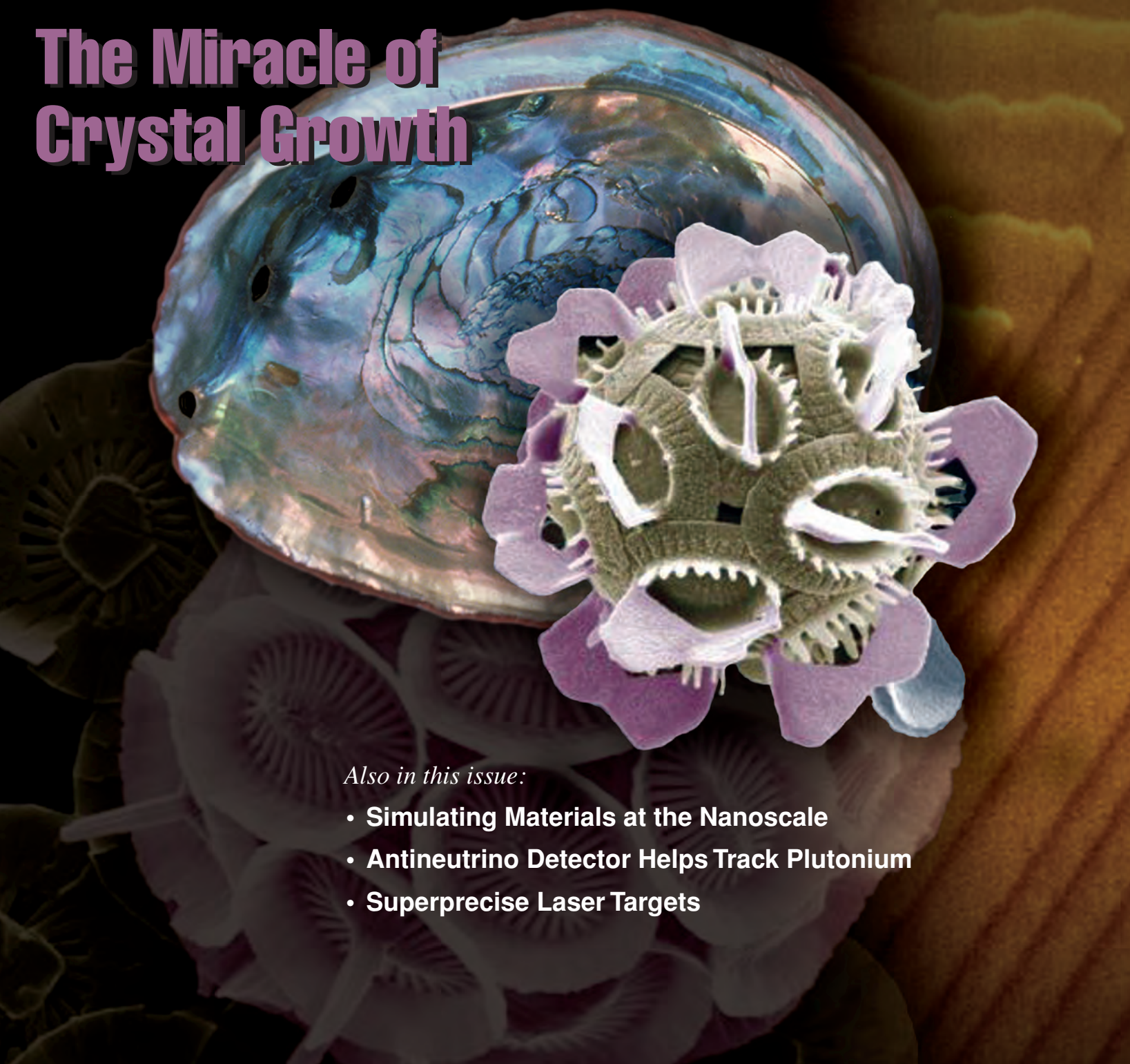
January/February 2006

Science & Technology Review

National Nuclear Security Administration's
Lawrence Livermore National Laboratory

The Miracle of Crystal Growth



Also in this issue:

- **Simulating Materials at the Nanoscale**
- **Antineutrino Detector Helps Track Plutonium**
- **Superprecise Laser Targets**

About the Cover

Understanding the growth processes that form the fascinating shapes and hierarchical designs of nature's biomineral structures, such as the molluscs shown on the cover, is key to addressing scientific challenges as diverse as synthesizing nanostructures, characterizing climate change, treating disease, and designing new materials for national security. As the article on p. 4 describes, Livermore researchers are using advanced microscopy and molecular modeling to provide insight on how crystals grow. The multidisciplinary collaboration, which includes researchers from other institutions, is studying the mineral calcium carbonate to determine the physical mechanisms that underlie biomineralization. (The mollusc image shown in front of the abalone shell is courtesy of Mark Geisen and Jeremy Young, copyright Natural History Museum, London.)

Cover design: Kitty Madison

About the Review

Lawrence Livermore National Laboratory is operated by the University of California for the Department of Energy's National Nuclear Security Administration. At Livermore, we focus science and technology on ensuring our nation's security. We also apply that expertise to solve other important national problems in energy, bioscience, and the environment. *Science & Technology Review* is published 10 times a year to communicate, to a broad audience, the Laboratory's scientific and technological accomplishments in fulfilling its primary missions. The publication's goal is to help readers understand these accomplishments and appreciate their value to the individual citizen, the nation, and the world.

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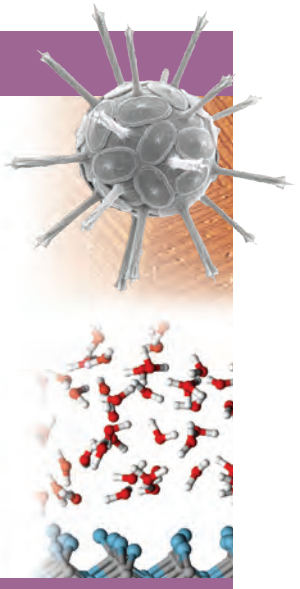

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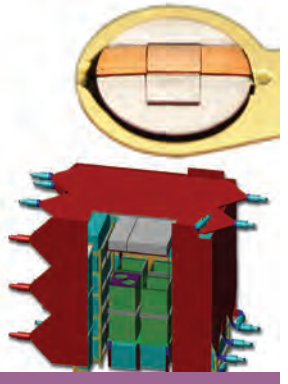

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Uncovering how crystals dissolve

Scientists from Lawrence Livermore, Virginia Polytechnic Institute, and State University of New York at Buffalo are discovering how quartz and other silicates erode during geochemical weathering. The team applied methods used in its studies on crystal growth (see the article on p. 4) and concluded that mineral dissolution could be understood through the same mechanisms as those in the growth processes.

The team expanded its equations on crystal growth rates to include dissolution rates and created a model that predicts how quartz dissolves as the surrounding fluid becomes less concentrated in silicon dioxide. "The rate at which a crystal dissolves is controlled by the density of layers, or steps, on the surface of the crystal," says Jim De Yoreo, who leads the Livermore team.

The team used atomic force microscopy to characterize surface changes and document dissolution of the quartz surfaces exposed to four chemical solutions. It then compared the results to those measured for other silicates. In each case, the dissolution processes differed depending on the temperature and solution composition. The findings, which appeared in the October 25, 2005, edition of the *Proceedings of the National Academy of Sciences*, have broad implications for other families of crystalline materials.

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BlueGene/L breaks another record

National Nuclear Security Administration (NNSA) Administrator Linton F. Brooks, Department of Energy Office of Science Director Raymond L. Orbach, and IBM Executive Vice President for Technology and Innovation Nicholas Donofrio were at Livermore on October 27, 2005, to join Laboratory leaders in dedicating IBM BlueGene/L and IBM Purple, which are both part of the Advanced Simulation and Computing (ASC) Program and serve NNSA's Stockpile Stewardship Program.

Administrator Brooks announced that the BlueGene/L supercomputer at Livermore's Terascale Simulation Facility reached 280.6 trillion operations per second (teraops) on the LINPACK benchmark, the industry standard to measure computing speed. In a demonstration of its capability, BlueGene/L ran a record-setting materials science application at 101.5 teraops sustained over 7 hours on the machine's 131,072 processors. It was the largest simulation of its kind ever attempted. The application used in the demonstration is important to NNSA's effort to ensure the safety, security, and reliability of the nation's nuclear deterrent.

The Purple and BlueGene/L systems will provide scientists and engineers working at Sandia, Los Alamos, and Lawrence Livermore national laboratories with just under half a petaop (1,000 teraops) of computing power—more than any other scientific computing facility in the world.

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Simulations show global warming dramatically increasing

Laboratory scientists used a coupled climate and carbon-cycle model to look at global climate and carbon-cycle changes that would occur if humans use the entire planet's available conventional fossil-fuel resources by the year 2300. The simulations showed that the global mean temperature would soar 8°C by 2300. In the polar regions alone, the temperature would spike more than 20°C, forcing the land in this region to change from ice and tundra to boreal forests. The implication is that polar ice caps would be depleted and ocean sea levels would rise by 7 meters over the next three centuries. In addition, the model predicts that the amount of atmospheric carbon dioxide would nearly quadruple to 1,423 parts per million (ppm) from today's level of 380 ppm.

The simulations showed that about 38 and 17 percent of the carbon dioxide released from the burning of all fossil fuels are taken up by the land and ocean, respectively. The remaining 45 percent remains in the atmosphere. According to lead author Govindasamy Bala of the Energy and Environment Directorate, the models predict large-scale migration of plants and severe disturbances to terrestrial ecosystems. This study revealed a dramatic change not only in the temperature of the oceans but also in their acidity content, which would be especially harmful for marine organisms with shells and skeletal material made of calcium carbonate. The team's research appeared in the November 1, 2005, issue of the American Meteorological Society's *Journal of Climate*.

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Commentary by Cherry A. Murray

Our Monthly Progress Report

THIS issue of *Science & Technology Review* (*S&TR*) marks the 30th anniversary of our unclassified monthly magazine and carries on a tradition that goes back to the founding of the Laboratory. In the fall of 1952, the Atomic Energy Commission received a written report on the first month of work at the newly formed Radiation Laboratory in Livermore, California. Much has changed in half a century. Lawrence Livermore National Laboratory now communicates with sponsors in many ways—both formal and informal—including *S&TR*, which is the direct descendant of that first report. Since 1952, we have been providing our Washington sponsors, and others, monthly news of scientific and technical accomplishments at the Laboratory.

The first reports, appropriately entitled *Progress Reports Monthly*, were classified and had limited distribution. Their focus was on the Laboratory's principal mission: to advance nuclear weapons science and technology. Breakthroughs in nuclear design—such as a thermonuclear warhead compact enough to be carried on submarine-launched Polaris missiles—and an active nuclear test program meant that we had much to tell.

In 1960, a scientific editor was named to manage the growing Laboratory's monthly report. Three years later, we began the tradition of selecting an up-and-coming scientist or engineer as scientific editor for a year. Those knowledgeable of the Laboratory's history will recognize some of the early names: Richard Wagner, Robert Barker, Bruce Tarter, Philip Coyle, and Robert Selden. All scientific editors have found the position a rewarding experience as well as a wonderful opportunity to meet colleagues and learn about programs throughout the Laboratory.

Growth at Lawrence Livermore in the 1970s transformed it into the multiprogram laboratory that it is today. National security is our defining mission, but with our special capabilities and multidisciplinary approach to problem-solving, we also can contribute to solving many national issues that require leading-edge science and technology. Director Roger Batzel decided to start an unclassified monthly companion report, *Energy & Technology Review* (*E&TR*), to cover the breadth of the Laboratory's science and technology. Its first issue in a glossy magazine format appeared in January 1976—exactly 30 years ago.

The rationale for the new magazine was as important then as it is now. We needed a widely distributed periodical to highlight progress in the Laboratory's programs. The intended audience is broad: our sponsors and other government officials, research partners, and the scientific community. The magazine also helps Livermore scientists keep abreast of work in other areas of the Laboratory. In addition, members of the general public are welcome to subscribe.

In the mid-1990s, Director (and former scientific editor) Bruce Tarter made another change. *E&TR* transformed into *S&TR* and became our principal monthly magazine (with two double issues each year). With research activities shifting to science-based stockpile stewardship, nonproliferation, and homeland security, it became even more feasible to provide informative unclassified coverage of the Laboratory's national security programs as well as our many unclassified areas of research.

