel from our three divisions.

The three divisions in CMS are responsible for the line management and leadership of the scientific, technical, and administrative staff. Each division maintains a close relationship with Laboratory programs, working with directorate and program leaders to ensure an effective response to programmatic needs. Together, the divisions provide us with the flexibility and agility to respond to change and to merge our science successes into program milestones.



The centers provide specific research environments to support needs in nanoscale novel materials development; biosecurity and nanobiotechnology research; forensic science for chemical, nuclear, and biological counterterrorism; applied nuclear science and nuclear radiochemistry; research and development of high explosives, pyrotechnics and propellants; and in-situ characterization of materials using nuclear magnetic resonance spectroscopy.



Awards and Recognition

The staff who make the science happen at Lawrence Livermore continue to receive recognition for their accomplishments from their peers through awards, honors, and fellowships from respected scientific societies. The awards and recognition section of this report highlights the many achievements in CMS during 2004.

Financial and Operational Information

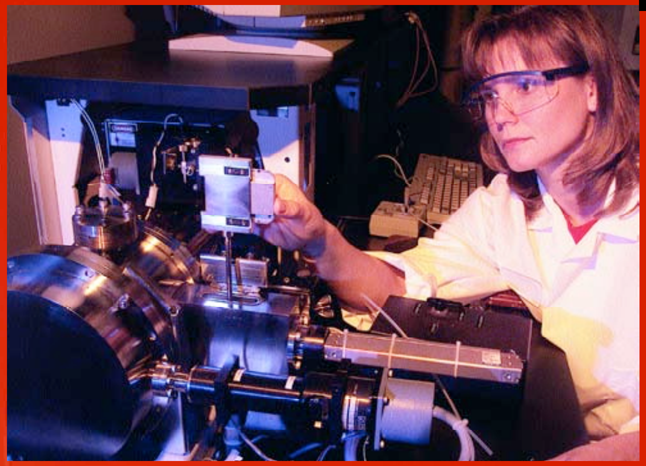
CMS is fully committed to the simultaneous excellence in both science and operations. In addition to the scientific and technical accomplishments in 2004, we have compiled our financial and operational data into a separate publication, Facts and Figures. This companion publication to the annual report intends to be a broad overview of budgetary, personnel, and other administrative information about Lawrence Livermore National Laboratory and our directorate. Facts and Figures is available for download from our website.

Looking Forward

The future we envision is arriving, and more rapidly than we expected. We have good reasons to be optimistic as 2005 unfolds and the Laboratory assumes increasing responsibilities in new national-security programs. CMS maintains an unambiguous role as both a partner and a technology leader for these responsibilities. More confident and committed than ever, we look forward to expanding frontiers of science and continuing our legacy of partnership with the Laboratory and the worldwide scientific community, as we apply science and technology to the important challenges of our time.

Sincerely,

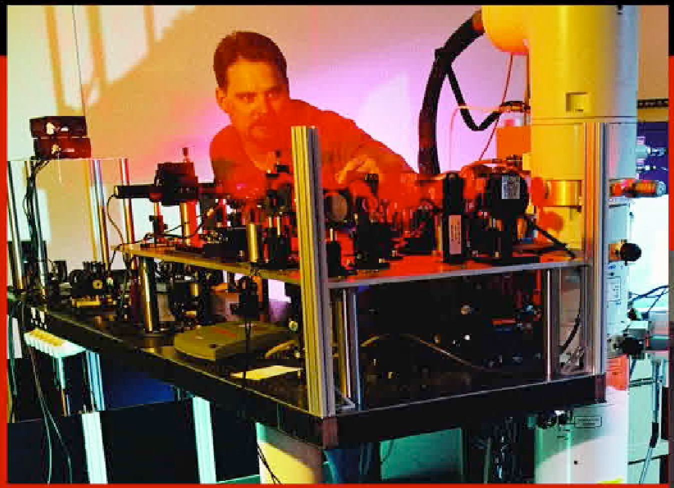
Tomás Díaz de la Rubia
Associate Director, Chemistry and Materials Science
Lawrence Livermore National Laboratory



CHEMISTRY AND MATERIALS SCIENCE

Research Themes

- Science at the intersection
- Materials properties and performance
- Chemistry under extreme conditions
- Applied nuclear science



Unraveling the Molecular Modulation of Kidney Stone Formation

For more information contact
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The primary constituent of kidney stones in patients with urolithiasis is calcium oxalate monohydrate (COM). Normal urine contains compounds such as citrate and proteins that inhibit crystallization of COM (Figure 1). Although these inhibitors provide protection, their precise roles have not been defined. Understanding the molecular features and physiologic effects of individual urinary proteins and small inhibitory molecules is essential for determining their roles in disease and defining strategies for designing therapeutic drugs.

We investigate the molecular mechanisms of tissue mineralization and pathogenesis by combining molecular modeling and in situ scanning probe microscopy. Using this method, we examine the thermodynamic and kinetic impacts of citrate and osteopontin on modulating the growth of COM and determine the stereochemical relationship between the growth modifier and atomic features on the crystal surface.

Relevance to CMS Research Themes

Our work focuses on biomolecular control of tissue mineralization and pathogenesis. This field integrates knowledge from materials physics, physical chemistry, biology, and medicine. The work aligns with the CMS strategic theme of science at the intersection of chemistry, materials science, and biology. Understanding how macromolecules dictate the shape, size, and properties of inorganic entities will strongly impact efforts in biological, chemical, and materials science and technology for national-security applications.

Major Accomplishments in 2004

We have found that COM grows on atomic steps at dislocations, and citrate and osteopontin each attack a different face of COM crystals. Figure 2 illustrates COM growth in a citrate-bearing solution. Citrate predominately inhibits growth on the (–101) face by forming a geometric match between the carboxylic groups and the calcium ions at the step edges. A triangular shape dislocation hillock becomes quite rounded and disc-shaped. Citrate has a much lesser effect on the (010) face.

Molecular modeling calculations show that the highest binding energy of citrate bounds to steps on the (–101) face is $-170\ \mathrm{kJ\cdot mol^{-1}}$ and only $-102\ \mathrm{kJ\cdot mol^{-1}}$ on the (010) face. Our experiental data, along with theoretical calculations, suggest that citrate modifies the shape and inhibits the growth of the COM by pinning-step motion, as indicated in Figure 3. In addition, the morphological change in step structure is consistent with that of the bulk crystal shape.

In contrast, osteopontin has the greatest effect on the (010) face, where the step height is similar to the size of the protein. Osteopontin also inhibits the step kinetics and changes its morphology.

These results suggest that, used simultaneously, citrate and osteopontin may work synergistically to inhibit overall growth of COM. In addition to designing drugs that reduce or eliminate kidney stones, these modifiers are effective at changing the shape of crystals and may provide materials scientists with strategies for growing designer crystals. The results also demonstrate the capability of combining molecular imaging and modeling tools for understanding events underlying aberrant crystallization in disease.

Scientific Impact

These results, which were recently featured as a cover story in the *Proceedings of the National Academy of Sciences*, showed for the first time the molecular mechanism of therapeutic agents and naturally occurring proteins that control the crystallization of calcium oxalate crystallization. In addition, the results showed that citrate and osteopontin protein act in concert to inhibit kidney stone growth.

Related Publications

S.R. Qiu, et al., "Molecular Modulation of Calcium Oxalate Crystallization by Osteopontin and Citrate," *Proc. Natl. Acad. Sci. USA* **101**, 1811–1815 (2004).

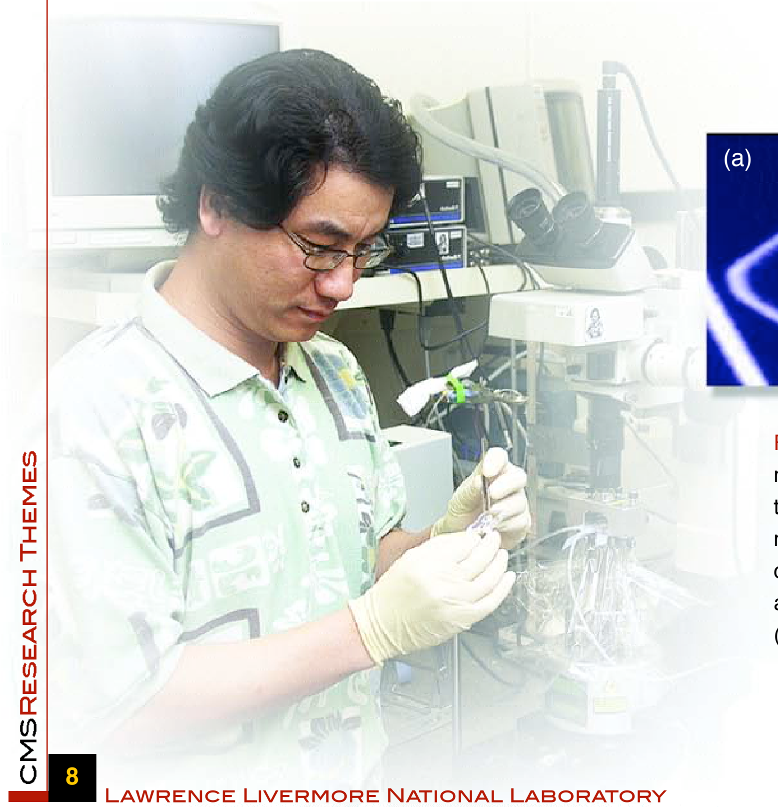
J.J. De Yoreo and P.M. Dove, "Shaping Crystals with Biomolecules," *Science* **306**, 1301–1302 (2004).

P.M. Dove, J.J. De Yoreo, and S. Weiner, Eds., *Reviews in Mineralogy and Geochemistry, Volume 54, Biomineralization* (Mineralogical Society of America Geochemical Society, Washington, D.C., 2003), pp. 57–93.

NEW FRONTIERS

By combining theoretical calculations with crystal growth theory, we will define the mechanism by which small molecules and proteins control the thermodynamics and kinetics of the COM growth and shape modification. We will also investigate the interaction between the COM crystal and synthetic peptides that mimic the acidic segments of osteopontin and are believed to be responsible for the inhibitory function.

Understanding the mechanisms by which peptides interact with the COM crystals reveals details of various amino acid sequences within proteins that control the crystallization of kidney stones in humans. Knowledge about the molecular modulation of kidney stones can be extended to studies of other biogenic materials in humans, such as the mineral phases of calcium phosphate—the main inorganic component in human teeth and bones. We expect that this knowledge will lead to the development of new drugs to fight oral and bone diseases and will also help researchers design strategies to remove heavy metals from groundwater.



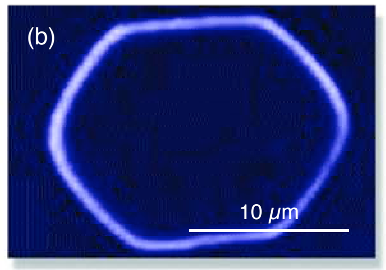


Figure 1. Scanning electron microscopy images show how the growth of calcium oxalate monohydrate—the main constituent of kidney stones—is affected by the (a) absence and (b) presence of citrate in solution.

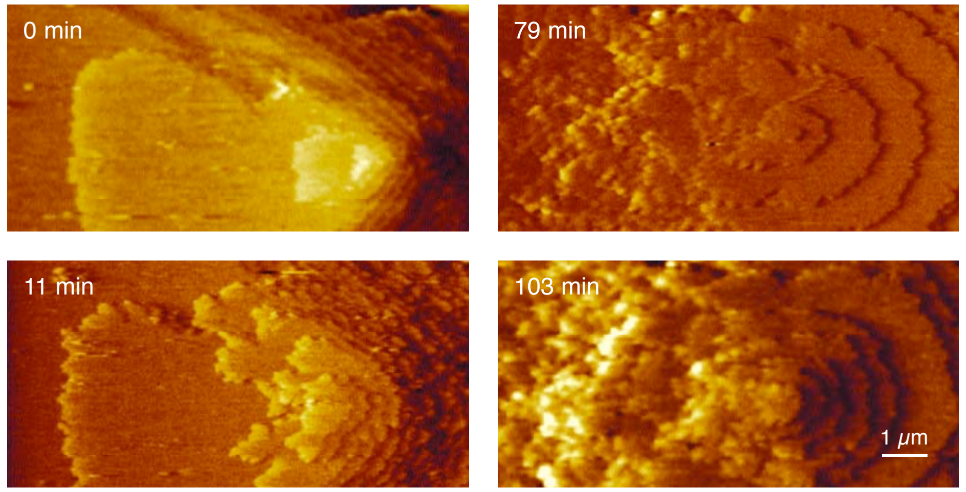


Figure 2. Atomic force microscopy images show the effect of citrate-bearing solution on the morphology of calcium oxalate monohydrate.

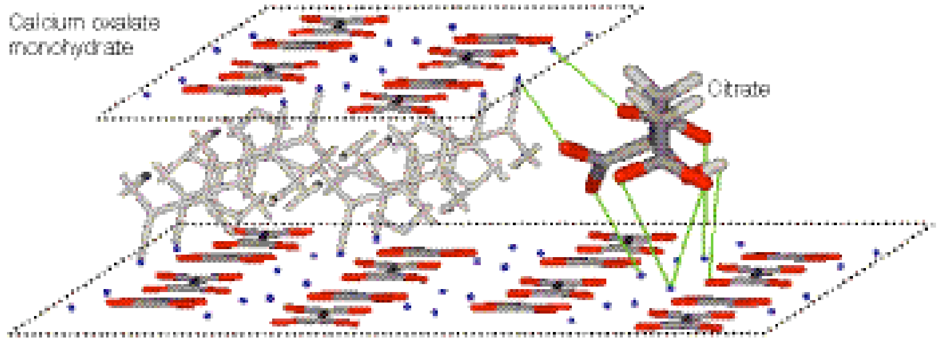


Figure 3. Molecular modeling calculations show the geometry of citrate with the highest binding energy to the acute step (light grey molecules) on the (–101) face. The green lines represent the chemical bonds between the citrate molecules and calcium ions, and the bonds between the hydroxyl groups and the oxalate ions. Other ions represented are Ca^{2+} (blue), O (red), C (dark grey), and H (off-white).

Smart Membranes for Bio-Organism Detection

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Identifying biological organisms that may have been engineered for the purpose of a biological attack is critical for national security. To address this need, we are coupling semiconductor nanotechnology with surface chemistry. We have synthesized arrays of functionalized pores in silicon membranes that can selectively capture and immobilize an organism ranging in size from spores (many micrometers) to viruses (tens of nanometers), as illustrated in Figure 1.

Creating channels in the membrane with controlled position, length, and diameter that range in size from micrometers to a few tens of nanometers represents a major challenge. Furthermore, in confined geometries such as nanochannels, controlling and characterizing the organic/inorganic interface require significant technological breakthroughs.

To identify bio-organisms, we are building a particle-characterization device based on a Coulter counter, with a fabricated pore that mimics an ion channel. As an organism is electrophoretically driven through the device, it generates an ionic current blockade event. The amplitude, duration, and shape of the electrical signal provide information on size, shape, and chemical composition of the organism (Figure 2).

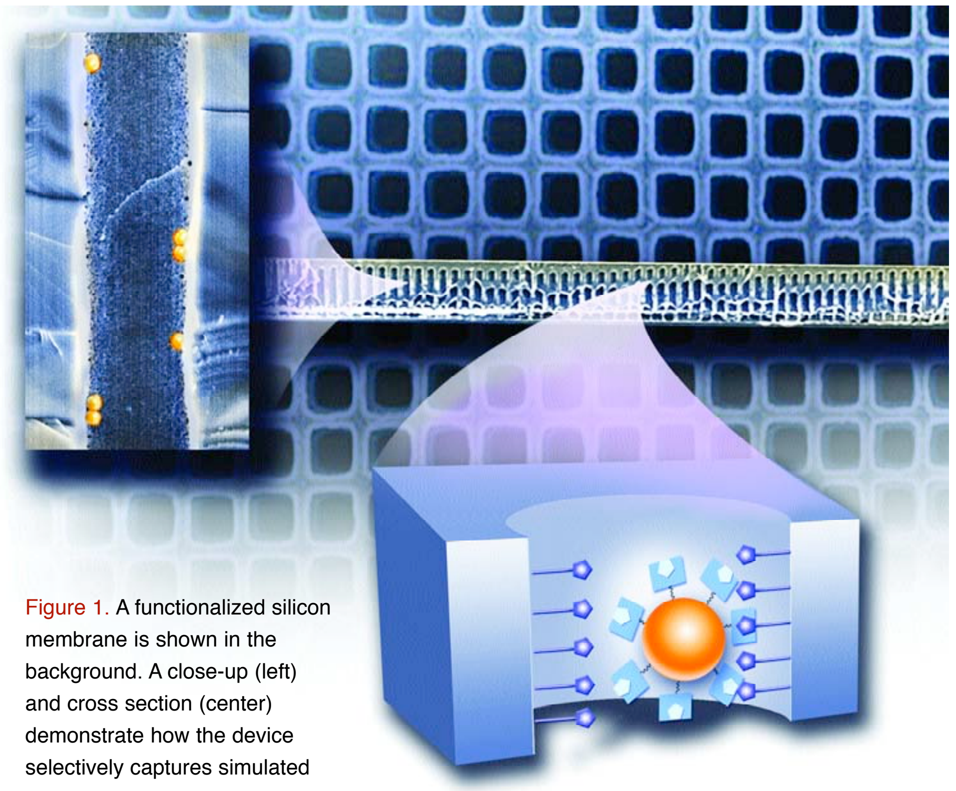


Figure 1. A functionalized silicon membrane is shown in the background. A close-up (left) and cross section (center) demonstrate how the device selectively captures simulated bio-organisms, represented in orange.

Relevance to CMS Research Themes

Understanding the interface between an inorganic platform and organic ligands is aligned with the part of the CMS strategic plan that is dedicated to systems integration. This work also supports Livermore's national-security mission by building a detection platform that will generate a profile of characteristics such as size, shape, and chemical functionality of unknown biological organisms. Once characterized, the electrical signatures of these organisms can be compared to others stored in a database.

Major Accomplishments in 2004

Our group demonstrated the first success of electrochemical etching to synthesize silicon membranes and showed their ability to selectively capture micro-organisms. We produced periodic arrays of functionalized pores with diameters down to 30 nm and aspect ratios (opening vs depth) up to 250, which had never been achieved before. To simulate micro-organisms, we coated fluorescent microbeads with an antibody. The membranes, functionalized with a particular antigen, selectively captured the matching antibody-coated beads while allowing the rest of the beads to flow through the membranes' pores.

We also demonstrated the utility of our devices for cell encapsulation applications with pore diameters in the ten-nanometer range. In such applications, the main challenge is to fabricate a porous capsule that allows the diffusion of a cell nutrient such as glucose, while blocking the diffusion of an antibody such as immunoglobulin, which may trigger foreign body responses.

In each application, we used a focused ion beam to machine single apertures down to a few tens of nanometers. Ionic current through these devices was recorded with DNA probes before and after functionalization, demonstrating the open nature of the apertures before and after functionalization. We also successfully achieved localized oxidation deposition at the entrance of the membrane aperture, which we characterized by energy dispersive x-ray spectroscopy and atomic force microscope spectroscopy.

We are now studying the dynamics of DNA probes as they flow through functionalized apertures (Figure 3) in order to demonstrate the selectivity of our Coulter counter. The next step will be to demonstrate selective bio-organism detection with engineered bacteriophages.

Scientific Impact

While research in membrane and single-pore technology is heading toward nanodevices for DNA detection, a gap has remained between objects as large as blood cells and those as small as DNA. More importantly, spatial localization of the ligands on artificial pores has not been achieved. Our group is closing the gap by machining single apertures to the 20–500-nm range to study virus and bacterium regimes. We used ion beam–assisted oxide growth around the apertures, followed by self-assembled surface chemistry, to demonstrate localization of the ligands at the aperture opening. This unique combination of controlled aperture geometry and surface chemistry should lead to the first selective Coulter counter for bio-organisms.

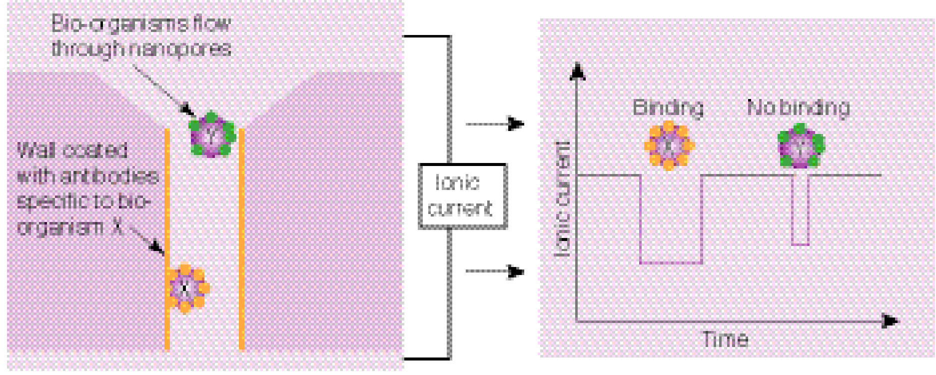


Figure 2. The scheme of operation shows a bio-organism traveling through a functionalized Coulter counter. An ionic current drives the bio-organism through an aperture. The amplitude of the blockade event reflects the size of the organism, and the duration of the event represents the affinity between the organism's outer coat proteins and the functionalized aperture wall.

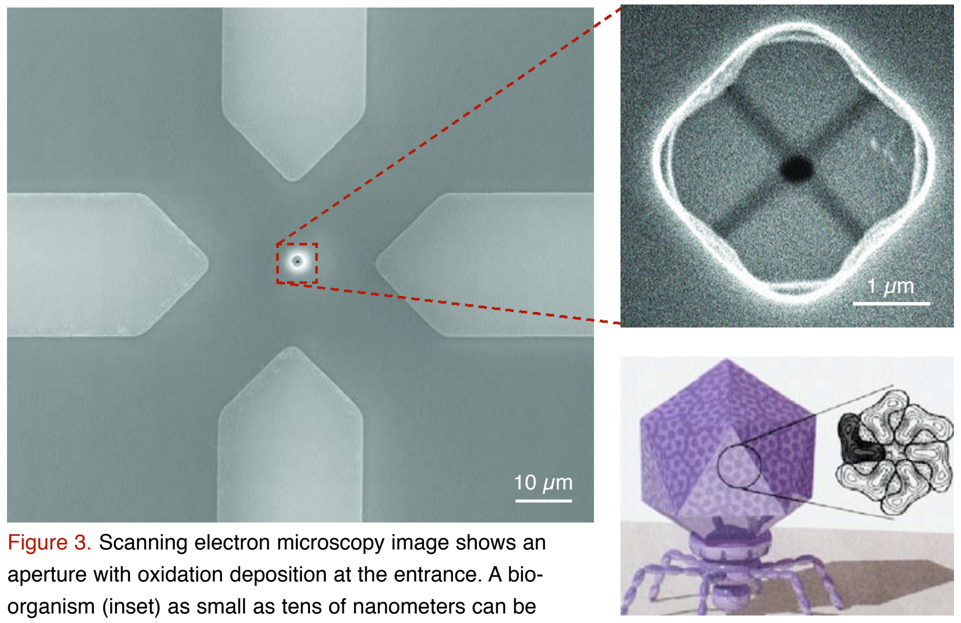


Figure 3. Scanning electron microscopy image shows an aperture with oxidation deposition at the entrance. A bio-organism (inset) as small as tens of nanometers can be detected.

Related Publications

S.E. Létant, et al., "Functionalized Silicon Membranes for Bio-Organisms Capture," *Nature Materials* **2**, 391 (2003).

S.E. Létant, et al., "Nanochannel Arrays on Silicon Platforms by Electrochemistry," *Nano Letters* **4**(9), 1705 (2004).

NEW FRONTIERS

When this new class of detection platforms is developed, scientists will be able to collect, concentrate, and analyze bio-organisms in real time. These engineered membranes are extremely versatile and could be adapted to recognize the fingerprints (size and membrane proteins) of any bio-organism of interest. To help achieve that goal, we will add in situ detection capabilities to our selective membranes. Possible applications for such an integrated device include: counter-terrorism, human health, and environmental monitoring.

A challenge will be to further control single-aperture functionalization, ultimately to where a single chemical unit is positioned at the entrance of a single aperture. Such a platform would lead to detectors for single molecules and to the sequencing of a single molecule of DNA.

Molecular Transport in Carbon Nanotubes

Improving our capability to detect and monitor chemical and biochemical agents is a critical component of LLNL's mission. Our group takes a molecular-level approach for materials transport and uses it to develop innovative nanostructures that can be used for biological agent detection as well as other applications such as water desalination and molecular separation.

Discovered in 1991, carbon nanotubes are extremely small, hollow cylinder structures that are endowed with exceptional conductivity and strength. Particularly, one-dimensional nanowires and nanotubes exhibit unusual physical properties, due to their reduced dimensionality and enhanced surface-volume ratio. We use carbon nanotubes as molecular wire templates and utilize their unique geometry, structure, and electrical properties to create novel functionality in two project areas. First, we are building a nanodevice that can detect pore-forming bacterial toxins. In another project, we are building a synthetic membrane that would utilize the inner diameter of the nanotube for mass transport and separation.

Relevance to CMS Research Themes

This work advances system integration strategies by developing sensing and surveillance components for a broad spectrum of chemical and biochemical applications. For example, one-dimensional phospholipids-based nanosensors will permit a large number of individual sensors to be packaged on the surface of a semiconductor chip and will enable the use of low-cost electrical detection to interrogate the sensors.

The tight integration of biomimetic and inorganic components in such a structure ensures the ultimate sensitivity of the device. Also, nanotube-based membranes can control access of the analyte molecules to the chip components with molecular precision. The technology can be applied to other relevant areas, including molecular sieving, desalination, and dialysis, all of which apply to research at the intersection of chemistry, materials science, and biology.

Major Accomplishments in 2004

The phospholipids, or lipids, in cell membranes are arranged as a bilayer (two molecules thick). We have successfully fabricated and characterized one-dimensional lipid bilayers, which represent a new class of nanostructures that combine carbon nanotubes with biomimetic membranes (synthetic membranes that mimic biological ones), as illustrated in Figure 1. By modifying carbon nanotubes with multilayers of polyelectrolyte polymers, we can control the nanotube surface functionality and add support and strength for the lipid bilayers.

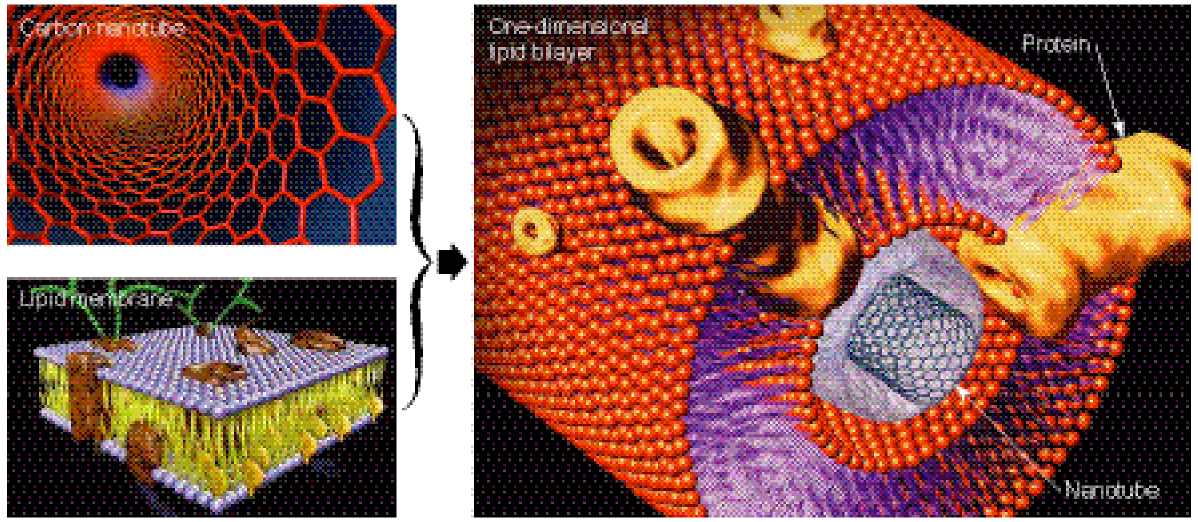
These nanotube templates enable formation of one-dimensional lipid bilayers in which a lipid bilayer spontaneously wraps around these nanostructures to form an insulating jacket. By applying the fluorescence-recovery-after-photobleaching techniques, we have confirmed that the lipid molecules in these nanostructures are mobile (Figure 2).

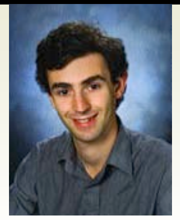
In our second project, we have developed a synthetic membrane by using carbon nanotubes with diameters of 0.6–10 nm for membrane pores. Graphite's inherently smooth surface enables a high flux of the permeate molecules. Recent simulations by our collaborators at the National Institutes of Health suggest that water exhibits unique effects upon one-dimensional confinement not seen in the bulk, and our aim is to produce a platform for investigation of these effects.

Using standard microfabrication techniques, we have produced patterned arrays of multiwall carbon nanotubes (Figure 3) with outer diameters of 20–50 nm and inner diameters of 6–12 nm. The arrays are coated with a conformal silicon nitride matrix to fill the gaps between the tubes and to produce a robust, freestanding membrane. Porosimetry measurements have confirmed that the membrane is void-free, with pores corresponding to the inner diameters of the multiwall carbon nanotubes.

Experiments are under way to characterize the transport characteristics of electrolytes through this membrane for applications in desalination and dialysis. Efforts are also under way to produce the single-wall nanotube version of this membrane (pores sizes from 0.6–2 nm), which would enable highly selective molecular separations as well as bring us closer to observation of confinement effects in water.

Figure 1. By combining carbon nanotubes and biomimetic membranes, we are creating a new class of nanostructures that have increased functionality.





For more information contact
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Scientific Impact

Our work on the one-dimensional lipid bilayers is one of the first demonstrations of unique nanostructures that tightly integrate biomimetic materials and inorganic nanostructures. This integration allows for the efficient transformation of biomolecular signals into measurable electrical responses, which results in many new opportunities to advance our study of molecular transport and to design a new generation of biosensors. Our development of artificial membranes will allow us to test the predictions from simulations that show unique effects of confinement in bulk water.

Related Publications

A.B. Artyukhin, et al., "Functional One-Dimensional Lipid Bilayers on Carbon Nanotube Templates," *J. Am. Chem. Soc.*, in press.

A.B. Artyukhin, et al., "Layer-by-Layer Electrostatic Self-Assembly of Polyelectrolyte Nanoshells on Individual Carbon Nanotube Templates," *Langmuir* **20**(4), 1442–1448 (2004).

J. Holt, et al., "Fabrication of a Carbon Nanotube-Embedded Silicon Nitride Membrane for Studies of Nanometer-Scale Mass Transport," *Nano Letters* **4**(11), 2245–2250 (2004).

New Frontiers

Carbon nanotube membranes provide a foundation for new types of materials and structures that can be used in many applications, including water desalination and ultra-tough composites with unique vapor transport properties. Our studies will make a significant contribution to fundamental studies of molecular transport in confined nanostructures and to the nascent field of nanofluidics. As we continue our work on fabricating structures based on one-dimensional bilayers, we will incorporate them into detection devices that utilize the unique functionality of membrane proteins. We will also investigate alternative uses for this technology for specific detection of chemical species. Finally, the one-dimensional bilayer provides unique capabilities for studying molecular transport in systems of reduced geometry and molecular-scale curvature.

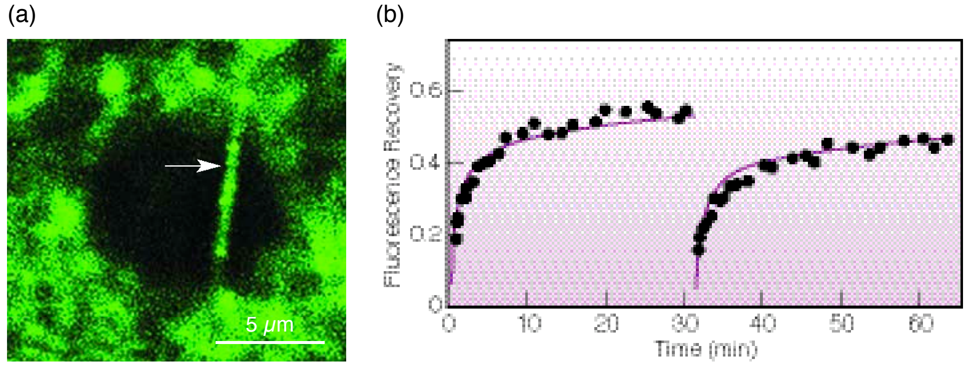

Figure 2. (a) A scanning confocal microscopy image shows a lipid bilayer on a carbon nanotube stretched across a transmission electron microscopy grid hole. (b) Two consecutive fluorescence-recovery curves verify the mobility of the membranes.

