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Chemistry and Materials Science 2004 Annual Report, Preview Edition

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Gabriele Rennie

May 18, 2005

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This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

CHEMISTRY AND MATERIALS SCIENCE

DIRECTORATE

Annual Report 2004

PREVIEW EDITION

CHEMISTRY AND MATERIALS
CMS SCIENCE DIRECTORATE

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June 2005

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U.S. Government Printing Office: 2004/683-155-44038

A message from



Tomás Díaz de la Rubia

Thriving from change is a constant element at LLNL. Through our commitment to scientific accomplishments, we have met the challenges posed by our evolving missions in 2004. It is the scientific breakthroughs that substantiate our strategic directions. Investments based on our strategic directions are bearing fruit, as illustrated in this preview of the 2004 Annual Report.

We describe how our science is built around a strategic plan with four organizing themes:

- Materials properties and performance under extreme conditions
- Chemistry under extreme conditions and chemical engineering in support of national-security programs
- Science supporting national objectives at the intersection of chemistry, materials science, and biology
- Applied nuclear science for human health and national security

We are particularly pleased with achievements within the “intersection of chemistry, materials science, and biology,” an emerging area of science that may reshape the landscape of our national-security mission. CMS continues to have an unambiguous role both as a technology leader and as a partner for all of the four theme areas. We look forward to expanding the frontiers of science and continuing our partnership with the worldwide scientific community, as we firmly respond to the changing environment with agility and flexibility.

Sincerely,

Tomás Díaz de la Rubia
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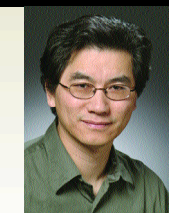
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Unraveling the Molecular Modulation of Kidney Stone Formation



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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 $-170 \text{ kJ}\cdot\text{mol}^{-1}$ and only $-102 \text{ kJ}\cdot\text{mol}^{-1}$ on the (010) face. Our experimental 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.

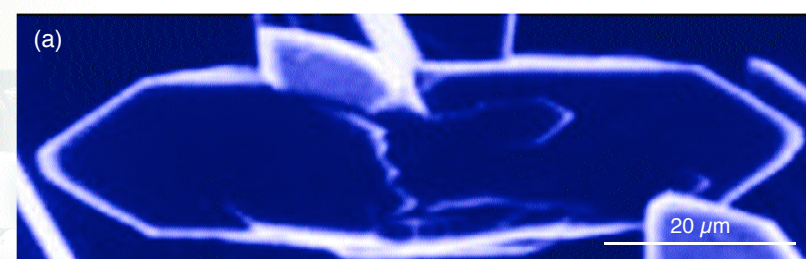
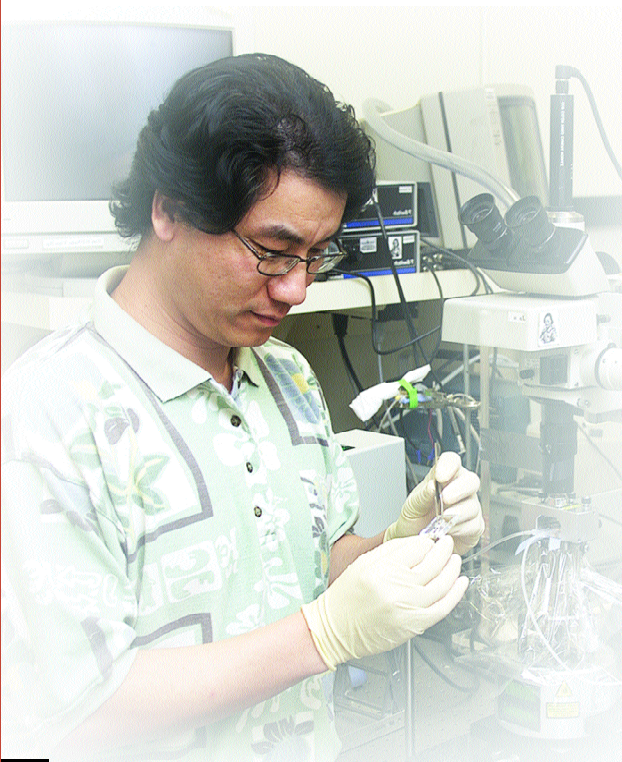


Figure 1. Scanning electron microscopy images show how the growth of calcium oxalate monohydrate—the main constituent of kidney stones—is affected by the (a) absence and (b) presence of citrate in solution.

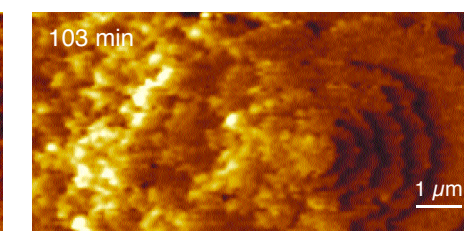
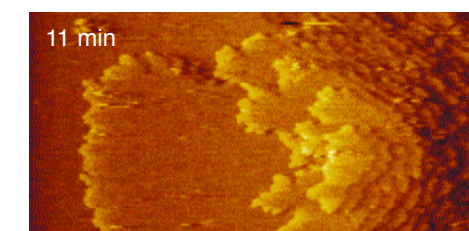
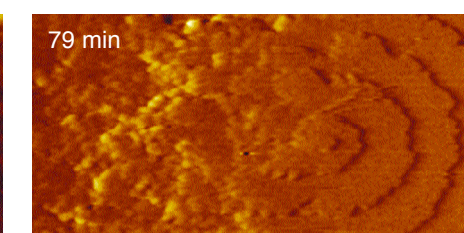
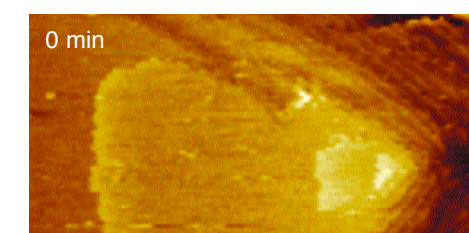
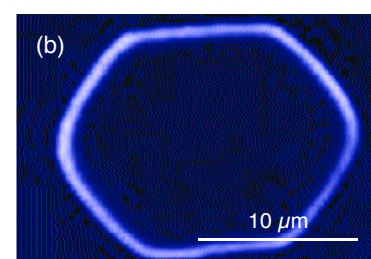
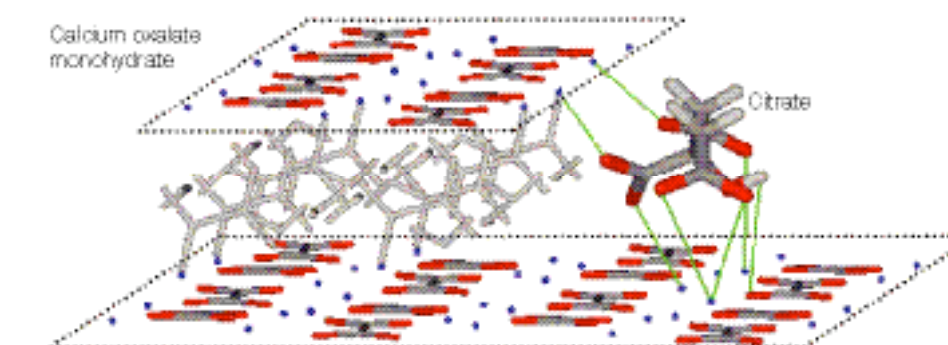


Figure 2. Atomic force microscopy images show the effect of citrate-bearing solution on the morphology of calcium oxalate monohydrate.

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 many 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).

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.

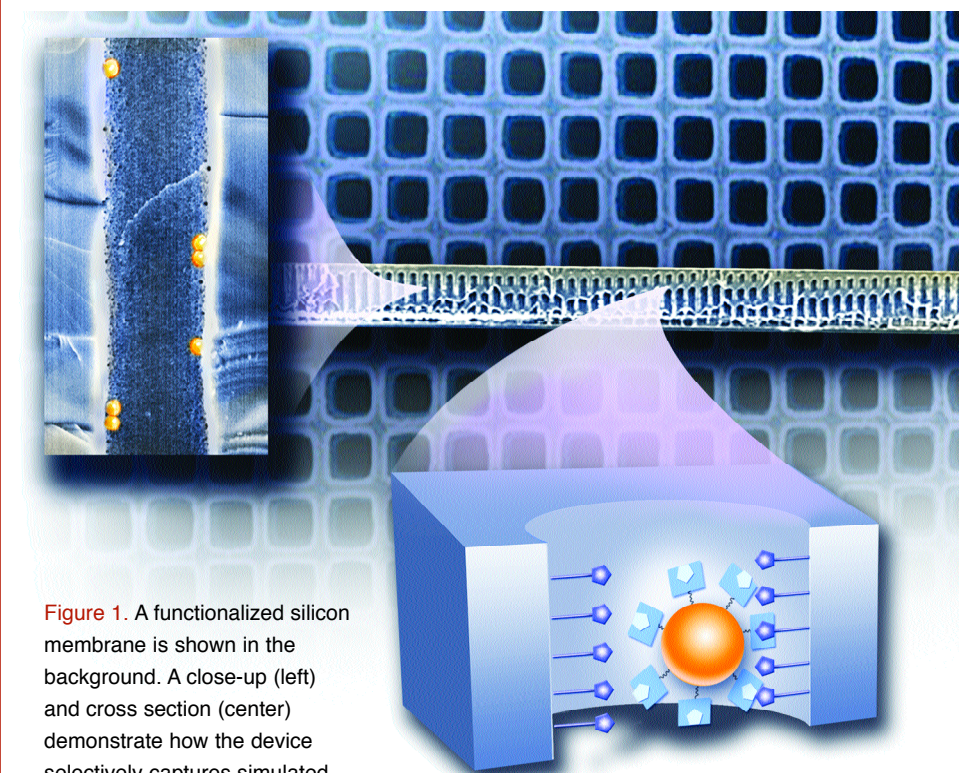


Figure 1. A functionalized silicon membrane is shown in the background. A close-up (left) and cross section (center) demonstrate how the device selectively captures simulated bio-organisms, represented in orange.

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.

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).