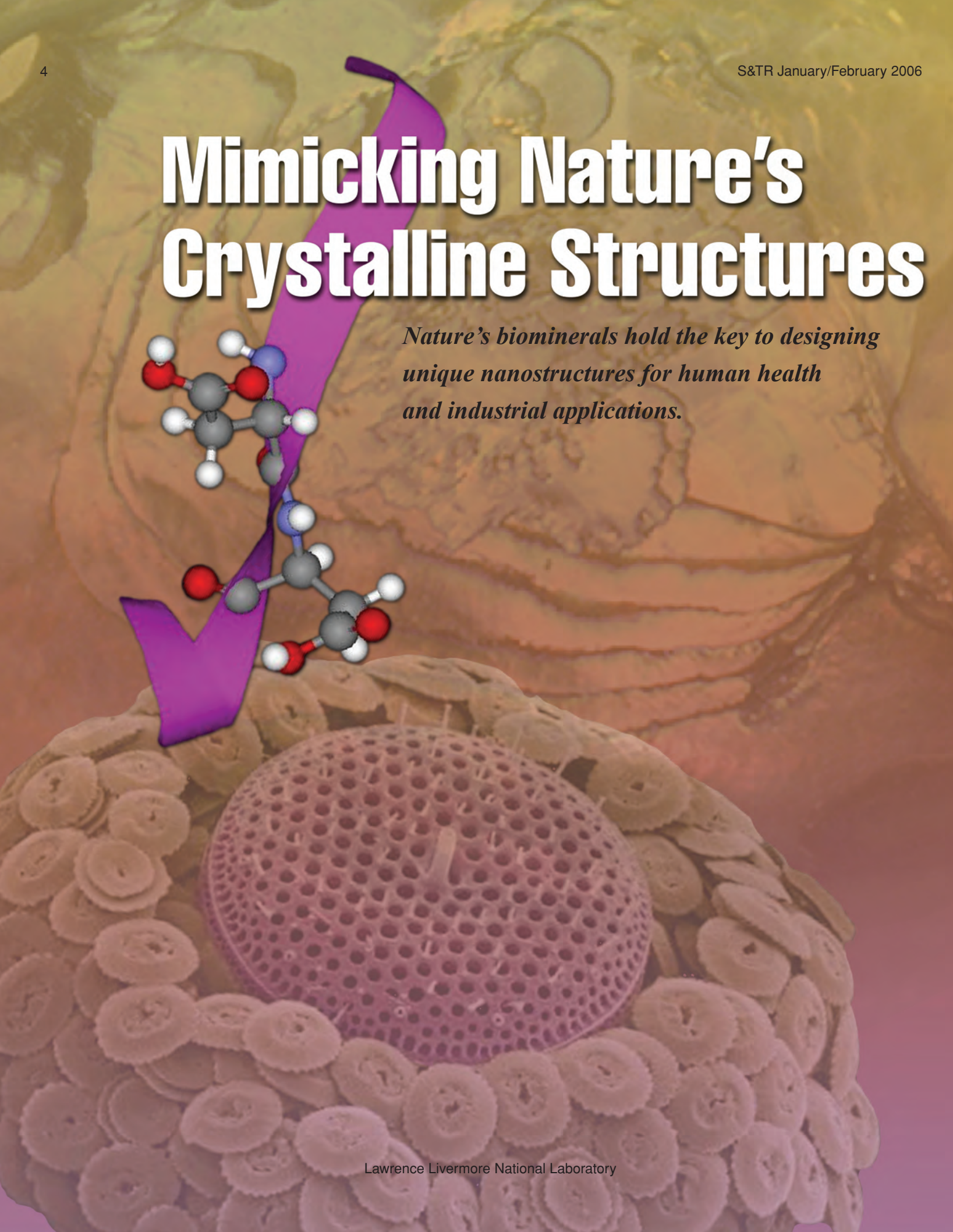
S&TR currently has over 9,000 subscribers, and the online magazine is one of the most visited of the Laboratory's Web pages. It is a frequent winner of awards from the Society for Technical Communication, including an Award of Excellence in the international magazine competition last year. We hope that we are serving our readers well and always welcome your feedback. For your convenience, all issues include a survey form for you to return to us.

From one perspective, this is *S&TR*'s 30th birthday. From another, the magazine is as old as the Laboratory and, like the Laboratory, always reinventing itself to meet current needs. In any case, the staff of *S&TR* is excited about carrying on the tradition of providing monthly reports on the outstanding science and technology being carried out at Lawrence Livermore National Laboratory.

■ Cherry A. Murray is deputy director for Science and Technology.

Mimicking Nature's Crystalline Structures

Nature's biominerals hold the key to designing unique nanostructures for human health and industrial applications.



SCIENTISTS and engineers have long envied nature's ability to design crystalline structures whose properties are often superior to those of similar synthetic materials. Through a process called biomineralization, proteins orchestrate the growth processes of many natural minerals into designs that confer exceptional properties. Scientists are eager to understand nature's biomineralization processes. The biological controls that determine the size, shape, and properties of crystals are key to addressing challenges as diverse as synthesizing nanostructures, characterizing climate change, treating disease, and designing new materials for national security applications.

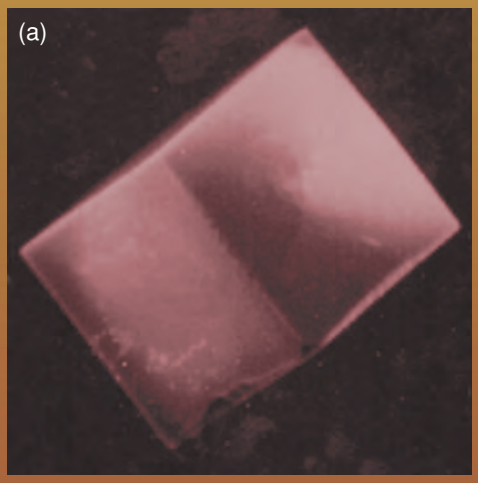
Researchers have been studying biominerals for decades and have known for some time that organic molecules can influence the shape and properties of a growing crystal. However, researchers have been limited in their ability to mimic biomineral growth for specific applications, because they lack a thorough understanding of how biominerals form. The limitations are evident by comparing a single calcite crystal (the most stable form of calcium carbonate) synthesized in the laboratory to a coccolith formed in nature. (See the figures at right.) The synthetic form has a simple rhombohedral shape (a prism with six faces, each a rhombus) and tends to grow randomly with no preferred orientation. In contrast, the coccolith exhibits a very organized, repeating crystal pattern.

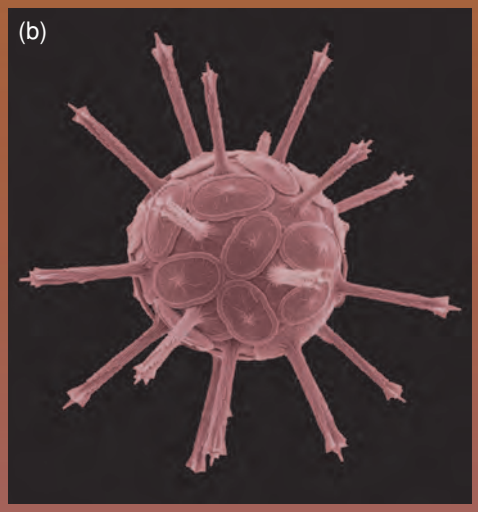
In an effort funded originally by the Laboratory Directed Research and Development (LDRD) Program and now by the Department of Energy (DOE), a Livermore team is using advanced microscopy techniques and molecular modeling to investigate the effects of interactions between biomolecules and calcium carbonate surfaces. The Livermore team, which includes physicists Jim De Yoreo, Roger Qiu, and Chris Orme, is collaborating with geochemist Patricia Dove of Virginia Polytechnic Institute, molecular biologist Daniel Morse of the University of California at Santa Barbara, biochemist John Evans of New York University, and theoretical physicist Andrzej Wierzbicki of the University of South Alabama.

The multidisciplinary collaboration is studying calcium carbonate because calcium-bearing minerals comprise about 50 percent of all known biominerals. The vast deposits of calcium carbonate laid down by marine organisms are the largest terrestrial reservoir of carbon and hold a historical record of the interplay between Earth systems and biological organisms stretching back to the Cambrian period. Moreover, the richness of calcium carbonate architectures suggests that the mineral can serve as an excellent model for determining the physical mechanisms that underlie biomineralization.

The Many Faces of Crystals

More than 300 identified crystal forms of calcite can combine to produce at least a thousand different crystal variations. Calcite, in its simplest form, grows as a rhombohedron. Similar to other solution-grown crystals, calcite grows when molecules land on the surface of a crystal seed and attach to the edge of a one-molecule-thick layer, called a step. The addition of molecules causes the layer to spread outward until it covers the face of the crystal. The layers form because the crystal contains defects, called dislocations.





(a) The simple shape of a synthetic calcite crystal is contrasted with (b) the complex and organized shape of a coccolith formed in nature. (This coccolith image and the other crystal images in the background at left are courtesy of Markus Greisen and Jeremy Young, copyright Natural History Museum, London.)

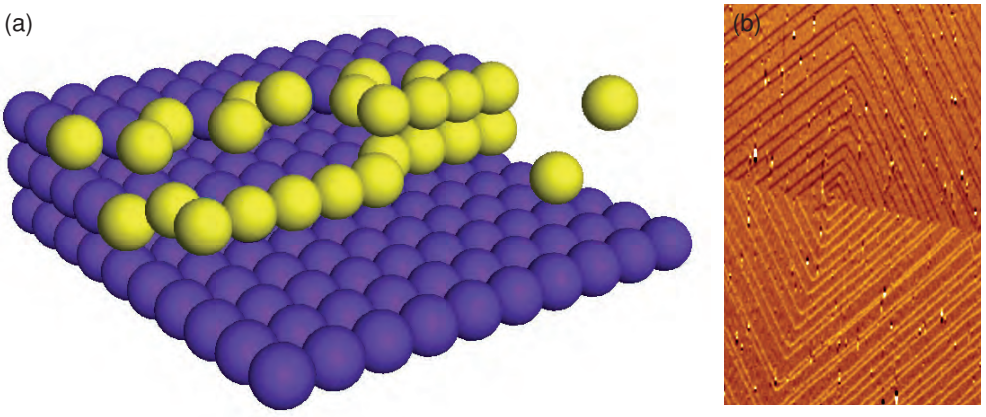
A dislocation will naturally generate a step at the surface of the crystal lattice. Because this step never goes away, as the layer grows outward, a spiral ramp of new layers, called a dislocation hillock, forms. Molecules continually adsorb and desorb from the step edges of these hillocks. If the concentration of molecules in the solution is high, the rate of adsorption will be greater than the rate of desorption, and the crystal will grow. If the reverse is true, the crystal will dissolve.

In the past, theories of solution crystal growth were based on the limited capabilities of imaging equipment such as the scanning electron microscope (SEM). The SEM allowed researchers to observe only one or two faces of a crystal and did not allow them to observe the growth mechanisms in real time and at the necessary size scales. More recently, the Livermore team was among the pioneers to use atomic force microscopy (AFM) for investigating the growth of crystals from solutions. AFM enables researchers to image and measure subnanometer changes on the surfaces of every face of a crystal in real time. (See the box on p. 7.) In 2001, the team received a Laboratory Science and Technology Award for its use of this technology in investigating the physical controls on biomineral growth.

To understand the growth mechanisms involved in biomineralization, researchers must know the orientation of a crystal's molecules and how they bond to each other. The molecules in a crystalline structure are arranged in a framework called a crystal lattice. The geometric and chemical relationships between the crystal lattice and organic modifiers, such as proteins, determine the interaction energy between modifier and crystal.

Because crystals found in biomineral structures often exhibit unusual faces not found in synthetic crystals, researchers originally thought that the addition of a modifier must lower the energy of those new faces, allowing the crystal to express a shape that wouldn't have otherwise been stable. "We discovered this theory was incorrect," says De Yoreo, who initiated the Livermore effort. "To understand how a particular additive affects crystal shape, we need to look at how it interacts at the growing steps of the crystal."

A modifier alters the shape and growth rate of a crystal by blocking the growth of certain steps or by increasing the rate at which new molecules attach to steps. Because the geometric and chemical relationships between modifier and crystal are different for each type of step, new crystal shapes can be generated. To understand the change in crystal shape, the team performed calculations that predicted which steps the modifier would bind to most strongly.



(a) A crystal grows when molecules land on the surface of a crystal seed and attach to the edge of a layer, called a step. (b) An atomic force microscope image of a pure calcite sample shows that as the molecules attach to a step, the layer spreads, forming a dislocation spiral, or hillock.

Proteins Modify Growth

In 2005, the team studied how peptide sequences from proteins of abalone and oyster shells—AP7-N, AP24-N, and n16-N—affect calcite growth. Using AFM, the team explored the adsorption of these proteins. Results showed that AP7-N and AP24-N inhibit growth at some of the calcite crystal's steps and accelerate growth in others, resulting in round dislocation hillocks. In contrast, n16-N interacts with corner sites and promotes the emergence of a new set of steps.

To test the importance of protein sequence on the structure of the three proteins, the team scrambled the sequence of peptides in the chain. The scrambled proteins no longer accelerated the step kinetics, illustrating directly that the structure, not simply the chemistry, is important for the effect on crystallization. This study is one of the first to systematically change protein sequence and use AFM to cross-correlate sequence and structure. The process provides a mechanistic understanding of the effects on crystal growth.

In another study funded by DOE, the team investigated whether the most acidic abalone nacre protein, AP8, alters calcite growth and whether differences in control mechanisms existed. The change in growth shape was similar to that seen with small molecules, but surprisingly, the team found that the molecular-scale kinetics are significantly accelerated by AP8. Moreover, although AP8 proteins are much larger than atomic steps, they modify the growth by step-specific interactions. The observed rounding of the step edges and accelerated kinetics indicate that these proteins act as surface-active agents to promote ion attachment at the calcite step.

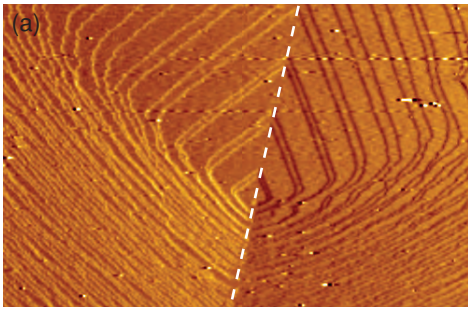
Qiu says, "The significant and exciting outcome of this work is that we can define a new role for biomolecules in controlling

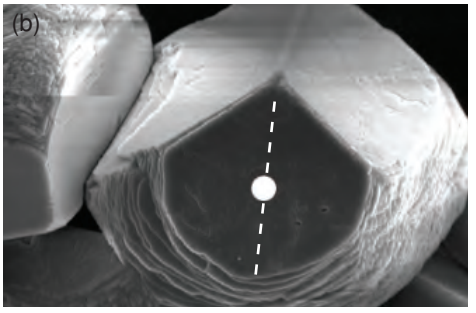
crystal growth. Specifically, acidic proteins promote crystallization, which is in stark contrast to an inhibitor of crystallization—a role that is generally postulated and observed for peptides and other small molecules." The results of the study also create a coherent picture of how protein-induced morphological changes at the molecular scale can guide the growth of a crystal to its macroscopic form.

Molecular models confirm that the step edges are the most favorable binding environment for the modifiers. The steps provide the greatest opportunity for the three-dimensional modifiers to make the largest number of bonds. De Yoreo says, "Although the mechanisms of growth modification are diverse, crystal shape is most controlled by the interactions that occur at the step edges of a crystal's faces. By knowing which steps the modifiers bind to most strongly, we can predict how they change the crystal shape." These findings are significant for applications in materials science, bioengineering, geosciences, and medical sciences.