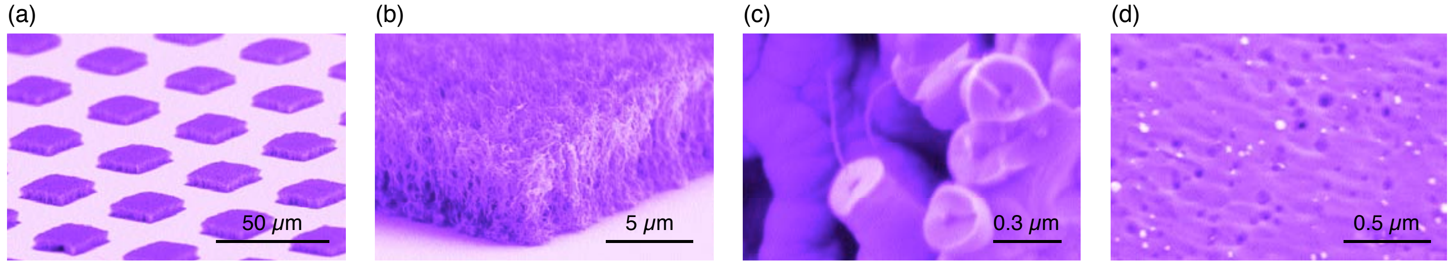

Figure 3. Patterned array of carbon nanotubes (a) and close-up (b) illustrate the typical high density, in excess of 10^{10} cm^{-2} (areal). Micrographs show conformal coating of silicon nitride around multiwall carbon nanotubes of 20–50 nm in diameter (c) and silicon nitride/carbon nanotube membrane (d), with pore sizes representative of the nanotube outer diameters.

Novel Approach for Identifying Bacterial Toxin Inhibitors

For more information contact

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The exposure of U.S. postal workers to *Bacillus anthracis*, commonly known as anthrax, in 2001 revealed a gap in the nation's overall preparedness against bioterrorism. The incidents underscored an urgent need to prevent, rapidly diagnose, and treat disease by developing antiviral drugs and antibiotics that would be effective on new pathogenic bacterial or viral strains. Developing new methods for fast and efficient synthesis and screening of small drug-like molecules with a high affinity against toxins should be one of the top priorities in the fight against bioterrorism.

In order to be useful, these new methods must provide high-throughput analysis and specific molecular binders that inhibit the toxins in a short period of time. To meet this need, we are developing an approach that uses living cells to generate libraries of small drug-like biomolecules, which are then screened inside the cell for activity. The advantage of this method is that both processes—biosynthesis of the library and screening—occur inside the cell, eliminating the need for in vitro screening. This approach considerably speeds up the process. Further, because screening takes place inside a complex biological cell consisting of thousands of proteins, only those proteins in the library with high specificity for the target will be selected.

Relevance to CMS Research Themes

The development of this novel approach introduces a technology that combines chemistry and biology for fast and efficient identification of high-specificity inhibitors, or ligands, to biological toxins. These ligands can be used as powerful antidotes against toxins. More importantly, because they can also be used as biosensors when attached to the appropriate platforms, they can help advance our national-security mission by providing an inexpensive and reliable detector system to improve response capability to bioterrorist attacks on the civilian population. This new combined approach may also be used to generate small drug-like molecules that are capable of interfering with deleterious protein interactions occurring in neurodegenerative diseases, such as Mad Cow and Alzheimer's.

Major Accomplishments in 2004

Our group is using this living combinatorial approach to find highly specific ligands capable of disabling the lethal factor (LF) toxin. This toxin, which is secreted by virulent strains of *B. anthracis*, kills its host cell immediately after contact. Key to our approach is the development of a method for the biosynthesis of libraries of small biomolecules and an efficient screening process that can be carried out inside the cell.

Circular peptides are one of the most common scaffolds used in nature to produce high-affinity, drug-like effectors such as antibiotics and immuno-suppressants. Circular peptides can be artificially created, or biosynthesized, inside the cell by using recombinant DNA expression techniques to produce vast libraries of these compounds, that is, libraries of cells that are each able to biosynthesize a particular cyclic peptide. By using engineered protein-splicing elements, we have been able to biosynthesize two cyclic proteins: (1) a SH3 domain of the oncogene cCrk protein—an ideal model for in vivo biosynthesis of polypeptides and (2) the cyclotide Kalata B1.

Cyclotides are a class of disulfide-rich proteins that have the feature of a cyclic backbone, as illustrated in Figure 1. Because of their unique circular backbone and knotted arrangement of the three disulfide bonds, cyclotides are exceptionally stable to thermal and enzymatic degradation. Further, their well-defined structures have been associated with a range of biological activities such as inhibition of neurotensin binding and uterotonic properties. These characteristics make cyclotides ideal candidates as molecular scaffolds for new ligand/drug design and discovery.

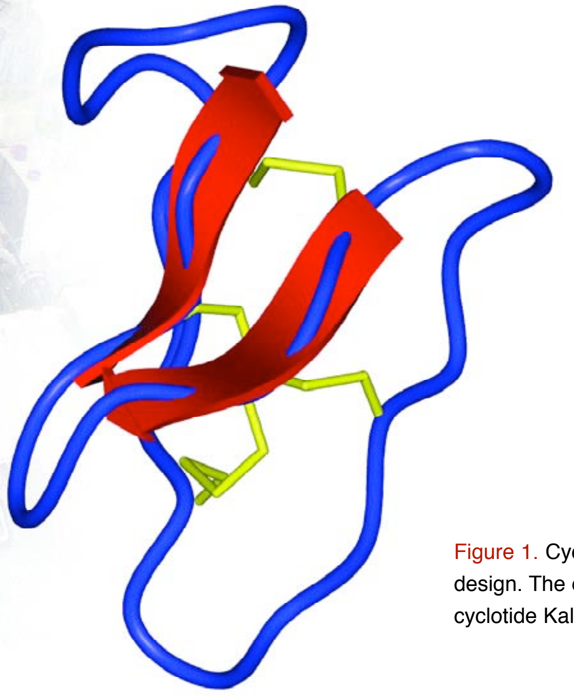

Figure 1. Cyclotides provide an ideal scaffold for a ligand design. The diagram at the left shows the structure of the cyclotide Kalata B1.

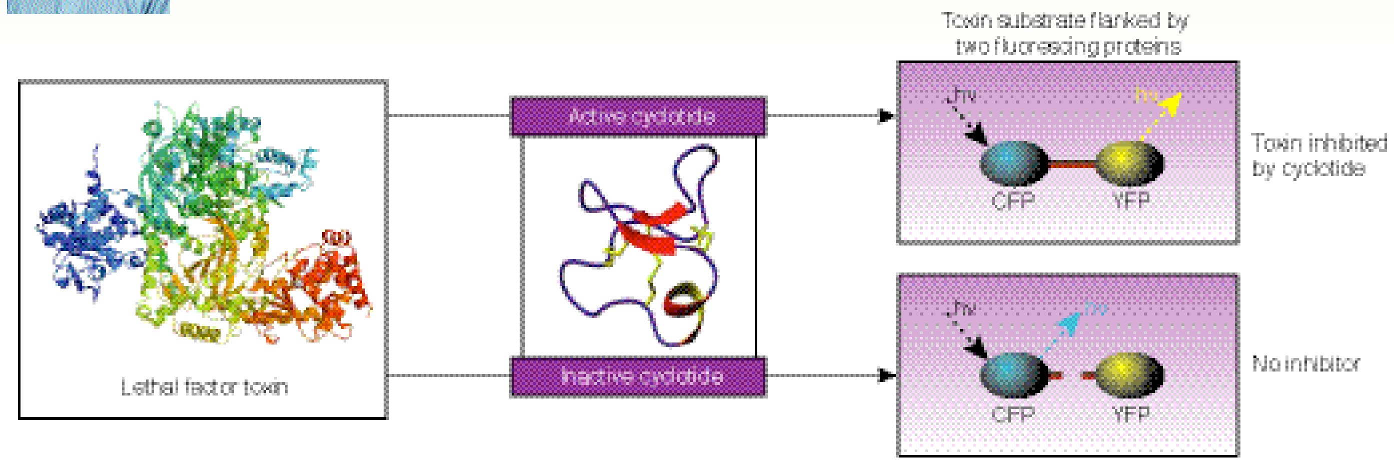

Figure 2. We have developed an in vivo approach for the screening of a cyclotide cell-based library against the lethal factor toxin produced by *B. anthracis*. The chameleon reporter directly senses the toxin activity and reports through a fluorescence change which cells express active inhibitors. In a cell with an active cyclic peptide inhibitor, we can measure the emission of the yellow fluorescent protein (YFP) fluorophore as the cyan fluorescent protein (CFP) fluorophore is excited.

We use fluorescent proteins as "chameleon reporters" in vivo during the screening process to find which cyclotides within the biomolecular library are able to inhibit the LF toxin produced by *B. anthracis* (Figure 2). The reporter monitors molecular interactions and changes color when it detects an interaction. The LF toxin is a Zn-protease that cleaves specific proteins critical for the survival of the targeted cell. The screening reporter uses the catalytic activity of the protease enzyme in combination with a fluorogenic substrate, which is composed of a short substrate of the protease and is flanked by two fluorescent proteins—cyan and yellow. Cyan fluorescent protein (CFP) and yellow fluorescent protein (YFP) are both engineered mutants of the naturally occurring green fluorescent protein and are designed to form a fluorescence resonance energy transfer (FRET) pair.

When the protease and the fluorogenic substrate are expressed in a cell that has biosynthesized an active cyclic peptide inhibitor, the protease is unable to cleave the fluorogenic substrate. This allows us to observe the FRET by measuring the emission of the YFP fluorophore as the CFP fluorophore is excited. In contrast, we observe no FRET in a cell that has not biosynthesized an active cyclic peptide inhibitor. By using in vivo fluorogenic enzymatic assay in combination with fluorescence-activated cell sorter technology, we are able to separate the cells capable of producing selective inhibitors. Also, DNA sequencing of the positive cells makes it possible for us to identify the active components of the library that can be later used in detection or disease treatment.

Scientific Impact

Our initial focus has been to produce high-affinity ligands that can disable bacterial and other biological toxins. However, this approach can easily be used to find small drug-like molecules capable of disrupting any biomolecular interaction. For example, the method can be used to find molecules that may disrupt the destructive mechanisms involved in cancer and neurodegenerative diseases such as Mad Cow and Alzheimer's.

Related Publications

J.A. Camarero and R. Kimura, "Expressed Protein Ligation: A New Tool for the Biosynthesis of Cyclic Polypeptides," *Protein Peptide Lett.*, in press.

J.A. Camarero, et al., "Biosynthesis of the Cyclotide Kalata B1 Using Protein Splicing," *Protein Sci.* **13**(1), 139 (2004).

J.A. Camarero, et al., "Peptide Chemical Ligation Inside Living Cells: In Vivo Generation of a Circular Protein Domain," *Bioorg. Med. Chem. Lett.* **9**, 2479–2484 (2001).

NEW FRONTIERS

We will develop a new method for the in vivo screening of biomolecular libraries using Darwinian selection, in which only the cells that produce ligands capable of disabling the target protein will be able to survive. This method will simplify the selection process by mirroring the way the human immune system works. The ability to biosynthesize cyclic peptides using protein-splicing technology has important implications for drug-development efforts. The capability to screen for biochemical events in an environment as complex as the cell's interior will provide valuable information. For example, peptide-based libraries are already showing to be effective in producing drug candidates in bacterial as well as mammalian systems.

Synthesis and Characterization of Nanoporous Metal Foam

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Among the most interesting accomplishments of materials science is the design and synthesis of new materials with engineered properties. Cellular materials—in particular, nanoporous metal foam—are one example. Through a process of casting, powder metallurgy, and sputter deposition, cellular materials with large pores (200 μm to 2 mm) can be produced. However, creating nanoporous metal foam with pores less than 100 nm requires unconventional techniques such as selective dealloying to achieve homogeneous pores and pore size distribution.

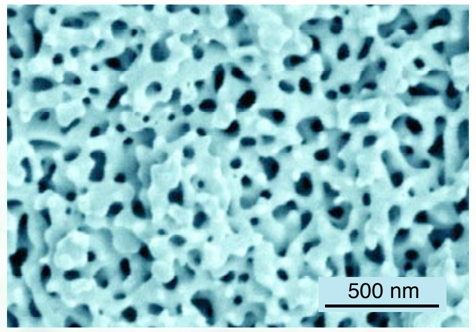

Figure 1. Scanning electron microscopy image of a synthesized porous gold sample shows the sponge-like morphology of interconnecting ligaments after selective dealloying.

Current research on nanoporous foam processing has focused on gold/silver alloys, and the challenges are to produce nanoporous foam of lower density from a range of metals and to understand the relationship of pore evolution and mechanical properties. Testing and characterizing the foam require new techniques as well as the development of foam scaling laws, which include factors such as nanoporosity and nanocrystallinity.

Relevance to CMS Research Themes

Lawrence Livermore's long-term strategic plan aims for the development and understanding of nanoscale materials science and technologies to achieve programmatic missions. Processing and characterization of nanoporous structures (pore size 10–50 nm) are necessary for this research endeavor. Most of the research on nanoporous materials has focused on synthesis, with much less attention given to characterization and mechanical behavior. Our studies of the processing, characterization, and mechanical behavior of these materials will accelerate the development of technologies that use these materials. Specifically, sophisticated targets for high-energy-density experiments demand new classes of designer materials with low densities and thoroughly characterized mechanical behavior. High-energy-density science will benefit from this work because our research will provide the foundation for the fabrication of highly tailored and complex targets.

Major Accomplishments in 2004

We have demonstrated for the first time that electrolytic dealloying leads to a nanoporous structure formed of nanocrystalline foam ligaments. In selective dealloying, the more electrochemically active element is dissolved, leaving behind a sponge-like morphology of interconnecting ligaments made from the less electrochemically active element (Figure 1). Using dealloying, we have prepared nanoporous gold (Au) samples by selective electrolytic dissolution of silver (Ag) from various Au/Ag alloys.

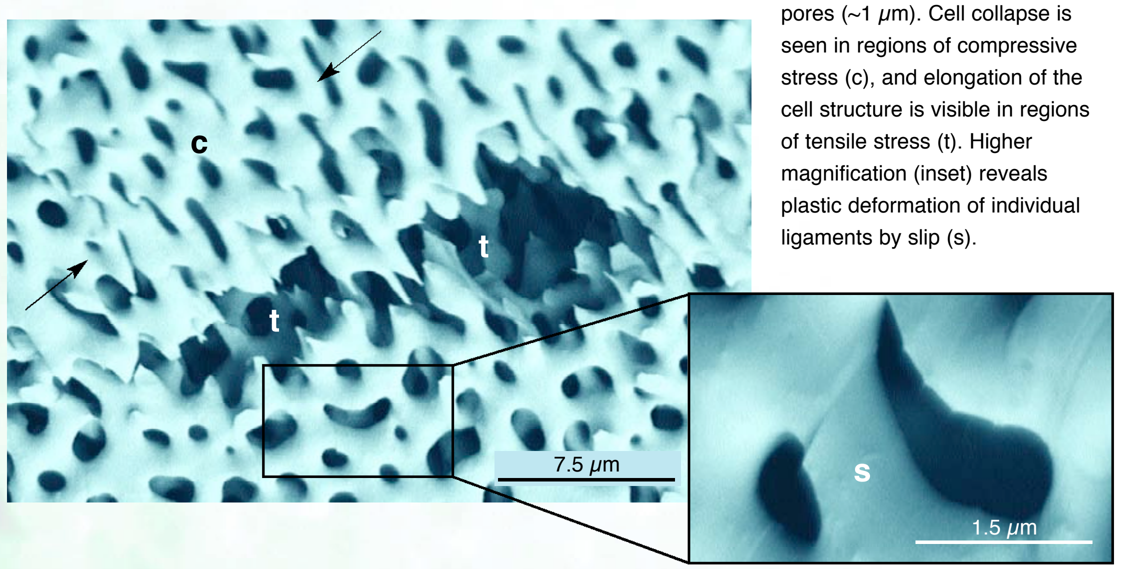

Figure 2. Scanning electron microscopy images show the fracture characteristics of a heat-treated sample of foam with large pores (~1 *μ*m). Cell collapse is seen in regions of compressive stress (c), and elongation of the cell structure is visible in regions of tensile stress (t). Higher magnification (inset) reveals plastic deformation of individual ligaments by slip (s).

Contrary to our results, previous research on free-corrosion dealloying (electroless) indicated that the dealloying process would not change the crystal grain structure to nanocrystalline. This discrepancy could suggest that electrochemically driven dealloying produces a higher supersaturation of gold adatoms, which in turn should increase the nucleation rate. The actual evolving morphology should be strongly influenced by the mobility of vacancies and adatoms and, in particular, by the presence of nucleation sites and thus the development of a nanocrystalline structure.

Even though nanoporous metals have recently attracted considerable interest—fueled by potential sensor and actuator applications—very little is known about their mechanical properties. To elucidate the yield strength of nanocrystalline gold, we have conducted both compression and tensile studies with nanoindentation and bending tests. Based on foam scaling laws, our results suggest that the nanoporous nanocrystalline gold is a high-yield, high-strength material that approaches the intrinsic yield strength of gold.

It is also important to understand how the ligament diameters affect when the materials would fail. We have deduced that the failure of a few ligaments triggers brittle fracture of the crystal lattice network. Interestingly, the failure mechanism of the ligaments seems to change with the ligament diameters. Our microscopic characterization of fracture surfaces has shown that in nanoporous gold with a ligament diameter of ~100 nm, the ligaments fail by plastic flow and necking (elongation of filaments). On the other hand, failure by slip (atomic plane movement) was observed for ligaments with a diameter of ~1000 nm. Figure 2 shows the fracture characteristics of a heat-treated sample. The heat treatment increases the ligament diameter from ~100 nm to ~1 μm.

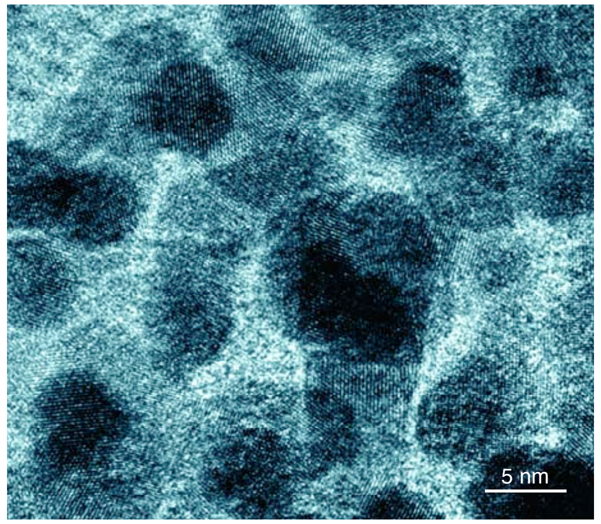

Figure 3. High-resolution transmission electron microscopy image shows compressed foam of nanocrystalline monolithic gold with grain sizes less than 10 nm.

Scientific Impact

Prior to our discovery, the general belief in the field was that there was no recrystallization during dealloying, and therefore the nanoporous foam was composed of single-crystal ligaments. We have shown for the first time that nanoporous foam synthesized by dealloying (free-corrosion or electrochemically driven) is composed of nanocrystalline ligaments.

We also introduced a two-step dealloying/compaction process to produce nanocrystalline monolithic gold (Figure 3). The compacted nanocrystalline gold exhibits an average grain size of less than 10 nm and hardness values of up to 4.5 times higher than the values obtained from polycrystalline gold. This two-step process presents an alternative route to producing monolithic nanocrystalline metals.

Related Publications

J. Biener, et al., "Nanoporous Au—a High Yield Strength Material," *J. Appl. Phys.* **97**, 024301 (2005).

A.M. Hodge, et al., "Monolithic Nanocrystalline Au Fabricated by the Compaction of Nanoscale Foam," *J. Mater. Res.* **20**, 554 (2005).

NEW FRONTIERS

Nanoporous gold foam is an example of a material that can be synthesized with engineered properties. Creating the foam with pores less than 100 nm through dealloying opens the possibility for many applications. For example, nanoporous gold foam could be used for research on surface-enhanced Raman spectroscopy. Currently, gold and silver nanoparticles help to enhance Raman scattering, and more recently, the use of gold nanoshells has been shown to significantly further increase the Raman scattering. The study of nanoporous foam as Raman enhancers and their comparison to nanoshells presents an interesting and technologically challenging project that could impact both the medical and scientific fields. Nanoporous foam could also be potentially used as actuators. Recently, a nanoporous platinum material demonstrated the basis for the first metal actuator, and many other applications are expected to arise for metallic actuators as new research becomes available.

Unraveling the Mysteries of Dislocation Formation

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Since the invention of the transmission electron microscope (TEM), materials scientists and physicists have investigated the structure of dislocation networks in crystalline materials to understand the origins of their unique mechanical strength. Dislocations—the carriers of plastic deformation in crystalline materials—often increase in density by several orders of magnitude during the deformation process. The interaction among dislocations and the topological rearrangements that occur in dislocation collisions are believed to be responsible for strain hardening, a remarkable property of metals in which a material's strength increases as deformation increases.

Two colliding dislocations may partially merge, or zip, into a junction bounded by two nodes. The behavior of dislocation nodes (where three or more dislocation lines connect) and the constraints they place on the motion of their lines are believed to strongly influence the heterogeneous microstructures that develop with large deformations. Unfortunately, the dislocations in these microstructures become so severely entangled that they can no longer be individually distinguished by TEM. With the development of the Parallel Dislocation Simulator (ParaDiS) code at LLNL, the elements of these highly entangled dislocation microstructures can now be investigated, providing a means for in situ computational microscopy.

Relevance to CMS Research Themes

Lawrence Livermore's stockpile stewardship mission requires an understanding of the thermo-mechanical behavior of metals that are subject to extreme loading conditions and high rates of strain. Under these conditions, dislocations behave in ways that experiments are unable to assess and the existing theory is unable to foresee. ParaDiS allows us to investigate these behaviors in microscopic detail to understand how the dislocation microstructure forms and how it affects the mechanical behavior of the material. This new understanding is used to develop predictive models of materials performance under extreme deformation conditions.

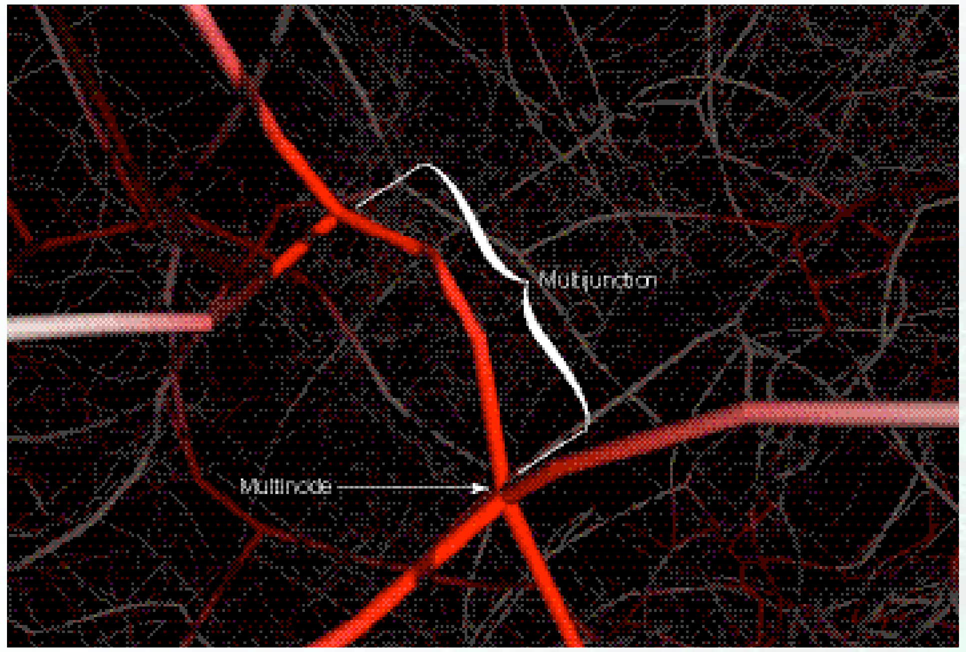

Figure 1. A dislocation dynamics simulation of strain hardening in bcc molybdenum shows a fragment of the dislocation network. Binary junctions connect the mass of dislocation lines (grey). Multinodes (red) complicate the topology by forming a strong skeleton throughout the network.

Major Accomplishments in 2004

The classic dislocation theory is an elegant approach resulting in useful analytical solutions for the energy and stress associated with dislocations. However, the solutions are singular and undefined on the dislocations themselves, making numerical calculations difficult. In previous attempts to develop a non-singular theory, either the theory was too complicated to be useful for a numerical implementation or it was simple but mathematically inconsistent. In response, we have developed ParaDiS, a massively parallel dislocation dynamics code that can follow large numbers of dislocation dynamics for a long enough time.

ParaDiS incorporates a new, non-singular continuum theory of dislocations that is both mathematically rigorous and analytically simple. In one of its early applications, the new theory provided an accurate description of the physics of dislocation nodes.

The new theory was instrumental in our recent discovery of multijunctions and multinodes that resulted from collisions of three or more dislocation lines. Multijunctions are significant in that they tie together three and, possibly, more lines into very tight knots that serve as strong anchors for the whole network. A multinode connects four (possibly more) dislocation lines together. Figure 1 shows a fragment of the dislocation network created in a very large dislocation dynamics simulation. We found that this ternary interaction in body-centered-cubic (bcc) metals is three to four times stronger than any binary interaction in the same metal and strong enough to pin dislocation lines indefinitely.

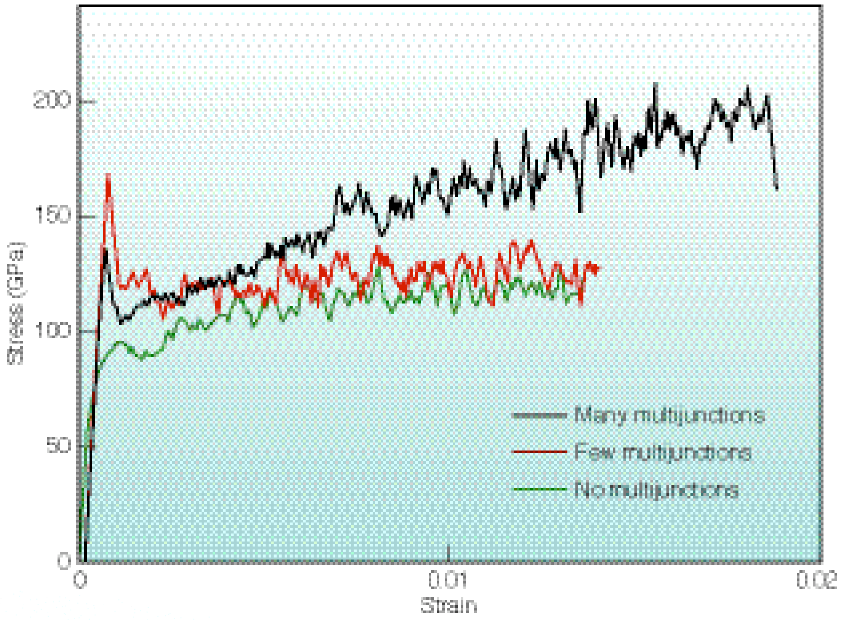

Figure 2. Stress–strain curves from a simulation on bcc molybdenum show that the formation of multijunctions significantly increases the hardening rate (line slope). Multijunctions that form in large numbers result in a well-defined slope (black) and are contrasted with the nearly flat lines when only few (red) or no (green) multijunctions are formed. (Simulation image courtesy of M. Tang.)

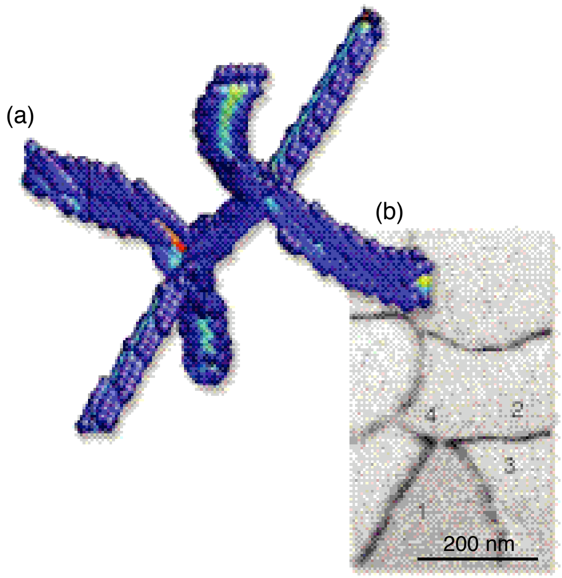

Figure 3. (a) An atomistic simulation based on an interatomic potential for molybdenum shows the formation of a multijunction. (b) A transmission electron microscopy image shows a symmetric 4-node (numbered 1–4) and verifies the existence of multijunctions and multinodes.

Scientific Impact

Because the multijunctions in dislocation networks are nearly indestructible, their existence is predicted to greatly affect the mechanical strength of metals. In particular, the existence of this element of dislocation microstructure offers an explanation to the unexplained large directional variation of strength observed in bcc single crystals.

In a series of large-scale dislocation dynamics simulations, we observed that the rate at which bcc metals harden during plastic straining is defined, to a large extent, by the presence or absence of the multijunctions (Figure 2). The existence of multijunctions was later confirmed by atomistic calculations and ultimately by experiments. Figure 3 shows an unmistakable signature of a multinode observed using TEM in a bcc single crystal of molybdenum deformed to 1 percent strain. The newly explained large variation in strength results in the propensity of many bcc alloys to localize their deformation in bands and affects their ultimate failure.

Related Publications

V. Bulatov, et al., "Scalable Line Dynamics in ParaDiS," *Supercomputing 2004*, Pittsburg, PA, http://www.sc-conference.org/sc2004/schedule/pdfs/pap206.pdf

W. Cai, et al., "A Non-Singular Continuum Theory of Dislocations," *J. Mech. Phys. Solids*, in press.

New Frontiers

Having predicted and observed the multijunctions of dislocations in bcc crystals, we need to understand the role that many-body collisions play in other materials. We have already predicted the existence of multinodes in face-centered cubic crystals and believe that confirmation of their existence by TEM observations will follow.

Our preliminary results also suggest that multijunctions and multinodes can be important missing pieces in the puzzling phenomenology of dislocation microstructure and strain hardening. We anticipate that new understanding of the topology of the highly entangled dislocation microstructures will compel researchers to generalize the models of material strength to include ternary and higher-order dislocation interactions.

Time-Resolved Observations of Electronic Structure

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The principal challenge of the emerging field of ultrafast materials dynamics hinges on our ability to characterize materials at both the time and length scales appropriate to the underlying physics. To probe the electronic and structural dynamics of molecules—in real time and with femtosecond resolution, we are using x-ray techniques, in combination with femtosecond lasers, to study the dynamics of metals during ultrafast laser irradiation.

These methods rely on the newest technological developments in x-ray sources and detection systems. Experimental protocols being developed to achieve the requisite time and spatial resolution not only bring our experiments into contact with theoretical studies but also inspire new theoretical tools. We are interpreting our experimental results using multiscale modeling techniques that account for electronic excitations and electron-ion equilibration in metals. This has seeded new theoretical ideas and has led to a continuum model of the electron fluid coupled to the ionic system.

Relevance to CMS Research Themes

Advancing the fundamental scientific understanding of the dynamic behavior of materials is essential for our national-security mission. Investigation of materials properties and performance is challenging because of the diversity and rapidity of the structural changes under extreme and dynamical conditions. By combining in-situ experimental diagnostics and new computational schemes, we are focusing on the fundamental aspects of how materials respond to strong shocks and extreme non-equilibrium conditions.

