Lawrence Livermore National Laboratory

Science & Technology Review

March 2016

Nanomaterials Advance Energy Research

Also in this issue:

Bioprinting Living Tissue

Insulators with a Quantum Spin

Protecting California's Water

About the Cover

Livermore researchers design and develop new materials with novel structures, functions, and properties. As the article beginning on p. 4 describes, the Department of Energy's Office of Basic Energy Sciences (BES) funds a portfolio of six materials research projects that are probing, manipulating, and simulating single atoms and molecules, discrete clusters of atoms and molecules, and large systems containing nanoscale components. One BES-funded effort is striving for a breakthrough in understanding the electrochemical systems in lithium-ion batteries, an important energy technology about which surprisingly little is known at the molecular level. The image on the cover shows a quantum-mechanical simulation of the solid–electrolyte interphase layer, where key reactions occur.

Cover design: Alexandria Holmberg

About *S&TR*

At Lawrence Livermore National Laboratory, we focus on science and technology research to ensure 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 eight 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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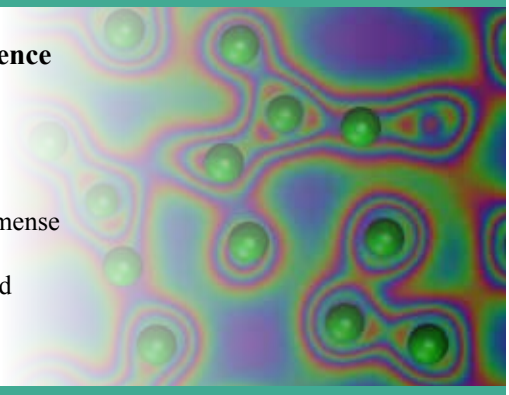

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Protein Curbs Spread of Prostate Cancer to Bone

Scientists from Lawrence Livermore, in collaboration with researchers from the University of California (UC) campuses at Merced and Davis, have found that a specific secreted protein inhibits prostate cancer metastasis to bone. Their research appears in the October 29, 2015, issue of the journal *Microarrays* and in the November 6, 2015, edition of *PLOS ONE*.

If prostate cancer is detected at early stages, the prognosis is favorable, but aggressive forms spread primarily to the skeleton. Bone tumors cause great pain, promote fractures, and ultimately represent the main cause of morbidity, with a 70 percent incidence documented by autopsies. Aimy Sebastian, a UC Merced graduate student conducting her Ph.D. thesis work under Livermore's Gabriela Loots (both are shown in the above photograph), led a study that identified the secreted bone protein sclerostin (SOST) as a key molecule dysregulated as a result of prostate cancer–bone microenvironment interactions. This study, published in *Microarrays*, shows that the lack of SOST in the bone microenvironment promotes the expression of genes associated with cell migration and invasion, including those in prostate cancer, suggesting that SOST has an inhibitory effect on prostate cancer invasion.

A second study, which included Livermore biomedical scientist Nicholas Hum, looked into the role of SOST in regulating prostate cancer invasion and metastasis. They found that prostate cancer cells producing more SOST had significantly lower rates of metastasis. With the help of UC Davis assistant professor Blain Christiansen, they also found that cells expressing more SOST induced significantly less osteolytic bone loss. These results provided strong evidence that SOST has an inhibitory effect on prostate cancer metastasis to bone.

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Using Hydrogen to Enhance Lithium-Ion Batteries

Lawrence Livermore scientists have found that hydrogen-treated graphene nanofoam electrodes in lithium-ion batteries show higher capacity and faster transport. A paper on their research appears in the November 5, 2015, edition of *Nature Scientific Reports*. "The performance improvement we've seen in the electrodes is a breakthrough that has real-world applications," says Jianchao Ye, a Livermore materials scientist who is lead author of the paper.

A lithium-ion battery is a rechargeable battery in which lithium ions move between the negative electrode to the positive electrode during discharge and recharge. The capacity, voltage, and energy density of lithium-ion batteries are ultimately determined by the binding between lithium ions and the electrode material. That binding can be affected by subtle changes in an electrode's structure, chemistry, and shape.

To study the involvement of hydrogen and hydrogenated defects in the lithium storage ability of graphene, Livermore scientists applied various heat treatment conditions combined with hydrogen exposure and looked into the electrochemical performance of three-dimensional graphene nanofoam electrodes, which are comprised mostly of defective graphene. The team's experiments and multiscale calculations show that low-temperature treatment of defect-rich graphene with hydrogen can improve rate capacity. Hydrogen reacts with the defects in the graphene, opening small gaps to facilitate easier lithium penetration, which improves the transport. Because hydrogen is most likely to bind near edges, lithium binding is enhanced in those areas, providing additional reversible capacity.

The Livermore team's research suggests that controlled hydrogen treatment may be used as a strategy for optimizing lithium transport and reversible storage in other graphene-based anode materials such as those used in electric vehicles and aerospace technologies.

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Scientists Discover Shifts in Climate-Sensitive Plankton

New research by Lawrence Livermore scientists and colleagues at the University of California at Santa Cruz, University of Colorado, and University of Kiel in Germany has revealed distinct differences in the ways plankton have responded to climate over the last thousand years. These results can be found in the November 26, 2015, edition of the journal *Science*.

Deep-sea corals act as living sediment traps, filtering out sinking organic matter that reaches them from the ocean surface before it is remineralized. That organic matter is known as export production. The components of phytoplankton organic matter are recorded in the growth bands of deep-sea coral skeletons. Thus a coral's skeleton acts as a strip-chart reminder of what the coral has fed upon, enabling researchers to reconstruct the relative contribution of different phytoplankton groups to the export production back through time.

The researchers found that the North Pacific Subtropical Gyre—a system of ocean currents that is also the largest continuous ecosystem on Earth—has undergone major shifts in phytoplankton community composition associated with large-scale regional climate change. An increase in nitrogen-fixing cyanobacteria over the last 150 years has resulted in greater food production by phytoplankton, which are making their own nitrogen-based fertilizer out of dissolved nitrogen. However, as the oceans have warmed, the surface water of the gyre has become more stable and allows fewer nutrients from below—including nitrogen—to be incorporated into the surface layer, where phytoplankton need nitrogen to grow and continue taking up carbon from the atmosphere. Therefore, although phytoplankton may have inhibited rising carbon dioxide levels over the last 100 years, "we cannot expect this to be the case in the future," says author Tom Guilderson. Climate change is predicted to continue to alter marine phytoplankton communities and affect productivity, biogeochemistry, and the efficacy of the biological pump.

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Commentary by Patricia Falcone

At the Forefront of Materials Science

ADVANCES in materials improve our lives, strengthen national security, and drive economic growth. Understanding, developing, and predicting the performance of advanced materials are an essential part of the job for Lawrence Livermore scientists and engineers working in programs ranging from the National Nuclear Security Administration's Stockpile Stewardship Program to lasers and clean energy. Over the past decade, the Laboratory's expertise in materials science has been driven largely by needs of researchers working at the National Ignition Facility and in stockpile stewardship. These scientists and engineers search for new materials with extraordinary properties and for an enhanced understanding of how materials behave under extreme conditions.

As the article beginning on p. 4 describes, Livermore currently has a portfolio of six research efforts funded by the Department of Energy's (DOE's) Office of Basic Energy Sciences (BES), the largest of the six divisions in DOE's Office of Science. BES research programs lead to new materials and chemical processes that are critical for all facets of energy production and storage. The competition for BES funding is fierce, and the work featured in the article is testimony to the very high quality of scientific research conducted at Livermore.

Together, Livermore's six BES-supported efforts reflect the three themes that characterize all BES research: time-, space-, or energy-resolved investigations of materials; control of materials at the nanometer scale (a billionth of a meter); and predictive modeling and simulations. One project's focus is using a Livermore-designed instrument that takes real-time snapshots of dynamic processes in materials. Other projects focus on understanding alloys that are resistant to radiation and thermal damage; designing and synthesizing materials and components that mimic those found in human cells; and developing advanced simulation tools that model and predict materials properties at the quantum level.

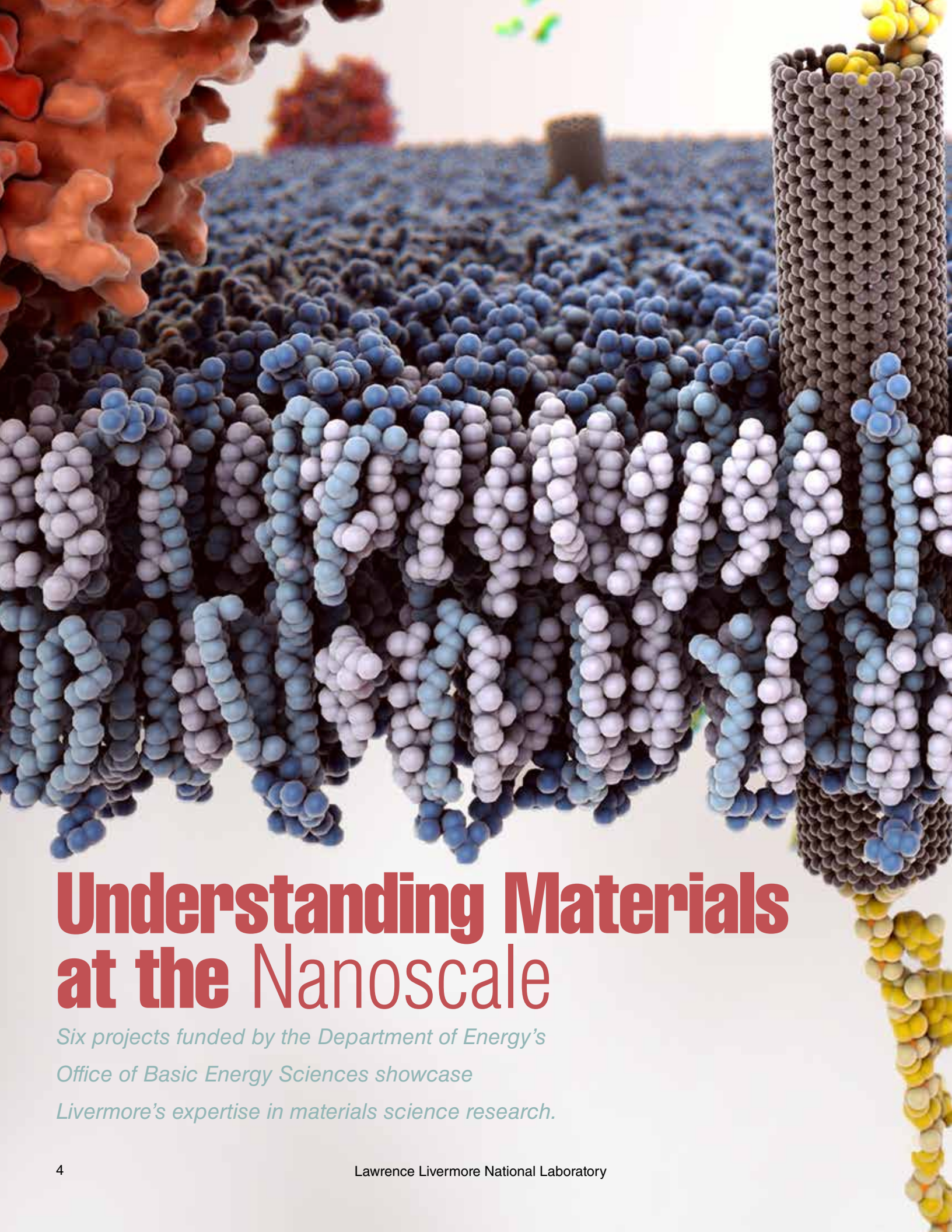
The BES-funded projects align with Lawrence Livermore's longstanding effort to understand materials at the molecular and atomic scales, especially under extreme pressure and temperature; design and manufacture new materials with unique properties; and find novel applications for these materials. Livermore-born products include specialty materials for carbon sequestration and desalinization, as well as substitutes for rare-earth elements in clean-energy products.

Besides funding hundreds of top researchers nationwide, BES also provides scientists with the latest generation of experimental tools, including the world's largest suite of synchrotron radiation light source facilities, neutron-scattering facilities, and electron-beam microcharacterization centers. Every year, more than 14,000 scientists and engineers use these capabilities to probe the properties of materials critical to fields ranging from geology to biology. Livermore researchers regularly use several large BES facilities, including the Advanced Light Source at Lawrence Berkeley National Laboratory, Argonne National Laboratory's Advanced Photon Source, and the Linac Coherent Light Source at SLAC National Accelerator Laboratory. At these centers, our scientists and engineers study high-energy-density states of matter—the physical conditions of materials in domains of great interest.

In addition to advancing our understanding of interactions of atoms and molecules in important domains, Livermore scientists have also made significant accomplishments in materials synthesis over the past decade. Livermore progress in advanced manufacturing technologies includes a variety of approaches to additive manufacturing, also known as three-dimensional printing, which enables the construction, layer by layer, of materials with previously unachievable properties. Our goal is also to accelerate the discovery of new materials, guided by powerful supercomputers running the latest molecular dynamics simulation codes. As well as the new materials themselves, we also want to make our advances in simulation and modeling available to the broader materials science community.