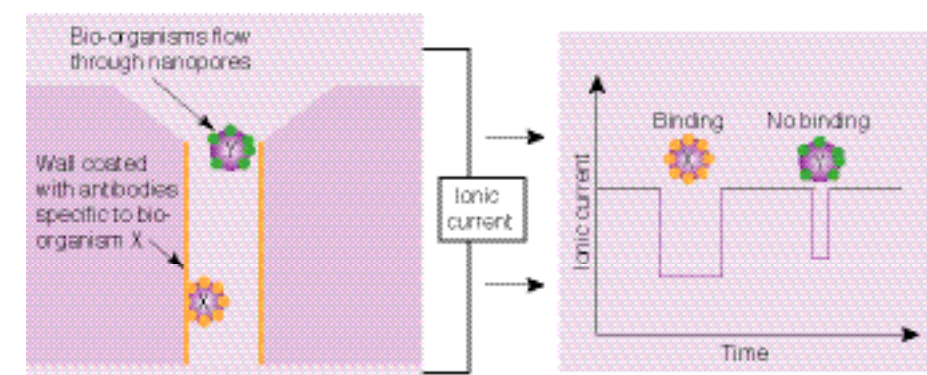


Figure 2. The scheme of operation shows a bio-organism traveling through a functionalized Coulter counter. An ionic current drives the bio-organism through an aperture. The amplitude of the blockade event reflects the size of the organism, and the duration of the event represents the affinity between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

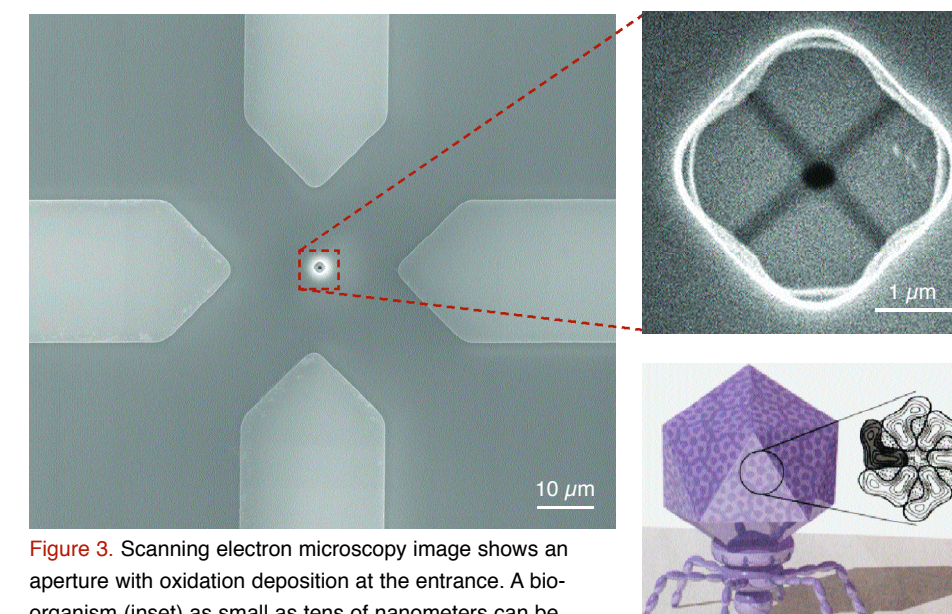


Figure 3. Scanning electron microscopy image shows an aperture with oxidation deposition at the entrance. A bio-organism (inset) as small as tens of nanometers can be detected.

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



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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

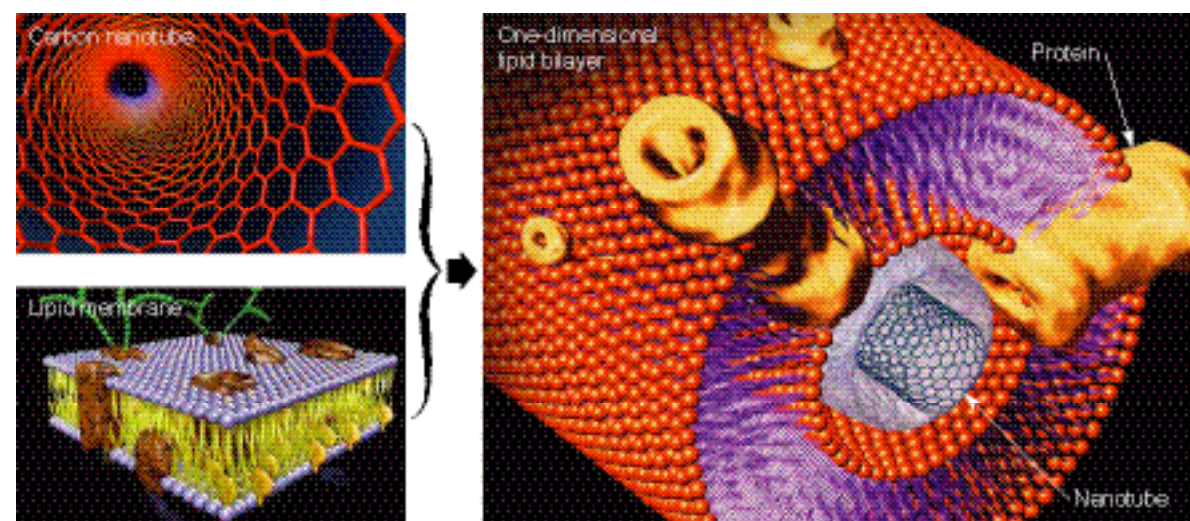
carbon nanotubes with multilayers of polyelectrolyte polymers, we can control the nanotube surface functionality and add support and strength for the lipid bilayers.

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

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



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 (pore 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.

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., "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).

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

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 1-D 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.

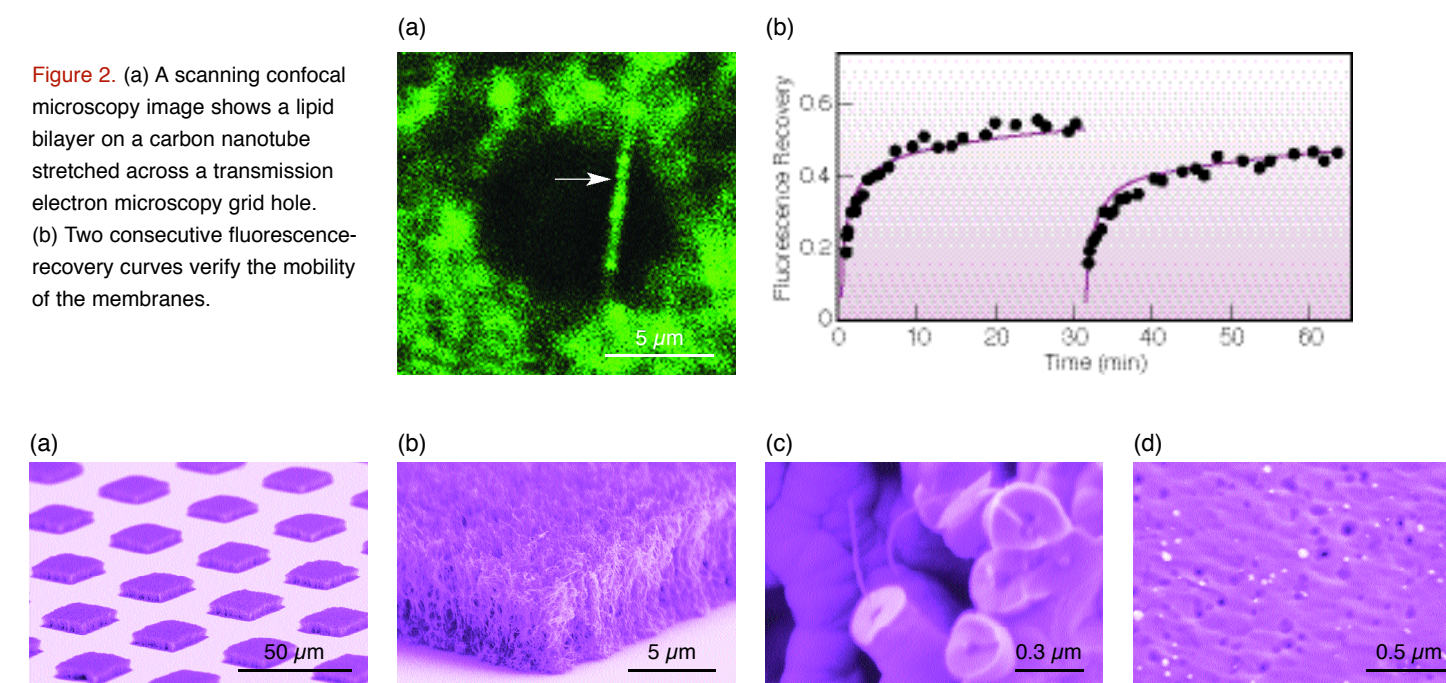


Figure 2. (a) A scanning confocal microscopy image shows a lipid bilayer stretched across a transmission electron microscopy grid hole. (b) Two consecutive fluorescence-recovery curves verify the mobility of the membranes.

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

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 immunosuppressants. 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

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



For more information contact

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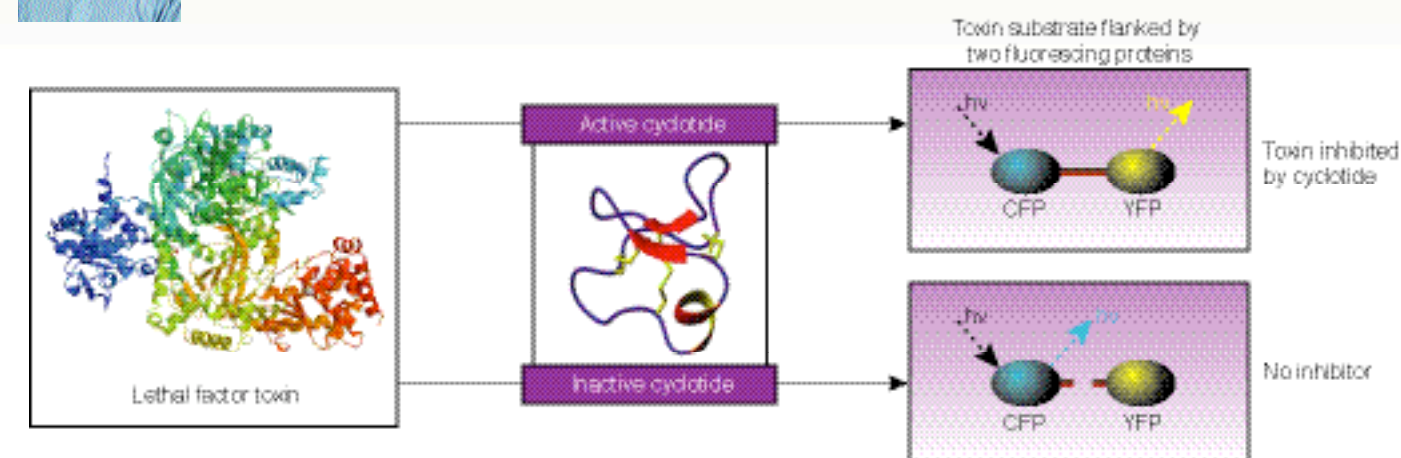


Figure 2. We have developed an in vivo approach for the screening of a cyclotide cell-based library against the lethal factor toxin produced by *B. anthracis*. The chameleon reporter directly senses the toxin activity and reports through a fluorescence change which cells express active inhibitors. In 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.

make cyclotides ideal candidates as molecular scaffolds for new ligand/drug design and discovery.