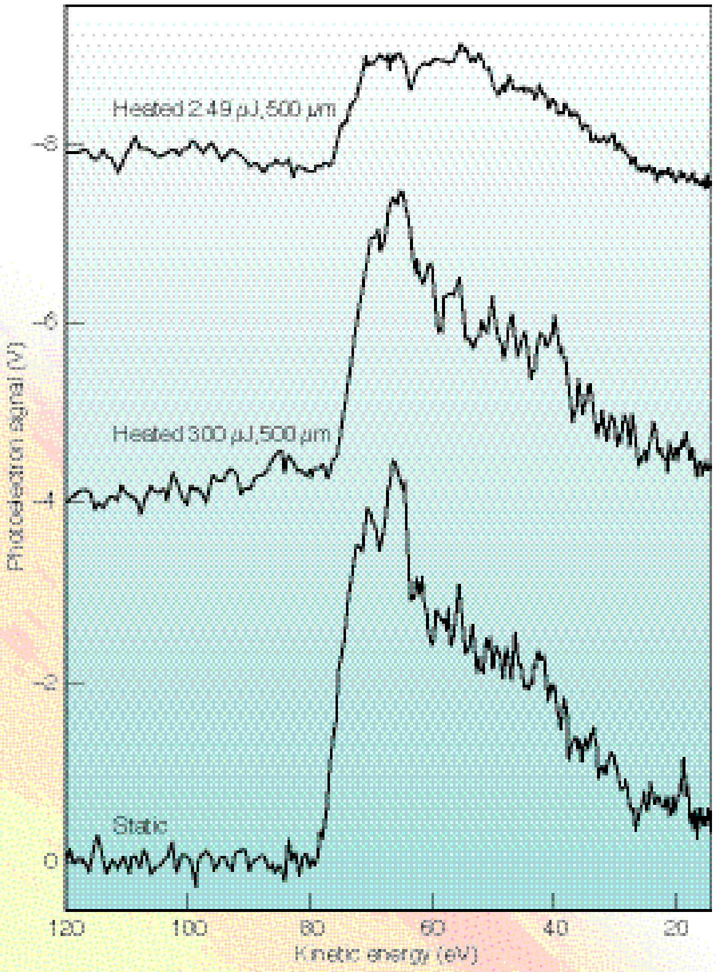

Figure 1. Photoelectron spectra for static versus laser-heated copper foil show how electrons respond to increasing laser heating.

Major Accomplishments in 2004

To probe ultrafast changes in the chemical and electronic structure of materials, we use the compact multipulse terawatt (COMET) x-ray laser to obtain the necessary high-photon flux (greater than 10^{12}/pulse), monochromaticity, picosecond pulse duration, and coherence. We have obtained the first photoemission spectra of laser-heated, ultra-thin copper foils showing changes in electronic structure.

COMET is ideal for studying the electron time-of-flight photoemission process (electrons ejected from solids by radiation), as its short-pulse laser irradiation creates a non-equilibrium electron distribution at elevated temperatures, while the lattice remains at room temperature. We illuminated ultra-thin polycrystalline copper foils with 10^8–10^9 x-ray-laser photons to measure how electrons respond to increasing laser intensity (Figure 1). We observe a strong *d*-state photoemission that corresponds to direct transitions from *d*-like occupied bands (high valency) to unoccupied bands (high conductivity) above the Fermi level (Figure 2). The data also indicate the high density of filled *d* states that are 2 eV below the Fermi level.

Many other interesting and important features evolve with increased laser heating, and at the highest temperatures, depopulation of the valence band *d* states also creates vacancies in the conduction band, thus allowing interband absorption below the edge, in this case, from 3*d* to 4*p* transitions in copper. Our ability to access this complex spectroscopy is fundamentally important in advancing our understanding of the dynamic non-equilibrium processes at play that precede materials disassembly.

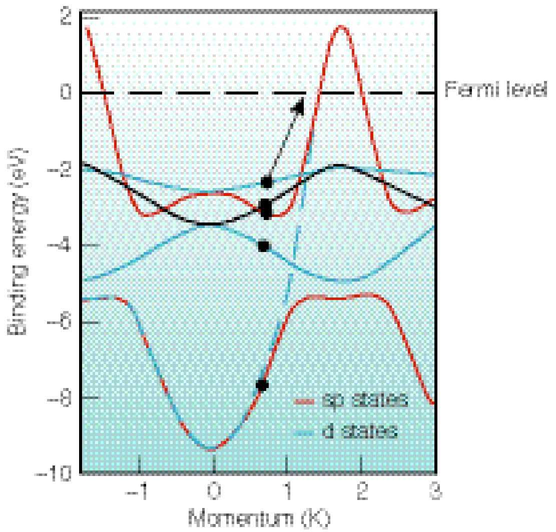

Figure 2. Schematic of photoemission process for copper illustrates a strong photoemission from direct transition from valance band to conduction band above the Fermi level.

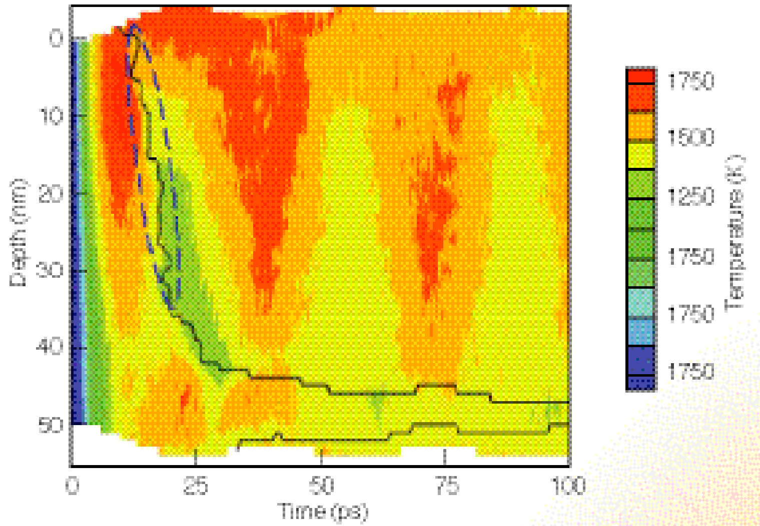

Figure 3. Temperature contour plot shows simulations of laser melting of a 50-nanometer nickel film. Strong electron–phonon coupling leads to a large temperature gradient in the film. Ultrafast melting of a large fraction (~35 nm) of the film is observed.

We have also observed that the peak of copper 3*d* state shifts toward lower kinetic energy (higher binding energy). Depopulation of the *d* band is predicted to affect its binding energy in this manner. We observed no broadening of the copper 3*d* state upon heating, which implies a non-equilibrium distribution of occupied states, or smearing of the Fermi-Dirac electron energy distribution. Increasing the laser energy further by a factor of ten generates a strong electron signal before reaching the valence band maximum, indicating the sample is in an ionized or non-equilibrium state.

In order to model laser interaction with metals, we combine classical molecular dynamics simulations with a model for the dissipative dynamics of the electron-ion system to bring the two systems into equilibrium with each other (Figure 3). Specifically, we have formulated a continuum description of the laser excitation and subsequent relaxation of the conduction band electrons and are applying first-principles methodology for determining the relevant material-specific characteristics. We are also extending the model to micrometer and larger length scales to predict structural information about voids and the ablated surfaces.

Scientific Impact

These experiments demonstrate the first picosecond time-resolved photoemission spectra of laser-heated, ultra-thin copper foils showing these changes in electronic structure. This study also included the first measurements of the disassembly dynamics of ultra-thin copper foil. The complementary relationship between these experiments and the newly developed, massively parallel hybrid atomistic-continuum model allows us to model the evolution of photomechanical damage in large-scale simulations of laser melting and spallation of nickel and copper thin films. In collaboration with UC Berkeley, this project provides a clear vision for ultrafast examination of extreme states of matter.

Related Publications

A.J. Nelson, et al., "X ray Laser-Induced Photoelectron Spectroscopy for Single-State Measurements," *Appl. Phys. Lett.* **85**(25), 6290 (2004).

L.V. Zhigilei, et al., "Computer Modeling of Laser Melting and Spallation of Metal Targets," in *Proc. Intl. Soc. Opt. Eng.* **5448**, 505 (2003).

New Frontiers

When it becomes operational in 2009, the Linac Coherent Light Source (LCLS) at the Stanford Linear Accelerator Center will be the world's first x-ray, free-electron laser. LLNL researchers will use the unique quality of the LCLS to create extreme states of matter at high temperature and density, to probe the ablation/damage process for high-energy-density science, and to study accompanying structural changes.

LCLS will be an important new experimental platform to study the interaction of intense x rays with matter. The unique attributes of the LCLS have the potential to revolutionize the experimental investigation of structural dynamics by directly following the time evolution of the electron density during the course of a biological, chemical, or physical transformation.

Ultrafast Dynamics of Metal Deformation

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Metallic materials exhibit a variety of response mechanisms during deformation processes, including dislocation production and motion, diffusion, stress-induced phase transformations, and twinning in the crystal structure. Which mechanism will dominate the deformation process depends upon temperature, pressure, and strain rate. While the movement and interaction of dislocations may dominate the overall response of metals, changes in the deformation mechanism create a fundamentally different environment in which these dislocations move and interact. For example, the appearance of a twinned lattice structure creates additional obstacles to dislocation motion.

Characterizing the mechanisms of deformation under extreme conditions of pressure, temperature, and strain rate is challenging. Although detailed, real-time observations at the relevant time and length scales of the dynamic process are not presently possible, we use detailed recovery-based observations on metals, along with hydrodynamic and molecular dynamic simulations, to infer the deformation behavior under extreme conditions. Our goal is to investigate material response to shocks and determine how different deformation mechanisms affect material properties. We will also compare material behavior across a wide range of loading conditions, utilizing multiple test platforms such as a gas gun, high explosives, and lasers.

Relevance to CMS Research Themes

Our stockpile stewardship mission demands a fundamental understanding of the behavior of solid metals under extreme conditions. To achieve this, new experimental and theoretical frameworks are required. Correctly modeling metal response to shock-wave passage and subsequent high-strain-rate deformation requires an understanding of the material response mechanisms across a wide range of pressure, temperature, and strain rate. Any numerical model used to predict this behavior must reflect the operative deformation mechanism, while changes in this underlying mechanism may require changes in the form of the model. Detailed, recovery-based experimental observations play a vital role in these efforts. The experimental and modeling methodology we use will help advance the development of robust numerical models of metal deformation under extreme conditions.

Major Accomplishments in 2004

We have conducted experiments utilizing different quasi-isentropic loading paths on a gas gun and a laser-based platform using both single-crystal and polycrystalline copper samples. Single-crystal copper samples (<100> orientation) recovered from the laser-based platform have shown a gradual transition, from a dislocation-dominated to a twin-dominated (although still dislocation-assisted) deformation response, over a pressure range of 20–50 GPa, as illustrated in Figure 1. Polycrystalline samples have shown an even more gradual shift, as might be expected from the relatively few crystallites oriented favorably in an easily twinned direction. Analysis of the gas-gun-driven material is currently in progress.

Our laser-based system, the Omega laser at the University of Rochester, utilizes short loading pulses and has rapid thermal transients. One advantage of this platform is that the shock wave forms over a relatively small distance, which allows us to investigate both the isentropic (shockless) and shock response in a single sample at a fixed peak pressure. We have made the first observations of a remarkable change in material response over this transition. In isentropic loading, the residual microstructure is dominated by dislocation cells, and in shock loading, it is dominated by stacking faults (Figure 2). Because the temperature and pressure differences between these loading paths are very small, we conclude that this behavior is due to strain-rate effects.

These experimental results support the molecular dynamics simulations conducted as a component of this work. The results have indicated that there is a pressure threshold of 50 GPa for twin formation in <100> copper. This twin nucleation threshold is lowered, in the case of a 20-GPa shock, by the presence of a void defect (Figure 3). These simulations also support the theory that the twin formation mechanism is one of coalescence wherein stacking faults on three adjacent planes join to form a "nanotwin" that may subsequently rapidly grow.

Scientific Impact

We have established a viable path toward understanding the dynamic response mechanisms of technically relevant materials. In addition, we have found that for these specimen-recovery experiments, a laser-based system minimizes the disturbance of the microstructure and allows for retention of some deformation structures that would be unstable on more traditional platforms. Comparison of results across platforms provides a rational basis for assessing the use of laser-based material testing strategies to provide technically valuable strength data. Additionally, the use of multiple platforms, possessing distinct differences in strain rate and hold time at peak pressure, yields a more complete understanding of the evolving features that take place in the microstructure during these transients.

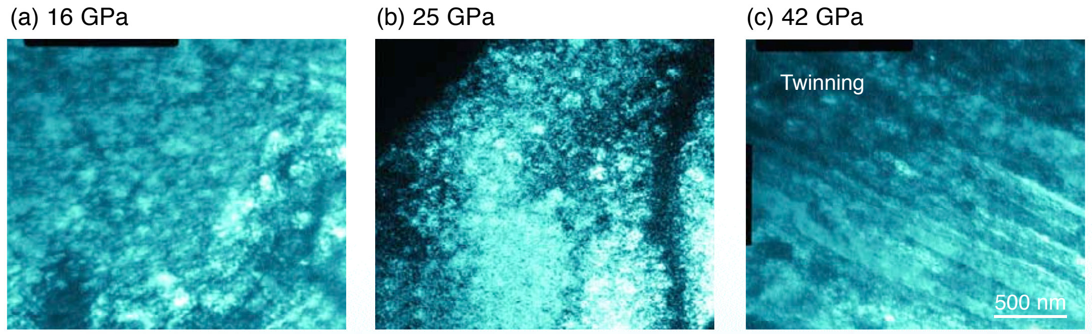

Figure 1. Transmission electron micrographs show residual deformation signatures from samples loaded to (a) 16 GPa, (b) 25 GPa, and (c) 42 GPa. A gradual shift from dislocation to twinning is evident.

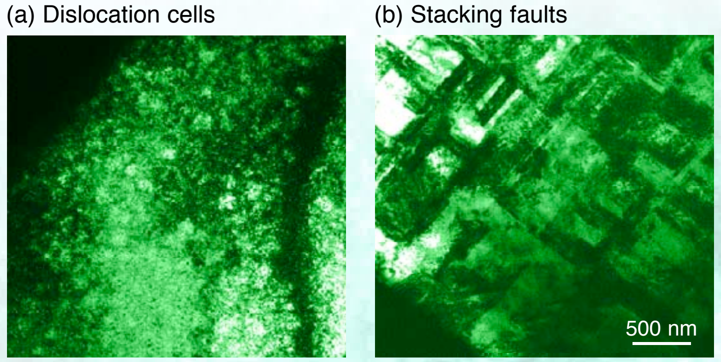

Figure 2. Transmission electron micrographs from a sample loaded to 25-GPa peak pressure show (a) dislocation cells under shockless loading and (b) stacking faults under shock loading.

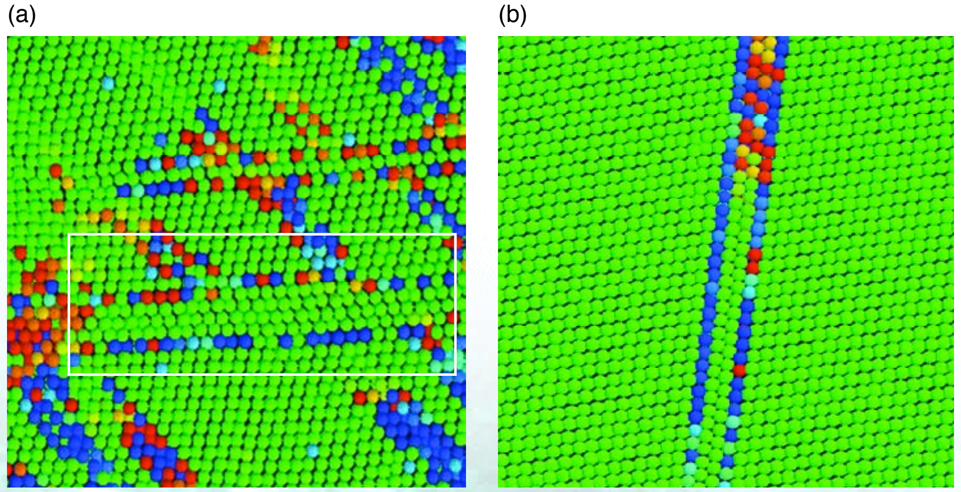

Figure 3. Molecular dynamics simulations show twin formation in single-crystal copper during (a) a 50-GPa shock in a perfect crystal and (b) a 20-GPa shock in a crystal containing a void (which collapses during shock passage).

Related Publications

L. Davila, et al., "Shock-Induced Void Collapse in fcc Metals," *App. Phys. Lett.*, in press.

J.M. McNaney, et al., "High-Pressure, Laser-Driven Deformation of an Aluminum Alloy," *Mettal. Trans. A*, **35**A, 2625–2631 (2004).

B.A. Remington, et al., "Materials Science under Extreme Conditions of Pressure and Strain Rate," *Mettal. Trans. A*, **35**A, 2587–2608 (2004).

NEW FRONTIERS

Looking ahead, we can hope to establish the upper and lower bounds on material constitutive response by measuring the shape of the recovered sample. In addition, the recovery techniques used here may be leveraged to provide containment capability in cases where it is desirable to contain the debris emitted from the test assembly.

Methodologies developed under this work are the first steps in providing valuable data to address the challenges of larger-scale experiments that measure the constitutive behavior of metals at ultrahigh pressures. For example, the current technique for measuring metal strength results in the presence of a partially ionized plasma in contact with the sample surface. A heat shield is used to prevent the associated thermal wave from affecting the experiment. Multilayer deposits along with recovery-based experimentation will allow us to assess the effectiveness of these heat-shield materials.

Emergent Materials Properties of Plutonium

The challenge of modern solid-state science is to identify new ways matter is organized and to develop a fundamental understanding of the physical principles involved in that organization. Solid-state science is currently confronted with what appears to be a new phenomenology, the quantum critical point (QCP), which defines a phase transition at absolute zero temperature.

What is extraordinary about quantum criticality is that its influence is felt at temperatures far above absolute zero, possibly to the melting point in some materials. Indeed, many enigmatic properties of materials for which we only have empirical descriptions and little or no understanding may one day be explained by QCPs.

Plutonium, a material of special interest to LLNL, may be poised on the edge of just such a QCP as we study its physical changes caused by radioactive decay. This possibility motivates us to investigate plutonium's thermodynamic properties at low or near zero temperature. Specifically, we are interested in low-temperature magnetization and magnetic susceptibility as a function of self-damage due to radioactive decay.

Relevance to CMS Research Themes

Plutonium's technological importance stems from its nuclear properties, however the physical properties of plutonium are defined by its electronic structure. While these properties are empirically well described, their fundamental origin is not. Characterization of the physical property changes accompanying radiation damage accumulation and the possible identification of a QCP will provide insight into plutonium's underlying nature and its organizing principles. This understanding is central to our work and to the broader scientific challenge of predicting material properties defined by electron correlations.

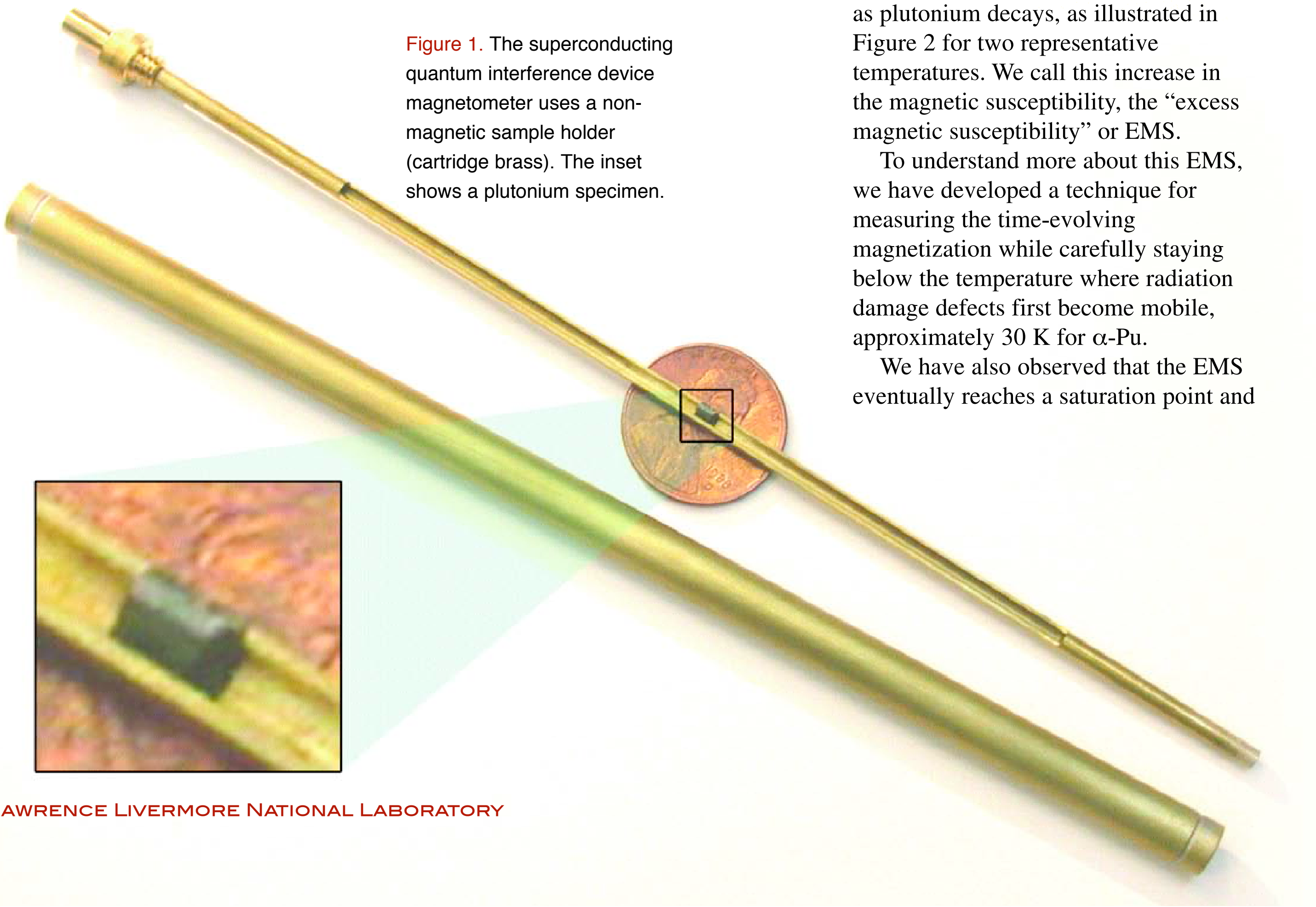

Figure 1. The superconducting quantum interference device magnetometer uses a non-magnetic sample holder (cartridge brass). The inset shows a plutonium specimen.

Major Accomplishments in 2004

Our principal goal is to learn how to "tune" plutonium in such a way as to move toward the point where its magnetic properties change. We have devised a novel approach to introduce structural disorder through the accumulation of radiation damage (displaced atoms) in plutonium. Using a superconducting quantum interference device magnetometer and a unique sample holder (Figure 1), we have performed the first magnetic damage accumulation and annealing studies and compared the results to those from previous, more traditional, resistance-based annealing studies.

The similarity to resistive annealing demonstrates the complex nature of defects on the magnetic properties of plutonium. This is the first observation that the magnetic susceptibility of plutonium increases due to self-damage as plutonium decays, as illustrated in Figure 2 for two representative temperatures. We call this increase in the magnetic susceptibility, the "excess magnetic susceptibility" or EMS.

To understand more about this EMS, we have developed a technique for measuring the time-evolving magnetization while carefully staying below the temperature where radiation damage defects first become mobile, approximately 30 K for α-Pu.

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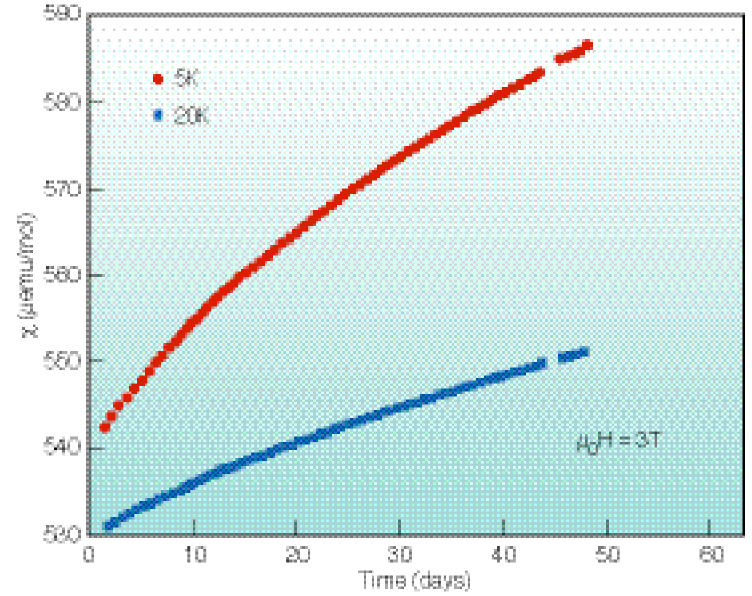

Figure 2. The isothermal magnetic susceptibility of plutonium increases with time, reflecting the accumulation of radiation damage. The gradual bending of the curves illustrates the approach to saturation as regions influenced by damage begin to overlap.

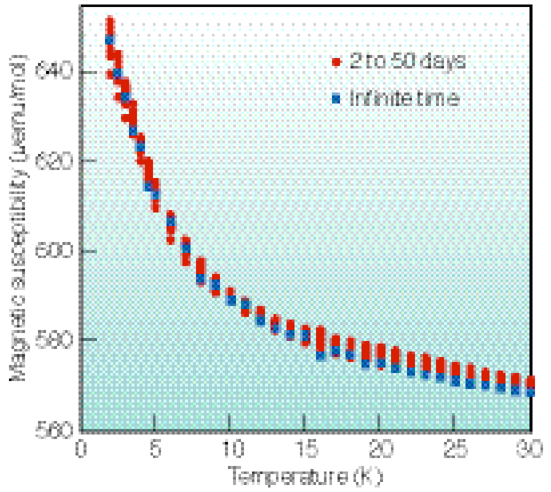

Figure 3. We measure the effects of radiation damage on the physical properties of plutonium at different times and temperatures. These data can be collapsed onto a universal time-independent curve. The elongated red data points represent plutonium magnetic susceptibility over 2 to 50 days. The blue data points are the extrapolation to infinite time.

We have also observed that the EMS eventually reaches a saturation point and no longer increases. That is, as alpha decay of plutonium proceeds, the rate of change of the EMS approaches zero. We observed that the total time and temperature dependent magnetic susceptibility $\chi(t,T)$ is well described by an exponential function:

$$\chi(t,T) = \chi_{Int}(\mathrm{T}) + \chi_{EMS}(T)(1 - e^{-t/\tau(T)})$$

where χ_{Int} is the annealed or initial susceptibility and χ_{EMS} is the excess susceptibility as time goes to infinity. The physical meaning of this observation is quite surprising. It says that a volume of space surrounding the radiation damaged region is affected magnetically. Initially these volumes are isolated from one another, but as time proceeds they begin to overlap. In about three months, almost all the crystal is affected. In fact, the magnetic susceptibility of these affected volumes is independent of time, and all the data represented in Figure 2 can be reduced to a single universal time-independent curve illustrated by Figure 3.

Because of its increased susceptibility, the region surrounding the damaged lattice is indicative of f-electron localization (more atomic-like). In a very real sense we have created a new phase of plutonium that is intrinsically correlated with the presence of lattice defects.

Scientific Impact

The existence of magnetism in plutonium has been a topic of controversy. Some theoretical models predict it, but experimentalists have not observed it despite numerous measurements. The observation that local magnetic behavior arises from self-damage strongly suggests that α-Pu is on the edge of becoming magnetic. Therefore, it may be possible to drive plutonium into a magnetic ground state by employing self-irradiation as a "tuning" variable.

Related Publications

S. McCall, et al., "Magnetic Properties of Radiation Damage in Pu," *Materialovedenie (MTV)*, in press.

Z.X. Zhou, et al., "Transport and Thermodynamic Properties of $Sr_3Ru_2O_7$ near the Quantum Critical Point" *Phys. Rev. B* **69**, 140409(R) (2004).

J. Custers, et al., "The Break-up of Heavy Electrons at a Quantum Critical Point," *Nature* **424**, 524 (2003).

New Frontiers

Acting like a negative pressure, the self-irradiation of α-Pu disorders and locally modulates the atomic lattice. We are pursuing further measurements on both α- and δ-Pu to help us map the phase diagram and locate, if it exists, the quantum critical point (QCP). In addition, by applying new techniques that allow a greater range of negative pressures, we expect to drive plutonium to a fully magnetic state and perhaps to the illusive QCP. Realization of a QCP may usher in a new understanding of the overall properties of plutonium and provide a new, albeit complex, fundamental description of its ground state.

Modeling the Many Faces of Water

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Although water is the most abundant substance on our planet and in our bodies, its properties still elude scientists. New theoretical studies of the liquid–vapor interface of water are revealing structural characteristics in the vicinity of the molecule's interfacial region. Using the same techniques, scientists are also probing whether the molecular arrangement of water is predominantly tetrahedral (each molecule surrounded by four others). At the same time, new experiments are measuring the properties of water under extreme interior planetary conditions.

The challenge for theorists is to provide a single model to describe water in all possible environments. To date, there is no universal model that can reproduce and predict properties of water throughout its phase diagram. Three classes of models are used in the majority of scientific studies. First, classical empirical models covering both rigid and polarizable ions seem to perform best under ambient conditions. A second approach builds a water model, one molecule at a time. A third model uses density functional theory (DFT) that contains explicit chemistry and charge transfer.

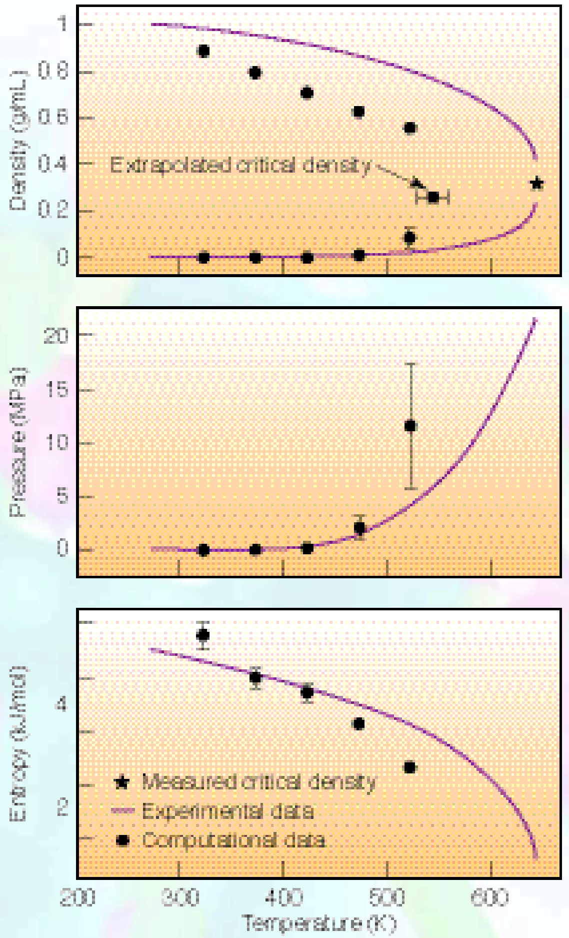


Figure 1. Phase diagram shows water at liquid–vapor interface (top curve), saturated vapor pressure (center), and heats of vaporization (bottom). Our ab initio model successfully describes, for the first time, the key thermodynamic variables of liquid–vapor interface.

Relevance to CMS Research Themes

Having a theoretical understanding of water has far-reaching implications to at least two CMS research themes. First, having the ability to model water in extreme environments is directly related to understanding chemistry under extreme conditions. Here, experimentalists and theorists are working together to examine molecular fluids that are exposed to high temperatures and pressures, and water is often used to help calibrate molecular systems. Second, water plays an extremely important role in the emerging area of understanding biomolecular matter in relation to life sciences. In various environments ranging from the interior of an enzyme to the surface of aerosols and proteins, having the theoretical tools to understand water is positioning LLNL to become an emerging leader in the study of the complex and important chemistry that is present under ambient conditions.

Major Accomplishments in 2004

We have taken a multifaceted approach to modeling water. First, our model for the water dimer (H_2O–H_2O) has proven to be highly accurate for larger clusters and the ambient liquid. This is the first time a model with gas-phase spectroscopic accuracy has been able to describe condensed-phase properties. This model has been used in both classical and quantum Monte Carlo simulations. We have also accomplished a high-level quantum chemical calculation of the water pentamer, $(H_2O)_5$, with unique hydrogen bonding structures.

To describe water outside of ambient conditions, we are performing pioneering calculations using both standard and newly developed methodologies. Using DFT, we have performed the first-ever calculations of the aqueous liquid–vapor interface containing 216 water molecules, and our results agree with recent experimental data. These calculations have led to questions on the accuracy of DFT beyond 1 g/cc and 298 K. Our group, in conjunction with many collaborators, has developed the first Monte Carlo calculations using the DFT interaction potential, and we successfully computed the phase diagram of liquid water at 1 atmosphere. These results provide the first accurate assessment of the thermodynamics of water and answer many questions regarding its transferability (Figure 1).