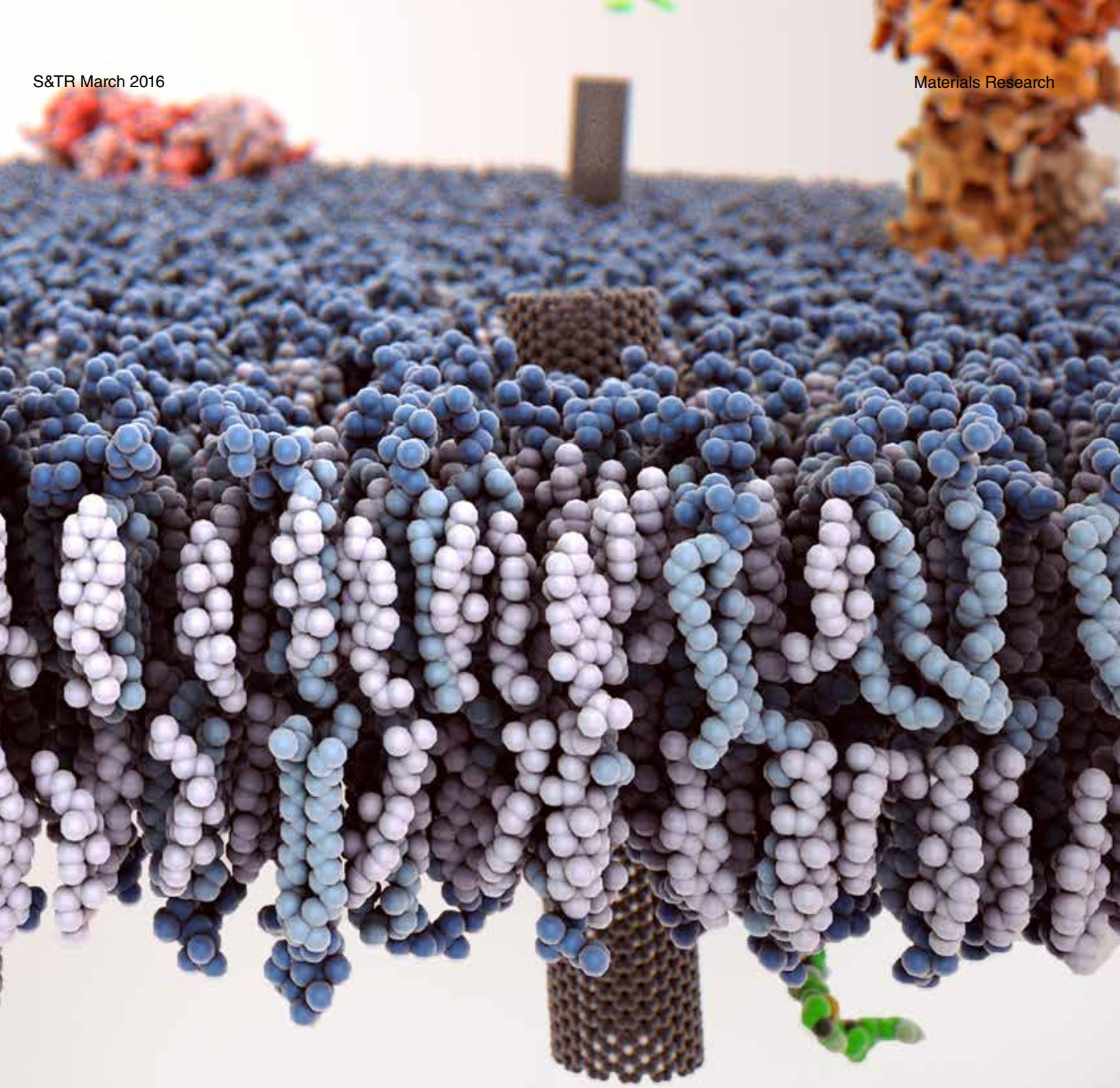
Opportunities such as this BES work enhance our capabilities in fundamental scientific research and support our national security missions. Support for basic research also helps to maintain a vibrant research environment here at the Laboratory and strengthens our recruitment of talented individuals, particularly promising young scientists. We value our work for BES tremendously, and we are striving to become more deeply involved in the vigorous basic science community that BES supports. Pushing the forefront of materials science is sure to provide more efficient and cost-effective clean-energy technologies, as well as strengthen our competencies in other mission areas.

■ Patricia Falcone is deputy director for Science and Technology.



Understanding Materials at the Nanoscale

Six projects funded by the Department of Energy's Office of Basic Energy Sciences showcase Livermore's expertise in materials science research.



In this rendering, a target molecule (yellow) passes through a nanotube porin (light brown) deliberately embedded in a cell membrane to introduce such molecules into a cell body. (Image courtesy of Scripps Research Institute.)

OVER the past 60 years, Lawrence Livermore scientists and engineers have successfully found materials solutions to a wide range of challenges in national security, including energy and environmental security. The development of new materials and manufacturing processes has long been recognized as the engine driving new scientific and technological innovations in these fields.

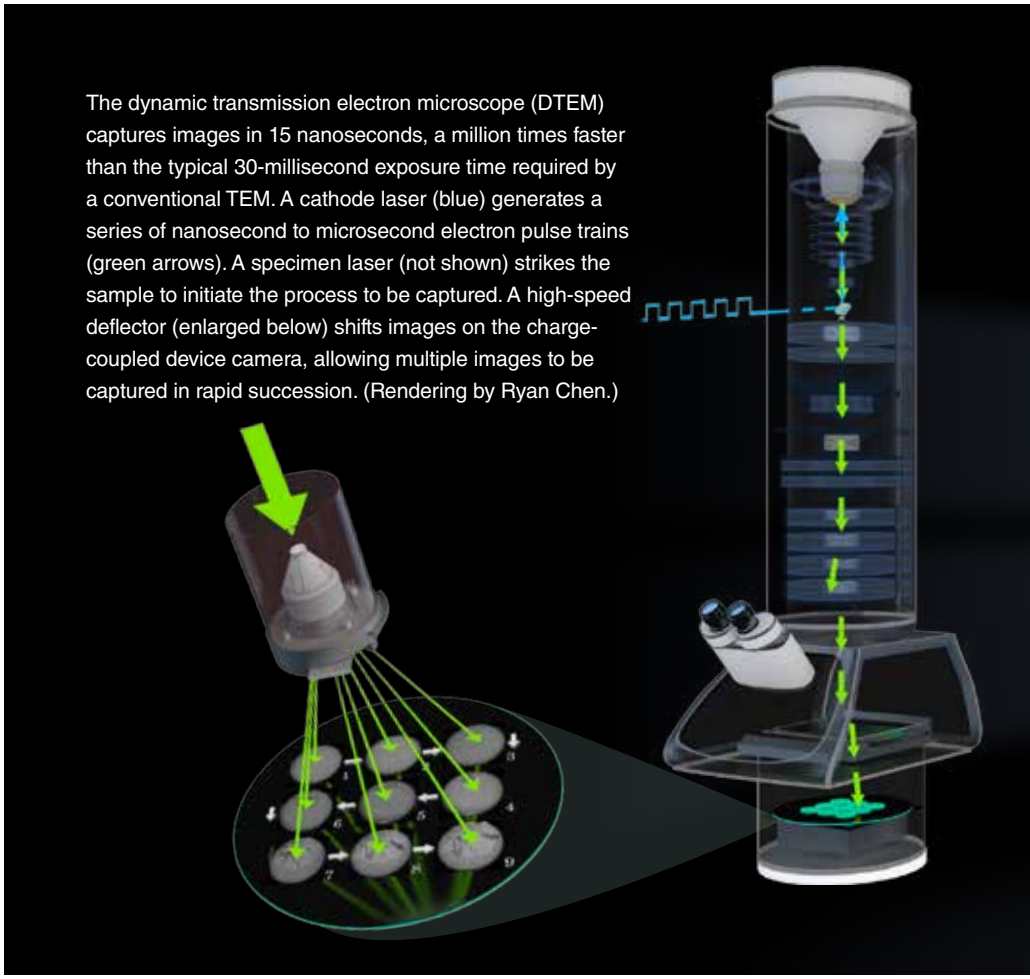
Livermore researchers routinely design and develop new materials with novel structures, functions, and properties, along with innovative methods for materials synthesis and manufacturing. Laboratory researchers are currently developing components with previously unobtainable properties, such as high stiffness combined with low density. (For example, one Livermore-developed

lightweight material can withstand a load of at least 160,000 times its own weight.) Current research thrusts include validated predictive models, atomic-scale characterization, materials synthesis and assembly, and advanced manufacturing, including three-dimensional (3D) additive manufacturing.

A portfolio of six materials research projects at Livermore is funded by the Department of Energy's (DOE's) Office of Basic Energy Sciences (BES). BES funds work at more than 160 research institutions nationwide and operates major scientific user facilities. BES supports fundamental research to understand, predict, and control matter at the atomic and molecular levels in the fields of condensed matter and materials physics, chemistry, geosciences, and aspects of physical biosciences. All efforts are focused on discovering new materials and chemical processes.

The six Livermore BES projects fall under three thematic areas: time-, space-, and energy-resolved materials investigations; nanoscale control of functional materials; and predictive modeling and simulations. These projects are strongly aligned with Livermore's motto of "Science and Technology on a Mission." Says Livermore physicist Eric Schwegler, "The Laboratory conducts much basic-science research in materials as a strategic investment because in the long term it aids our diverse national security missions. Scientific and technological breakthroughs have historically originated with basic-science activities."

The six projects also dovetail with several efforts in materials science funded by Livermore's Laboratory Directed Research and Development (LDRD) Program, which is designed to anticipate future national security needs and avoid technological surprise from adversaries. Together, the BES and LDRD efforts comprise part of the Laboratory's materials strategy, particularly its Accelerated Materials and Manufacturing Initiative. This initiative is aimed at accelerating the design, fundamental understanding, and deployment of new manufacturing processes and new materials with novel structures, functions, and properties. These endeavors draw together not only postdocs and graduate students working at Livermore but also collaborators at other national laboratories and universities.

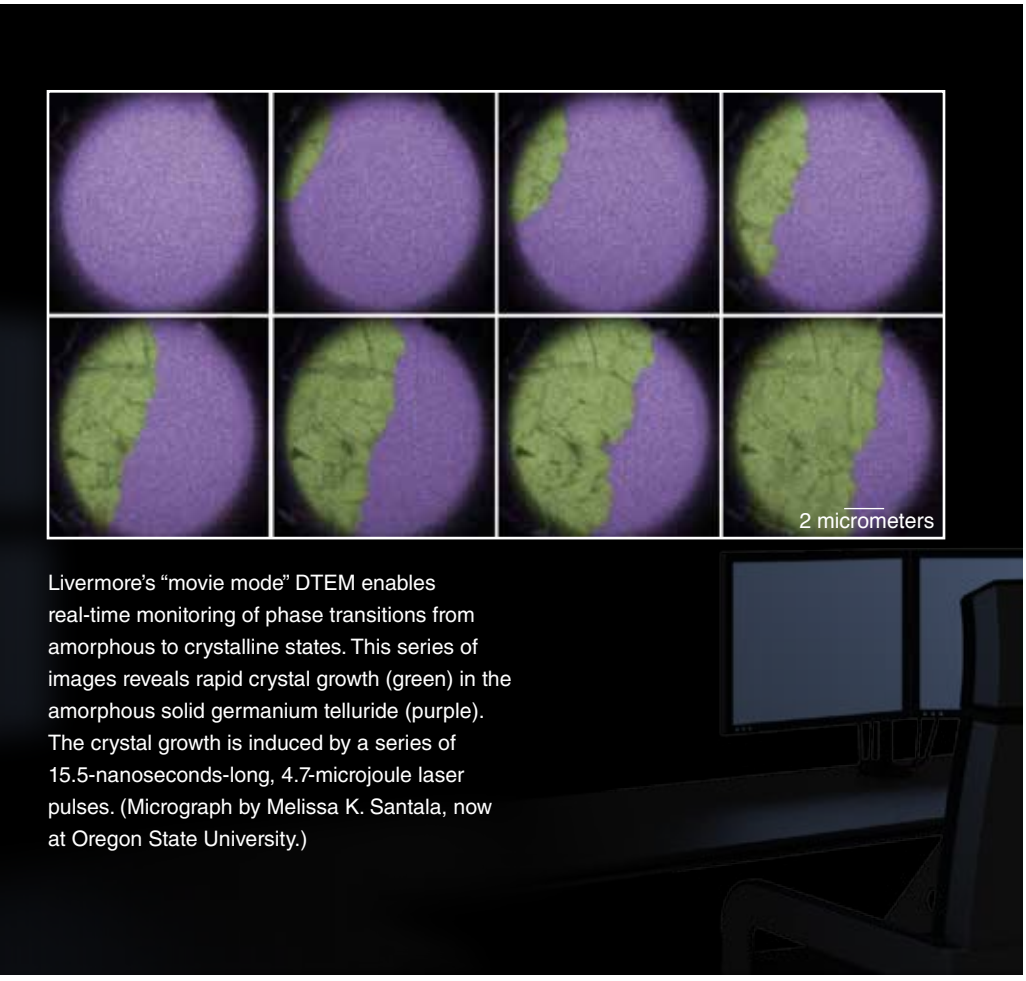


The dynamic transmission electron microscope (DTEM) captures images in 15 nanoseconds, a million times faster than the typical 30-millisecond exposure time required by a conventional TEM. A cathode laser (blue) generates a series of nanosecond to microsecond electron pulse trains (green arrows). A specimen laser (not shown) strikes the sample to initiate the process to be captured. A high-speed deflector (enlarged below) shifts images on the charge-coupled device camera, allowing multiple images to be captured in rapid succession. (Rendering by Ryan Chen.)