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, p. 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.

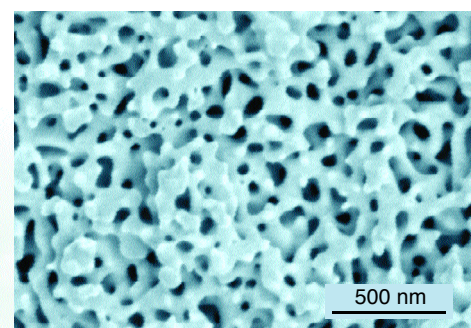
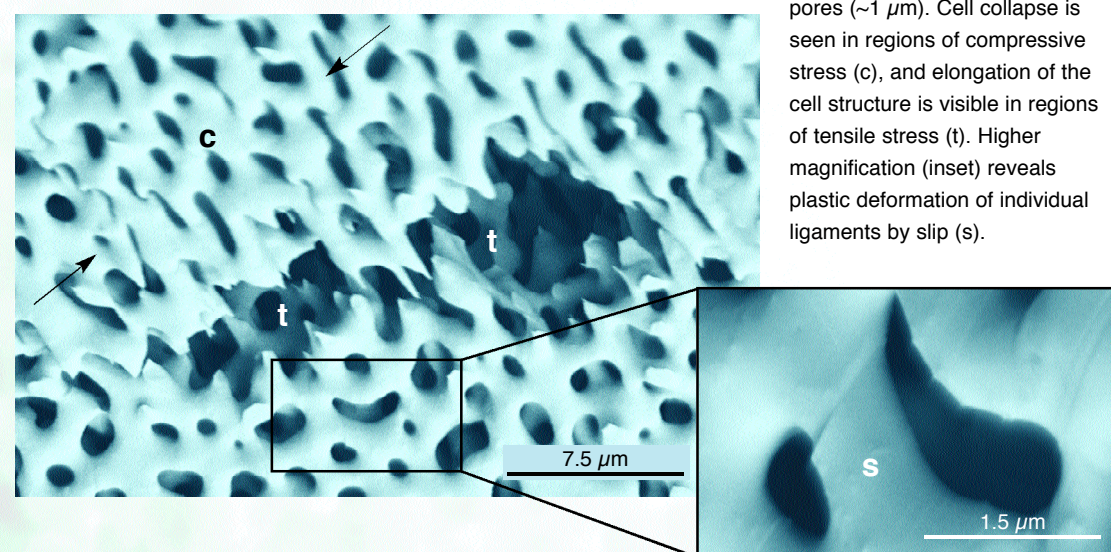


Figure 1. Scanning electron microscopy image of a synthesized porous gold sample shows the sponge-like morphology of interconnecting ligaments after selective dealloying.

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 ($\sim 1 \mu\text{m}$). 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 $\sim 1 \mu\text{m}$.

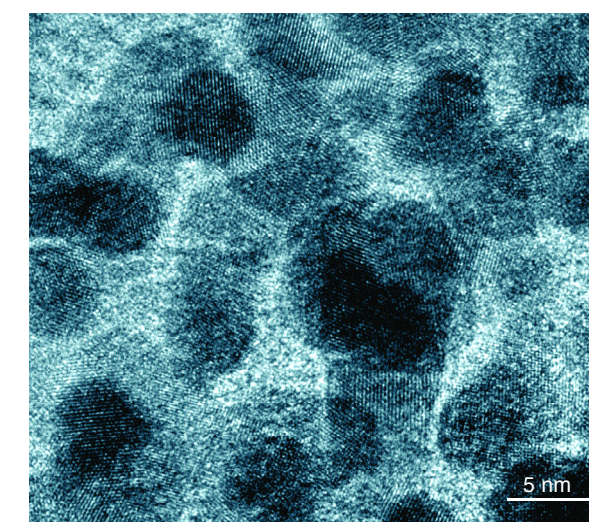


Figure 3. High-resolution transmission electron microscopy image shows compressed foam of nanocrystalline monolithic gold with grain sizes less than 10 nm.

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.

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

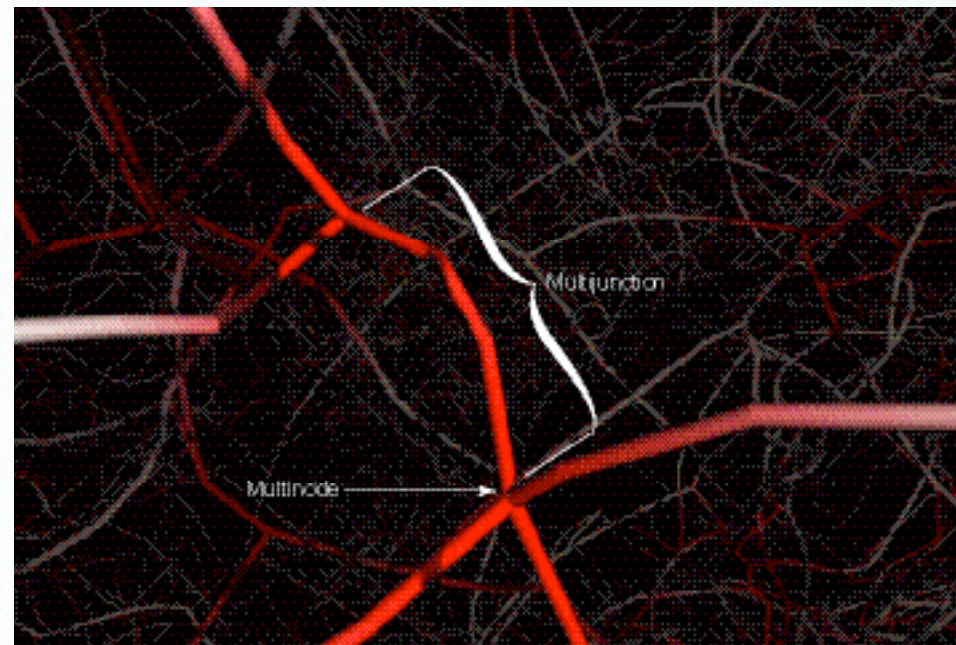


Figure 1. A dislocation dynamics simulation of strain hardening in bcc molybdenum shows a fragment of the dislocation network. Binary junctions connect the mass of dislocation lines (grey). Multinodes (red) complicate the topology by forming a strong skeleton throughout the network.

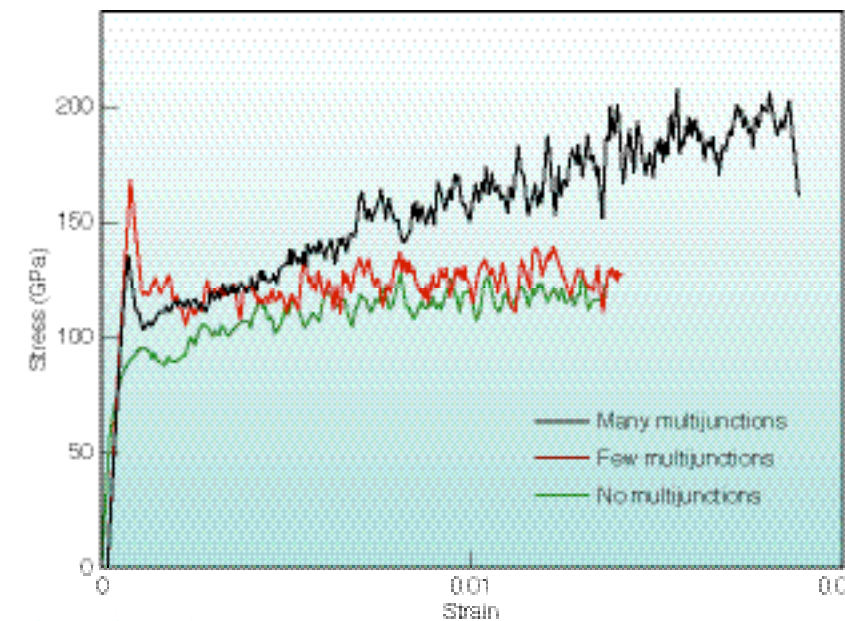


Figure 2. Stress-strain curves from a simulation on bcc molybdenum show that the formation of multijunctions significantly increases the hardening rate (line slope). Multijunctions that form in large numbers result in a well-defined slope (black) and are contrasted with the nearly flat lines when only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

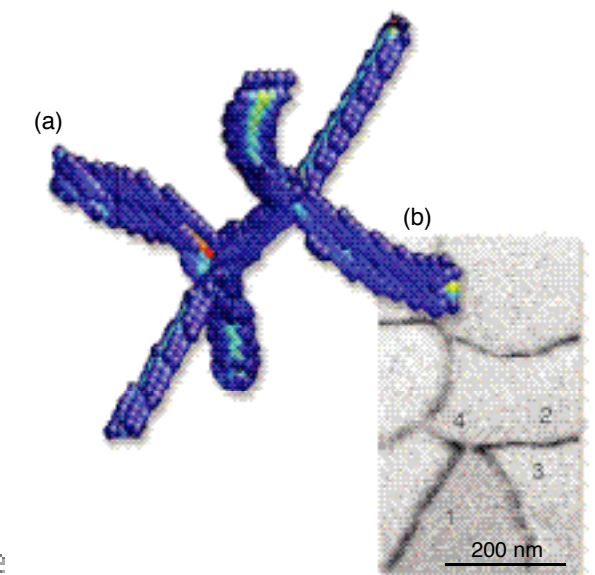


Figure 3. (a) An atomistic simulation based on an interatomic potential for molybdenum shows the formation of a multijunction. (b) A transmission electron microscopy image shows a symmetric 4-node (numbered 1-4) and verifies the existence of multijunctions and multinodes.