Our simulations of water under the extreme conditions of planetary interiors (2000 K and 115 GPa) indicate that water undergoes several transformations. At higher densities, the oxygen atoms form a glassy state, while the hydrogen atoms diffuse extremely rapidly by jumping between oxygen lattice points. Due to the extremely high hydrogen mobility, water is in a *superionic* state. Its presence had been predicted previously, but at significantly lower temperatures and pressures. Water in this superionic phase consists of extensive transient networks of O–H bonds, which are predominantly covalent (Figure 2). We find that at the superionic phase transition, molecular species are too short-lived to be described as molecules or ionic conductors and are better described as ensembles of transition states.

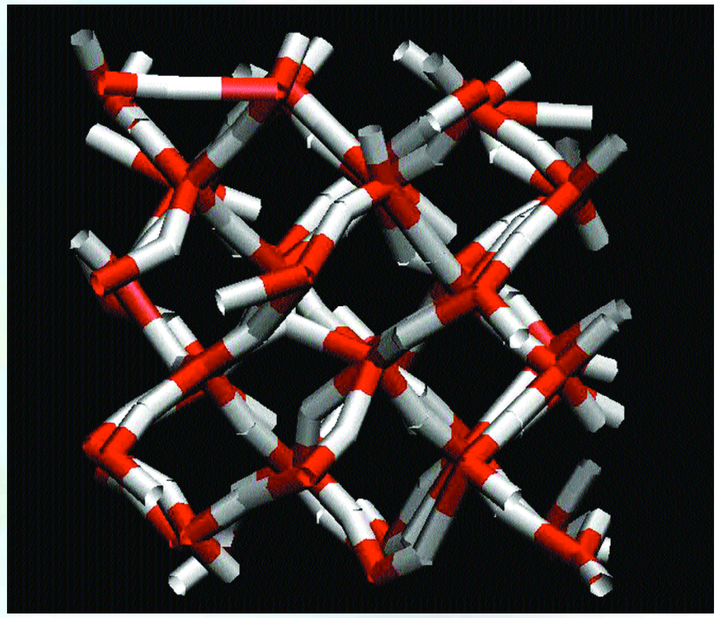
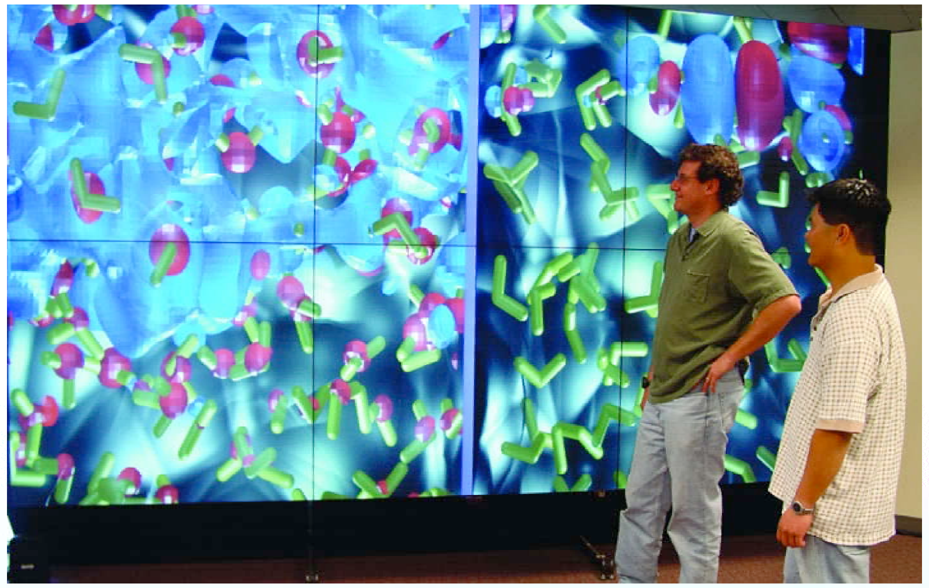


Figure 2. Simulation of water at superionic phase shows that at 115 GPa, a well-defined network of predominantly covalent bonds between oxygen (red) and hydrogen (white) forms.



Scientific Impact

Studying the structure of water under a variety of conditions benefits many areas. Many of the predictions of water using the density function theory have been performed without knowledge of whether water has a stable liquid phase. Furthermore, given that no single model of water will be able to describe water in all environments, a detailed knowledge of the performance of more efficient models will allow us to more confidently approach problems ranging from biology to atmospheric science.

Related Publications

N. Goldman, et al., "A First-Principles Potential Energy Surface for Liquid Water from VRT Spectroscopy of Water Clusters," *Phil. Trans. R. Soc. A* **363**, 493–508 (2005).

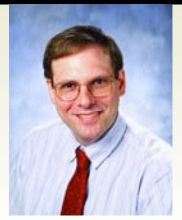
I.F.W. Kuo and C.J. Mundy, "An Ab Initio Molecular Dynamics Study of the Aqueous Liquid–Vapor Interface," *Science* **303**, 658–660 (2004).

I.F.W. Kuo, et al., "Liquid Water from First-Principles: Investigation of Different Sampling Approaches," *J. Phys. Chem. B* **108**, 12990–12998 (2004).

NEW FRONTIERS

New studies of water at the liquid–vapor interface have furthered our understanding that leads toward a single model to describe water in all possible environments. In the future, we will look at the chemical reactivity of water in environments that strongly modify its usual properties. In particular, we will examine acid-base reactions in aqueous solutions under conditions of high pressures and temperatures. We also plan to examine acid-base reactions in small water clusters, where surface effects play a dominant role in chemical reactivity. These studies will lead to more efficient models that allow researchers to probe hydrogen-bonded network structure in water and gain fundamental understanding of its unusual chemical and physical properties.

Formation of Methane under the Earth's Mantle



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Methane is the most plentiful hydrocarbon in the Earth's crust and a main component of natural gas. However, oil and gas wells are typically only drilled 5–10 km beneath the surface. At these depths, the interior pressures of the Earth are equivalent of a few thousand atmospheres.

We have collaborated with a team of scientists from Carnegie Institution's Geophysical Laboratory, Harvard University, Argonne National Laboratory, and Indiana University in South Bend to conduct a series of experiments and theoretical calculations, which have shown that methane forms under the high-pressure conditions that occur in the Earth's upper mantle at depths of 100–200 km. The results of our studies indicate that methane could be formed by non-biological processes under the Earth's surface.

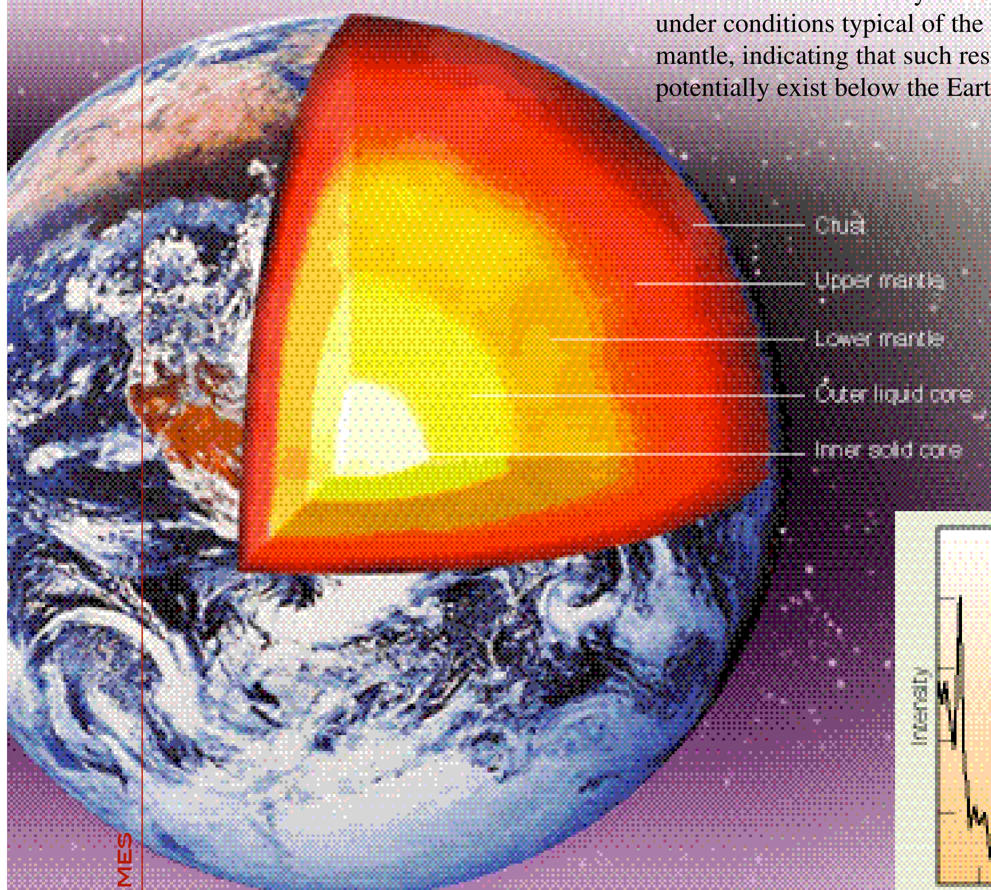
Relevance to CMS Research Themes

This research combines experiments and theory to understand chemical reactions under extreme conditions. Our experiments show that hydrocarbons can be created from a non-biological source—not just from the decomposition of living organisms. Also, our calculations show that methane is thermodynamically stable under conditions typical of the Earth's mantle, indicating that such reserves could potentially exist below the Earth's surface for millions of years. In addition to providing data that may indicate that the Earth holds limitless energy reserves, these studies will help to improve our ability to predict chemical processes under similar conditions, such as a high-explosive detonation.

Major Accomplishments in 2004

We conducted in situ high pressure–temperature experiments specifically designed to detect methane formation under geologically relevant conditions for the Earth's upper mantle. For the experiments, we created simultaneous high-pressure and temperature conditions in a diamond anvil cell by using both resistive heating (temperatures lower than 600°C) and laser heating (temperatures higher than 1,000°C) methods. Samples that contained natural $CaCO_3$–calcite, FeO–wüstite, and distilled H_2O were squeezed in the diamond anvil to produce the extreme conditions.

Through a combination of Raman spectroscopy, synchrotron x-ray diffraction, and optical microscopy, we performed a series of in situ analyses. Particularly, in situ Raman spectroscopy proved essential because of its high sensitivity to the C–H stretching vibrations of molecular species; it was also useful for examining amorphous or poorly crystalline phases. The synchrotron x-ray diffraction provided a means to identify crystalline phases and helped determine the reactions.



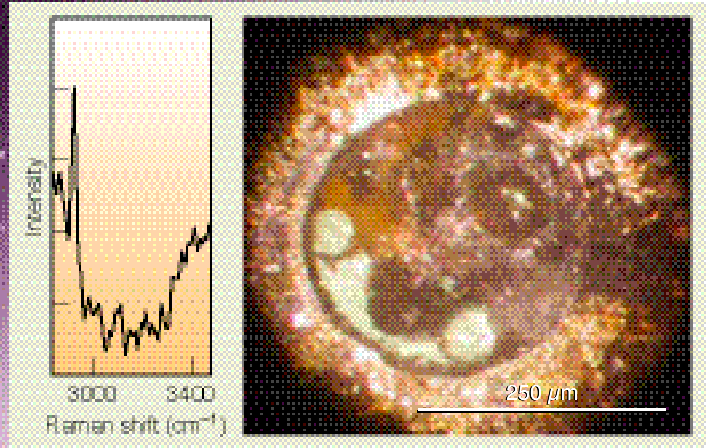


Figure 1. Methane-containing bubbles (right) are formed from decompression to approximately 0.5 GPa after laser heating at 5.7 GPa. Bubbles are visible near the bottom, left side, and slightly right of center of the diamond anvil sample. The Raman spectra show an absence of O–H stretching vibrations because the bubble has displaced the surrounding H_2O.

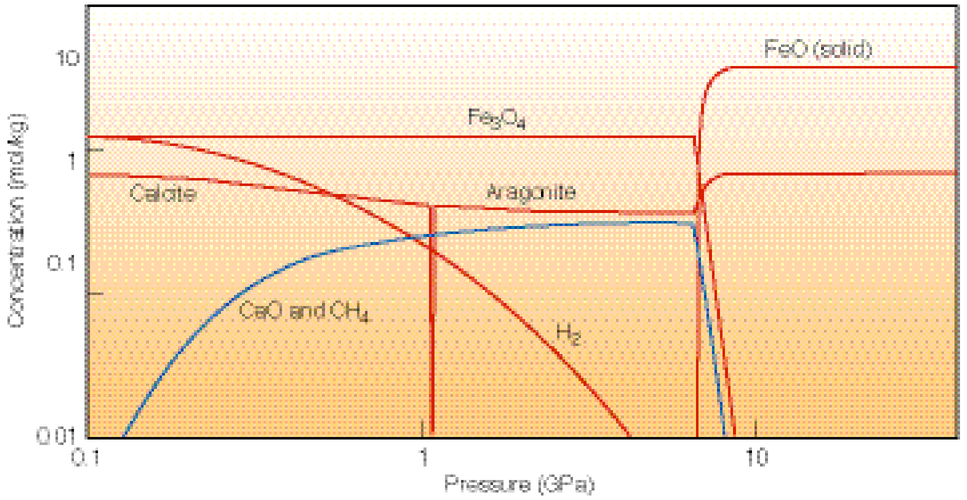


Figure 2. Our results of thermochemical calculations show that, at 500ºC, CH_4 (methane) is predicted to be prevalent at pressures up to 10 GPa.

As shown in Figure 1, hydrocarbon-rich regions are found in our diamond anvil sample after laser heating at ~1500°C at 5.7 GPa. The hydrocarbon is clearly identified as methane-based by the sharp band at 2972 cm^{-1} matching the position of bulk methane at this pressure. The sample exhibited considerable heterogeneity. It is important to note that, in this experiment, the diamond anvils do not show evidence of reaction with the sample material. Raman measurements of laser-heated experiments typically are very challenging because the samples are fine-grained and fluorescent after heating, and a layer of opaque material across the diamond surface often obscures the interior of the sample chamber from optical measurements.

We have obtained further insight into the chemical processes involved in high-pressure methane production by conducting new thermochemical modeling. Our aim is to address the temperature and pressure dependence of the methane-forming reaction. Specifically, it is important to determine if the high-pressure formation of methane is indeed favored at lower temperatures, or if this is an experimental artifact (laser versus resistive heating). By using our Cheetah thermochemical code, we calculated the high-pressure chemical equilibrium. Figure 2 shows that methane is thermodynamically stable at 500ºC at pressures up to 10 GPa.

Scientific Impact

The Earth's mantle is a dense, hot layer of semi-solid rock approximately 2,900 km thick. It contains more iron, magnesium, and calcium than Earth's crust, and it is hotter and denser because temperatures and pressures inside the Earth increase with depth.

Because of the firestorm-like temperatures and crushing pressures in the Earth's mantle, molecules behave very differently than they do on Earth's surface. At temperatures lower than 1500ºC, we have found optical changes indicative of methane formation, and at temperatures above 1500ºC, the carbon in calcite forms carbon dioxide rather than methane. This implies that methane may be present at depths between 100–200 km, and it may be more prevalent in the mantle than previously thought. Because of the vast size of Earth's mantle, hydrocarbon reserves in the mantle could be much larger than reserves in Earth's crust.

Related Publications

H.P. Scott, et al., "Generation of Methane in the Earth's Mantle: In Situ High Pressure–Temperature Measurements of Carbonate Reduction," *Proc. Natl. Acad. Sci.* **101**, 39 (2004).

N. Wade, "Petroleum from Decay? Maybe Not, Study Says," *The New York Times*, September 14, 2004.

NEW FRONTIERS

Our research combining experiments with theoretical calculations indicates that methane is produced and thermodynamically stable under conditions typical of the Earth's mantle.

We intend to study the phase diagram and stability of other simple molecular compounds under high-pressure and temperature conditions. We are extending our experimental and computational techniques to study water under conditions of giant planetary interiors. For example, we use first-principles molecular dynamics calculations and Raman spectroscopy to investigate the existence of a novel "superionic" phase of water. In this phase, oxygen atoms are fixed while hydrogen atoms diffuse freely. These techniques can improve our ability to predict a host of chemical processes under extreme conditions that are previously unattainable.

Probing Materials under Extreme Conditions

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Most of the chemical and physical processes that occur in our universe take place under conditions that seem extreme to us on Earth. Nevertheless, the study of these processes under controlled conditions in the laboratory will yield great insight as well as provide quantitative estimates of a host of physical properties that are of direct importance to many diverse disciplines.

There are many systems whose behavior under extreme conditions is of great relevance to both fundamental science and also to the essential mission of LLNL. The present challenge is to develop the corresponding experimental tools and also the computational machinery to investigate and model these systems.

Relevance to CMS Research Themes

The development of effective diagnostic tools to elucidate the nature of extreme-conditions phenomena has been at the core of Livermore's mission. The overarching aim of our research is to extend the range of these tools to conditions that have hitherto precluded investigation. The results of our work can be applied to unique chemical and physical processes of paramount concern to national security.

Major Accomplishments in 2004

In spite of recent advances in diamond anvil cell techniques, accurate determination of the elastic and vibrational properties of materials under static pressures exceeding 100 GPa remains a challenge. We have successfully demonstrated the utility of a new instrument that employs the technique of impulsive stimulated light scattering (ISLS) to measure acoustic velocities to pressures in excess of one million atmospheres. Developed by Livermore scientists, this unique instrument allows us to study both transparent and opaque materials in order to determine their elastic properties.

ISLS and Raman Spectroscopy: Our system enables us to make acoustic wave velocity measurements under previously inaccessible conditions. The instrument provides exceptionally precise and accurate data. We have demonstrated its ability to determine either the entire elastic tensor or selected tensor elements of single crystals (including germanium and cobalt) and also the shear and compressional elastic moduli of polycrystalline aggregates (including tantalum and iron).

Using ISLS and our unique Raman spectroscopic system, we have determined the sound velocities of hexagonal close-packed iron to pressures approaching 120 GPa—corresponding to depth near the mantle–core boundary in the Earth's interior. Once thermodynamically scaled to the Earth's core temperatures, our data clearly imply that the Earth's solid inner core consists of pure iron. These results also agree with velocity data obtained through shock-wave measurements.

Our study of cobalt—analogous in some ways to iron—is also important for a better understanding of the composition and structure of the Earth's interior. For the first time, we have obtained direct measurements that indicate a pressure-induced collapse of magnetic ordering in cobalt that drives it to a nonmagnetic state and is likely to dramatically change its physical properties. This behavior is consistent with a prior theoretical model postulating magnetic suppression.

Ring Compression: We have developed a combined experimental and computational technique to determine the coefficient of friction between diamond and metal under high pressure in the diamond anvil cell. As an example, we have performed the first-ever application of the ring-compression test to determine the coefficient of friction between molybdenum and diamond under high hydrostatic pressure (Figure 1). This type of knowledge is useful for the determination of yield strengths of materials under pressure and for fully interpreting the results of various types of experimental investigations of high-pressure rheology.

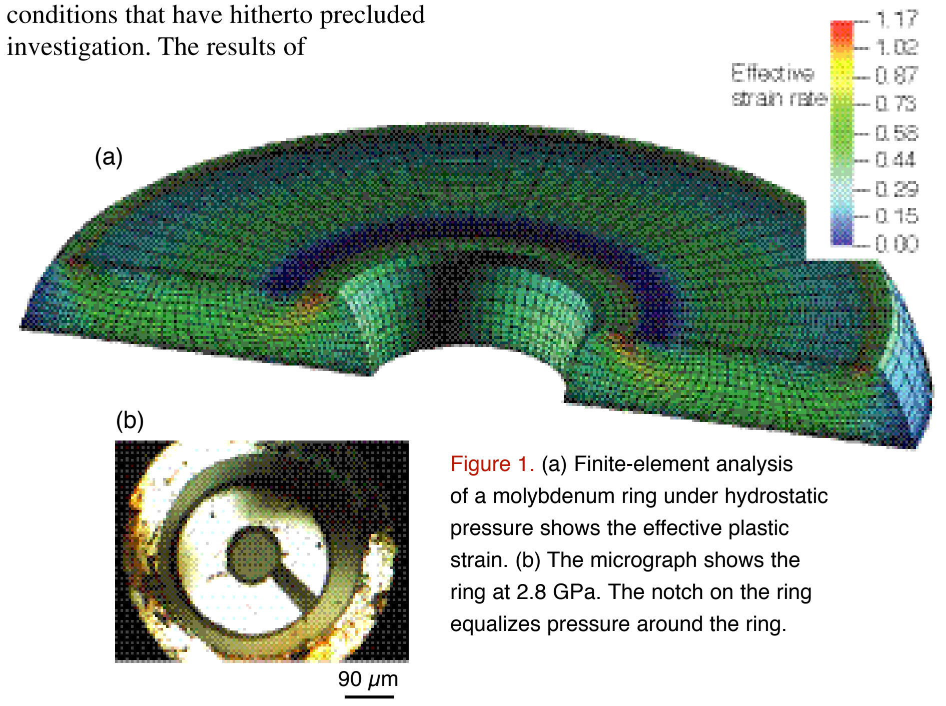

Figure 1. (a) Finite-element analysis of a molybdenum ring under hydrostatic pressure shows the effective plastic strain. (b) The micrograph shows the ring at 2.8 GPa. The notch on the ring equalizes pressure around the ring.

Laser Heating: Working side-by-side with theoreticians as well as computational scientists, we continue to apply novel diagnostic techniques in the discovery of many never-seen-before materials properties that can be validated by both experimental and computational results. For example, using Raman scattering and laser heating, we have observed for the first time the existence of a novel *superionic* phase of water above pressures of 50 GPa and temperatures of approximately 1000 K (Figure 2). Superionic water could be plentiful inside giant planets such as Neptune. Water under these conditions should be highly conductive, thanks to mobile protons that move through a fixed sub-lattice of oxygen ions.

We have also recently used our combined Raman/laser heating system to extend the melting curve of nitrogen to much high pressures than previously known and to investigate the behavior of cubic boron nitride at pressures of up to 40 GPa and temperatures in excess of 1700 K. We have used the results of the latter investigation to develop the first high pressure scale above 1000 K. Using laser heating, we have also synthesized the world's second known noble metal nitride: iridium nitride. This compound forms above 47 GPa and 1600 K. This work confirms the ability of the diamond cell to synthesize novel materials.

Scientific Impact

Advancing our understanding of mechanical properties at extreme conditions allows us to develop the capabilities required to address many scientific challenges. For example, the shear moduli of many actinides above a few tens of GPa or at simultaneous high temperatures are still unknown. There is a lack of experimental data on how the magnetic properties of these metals coupled with strength parameters at high pressure–temperature conditions, neither has it been accurately determined how yield strength responds to simultaneous uniaxial compression at high pressures.

The results of experimental investigations of the physical and chemical nature of materials can be used as an excellent test of ab initio theoretical approaches to model the behavior of materials.

Related Publications

A.F. Goncharov and J.C. Crowhurst, "Pulsed Laser Raman Spectroscopy in the Laser-Heated Diamond Anvil Cell," *Rev. Sci. Instrum*, in press.

A.F. Goncharov, et al., "Dynamic Ionization of Water under Extreme Conditions," *Phys. Rev. Lett.* **94**, 125508 (2005).

J.C. Crowhurst, et al., "Determination of the Coefficient of Friction Between Metal and Diamond under High Hydrostatic Pressure," *Appl. Phys. Lett.* **85**(22), 5188–5190 (2004).

A.F. Goncharov, J.C. Crowhurst, and J.M. Zaug, "The Elastic and Vibrational Properties of Co to 120 GPa," *Phys. Rev. Lett.* **92**(11), 115502 (2004).

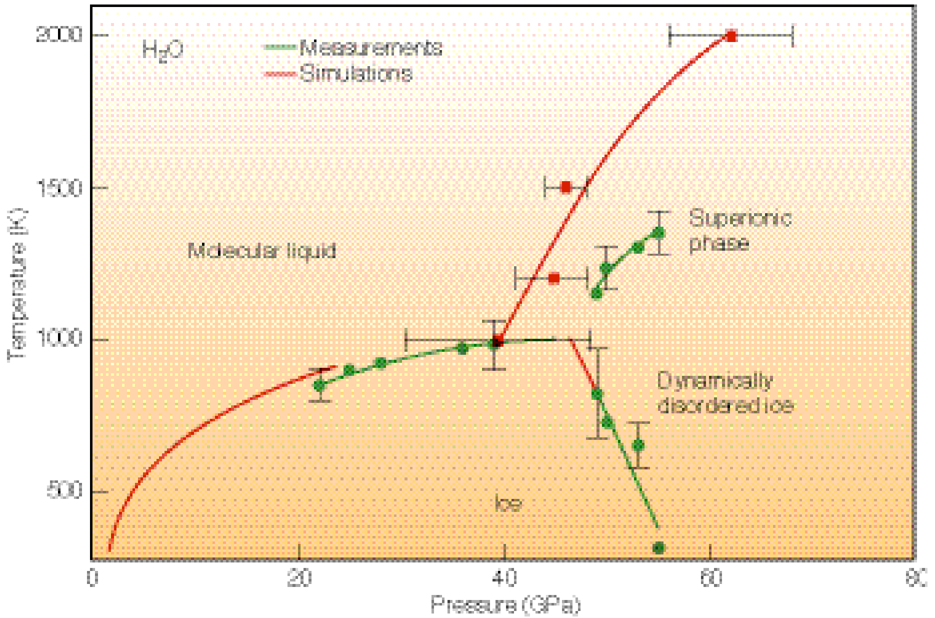

Figure 2. Phase diagram of H_2O shows that under high temperatures and pressures, water exists in a superionic phase. For the first time, experimental measurements (green) and computational data (red) have verified its existence.

NEW FRONTIERS

Bench-top ISLS or Raman instruments collect precise data in seconds or minutes. In the future, we will augment these tools to study samples at high pressures and at thousands of degrees to determine physical properties over a more extensive domain of phase space and through state changes. In order to execute traditional vibrational spectroscopy above 2000 K, we will employ our advanced, high-frequency short-pulsed laser and fast-detection technologies. We will continue to study materials such as ammonia and hydrogen fluoride. In 2009, we will have access to the Linac Coherent Light Source at Stanford's Synchrotron Radiation Laboratory, which will deliver 10^{12} photons (0.8–8 keV) in 130-femtosecond pulses, to determine the transient structure of shock-loaded samples.

Structure Control in Sol-Gel Materials

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Sol-gel is a chemical synthesis process that offers a versatile approach to the design of advanced materials for a range of applications, including catalysis, separation technology, ceramics, sensors/detectors, and nanoelectronics. In the sol-gel process, reaction precursors transform into nanometer-size particles (sol) that link up with one another to form a three-dimensional solid network (gel). This technique provides compositional and structural control on the nanometer scale as well as access to various forms of the desired material, such as powders, films, fibers, and monoliths.

We have developed a new sol-gel method that greatly expands the types of materials that can be prepared. To fully exploit this new technique, however, we need a fundamental understanding of the mechanisms that drive the chemistry and how these mechanisms influence the physical properties of sol-gel materials.

To obtain these insights, we are utilizing nuclear magnetic resonance (NMR) spectroscopy as an *in-process* characterization tool to monitor particle formation and organization in these novel materials. NMR is ideally suited for this task because the technique can track transformation in either liquids or solids in an elementally selective and non-destructive manner. In addition, NMR observables are directly related to kinetic and thermodynamic processes that control macromolecular formation, which, in turn, affects the bulk physical properties.

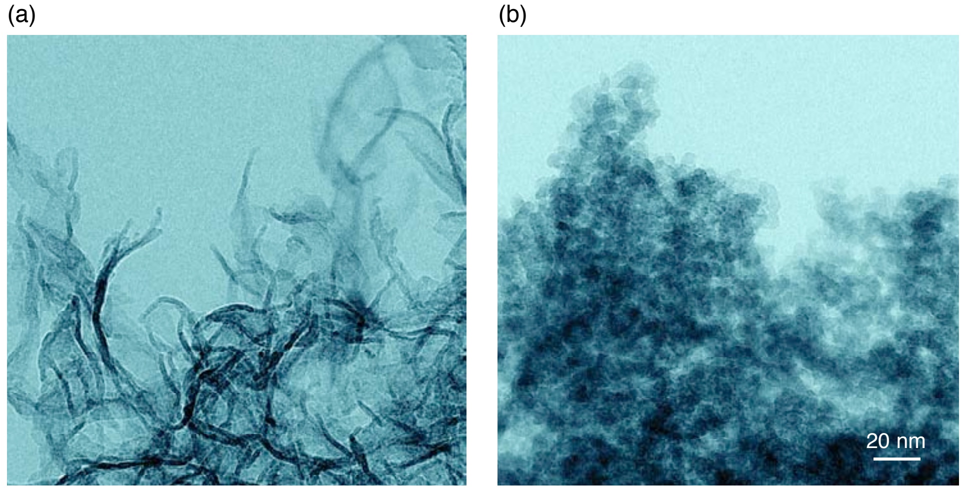

Figure 1. High-resolution transmission electron microscopy images show two alumina aerogels prepared using different sol-gel precursors: (a) $AlCl_3$ and (b) $Al(NO_3)_3$. The two resulting alumina aerogels have identical chemical composition but very different materials properties.

Relevance to CMS Research Themes

Ongoing development of advanced materials is an integral component of the science and technology efforts at Lawrence Livermore. CMS supports this endeavor through the investigation of chemistry and materials under extreme conditions. The synthetic methods we have developed provide the ability to examine new or alternative synthetic routes and meet design criteria such as composition, purity, yield, and physical properties. Applying sol-gel chemistry to the synthesis and processing of advanced materials is part of a broad effort that includes preparing and characterizing a wide range of designer materials, such as very low-density metal and metal-oxide foam, stronger and tougher nanoceramics, and energetic nanocomposites. Furthermore, this work contributes to the fundamental science and technology of sol-gel chemistry.

Major Accomplishments in 2004

By combining sol-gel chemistry and advanced NMR techniques, we are gaining detailed insight into the relationship between synthesis and the macroscopic properties in sol-gel materials. We have used NMR to monitor structure formation in two types of aluminum oxide (Al_2O_3) aerogels. By changing a single synthetic variable—specifically, the anion of the sol-gel precursor—in the sol-gel reaction, aerogels that have identical chemical composition can be generated to possess dramatically different morphologies and mechanical properties. The materials shown in Figure 1a display fibrous morphology that is substantially stronger than the more random cluster aggregation shown in Figure 1b.

To understand the reactions that occur during synthesis, we use solution and solid-state NMR techniques to follow the kinetics of the nucleation and growth of the sol-gel architecture for both types of the aluminum oxide. NMR experiments for ^{27}Al provide information regarding aluminum speciation (4-, 5-, or 6-coordinate Al^{3+} species) in the sol-gel building blocks, as illustrated in Figure 2, while NMR experiments for ^{17}O provide insight into the connectivity of these building blocks.

We are also characterizing the transformations that occur in the gel state (mixture of both solid and liquid phases) of the sol-gel reaction process (Figure 3). These gel-state NMR experiments represent the first time this technique has been applied to sol-gel transformations in non-silica systems and provide a crucial link between traditional solution and solid-state experiments. We will establish the relationships between the initial reaction conditions and the resulting bulk properties of the sol-gel materials. Ultimately, this knowledge will be applicable to the fabrication of other material compositions, allowing us to expand the technological potential of sol-gel science.

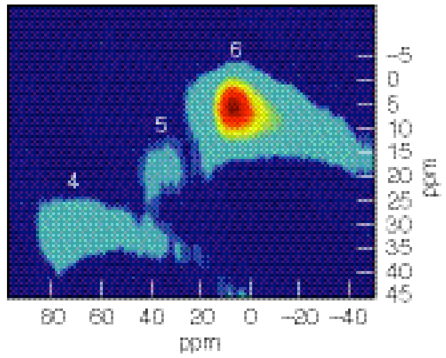

Figure 2. Two-dimensional ^{27}Al nuclear magnetic resonance spectra provide information regarding three species (4-, 5-, and 6-coordinate) of aluminum ion, Al^{3+}.

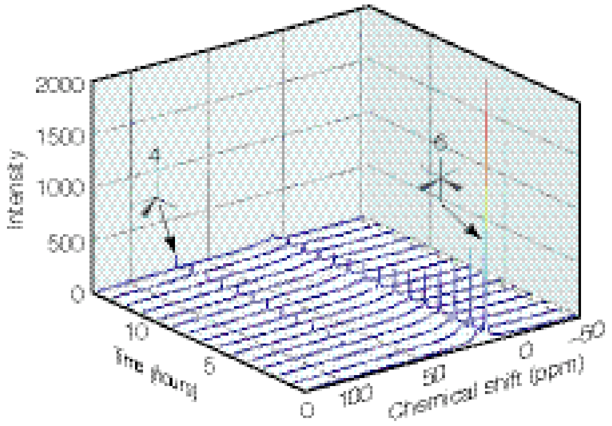

Figure 3. We are using nuclear magnetic resonance spectra to characterize the sol-gel transformation process. Here the gel-state spectra of an alumina aerogel show the formation of 4- and 6-coordinate Al^{3+} species.