Inhibiting Kidney Stones

Not all biomineralization processes are aimed at growing crystalline structures. Many organisms rely on arresting crystal growth in order to survive. For example, arctic fish must live in subfreezing environments without developing ice crystals in their blood. If it were not for the inhibitory effect of certain proteins, the supersaturation of calcium phosphates and oxalates in human blood and urine would be enough to turn a human into a proverbial pillar of salt. Understanding how proteins





(a) An atomic force microscope image shows that the AP8 protein alters the step morphology of a growing calcite crystal by accelerating the growth kinetics. (b) A scanning electron microscope image shows the shape of a calcite crystal grown in the presence of AP8 protein. The morphology in the upper portion remains the same, but the morphology in the lower portion is modified.

Measuring the Topography of Materials

The atomic force microscope (AFM) has been used since 1986 to produce topographic maps of nanostructures. An ultrasharp tip scans across a sample's surface, and a computer records the path of the tip, slowly building a three-dimensional image. When force and displacement data are combined in various algorithms, the resulting calculations reveal information on mechanical properties, such as hardness, and any other reactions to an applied force.

Unlike the scanning electron microscope, which provides a two-dimensional image of a sample, the AFM provides a true three-dimensional surface profile. Additionally, samples viewed by AFM do not require special treatment that would destroy the sample. AFMs also do not need to operate in a vacuum environment, as do electron microscopes. The AFM can be used on materials that don't conduct electricity. The microscope is unique in its ability to measure the mechanical properties of both hard and soft materials. The latter has traditionally been more difficult because soft materials, such as biological tissues, are part solid and part fluid.

Although the AFM produces a smaller image area than electron microscopes (micrometers versus millimeters, respectively), it can image and manipulate matter at the nanoscale, allowing researchers to both study a molecule's structure and properties and organize molecules into predetermined patterns.

Roger Qiu uses atomic force microscopy to investigate how a naturally occurring protein (osteopontin) can control the growth of a kidney stone.

and other biomolecules—including therapeutic agents—inhibit mineralization is crucial for controlling a variety of disorders.

An example of such a disorder is the formation of stones in the human urinary tract. Through funding from the National Institutes of Health, Livermore's biomineralization team is collaborating with Wierzbicki, physical chemist George Nancollas from State University of New York at Buffalo, and nephrologist John Hoyer from Children's Hospital in Philadelphia to investigate the influence of modifiers in inhibiting the growth of kidney stones.

Kidney stones are composed of up to 95-weight-percent calcium oxalate. Calcium oxalate exists in two forms—calcium oxalate monohydrate (COM) and dihydrate (COD). Although normal human urine contains COM and COD, stone formation is suppressed by a number of protein inhibitors and small molecules such as citrate and magnesium.

The Livermore team combined molecular modeling with AFM to provide the first molecular-scale views of COM modification by two urinary constituents, citrate and the protein osteopontin. The team found that while both molecules inhibit the growth kinetics and modify growth shape, they do so by attacking different faces on the COM crystals. Citrate has a stronger binding energy on the steps of one face than on the steps of the other faces. The results also suggest that when citrate and osteopontin are added simultaneously, a greater inhibitory effect on COM growth exists than when either is applied alone. The results have significant implications for kidney stone disease therapy.

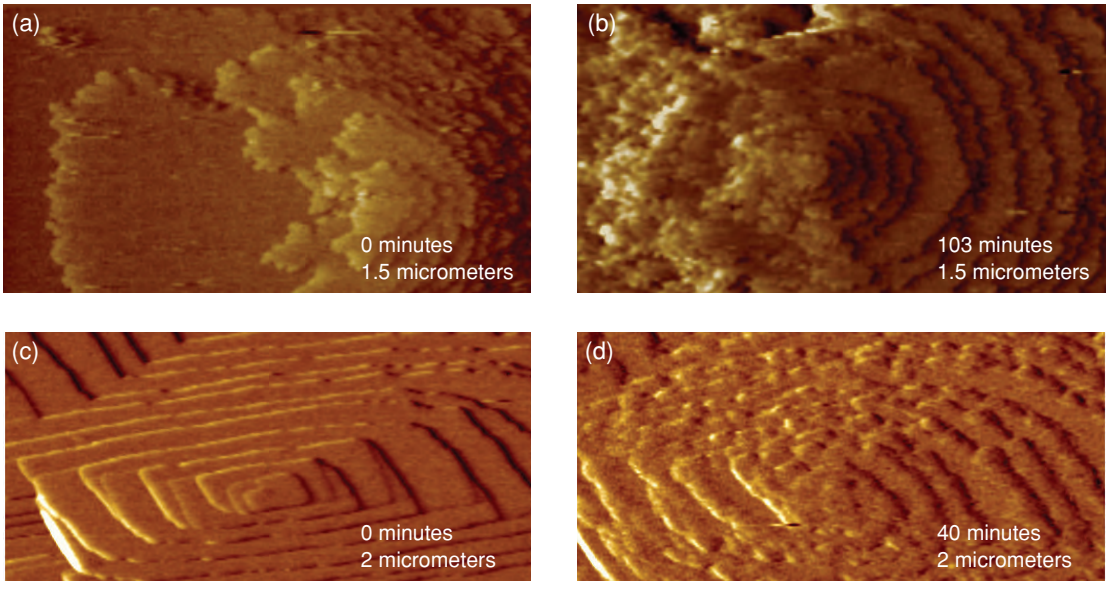
Qiu says, "We don't completely understand kidney stones. For example, we would like to know how proteins control the nucleation of stones, that is, the growth of new crystals." Qiu wants to create a synthetic cell surface for realistically studying nucleation kinetics and how additives may affect nucleation. "In the case of kidney stones, the problem can be addressed at a few different points along the pathway," he says. "We could address it at the nucleation point or at the transformation of COD to COM. Using a synthetic cell would provide us with the most realistic model to understand the starting point of kidney stone formation."

Applications to Energy and Security

Much of Livermore's early AFM work on crystal growth focused on the need to better understand potassium dihydrogen phosphate (KDP) crystal growth for use on the Laboratory's National Ignition Facility (NIF), which when completed will be the largest laser and optical instrument ever built. (See *S&TR,* September 2002, pp. 20–29.) In 1983, Novette, one of NIF's predecessors, was the first laser to be engineered with optical frequency converters made of KDP crystals. The crystals convert infrared light at a wavelength of 1,053 nanometers to a shorter wavelength of 351 nanometers.

For NIF's optics, about 600 large slices of KDP are needed. Using traditional crystal growing methods, it would have taken 15 months to grow that number at the large sizes needed. In the early 1990s, a fast-growing method, pioneered in Russia and perfected at Livermore, produced crystals at the required size in just days. The development team won an R&D 100 Award in 1994 for developing the process that produced high-quality KDP crystals for inertial confinement fusion lasers. Their process had, in only 27 days, produced a KDP crystal measuring 44 centimeters across.

The results of the biomineralization studies conducted by the Livermore team may help NIF researchers in another effort. In inertial confinement fusion, a large amount of laser energy is delivered onto a target containing fusion fuel. The type



Atomic force microscope images show at the molecular scale that citrate and a naturally occurring protein, osteopontin, inhibit the growth and change the shape of calcium oxalate monohydrate by attacking the steps on different faces. While citrate strongly affects the steps on the top face (a–b), osteopontin tackles the steps on the side face of the crystal (c–d).

of target envisioned for NIF ignition experiments (those designed to liberate more energy than the fusion fuel absorbs) is a 2-millimeter-diameter capsule containing deuterium–tritium (D–T) gas surrounded by a solid D–T layer.

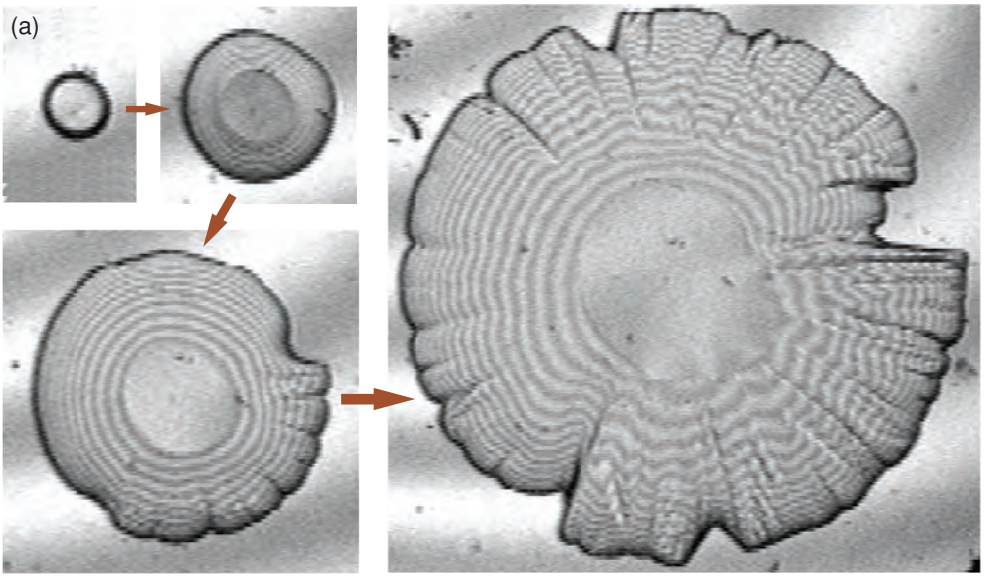
The specifications for the solid D–T layer are extremely demanding. Surface roughness and defects in the layer can promote hydrodynamic instabilities. Physicist Bernie Kozioziemski, who is on the team developing D–T layers for the ignition capsules, says, "The capsule needs to have a perfect seam between the D–T solid and the D–T gas inside. Any deviation from a perfect sphere indicates roughness either because the crystals are not smooth or because they are not joining well."

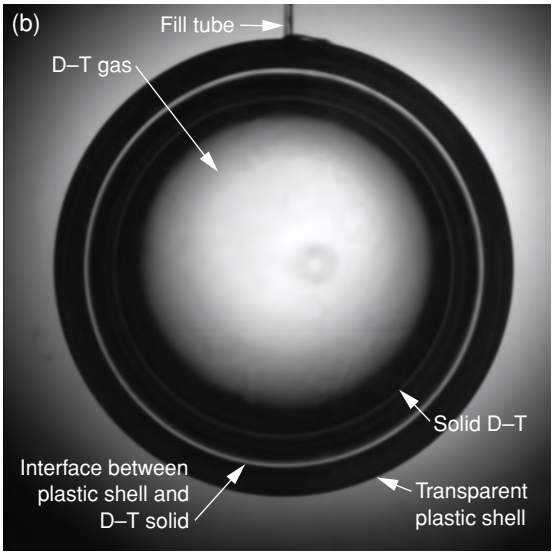
Solid D–T layers are formed by slowly cooling liquid D–T to its freezing temperature. Even the smallest crack may spread as the liquid is cooled to the required temperature. Growing perfectly uniform D–T layers that are free of defects has been a challenge because of the random orientations in the crystals' initial growth patterns. The team plans to determine the optimal growth orientation for crystals and then find a way to grow this pattern repeatedly for each NIF ignition experiment. One possible approach is to mimic biological organisms by creating a nanoscale template to form a single seed crystal with a preset orientation in an ignition capsule, and then allow the seed to propagate. Comparing the smoothness of D–T layers grown from different seed crystal orientations would quickly indicate the ideal orientation.

Understanding crystal formation is also important in maintaining high explosives (HE) for stockpile stewardship. Researchers need to know how HE evolves over time. "Many of the powders used in HE may form crystals after a length of time," says Qiu. "As crystals form, the surface-area-to-volume ratio is decreased, which may affect safety and performance." Researchers can solve problems with crystal formation in HE by using AFM to examine how HE crystals evolve under different environmental conditions. Uncovering the formation mechanism will allow researchers to design an effective means to suppress HE crystallization. In addition, researchers can explore the use of compounds that, like modifiers of biominerals, will control the crystallization process.

Mapping Dissolution Mechanisms

Just as molecules most readily attach to the crystal at steps during growth, when molecules leave the crystal during dissolution, they do so more easily by detaching from the steps, the sites where they have fewer bonds. Understanding dissolution mechanisms has important implications for studies of metal corrosion, a critical issue for DOE's Yucca Mountain Project. Yucca Mountain, Nevada, is the proposed location to store about 70,000 tons of waste from civilian nuclear power plants and highly radioactive waste from defense-related activities at DOE facilities. Livermore scientists have contributed to the project by characterizing the proposed underground site, determining the effects on the site from





(a) Interferometric images of a growing deuterium–tritium (D–T) crystal show a layer of the crystal that is growing more rapidly than those in the center, leading to a rough surface. (b) Visible light illuminates a transparent plastic shell in which D–T crystals have fused together to form a perfect circle, or interface, between a solid layer of D–T and the shell's center of D–T gas. Liquid D–T is poured into the fill tube at the top, and the liquid is slowly cooled to form the solid layer.

storing high-temperature radioactive wastes, and selecting and characterizing corrosion-resistant materials for the waste packages. (See *S&TR*, April 2004, pp. 10–16.)

The current repository design calls for waste to be stored in a package consisting of two nested canisters—an outer canister made of a highly corrosion-resistant metal (Alloy 22) and an inner canister made of a tough, nuclear-grade stainless steel (316NG). The proposed outer canister made of Alloy 22 consists of about 60-percent nickel, 22-percent chromium, 13-percent molybdenum, and 3-percent tungsten. Alloy 22 is extremely corrosion resistant at the high temperature and low humidity expected to prevail for hundreds to thousands of years in a repository. However, because it corrodes very slowly, Alloy 22 is difficult to study on laboratory time scales. Therefore, Orme's team conducted studies using Inconel 600, an alloy of nickel–chromium–iron.

To determine how the chemical bonding at the metal surface dictates the initiation of corrosion, Orme and metallurgist Chris Schuh (a former Lawrence Fellow now at the Massachusetts Institute of Technology) combined electron backscatter diffraction (EBSD) with AFM. EBSD can identify the orientation of each crystal grain at the surface of a sample and create a spatial map of the orientations. After exposing the mapped sample to a corrosive environment, such as diluted hydrochloric acid, the team can then use AFM to determine which orientations dissolve faster than others by measuring the relative heights of different crystallographic orientations. Orme says, "One of the promising aspects of this work is that all facet orientations can be tested simultaneously, making it much easier to identify trends in how materials interact with their environment."