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.

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>

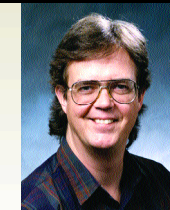
W. Cai, et al., "A Non-Singular Continuum Theory of Dislocations," *J. Mech. Phys. Solids*, in press.

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.

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 *3d* to *4p* transitions in copper. Our ability to access this complex spectroscopy is fundamentally important in advancing our understanding of the dynamic

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

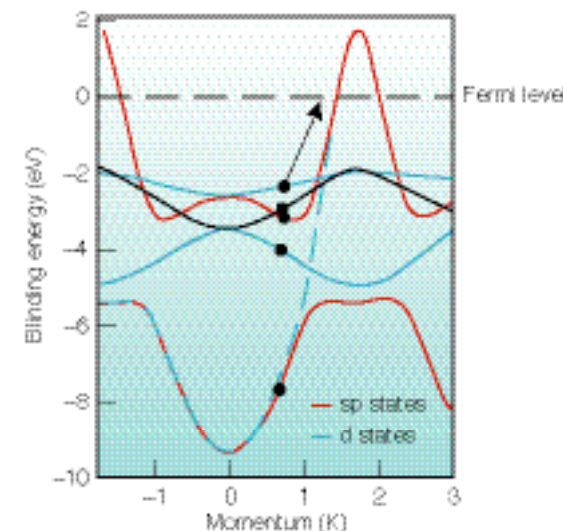
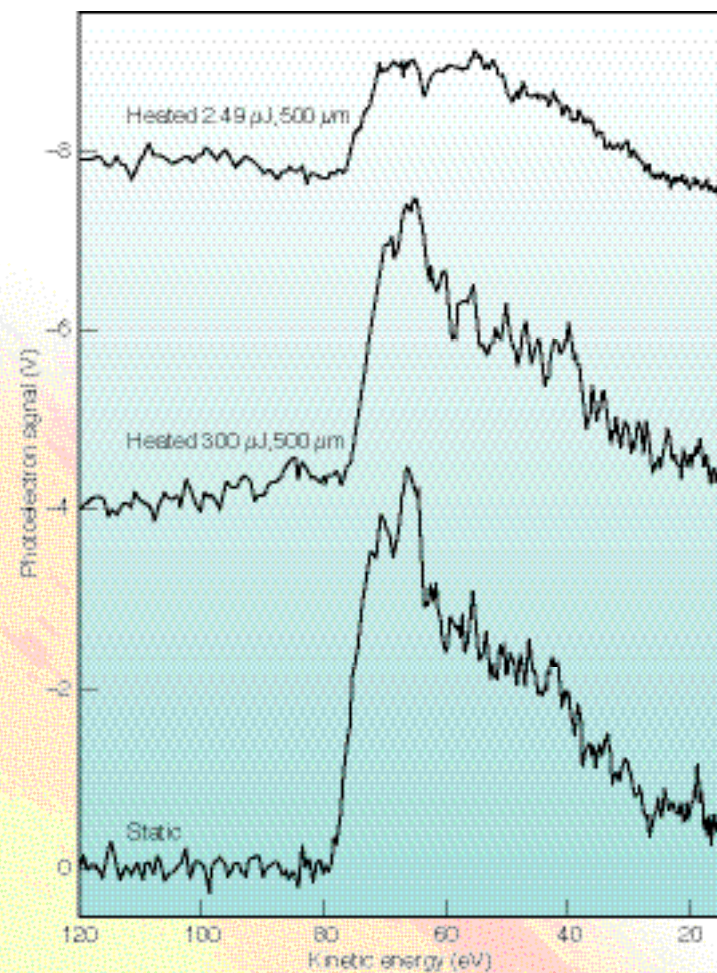


Figure 2. Schematic of photoemission process for copper illustrates a strong photoemission from direct transition from valence band to conduction band above the Fermi level.

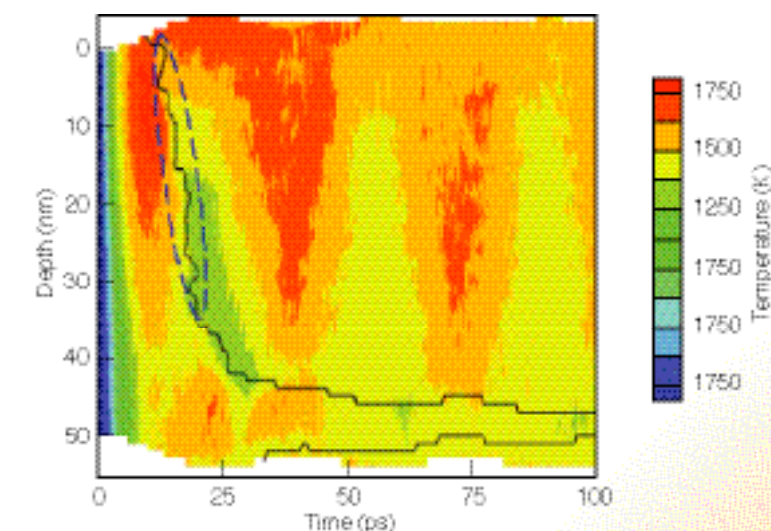


Figure 3. Temperature contour plot shows simulations of laser melting of a 50-nanometer nickel film. Strong electron-phonon coupling leads to a large temperature gradient in the film. Ultrafast melting of a large fraction (~35 nm) of the film is observed.

non-equilibrium processes at play that precede materials disassembly.

We have also observed that the peak of copper *3d* 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 *3d* 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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Metals 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.

Related Publications

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

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

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

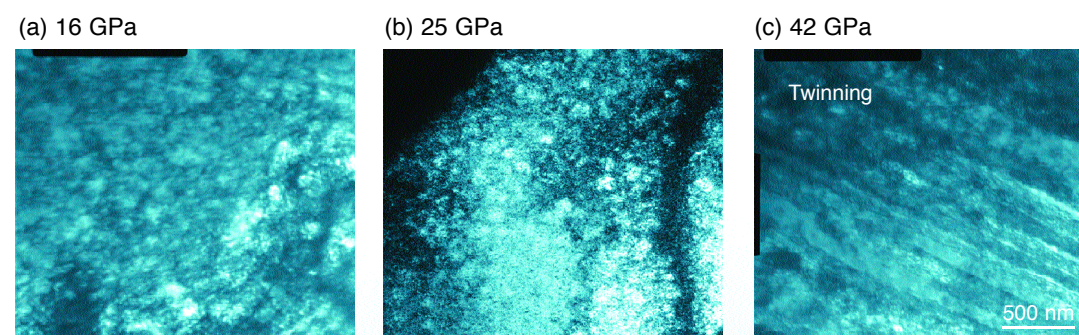


Figure 1. Transmission electron micrographs show residual deformation signatures from samples loaded to (a) 16 GPa, (b) 25 GPa, and (c) 42 GPa. A gradual shift from dislocation to twinning is evident.

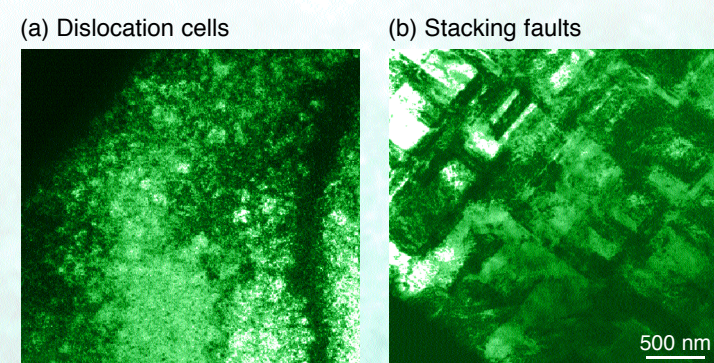


Figure 2. Transmission electron micrographs from a sample loaded to 25-GPa peak pressure show (a) dislocation cells under shockless loading and (b) stacking faults under shock loading.

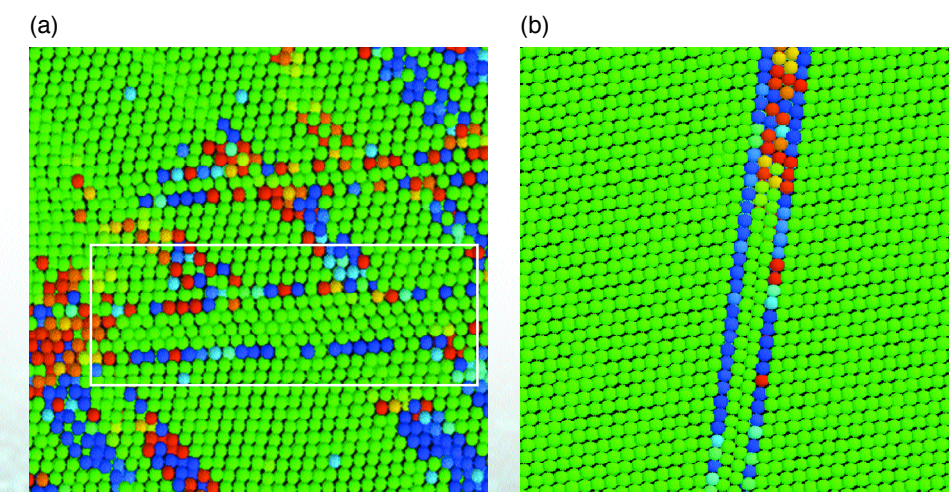


Figure 3. Molecular dynamics simulations show twin formation in single-crystal copper during (a) a 50-GPa shock in a perfect crystal and (b) a 20-GPa shock in a crystal containing a void (which collapses during shock passage).

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



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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.

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.