Much of the research is conducted at the subnanometer (less than one billionth of a meter) scale—the level of atoms and electrons. New scientific understanding and technologies are emerging through the probing, manipulation, and simulation of single atoms and molecules, discrete clusters of atoms and molecules, and large systems with nanoscale components.

Solid–Solid Transformations

Materials can undergo phase transformations—rearrangements in their crystal structure—in their solid state as a result of changes in temperature or pressure. A few metals, such as iron, can undergo several solid-to-solid phase changes before they melt. Studies of solid–solid phase transformations have been conducted since the Industrial Revolution, sparked by the discovery that different processes confer different properties, such as strength and resistance to corrosion. Today, modern tools such as the Livermore-designed dynamic transmission electron microscope (DTEM) permit, for the first time, detailed understanding and characterization of dynamic processes in materials as they take place, in particular rapid phase transformations and crystal growth (see *S&TR*, September 2013, pp. 4–11).



Livermore's "movie mode" DTEM enables real-time monitoring of phase transitions from amorphous to crystalline states. This series of images reveals rapid crystal growth (green) in the amorphous solid germanium telluride (purple). The crystal growth is induced by a series of 15.5-nanoseconds-long, 4.7-microjoule laser pulses. (Micrograph by Melissa K. Santala, now at Oregon State University.)

"We're interested in how quickly solid–solid transformations occur," explains Livermore metallurgist Geoff Campbell. Understanding these phase transformations and learning how to manipulate them could lead to breakthroughs in how materials can be processed to yield new attributes. Campbell is working with Livermore researchers Joseph McKeown and postdoc Tian Li on a BES-funded project to study the dynamics of phase transformation (nucleation and growth), microstructure, and thermodynamics in nanoscale systems evolving on timescales of nanoseconds to microseconds.

The Livermore team is investigating, at the nanoscale, the physical mechanisms and kinetics controlling solid–solid phase transformations, concentrating on the crystallization of amorphous solids, such as germanium. This type of solid lacks the long-range order found in crystals but may exhibit order on the short (nearest neighboring atom) or medium (several nearest neighboring atoms) range. Dynamic imaging or "movie mode" DTEM enables phase transitions from amorphous to crystalline states to be monitored in real time. Investigators acquire consecutive images—only 120 nanoseconds apart—of the microstructure of amorphous solid germanium evolving under heat or pressure. "We can see the nucleus of a new phase appear and grow with each frame," says Campbell. Successive images track and quantify the nucleation and growth of the crystalline microstructure.

The kinetics of phase transformations are influenced by the initial amorphous structure. The researchers are using sputtering and bombardment with argon ions to create thin films of germanium, with each method resulting in a different amorphous structure. The team then uses fluctuation electron microscopy (FEM) to characterize the structure of amorphous solids formed under different conditions. FEM measures the medium-range order needed to distinguish amorphous states from one another.

In collaboration with Schwegler's group, Campbell's team is conducting quantum simulations that are informed by the FEM data with the goal of finding the atomic arrangements (seeds) responsible for the changes in crystal growth rate. "The simulations help us understand the relative internal energies of different microstructures," explains Campbell. "We compare the observed differences in the kinetics with the predictions of simulations to reveal fundamental controlling mechanisms for the solid transformation process."

Radiation-Resistant Materials

Advanced nuclear energy reactors will require materials to perform for long periods in elevated temperatures and high-radiation conditions. Conventional engineered metals and alloys lack the required microstructural stability in the extreme environments envisioned for future reactor designs.

Crystalline metals are collections of grains arranged irregularly, with each grain oriented differently in space. Each grain represents a small single crystal ranging in size from nanometers to centimeters. Where two or more grains meet is called a grain boundary. Together, grain boundaries form an interconnected network, akin to a crude skeleton (see *S&TR*, December 2014, pp. 16–19). The 3D arrangement of the grain boundaries, and how they interact, affects a material's mechanical,

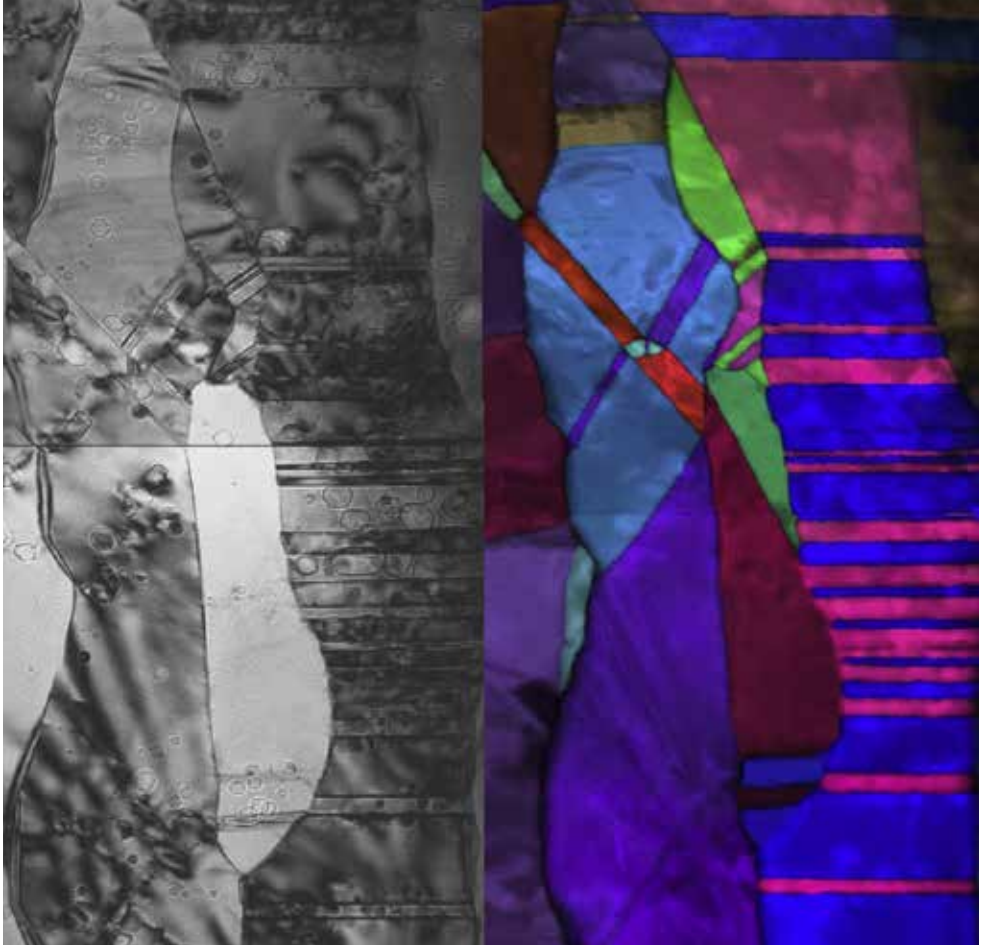
thermal, chemical, and electrical properties, including its tendency to crack or corrode. As a result, controlling the types and arrangement of grain boundaries offers the possibility of tailoring a material's properties to withstand harsh radiation and thermal environments, for instance.

In another BES-funded effort, Livermore researchers Mukul Kumar and Vasily Bulatov are hoping to help scientists and engineers design new materials for next-generation nuclear reactors. Using transmission electron microscopy, scanning electron microscopy, and 3D high-energy x-ray diffraction microscopy, the team generates microscopy data and compares the results with advanced simulations. The researchers are working mainly with copper, which has a face-centered-cubic structure, meaning atoms are located at each of the corners and centers of all the cubic faces. Many common metals and alloys, such as austentic stainless steels and nickel-based superalloys, share this grain structure.

Kumar explains that microstructures evolve as boundaries move in response to external factors such as heat—some grains grow, others shrink. The net effect is fewer but larger grains. When subjected to radiation, point defects appear and move around in the crystalline lattice. These defects can reach grain boundaries and annihilate one another, or they can combine and eventually form a large void, distorting the metal.

The team previously showed that grain-boundary networks in polycrystalline microstructures can be stabilized against thermal damage. Researchers are currently studying whether optimized networks can also enhance microstructural stability in a high-radiation environment. Kumar's vision is a boundary network in which high-free-energy (random) grain boundaries act as efficient "sinks" for radiation-induced defects, while more stable boundaries anchor the network.

Experiments by Kumar's team showed that nanocrystalline materials exhibit poor stability under high temperatures and do not survive radiation damage, either. "People had thought that nanomaterials' extremely small grain boundaries would be sufficient to resist radiation damage," says Kumar. However, many ways exist to combine grains, and some combinations are more susceptible to radiation damage than others. "We need to combine some boundaries that absorb defects with those that resist movement and can limit any cracks that appear," he explains.



(left) A TEM image shows the topology of grain boundaries in nanocrystalline copper subjected to radiation-resistance testing. (right) Arbitrary colors used to highlight grains reveal radiation-induced voids clustering near the highly ordered, parallel-sided boundaries of grains colored magenta.

Determining microstructure properties requires proper modeling. The team modified existing quantum Monte Carlo (QMC) simulation codes to better represent the physics of grain boundary evolution. They developed a highly sensitive model that permits the study of a vast configuration of grain boundary networks to fully understand the composition of boundaries that confer thermal and radiation resistance.

Mimicking Nature's Molecules

An important part of Livermore's BES portfolio is biomimetic materials research, which focuses on designing and synthesizing materials with properties that are found only in nature—such as self-repair and adaptability to changing environments—or that mimic biological functionality using different molecular scaffolds. This project's emphasis is on creating robust and scalable materials and systems that work with the effectiveness of the molecules and processes of the biological world. Possible applications of biologically inspired synthetic materials include sensors, membranes for pharmaceutical filtration, drug delivery, platforms for nanofluidic studies, bioelectronic interfaces, and artificial cells.

One focus of the project is developing synthetic biomimetic pores called carbon nanotube porins, which mimic the characteristics of biological channels, in particular their transport functions

and their ability to self-assemble into a range of membrane systems. The project uses an array of transport studies to understand pore permeability, along with small-angle x-ray scattering and scanning transmission x-ray microscopy to probe the porins' atomic-level structures. This work seeks to understand the fundamental characteristics of the transport of biomolecules in a fully synthetic scaffold. The Livermore-led team includes Alex Noy, Tony Van Buuren, Jonathan Lee, postdocs Huanan Zhang and Ramya Tunuguntla, and Lawrence Fellow Tuan Anh Pham, as well as collaborators from Lawrence Berkeley and Pacific Northwest national laboratories, the University of California (UC) at Davis, and Spain's University of the Basque Country.

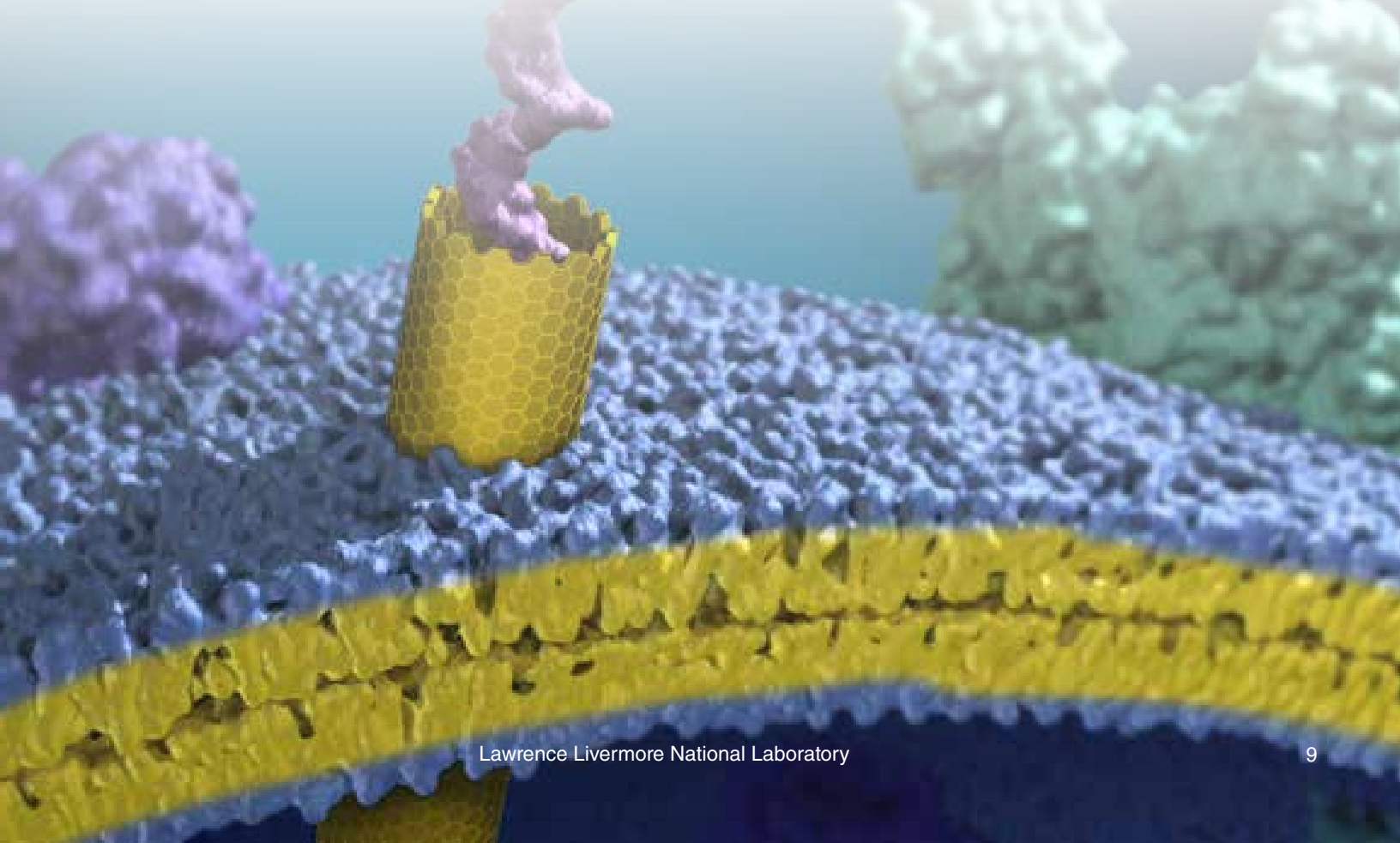
Physical chemist Noy's team has demonstrated that carbon nanotubes can be coaxed to form functional pores in biological membranes. Carbon nanotubes already have smooth and narrow pores that enable efficient transport. To convert them into nanotube porins, Noy's team dices them into very short segments and combines them with lipid molecules. The result is a dimensionally and functionally similar synthetic analogue of a biological channel (see *S&TR*, June 2015, pp. 16–19). "We can learn from nature," observes Noy, "but we don't necessarily have to imitate it."