In the studies with Inconel 600, the team expected the results to show that the metal grains with the fewest number of neighbor bonds at the surface corrode the fastest for the same reason that steps dissolve the fastest. Instead, the low-bonded facets were somehow better protected from dissolution than other facet orientations.

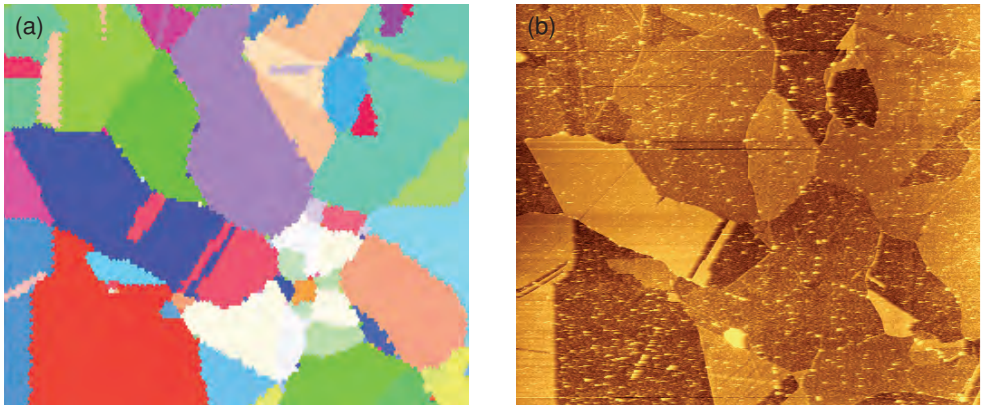
To sort out this puzzle, the team enlisted postdoctoral researchers Jeremy Gray and Bassem El-dasher to carry out a series of experiments, placing Alloy 22 in increasingly corrosive environments. The researchers found that in the most aggressive environments, dissolution occurred as expected, according to the bonding of the metal. However, in less corrosive environments where oxides can form, the order changed. In highly corrosion-resistant materials, the metal is protected by a very thin layer of oxide, which like paint, provides a barrier between the environment and the metal, preventing it from dissolving. However, unlike paint, the oxide continually reforms if oxygen is present.

Orme says, "The interesting twist here is the competition between metal dissolution and oxide growth. Both processes occur at the most reactive locations on the crystal, and it is a delicate balance to determine which will prevail." The facets most susceptible to corrosion are also those most able to form a protective coating.

Materials scientists will continue to glean information about the crystal growth process from the fascinating shapes and hierarchical designs of nature's biomineral structures. "We've come a long way in our understanding of crystal growth," says De Yoreo. "We understand many of the basic mechanisms by which modifiers control growth rate and shape. We also know more about surface science because of these studies. However, everything we've done so far has been in the laboratory. We, admittedly, still understand little about how organisms in nature control nucleation or how they form such remarkable crystalline architectures."

As Livermore researchers continue to unlock nature's secrets of crystallization, they can look forward to applying this knowledge to many applications in materials science, geochemistry, and medicine and toward the fabrication of new classes of materials.

—Gabriele Rennie



(a) A 100-micrometer-square section of an electron backscattered diffraction image of an Inconel crystal shows grain orientations. The colors represent different orientations. (b) An atomic force microscope image of the same area etched with hydrochloric acid shows the susceptibility of each orientation to corrosion. Dark areas in the image indicate orientations that are most susceptible.

Key Words: abalone nacre, Alloy 22, atomic force microscopy (AFM), biomineralization, calcite, calcium carbonate, calcium oxalate dyhydrate (COD), calcium oxalate monohydrate (COM), corrosion, deuterium–tritium (D–T) gas, electron backscatter diffraction (EBSD), potassium dihydrogen phosphate (KDP) crystals.

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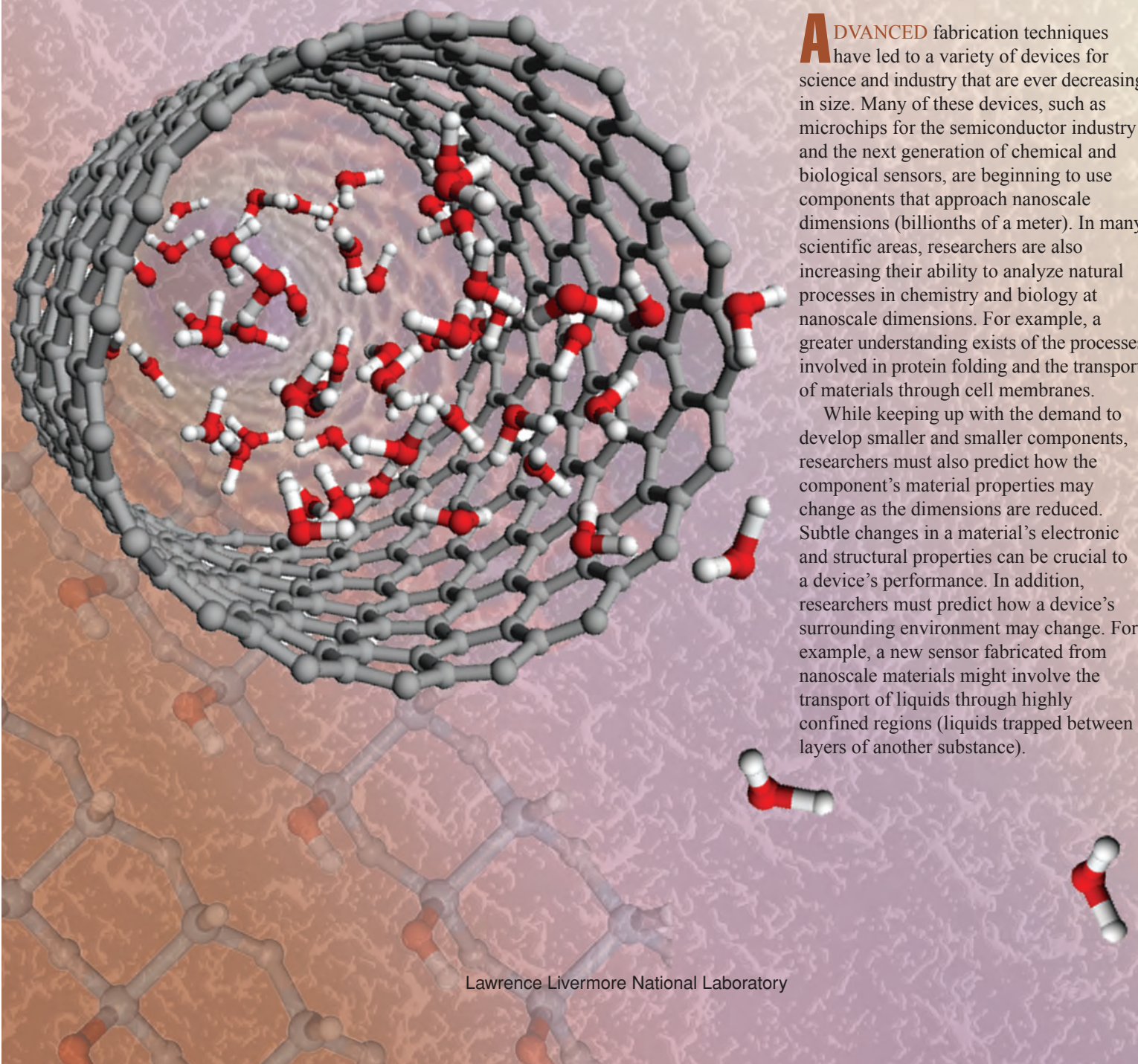
Simulating Materials for Nanostructural Designs

Models of the interaction between water and semiconductor surfaces at the nanoscale show that changes in both affect the performance of nanodevices.



ADVANCED fabrication techniques have led to a variety of devices for science and industry that are ever decreasing in size. Many of these devices, such as microchips for the semiconductor industry and the next generation of chemical and biological sensors, are beginning to use components that approach nanoscale dimensions (billionths of a meter). In many scientific areas, researchers are also increasing their ability to analyze natural processes in chemistry and biology at nanoscale dimensions. For example, a greater understanding exists of the processes involved in protein folding and the transport of materials through cell membranes.

While keeping up with the demand to develop smaller and smaller components, researchers must also predict how the component's material properties may change as the dimensions are reduced. Subtle changes in a material's electronic and structural properties can be crucial to a device's performance. In addition, researchers must predict how a device's surrounding environment may change. For example, a new sensor fabricated from nanoscale materials might involve the transport of liquids through highly confined regions (liquids trapped between layers of another substance).

Understanding how the structural and dynamic properties of a liquid, such as water, changes as it passes through these confined regions is extraordinarily challenging for both experimentalists and theorists.

A Livermore team, led by physicist Eric Schwegler, is developing computational tools to simulate the electronic and structural properties of confined water at the nanoscale as it comes into contact with materials such as silicon carbide and graphite sheets. Their work will help researchers predict how the properties of a liquid might be altered in a nanoscale confinement.

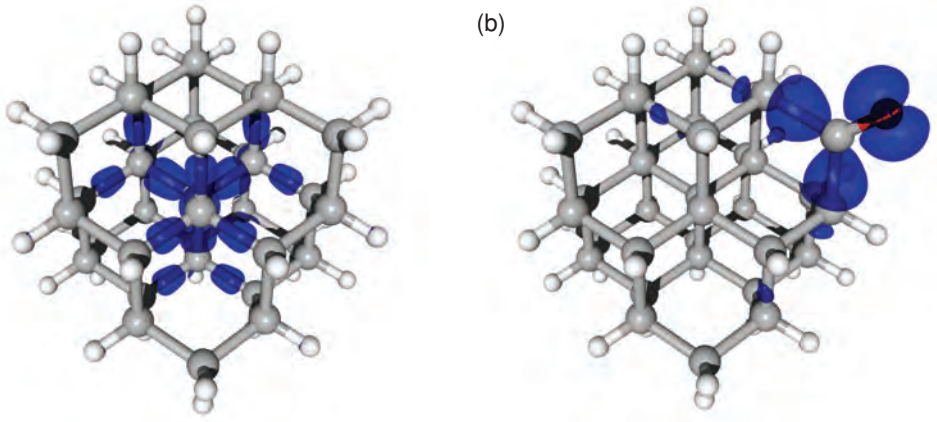
Measuring Nanosize Materials

In the past few years, Livermore has conducted research funded by the Laboratory Directed Research and Development (LDRD) Program on a wide range of semiconductor nanostructures—also known as nanodots or quantum dots. Nanodots are tiny atomic structures just a few nanometers in size, about 100,000 times smaller than the width of a human hair. (See *S&TR*, April 2002, pp. 4–10.)

A nanosize quantity of material can have very different basic properties than the same material in its bulk form. Nanodots have unique and interesting properties such as the ability to emit different colors of light depending on their diameter. Because silicon in bulk form is compatible with biological materials, researchers believe the material may be useful in nanosensors to detect biological and chemical warfare agents.

Schwegler, who leads Livermore's Quantum Simulations Group, says, "When reduced to the nanoscale, a material's shape and crystalline structure can change as well as its electronic and optical properties and melting and boiling temperatures." The Livermore team, which includes physicists Francois Gygi, Giulia Galli, and Andrew Williamson and postdoctoral researchers Giancarlo Cicero and David Prendergast, hopes that modeling the interactions of water with potential confining materials, such as silicon carbide, graphite sheets, and carbon nanotubes, will advance theoretical understanding of confined fluids at the nanoscale. The researchers also hope to provide experimentalists with models of

(a) (b)



In silicon quantum dots, the wavelength of light that is absorbed depends strongly on the cluster's size and surface chemistry. (a) The purple cloud in this silicon cluster covered with hydrogen atoms represents regions where light will be absorbed. (b) When two of the hydrogen atoms on the surface are replaced by oxygen, the light-absorbing region moves, and the optical properties of the cluster are altered.

Carbon Nanotubes—Small but Strong

Strictly speaking, a nanotube can be any tube with nanoscale dimensions. Nanotubes are most commonly made of carbon, but they have also been produced from materials such as boron nitride and gallium nitride. Carbon nanotubes are unique nanostructures with remarkable electronic and mechanical properties. These cylindrical structures are based on the hexagonal lattice of carbon atoms that form crystalline graphite. An ideal nanotube consists of a network of lattices rolled to form a seamless cylinder. Single-wall nanotubes are the fundamental cylindrical structure and form the building blocks of both multiwall nanotubes (nanotubes within nanotubes) and the ordered arrays of single-wall nanotubes called ropes. In the 1990s, researchers found a way to efficiently produce bundles of single-wall nanotubes. This discovery has provided opportunities for quantitative experimental studies on carbon nanotubes.

The tubes, which can be used as nanoscale wires and electrical components, act as conductors or semiconductors depending on the direction they are rolled. The one-dimensional fibers that compose nanotubes exhibit an electrical conductivity as high as copper, a thermal conductivity as high as diamond, and a strength 100 times greater than steel at one-sixth the weight.

Electronic circuit technology cannot continue to shrink by orders of magnitude and provide corresponding increases in computational power. Nanocomposites, however, offer dramatic opportunities to further advance the downsizing of circuit dimensions and the development of novel computer technologies.

what they should expect to find when examining interactions between water and other materials, such as carbon nanotubes, at similar scales. (See the box on p. 12.)

Researchers have used experimental techniques such as neutron and x-ray diffraction to characterize the properties of bulk water. However, detailed information on liquids confined at the nanoscale has been limited because of the difficulty in probing the solid–liquid interface in nanosize devices. Theoretical and computational studies have also been limited because these complex, multicomponent systems require large-scale simulations to be realistic. Past studies have been restricted to computationally inexpensive models based on classical molecular dynamics (MD).

In classical MD simulations, researchers use calculations that describe the motion of molecules according to forces defined by empirical interaction potentials. These potentials are determined by observing how molecules behave in a given phase at a specific temperature and pressure. Researchers then compute the trajectories of the molecules in small time steps by integrating Newtonian equations of motion. Because empirical potentials describing the interactions between the atoms of the system must be supplied as input before the simulations can be carried out, classical MD is limited in the information it can provide about complex systems whose interactions are not well characterized.