We have also observed that the EMS eventually reaches a saturation point and

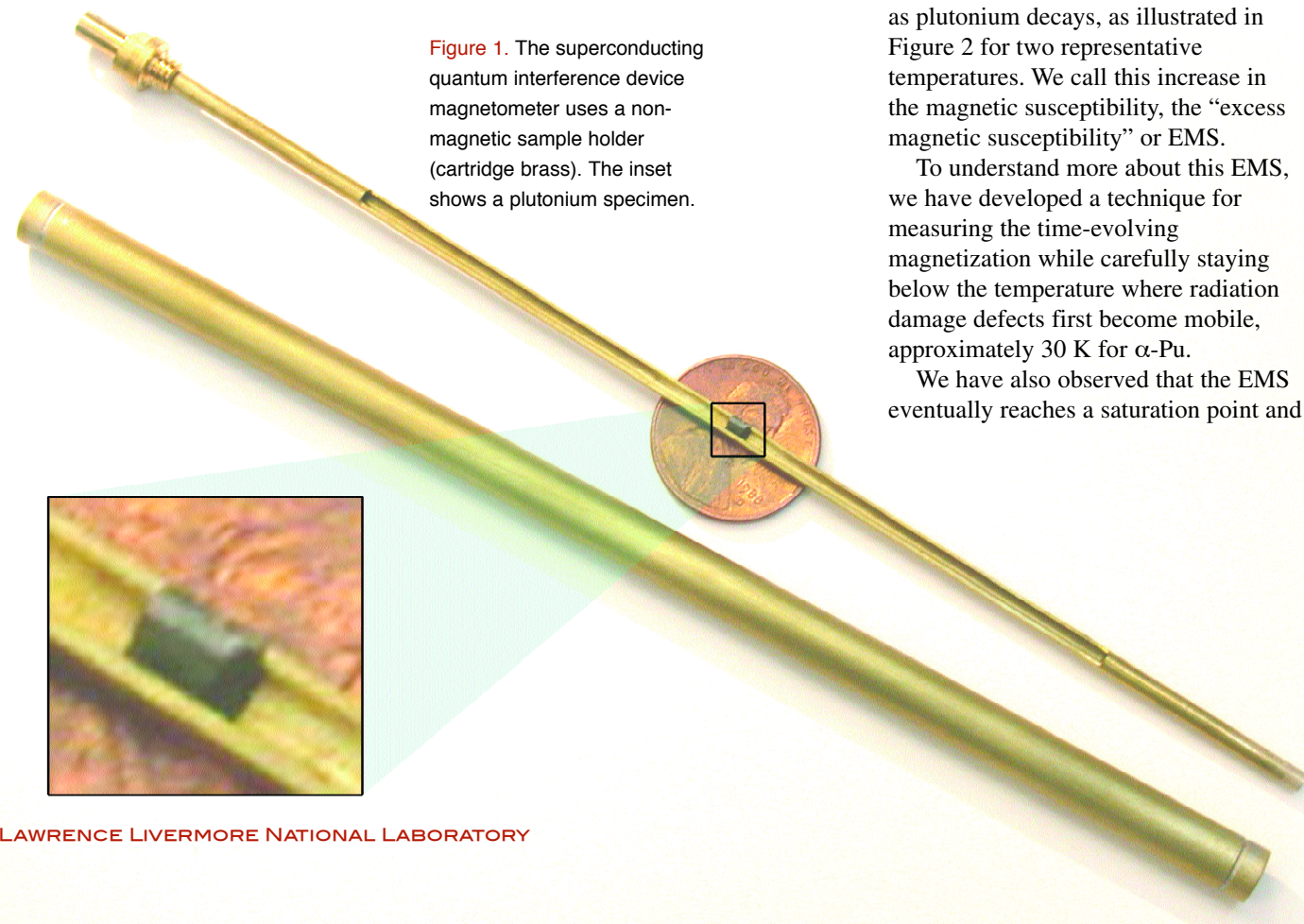


Figure 1. The superconducting quantum interference device magnetometer uses a non-magnetic sample holder (cartridge brass). The inset shows a plutonium specimen.

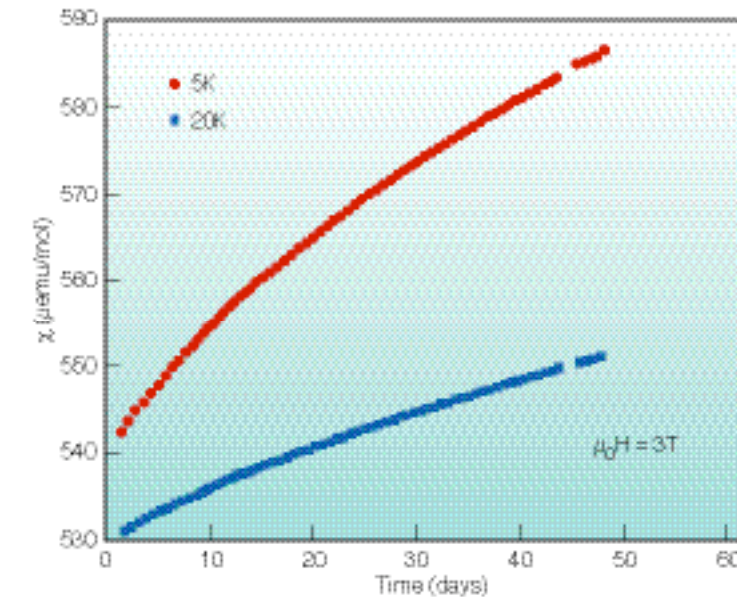


Figure 2. The isothermal magnetic susceptibility of plutonium increases with time, reflecting the accumulation of radiation damage. The gradual bending of the curves illustrates the approach to saturation as regions influenced by damage begin to overlap.

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:

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

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

Z.X. Zhou, et al., "Transport and Thermodynamic Properties of $\text{Sr}_3\text{Ru}_2\text{O}_7$ near the Quantum Critical Point" *Phys. Rev. B* **69**, 140409(R) (2004).

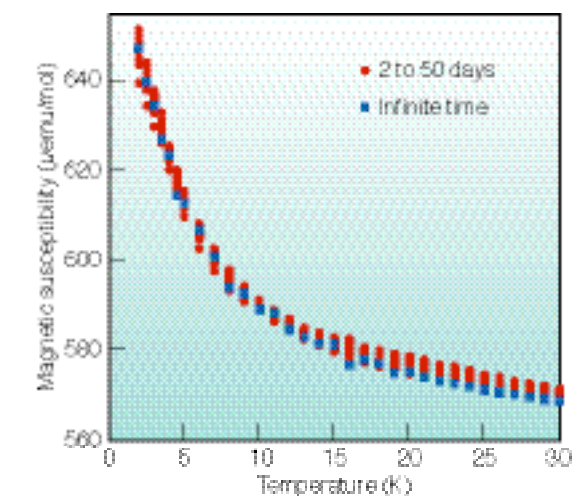


Figure 3. We measure the effects of radiation damage on the physical properties of plutonium at different times and temperatures. These data can be collapsed onto a universal time-independent curve. The elongated red data points represent plutonium magnetic susceptibility over 2 to 50 days. The blue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

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

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

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.

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

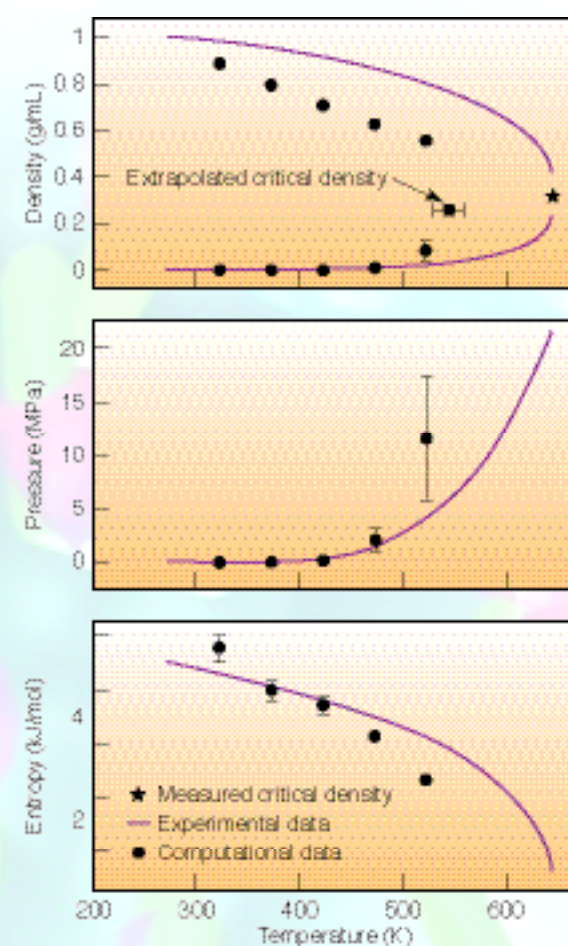


Figure 1. Phase diagram shows water at liquid-vapor interface (top curve), saturated vapor pressure (center), and heats of vaporization (bottom). Our ab initio model successfully describes, for the first time, the key thermodynamic variables of liquid-vapor interface.