Scientific Impact

Nanotechnology has applications in a broad range of fields, from electronics and biology to energy and physics. Advances in these areas require new methods for the preparation of nanomaterials with desired size, morphology, and composition. Therefore, synthesis and processing of nanomaterials are an essential aspect of nanotechnology. Sol-gel chemistry produces materials that are inherently nanostructured and thus holds the potential for technological innovations in a number of important areas. A fundamental understanding of the mechanisms associated with sol-gel chemistry will lead to the design of new nanostructured materials as well as further our understanding of structure–property relationships.

Related Publications

T.F. Baumann, et al., "Synthesis of High-Surface-Area Alumina Aerogels without the Use of Alkoxide Precursors," *Chem. Mater.* **17**(2), 395–401 (2005).

I.L. Moudrakovski, et al., "Probing the Geometry and Interconnectivity of Pores in Organic Aerogels Using Hyperpolarized ^{129}Xe NMR Spectroscopy," *J. Am. Chem. Soc.* **126**, 5052–5053 (2004).

NEW FRONTIERS

Advancements in sol-gel chemistry are leading to new applications that are continuing to evolve. For example, we are leading the development of new materials used in high-energy-density physics experiments, an area that is critical to our national-security mission. We are using our sol-gel process to prepare materials for sensors/detectors, catalysis, and energetic materials. We also have burgeoning efforts in the areas of ceramics, hydrogen storage, and waste remediation, all of which involve novel nanostructured materials prepared by using sol-gel chemistry. Our ultimate goal in this effort is to establish correlations between synthetic variables and material properties analogous to those that have been used to develop structure–property relationships in organic polymer systems.

Tracing Iodine-129 from Nuclear Fuel Reprocessing Facilities

Iodine exists in many organic and inorganic chemical forms that are thermodynamically stable in multiple oxidation states. Its complex chemistry renders it ideal to use as a tracer. Isotopic tracers are an important component for LLNL's counterproliferation efforts because they can be used as fingerprints to help identify and characterize nuclear fuel reprocessing activities. Iodine-129, in particular, is produced as a result of nuclear reprocessing. Characterizing ^{129}I speciation in the environment is the key to understanding its mobility and absorption into the environment. The current challenge to interpreting ^{129}I levels is the lack of knowledge about its residence times and chemical transformations.

We are developing new analytical techniques to improve measurements of key parameters used to predict and model dispersal of ^{129}I from reprocessing emissions in relevant environmental matrices. The results of this research will provide the scientific basis for predicting the transport and biological uptake of ^{129}I released from fuel reprocessing facilities and will allow unambiguous identification of its source.

Relevance to CMS Research Themes

The methodologies we use provide the basis for extending the geographic range for effective sampling, choosing the best sample matrix type and determining the timing of ^{129}I releases. Together, these will form a powerful tool for monitoring the source and history of ^{129}I emissions from nuclear fuel reprocessing facilities. Iodine-129 is also an important radionuclide in the long-term dose assessment for the Yucca Mountain nuclear-waste disposal site and the Nevada Test Site. In addition, our studies advance areas of nuclear science for human health. For example, at the heart of dose estimate uncertainties are unknowns regarding the chemical form and biologic pathway of ^{129}I to the human thyroid.

Major Accomplishments in 2004

We use x-ray absorption fine-structure (XAFS) technique to identify speciation of iodine in solids and to characterize the near-neighbor atomic bonding and coordination information. This is the first time XAFS has been applied to natural, environmental samples for analysis of iodine near-neighbor information.

In addition to measuring the oxidation state and local bonding geometry of iodine, XAFS quantifies the number and species of iodine atomic neighbors as well as the iodine-neighbor bond lengths. We have measured iodine XAFS spectra for a number of environmental samples, including iodine-containing marine samples and a number of iodine-sorbed minerals. XAFS spectra can be gathered into several groups, including inorganic and organic chains, organic ring molecules, and mineral structures. The results shed light on the nature of the carbon-iodine bond, which determines the residence time for organo-iodine compounds during biogeochemical cycling of biological, geological, and chemical processes.

Examination of iodine species, with due attention to potential inter-conversion among species, is essential in interpreting the behavior of iodine in the environment. Using results from bench-top soil column experiments, we can model the differential distribution of iodine and ^{129}I in various chemical forms. Specifically, we focus on the sorption and transport behavior of iodine species (iodide, iodate, and 4-iodoaniline). In some clay minerals, we observed appreciable iodate reduction to iodide, probably mediated by the structural iron (Figure 1). We interpreted the sorption and transport behavior of different iodine species with respect to the physicochemical characteristics of the geological media, which exhibit a wide range in organic matter, clay mineralogy, soil pH, and texture.

We continue to develop new analytical methods for analyzing inorganic iodine forms and ^{129}I in complex environmental matrices. Employing a new multi-collector inductively coupled mass spectrometer (IsoProbe MC-ICPMS), we are analyzing ^{129}I/^{127}I in aqueous samples from affected environments such as the Nevada Test Site. Compared to the more sensitive technique of accelerator mass spectrometry, the method has advantages both in ease of sample preparation (allowing higher throughput) and in the potential addition of speciation information.

For more information contact

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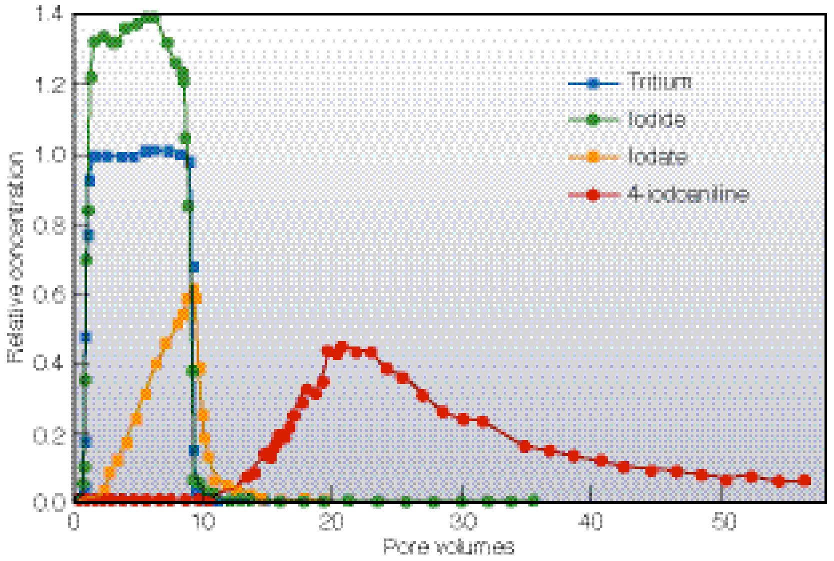


Figure 1. Experimental results of sorption and transport of iodine species in surface soil from a former nuclear production site are shown. Tritium is included as a comparison tracer because it is easily transported with no retardation. The transport of iodate and 4-iodoaniline is retarded due to interaction with clay materials and organic matter.

Figure 2. LLNL's Center for Accelerator Mass Spectrometry performs extremely sensitive measurements to detect the fingerprints of nuclear reprocessing emission.

Scientific Impact

Although nuclear fuel reprocessing contributes to increased levels of ^{129}I in the environment, trace levels are found in nature. Local oxidation/reduction conditions and biological activity have caused anthropogenic ^{129}I to be out of chemical equilibrium with naturally occurring ^{129}I. Experimental studies allow us to predict the likely chemical form of ^{129}I from fuel reprocessing emissions and to interpret the ^{129}I to ^{127}I ratios in downstream or downwind matrices with respect to the source, mode of transport, and mechanism of incorporation.

Analysis of data acquired during this study suggests that soils with significant organic matter will sequester ^{129}I efficiently, and aqueous matrices such as river water are highly sensitive to input of ^{129}I that originates in the atmosphere. In terms of dose estimates, our results indicate that atmospheric transport and inhalation may be a more significant pathway than previously thought, and ^{129}I remains out of equilibrium with stable iodine in the environment for up to several months.

Related Publications

Q. Hu and J.E. Moran, "Simultaneous Analyses and Applications of Multiple Fluorobenzoate and Halide Tracers in Hydrologic Studies," *Hydrol. Process.*, in press.

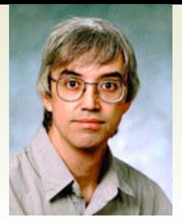
Q. Hu, et al., "Sorption and Transport of Iodine Species in Sediments from the Savannah River and Hanford Sites," *J. Contam. Hydrol.*, in press.

K. Schwer, et al., "Near-Conservative Behavior of Iodine-129 in the Orange County Aquifer System, California," *Applied Geochemistry*, in press.

NEW FRONTIERS

The ability to determine iodine speciation, coupled with major advances in ^{129}I analysis at LLNL's Center for Accelerator Mass Spectrometry (CAMS), is opening a new field in tracer technology (Figure 2). Because CAMS requires only a small sample and can perform extremely sensitive measurements, fuel reprocessing emission fingerprints can be detected at greater distances and in more environmental matrices long after the emission. Using ^{129}I as a tracer in fuel reprocessing emissions provides an advantage over the traditionally used ^{85}Kr because as a noble gas, ^{85}Kr disperses rapidly in the atmosphere without a trace. The next advance will be to apply speciation information derived from these experiments and measurements of ^{129}I at CAMS to field-test ^{129}I as a tracer of fuel reprocessing emissions.

Age-Dating Groundwater to Assess Contamination



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Quantitative characterization of groundwater replenishment (known as recharge) and flow paths is essential to water resource management and environmental remediation. In response to a request for assistance from California's Water Resources Control Board, LLNL is assessing the vulnerability of the state's 16,000 municipal water wells to contamination by conducting focused studies on the nitrate and emerging contaminants in groundwater.

Both radioactive and stable isotopes can provide information about a groundwater's age, which refers to the last time the water was in contact with the atmosphere. Younger water is more susceptible to contamination; therefore, it requires close monitoring.

Livermore is one of only two facilities in the world with high-throughput capability for age-dating analyses and is unique in using isotopic tracers to characterize groundwater travel times and flow paths.

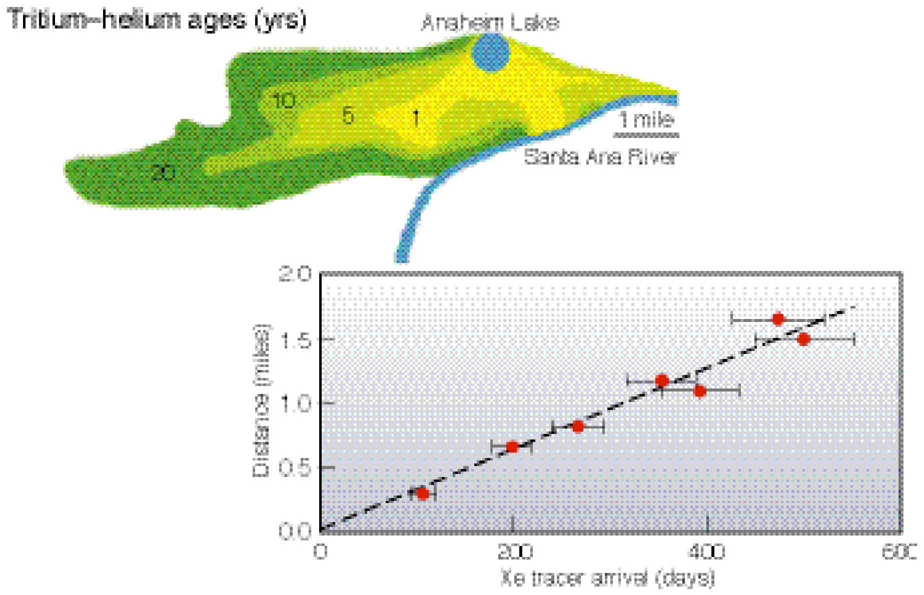

Figure 1. Groundwater age and travel distances are shown for a recharge facility in Orange County, California. Tritium–helium age dating is used for groundwater measured in years, and ^{136}Xe is used as a tracer for groundwater with ages in days.

Relevance to CMS Research Themes

Mass spectrometry using noble gases, which are chemically inert, was originally developed at LLNL for nuclear test diagnostics. Over the years, its applications have been extensive in research for our national-security mission. The technology is also used to understand radionuclide sources and transport in the ground at the Nevada Test Site.

These programs are closely aligned with our mission to tackle environmental issues that affect water safety and nuclear waste cleanup. Noble gas methods are also used in other research, including studies on groundwater flow and pathogen transport, subsurface nitrate transport and biogeochemistry, and transport of xenobiotics during land application of wastewater.

Major Accomplishments in 2004

Our unique approach uses noble gas spectrometry to quantify groundwater flow through tritium–helium age dating and xenon tracer studies (Figure 1). Tritium–helium age dating measures groundwater in units of years, and isotopically enriched xenon tracers measure groundwater with ages in days.

One drawback of using age to assess vulnerability is that "old" groundwater may contain a small fraction of very young water that is highly contaminated. To address this possibility, LLNL, in collaboration with the United States Geological Survey (USGS), also measures recently released volatile organic compounds such as MTBE (methyl tert-butyl ether) at very low levels.

We have found that coastal aquifers, particularly in the Los Angeles Basin and Santa Clara County, are well protected by extensive low-permeability zones that act as barriers to vertical contaminant transport (Figure 2). Although their young water shows low levels of common organic contaminants, their old (deep) water is free of anthropogenic contaminants. The absence of contamination in deeper groundwater is remarkable considering that these basins are located in some of the most highly compromised areas in the state with respect to contaminated surface sites.

We have found the reverse situation for California's Central Valley, especially northern California where the principal aquifers are not well protected. Common solvent contaminants are present in both young and old groundwater in the Sacramento Valley, a distribution requiring more than one transport path for contamination. California's Central Valley is rapidly developing, and significant effort will be necessary to prevent surface contamination from affecting the drinking water supply.

Scientific Impact

The ability to characterize groundwater flow is essential to understanding contaminant and pathogen transport. We have developed a new method to calibrate and validate high-resolution simulations of groundwater flow and contaminant transport to rapidly determine groundwater ages for large numbers of samples. By using noble gas mass spectrometry, we have characterized the flow of water within a basin to determine the spatial distribution of groundwater age. We are also using noble gas methods to determine the water temperature and the abundance of dissolved gases above the equilibrium solubility limit in water. These parameters are directly related to the elevation, seasonality, and soil conditions during natural replenishment of groundwater. Our large data set has revealed strong regional differences in water recharge that have not been previously well understood.

Related Publications

J.F. Clark, et al., "Geochemical Imaging of Flow near an Artificial Recharge Facility, Orange County, California," *Ground Water* **42**(2), 167–174 (2004).

J.E. Moran, et al., "A Contamination Vulnerability Assessment for the Sacramento Area Groundwater Basin," Lawrence Livermore National Laboratory (http://www.waterboards.ca.gov/gama/docs/cas_llnl_sac.pdf).

L.K. Rademacher, J.F. Clark, and G.B. Hudson, "Temporal Changes in Stable Isotope Composition of Spring Waters: Implications for Recent Changes in Climate and Atmospheric Circulation," *Geology* **30**(2), 139–142 (2002).

NEW FRONTIERS

Because most anthropogenic groundwater contamination has occurred in the past 50 years, our research using age dating and tracer studies has been useful for assessing the vulnerability of groundwater to contamination. The next step will be to develop new tools to characterize components in younger groundwater.

For example, ^{85}Kr, produced by nuclear reprocessing, has a similar half-life to tritium, but a very different source function. Because the activity of ^{85}Kr in groundwater is sensitive to the fraction of very young groundwater (less than 10 years old), we are planning to develop a low-level method that uses ^{85}Kr for water resource investigations. We are also continuing our research to determine how noble gases are incorporated into infiltrating groundwaters, during both natural and artificial recharge, as well as the use of isotopically enriched noble gases as tracers of groundwater processes.

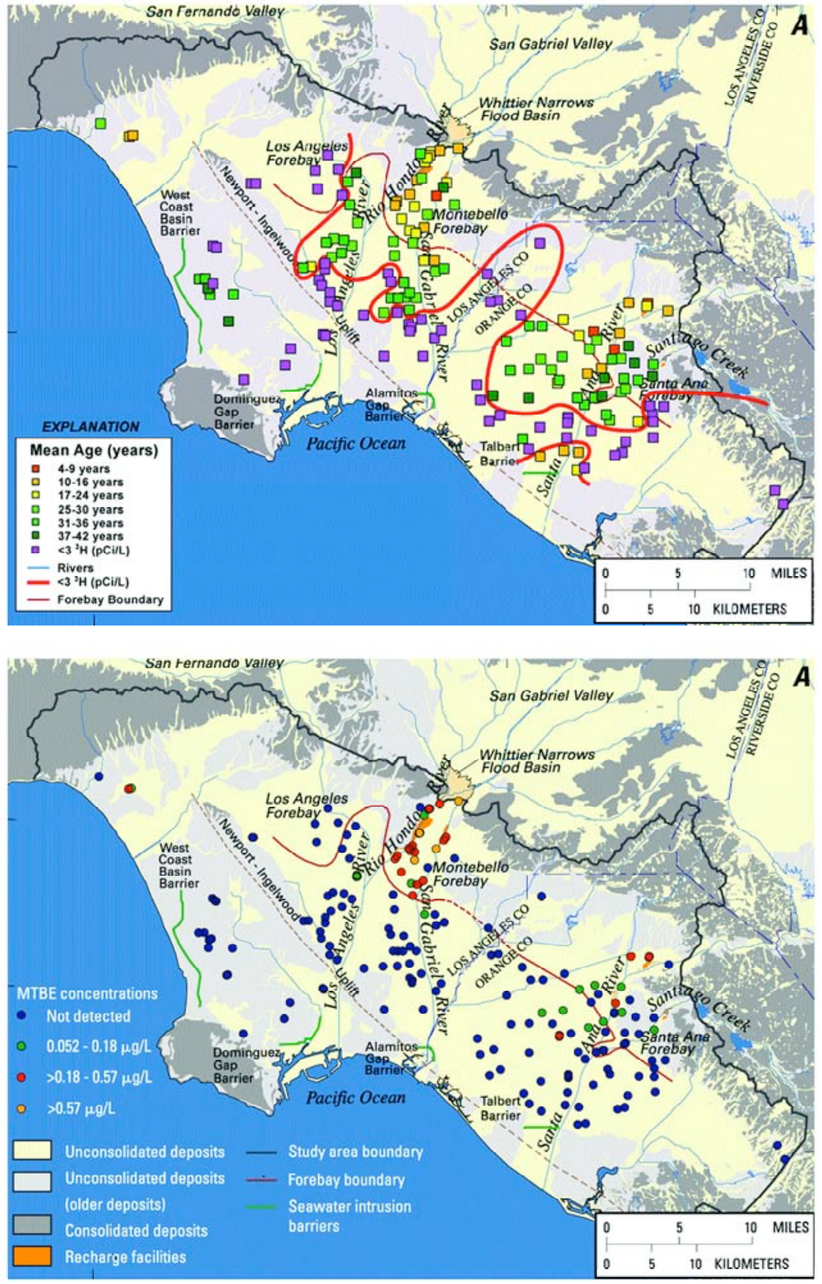

Figure 2. A map of the Los Angeles Basin shows the levels of the organic contaminant MTBE found in groundwater. MTBE is found only in shallow, young groundwater, demonstrating that deep groundwater is protected from surface contamination. (Images courtesy of the USGS.)

Isotopic Composition of Interplanetary Dust Particles

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Interplanetary dust particles (IDPs) are extremely small grains derived from primitive solar-system bodies such as asteroids or comets. These dust grains carry traces of isotopes that may have originated in stars older than our solar system. Laboratory observations of these particles at the nanoscale can advance our understanding of the origin and formation of solar system and galactic processes.

For example, IDPs that contain submicrometer grains with nonsolar isotopic composition can be confirmed as originating from interstellar space (Figure 1). The NanoSIMS, a new-generation ion microprobe with unprecedented spatial resolution, provides our researchers a unique capability to measure isotopic composition in IDPs (Figure 2). NanoSIMS is also used in other cosmochemistry projects, including the study of the abundances of short-lived nuclides in meteorites.

Relevance to CMS Research Themes

Identifying and characterizing IDPs at the nanoscale is part of a larger effort that utilizes an array of microanalytical techniques for materials characterization. In addition to furthering our understanding of astrophysics and cosmochemistry, this research contributes to our national-security mission. Determining the origin of samples with unknown provenance based on chemical and isotopic signatures applies not only to investigations of meteorites, interplanetary dust, and samples returned from planetary missions, but also to interdicted nuclear materials and radionuclides in tumor cells.

Major Accomplishments in 2004

In collaboration with the Institute of Geophysics and Planetary Physics at Lawrence Livermore, we used the NanoSIMS to identify and report the first discovery of nitrogen isotopic anomalies in a hydrous IDP (Figure 3). In contrast to anhydrous IDPs that are most likely from cometary origins, hydrous IDPs are thought to have asteroidal origins. The preservation of nitrogen isotope anomalies in submicrometer amorphous carbon grains in a hydrous IDP provides information on the temperature and duration of aqueous alteration in the asteroidal parent body.

Preparing samples from bulk materials is a critical step in nanoanalytical studies. Advances in the use of the focused ion beam (FIB) to ablate and isolate grains have revolutionized the success achievable from the NanoSIMS. Using a field-emission-gun transmission electron microscope, we can determine the composition of a single slice of a grain taken from the FIB.

Using a new-generation, scanning transmission electron microscope fitted with a high-resolution electron energy-loss spectrometer, we can identify the sources of spectral signatures observed in the interstellar medium. In particular, we have identified the possible origins of an astronomical feature—known as the 2175-angstrom extinction feature—which is the strongest spectral signature of interstellar dust. Our research has identified two likely sources of the 2175-angstrom feature—organic carbon and amorphous silicates—both of which are abundant in both IDPs and in the interstellar medium.

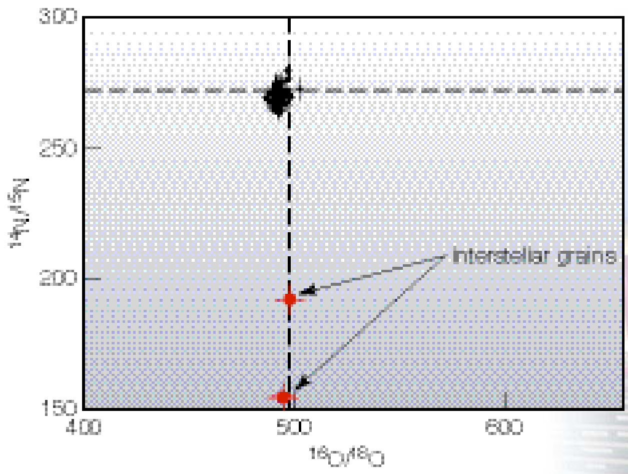


Figure 1. An isotope-ratio plot of nitrogen and oxygen shows the composition of an interplanetary dust particle. The two red circles represent interstellar grains identified within the IDP. The carbon interstellar grain has a ^{14}N/^{15}N ratio of 192±4, compared to the solar ratio (dotted line) of 272. The black circles represent remaining areas of the interplanetary dust particle that have a solar isotopic composition.

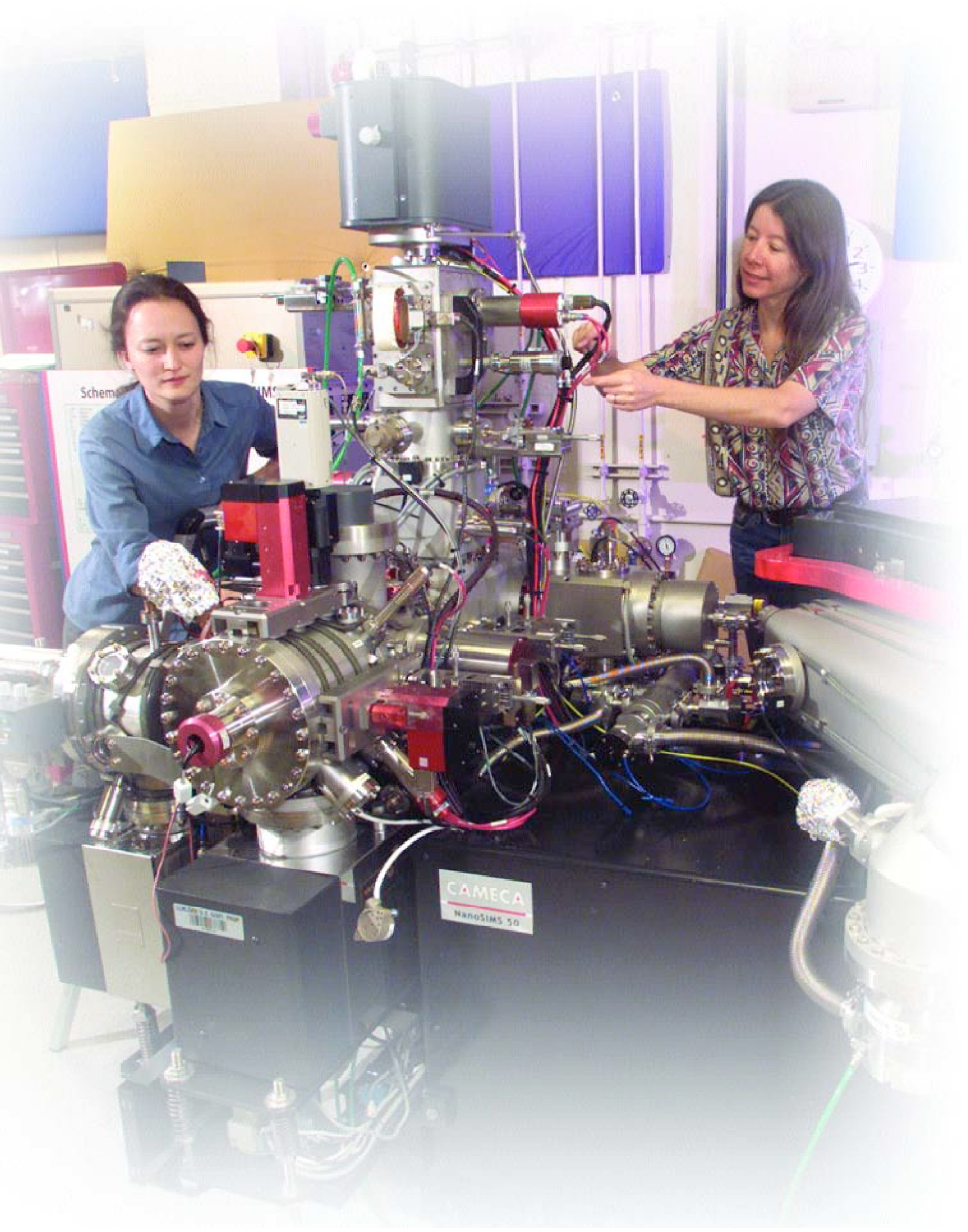


Figure 2. The NanoSIMS, a new–generation ion microprobe, was used to report the first discovery of nitrogen isotopic anomalies in a hydrous IDP.

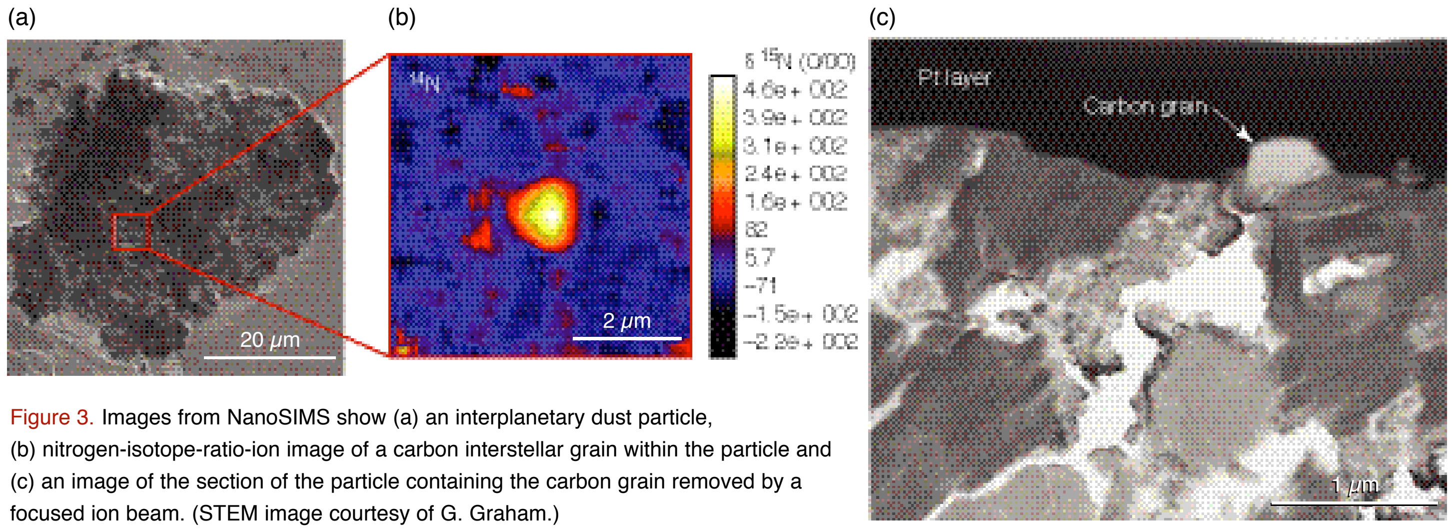


Figure 3. Images from NanoSIMS show (a) an interplanetary dust particle, (b) nitrogen-isotope-ratio-ion image of a carbon interstellar grain within the particle and (c) an image of the section of the particle containing the carbon grain removed by a focused ion beam. (STEM image courtesy of G. Graham.)

Scientific Impact

Because much of what is known about our solar system comes from comparing spectral studies of space with laboratory studies of interstellar grains, this research is essential to further our understanding of solar system materials. Specifically, the presence of both organic carbon and amorphous silicates may help explain the variability of the 2175-angstrom feature, as the relative abundances or physical state of the carriers can be expected to vary from one line of sight to another. In addition to the study of IDPs, we are also conducting studies of presolar silicon carbide grains and early solar system chronology using short-lived radionuclides.

Related Publications

J. Bradley, et al., "An Astronomical 2175 Å Feature in Interplanetary Dust Particles," *Science*, **307**, 244–247 (2005).

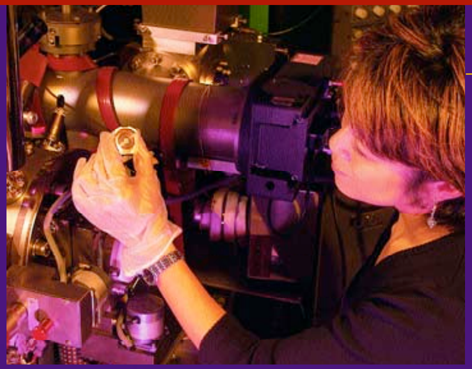
A.N. Krot, et al., "Chronology of the Early Solar System from Chondrule-Bearing Calcium-Aluminum-Rich Inclusions," *Nature*, **434**, 998–1001 (2005).

M. Wainwright, et al., "Studies on Bacteria-like Particles Sampled from the Stratosphere," *Aerobiologia*, **20**, 237–240 (2004).

NEW FRONTIERS

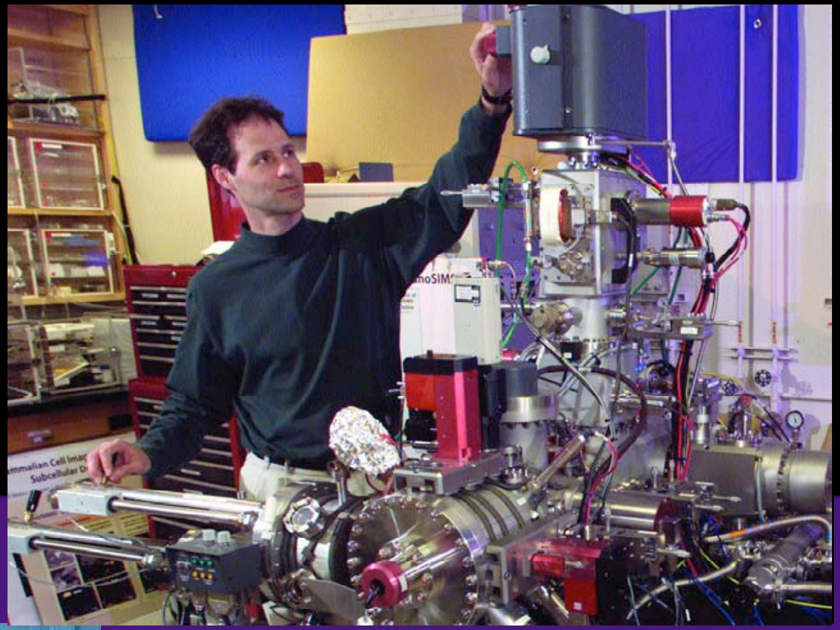
By combining microanalytical technologies such as multibeam FIB, NanoSIMS, and our recently installed high-resolution scanning transmission electron microscope (named SuperSTEM), we are at the forefront of nanoscale characterization. A direct application of our IDP studies will be to analyze samples from NASA's STARDUST mission, which is scheduled to return to Earth in January 2006 with dust from the comet Wild 2. We will study the comet particles to learn more about the fundamental materials that assembled to form the solar system 4.6 billion years ago.