Coupling a Supercomputer and Code

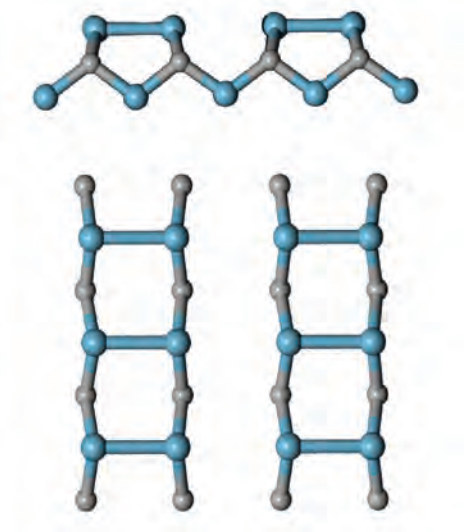
To model complex systems without using predefined empirical potentials, researchers must use codes based on first principles. In 2004, Gygi developed Qbox, a first-principles MD code. First-principles MD simulations use the laws of quantum mechanics to describe the electrons in a system. The data are then used to accurately compute the interactions between atoms without experimental input. The Qbox code calculates the electronic structure of a system using methods based on density functional theory, which defines a molecule's energy and electronic structure in terms of its electron density. Galli, who along with Gygi is now a professor at the University of California at Davis, says, "At the nanoscale, predicting the behavior of water is extraordinarily challenging, and experimental data are sparse. Quantum simulations allow us to make predictions, even if little or no experimental data are available."

Modeling complex interfacial systems with first-principles MD has been challenging even with today's supercomputers. The Livermore group is using the Laboratory's Thunder machine, which can execute 23 trillion operations per second. Thunder is funded by Livermore's Multiprogrammatic and Institutional Computing Initiative, which grants scientists engaged in leading-edge research access to computer time. In 2004, Schwegler's team was awarded one of the largest time allotments on Thunder as part of Livermore's computational grand challenges.

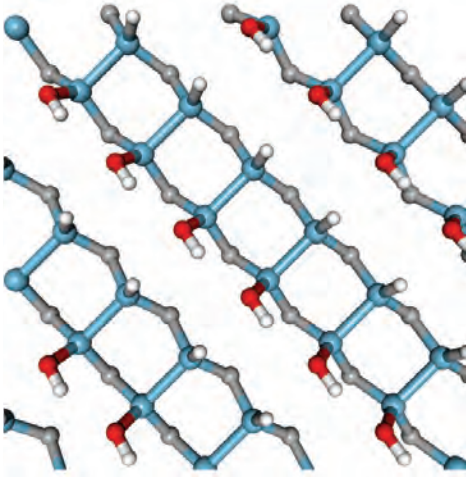
Together, Thunder and the Qbox code can efficiently calculate systems involving hundreds of atoms, allowing researchers to study nanotechnology and biochemistry applications. These same tools are used to conduct research on condensed matter subjected to extreme temperatures and pressures. For example, in 2004, Livermore researchers used Qbox to predict a new melting curve of hydrogen at extremely high pressures. (See *S&TR*, January/February 2005, pp. 4–13.)

Different Reactions to Water

The team used first-principles MD simulations to model the properties of confined liquid water as it interacts with silicon carbide surfaces, graphite sheets, and carbon nanotubes. The models simulated systems containing between 500 and 600 atoms for 20 to 25 picoseconds. Schwegler says, "The combination of a highly optimized and robust code such as



Silicon carbide is composed of alternating layers of carbon (gray) and silicon (blue) atoms.



Silicon atoms (blue) exhibit a hydrophilic (water-binding) characteristic and form bonds with water molecules (red and white). In contrast, carbon atoms (gray) possess a hydrophobic (water-repelling) characteristic and do not easily form bonds with water.

Qbox running on Thunder enabled us to simulate such complex systems."

Surfaces made of silicon carbide were chosen for the study because the material's high electrical conductivity is useful in electronic devices. In addition, the material's high mechanical, thermal, and chemical stability are characteristics that make it a promising candidate for use in biocompatible devices. Silicon carbide is made of alternate layers of carbon and silicon atoms. Consequently, the material has two possible surfaces with quite different electronic and structural properties. These properties have a strong effect on the material's relationship with water. In particular, surfaces rich in carbon atoms have a hydrophobic (water-repelling) character, while surfaces rich in silicon atoms are strongly hydrophilic (water-binding).

The team designed the simulations by "slicing" solid silicon carbide so calculations could be run for surfaces that terminated with either silicon or carbon atoms. For the strongly hydrophilic surfaces that terminated with silicon atoms, the simulation results indicated that water molecules near the surface tend to spontaneously dissociate into a hydrogen or an oxygen–hydrogen group, completely covering the hydrophilic surfaces. In contrast, water molecules approaching the carbon-terminated surfaces remained floating above the silicon carbide, which is characteristic of a hydrophobic interaction.

The team also examined the effects of water confined by carbon graphite sheets and carbon nanotubes, which have hydrophobic surfaces similar to the carbon-terminated silicon carbide slices. By studying how the properties of water change as it is sandwiched between two sheets of graphite or as it fills the interior of a carbon nanotube, the researchers could examine the differences between one- and two-dimensional confinement by a hydrophobic material. Surprisingly, the results indicated that hydrophobic surfaces tend to have a more pronounced effect on the structural and dynamical properties of confined liquid water than do hydrophilic surfaces.

Designing Novel Nanostructures

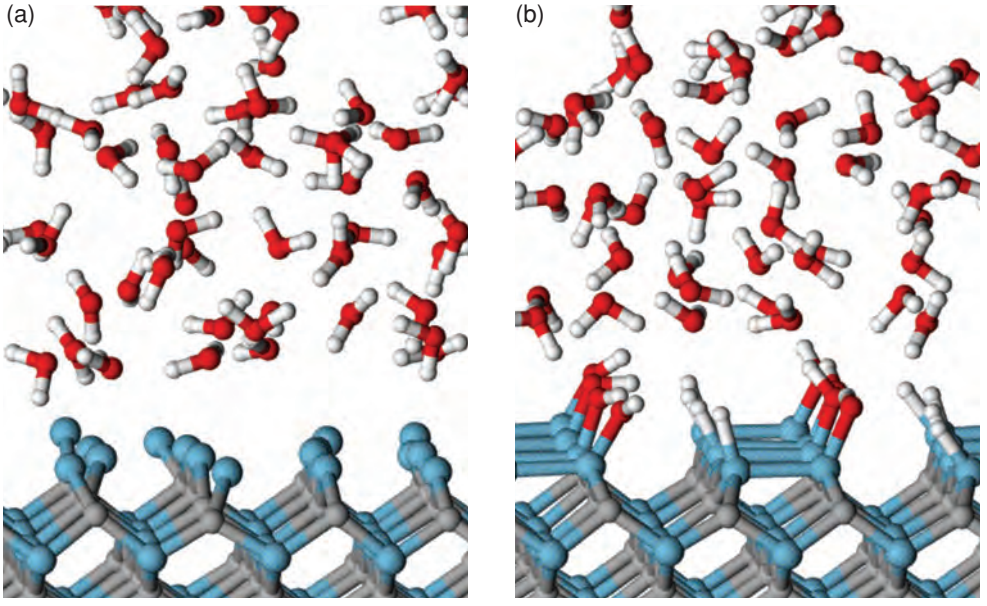
The team's findings suggest that researchers may be able to prepare nanoscale materials with specific hydrophilic and

The Love–Hate Relationship with Water

Why does water bead on some surfaces and not on others? People rely on water to bead rather than be absorbed on raincoats and freshly waxed cars. On the other hand, most forms of life depend on the ability to rapidly transport water through cell walls via membrane channels. These two competing tendencies, which scientists refer to as hydrophobic (water repelling) and hydrophilic (water binding), depend on the material with which the water molecules are interacting.

Scientists take advantage of hydrophilic and hydrophobic tendencies of materials to develop commercial products. For example, laundry soap works because one part of the soap molecule is hydrophilic and the other is hydrophobic. The hydrophilic part allows the hydrophobic fatty acids to come into contact with other hydrophobic substances such as the dirt on the surface being cleaned. When the grime adheres to the soap's fatty acids, it becomes encapsulated in droplets of water. Dirt, oil, and bacteria can then be washed away in this suspended state.

Researchers hope that with a better understanding of how water interacts with a material's properties at the nanoscale, they can design nanoscale devices for many applications in science and industry. The developments will include new sensor technologies for detecting biological threat agents as well as nanofluidic devices for medical applications.



(a) A first-principles simulation shows water molecules (red and white) approaching a layer of silicon carbide that terminates with silicon atoms (blue). (b) As the water molecules approach the material's surface, they dissociate into hydrogen (white) or oxygen–hydrogen groups (white and red) and bond with the silicon carbide.

hydrophobic patterns that are most compatible for an intended purpose. Controlling the properties of a surface by patterning regions with hydrophilic and hydrophobic characteristics is important for DNA and protein attachments.

The simulation studies also strengthen the link between theory and experiment. Experimental measurements of a material's properties often require a theoretical model for interpretation. For example, equations must be used to transform observed x-ray diffraction data into information on the structure of a crystalline material. The Livermore simulations provide structural models that can be used as a basis for transforming the results of specific measurements into detailed information about molecular behavior.

In studies on confined water, of which most experimentalists have little or no experience, the Livermore team is hoping to find unique signatures of the interaction between materials and water confined at the nanoscale. The fingerprints could provide information about properties that are directly related to optical and x-ray absorption experiments—powerful methods used to obtain detailed structural information on the materials interacting with water. For example, simulations using first principles supply accurate structural and dynamic information on such properties as electronic charge densities, polarization effects, and various absorption spectra associated specifically with electronic transitions. Also, by tracking the position of every atom over relevant time scales, the simulations provide useful data on important molecular vibrations in confined water measured during infrared absorption experiments. Prendergast says, "The simulations give us access to structural, electronic, and vibrational properties at the nanoscale that have not yet been accessible by experimental methods."

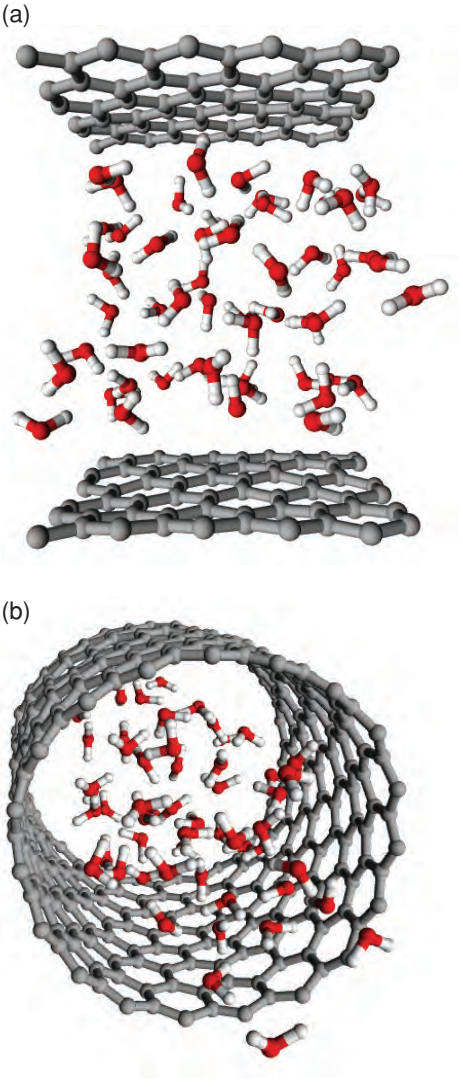
Some of the most promising experiments on water have been based on x-ray absorption measurements, where the interpretations rely heavily on theoretical models. Traditionally, x-ray absorption experiments have been used to probe the electronic structure of high-atomic-number (high-Z) materials such as transition metals and radioactive materials. This research requires the use of high-energy, deep-penetrating x-ray beams from sources such as the Advanced Light Source at Lawrence Berkeley National Laboratory and the Stanford Linear Accelerator Center. However, for materials composed of low-atomic-number (low-Z) elements, such as oxygen, carbon, or hydrogen, the energies at which x rays are absorbed are relatively low and tend to be absorbed by the standard sample containers that are used.

Recently, several experimental groups have devised new methods to probe low-Z materials such as water and other organic molecules. In one method, researchers avoid the use of a container by using a microjet stream of water in a high vacuum to measure the water's absorption of x rays. (See *S&TR*, November 2001, pp. 20–23.) Another approach measures the energy loss of high-energy x rays as they interact with a material encased in beryllium, which is transparent to x rays. Experimentalists can also measure various emission processes that occur after the absorption of x rays, such as the ejection of electrons, ions, and lower energy radiation from the surface of a material.

Detecting Organisms at the Nanoscale

Understanding how hydrogen bonding and hydrophilic and hydrophobic characteristics are affected at the nanoscale will further studies on fluid flow in the confined environments of nanoscale channels. The simulation data provided by Schwegler's team is helping Livermore researchers design nanofluidic devices that will serve the Laboratory's national security mission, which includes developing technologies to detect and identify biological organisms that may have been engineered for the purpose of a biological attack.