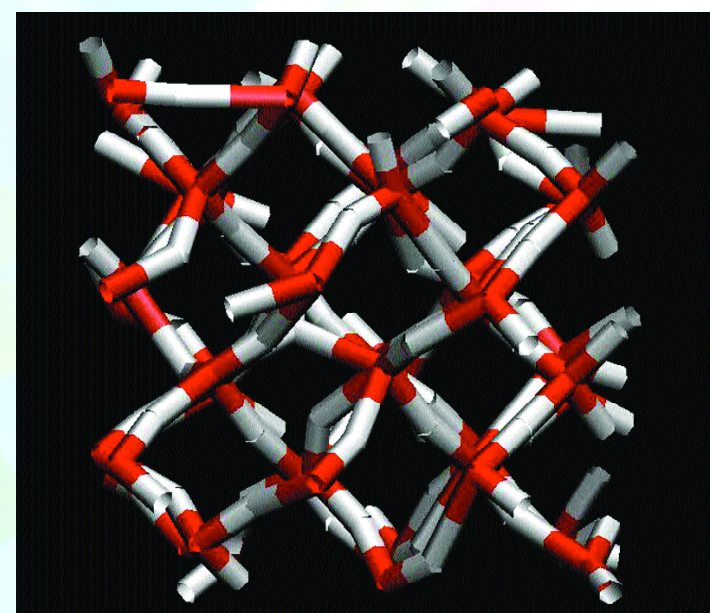
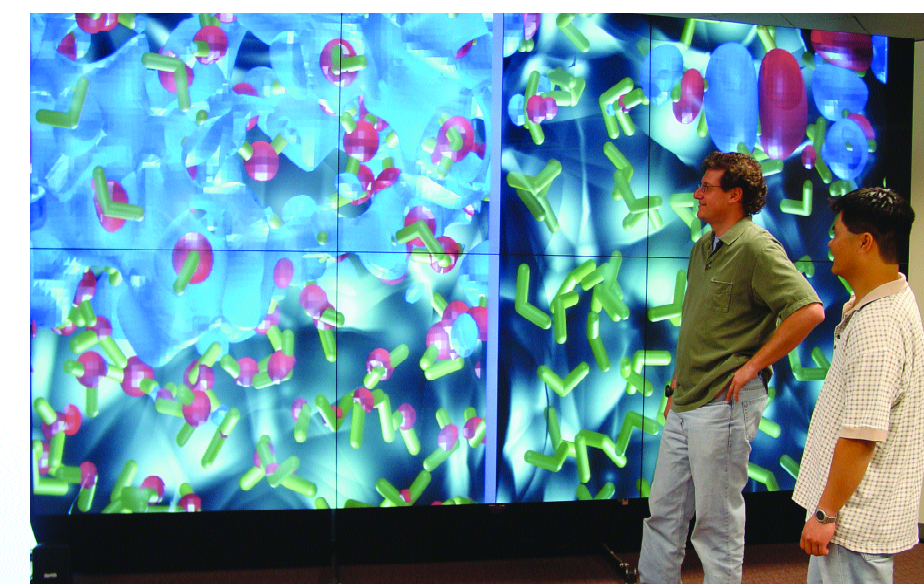


Figure 2. Simulation of water at superionic phase shows that at 115 GPa, a well-defined network of predominantly covalent bonds between oxygen (red) and hydrogen (white) forms.

model for the water dimer ($\text{H}_2\text{O}-\text{H}_2\text{O}$) 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 transitions states.

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

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).

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).

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.

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 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 CaCO₃–calcite, FeO–wüstite, and distilled H₂O 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

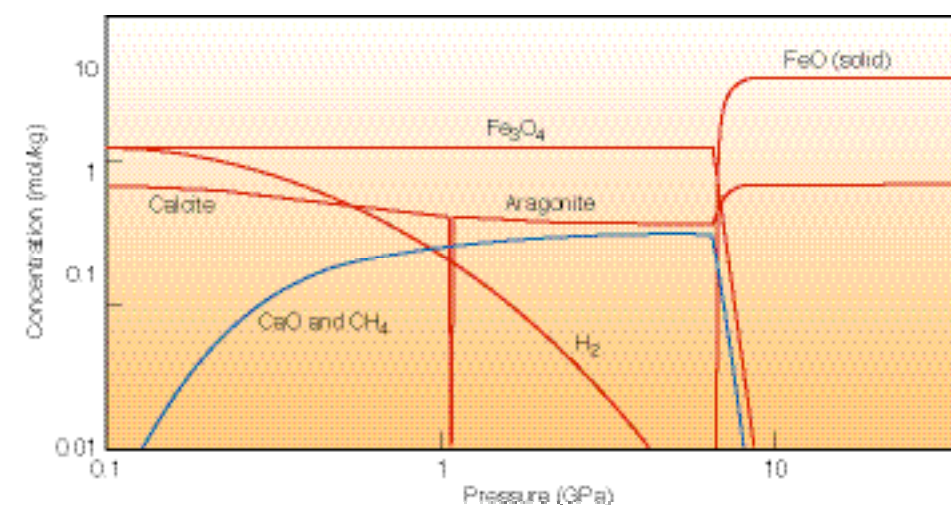


Figure 2. Our results of thermochemical calculations show that, at 500°C, CH₄ (methane) is predicted to be prevalent at pressures up to 10 GPa.

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.

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 500°C 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 1500°C, we have found optical changes indicative of methane formation, and at temperatures above 1500°C, 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.

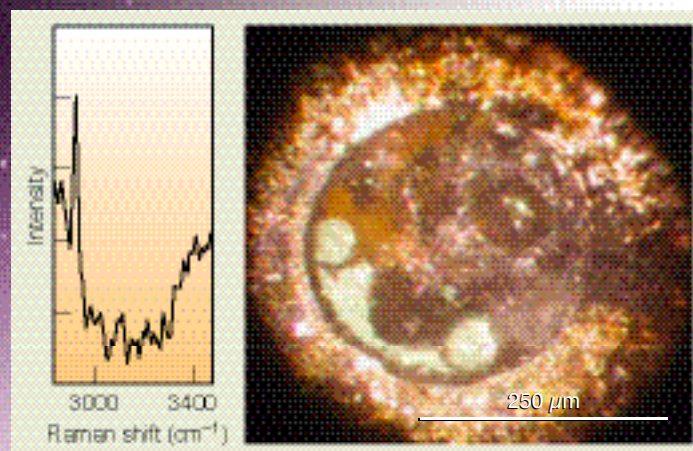
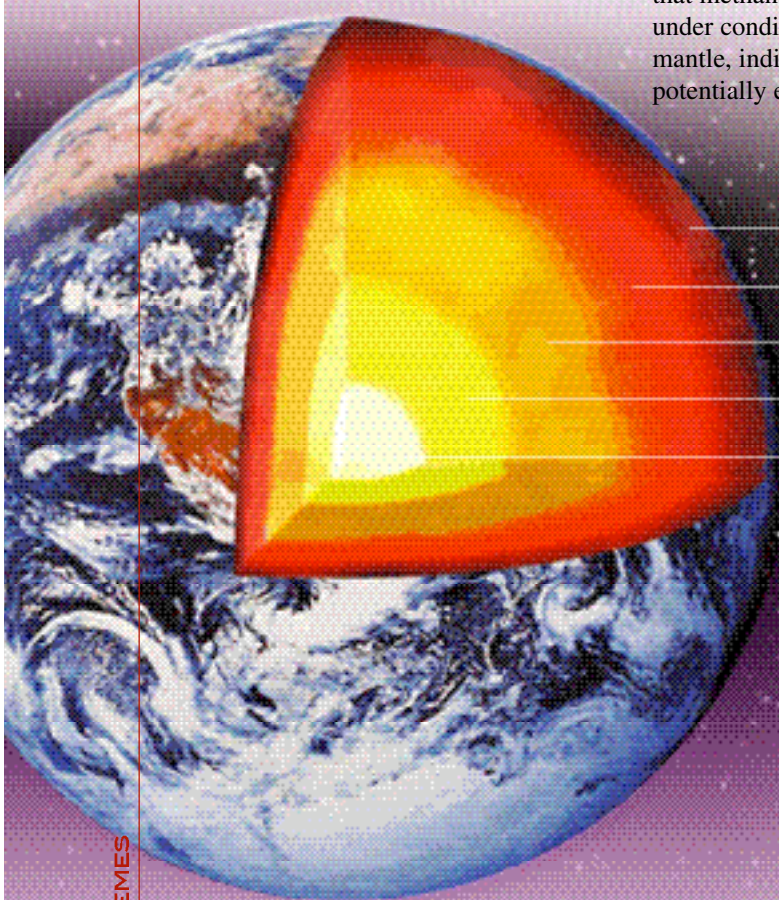


Figure 1. Methane-containing bubbles (right) are formed from decompression to approximately 0.5 GPa after laser heating at 5.7 GPa. Bubbles are visible near the bottom, left side, and slightly right of center of the diamond anvil sample. The Raman spectra show an absence of O–H stretching vibrations because the bubble has displaced the surrounding H₂O.

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—analogueous 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.

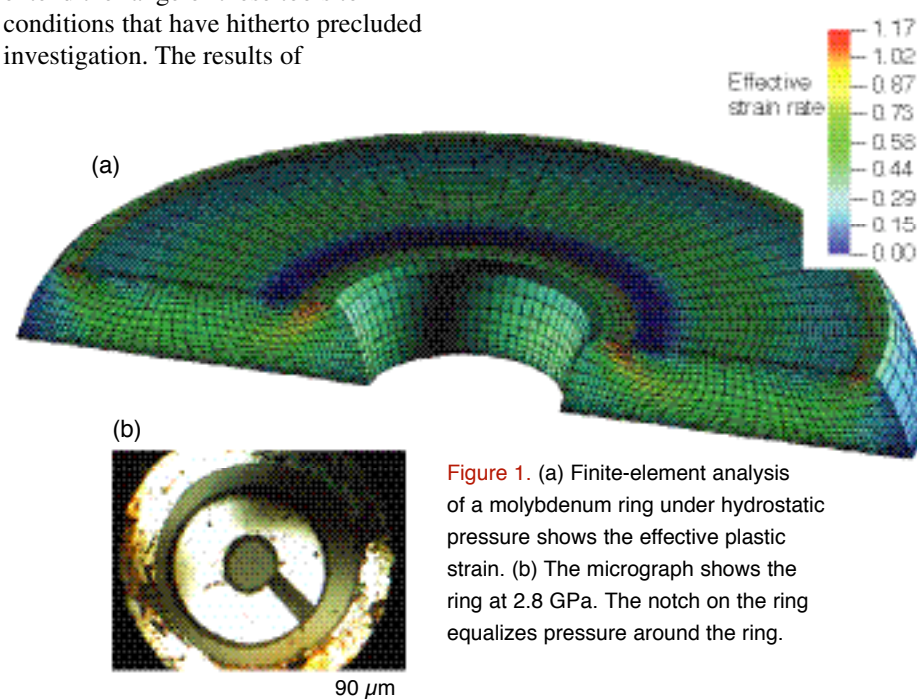


Figure 1. (a) Finite-element analysis of a molybdenum ring under hydrostatic pressure shows the effective plastic strain. (b) The micrograph shows the ring at 2.8 GPa. The notch on the ring equalizes pressure around the ring.