CHEMISTRY AND MATERIALS SCIENCE



Dynamic Teams

- **Divisions**
- **Centers**
- **Institutes**



Materials Science and Technology Division

Providing a fundamental scientific capability for predicting the properties and performance of materials under extreme conditions

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The Materials Science and Technology Division (MSTD) supports major Laboratory programs and executes world-class R&D in a wide range of disciplines. Our program elements are aligned with specific projects supporting the U.S. Stockpile Stewardship Program, the National Ignition Facility (NIF), the Yucca Mountain Project, and the nation's counterproliferation efforts.

We are pursuing conventional-scale and nanoscale technologies in areas that include metallurgy, actinide science, materials synthesis, nanobeam characterization, high-performance computational materials science, electrochemistry, ceramics, solid-state physics and chemistry, surface and interface science, ultrafast science, and coatings and multilayered materials.

Strategic Theme-Related Accomplishments in 2004

MSTD is aligned with the CMS research theme of *materials properties and performance under extreme conditions*. The division supports the Nanoscale Synthesis and Characterization Laboratory (NSCL), and many of our research efforts are described in that section of this report. The following are highlights of additional MSTD accomplishments in 2004:

Materials Dynamics: We continue to employ multiple approaches—including time-resolved dynamic observations, recovery-based observations, and large-scale computational modeling—to better understand the dynamic response of materials under high-pressure, rapid shock-loading conditions. For example, to study shock propagation and phase transitions of titanium and vanadium under shock loading, we are using extended x-ray absorption fine structure measurements at the nanosecond time scale.

Our studies of material deformation mechanisms demonstrate, for the first time, control of high pressure, high-strain-rate loading conditions on a laser-based system. Experimental studies of shock-induced melting and refreeze-on-release phenomena are beginning to address complex issues of microstructure formation under highly transient conditions. The division's non-equilibrium molecular dynamics models are examining defect production and movement as well as melting phenomena and have provided extraordinary details of material response to shock-wave loading in single crystals and polycrystalline metals (Figure 1).

Ultrafast Science—Dynamic Transmission Electron Microscope: In addition to x-ray and optical techniques, we are using electrons as an ultrafast probe. The transmission electron microscope (TEM), which images at high spatial resolution, allows us to study defects in materials that often control material behavior. We are constructing a dynamic transmission electron microscope (DTEM), which will capture microstructural dynamics at nanosecond and nanometer scales, allowing us to study the mechanisms by which defects transform materials from one state to another (Figure 2). Our DTEM will use an electron-capable digital camera system in place of the film traditionally used in a conventional TEM. The images we are currently acquiring will help us to further understand performance requirements necessary for future single-shot investigations. As shown in Figure 3, the pulses produced by a DTEM are intense enough that an image can be observed directly on a phosphor screen.

Computational Materials Science: We have efforts under way—including the massively parallel ParaDiS code covered elsewhere in this report—to study the effects of radiation damage and ensuing dislocation dynamics on the mechanical performance of a wide variety of materials. Particularly, we employ density-functional theories in our models to understand the nature of the electronic properties of the six solid phases of plutonium found at ambient pressure. This year, we have extended a model to include both spin-orbital coupling and orbital polarization effects. This extended model has been able, for the very first time, to accurately simulate the total energies, crystal structures, atomic densities, and magnetic moments of plutonium.

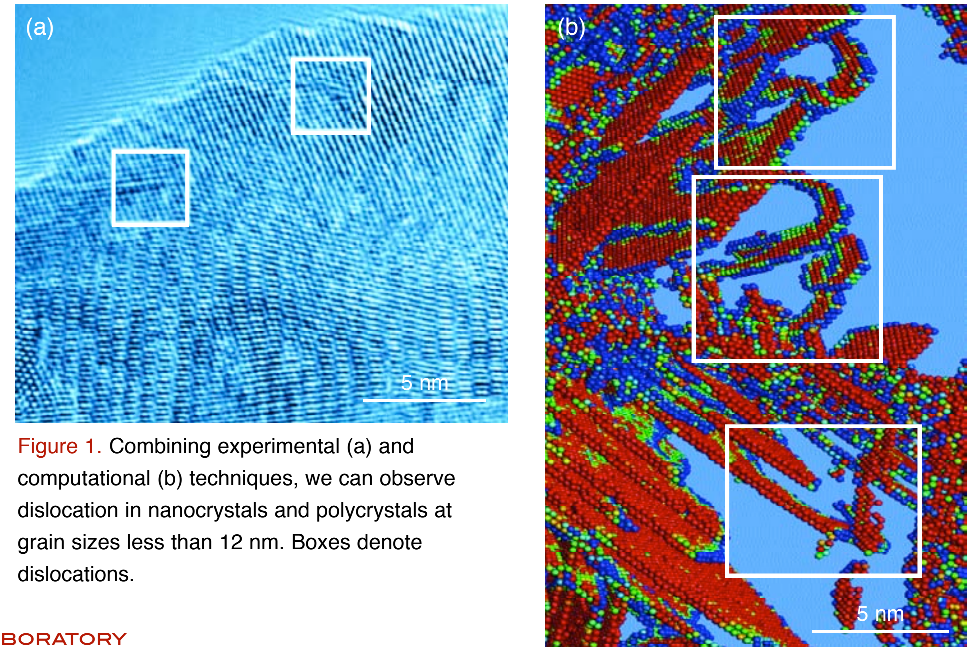

Figure 1. Combining experimental (a) and computational (b) techniques, we can observe dislocation in nanocrystals and polycrystals at grain sizes less than 12 nm. Boxes denote dislocations.

Radiation Detectors: We continue to provide novel materials innovations to our national-security programs. We have successfully demonstrated the synthesis and fabrication of a radiation detector that can be deployed and interrogated remotely.

Using fluorescent photochromic materials, we have developed radiation dosimeters that are small and inexpensive to produce. As radiation converts photochromic molecules in the sensor into fluorescers, a laser system can interrogate the fluorescence level remotely to detect radiation dosage. We have already demonstrated functional high-sensitivity dosimeters and will continue optimization this year. This technology is already making contributions to the nation's nonproliferation efforts.

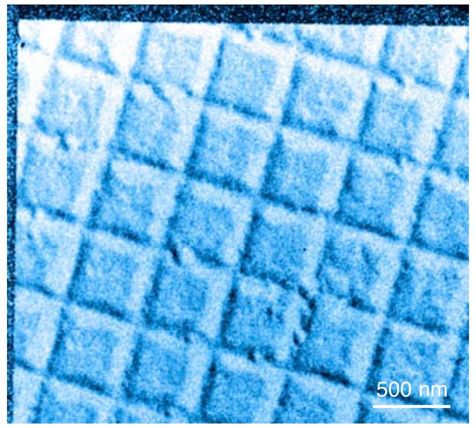

Figure 3. Image of a diffraction grating produced in the DTEM pulsed mode of operation.

State-of-the-Art Technologies

MSTD has developed strategic technologies for predicting the properties and performance of materials under extreme conditions. Our focus has been on the following scientific areas:

- Synthesis of high-performance materials, including extreme-low-density materials for NIF targets, multilayer coatings for extreme-ultraviolet lithography, and thin films for low-temperature welding
- Laser-matter coupling and dynamic response of materials, with particular applications to NIF experiments and stockpile stewardship
- Long-term corrosion studies to provide corrosion-resistant materials for nuclear waste repositories
- Experimental facilities for the study of dynamic properties of materials at unprecedented spatial and temporal resolution
- New materials for remotely interrogated radiation detection

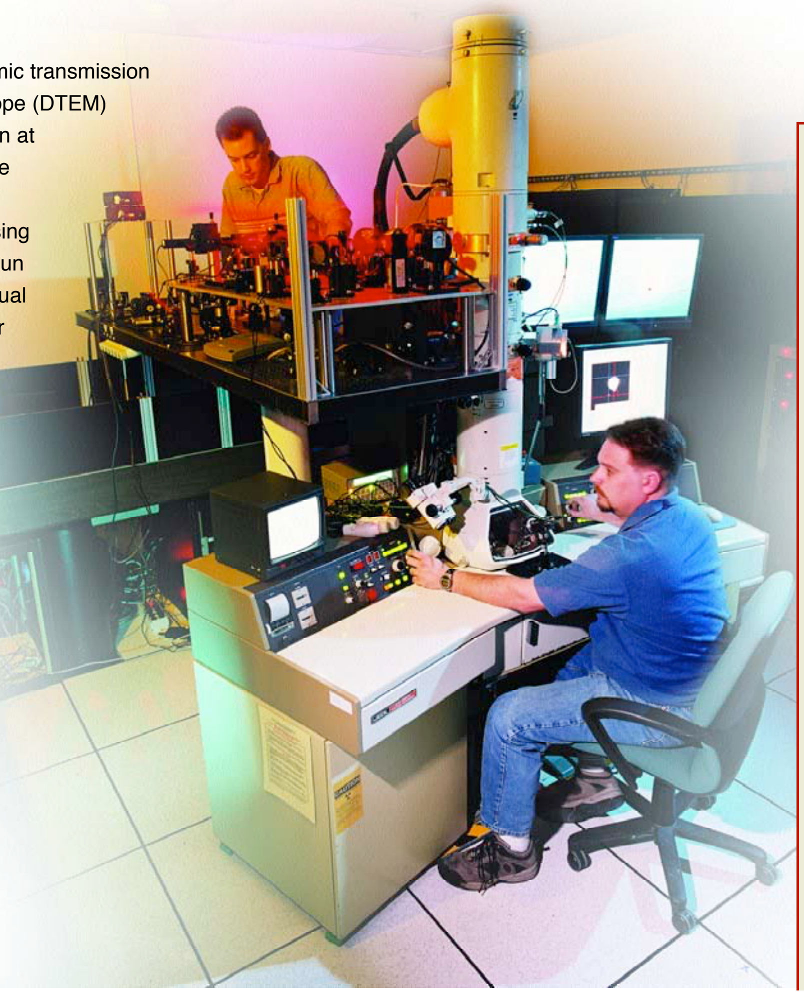

Figure 2. A dynamic transmission electron microscope (DTEM) under construction at LLNL will add time resolution to the microscope by using a photoelectron gun in place of the usual thermionic emitter and a single electron-sensitive digital camera.

NEW FRONTIERS

MSTD will continue to develop a comprehensive program that combines advanced experimental facilities with massively parallel computing to investigate the properties and performance of materials under extreme conditions. A particular focus will be to expand our capabilities in the area of ultrafast science including x-ray, optical, and ultrafast electron microscopy and diffraction.

We expect that the properties of new materials developed using our innovative materials synthesis approaches will be useful to many novel and unexpected applications. These unique approaches and experimental facilities will also help attract leading university collaborators and outstanding young scientists to Lawrence Livermore.

Chemistry and Chemical Engineering Division

Science and engineering that investigate the chemical properties, reactivity, and synthesis of energetic and optical materials

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The Chemistry and Chemical Engineering Division (CChED) focuses on discipline-based science and technology in the fields of chemistry, advanced materials synthesis, and chemical engineering while simultaneously providing key support to the Laboratory's programs in the areas of energetic materials, optical materials, and chemical detection.

Strategic Theme-Related Accomplishments in 2004

CChED is aligned with the CMS research theme of *chemistry under extreme conditions and chemical engineering in support of national-security programs*. Chemistry under extreme conditions involves processes at very high pressures and temperatures—conditions that are often found in nuclear weapons performance studies, laser fusion experiments in the National Ignition Facility (NIF), and planetary interiors. Many of the division's recent accomplishments are reflected elsewhere in this annual report. The following are additional noteworthy accomplishments by CChED personnel in 2004:

Chemistry Under Extreme Conditions: We are using both experiments and computer simulations to study interactions of shock waves in crystals to understand ultrashort time- and length-scale dynamical phenomena in shock waves. We have developed a new impulsive stimulated light scattering instrument that uses surface acoustic waves to study elastic stiffness in solids at extreme conditions (Figure 1).

Figure 1. We have successfully demonstrated the utility of a new instrument that employs the technique of impulsive stimulated light scattering to measure acoustic velocities in materials at pressures in excess of one million atmospheres.

Optical Materials for Laser Experiments: Our improvements to the quality and speed of production of large optics for NIF, the world's largest laser system, have produced world-record KDP (potassium dihydrogen phosphate) crystals, as seen in Figure 2. We have also developed the first disposable debris-shield optics for the NIF Early Light target chamber, which will greatly reduce contamination-induced damage to the main debris shields.

CChED has continued to develop new technologies for producing the world's largest and most accurate diffraction gratings, which are used in petawatt lasers to allow for safe amplification of laser beams. Recently, the first-ever 80-cm-aperture production gratings (Figure 3) were delivered to the Janus Intense Short Pulse laser at Livermore. Based on multilayer dielectric reflection technology, this new generation of diffraction gratings can diffract greater than 99 percent of the incident light while absorbing almost none of the laser beam's energy.

Figure 2. Two KDP crystals produced by using rapid crystal growth techniques are shown.

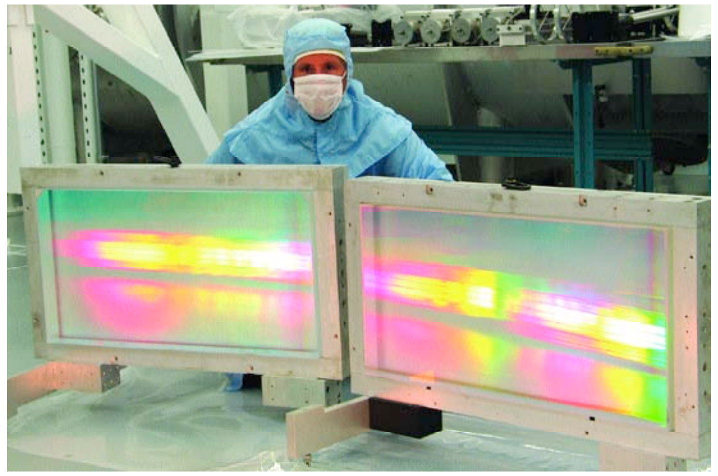

Figure 3. These first-ever 80-cm-aperture production gratings are composed of multilayer dielectric reflectors.

Target Materials for Laser Experiments: We continue to provide novel materials for environmental, nonproliferation, optical/laser, and energetic materials applications. Our latest focus has been on the development of ultra-low-density materials in support of laser target applications. For example, we are using in situ nuclear magnetic resonance to study the dynamics of aerogel formation in alumina. The results will improve our ability to produce materials with specific properties. We have also demonstrated that a templating technique may be used to produce a new class of aerogel with densities less than 100 mg/cc. By applying dextran pyrolytic templating, we have produced silver foams with 1-mm pores at 4 percent full density, which represents a significant advance in this field.

Computational Chemistry: Our computational chemists have made noteworthy advances in a variety of projects, including first-principles studies of water, with an emphasis on the potential energy surfaces of multiple water molecules. In support of the national Stockpile Stewardship Program, our studies have shed light on the effects of water on the interfacial structure and dynamics of the composite materials silica and polydimethylsiloxane in our aging nuclear stockpile. This work helps explain how dehydration might affect polymer stiffness in nuclear weapons stiffening over time and under very arid conditions. We have also used theoretical calculations to study the behavior of crystalline TATB (1,3,5-tri-amino-2,4,6-trinitro benzene, a commonly used energetic material in nuclear weapons) at pressures from atmospheric to 7 GPa, reproducing observed highly anisotropic behavior and suggesting explanations based on structural features of the molecule.

In other computational chemistry efforts, our group received a prestigious award from the Society of Automotive Engineers for its work explaining how the addition of oxygenated hydrocarbon molecules, such as methanol, dimethyl ether, and selected biodiesel fuels, can reduce soot emissions from diesel engines. The oxygenated species encourage the production of carbon monoxide and reduce production of significant soot precursors such as acetylene and butadienes. These results also explain a number of other observations about soot production in engines and the combustion of aged munitions.

State-of-the-Art Technologies

CChED continues to develop new optics manufacturing techniques for NIF. Better understanding of the crystallization and growth process has led to improved performance with lower levels of crystal growth defects, reducing bulk damage. Our expertise is helping researchers to characterize mechanisms of surface damage and etch-pit growth and use new sol-gel coatings to design effective mitigation schemes.

Through a new collaboration with Lawrence Berkeley National Laboratory, we are using a high-pressure and temperature x-ray synchrotron beam line at the Advanced Light Source to monitor chemical reactions in the diamond anvil cell. In one of the first experiments, we studied reactions in white phosphorus. Other work includes using an internally heated diamond anvil cell that can achieve a pressure of 10 GPa and a temperature of 2300 K for studying a wide range of high-pressure reactions and materials properties.

New Frontiers

Through several research collaborations, we are working to advance our understanding of energetic materials and nanocomposites. Through an interdisciplinary approach that combines experimental studies and theoretical calculations, we can more fully comprehend dynamic chemical processes at high temperatures and pressures.

We must use our expertise and advanced tools to fully understand the fundamental issues that govern the safety and performance of our national defense systems, elucidate biochemical processes, understand solid-state nanoparticle chemistry, and augment homeland security agendas. For example, there is a tremendous scientific opportunity to conduct pioneering scientific work in fundamental chemistry at pressures above 1 kbar that has direct applications to the Laboratory's core mission and to address outstanding questions in geochemistry and astrochemistry.

Chemical Biology and Nuclear Science Division

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To provide unique and integrated solutions to issues at the intersection of chemical, biological, and nuclear science and to sustain a strong and viable life-sciences expertise

The Chemical Biology and Nuclear Science Division (CBND) supports program areas that include the U.S. Stockpile Stewardship Program, homeland security, counterproliferation, and energy and environment. The division has exceptional expertise in radiochemistry, radiation detection, nuclear sciences, groundwater chemistry, biochemistry, and bioanalytical science. CBND also provides a majority of the technical staff in CMS institutes and centers, including the Glenn T. Seaborg Institute, the BioSecurity and Nanosciences Laboratory, and the Forensics Science Center.

Figure 1. A drill rig at the Nevada Test Site allows researchers to extract soil samples for radiochemistry analyses of isotopes dating from the period of nuclear testing.

Strategic Theme-Related Accomplishments in 2004

CBND is aligned with the CMS research themes of *science in support of national objectives at the intersection of chemistry, materials science, and biology*, as well as in *applied nuclear science for human health and national security*. The following are highlights of CBND accomplishments in 2004:

Biological Trace Particle Detection: Developed by Livermore scientists to fight bioterrorism, the BioAerosol Mass Spectrometry (BAMS) system can identify spore species in less than one minute. In 2004, we made significant improvements that will increase throughput by several orders of magnitude and lower detection limits for trace populations of particles. We have improved the particle tracking system by increasing the number of probes and analyzing lasers from two to six. We have also developed an advanced algorithm on a field programmable gate array, which can process data in real time. This year, we successfully participated in several government-run field capability tests and demonstrated system performance and spectrometer sensitivity limits.

New Radioanalytical Tools: We continue to provide analyses on environmental and hazardous waste samples that cannot otherwise be analyzed at commercial facilities. These analyses are certified by the State of California and qualified by the Department of Energy Environmental Management Consolidated Audit Program. A major effort this past year has been to support a $20 million project to downgrade the hazard category of the Heavy Element Facility at LLNL from a nuclear facility to a radiological facility, by providing gamma spectroscopy and radioanalytical support to identify and remove items with high activities of exotic actinide radionuclides.

During the period of underground nuclear weapons testing, CBND performed analyses on device performance by extracting debris, known as drillbacks, from the soil surrounding a test and using radiochemistry for diagnostics. Because drillbacks were usually conducted within days of a test, debris selection criteria were based on isotopes with rather short half-lives. In 2004, we led a project that drilled back soil samples near a previous nuclear test and performed a series of analyses based on a new set of radioactive decay sequences, establishing new radioanalytical tools for the future (Figure 1). In addition, isotope analyses of melt glass and groundwater samples from the drillback samples have revealed how radionuclides are partitioned between solid and liquid phases. These results have been used to build predictive models of contaminant transport rates in groundwater, which are useful for the environmental management programs at the Nevada Test Site for the Department of Energy.

Radiation Detectors: We have developed a new, innovative large-area gamma-ray detector with a nanoporous silicon structure that uses quantum confinement to provide tunable frequency output and improved signals. This class of new detectors will be used for national security applications. We are also building a neutron detector with semiconductor nanowires embedded in a boron matrix. The length-to-diameter ratio of the silicon nanowires is approximately 10:1 (Figure 2). These features will allow the detector to operate at room temperature, be less costly to produce, and provide higher energy resolution than that of previous sensors. We are also pursuing a new approach to fabricate neutron detectors based on a single-crystal diamond fabricated by the chemical vapor deposition technique. The diamond neutron detector should exceed the performance of natural diamond gemstones, providing an excellent neutron spectrometer for the International Thermonuclear Experimental Reactor or the National Ignition Facility.

Other highlights of CBND activities in 2004 include the development of an automated titration system to make corrosion studies more efficient and an innovative photocatalytic nanolithography technique to study pattern surfaces efficiently and contribute to future bio-detection systems. CBND scientists also contributed to homeland security by leading a feasibility study for detection and identification of radioactive materials in cargo containers in the New York City area.

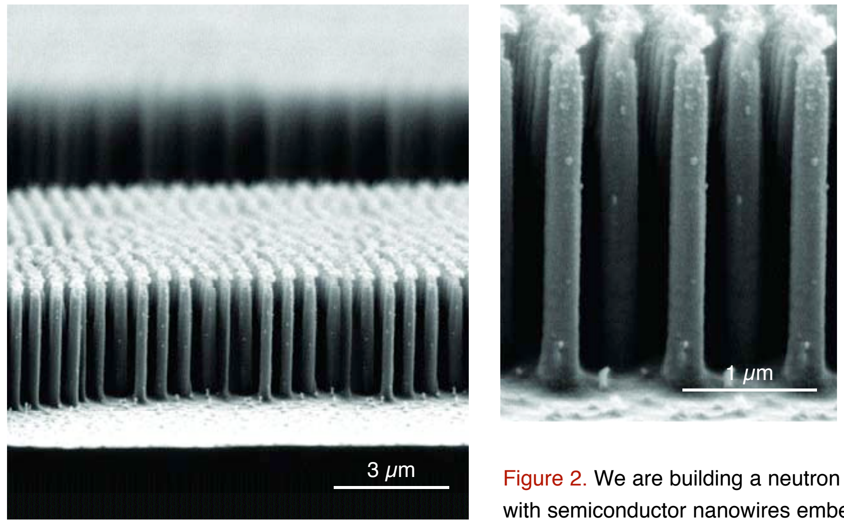


Figure 2. We are building a neutron detector with semiconductor nanowires embedded in a boron matrix. These scanning electron micrographs show silicon nanopillars each approximately 200 nm diameter with 1:9.5 aspect ratio made by nanosphere lithography and deep reactive ion-etching technique.

State-of-the-Art Technologies

CBND possesses unique expertise that is applied toward a wide range of analytical chemistry disciplines. For example, our support for the Department of Homeland Security focuses on capabilities in radiation sensing and imaging, nuclear attribution technologies, and air-sea-land port-of-entry protection. The skills and equipment used for radioanalytical studies of nuclear tests is now being used to produce and observe the radioactive decay of new elements 113 through 116.

CBND is home to one of only ten NanoSIMS (Secondary Ion Mass Spectrometer) in the world. The spectrometer, which has unique capabilities of nanometer-scale spatial resolution and part-per-million sensitivity, is being used in studies of biological materials, molecular targeting for cancer therapy, cosmochemistry, and particle characterization for forensics. Additional state-of-the-art analytical instruments are in regular use in our laboratories.

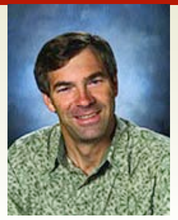
NEW FRONTIERS

CBND provides expertise to many major LLNL programs, each with ambitious future goals. In the area of chemical biology, a particularly important future program is the national Genomics:GTL (formerly Genomes to Life), in which CBND plans to participate in both the basic research and facility initiatives.

In support of the U.S. Stockpile Stewardship Program, our radioanalytical study on drillback soils is expected to lead to important new research. The BAMS project is ready to advance methods on screening for biological agents and high-explosives compounds in real-time field applications in support of homeland security. Many environmental programs are benefiting from the water R&D initiatives led by CBND. With each of these major LLNL programs likely to grow in the coming years, CBND is well positioned to contribute leadership and expertise in the areas of biological, chemical, and nuclear science.

BioSecurity and Nanosciences Laboratory

Science to protect the nation against biological threats and natural disease outbreaks



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The BioSecurity and Nanosciences Laboratory (BSNL) is a multidisciplinary, multiprogrammatic initiative at Lawrence Livermore. The BSNL mission is to provide the nation with biochemical and biomaterials expertise to detect and identify harmful molecules that threaten human health and national security. Principal research areas include proteomic analysis, bioaerosol science, pathogen signatures, bio-organic synthesis, nanofabrication of device platforms, and cellular- and molecular-scale measurements.

Strategic Theme-Related Accomplishments in 2004

BSNL scientists conduct multidisciplinary research to help our nation's homeland security organizations counter biological weapons, to understand the molecular machinery of the cell, and to fight life-threatening diseases. Its focus is in alignment with the CMS research theme of *science in support of national objectives at the intersection of chemistry, materials science, and biology.*

Pathomics is the study of changes in protein and metabolite expression levels in response to disease-causing agents, or pathogens. In 2004, BSNL pathomics scientists improved our ability to identify specific pathogens in blood samples by coupling liquid chromatography with mass spectrometry, using protein samples from humans and from *Yersinia pestis*, or plague bacteria. Our scientists used separation with liquid chromatography to improve the dynamic concentration range of the spectrometer, identify unique peptides produced from each protein, and produce a more accurate signature of pathogens.

Identifying human pathogens and characterizing their surfaces is critical in understanding how pathogens cause disease and in developing detectors and vaccines for biodefense and medical applications. BSNL scientists continue to push the limits of atomic force microscopy (AFM) in imaging individual proteins and spores. During 2004, we approached a 2-nm resolution in revealing the structure of a small virus's capsid—the protein shell covering the viral core (Figure 1). Our results show that viruses from different but closely related families can be differentiated by AFM on the basis of their capsid structure.

As a cell responds to its changing environment, pieces of DNA in its nucleus are constantly being compressed and expanded like an accordion. Understanding the compaction and expansion states of DNA is an important step toward detecting and treating diseases through biochemistry. Working with UC Davis, BSNL scientists use high-resolution AFM to study how DNA interacts with selected proteins. By adding varying amounts of Abf2p—a protein found in yeast mitochondria—to a DNA solution, the researchers have found that when this protein binds to the DNA, it produces a sharp kink in the otherwise fairly loose, open DNA strand (Figure 2). Adding more protein produces more kinks—each kink angled roughly 102 degrees. When sufficient Abf2p protein is added, the DNA collapses into a compact globular structure, which protects the DNA from oxidative reactions that can cause Parkinson's and other diseases.

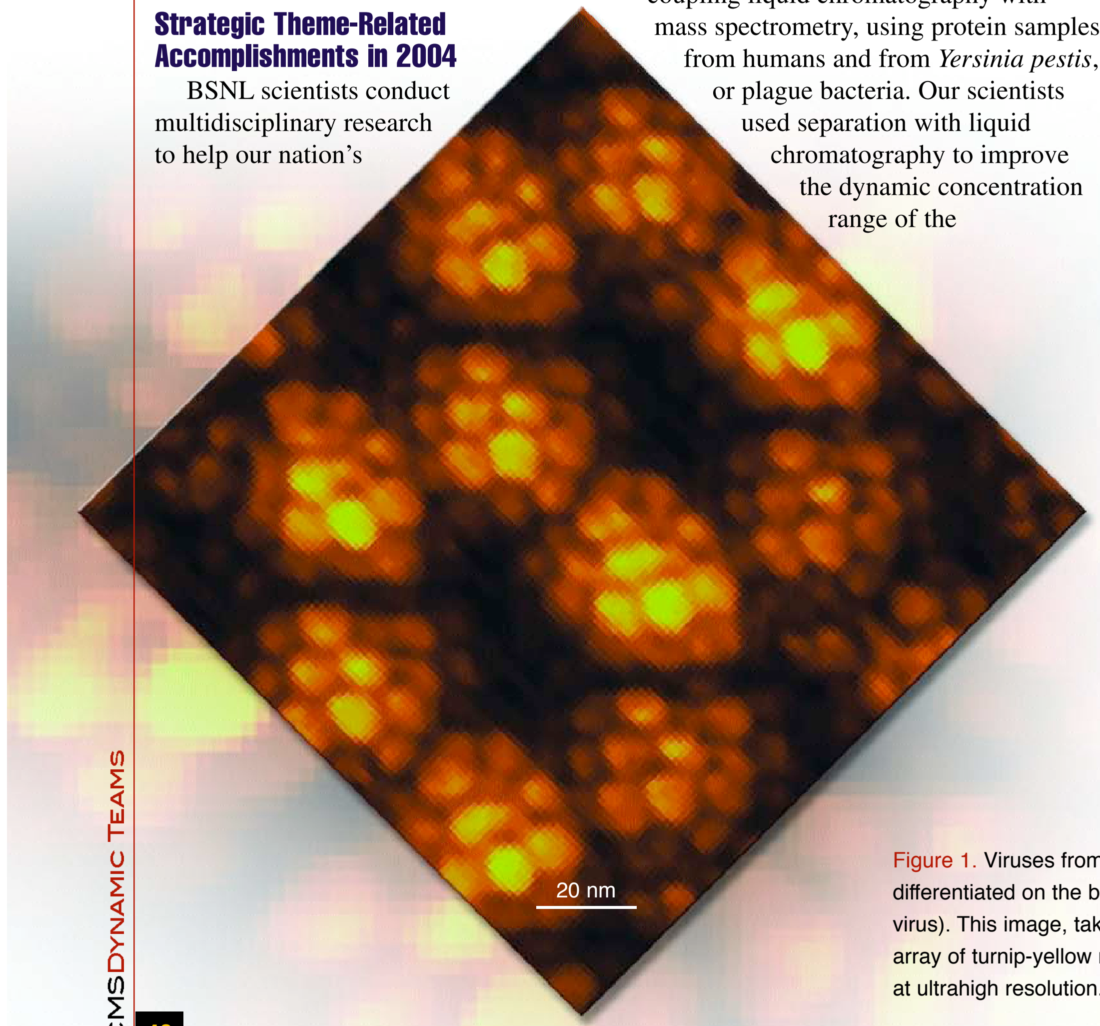

Figure 1. Viruses from different but closely related families can be differentiated on the basis of their capsid structure (the protein shell of a virus). This image, taken by our atomic force microscope, of a crystalline array of turnip-yellow mosaic viruses shows the detailed capsid structure at ultrahigh resolution.

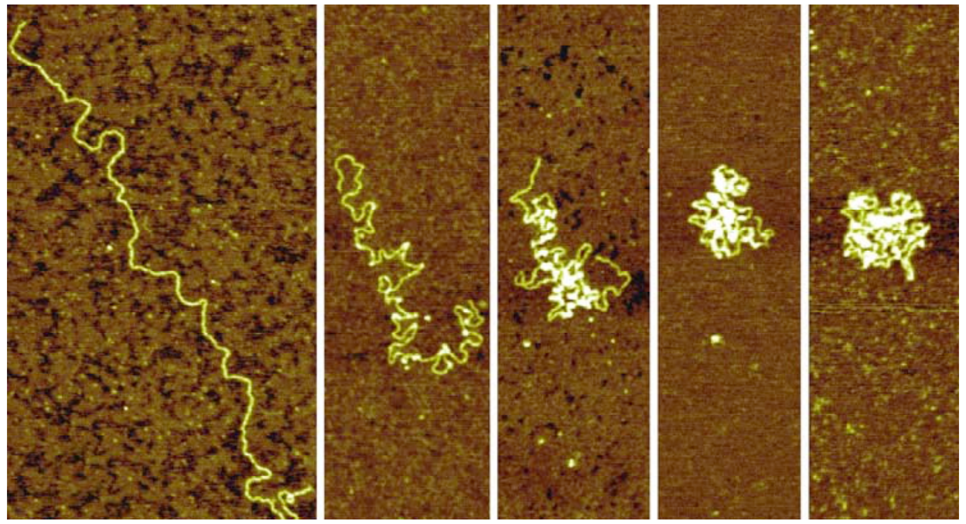

Figure 2. Progressive AFM images show the compaction of DNA caused by increasing the amounts of Abf2p yeast protein. Understanding the compaction of DNA is an important step toward detecting and treating diseases.