Natural and synthetic ion channels can also act as components of much more complicated systems that convert ionic signaling into an electrical response. To make such systems possible, the team developed a bioelectronics device platform in which a silicon nanowire transistor is shielded by a lipid bilayer membrane. Researchers then inserted light-driven proton pumps—bacteriorhodopsin proteins—into the bilayer. Light caused the protein to pump protons toward the nanowire, which in turn produced changes in the output current of the nanowire transistor. Similar biologically controlled devices that seamlessly integrate biological functionality into electronic circuits could find uses in future generations of interfaces between people and machines.

Starting from First Principles

Schwegler, leader of Livermore's Quantum Simulations Group, notes that predictive simulation tools are playing an increasingly important role in Livermore's materials research. The term "quantum simulations" refers to the use of computational methods that provide numerical solutions to the fundamental laws of quantum mechanics in an approximate yet nonempirical manner. Progress in quantum simulations of condensed and molecular systems, combined with the development of algorithms and optimized codes running on

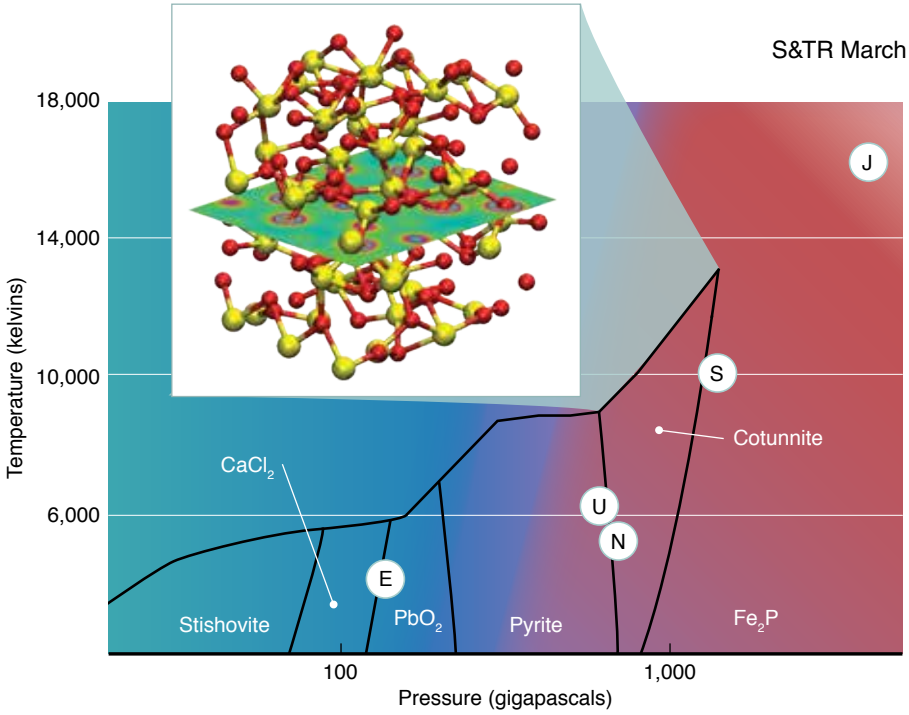
Livermore-developed carbon nanotubes spontaneously insert into both artificial and natural cell membranes, reproducing the functions of biological channels. In this rendering, a carbon nanotube (yellow) has inserted into a cell membrane (blue and yellow), with a single strand of DNA passing (violet) through the nanotube. (Image courtesy of Xavier Studios.)



high-performance computers, has opened the possibility of using truly predictive simulation tools to address the complexity of materials at the microscopic level. Numerous properties can now be inferred directly without input from experiment.

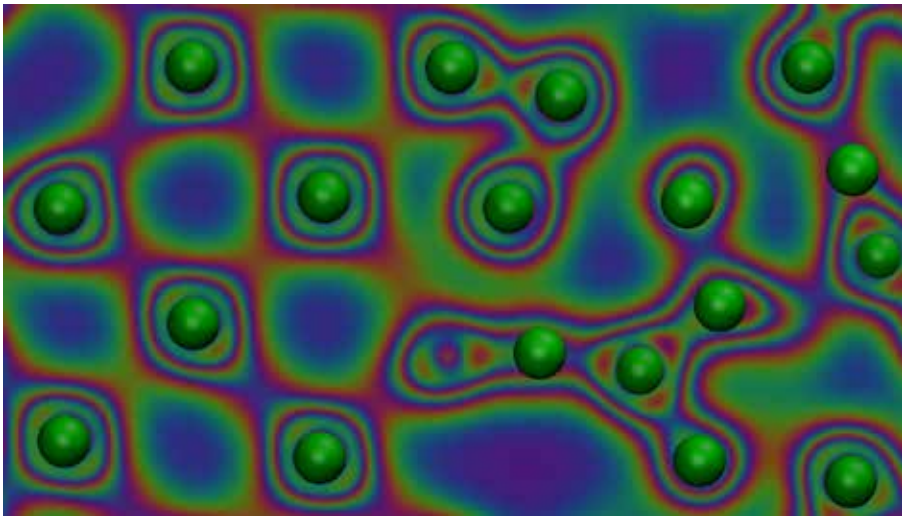
The main supercomputer codes that Livermore scientists use to model materials at the quantum level are based on density functional theory and QMC techniques. Both approaches start from first principles—that is, with no input other than the laws of quantum mechanics. Density functional theory is based on a Hohenberg–Kohn theorem positing a one-to-one correspondence between the electron density and energy of a system. Determining electron density therefore makes it possible to determine a wide range of properties—such as the forces acting between atoms—which in turn can be input into a molecular dynamics simulation to describe the system's motion in time. Together, these simulations provide an accurate, atomic-scale model of matter for applications in chemistry, materials science, and nanotechnology.

A BES-funded project at Livermore, UC Davis, and the University of Chicago is focused on advancing a high-performance, open-source software infrastructure called Qbox. Downloadable free of charge and in use at major supercomputer centers everywhere, Qbox is increasingly used as a predictive tool in the exploration of properties of new materials for batteries, solar energy conversion, light-emission devices, dielectric materials, and phase-change materials for optical storage.



A phase diagram of silicon dioxide (SiO_2) as revealed by quantum-mechanics simulations shows that as SiO_2 compresses, it goes through different solid phases having crystal structures that correspond to the compounds listed, including calcium chloride ($CaCl_2$), lead dioxide (PbO_2), and iron phosphide (Fe_2P). Circled letters stand for Earth, Uranus, Neptune, Saturn, and Jupiter and indicate the pressure and temperature believed to exist at each planet's center. (inset) Yellow and red represent silicon and oxygen, respectively, in the cotunnite-type crystal structure of SiO_2.

Schwegler is working with postdoc Amit Samanta to implement advanced sampling algorithms that direct Qbox to find and characterize rare reactions. For example, theoretical analyses of phase transition mechanisms (such as solid to liquid) are often not feasible with standard simulation methods because such transitions involve rare events that take place over time periods many orders of magnitude greater than a supercomputer can accommodate. Using the group's newly developed algorithms, Qbox can



Advanced sampling algorithms developed for use with the Qbox quantum simulation code look for rare reactions of interest to researchers. A simulation depicts germanium transitioning suddenly from an ordered crystalline solid to a disordered liquid in response to heat. Green represents germanium atoms. Red and blue represent a high probability and zero probability of electrons, respectively.

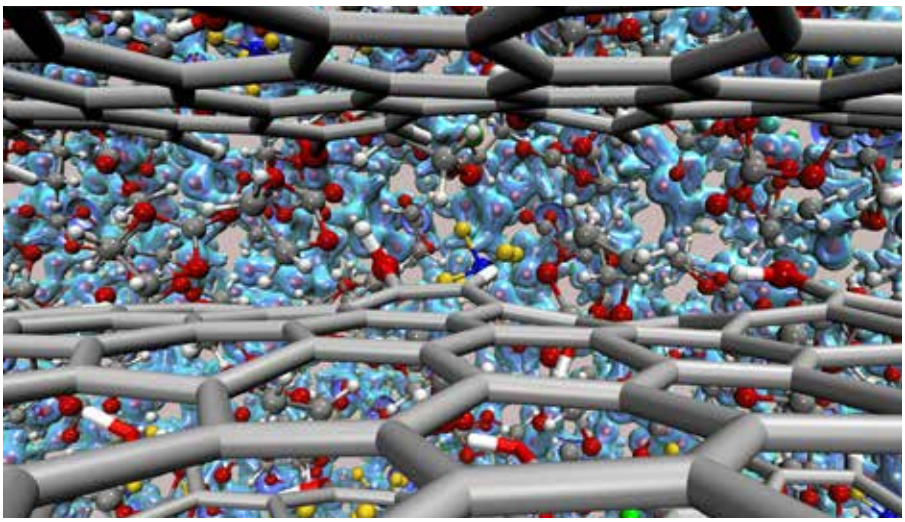
overcome the time limitations of even the most powerful supercomputers with a methodology that is far more computationally efficient than a typical "brute force" approach. Schwegler sees the advanced algorithms accelerating the process of discovery and optimization of new materials properties in the immediate term and, in the longer term, producing data that will be passed to specialized codes designed to work on longer time and length scales. One benefit of this approach would be the ability to predict how materials are likely to perform over decades of use.

Two Computational Breakthroughs

The popular lithium-ion battery is found in products ranging from electric cars to laptop computers. In this battery, the negative electrode is made of graphite, the positive electrode of a metal oxide, and the electrolyte a lithium salt dissolved in an organic solvent. The functioning of the battery depends on the movement of lithium ions between the electrodes. "We aim to achieve a breakthrough in understanding these electrochemical systems," declares Livermore physicist John Pask, who leads an effort including Livermore's Vincenzo Lordi, Erik Draeger, and postdoc Mitchell Ong, along with collaborators from Lawrence Berkeley National Laboratory and UC Berkeley. Divided into two parts, the effort is funded by both BES and the Advanced Scientific Computing Research Program, through the Scientific Discovery through Advanced Computing Program, known as SciDAC.

In the first part, the researchers are developing and implementing two computational breakthroughs in electronic structure methods: discontinuous Galerkin (DG) and pole expansion and selected inversion (PEXSI). Working together, DG and PEXSI overcome the traditional computational bottlenecks faced when researchers attempt to simulate large numbers of atoms using quantum-mechanical methods. The DG technique collapses the size of the matrix problem that must be solved by including both atomic and local-environmental physics into the computation. The PEXSI methodology directly computes electronic density, total energy, and ionic forces without computing individual electronic orbitals, eliminating the usual cubic scaling of solution time with the number of atoms, which has severely limited the physical systems to which quantum mechanics can be applied.

In developing the DG–PEXSI approach, the team first focused on advancing Qbox—increasing its speed and the number of atoms it can simulate—and using the enhanced Qbox code to verify DG–PEXSI at every stage. The team is close to achieving the scales of length (10,000 atoms) and time (50 picoseconds) needed to obtain a detailed quantum-mechanical understanding of the solid–electrolyte interphase layer in lithium-ion batteries, the second main thrust of the project. Progress in improving these batteries has been hindered by an incomplete understanding of the formation and evolution of this critical layer between anode and electrolyte. "No one understands what's going on at the interfaces," says Pask. He explains that although most research is based on experiments, the chemistry is extremely complicated. "To really understand what's going on in the solid–electrolyte interface and other complex, mixed-phase systems, we need quantum-mechanical methods," states Pask. By making quantum-mechanical calculations possible at the necessary length and timescales, DG–PEXSI promises to pave the way for breakthroughs in battery performance, lifetime, and safety. The team's calculations have already shown that the more tightly ions are solvated in an electrolyte, the lower their mobility, contrary to what may be expected based on chemical theory. This discovery alone has the potential to advance the design of lithium-ion battery electrolytes. When complete, DG–PEXSI will be available as open source so that researchers around the world will be able to solve



Livermore's new methodology combining the discontinuous Galerkin (DG) and pole expansion selected inversion (PEXSI) electronic structure methods depicts the interface of a graphite anode (hexagonal mesh) and an electrolyte in a lithium-ion battery. The distance between graphite layers is about 2 nanometers. The DG–PEXSI code promises to obtain a detailed quantum-mechanical understanding of the critical reactions that occur at the anode.

large quantum-mechanical problems currently inaccessible and with less required computation.