Nanofluidic devices move fluids through a maze of microscopic channels that have been fabricated with the lithographic techniques used to make microelectronics. Livermore physicist Sonia Létant is leading an LDRD-sponsored project to synthesize arrays of functionalized pores in silicon membranes that can selectively capture and immobilize an organism ranging from



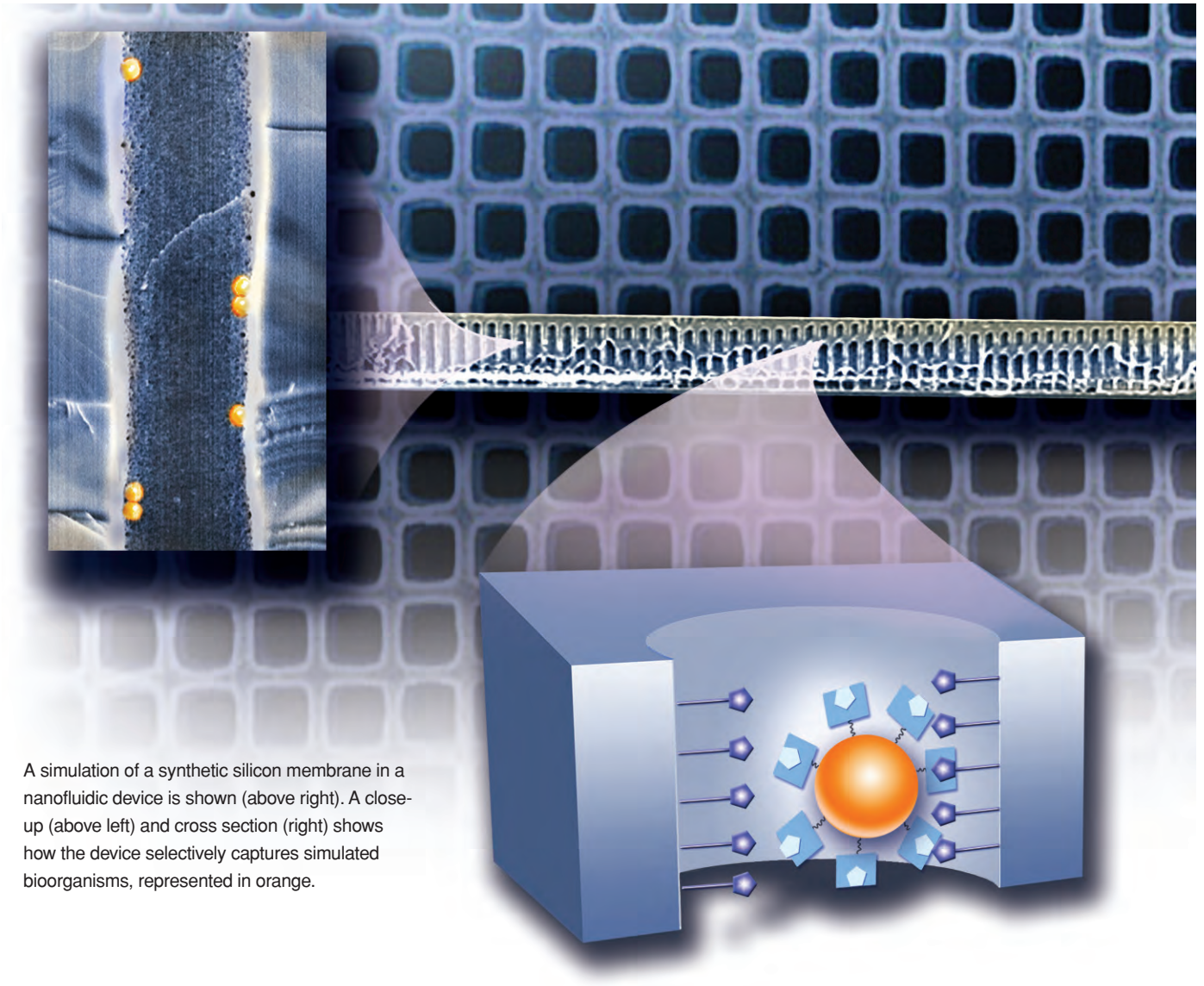
Simulations of water molecules (red and white) confined between (a) carbon graphite sheets and (b) carbon nanotubes demonstrate carbon's hydrophobic tendency.

spores (many micrometers) to viruses (tens of nanometers). The Livermore team is the first to use electrochemical etching to synthesize silicon membranes with pore diameters as small as 30 nanometers. To test the device, the team coated fluorescent microbeads with an antibody and equipped the membranes with a particular antigen. The device selectively captured the matching antibody-coated beads and allowed the remaining beads to flow through the membranes' pores.

To identify organisms, Létant's team is also building a nanofluidic device with a single synthetic pore that mimics an ion channel. As an organism travels through the device, the organism generates a charged current. The amplitude, duration, and shape of the electrical signal provide information on the size, shape, and chemical composition of the organism. Once characterized, the electrical signatures of the organism can be compared to others stored in a database.

In another LDRD-sponsored project, physical chemist Alex Noy is developing innovative nanostructures that can be used for biological-agent detection, water desalination, and kidney dialysis. (See *S&TR*, May 2004, pp. 4–11.) Noy's team is using carbon nanotubes as molecular wire templates to build a nanodevice that can detect bacterial toxins. The team has successfully fabricated and characterized one-dimensional lipid bilayers, which represent a new class of nanostructures. The nanostructures combine carbon nanotubes with synthetic membranes that mimic biological ones.

Physicist Olgica Bakajin is leading an effort to build synthetic membrane pores using carbon nanotubes with diameters between 0.6 and 10 nanometers. The



A simulation of a synthetic silicon membrane in a nanofluidic device is shown (above right). A close-up (above left) and cross section (right) shows how the device selectively captures simulated bioorganisms, represented in orange.

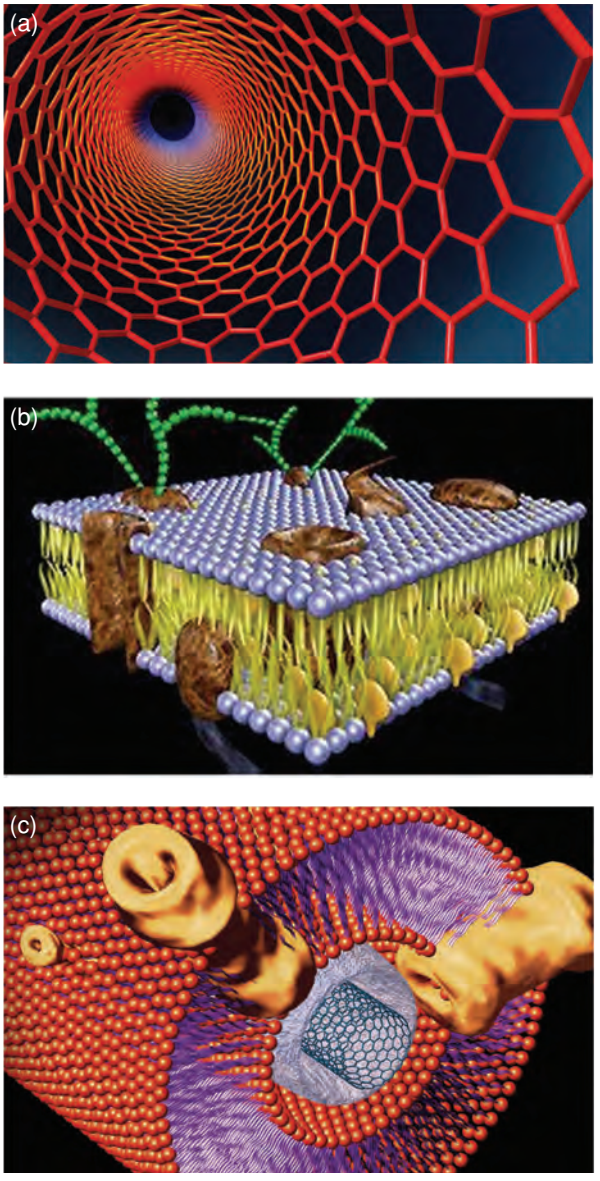
nanodevice will be used to study the effects of confined water not seen in bulk water. Experiments are also under way to characterize the transport of electrolytes through this synthetic membrane for desalination and dialysis applications. The combination of the membrane material's exceptional conductivity and strength and its compatibility with biological materials has resulted in carbon nanotube development becoming a rapidly growing field. Noy says, "Carbon nanotubes are ideal for packaging a large number of individual sensors on the surface of a semiconductor chip. Also, nanotube-based membranes can precisely control how other molecules access the chip components."

Understanding Life's Building Blocks

Protein folding is another research area that will benefit from simulated confined-water studies at the nanoscale because protein-folding experiments are difficult to conduct. (See *S&TR,* December 2004, pp. 12–17.) Computational studies of protein folding have been limited by time-scale capabilities and by the use of predefined parameters fitted to the properties of bulk water. Yet, the confined state of water is expected to be important in folding processes in a hydrophobic environment.

Simulations are playing an increasingly important role in understanding matter at the nanoscale and in predicting the properties of nanomaterials. Understanding the basic science issues involved in the properties of confined liquids is relevant to the development of sensor technologies based on nanoscale materials. Schwegler says, "We expect that we will be able to simulate alternative nanostructures with specific, targeted properties. In turn, this work will open the possibility of designing optimized materials entirely from first principles."

—Gabriele Rennie



By combining (a) carbon nanotubes and (b) synthetic cell membranes, (c) a new class of nanostructures with increased functionality is created. Nanostructures can be used in sensors and potentially in humans.

Key Words: confined water, hydrophilic, hydrophobic, nanofluidic devices, nanostructures, Qbox code, silicon carbide.

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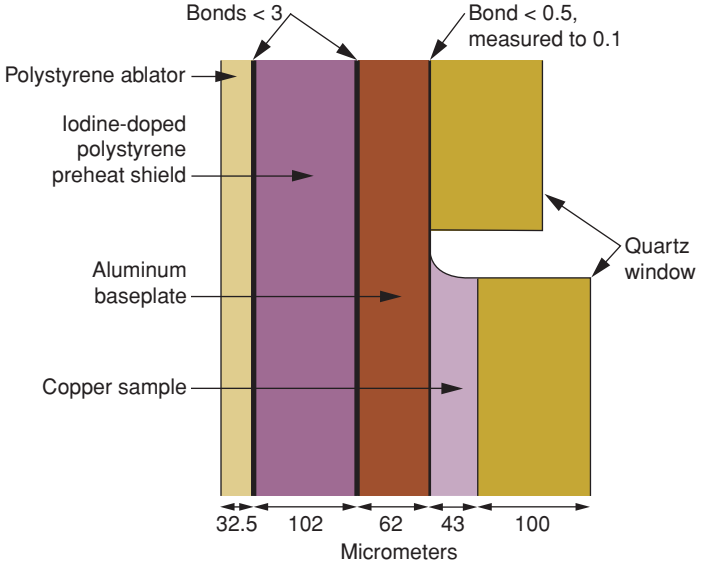
Zeroing In on New Targets

WHEN the National Ignition Facility (NIF) is completed and its 192 lasers are ready to fire, the force of the world's most powerful laser facility will likely be aiming at a very small and precisely fabricated target. Physicists preparing high-energy-density experiments intended for NIF are turning to Livermore engineers to help design, fabricate, and characterize super-tiny targets with minute tolerances.

NIF will be used to achieve ignition and to better understand physics at extremely high energy densities. The facility is critically important to ensuring the safety and reliability of the nation's nuclear weapons stockpile. Experiments on NIF will direct the force of a laser onto a target smaller than a poppy seed. Livermore's High Energy Density Physics (HEDP) Program, led by Charlie Verdon, has responsibility for an important series of experiments that will be conducted when NIF is completed. At present, experiments are being conducted on the OMEGA Laser at the University of Rochester's Laboratory for Laser Energetics. They include the measurement of key properties in materials such as equation of state (EOS), strength, opacity, and radiation transport.

Although precision and accuracy are always important in conducting scientific experiments, the specifications for the EOS targets are extremely precise and stringent. Because the results of the EOS laser experiments will be compared with computer simulations of expected material behavior, the exact size, shape, and orientation of each target must be known. Verdon says, "We are making significant advances in our target fabrication capabilities in order to achieve the desired physics understanding." A close collaboration between the physicists designing the experiments and the engineers fabricating the targets must occur to ensure the successful achievement of experimental goals.



Laser targets used to investigate the equations of state (EOS) of copper are composed of bonded layers of copper and aluminum foils and quartz windows (all units shown are in micrometers). The various layers of each EOS target must be fabricated to a uniform thickness for the experimental results to be accurate.

Putting Their Heads Together

Matthew Bono of the Engineering Directorate is involved in just such a collaboration. Bono and others from the target fabrication team are working with researchers from the Physics and Advanced Technologies Directorate to produce targets for experiments that will measure the EOS of copper.

Because of the accuracy desired in the experiments, the target specifications require a level of precision 10 times more stringent than that of most laser targets. Successfully designing the experiment and fabricating such precise targets requires a concerted effort by those involved. "As the designers of the experiments, we need to communicate with the target fabrication team to ensure the target can be realistically built while achieving the goals of the experiment," says physicist Peter Celliers.

Among the challenges in designing the targets is minimizing the variation in thickness of the materials that make up each target. The targets are composed of several layers of differing materials that are 4 millimeters in diameter and roughly the thickness of a piece of paper. These layers are stacked and bonded together to form the target.

According to Bono, one challenge is finding practical manufacturing solutions that will enable the team to deliver targets whose initial designs have proven difficult to build. When faced with challenges such as the EOS target, the engineers, machinists,

materials scientists, and metrology experts on the team must often develop new capabilities that will lead to a successful manufacturing and metrology strategy. The result of the close collaboration between the target fabrication team and the physicists is a target design that satisfies all of the physics requirements and can be manufactured at an acceptable cost.

Shocking Copper

Livermore's expertise in target fabrication has proven critical for the upcoming EOS experiments on copper. In these experiments, the laser energy is directed onto the target's polystyrene ablator, which generates a shock wave that passes through an iodine-doped preheat shield. (See the figure on p. 18.) Part of the shock is transmitted through a layer of aluminum and then a quartz window, while the other part of the shock passes through the aluminum, then through the copper, and finally through another quartz window. To accurately measure the shock velocity, scientists must know precisely when the shock enters and exits both the aluminum and the copper as well as the thicknesses of the two metals.

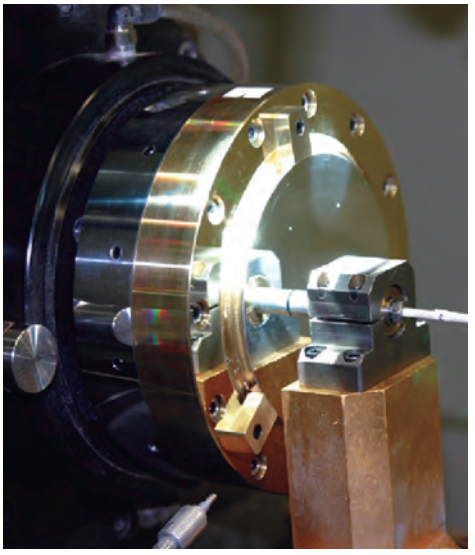
Because the shock must travel uniformly through the layers, the acceptable variation in the thickness of some layers is 0.1 micrometer. This thickness uniformity represents a tenfold increase in the level of precision of previously fabricated targets and was beyond the scope of standard target-fabrication practices at the onset of the effort.