BSNL is also developing cutting-edge approaches in protein engineering techniques to study the affinity and selectivity of ligands as they bind to a specific site on a protein. New methods to identify high-affinity ligands can aid in the drug discovery process, in addition to targeted drug delivery. Our approaches take advantage of the powerful forces of selection and amplification from within the context of in vitro or whole-cell platforms that provide for a high degree of control and certainty. Combined, these approaches should provide rapid access to high-affinity ligands for virtually any molecular target. Integrating these ligands with other BSNL science and research elements will allow us to develop next-generation technologies for biodetection, environmental biology research, and human health applications.

Finally, we continue our collaboration with UCLA scientists to use confocal microscopy combined with a unique microfluidic chip to refine the single-molecule measurement of protein-folding dynamics.

State-of-the-Art Technologies

BSNL has brought together a unique suite of analytical tools that provide advanced characterization capabilities at the molecular to single-organism level. Our investment in single-molecule optical detection systems supports the development of ultrasensitive detection and also research into protein–protein interactions. We have also acquired the most precise mass spectrometry systems available for high-throughput protein analysis and profiling chemical signatures across individual cells. Of particular note is the NanoSIMS (Secondary Ion Mass Spectrometer) used for chemical isotope imaging. This instrument is only one of two in the country, with spatial resolution down to 50 nm. We are using it to study microbial communities—important in bioremediation—and bacterial spores—relevant to homeland security.

The BSNL atomic force microscopy laboratories can spatially determine a structure at the single-protein level, measure interaction forces at the single-molecule level, and chemically pattern surfaces at 10-nm-length scales. These laboratories enable BSNL scientists to pursue a wide range of biosecurity and fundamental biosciences research.

NEW FRONTIERS

Prions cause several degenerative disorders such as Mad Cow disease, another degenerative disease in sheep called scarpie, and variant Creutzfeldt-Jacob disease in humans. Its detection had been difficult until very recently when scientists discovered that prion proteins could be detected by an immunofluorescence test or in blood.

Our team is developing techniques to detect prions in sheep blood serum. In addition, we are using microfluidic channels and an optical microscope to detect fluorescence from the prions. This project involves a challenging and important technical task in chemical biology, and it illustrates very convincingly the significant features of the BSNL, with the combination of multiple state-of-the-art analytical techniques and a multidisciplinary team to address a problem that has thus far defied analysis.

Energetic Materials Center

A national resource for research and development of explosives, pyrotechnics, and propellants

The Energetic Materials Center (EMC) is operated jointly by the CMS and Defense and Nuclear Technologies directorates at Lawrence Livermore to conduct research and development on the performance of high explosives. Initially established in 1952 as a core element of the nuclear weapons program, the EMC has grown to also support research and development for advanced conventional weapons, rocket and gun propellants, homeland security, demilitarization, and industrial applications of energetic materials. The EMC applies advanced theoretical, computational, and experimental techniques to provide a detailed understanding of the chemistry and physics of energetic materials and their applications to national defense, and the performance of high explosives and how their performance may change over time.

Strategic Theme-Related Accomplishments in 2004

Research conducted by the EMC is aligned with the CMS theme of *chemistry under extreme conditions and chemical engineering in support of national-security programs.*

To better understand the performance of high explosives, we must first obtain their equation-of-state information. However, accurate data on their properties at high pressures are difficult to obtain, as explosive materials react quickly to the extreme pressures typically produced by strong shock waves in an experiment. In recent experiments, we have successfully obtained new measurements of explosives reactions at pressures up to 35 GPa, using the Z Machine at Sandia National Laboratories (Figure 1). These isentropic, or shockless, experiments offer a new tool to determine materials properties without initiating chemical reactions in explosive samples.

We have also developed the capability to perform three-dimensional x-ray computed tomography in the High Explosives Applications Facility (HEAF) at LLNL to characterize the structure of internal voids inside bulk explosives. These voids have very significant influences on initiation and sensitivity of high explosives; however, their size distributions have not been previously measured. This type of nondestructive analysis produces a map of the material density throughout the volume of an explosive and can be particularly valuable in determining the location of inhomogeneities and voids resulting from explosives manufacturing as well as any possible effects from aging and thermal cycling.

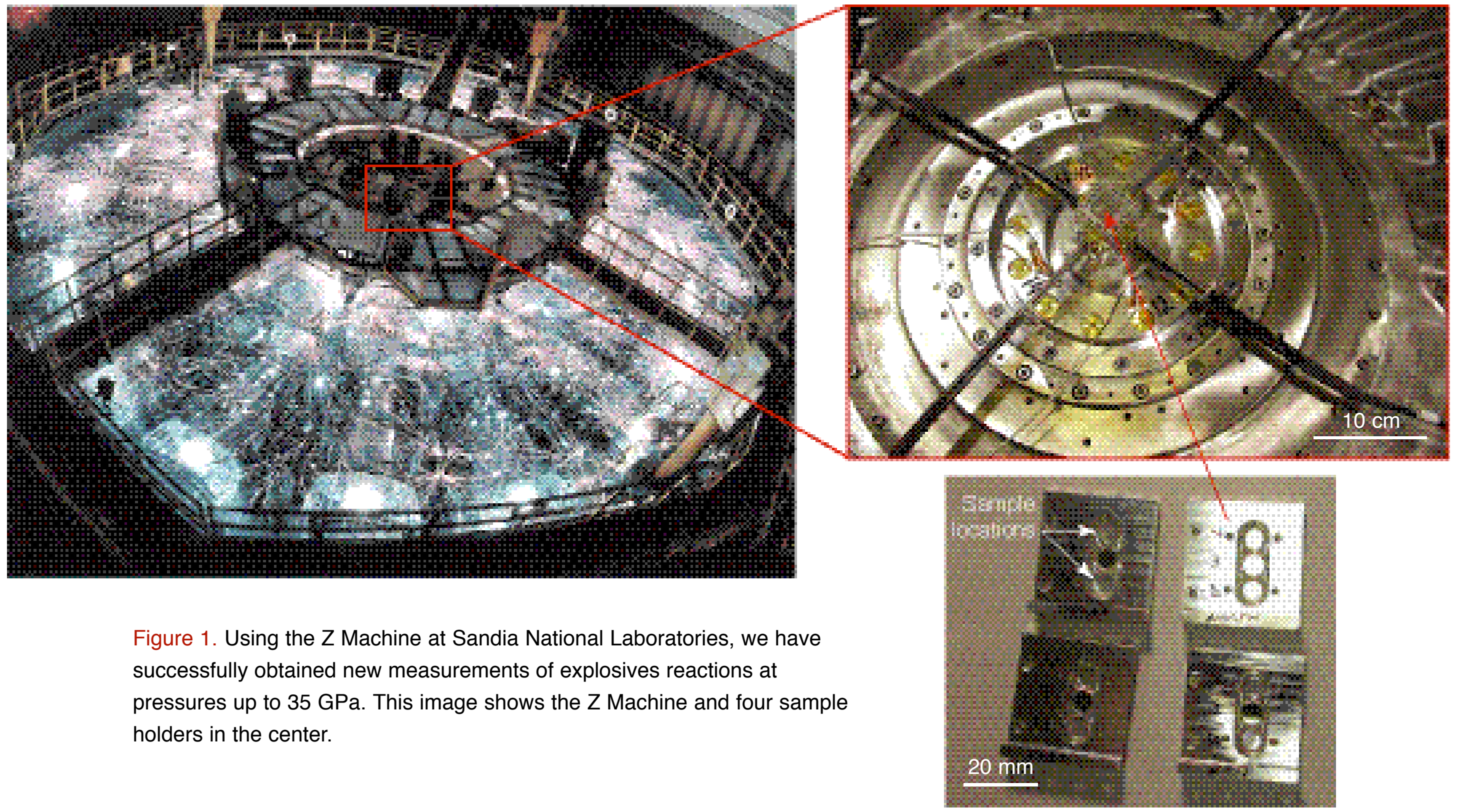

Figure 1. Using the Z Machine at Sandia National Laboratories, we have successfully obtained new measurements of explosives reactions at pressures up to 35 GPa. This image shows the Z Machine and four sample holders in the center.

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Our thermodynamics code, CHEETAH, is widely used as the premier high-explosives modeling environment. In the latest release in 2004, Version 4 incorporates detailed chemical kinetic models for combustion of RDX and TNT, two common high explosives. Together with careful experimental validations, we are using computational quantum chemistry methods in CHEETAH to study fundamental properties of energetic molecules. Knowledge of these properties can be critical in predicting materials behavior, which can change dramatically over the range of pressures and temperatures of interest.

For example, our theoretical predictions indicate that the explosive TATB would experience a significant volume reduction when the pressure reaches approximately 11 GPa. X-ray diffraction experiments at the Lawrence Berkeley National Laboratory's Advanced Light Source have confirmed this prediction.

In our quest to discover novel materials, we continue to conduct computational studies of hybrid fullerenes, in which some or all of the carbon atoms in a fullerene molecule have been replaced by nitrogen atoms. We investigated the condensed phase properties of $C_{48}N_{12}$ (Figure 2), showing that its ground-state solid has a face-centered-cubic structure and behaves like a semiconductor. While these computational studies were initially pursued as basic science research, our research has shown that these hybrid heterofullerenes are high-energy molecules similar to explosives and may eventually have a wide range of practical applications.

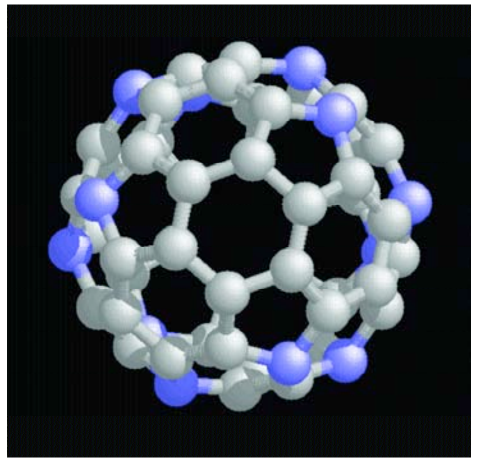

Figure 2. Hybrid fullerenes represent a new class of novel materials that behave like high explosives. Our computational model shows the ground-state structure of hybrid fullerene $C_{48}N_{12}$ with carbon atoms in grey and nitrogen atoms in purple.

State-of-the-Art Technologies

The EMC uses unique facilities to test high explosives and help understand and control their chemistry. These energetic materials are characterized by nanosecond reactions that drive microsecond detonation processes and are tested in facilities including:

- HEAF and Site 300, where explosives synthesis, formulation, characterization, processing, and testing are conducted.
- The Contained Firing Facility at Site 300 and the Big Explosives Experimental Facility at the Nevada Test Site, where fully diagnosed explosives detonations are conducted.
- The Forensic Science Center, where explosive detection methods are developed in support of homeland security programs.

In our dynamic experiments, we apply high-fidelity, high-speed diagnostics—including x-ray radiography, high-speed photography, laser velocimetry, and embedded particle velocity and pressure gauges. The coupling of experimental results with multiscale simulations provides us with a unique ability to apply the latest scientific developments to the challenges posed by energetic materials.

NEW FRONTIERS

The combination of cutting-edge computational analysis and highly diagnosed experiments will provide advances in energetic materials research. We are focusing on four major categories: performance, safety, reliability/surveillance, and new materials. The new diagnostic tools we use to observe the propagation of a detonation wave will enable the development of improved tools to analyze the performance of existing and new materials. These tools will also help us to develop more effective applications of insensitive explosives in the stockpile and in conventional weapons. Similarly, this approach will lead to the ability to evaluate the response of energetic materials to a wide variety of stimuli, providing a scientific basis for resolving safety questions and improving designs with respect to safety.

We continue to focus on detailed understanding of the aging effects in energetic materials, with the goal of identifying potential age-related changes and extending the projected lifetime of energetic materials. Finally, we are developing novel energetic molecules, formulations, and nanoenergetics to support improved safety and performance in the nuclear weapons stockpile as well as the trend toward small, high-value weapon systems that require innovative materials.

Forensic Science Center

Supporting national-security needs in chemical, nuclear, biological, and high-explosives counterterrorism

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The Forensic Science Center (FSC) provides advanced analysis for Livermore's national-security programs in chemical, nuclear, and biological counterterrorism. While serving the immediate, short-term needs in these areas, the center also develops a technology portfolio to support long-term missions.

We are strongly engaged in international and national interests through a variety of federal agencies, including the Federal Bureau of Investigation (FBI), the Department of Homeland Security (DHS), and the Food and Drug Administration. From these agencies, the FSC routinely receives unknown samples for analysis and identification. Our unique forensic capabilities contribute significantly in the nation's efforts to interdict dangerous materials and defeat terrorism. We leverage this expertise in a number of ways to support established collaborations and provide leadership to emerging national and interagency efforts in the areas of national security, nonproliferation, and intelligence support.

Strategic Theme-Related Accomplishments in 2004

Our work at the FSC supports two CMS research themes: (1) *science in support of national objectives at the intersection of chemistry, materials science, and biology* and (2) *applied nuclear science for human health and national security*.

The FSC is certified by the Organization for the Prohibition of Chemical Weapons (OPCW)—an international treaty-implementing body of the Chemical Weapons Convention—to analyze samples for the possible presence of chemical warfare agents. To maintain certification, the FSC participates in ongoing proficiency tests in which one OPCW laboratory creates and sends samples to participating laboratories for analysis. Each laboratory must correctly identify all of the potentially dangerous ingredients to remain certified or to obtain certification.

In 2004, the FSC was asked to prepare and distribute samples. Nine different suspect chemicals were used, two of which were synthesized in the FSC and seven others obtained from commercial sources (Figure 1). The samples were "spiked" with chemical interference and reportable compounds that included chemical weapons precursors and degradation products at concentration levels ranging from 5 to 500 ppm to represent a possible inspection scenario. As a control, FSC scientists conducted stability tests and forensic analysis of the samples using several techniques that included nuclear magnetic resonance and gas chromatograph–mass spectrometry.

The FSC is emerging as a critical scientific center for national security. In 2004, the FBI, in collaboration with the DHS, began the groundwork for a set of forensic networks that specialize in biological, chemical, and radiological forensic analysis. Through DHS and FBI funding, the FSC is developing a set of protocols and enhanced forensic analysis capabilities to support the growing national mission in forensic analysis and attribution. Our center has also been named a member of the Food Emergency Response Network, a national sentinel laboratory system that monitors and analyzes potential threats to the nation's food supply.

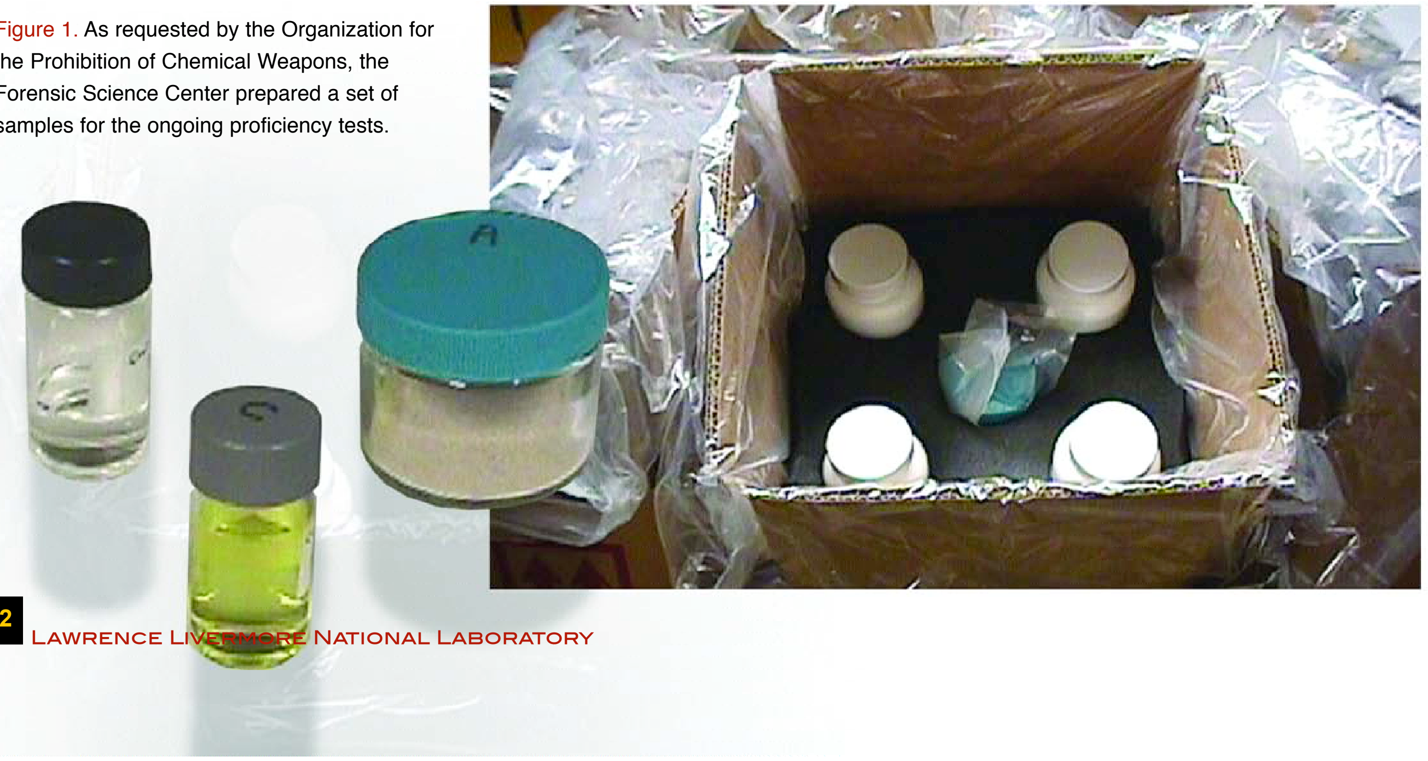


Figure 1. As requested by the Organization for the Prohibition of Chemical Weapons, the Forensic Science Center prepared a set of samples for the ongoing proficiency tests.

Figure 2. The Forensic Science Center has developed a field-deployable analysis kit using thin-layer chromatography (TLC) to assess the stability of munitions and propellants. Previously only available in a laboratory, the new portable TLC kit can reduce the assessment time from days or weeks to minutes and avoid transport of potentially dangerous samples.

We also participated in TOPOFF 3—the most comprehensive terrorism response exercise ever conducted. The exercise involved 10,000 participants from more than 275 organizations in the United Kingdom, Canada, and the United States. The event simulated biological and chemical releases, potential human injuries that might occur as a result, and response actions taken under such a scenario. The FSC provided technical expertise on a 24/7 basis to inquiries from responders over a wide range of subject areas in chemical and biological science and technology.

State-of-the-Art Technologies

We are continually searching for new ways to combine analytical methods with challenging new applications, as well as packaging the tools into smaller, more sensitive configurations to provide portability and flexibility in the field. These compact instruments serve as mobile chemistry laboratories that greatly expedite data acquisition and decision making.

During the past year, the U.S. Army completed a validation test of a field-deployable analysis kit developed by the FSC for assessing the stability of munitions and propellants. This kit (Figure 2) uses thin-layer chromatography (TLC), a technique previously only available in a laboratory. The new portable TLC kit enables a trained technician to test a sample immediately in the field, reducing the assessment time from days or weeks to minutes and avoiding transport of potentially dangerous samples. This valuable technology has now been transferred to a commercial partner.

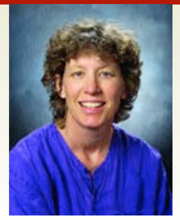
We have continued work on a new technology for rapid colorimetric testing of explosives using a chromometer. One of the greatest national-security concerns is the utilization of explosives in improvised explosive devices. New technology designed at the FSC allows for the rapid testing of over 30 different explosives and can be implemented by first responders with minimal training. The equipment has been field-tested in several "real-world" scenarios and has outperformed other potential field-deployable systems.

NEW FRONTIERS

FSC scientists will continue to expand their capabilities in analytical science, instrument development, nuclear forensic analysis, and new molecular and nanostructured materials synthesis. Future scientific theme areas include next-generation chemical and explosives detection, as well as bioforensics emphasizing chemical and physical signatures. Working with the DHS, the FBI, the Department of Energy, and other pertinent agencies, FSC is strengthening programmatic connections that will use FSC and other unique resources at Lawrence Livermore. Our center is increasing its role as a resource for chemical, biological, radiological, and explosives expertise assistance and is poised to move rapidly to respond to the growing needs of national security.

Glenn T. Seaborg Institute

Fostering research in fundamental and applied nuclear science and technology



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The Glenn T. Seaborg Institute (GTSI) was formed in 1991 to provide scientific leadership in nuclear and bionuclear research. Our expertise includes the development of advanced detection techniques to identify and characterize the effects of radioactive and nuclear-proliferation materials. Our research also contributes toward promoting a clean environment and assisting in the detection and treatment of disease. Efforts at GTSI focus on:

- Science that advances the safety and reliability of the nation’s nuclear-weapons stockpile
- Research to reveal new ways to counter terrorism and deter the proliferation of nuclear materials
- Applying radiation science to improve human health
- Scientific methodologies for assessing the vulnerability of the drinking-water supply and for characterizing the environmental impact of nuclear testing
- Science education to enhance public understanding and student involvement in nuclear research

The institute maintains a world-class nuclear-science workforce to address our evolving national-security needs. In addition, we are fully engaged in the training and development of next-generation nuclear scientists by hosting interns and summer students from top universities around the country.

Strategic Theme-Related Accomplishments in 2004

Research conducted by the GTSI aligns with the CMS research theme of *applied nuclear science for human health and national security*.

To study materials involved in nuclear processes at the nanoscale level, GTSI utilizes an array of unique technologies such as the 200-keV Scanning Tunneling Electron Microscope (STEM) and nanoscale-resolution Secondary Ion Mass Spectrometer (NanoSIMS). In collaboration with the Institute of Geophysics and Planetary Physics at LLNL, GTSI scientists use the STEM and nanoSIMS to analyze interplanetary dust particles and determine if the particles were formed before or after the formation of the solar system. Researchers look for the abundance of specific elements in a sample and profiles of oxygen, magnesium, silicon, iron, and sulfur features, all of which provide information on a particle’s formation and evolution (Figure 1).

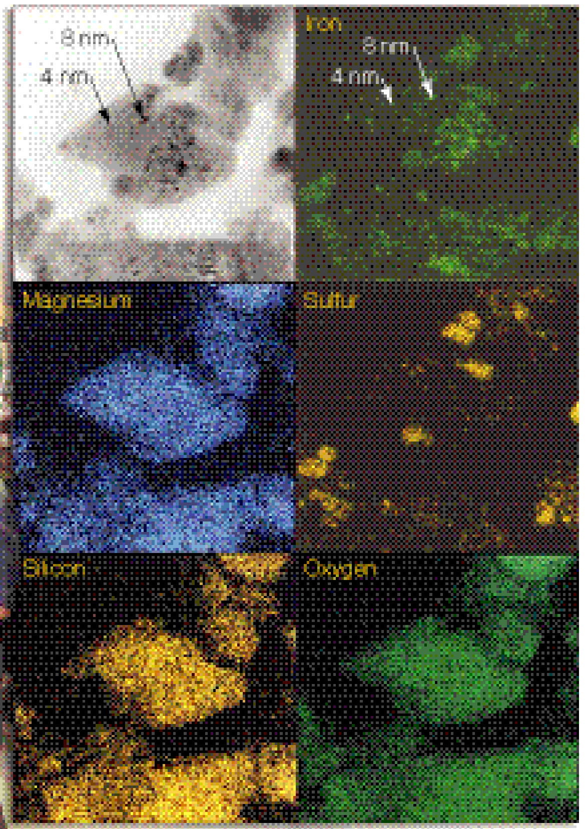
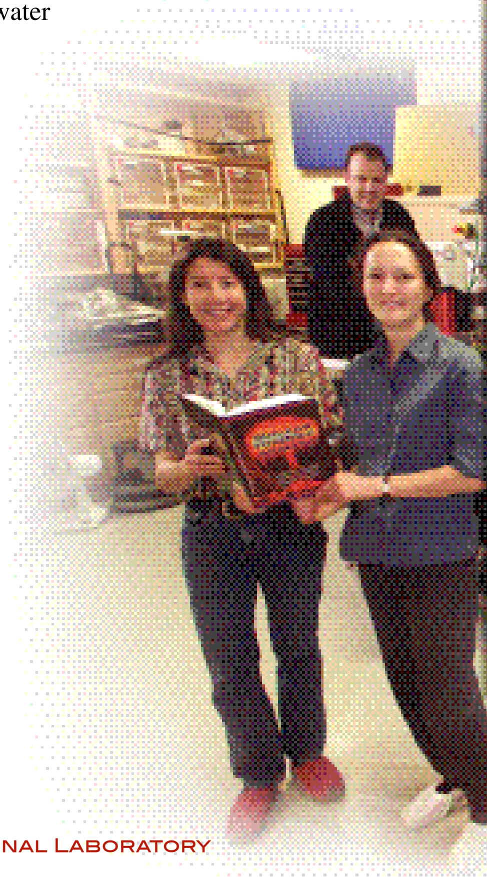


Figure 1. Transmission electron microscopy images of a dust particle from Earth’s upper atmosphere show the total energy emitted from the particle (top left) and the energy distribution for each of the elements in the particle.



GTSI is contributing to biosecurity efforts by using the nanoSIMS to identify elemental and isotopic signatures of anthrax and other dangerous pathogens. We are combining genetic typing with new, state-of-the-art bioforensics technology. We can, for the first time, fingerprint individual spores from a very small sample to help determine the origin of biological weapon agents.

GTSI continues to develop new gamma radiation detection devices for applications ranging from biomedical research and nuclear medicine to national security and astrophysics. Recent efforts have been focused on Compton scattering-based imagers, which provide high source resolution and sensitivity. These detectors use layers of two-dimensional, high-purity germanium arrays to deduce the incident direction of the gamma rays. While the main goal of this detector is finding clandestine nuclear material, it could also be used with radiolabeled tracers to detect unique molecular characteristics of early cancers.

To improve the accuracy of dose determination in radiation therapy, we have developed a new anthropomorphic phantom—a human-body model used in calculating dosage delivery—with an adjustable thickness. The Radiation Phantom with Humanoid Shape and Adjustable Thickness (RPHAT) image system will provide physicians the ability to adjust dosages and target delivery sites according to the weight of each patient. Figure 2 shows the difference in radiation dose and delivery sites for two prostate radiotherapy patients of different weights.

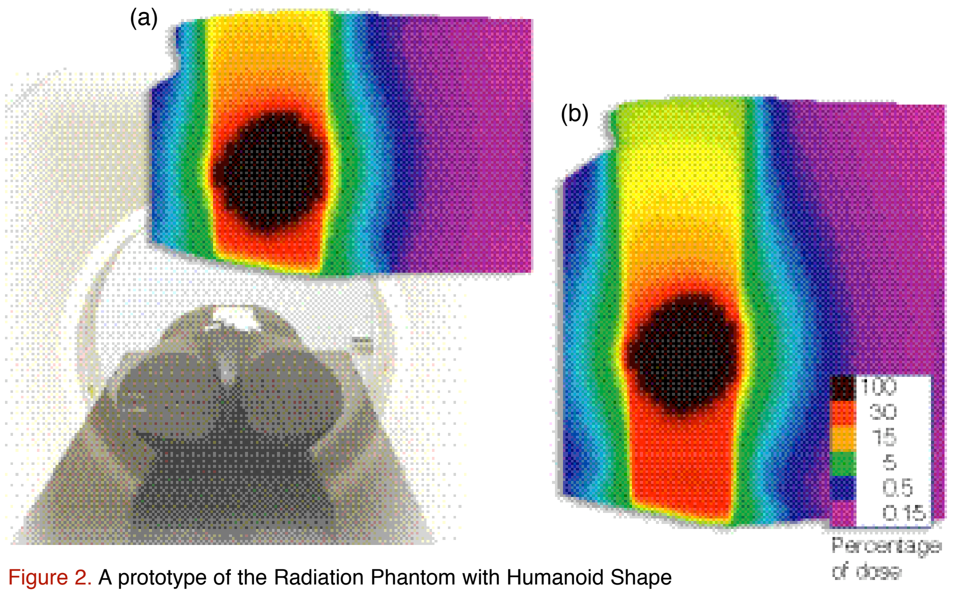


Figure 2. A prototype of the Radiation Phantom with Humanoid Shape and Adjustable Thickness, or RPHAT, model (bottom) is entering a CT scanner. The RPHAT-enabled calculations show dose distributions for a thin radiotherapy patient (a) and a heavier patient (b).

Our expertise in isotope science also contributes to improving the environment, specifically in addressing the growing concern of the vulnerability of groundwater to contamination. For example, in California, which relies on groundwater for 50 percent of its water needs, the leading cause for the closure of many drinking water supply wells is nitrate contamination. Scientists in the GTSI have been using its state-of-the-art mass spectrometry capability to conduct studies using noble gas to determine which wells might be at risk for contamination.

An integral part of the success of LLNL research is attracting young scientists to ensure continuing expertise in basic and applied sciences. GTSI’s Nuclear Science Internship Program, sponsored by the Department of Energy, provides nuclear science students with individual mentors in nuclear and analytical chemistry. During the summer of 2004, GTSI hosted 20 college graduate and undergraduate students from around the country.

State-of-the-Art Technologies

The GTSI utilizes a number of unique facilities and capabilities to advance its programmatic activities, and these technologies often contribute toward other areas of basic science research. For example, the STEM and nanoSIMS—two tools used in work for homeland security, nonproliferation, and national security—also benefit efforts in nuclear astrophysics, new element discovery, nuclear medicine, and environmental research. Through their applications in these areas, scientists refine and develop new techniques for the two facilities. We also train young scientists to use the analytical tools to address problems ranging from attribution of elements in cosmology to solving water pollution. Similarly, the Compton gamma detectors that are being developed for national-defense applications will benefit areas of nuclear medicine.

NEW FRONTIERS

Nuclear science represents a key enduring capability at LLNL. Our goal is to continue to enhance the impact of nuclear and bionuclear science for important national problems such as homeland security, health, and the environment. We are also committed to recruiting and training young scientists pursuing careers in applied nuclear science so that we can ensure continuing scientific expertise in this important discipline.

Center for National Security Applications of Magnetic Resonance

Probing the structure and dynamics of molecules and materials for science in the national interest

For more information contact

Robert Maxwell (925) 423-4991, maxwell7@llnl.gov

The Center for National Security Applications of Magnetic Resonance was created in 2003 to explore biological characterization and meet national defense challenges. The center is a multidisciplinary, state-of-the-art, nuclear magnetic resonance (NMR) facility, housing instruments with unique capabilities and a strong research staff with diverse interests.

NMR uses large magnetic fields and radio-frequency spectroscopy to probe the structure and dynamics of molecules and materials. The center provides a powerful resource for exploring the chemical, physical, and mechanical properties of biological, organic, and inorganic materials. Current projects include studies of sol-gel architectures for chemical synthesis and the structure of high-molecular-weight organic and inorganic complexes.

Strategic Theme-Related Accomplishments in 2004

The wide range of fundamental analyses the center provides is aligned with all four of the CMS strategic theme areas.

One powerful feature of the NMR technique is its ability to examine reacting environments in situ without disturbing the processes in progress. Using NMR spectroscopy as an in situ characterization tool, we successfully monitor particle formation and organization of new aerogel materials in an elementally selective and nondestructive manner. Aerogel materials synthesized using the sol-gel technique are becoming increasingly important in major LLNL programs. Unfortunately, the detailed chemical processes that control the final aerogel morphology and properties are not yet known. That the materials and conditions could only be observed and measured at the beginning and end of the sol-gel process has been an obstacle to progress. During 2004, we successfully probed the influences of such factors as pH, type of solvent and precursor, and extraction technique on the properties of aerogel.