Advanced QMC

In the world of simulation, getting as close to reality as possible involves an approach called QMC, which computes the electronic structure of atoms, molecules, and solids to accurately solve Schrödinger's differential equations. Although broadly used to understand the thermodynamic properties of materials, the approach is very expensive in terms of computational horsepower. Miguel Morales-Silva is part of a broad BES-funded effort to develop a next-generation implementation of QMC, called QMCPACK (for "QMC package"), based on continuum real-space QMC. The group is building a platform for theoretical development, broad scientific application, and use in changing computing environments. "QMC used to be a method only for experts," says Morales-Silva. "We want it to become a routine tool for general calculations." The effort includes scientists from Oak Ridge and Argonne national laboratories; Sandia National Laboratories in Albuquerque; and the University of Illinois Urbana-Champaign. At Livermore, Randy Hood, postdoc Roman Nazarov, and graduate student Raymond Clay are also contributing.

QMC methods are first being applied to catalysis, defects, and materials under high pressures, reflecting the research interests of the collaborating institutions. For Livermore, that means determining the equations of state (the relationship between pressure, density, and temperature) of light elements such as hydrogen and hydrogen–helium mixtures, but researchers are working to extend the code's applicability to very heavy elements. Another goal of the project is ensuring that the advanced code keeps up with changing architectures in high-performance computing. For example, newly emerging supercomputers are based on specialized graphics processors instead of central processing units.

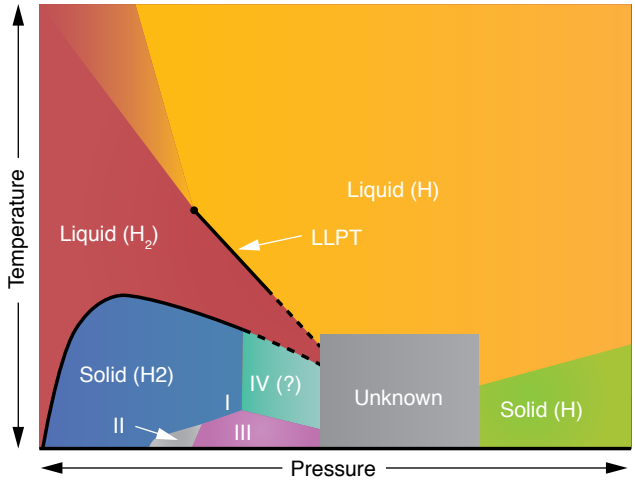
The group is also working to make the code available to a much larger and nonexpert population of investigators. They have made several public releases of the open-source QMCPACK code and developed a QMCPACK website (www.qmcpack.org). The new releases include automation tools that significantly enhance productivity for new and expert users. In 2014, the group organized a training workshop for postdocs and graduate students at Argonne. Another workshop is planned for 2016 at the University of Illinois Urbana-Champaign. In addition, smaller workshops are held regularly for experts in the field.

The outcome of this collaboration is sure to increase productivity and fundamentally alter how QMC data are produced and used by the materials and chemistry community at large. "Our work will provide direct answers to fundamental materials science questions and establish benchmark levels of accuracy," says Morales-Silva.

The Immense Challenges Ahead

The six BES-funded projects at Livermore are an attempt to tackle immense scientific challenges associated with accelerating the fundamental understanding, design, and deployment of new materials and manufacturing processes. The goals are ambitious. For example, advances in simulation and modeling aim to one day enable "chemistry by design" across multiple time and length scales. Livermore researchers are acutely aware that materials and biomaterials research are the foundation for advancing national security and quality of life.

—Arnie Heller



Quantum Monte Carlo calculations are helping to better define the phase diagram of hydrogen (H). Livermore researchers are focusing on the liquid–liquid phase transition (LLPT) from a molecular liquid (H_2, an insulator) to atomic liquid (metal), as well as hydrogen's various crystalline phases, in particular the unknown region near the lower middle part of the diagram.

Key Words: bacteriorhodopsin, carbon nanotube, discontinuous Galerkin (DG), dynamic transmission electron microscope (DTEM), fluctuation electron microscopy (FEM), high-energy x-ray diffraction microscopy, Laboratory Directed Research and Development (LDRD) Program, lithium-ion battery, nanotube porin, Office of Basic Energy Sciences (BES), pole expansion selected inversion (PEXSI), Qbox, QMCPACK, quantum Monte Carlo (QMC), scanning electron microscopy, scanning transmission x-ray microscopy, small-angle x-ray scattering, transmission electron microscopy (TEM).

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Bioprinting Extends the Frontiers of Medical Treatment

Biomedical engineer Monica Moya holds a petri dish containing a combination of two printed bioinks. Each bioink contains living cells that, after printing, grow to create a living tissue patch fed by a vascularized network analogous to the body's blood vessels. (Photograph by Lanie L. Rivera.)

THREE-dimensional (3D) printing continues to drive innovations in many disciplines, including engineering, manufacturing, aerospace, global security, and medicine, to name only a few. Most 3D products are made of plastics or metals, but cutting-edge 3D printing techniques have been leveraged in the biomedical engineering field using bioinks—a fluid with biological components—to manufacture vascularized tissue. Once refined, this approach could be used to engineer complete human organs for implantation and to assess medical treatments.

A Lawrence Livermore team, led by biomedical engineer Monica Moya and supported by Livermore's Laboratory Directed Research and Development Program, has been refining a bioprinting approach for two years. The process involves producing and printing bioinks with cell-containing materials and a viscosity similar to that of honey. A bioprinter deposits the bioink into a specially designed sectioned device that acts as a sort of dynamic petri dish, establishing a feeding system to direct the growth of a vascularized network.

The team has already created vascularized tissue patches and envisions some day establishing hierarchical vascular networks similar to those in the human body, as a step toward developing

larger 3D organs. Moya says, "Having a hierarchical, vascularized patch of tissue—meaning tissue with vessels that can be connected to and perfused—has great potential for medical implantation." These patches could transform approaches to organ repair, disease remedy, toxicology, and medical treatment testing.

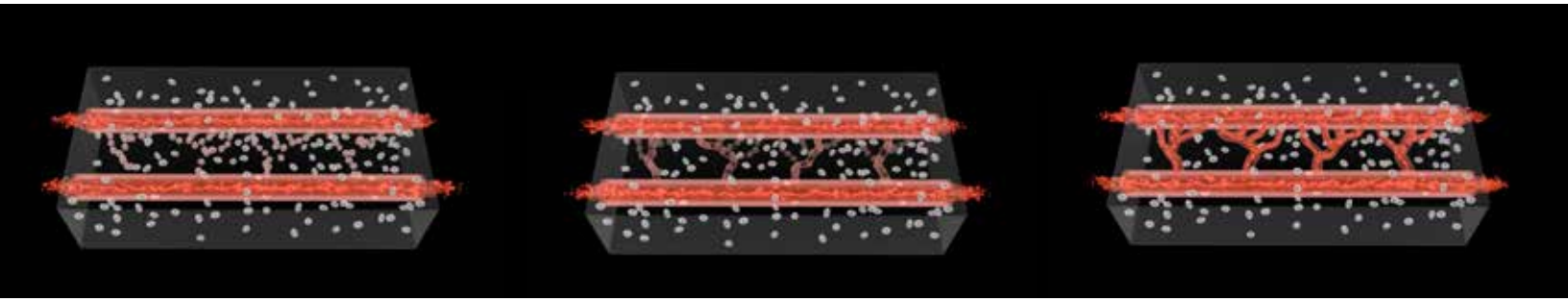
A Dish for Feeding

The team uses two different bioinks, each with ingredients engineered for specific printing approaches. All bioink components are derived from materials found in the human body or elsewhere in nature and modified for printability. The first type of bioink is self-assembly bioink, which forms the tissue material and contains endothelial cells, fibrin, and fibroblast cells. This bioink is printed into the center section of the petri dish, with its endothelial cells forming the lining of blood vessels and generating the microvascular structure (see the box on p. 15).

The fibrin in the self-assembly bioink results from the interaction of fibrinogen and thrombin, a combination of materials that the body uses to clot bleeding and form scabs. In the bioink, fibrin provides a temporary scaffold for tissue formation. The fibrin-based scaffold cues the fibroblast cells, which create structural supports, to go to work much like the cells would react to heal a wound. In this case, the cells replace the temporary scaffold with a more permanent structure, thus forming the vascular networks.

The self-assembly bioink is lined on two sides by printed biotubing, which is formed using a second bioink consisting of fibroblast cells and alginate, a biocompatible, viscous polysaccharide obtained from seaweed. The tubular structure is created by flowing the substance through a coaxial needle—a needle within a needle. Once laid down in the desired pattern, the tubing is locked into place by introducing calcium into the inner portion of the alginate tube. There, the positively charged

Surrounded by the self-assembly bioink, strands of biotubing consist of fibroblast cells and alginate, a biocompatible, viscous polysaccharide generated from seaweed. The tubular structure is created by flowing the substance through a coaxial needle. (Photograph by Lanie L. Rivera.)



(left to right) To create vascularized tissue patches, coaxial channels are printed in a "dynamic" petri dish, where the printed product evolves after the material is initially laid down by the bioprinter. The innate network-forming instinct of the living cells in the mixture results in the growth of vascular networks, which supply nutrients to the cells that comprise the tissue. (See the full animation online at str.llnl.gov.)

calcium ions react with the negatively charged alginate, hardening the latter. Although stiff, the hardened biotubing is permeable to nutrients—much like blood vessels in the human body—so that fluid infused into the tubing diffuses into the surrounding tissue environment.

Priming the Pump

In this project, Moya's team used a commercially available 3D printer for inorganic materials, which presented some hurdles. Cells cannot survive the high temperatures reached inside the printer's nozzles. Similarly, nozzle size presented a challenge—the narrow openings that enable high-resolution deposition can also subject cells to damaging levels of shear stress. To mitigate these issues, co-investigator Elizabeth Wheeler, who specializes in bioengineering and microfluidics, replaced the existing fluidics system with one suitable for bioprinting.

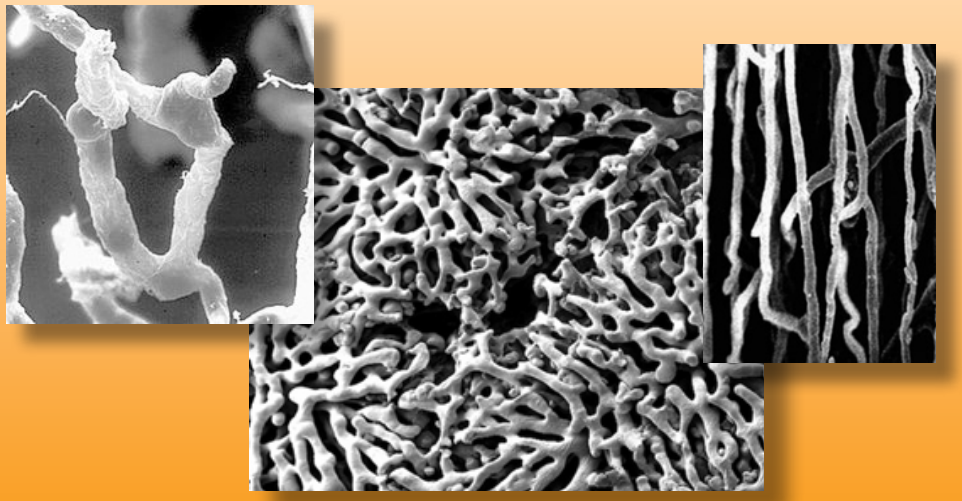
Wheeler notes that biomaterials are sensitive to flow rate, which must also be balanced with bioink viscosity. Immediately before the pumping and printing, the printer mixes the components of the self-assembly material, which immediately start to gel, altering the bioink's viscosity and affecting the rate of extrusion. The team conducted rheology tests to help understand the exact point at which the materials gel. For printing, the ink should be in a liquid state, but not too watery—otherwise the gel will form puddles when it hits the print stage. The bioink may spray out if deposited too quickly but could clog the nozzles if deposited too slowly. "Elements of bioprinting, including the printer specifications, pose a sort of Goldilocks problem—everything has to be just right," explains Wheeler.

The Vessel Venture

Once printed, the fibrin-and-cell bioink begins to generate vascular networks, directed by the cells' innate blueprint to form networks. "In contrast with additive manufacturing techniques, what we print is not the end product but the building block," notes Moya. "The cells self-assemble into the final form of the tissue patch." In the human body, vascular networks organize according to biochemicals (such as nutrients and other growth factors) or mechanical gradients (flow or pressures). Cells pay attention to these cues because in the body they guide the cells

One Size Does Not Fit All

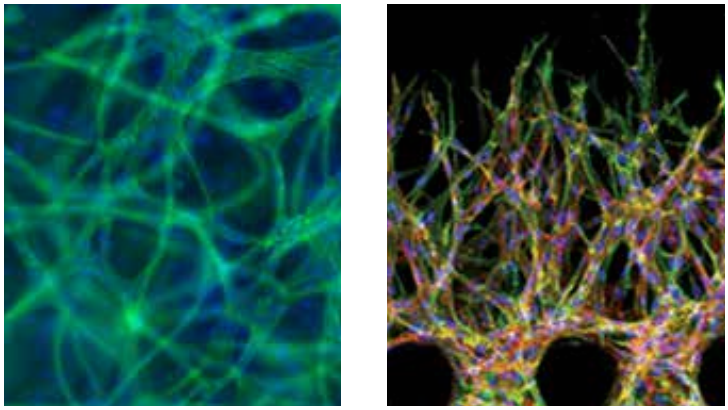
In the bioprinting approach used by Moya and her team, endothelial cells are taken from various organs. Although these cells have innate cues that spur vascular network formation, endothelial cells also establish different networks depending on the organ from which they originate. For example, the liver, which functions as the body's filter, has more pliable vessel networks to enable the organ's filtering function. In contrast, endothelial cells from the brain produce tight vessel networks that limit what crosses from the blood vessels into the brain. In short, each type of endothelial cell comes with a different type of vasculature—a challenge that the bioprinting of vessel networks must address. The Livermore team therefore focuses on creating bioinks that are compatible with all endothelial cell types and that leverage the endothelial cells' intrinsic ability to form networks suited to their specific environment.