Know How to Hold 'Em

Several fabrication methods were considered before selecting one that used a combination of diamond turning, deposition, and precision assembly. Because no practical methods currently exist to measure the targets adequately once they are built, the manufacturing process had to be designed to incorporate the required measurements of the components as they were fabricated and assembled.

Each target was built on a 100-millimeter-diameter aluminum disk that eventually became its paper-thin baseplate. To obtain components with uniform thickness, the team used a special vacuum chuck to hold the disk perfectly perpendicular to the machine tool. The vacuum chuck held the disk on a large number of very small concentric supports (only 50 micrometers wide), which were separated by much wider grooves. This small area of contact minimized the risk of dust or debris interfering between the baseplate and the chuck.

After diamond-turning both sides of the aluminum baseplate, a band of copper was deposited on the disk to form the copper sample of the target. The interface between the aluminum and the copper is crucial to the experiment. For the best possible interface, the copper was deposited directly on the aluminum using a combination of sputtering and electroplating. The sputter-seeded electroplating began with the removal of the oxide layer from the aluminum using an ion mill. Then a few micrometers of copper were sputtered onto the aluminum. Additional copper was electroplated onto the sputtered material, which was then diamond-turned to the correct thickness. All subsequent assembly operations and metrology were performed directly on the diamond-turning machine, which maintained the reference surfaces required to measure the thickness and uniformity of each layer of the target with the needed accuracy.



A special vacuum device holds the face of each disk perfectly perpendicular to the machine tool, which allows the components to be machined with uniform thickness.

After diamond-turning the aluminum disk to a paper-thin foil, several pads of iodine-doped polystyrene were bonded to it to form the preheat shields. The pads were epoxied in place using a special assembly fixture mounted directly on the machine tool. These pads were measured to determine the thickness of the adhesive layer and then machined to the required thickness. The process was repeated with polystyrene pads that formed the ablators. Because the workpiece remained on the vacuum chuck throughout this process, all surfaces were machined parallel to each other.

To create individual laser targets, the team cut 4-millimeter-diameter pieces of the bonded layers from the larger disk using an excimer laser. Quartz windows were then bonded onto the aluminum and the copper, and the target was bonded to a gold support ring, as shown in the figure on p. 20.

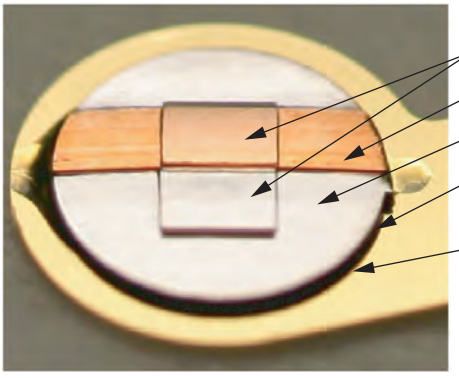
Measure by Measure

Because the amount of precision required to make and measure these targets is beyond those of industrial applications, some of the machines and tools to produce the targets must also be custom designed and fitted. “We often modify commercially available equipment to meet our requirements,” says Bono. “If we can’t buy a piece of equipment adequate for our needs, we make it ourselves.” Recent examples include a tool holder and an assembly station used to put together the tiny components.

Metrology tools used to precisely measure and characterize the final target may also need to be redesigned or retrofitted. “You can’t make what you can’t measure,” says Bono, echoing a maxim from the trade. “We have many capabilities for precision machining, but advanced capabilities for metrology are limited.” To meet the future needs of target production, the team is developing various metrology devices designed for targets at the mesoscale. Among these devices are an absolute thickness measuring machine and a four-axis coordinate measuring machine with submicrometer resolution. The team has also begun using a radiographic device with a millimeter-wide field of view that uses x rays to image an object with submicrometer resolution.

Looking to the Future

Targets for future experiments on NIF will become more complex with more demanding requirements. Close collaboration between physicists and engineers will be essential to designing targets that meet physics requirements and are manufacturable. Materials scientists will need to produce novel raw materials that allow physicists to study important issues. Engineers will need to develop new manufacturing processes that enable Livermore’s machinists to fabricate the targets. Metrologists and nondestructive evaluation experts will face one of the most important challenges as they develop and use advanced characterization methods to measure the completed targets. The requirements for measuring the targets are often just as challenging as manufacturing them.



A finished EOS target is bonded to a 5-millimeter gold support ring.

The successful delivery of the copper EOS targets has contributed to the feasibility and time and cost effectiveness of future experiments. “In addition,” says Bono, “as we develop new fabrication techniques, they become a part of our tool box. The work we did on this copper target has already enabled a significant cost savings for another project.”

That’s right on target.

—Maurina S. Sherman

Key Words: copper targets, equations of state (EOS), laser targets, machine tools, National Ignition Facility (NIF), precision machining, shock velocity, target fabrication.

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Monitoring Nuclear Reactors with Antineutrinos

As fissile materials are being created and destroyed in a nuclear reactor, tracking their inventory can be a tricky business. The International Atomic Energy Agency (IAEA), which is the United Nations agency responsible for monitoring civil nuclear facilities and nuclear inventories in nonnuclear weapons countries, uses a variety of accounting and surveillance techniques for this purpose. However, no easy method exists for peering into an operating reactor to accurately determine how much plutonium or uranium is present in the fuel rods in real time.

A team from Lawrence Livermore and Sandia national laboratories has designed a detector that uses an elusive elementary particle—the antineutrino—to make real-time measurements of plutonium as it is created in the heart of a nuclear reactor. This antineutrino detector can potentially help the IAEA and other agencies achieve the important goal of tracking global inventories of fissile materials, such as plutonium, to ensure these materials are not being diverted into weapons.

In the Heart of a Reactor

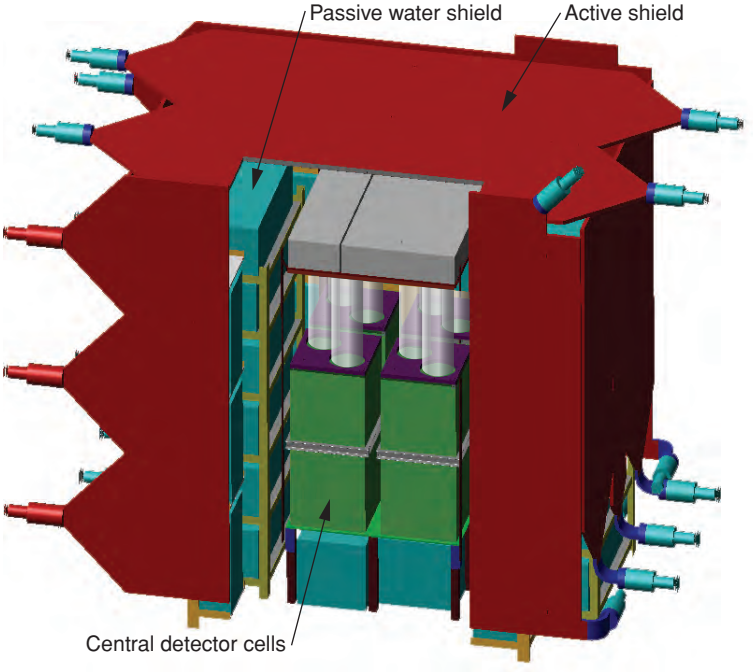
Antineutrinos are a by-product of the fission process that occurs in a nuclear reactor. Fresh reactor fuel rods contain uranium-238 and uranium-235, with the latter being the main fission isotope. When a fissile isotope absorbs a neutron, the isotope's nucleus can split into two energetic daughter nuclei and a shower of neutrons and gamma rays. The neutrons then cause more fissions, and the daughter nuclei decay, three times each on average, emitting an antineutrino with each decay. Uranium-238 can also capture neutrons, and some of these captures result in uranium-239, which decays to plutonium-239. Plutonium-239 can also fission, and its daughter nuclei produce antineutrinos as well.

Over a broad range of antineutrino energies, the number of antineutrinos emitted by plutonium-239 differs substantially from the number emitted by uranium-235. As plutonium-239 builds up in the reactor over time, the antineutrino count rate measured in a detector will drop, by about 5 to 10 percent over the reactor fuel cycle.

Detecting the Elusive Antineutrino

Antineutrinos are elusive by nature. Similar to their counterpart, the neutrino, antineutrinos are electrically uncharged, nearly massless, and rarely interact with matter. For example, about one interaction occurs when a beam of 10^{11} antineutrinos passes through Earth's diameter. (See *S&TR,* April 2003, pp. 13–19.) The high flux rate of antineutrinos from reactors—about 10^{21} per second—partially compensates for the low-interaction probability. The Livermore–Sandia detector makes use of the inverse beta-decay interaction, in which an antineutrino interacts with a free proton in the detector to create a neutron and positron (positive electron) that provide a measurable signature.

The detector consists of three subsystems: the central detector and two shields. The central detector, in which the antineutrinos are detected, consists of four stainless-steel cells filled with a cubic meter of liquid scintillator. The scintillator contains plenty of quasi-free protons and is laced with gadolinium atoms. When an



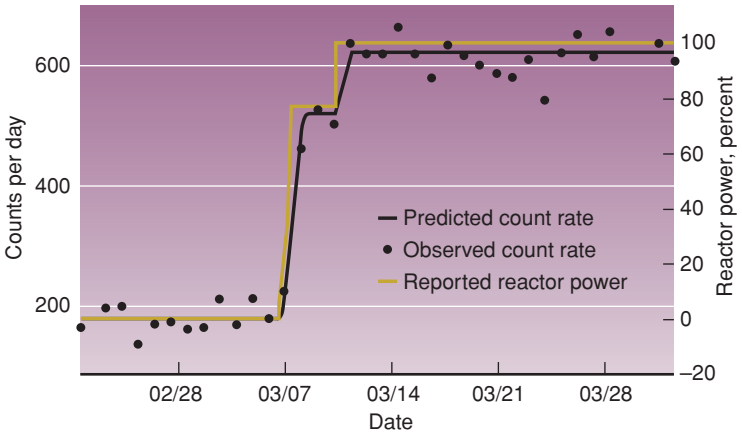
The prototype antineutrino detector consists of three subsystems: a central detector and two shields. Photomultiplier tubes above the central detector cells detect the antineutrino's signature.

antineutrino interacts with a proton, the created positron soaks up most of the antineutrino energy, converting it into a flash of visible photons as it induces scintillation. A fraction of a nanosecond later, essentially simultaneously, another flash is created when the positron annihilates with a nearby electron, producing gamma rays that also induce scintillation. About 30 microseconds later, a third flash of light is produced from the neutron when it is captured by and excites a gadolinium nucleus. The nucleus de-excites by emitting high-energy gamma rays, which again induce scintillation. The flashes of light are detected by photomultiplier tubes above the scintillation fluid and form a signature for the antineutrino interaction.

The central detector is surrounded on all sides by a passive water shield. This shield attenuates gamma and neutron backgrounds. A second active shield placed outside the water shield detects and "vetoes" penetrating cosmic ray–related signals, which can mimic antineutrinos.

Scientists have two ways of tracking the amount of plutonium-239 and uranium-235 in a working reactor. One method involves examining changes in the total rate of detected antineutrinos over time; the second involves looking at changes in the antineutrinos' energy spectrum.

By monitoring the rate at which antineutrinos are produced during the fission process, scientists can track the amount of fissile material in the reactor core. Because uranium-235 produces antineutrinos in greater abundance than plutonium-239 over a certain energy range, the rate of antineutrino production can be correlated to the amounts of specific fissile elements in the reactor core. "As the reactor core goes through its irradiation cycle, the amount of uranium decreases and the amount of plutonium increases," says physicist Adam Bernstein, who heads the project at Lawrence Livermore. "Because the plutonium produces fewer measured antineutrinos than does the uranium, we can use the change in antineutrino rate over time to estimate how much plutonium has been created." This drop in rate typifies the standard pressurized-water-reactor (PWR) fuel cycle.



Data recorded over a one-month period in 2005 as the reactor "ramped up" to full power shows that the antineutrino count rate measured by the detector closely matched the predicted count rate.

For example, at the start of a PWR fuel cycle, the antineutrino count rate may be 1,000 per day. By the end of the cycle, that number would decrease to 900 per day, depending on the reactor type and fuel loading. "If anyone removes plutonium along the way or alters the operating parameters to increase plutonium production, those changes will show up in the antineutrino count rate," says Bernstein. The correlation, known as the burn-up effect, can help provide a real-time inventory of the amount of plutonium and uranium isotopes in the reactor core. This method requires the reactor power to be measured independently; otherwise, the operator could mask the reduction in antineutrino rate caused by increased plutonium production simply by raising the power level.

The second method does not depend on knowing the reactor power. Because the detector is sensitive to the antineutrino energy and because the energy spectra of antineutrinos emitted by plutonium-239 and uranium-235 are different, scientists can determine the relative amounts of plutonium and uranium in the reactor by measuring ratios between the low- and high-energy parts of the energy spectrum. This ratio technique removes the need for an independent power measurement—albeit at the expense of a longer counting time—to achieve the necessary statistical precision.

Future Bright for Detector

"To be useful to the IAEA, the detector must be easy to operate, reliable, cost-efficient, and capable of uninterrupted operation for months or years at a time," says Bernstein. "We've shown that our small detector of relatively simple design can be installed in a convenient location outside the reactor's containment area, that we can count hundreds of antineutrinos per day, and that reactor power levels can be tracked on a time scale of hours. We have preliminary evidence for the burn-up effect in the data we've accumulated to date, which will be confirmed as more data are acquired. We've also demonstrated that the detector can run stably, continuously, and automatically for months. We can even calibrate the detector automatically, relying on energy peaks present in the natural radioactive background."

Since 2003, the 1-ton prototype has been recording data at the San Onofre Nuclear Generating Station in San Clemente, California,

in a room about 25 meters away from the reactor core. The detector is 17 meters below ground, and the total footprint, including shielding, is about 2 by 3 meters. The antineutrino rate is calculated hourly on a local, dedicated data-processing computer, and summary data are uploaded continuously to a secure Web site.