To improve our understanding of hydrogen storage mechanisms, we have also been using a range of NMR techniques combined with computational modeling. Storing hydrogen using either titanium-doped sodium–aluminum hydrides or metal-doped, carbon-based aerogels for new energy applications was observed to be quite effective. However, in neither case the mechanisms of hydrogen absorption were known. Our NMR studies have provided a distinctive method of identifying the bonding and absorption of hydrogen in these materials. In collaboration with Sandia National Laboratories, we performed ^{27}Al solid-state NMR studies on the sodium–aluminum hydrides and explained how the titanium doping enhanced the hydrogen absorption (Figure 1). We are also beginning to apply our NMR techniques to carbon-based aerogels.

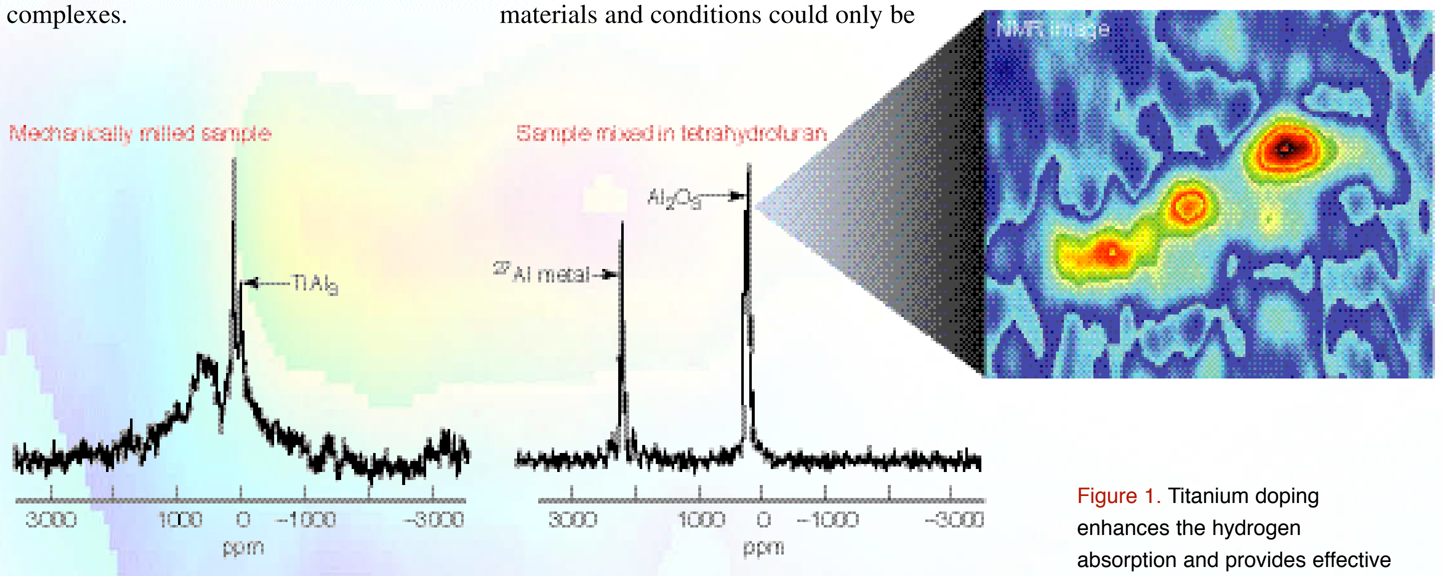


Figure 1. Titanium doping enhances the hydrogen absorption and provides effective hydrogen storage. NMR analysis revealed the formation of titanium compounds in two heavily doped (33.3 at.%) samples of sodium–aluminum hydrides.

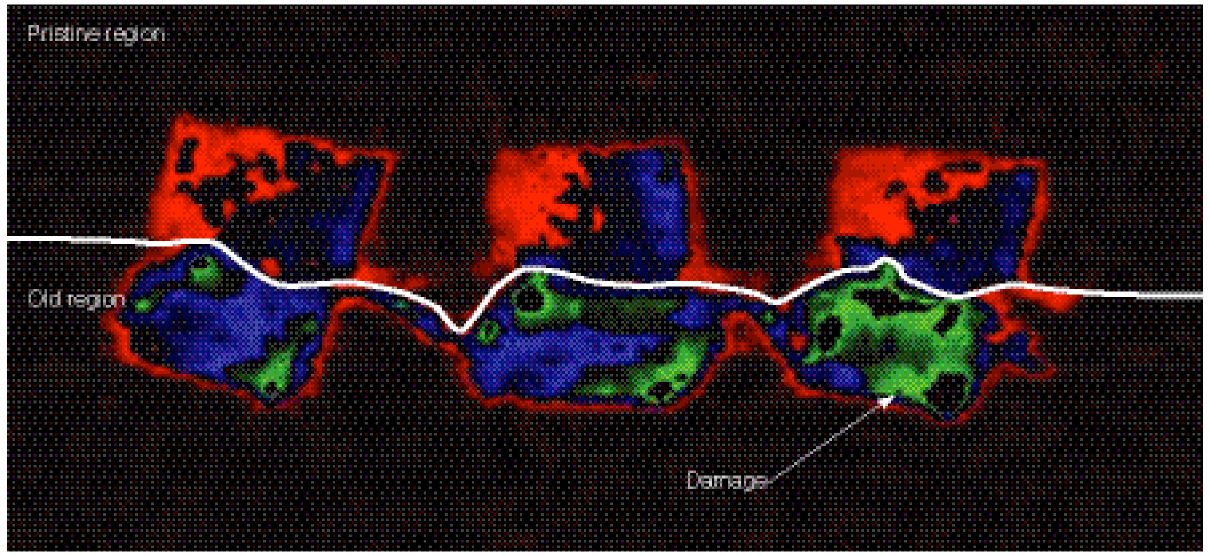


Figure 2. We employ magnetic resonance imaging to compare damaged section and pristine section of a DC745 polymer, a non-nuclear component in nuclear weapons.

A major concern of the U.S. Stockpile Stewardship Program is how non-nuclear components in weapons respond to long periods of stress. For example, composite polymer materials with silica fillers can degrade when stored under extreme conditions. Ionizing radiation and thermal degradation can cause changes of crosslink density and motional dynamics of the polymers. Employing NMR analysis as a diagnostic tool, we are screening replacement polymer parts and samples obtained from surveillance testing of existing weapons components. NMR provides an excellent tool to probe radiation damage in the polymers. For example, we used magnetic resonance imaging (MRI) to create a spatial map of crosslink density in the polymers to detect damaged areas that are not normally visible (Figure 2).

State-of-the-Art Technologies

The center includes NMR spectrometers with operating frequencies of 300, 400, 500, and 600 MHz. As a partner in a northern California consortium, the center is acquiring a new, powerful 900-MHz spectrometer to be located at UC Berkeley. Other capabilities include MRI and low-field, bench-top spectrometers (15, 20, and 85 MHz). These facilities and the expertise are especially valuable to stockpile stewardship research and particularly to materials aging studies.

NMR is especially valuable because it can examine the material in situ, without having to subject the material to environments that can change the state of the material and invalidate the measurements. In each area of study, NMR is used in conjunction with other experimental and computational tools to examine the evolution of the materials in question. In addition, using NMR expertise to integrate structural biology with materials characterization will provide a complementary resource of skills and knowledge that serves as a model of beneficial consolidation of facilities and scientists.

NEW FRONTIERS

The use of NMR to provide structural chemistry information about specific materials is well established. However, we are now learning to use NMR techniques to provide key mechanistic information about extremely complex chemical and physical problems that have long evaded fundamental explanations. We are using NMR to study carbon evolution in soils and in the ocean to better understand the carbon cycle and possible opportunities for carbon sequestration. We are also studying the binding of biological molecules in a variety of applications in radio-immunotherapy, DNA damage, cancers, and bioterrorism. Many of these applications will benefit from our continuing development of an easily transportable NMR scanner with a radio-frequency coil that is less than 500 μm. The dramatically reduced size of such an instrument could provide a portable platform for detecting chemical and biological weapons and for imaging micro-organisms such as microbial biofilms.

Nanoscale Synthesis and Characterization Laboratory

To provide enabling capabilities for fabricating advanced nanoscale structures with novel properties

For more information contact
Alex Hamza (925) 423-9198, hamza1@llnl.gov

Advances in nanoscience and nanotechnology are poised to offer sweeping changes in the way we optimize materials and their functions. The Nanoscale Synthesis and Characterization Laboratory (NSCL) was formed in 2004 to create and exploit interdisciplinary research and development opportunities in nanoscience and nanotechnology. Through advanced synthesis, fabrication, and atomic-scale characterization, the NSCL will develop many new materials and nanostructures that may have far-reaching potentials beyond our immediate applications in national security.

The NSCL is investigating four science and technology areas: nanoporous materials, advanced nanocrystalline materials, three-dimensional nanofabrication technologies, and nondestructive characterization. Among the diverse set of potential applications, our initial focus is to fabricate millimeter-size target capsules for high-power laser experiments. One goal is to maintain hydrodynamic stability of target materials under extreme conditions.

Figure 1. Attracting members from many leading nanoscience groups in the country, the newly formed Nanoscale Synthesis and Characterization Laboratory is already making significant scientific breakthroughs.

Strategic Theme-Related Accomplishments in 2004

Research at the NSCL aligns with the CMS research theme of *materials properties and performance under extreme conditions*. Although the NSCL is still very young, its interdisciplinary research team, including new members from leading nanoscience groups in the country, has made significant advances in important technical areas (Figure 1).

Nanoporous Materials: Nanostructures with pore sizes less than 50–100 nm have many unique structural and transport properties that are ideal for a wide range of modern technologies. Controlling the pore size and increasing the material strength are the two key technological challenges in making these materials. We successfully apply three different strategies for the production of nanoporous materials: dealloying, synthesizing low-density metal oxide aerogels, and depositing atomic layers on silica aerogel monoliths.

Dealloying refers to the selective removal of one element from alloys by leaching or corrosions, whereby a porous structure with a lower density is produced. We used the dealloying of silver/gold alloys to produce gold metal foam at 7.5% of the original material density and with pore sizes as small as 20 nm (Figure 2). Nanoporous gold normally displays a brittleness that cracks upon compression; however, when nanoporous gold foam is produced by dealloying, it deforms or compresses microscopically in a ductile manner. These unexpected properties may lead to an important new class of high-yield-strength, low-density materials ideally suited in target design for high-energy-density physics experiments.

Another approach to synthesize low-density, nanoporous materials involves a new sol-gel process to produce titania (titanium dioxide) aerogels with less than 10% of its normal density. Using high-resolution transmission electron microscopy and x-ray absorption near-edge structure spectroscopy, we also characterized their structural and electronic properties. This new form of titania appears to have unique properties ideally suited for catalytic, photovoltaic, and gas sensor applications.

By directly depositing layers of zinc-sulfide or cadmium-selenide nanocrystals onto silica aerogels, we also produced a new class of aerogels that have a high surface area and ultralow density. The new aerogels exhibit quantum confinement and other unique electronic and physical properties.

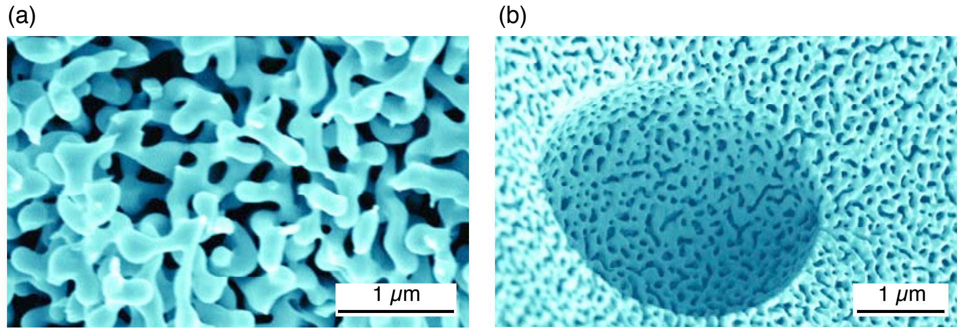


Figure 2. (a) By applying selective dealloying, we have successfully synthesized the first nanoporous gold foam with a pore size that is less than 100 nm. (b) This new class of materials exhibits novel properties. Under high strains, the gold foam is highly ductile and can be compacted by an indentation tip.

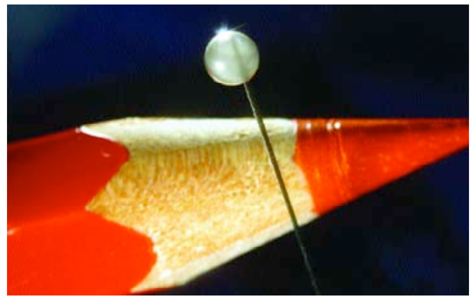


Figure 3. Using chemical vapor deposition, we have produced the first diamond capsule that is ten times harder than the conventional beryllium materials.

Nanocrystalline Materials: We produced the first-ever samples of nanocrystalline gold by compacting gold-metal foam produced by dealloying. During compression, the nanocrystalline character of the foam is retained all the way to full density, with a grain size less than 10 nm and hardness nearly five times greater than the original polycrystalline gold.

Advanced High-Strength Metals: In 2004, we synthesized the first samples of nanocrystalline tantalum. Using transmission electron microscopy and nano-indentation to characterize its hardness and strength, we found ultrahigh strength and unique deformation mechanisms.

In other studies, we used plasma-assisted chemical vapor deposition to produce a thick (100 μm) diamond film that may have advantges over beryllium coatings (Figure 3). The diamond film is an extremely strong surface coating, almost ten times harder than beryllium coating.

Nanofabrication: We have investigated multiple approaches to sculpt materials varying from low-density carbon foams to full-density metals, using computational and experimental tools. Laser ablation of carbon foam was found to produce a smoother but still highly porous surface, in contrast to ablating copper, nickel, and aluminum surfaces, which became pitted and cratered. The ability to polish the surfaces of our millimeter-size targets will be critical in laser compression experiments.

Nondestructive characterization: We are using atomic-force microscopy to probe the structure of bonds between surfaces of disparate materials, as part of a larger effort to understand and ultimately control complex bonding processes. Also in 2004, we began to assess the potential of high-spatial-resolution x-ray imaging and noncontact laser ultrasonics to nondestructively characterize mesoscale objects.

State-of-the-Art Technologies

In addition to a multitude of nanofabrication and characterization tools, the NSCL will use a newly installed dynamic transmission electron microscope with its ultrafast electron diffraction instrument. We collaborate with leading nanomaterials scientists on national user facilities such as the Advanced Light Source at Lawrence Berkeley National Laboratory, the Advanced Photon Source at Argonne National Laboratory, and others in the U.S. and at international sites.

NEW FRONTIERS

The advent of novel nanostructures with extraordinary properties is leading to a new class of materials that will enable many revolutionary applications. The NSCL intends to fabricate nanomaterials with characteristics that will meet the emerging requirements of our mission. In order to understand and control every step in the synthesis of these materials, we intend to establish predictability in a wide range of applications beyond our initial focus of laser target fabrication. We expect advances in nanoscience at Lawrence Livermore to significantly impact the future development of nano-celluar materials and nano-structured materials.

Postdoctoral Fellows and Graduate Students

For more information contact

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The CMS Postdoctoral Program continues to attract excellent young scientists to Lawrence Livermore. They come from top universities around the world, bringing fresh ideas and leading-edge skills to our community. Many of our postdoctoral fellows are making significant contributions to key Laboratory programs and carrying out excellent basic science research, while still maintaining close ties to external collaborators. Approximately 40 postdoctoral researchers in CMS conduct work within a wide range of scientific disciplines. There are also about 15 graduate students pursuing degrees within CMS, each under the supervision of a CMS scientist and a faculty thesis advisor. The postdoctoral and graduate students, grouped according to our current strategic research areas, include the following:

Nuclear Magnetic Resonance

Anh-Tuyet Tran (UC Davis) is working on biological applications of nuclear magnetic resonance, particularly on chemical synthesis of adducts formed by DNA with heterocyclic amines—the carcinogens present in cooked foods and cigarette smoke. Graduate student **Anant Paravastu** (UC Berkeley) is studying optical pumping of semiconductors.

Nanoscale Materials Science and Technology

Robert Meulenberg (UC Santa Barbara) is studying materials that are highly luminescent in the infrared by using rare-earth (lanthanide) doping on group IV nanocrystals. **Raluca Negres** (Central Florida) is studying defect-reactions associated with laser-induced damage in nonlinear optical crystals. **Yinmin "Morris" Wang** (Johns Hopkins) is working on deformation mechanisms of nanocrystalline materials and synthesis techniques for fabrication of high-energy-density experimental targets for the National Ignition Facility. **Trevor Willey** (UC Davis) is using small-angle x-ray scattering for determining nanostructure in explosives and aerogels and the evolution of electronic structure in sub-nanometer diamond-like carbon (diamondoids) and using near-edge x-ray absorption fine structure spectroscopy to examine the orientation of molecular monolayers. **Thomas LaGrange** (Swiss Federal Institute of Technology) is working on nanoscale materials to provide high-energy-density experimental targets.

Nuclear Materials Stewardship

Bassem El-Dasher (Carnegie Mellon) and **Jeremy Gray** (UC Davis) are studying the phase stability and crystalline interface behavior of the welds to be utilized in the Yucca Mountain waste containment outer barrier. Bassem recently received the Henry Marion Howe Award from the American Society for Metals for a paper he co-authored and was published in the journal, *Metallurgical and Materials Transactions*.

Correlated Electron Systems and Alloy Properties

Tom Trelenberg (Florida State) has been studying formation of thin films and nanocrystals by laser ablation and subsequent thin-film characterization. **Sung Woo Yu** (Universität Bielefeld, Germany) is using spin-resolved photoemission spectroscopy to investigate electron correlations in complex systems. **David Clatterbuck** (UC Berkeley) continues to contribute to measurements of the phonon dispersion curves and studying phase transformation behavior of plutonium using synchrotron radiation-based methods. **Martin Butterfield** (Loughborough, U.K.) has been carrying out spectroscopic studies of actinides, and **Scott McCall** (Florida State University) has been searching for a quantum critical point in plutonium/americium alloys with low-temperature experiments on low-temperature physical properties such as magnetization, resistivity, and specific heat. **Michael Armstrong** (University of Rochester) is working on applications of the dynamic transmission electron microscopy for ultrafast diagnostics.

High-Performance Computing

Masato Hiratani (Michigan Tech) is carrying out stochastic computer simulations of dislocation dynamics under various conditions such as irradiation and annealing and incorporating analysis tools such as pattern analysis and chaos and fractal theory. **I-feng Will Kuo** (UC Irvine) has been carrying out classical and quantum mechanical supercomputing studies of bulk and interfacial properties of water and selected problems in biochemistry. **Aaron Golumbfskie** (UC Berkeley) has been simulating complex multidimensional systems in cell biochemistry and energetic materials. **Nir Goldman** (UC Berkeley) has used first-principles molecular dynamics to study superionic phases of simple molecules, including water. Lawrence Fellow **Evan Reed** (MIT) is using computational and theoretical techniques to study optical emission from shock waves in crystals and developing multiscale simulation methods for shock waves.

Biophysical and Interfacial Science

The BioSecurity and Nanosciences Laboratory and other biophysical research areas currently have the greatest number of postdoctoral researchers in CMS, reflecting the emphasis on Laboratory Directed Research and Development and other discretionary funding sources for this subject area. As part of the Physical Biosciences Institute, **Amy Hiddessen** (University of Pennsylvania), **Chris Jeans** (Imperial College, U.K.), **Ted Laurence** (UCLA), **Nan Shen** (Harvard) and **Todd Sulchek** (Stanford) moved into CMS from the Biosciences Directorate during the past year. These researchers are working on a variety of biochemical systems involving host/pathogen interactions, protein–protein binding, and single-molecule detection. **Marco Plomp** (University of Nijmegen, The Netherlands) is using atomic force microscopy to study the nanoscale structure of viruses and spores. **Julie Smith** (University of Western Australia) is using the NanoSIMS to study chemical signatures in biological weapons, early earth geochemistry, and the isotopic composition of extraterrestrial materials. **Michael Stadermann** (University of North Carolina) is investigating the use of carbon nanotubes in gas chromatography and as transducer elements in chemical sensors, and **Jason Holt** (California Institute of Technology) is developing carbon nanotube–based permeable membranes for a variety of separation processes such as desalination and dialysis to understand the fundamentals of nanoscale fluid mechanics. **Jonathan Lee** (Cambridge, U.K.) is using x-ray absorption spectroscopy for structural studies of biomimetic inorganic crystal growth on organic templates, and **Richard Kimura** (UC Davis) is developing methods with protein-splicing tools for biosynthesis of cyclic peptides containing cysteine knots. **Brian Dick** (University of Alberta, Canada) is studying thin films and microfabrication. **Jennifer Giocondi** (Carnegie Mellon) is conducting experiments aimed at understanding the modulation of the crystal growth of calcium phosphate biominerals by ionic and organic modifiers. **Youngeun Kwon** (University of Chicago) is developing protein microarrays by using chemical synthesis of proteins and engineering of biologically expressed proteins. **Saphon Hok** (UC Davis) is using dynamic combinatorial chemistry for target-driven ligand development to identify synthetic high-affinity ligands for tetanus toxin C fragments. **Tim Ratto** (UC Davis) is using molecular recognition force spectroscopy to study surfaces at the nanoscale, investigating the adhesive properties of bacterial spores to decontamination materials, and designing fluidic membranes for protein production and analysis.

Other Programs

Thaddeus Norman (UC Santa Cruz) is using the diamond anvil cell to carry out research on materials at extremely high pressures. **Keith Coffee** (UC Riverside) is part of the BioAerosol Mass Spectrometry program, studying the feasibility of using a combination of aerosol particle size, fluorescence, and mass-spectrum signatures for detection and identification of harmful biological particles such as bacterial cells and spores, viruses, or chemical toxins. **Michael Singleton** (Washington University) is working on groundwater contamination by nitrates in California. **David Campbell** (Florida State) is examining the challenges inherent to mobile radiation detection systems for homeland-security applications. Additionally, he is engaged in the refinement of pulse-shape analysis algorithms for segmented high-purity germanium detectors.

Awards and Recognition in 2004

Professional Society Honors

Bryan Balazs, Deputy Enhanced Surveillance Campaign Leader, received the 2004 Petersen Award from the California Section of the American Chemical Society. The Petersen Award, presented each year at the section's annual awards meeting, recognizes a section member with the most cumulative service to the local group.

Patrice Turchi, a CMS physicist, has been elected as chairman of the Electronic, Magnetic, and Photonic Materials Division of the Minerals, Metals and Materials Society, after serving as vice-chairman for more than two years.

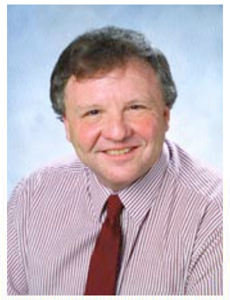
Craig Tarver, a scientist in the extreme chemistry capability area; **Lou Terminello**, materials program leader for LLNL's Defense and Nuclear Technologies directorate; and **David Eaglesham**, former deputy associate director for science and technology, became Fellows of the American Physical Society. Tarver was honored for "his contributions to shockwave physics and in particular his development and implementation of the ignition and growth model for reactions in energetic materials and the non-equilibrium ZND theory for detonating energetic materials." Terminello was recognized for "his innovative use of synchrotron radiation spectroscopy in revealing the electronic and atomic structure of new materials." Eaglesham was awarded for "his seminal discoveries and technical leadership in semi-conductor crystal growth and structural defects in epitaxial materials."

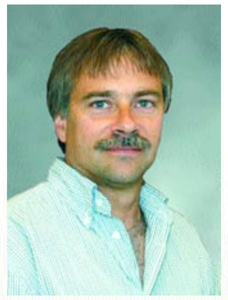

Bryan Balazs


Bill Pitz

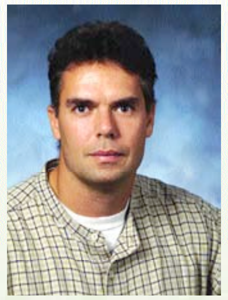

Patrice Turchi


Charlie Westbrook


Craig Tarver


Jerry Britten


Lou Terminello


Anthony Van Buuren

In 2004, **Bill Pitz** and **Charlie Westbrook** were notified of winning the Society of Automotive Engineers' 2003 Arch T. Colwell Merit Award for the best paper presented at society meetings. Their paper, "Effects of Oxygenates on Soot Processes in DI Diesel Engines: Experiments and Numerical Simulations," was written with four coauthors from Sandia National Laboratories. Their work was deemed the best among 2,492 papers published for meetings of the Society of Automotive Engineers during 2003.

Scientific Achievements

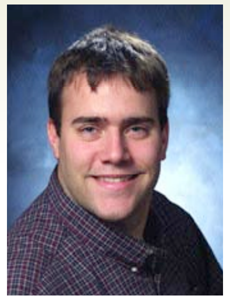
LLNL Director Michael Anastasio presented the fifth annual Science and Technology Awards to two teams of scientists. **Jerry Britten** led the team that developed the processing methods and tooling that produced both the world's largest multilayer dielectric reflection grating and the world's highest laser damage-resistant gratings. This technology provides optics for high-energy, short-pulse lasers. Until this breakthrough was made, no gratings were available for any of these lasers. Fellow CMS employees on the team included **James Peterson**, **Curly Hoaglan**, and **Leslie Summers**. **Anthony Van Buuren** was a member of the second team that won the S&T award for their discovery of bucky-diamond and unraveling the atomic structure of silicon and germanium nanoparticles. The team's research focuses on how the properties of materials change as they are squeezed and made smaller.

Among the American Institute of Physics (AIP) top physics stories for 2004, one Livermore project made the AIP hit parade: the discovery of element 115 at the Joint Institute for Nuclear Research in Dubna, Russia. CMS participants included **Jackie Kenneally**, **Ken Moody**, **Mark Stoyer**, **Josh Patin**, **Ron Lougheed**, **Dawn Shaughnessy**, **John Wild**, and **Nancy Stoyer**.


Jackie Kenneally


Ken Moody


Mark Stoyer


Josh Patin


Ron Lougheed


Dawn Shaughnessy

Leadership Positions

Dick Quigley, a CMS excess acquisitions coordinator, started a four-year term on the Board of Directors of the Alameda County Flood Control and Water Conservation District.

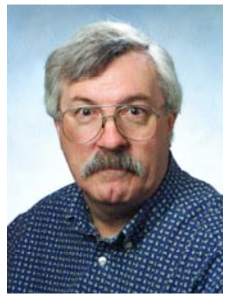
Editorships

Many CMS scientists play important roles in their respective professional societies, with about 13 CMS researchers serving as editors or on the editorial boards of technical journals. These scientists provide a valuable connection between CMS and researchers at universities, other national laboratories, and important industries.

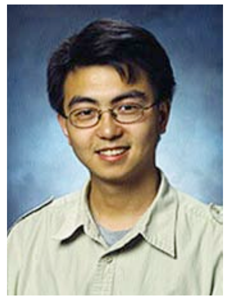
Patents and Licenses

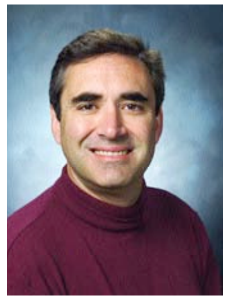
CMS scientists and engineers participated in groundbreaking research that resulted in a number of patents in 2004:

Invention Disclosures	34
Patent Applications	19
Patents Issued	8
Licenses Executed	3


John Wild


Nancy Stoyer


Wei Cai


Mark Lane


Geoff Campbell


Vicki Mason-Reed


Wayne King


Michael Fluss

Postdoctoral Fellows

Former Lawrence Fellow **Wei Cai**, now an assistant professor of mechanical engineering at Stanford University, was named a Frederick E. Terman Fellow. The Terman fellowship program was established in 1994 with a gift from William R. Hewlett and David Packard.

Other Recognitions

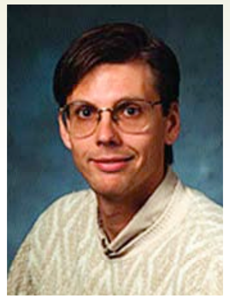
Mark Lane and **Bryan Balazs** of CMS were part of a team receiving a DOE Weapons Recognition of Excellence Award. The team was honored for their work on an aggressive project plan for high-priority testing and evaluation of existing and potential nuclear weapons capability.

Geoff Campbell and **Vicki Mason-Reed** also received a DOE Weapons Recognition of Excellence Award. Geoff and Vicki were members of the case dynamics team, which developed two new experimental platforms and a suite of analysis tools and methodologies to study high explosives-driven radiation-case dynamics.

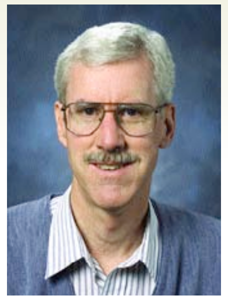
Wayne King, acting division leader of Materials Science and Technology Division, was awarded the Thiel College Distinguished Alumnus Award.

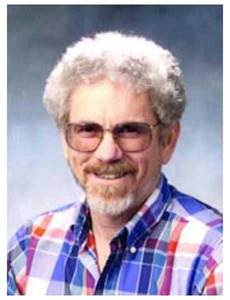
The *CMS 2003 Annual Report* received a Distinguished Award in the annual reports category of the Society for Technical Communication international competition. **Stephanie Shang**, **Charlie Westbrook**, and **Michael Fluss** organized almost 30 CMS contributions to the annual publication.


Christine Orme

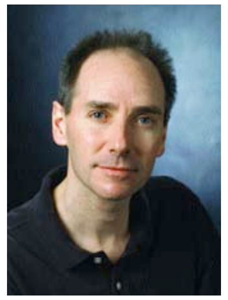

Brian Wirth


David Eaglesham


Carl Melius


Ian Hutcheon


Joe Satcher


Christian Mailhiot


Mukul Kumar


Jeffery Colvin


Luke Hsiung

Two CMS scientists received the prestigious Presidential Early Career Award for Scientists and Engineers. **Christine Orme** and **Brian Wirth** (now a UC Berkeley faculty member) were recognized in a White House ceremony for groundbreaking accomplishments early in their careers and for their potential for future leadership.

University Collaborations

The research activities of CMS members frequently include technical interactions with leading groups and individuals at universities in the United States and other countries. Various university research programs have been identified as particularly desirable and valuable, leading CMS to provide funding to these programs to facilitate interactions (for example, by granting graduate students and faculty special access to the Laboratory). There were more active collaborations in 2004 than in the previous year.

Dr. S.M. Yalisove of University of Michigan, Ann Arbor, partnered with **David Eaglesham** on implementing characterization tools.

Dr. Dudley R. Herschbach of Harvard University partnered with **Carl Melius** in research on chemical reactivity at high pressure.

Dr. Brenda Anderson of the Stony Brook State University of New York partnered with **Ian Hutcheon** in work on the imaging of NanoSIMS.

Dr. Mildred Dresselhaus of the Massachusetts Institute of Technology partnered with **Joe Satcher** to study carbon aerogels.

Dr. Brian Wirth of the University of California, Berkeley, partnered with **Christian Mailhiot** in studying materials degradation and deformation.

Dr. Chris Schuh of the Massachusetts Institute of Technology partnered with **Mukul Kumar** in work on a higher order correlation of data.

Dr. Stephen Quake of the California Institute of Technology partnered with **David Eaglesham** to work on microfluidics technology.

Dr. Todd Ditmire of the University of Texas partnered with **Jeffrey Colvin** in researching optical diagnostics techniques.

Dr. Hanchen Huang of Rensselaer Polytechnic Institute collaborated with **Luke Hsiung** to conduct simulations of interface dislocation and deformation.

2004 R&D 100 Award

Each year,* R&D Magazine *recognizes the 100 most technologically significant products of the year. CMS scientists contributed to one of the R&D 100 Awards for 2004.

AUTONOMOUS PATHOGEN DETECTION SYSTEM

Livermore researchers have been developing a new instrument that can provide a rapid early warning system for the detection of pathogens, such as anthrax. The development of this instrument—the Autonomous Pathogen Detection System, or APDS—has won a 2004 R&D 100 Award.

The lectern-size APDS can monitor the air continuously for biological threat agents and analyze samples within an hour. As the APDS collects air samples, it runs them through two different identification systems to reduce the probability of false alarms. The first system employs an immunoassay detector based on small-diameter polystyrene beads, commonly known as microbeads, technology. A positive result from the first identification system triggers the second test, which runs a separate analysis using the polymerase chain-reaction technique to detect DNA signatures of pathogens.

Results from the system are transmitted wirelessly every hour to a control center. Such systems have been deployed at various locations around the country, where they can provide continuous monitoring for up to seven days, unattended.

The Autonomous Pathogen Detection System monitors the air continuously for biological threat agents and uses two identification technologies to reduce the probability of false alarms. It can measure up to 100 different agents per sample and reports identified agents within an hour.