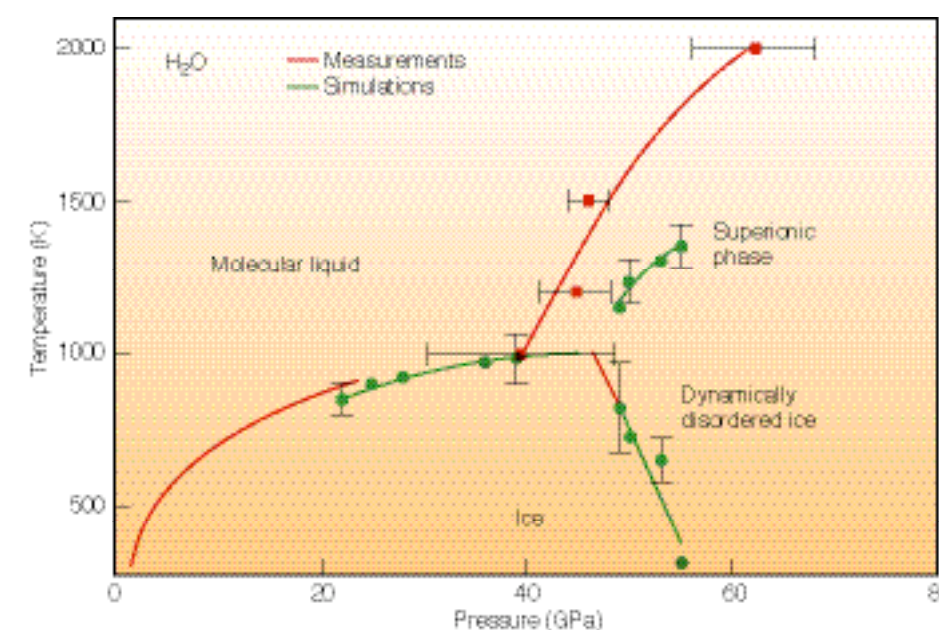


Figure 2. Phase diagram of H₂O shows that under high temperatures and pressures, water exists in a superionic phase. For the first time, experimental measurements (green) and computational data (red) have verified its existence.

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

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

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

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 10¹² 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.

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

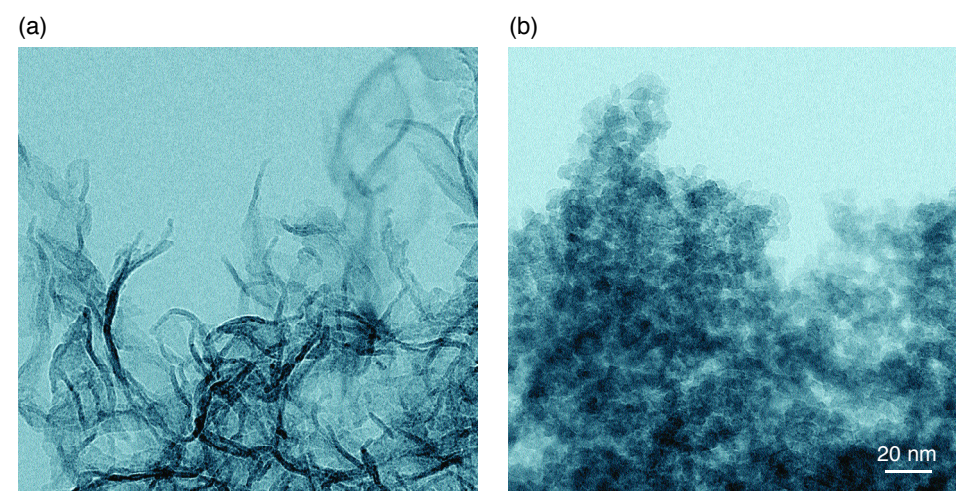


Figure 1. High-resolution transmission electron microscopy images show two alumina aerogels prepared using different sol-gel precursors: (a) AlCl_3 and (b) $\text{Al}(\text{NO}_3)_3$. The two resulting alumina aerogels have identical chemical composition but very different materials properties.

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

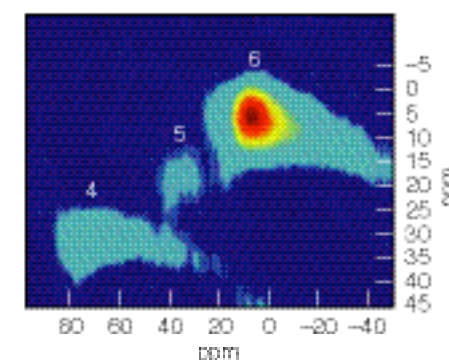


Figure 2. Two-dimensional ^{27}Al nuclear magnetic resonance spectra of one- and provide information regarding three species (4-, 5-, and 6-coordinate) of aluminum ion, Al^{3+} .

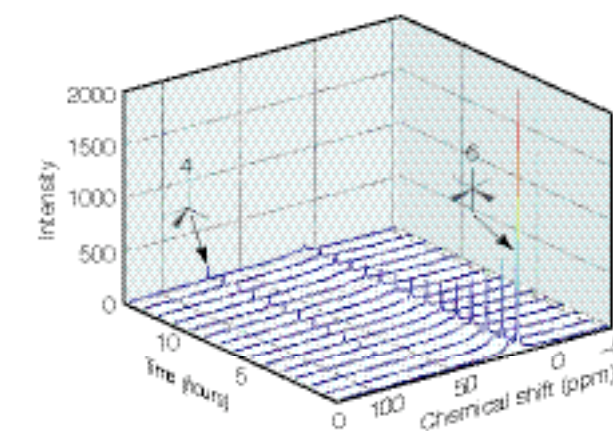


Figure 3. We are using nuclear magnetic resonance spectra to characterize the sol-gel transformation process. Here the gel-state spectra of an alumina aerogel show the formation of 4- and 6-coordinate Al^{3+} species.

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.

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



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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 $^{129}\text{I}/^{127}\text{I}$ in aqueous samples from affected environments such as the

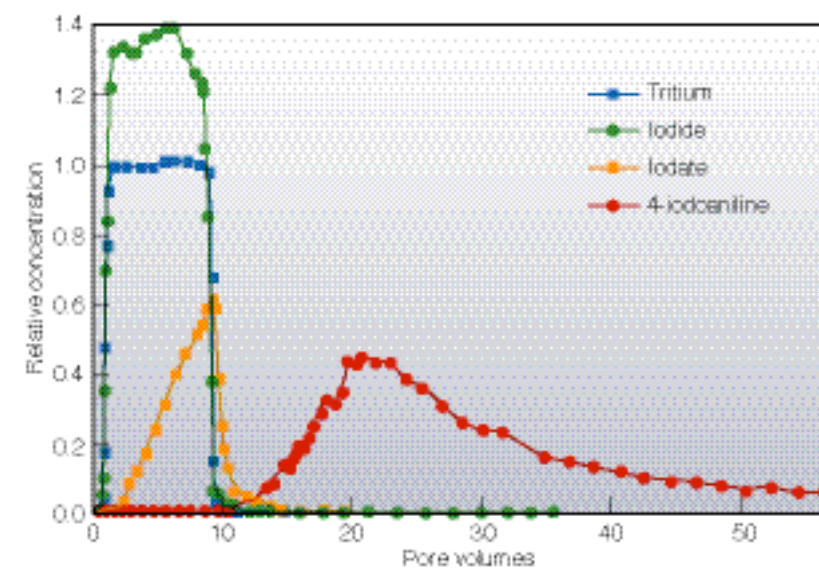


Figure 1. Experimental results of sorption and transport of iodine species in surface soil from a former nuclear production site is shown. Tritium is included as a comparison tracer because it is easily transported with no retardation. The transport of iodate and 4-iodoaniline is retarded due to interaction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

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.

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.

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

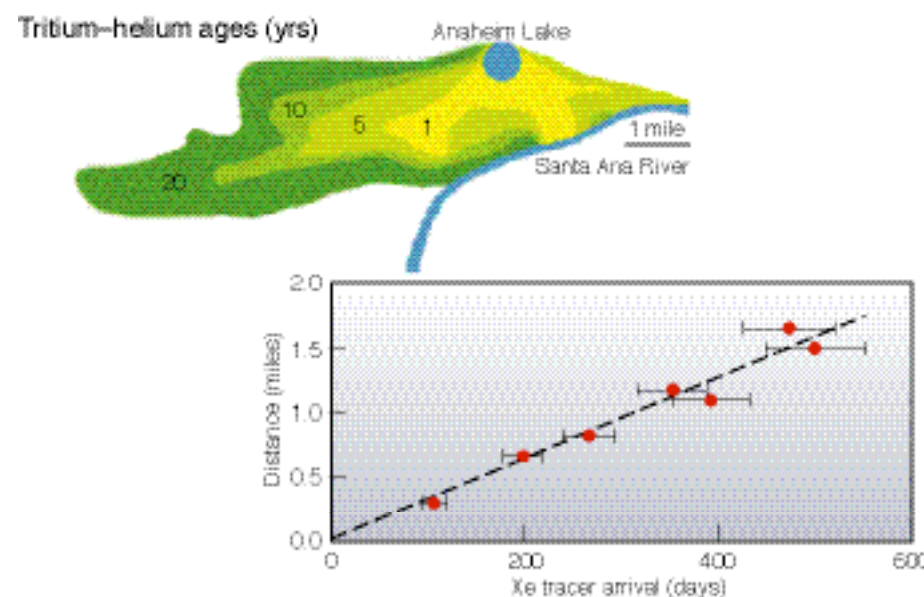


Figure 1. Groundwater age and travel distances are shown for a recharge facility in Orange County, California. Tritium-helium age dating is used for groundwater measured in years, and ^{136}Xe is used as a tracer for groundwater with ages in days.

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.