Scanning electron micrographs show the vasculature of (left) a brain capillary network, (center) hepatic sinusoids in the liver, and (right) capillaries running along muscle fibers. (Images courtesy of *PLOS Biology*; the *Journal of Hepatology*; and the *Muscle, Ligaments and Tendons Journal*, respectively.)

to arteries that carry oxygenated blood and nutrients to the surrounding tissues. However, in the bioink mixture, the cells are surrounded by a nutrient-rich chemical solution without variance in chemical or mechanical cues. As a result, they form undirected, spaghetti-like networks.

In the airtight device where the tissue patch forms, the biotubing acts as feeding tubes for the self-assembly material, supplying a sugary, protein-laden, oxygenated liquid whose nutrients sustain cell life and fuel vascular network formation. Nutrient density is tailored to direct vascular network growth, in a manner similar to how cells in the body propagate toward nutrient-dense areas, where they receive biochemical and mechanical cues to create a hierarchical vascular network. Most cells in the body are within 100 to 200 micrometers—approximately the thickness of human hair—of a vascular source of nutrients. Moya intends to mimic this hierarchy by more specifically dictating nutrient diffusion and concentration. "We harness the cells' own engineering potential by printing the cells into an initial configuration, then altering the environment with chemical flow to guide cell growth," adds Wheeler.



Directing vascular network growth using nutrient concentration gradients is a strategy that Livermore is pursuing to create a hierarchical network similar to that naturally formed in the human body. (left) An equal distribution of nutrients results in a spaghetti-like vascular network, whereas (right) a gradient in nutrition concentration creates a greater density of blood-vessel analogues where nutrients are denser. (Image on right courtesy of the Royal Society of Chemistry.)

Eventually, the ionic interaction between the alginate and calcium will deteriorate, and the biotubing will break down. By that time, the endothelial cells will have rebuilt the manufactured vessels to establish a new network. "Similar to implantation of artificial veins or arteries, the material needs to be rigid in the beginning, with an understanding that eventually it will dissolve, and cells will replace it with their own version," says Moya. Allowing cells to transform the tissue naturally increases the potential for the patch of artificial tissue to better integrate with the body.

Flowing Forward

Moya and Wheeler's team has successfully produced vascularized tissue patches 1 centimeter by 1 centimeter in size and containing biotubing up to 1 millimeter wide. They hope to soon achieve even larger tissue patches, as well as a perfusable, or flow-enabling, hierarchical vascular network. This effort will be aided by a new, higher resolution bioprinter recently installed at Livermore. "The prize in the sky is to be able to print organs," says Moya. "To do that requires having stable vasculature in place, which is what we have established." Bioprinting complete organs could potentially mitigate some of the complications associated with current transplantation processes, such as transplant rejection and organ shortages.

Although bioprinting a full-size human organ is far in the future, the ability to print small tissue patches and small-scale organs has the immediate potential to impact the development of drugs and the testing of medical treatments. Embedding targeted cells into these bioprinted patches could even have therapeutic potential. For example, Type 1 diabetes, a disease caused by low insulin production, could be remedied by embedding insulin-producing islet cells into a vascularized tissue patch, which could be implanted anywhere in the body. Achievements at the frontier of bioprinting will transform medical applications, including drug research, toxicology, and treatment testing, furthering Lawrence Livermore's contribution to human medicine.

—Lanie L. Rivera

Key Words: bioink, biomaterial, bioprinting, endothelial cell, biotubing, self-assembly bioink, three-dimensional (3D) printing, tissue patch, vascular networks, vessels.

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Taking Topological Insulators for a QUANTUM SPIN

Livermore researchers used a designer diamond anvil cell—which features tungsten metal microcircuits fabricated on the 300-micrometer-wide polished tip of a diamond—to investigate the high-pressure behavior of different ratios of bismuth and telluride as topological insulators (TIs). A TI behaves like an insulator in its interior yet conducts electricity along its surface, despite having the same chemical composition throughout.

MATERIALS can be categorized by their electrical conductivity—that is, the ease with which charged particles, electrons, can travel throughout the material. In conventional conductors (such as copper), the outer electrons of their atoms are loosely bound and require little to no additional energy to move from atom to atom and molecule to molecule. The electrons in semimetals and semiconductors (for instance, silicon) are more tightly bound to the nucleus of each atom—thus more energy is required to dislodge them—while the electrons in insulators (such as rubber) need the most energy to move freely. A topological insulator (TI) defies easy classification, however. It behaves like an insulator in its interior yet conducts electricity along its surface, despite having the same chemical composition throughout.

In a TI, an electron's orbital motion around the nucleus of the atom interacts with its spin—a physical property similar to the clockwise or counterclockwise rotation of a planet around its own axis—such that spin and orbital motion are coupled. (When driven by an electric field, all of a conductor's electrons will move in the same direction, independent of their spin; electrons in TIs with opposite spin move in opposite directions.) The coordinated electrons mostly end up revolving in place, but at the edge or surface of a TI, they form a current.

What truly sets these surface currents apart from those observed in conventional materials, however, is their topological properties. Topology is a broad field of study concerned with classifying the structure of an object. Imagine a donut made from Play-Doh: the donut has one hole, but it can be continuously deformed into a teacup with a handle, making these two objects part of the same topological class. Generating a donut from a ball shape, however, would require tearing a hole, which would put it into a different topological class. Similarly, the bulk electronic structure of a TI belongs to a topological class different than that of the air around it. The TI's surface state connects these two disparate topologies. Any surface currents around the TI are very difficult to disrupt and possess high electrical conductivity because these surface currents derive from topology rather than the chemistry of the bulk materials.

New Materials, New Applications

With their special surface properties, TIs could be ideal building blocks for faster, cheaper, and more energy-efficient electronics, such as spin-related electronics. Called spintronics, these devices comprise a nascent field that aims to manipulate the spin state of electrons to represent ones and zeroes, instead of the presence and absence of electrons used in conventional computing. Researchers have also theorized that the collective motion of electrons inside TIs will give rise to several particles predicted by high-energy physicists, including chargeless Majorana quasiparticles, which could be harnessed for transmitting information in a practical quantum computer. These computers use the laws of quantum mechanics to perform calculations and are predicted to perform tasks such as database searches and code breaking exponentially faster than today's binary computers.

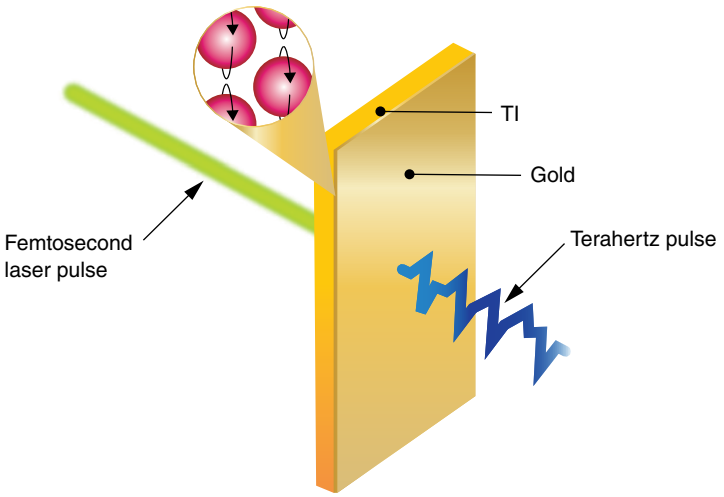
Although potential TI applications are generating excitement in the research community, TIs have only been synthesized and studied experimentally since 2008—more basic and applied research will be needed before realizing any TI-based quantum devices. To this end, Lawrence Livermore scientists, with funding from the Laboratory Directed Research and Development Program, are currently investigating two aspects of these materials. Jason Jeffries's team is using pressure to induce structural changes in TIs to better understand their properties, while Dongxia Qu is exploring the feasibility of using the TI surface current as a means of generating magnetic spins for spintronics. Qu's and Jeffries's work is poised to propel scientists' understanding of these rather new and strange materials a quantum step ahead.

Superconducting Surprise

Jeffries and his colleagues are employing compression experiments to shed light on how the atomic and electronic structure of TIs relate to their electron transport properties. Their experimental data will be used to bolster modeling accuracy for these and similar materials. The team has explored pressure-related changes in a series of bismuth telluride materials at up to 50 gigapascals using two kinds of diamond anvil cells (DACs). Small mechanical presses, DACs enable researchers to observe and measure a material's properties under extreme static pressures of up to 600 gigapascals and to vary those pressures slowly, over the course of many hours. (See *S&TR*, December 2004, pp. 4–11.) For structural studies, they loaded a standard DAC with bismuth telluride and performed x-ray diffraction experiments on it at Argonne National Laboratory's Advanced Photon Source (APS). A designer DAC, which is equipped with metallic microprobes, was used to measure electrical resistivity and other transport characteristics. Jeffries explains, "Designer DACs let us really interrogate the electronic system at high pressure. For example, is it a metal or a semiconductor? And how exactly is it conducting?"

At standard (atmospheric) pressure, materials with different ratios of bismuth and telluride have distinct properties—for instance, one is a semimetal, while another is one of the best-studied TIs. When compressed, the various bismuth-based samples underwent multiple transformations, documented through both structural and electronic measurements. Eventually, they all transitioned to the same bismuth–telluride alloy, which is a superconductor (that is, a material that conducts electricity without resistance). Jeffries notes that such universal behavior from a material series under pressure is unusual and somewhat surprising, but studying it may help the team to understand the subtle variations that lead to TI and superconducting states in these systems.

Jeffries's team has also investigated the TI samarium hexaboride at pressures up to 35 gigapascals. Samarium hexaboride is an ideal TI to study because the bulk of the material is truly insulating. Most other TIs have some internal current due to impurities within the material, and this current can interfere with measurements of the surface current. Using a standard DAC and various x-ray techniques at APS, they explored the material's transition under pressure from an insulator to a conductor. For example, they used resonant x-ray emission spectroscopy to probe the local electronic configuration of atoms and better understand how the electrons responded to the transition. They found that unlike samarium sulfide, which is considered a rather analogous material, samarium hexaboride does not undergo an abrupt change in its electronic



A spin-based terahertz emitter married to a TI layer is capable of greater bandwidth, for better imaging resolution in applications such as airport screening and medicine. In a process called spin injection, a 20-nanometer-thick TI is layered over a 2-nanometer-thick gold sample, and its surface is bombarded with a femtosecond laser pulse. Through the inverse-spin Hall effect, spin currents are converted to charge currents.

configuration as it transitions from an insulator to a conductor. This surprising result may indicate that the topological nature of the system varies continuously with pressure, which would have implications in TI applications.

Controlling Spin with Light

Qu has also probed the characteristics of bismuth-based TIs, but using magnetic fields and sensitive measurements rather than pressure experiments. To measure bismuth telluride's quantum oscillations, she created a temperature gradient in a sample, exposed the sample to a strong magnetic field, and looked for variations in the resulting voltage. Studying these oscillations, which relate to surface electron transport behavior, helps to provide a better picture of the material's electrical properties. She has also gauged the mobility of bismuth selenide's surface electrons by precisely measuring its resistivity and conductivity. "Mobility is a measure of how long an electron can move around before it is scattered," Qu explains. "The higher the mobility, the less chance that electrons will be scattered in the material." She found that the mobility was very high and relatively impervious to material impurities, confirming the robustness of the TI's surface current.

Qu's latest work leans more heavily to the applied side. She is leading an effort to make a prototype compact terahertz radiation emitter for imaging applications through a process called spin injection. She layers a 20-nanometer-thick TI over a 2-nanometer-thick gold sample and bombards the surface of the TI with a femtosecond laser pulse. The laser energy creates a population of electrons with a predetermined spin speed and direction. These "spin-preprogrammed" electrons accumulate at the gold–TI interface and then diffuse into the gold, where they cause the gold electrons to move in unison. This mass behavior generates an electrical current, which, in turn, makes the TI–gold structure emit electromagnetic radiation—a manifestation of a phenomenon called the inverse spin Hall effect, by which spin currents are converted to charge currents. The emitted radiation can be measured and analyzed with the help of a specially developed terahertz spectrometer.

The resulting device has demonstrated broader bandwidth and higher energy emissions (20 terahertz instead of 3 terahertz) than other spin-injection methods can produce, which could enable, for instance, higher resolution screening for airports and medical uses. Other potential applications include radar, basic science research, and wireless communications. Qu and her colleagues are aiming to develop a practical, fiber-laser-pumped, terahertz emitter within the next year.

Qu's process offers several advantages over the standard method for controlling electron spin, which uses magnetic fields and materials. "With normal ferromagnetic materials," she notes, "we align the spin using a magnetic field and then inject spin in a normal semiconductor. But if we inject current with a TI, the spins automatically align in one direction, without a magnetic field." Furthermore, TIs are more efficient at generating spin—that is, they can make the electrons spin faster—and the process allows researchers more control over the electrical and spin properties of the resulting device, through tuning of the laser pulse properties. Her work thus offers a promising avenue for the development of other spintronic devices.