The team is now refining the estimate of the detector's sensitivity to the reactor's plutonium inventory as well as working with the IAEA and other agencies to understand how this new technology will fit into existing regimes. Bernstein says, "We're encouraged by the interest from the IAEA and from safeguards and physics experts in Brazil, France, and Russia. The blending of practical application and fundamental particle physics has clearly struck a chord in these communities."

Other avenues of research have also opened. The detector built by the Livermore–Sandia team uses inverse beta decay to detect antineutrinos, but another method also exists: coherent scattering from nuclei, in which an antineutrino, zipping past the nucleus of an atom, causes the nucleus to "shake" and shed a few electrons in the process. The team has designed and proposes to build a small, liquid–gas argon detector to observe this never-before-seen antineutrino interaction. An antineutrino detector based on coherent elastic scatter would take up much less space and weigh much less than the 1-ton detector currently being fielded.

"The IAEA considers 8 kilograms of plutonium to be a proliferation concern," says Bernstein. "About 400 civilian power reactors worldwide create thousands of kilograms of plutonium annually. An antineutrino detector, whether based on inverse beta decay or coherent scattering, could be used to help make the world safer by giving international organizations, such as the IAEA, another tool for determining whether a country is making extra plutonium in its civilian reactors—plutonium that could be diverted to a weapons program."

—Ann Parker

Key Words: antineutrino detector, coherent elastic scatter, International Atomic Energy Agency (IAEA), inverse beta decay, nuclear power reactor, plutonium, uranium.

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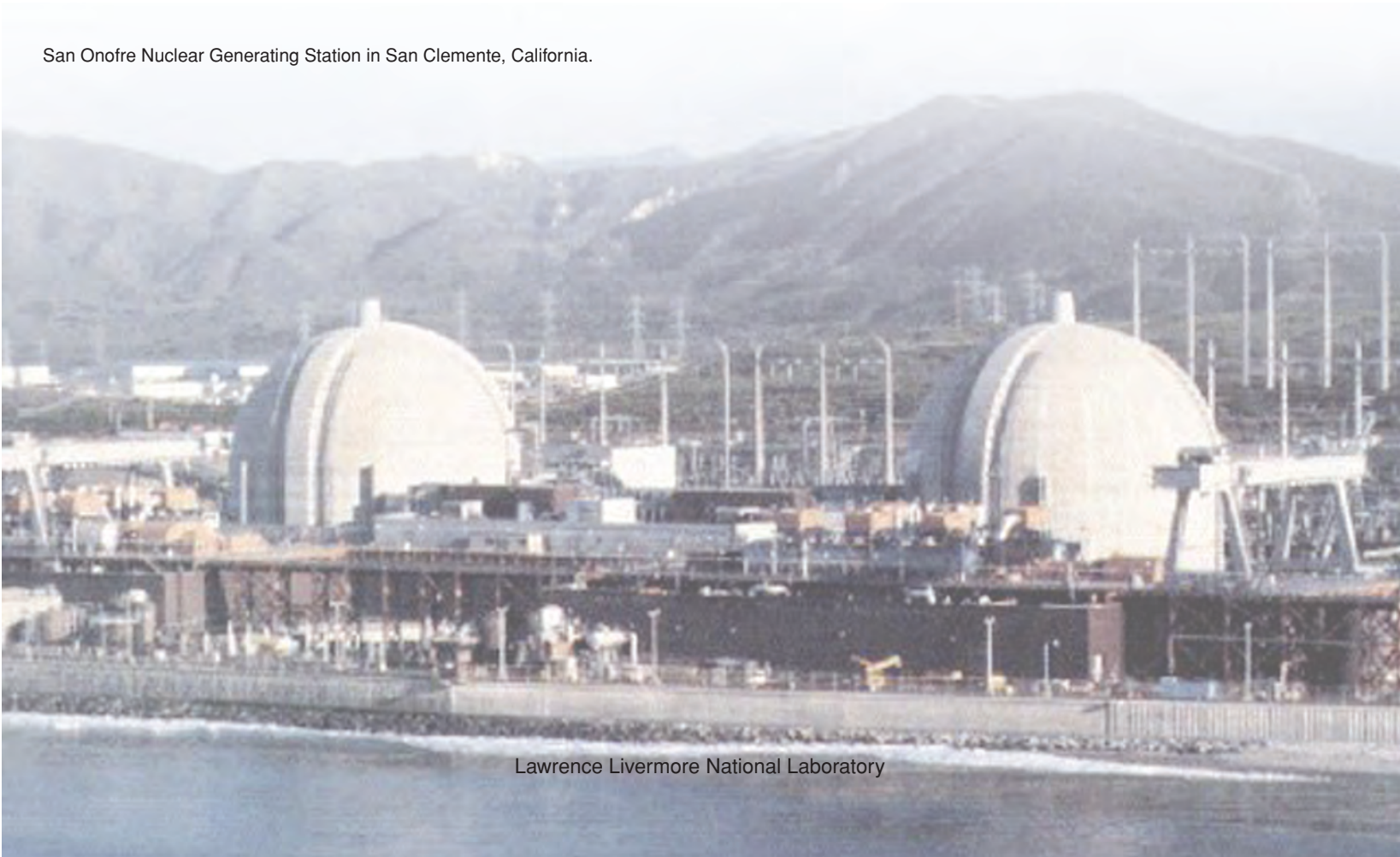
San Onofre Nuclear Generating Station in San Clemente, California.



Each month in this space, we report on the patents issued to and/or the awards received by Laboratory employees. Our goal is to showcase the distinguished scientific and technical achievements of our employees as well as to indicate the scale and scope of the work done at the Laboratory.

Patents

Real-Time Detection Method and System for Identifying Individual Aerosol Particles

Eric Evan Gard, David Philip Fergenson
U.S. Patent 6,959,248 B2
October 25, 2005
A method and system of identifying individual aerosol particles in real time. Sample aerosol particles are compared against and identified with substantially matching known particle types by producing positive and negative test spectra of an individual aerosol particle using a bipolar single-particle mass spectrometer. Each test spectrum is compared to spectra of the same respective polarity in a database of predetermined positive and negative spectra for known particle types. A set of substantially matching spectra is obtained. Finally, the identity of the individual aerosol particle is determined from a set of substantially matching spectra by determining a best-matching one of the known particles types having both a substantially matching positive spectrum and a substantially matching negative spectrum associated with the best-matching known particle type.

Chemical Microreactor and Method Thereof

Jeffrey D. Morse, Alan Jankowski
U.S. Patent 6,960,235 B2
November 1, 2005
A chemical microreactor suitable for the generation of hydrogen fuel from liquid sources, such as ammonia, methanol, and butane, through steam-reforming processes when mixed with an appropriate amount of water contains capillary microchannels with integrated resistive heaters to facilitate the occurrence of catalytic steam-reforming reactions. One such microreactor employs a packed catalyst capillary microchannel and at least one porous membrane. Another employs a porous membrane with a large surface area or a porous membrane support structure containing a plurality of porous membranes having a large surface area in the aggregate, that is, greater than about 1 square meter per cubic centimeter. The packed catalyst capillary microchannels, porous membranes, and porous membrane support structures may be formed by a variety of methods.

Bonded Polyimide Fuel Cell Package and Method Thereof

Jeffrey D. Morse, Alan Jankowski, Robert T. Graff, Kerry Bettencourt
U.S. Patent 6,960,403 B2
November 1, 2005
Described herein are processes for fabricating microfluidic fuel-cell systems with embedded components in which microscale features are formed by bonding layers of DuPont Kapton™ polyimide laminate. A microfluidic fuel-cell system fabricated using this process is also described.

Awards

Climate scientist **Benjamin Santer** received a **Distinguished Scientist Fellowship** for climate-change research from the **Department of Energy's Office of Biological and Environmental Research**. Santer, who works in the Program for Climate Model Diagnosis and Intercomparison, will receive $1.25 million over 5 years, contingent on his continued employment at Lawrence Livermore. The award citation says, "His work is marked by its depth and insight, and he is known for thoroughly exhausting all avenues in his pursuit of a solid answer or conclusion." Santer is a leading scientist in the identification of human-caused climate change using both observations and simulations, and he has contributed to several reports of the Intergovernmental Panel on Climate Change.

Abstracts

Mimicking Nature's Crystalline Structures

Understanding biomineralization processes is key to addressing scientific challenges in areas as diverse as human health, the environment, and materials science. Livermore scientists are collaborating with Virginia Polytechnic Institute, University of California at Santa Barbara, and University of South Alabama to investigate the effects of interactions between biomolecules and calcium carbonate and calcium oxalate surfaces. Using advanced microscopy techniques and molecular modeling, the team found that some proteins significantly accelerate growth and alter crystal shape while others inhibit growth. The researchers have also conducted for the first time molecular studies on kidney stone formation. They demonstrated how two urinary constituents, citrate and the protein osteopontin, inhibit stone formation and growth. When combined, the two also have a greater inhibitory effect on stone growth than either alone. The results of the biomineralization studies may also help in designing ignition capsules for Livermore's National Ignition Facility and in maintaining high explosives for stockpile stewardship. In addition, understanding crystal dissolution mechanisms are important for studies of metal corrosion, a critical issue for the Department of Energy's Yucca Mountain Project.

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Simulating Materials for Nanostructural Designs

The demand to design smaller and smaller devices for science and industry is requiring components that approach nanoscale dimensions. While keeping up with this demand, researchers must also predict how the material's properties and the surrounding environment may change as the device dimensions are reduced. Livermore researchers are using first-principles simulations to model the interaction between water and the materials used to manufacture nanoscale devices such as silicon carbide, graphite sheets, and carbon nanotubes. These materials are increasingly being used to manufacture sensor devices because of the materials' strength and high electrical conductivity. Silicon is also the preferred material for many biological applications because of its compatibility with biological materials.

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U.S. Government Printing Office: 2006/570-077-10015

Technicians Make Things Happen

Technicians, who comprise more than 20 percent of the Laboratory's workforce, are essential to Livermore's success in team-science research and technology development.

Also in March

- *The multichannel x-ray system Hydra records the changes occurring in metals during a high-explosives shock, revealing phenomena not predicted by material models.*
- *High-flying balloon gathers images from x-ray sources that are out of this world.*
- *Measurements of carbon-14 in samples from the Amazon River basin indicate that the cycle time for carbon dioxide may be shorter than scientists had believed.*

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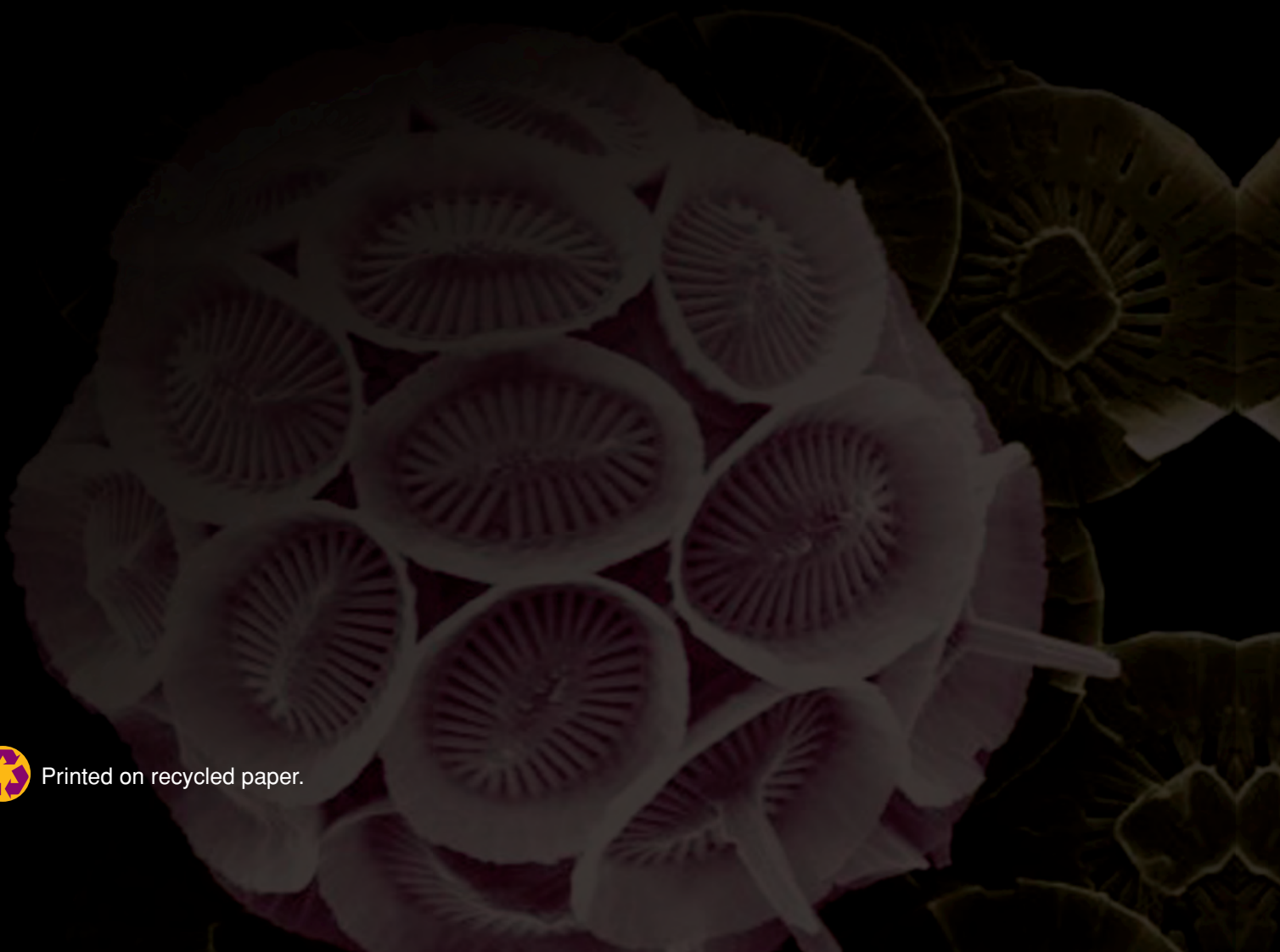

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