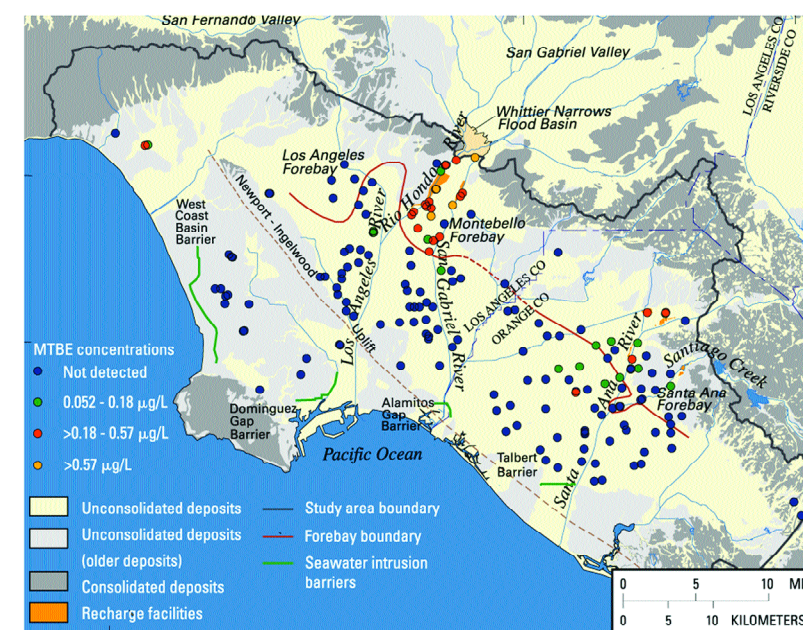
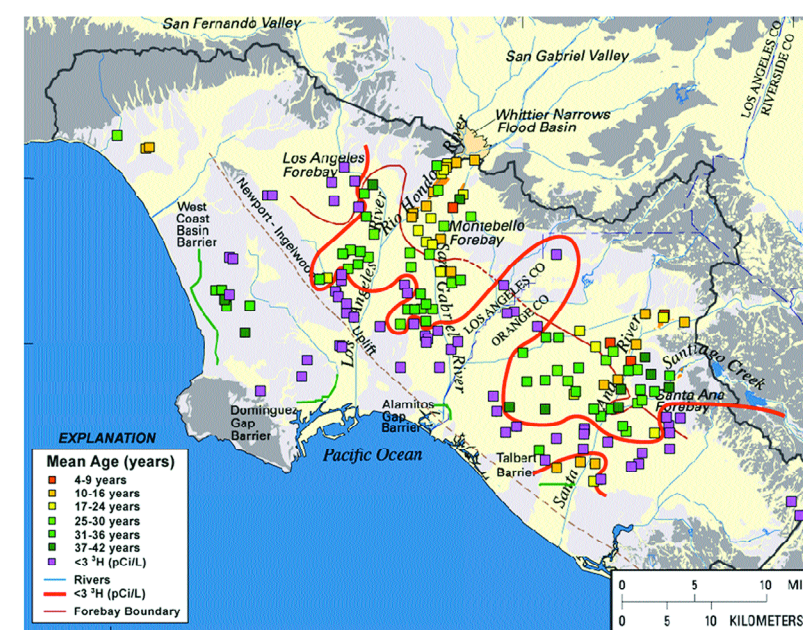


Figure 2. A map of the Los Angeles Basin shows the levels of the organic contaminant MTBE found in groundwater. MTBE is found only in shallow, young groundwater, demonstrating that deep groundwater is protected from surface contamination. (Images courtesy of the USGS.)

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

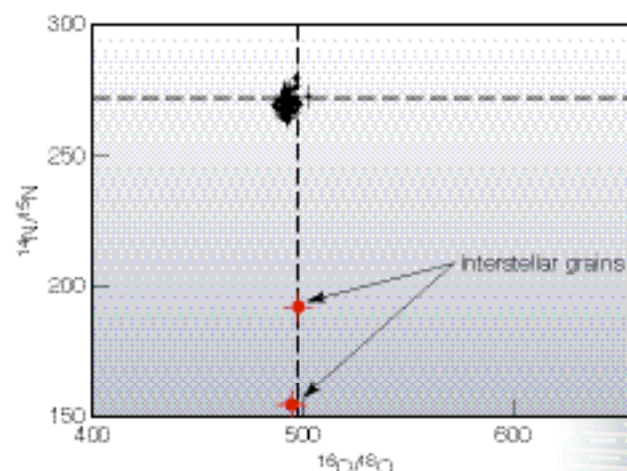


Figure 1. An isotope-ratio plot of nitrogen and oxygen shows the composition of an interplanetary dust particle. The two red circles represent interstellar grains identified within the IDP. The carbon interstellar grain has a $^{14}\text{N}/^{15}\text{N}$ ratio of 192 ± 4 , compared to the solar ratio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

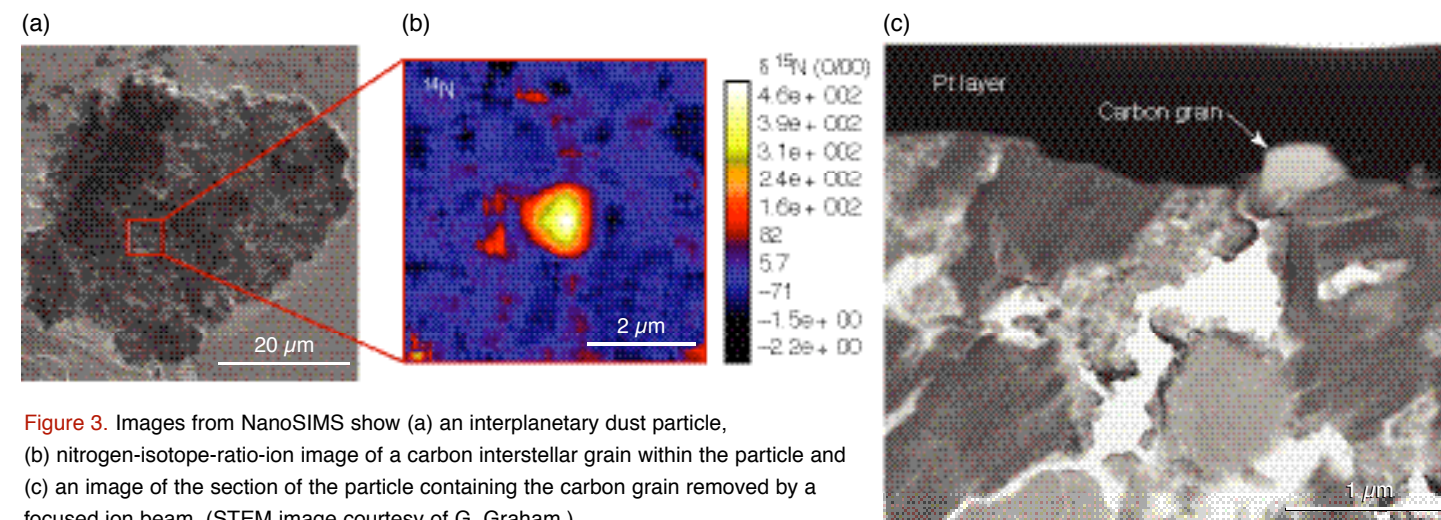
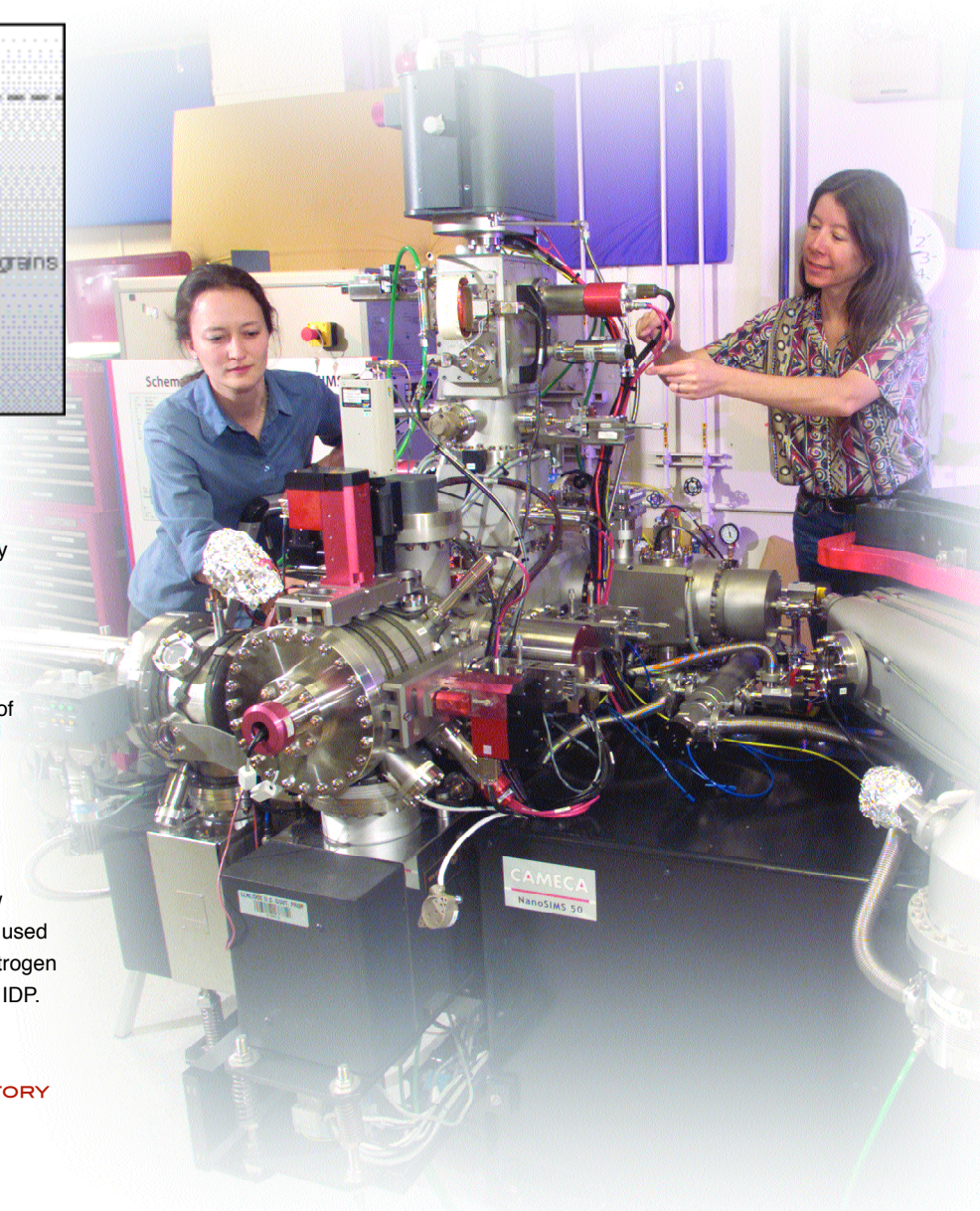


Figure 3. Images from NanoSIMS show (a) an interplanetary dust particle, (b) nitrogen-isotope-ratio image of a carbon interstellar grain within the particle and (c) an image of the section of the particle containing the carbon grain removed by a focused ion beam. (STEM image courtesy of G. Graham.)

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.

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.