Despite a few years in the scientific spotlight, TIs remain somewhat elusive materials. Their properties can be difficult to observe, and many of their applications remain more in the realm of conjecture than reality. Efforts such as Jeffries's and Qu's, however, represent appreciable progress toward the characterization and utilization of TIs, which benefits Livermore investigations into quantum computing, spintronics, device physics, materials science, and even actinide science.

—Rose Hansen

Key Words: Advanced Photon Source (APS), bismuth selenide, bismuth telluride, compression, conductor, diamond anvil cell (DAC), femtosecond laser, insulator, inverse spin Hall effect, Majorana particle, quantum computer, quantum mechanics, resonant x-ray emission spectroscopy, samarium hexaboride, spin injection, spintronics, terahertz emitter, topological insulator (TI).

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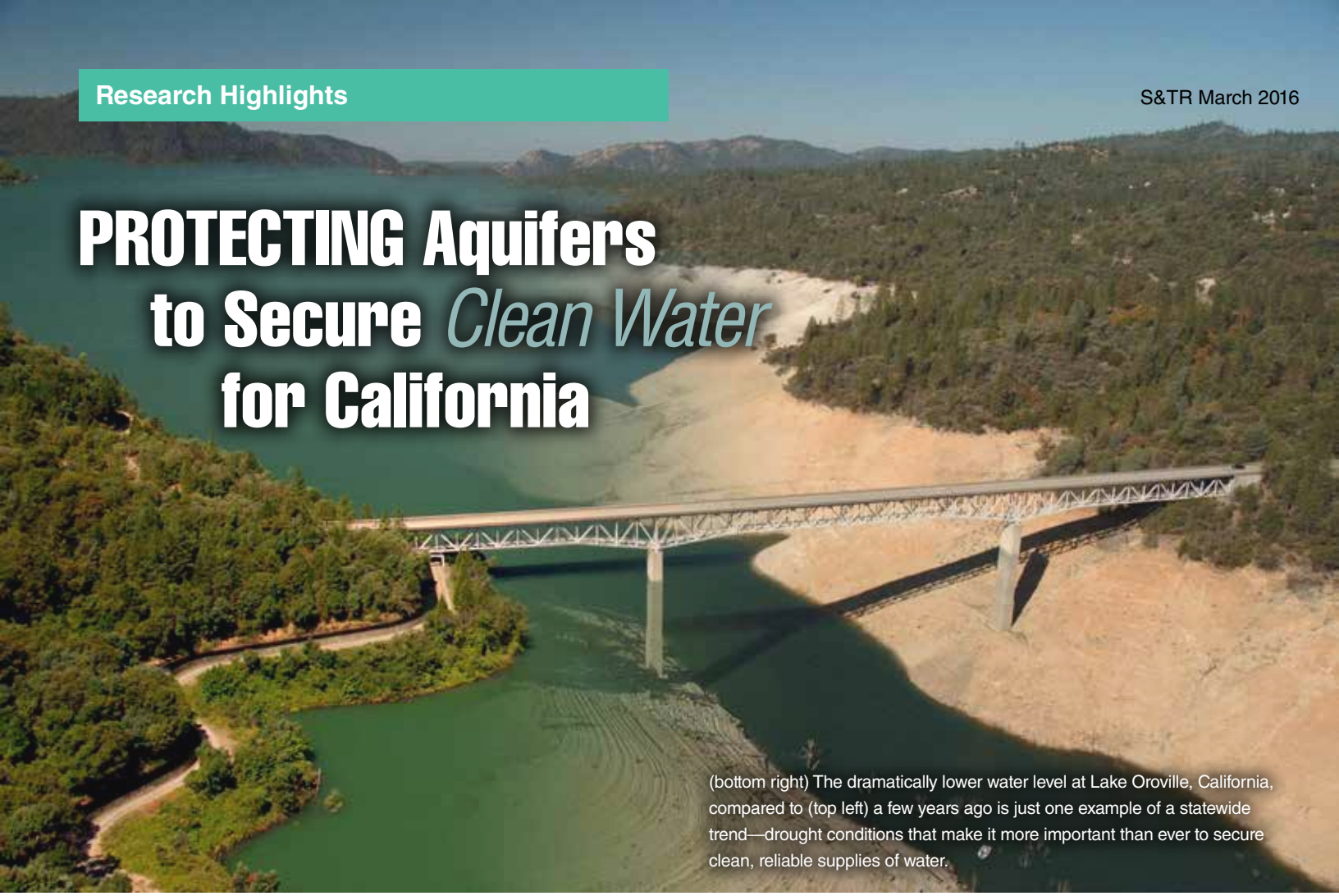
PROTECTING Aquifers to Secure *Clean Water* for California



(bottom right) The dramatically lower water level at Lake Oroville, California, compared to (top left) a few years ago is just one example of a statewide trend—drought conditions that make it more important than ever to secure clean, reliable supplies of water.

MORE than half of California's drinking water comes from aquifers—underground reservoirs of water that are recharged when rain and snowmelt percolate down through the soil. California has hundreds of aquifers, ranging from 1 to 90 square kilometers in surface area. Now in the midst of a multiyear drought, however, the state is facing a serious challenge as it tries to ensure ample water supplies. Reservoirs for a time had dipped below half of their historical levels, with precipitation far below average and even snowpack levels, which traditionally provide significant water storage, drastically low. Furthermore, many shallow private drinking-water wells are being abandoned because of increased use of the surrounding groundwater, primarily by farmers, to the point where the falling water table leaves the well "high and dry."

Securing clean water is another sobering concern for Californians. Groundwater from aquifers and wells provides 40 percent of the state's total water supply in a normal year, but in addition to changing precipitation patterns, contaminants also threaten California's precious water sources. As pristine underground aquifers are consumed at an increasing rate, water quality—not just quantity—must be addressed.

A team of Livermore researchers with expertise in isotope geochemistry is developing new methods to help characterize California's underground aquifers. Using naturally occurring and anthropogenic radioactive isotopes, they can determine when the water was recharged from surface water that percolated down through the soil and into the aquifer. This recharge time, or "water age," is helping Laboratory researchers determine the source of contaminants and the flow of groundwater. Researchers also use the isotopic composition of pervasive pollutants, such as nitrate, to determine the source of contamination.

One State, Multiple Efforts

Livermore geochemist Brad Esser is the technical lead for the Laboratory's involvement in the California Groundwater Ambient Monitoring and Assessment (GAMA) Special Studies program, which is developing new tracers to monitor recent groundwater recharge. This program is a partnership between the California State Water Resources Control Board; Lawrence Livermore; California State University, East Bay; and the U.S. Geological Survey (USGS). Esser also runs the Laboratory's

Environmental Monitoring Radioanalytical Laboratory, which monitors the radioactivity in air, soil, and water at both the Livermore main site and Site 300, the Laboratory's remote research and development facility (see *S&TR*, July/August 2004, pp. 4–13).

Past GAMA Special Studies program research focused on gaining a better understanding of the source and transport of nitrate contamination in drinking water aquifers. Current research efforts focus on meeting persistent needs in California water resource management by identifying appropriate areas for managed aquifer recharge in response to the drought and developing new age tracers to permit the use of treated wastewater. Esser's team of four researchers is developing methods to characterize the different age components in a single groundwater sample. The team also provides groundwater age data to the GAMA Priority Basin and Shallow Aquifer Assessment, a statewide monitoring program led by USGS. The State of California funds these efforts.

The Trickle-Down Effect

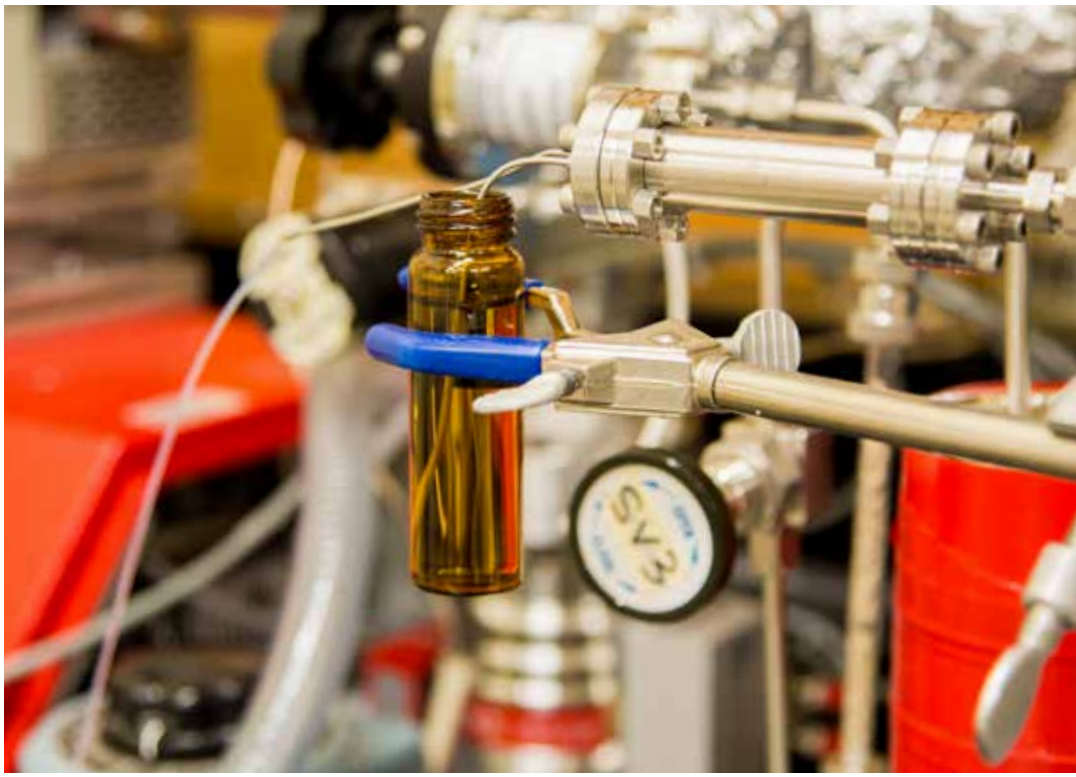
Laboratory researchers can determine the source, history, and likely fate of contaminants in groundwater from factors such as groundwater age and isotopic composition. When studying contaminants such as nitrate, researchers also look for the presence of their degradation products. These measurements indicate whether the contaminant is natural, whether it results from past events or ongoing activities, and whether it is being naturally degraded in the aquifer, for instance. In addition, water age can be used to identify vulnerable aquifers and wells. Younger waters have had less time in the subsurface for filtration and the breakdown of harmful compounds.

Although compounds such as nitrate occur naturally and are essential to life, their intensive use in the modern age has led to the harmful contamination of groundwater. "Post–World War II industrialization of irrigated agriculture and animal operations in California has been a major source of contamination," says Esser. Younger waters are also more vulnerable because of the dramatic increase in nitrogen loading in California since World War II. The use of synthetic nitrogen fertilizers and the size and number of confined animal feeding operations, such as dairies, increased dramatically in the last half of the 20th century. Therefore, groundwater recharged over this time is more likely to contain anthropogenic nitrogen than is older water.

"Water managers want to know if the water is renewable or nonrenewable, and how vulnerable it is to contamination," says Esser. "If you are tapping water that is thousands of years old, then you are mining precious, nonrenewable groundwater. If you are using water that is ten years old, then you know it's recharging and therefore is renewable," he explains. "On the other hand, younger water is more vulnerable because contaminants are more widespread now than one hundred years ago. So we have to try to determine whether, say, the nitrate we are seeing today is a result of some activity that is happening at the surface now or that happened decades ago."

Esser explains that water age is a complicated concept because water produced by a well doesn't have a single age. Large wells may access groundwater from more than one aquifer, and the same well can be fed by both younger and older

The noble gas membrane inlet mass spectrometer (NG-MIMS) is a simple benchtop instrument developed at Livermore to measure dissolved noble gases in water samples. For instance, NG-MIMS can detect the arrival of introduced xenon to establish the underground travel time of water.



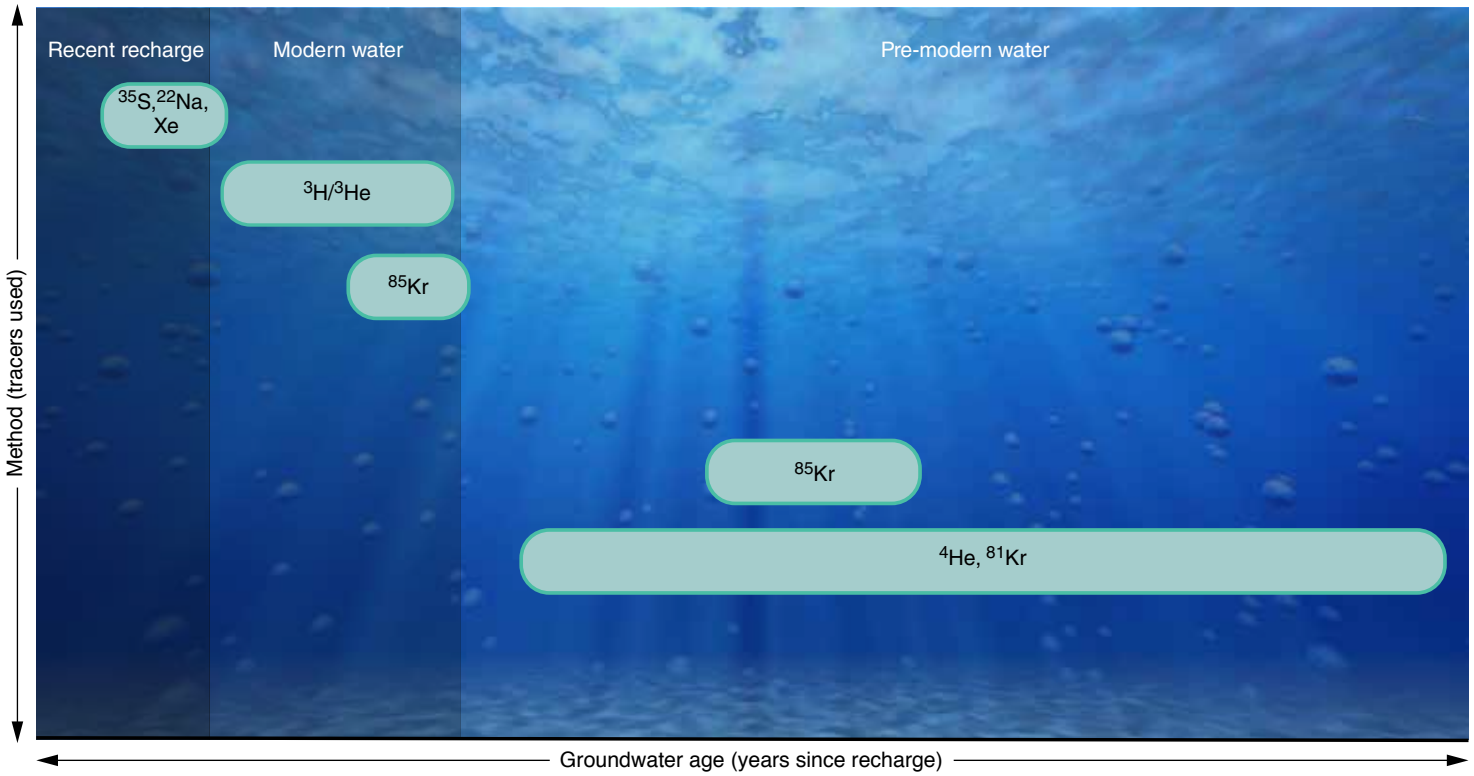
water sources. The challenge is figuring out how to pull that information apart and use it to determine both the history and the future vulnerability of the water and its contaminants.

Testing with Tracers

Livermore's GAMA-related program tests groundwater using a number of tracers that tell how long the water has been in the subsurface. Xenon, a noble gas, and sulfur-35, a radioactive isotope produced naturally, are among the latest tracers that the GAMA group uses to test groundwater that is weeks to months old. Xenon is introduced to a recharge pond or injection well and then detected at a monitor or production well using a noble gas membrane inlet mass spectrometer—a simple benchtop instrument developed at Livermore. The time between introduction and first detection is related to groundwater age. Sulfur-35 is measured in groundwater samples after preconcentration from large-volume water samples using a method also developed at Livermore. The radioactive decay of sulfur-35 can be used as a clock to determine groundwater age.

The team is also developing krypton-85 as a tracer to complement Livermore's signature tritium tracers, used to determine the mean age of "modern water"—water aged less than 50 years. Tritium, an isotope of hydrogen, is naturally produced in Earth's upper atmosphere by cosmic rays. In the early 1960s, atmospheric nuclear testing introduced a large amount of tritium into the atmosphere. Today, many public drinking water wells in California produce water with measurable tritium. Water recharged before 1950, however, does not contain tritium. Krypton-85 has a similar half-life to tritium and is released into the atmosphere through the reprocessing of nuclear fuel. Although tritium's atmospheric concentration has been falling over the last several decades, the atmospheric concentration of krypton-85 has been rising. The use of these tracers can permit the determination of not only the average age of modern water but also the ratio of modern to "pre-modern" water.

The Laboratory is one of two high-throughput noble gas mass spectrometry laboratories in the nation with the capability to measure tritium and noble gases. Through



California's Groundwater Ambient Monitoring and Assessment (GAMA) program uses multiple tracers to determine the age of groundwater, including tritium (^{3}H), radiocarbon, radiogenic helium-4 (^{4}He), and krypton-81 (^{81}Kr). Livermore's GAMA team is also developing krypton-85 (^{85}Kr) as a tracer for dating "modern water" and both sulfur-35 (^{35}S) and xenon (Xe) as tracers for recent recharge, that is, water less than two years of age. Under a project supported by the Laboratory Directed Research and Development Program, the team is also developing sodium-22 (^{22}Na) as a tracer of modern groundwater of intermediate age (2–10 years).

the GAMA Priority Basin program over the last 10 years, USGS and Livermore have provided the California Water Board with thousands of groundwater ages. Esser notes, "We're just beginning to understand where we are pumping out very old groundwater, which recharges too slowly to be considered a renewable resource, and where the very young groundwater is present, indicating an area suitable for managed aquifer recharge."

California and Livermore—a Strong Partnership

Over the past 15 years, Livermore has been a strong ally to California in managing groundwater resources. In response to the discovery of methyl tertiary-butyl ether—a gasoline oxygenate released into groundwater from leaking underground fuel tanks in California drinking water wells in the late 1990s—Livermore developed Geotracker, a geographic information system database that tracks the proximity of drinking water wells to leaking underground fuel tanks. Livermore proposed that groundwater age could be a simple metric to identify wells that were particularly susceptible. This research led to the establishment of the California Aquifer Susceptibility program, a partnership between the California Water Board, USGS, and Livermore from 2000 to 2003.

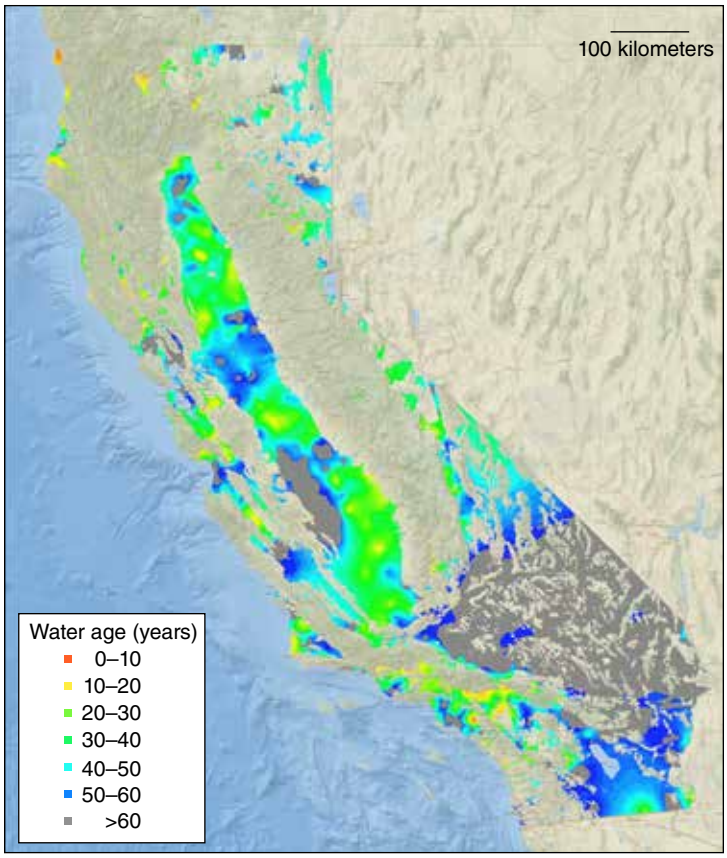
In 2003, Livermore's Laboratory Directed Research and Development (LDRD) Program funded an Esser-led investigation of nitrate biogeochemistry and reactive transport in California groundwater. The Laboratory was an influential force behind the California Water Board's decision to establish the GAMA Special Studies program in 2003. The tools developed in the course of that program were used in subsequent state-funded Special Studies projects.

Livermore continues to invest in California groundwater studies. In a 2008 LDRD-funded effort, Livermore researcher Mike Singleton explored the impact of climate change on high-elevation groundwater basins using a new sampling system to characterize recharge mechanisms and groundwater residence times in Sierra aquifers.

Currently, Livermore scientist Ate Visser is leading an LDRD-funded project to track water through the "critical zone"—the thin layer of vegetation, soil, and sediment overlying groundwater aquifers—to assess drought vulnerability. This collaboration between Livermore, the University of California at Merced, and the Colorado School of Mines will develop new tracers and technologies to better characterize the water cycle at the surface and in the subsurface.

"Water is a national security issue," states Esser. "Both for residential use and for agriculture, we need water to live and to maintain farming systems." Although California remains the immediate focus of Esser's efforts, Livermore's tools and methods are applicable throughout the country and beyond.

—Kristen Howard



The GAMA program has so far determined the age of over 4,000 California groundwater samples using tritium as a tracer. A map graphically represents the results of 2,589 samples. Of these, 1,630 samples—or 63 percent of the total—had a mean groundwater age of approximately 60 years, indicating California's reliance on relatively old water that is replenished slowly.

Key Words: age tracer, aquifer, California Aquifer Susceptibility program, Environmental Monitoring Radioanalytical Laboratory, Geotracker, Groundwater Ambient Monitoring and Assessment (GAMA) Special Studies program, groundwater isotopic composition, methyl tertiary-butyl ether (MTBE), noble gas mass spectrometry, water age, water contamination.

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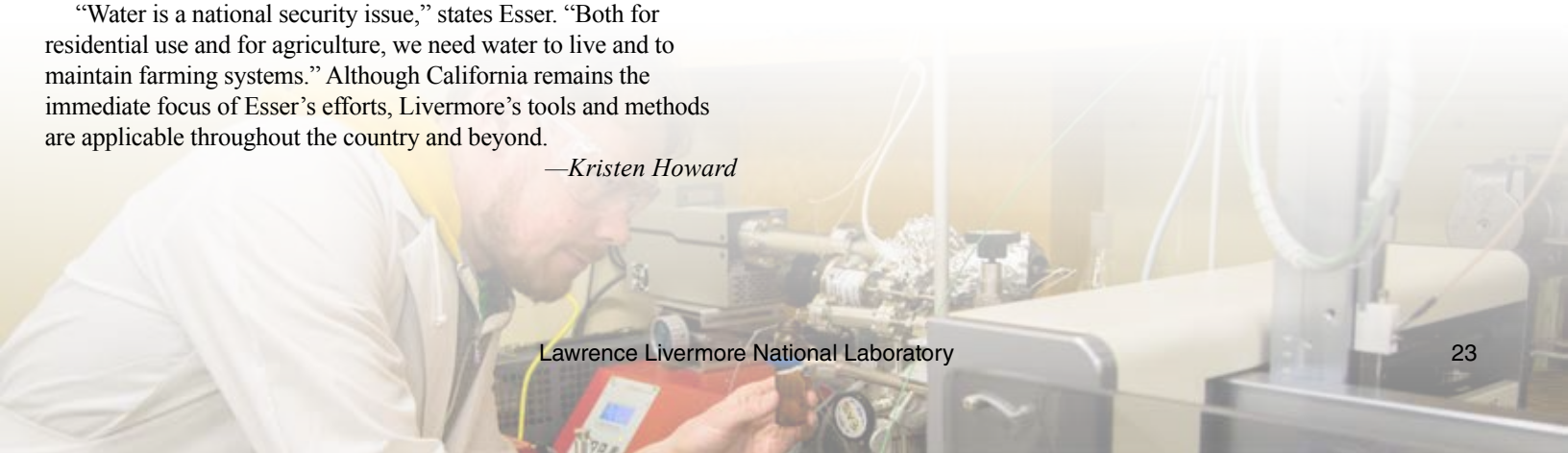

In this section, we list recent patents issued to and awards received by Laboratory employees. Our goal is to showcase the distinguished scientific and technical achievements of our employees as well as to indicate the scale and scope of the work done at the Laboratory. For the full text of a patent, enter the seven-digit number in the search box at the U.S. Patent and Trademark Office's website (http://www.uspto.gov).

Patents

Isotope Specific Arbitrary Material Sorter
Christopher P. J. Barty
U.S. Patent 9,205,463 B2
December 8, 2015

Phase-Sensitive Two-Dimensional Neutron Shearing Interferometer and Hartmann Sensor
Kevin L. Baker
U.S. Patent 9,207,194 B2
December 8, 2015

Energy Storage Management System with Distributed Wireless Sensors
Joseph C. Farmer, Todd M. Bandhauer
U.S. Patent 9,209,501 B2
December 8, 2015

Methods for Point-of-Care Detection of Nucleic Acid in a Sample
Jane P. Bearinger, Lawrence C. Dugan
U.S. Patent 9,222,126 B2
December 29, 2015

Awards

Roy Musselman and **Scott Futral** were acknowledged for their contributions to simulations conducted on Livermore's **Sequoia supercomputer** that were recognized with the **2015 Gordon Bell Prize**, which was presented last December at the 2015 Supercomputing Conference (SC15). The simulations, led by University of Texas researchers, examined tectonic plates and convection in Earth's mantle. "These advances will open the door to addressing such fundamental questions as what are the main drivers of plate motion and what are the key processes governing the occurrence of great earthquakes," says Professor Georg Stadler of New York University's Courant Institute of Mathematical Sciences. Using Sequoia's peak performance, the simulations achieved an unprecedented 97 percent efficiency in software scalability, a new world record. "I'm gratified that Sequoia continues to contribute to groundbreaking calculations in computational science," says Futral. Capable of 20 petaflops (quadrillion floating-point operations per second), the IBM Blue Gene/Q system is ranked third on the Top500 list of the world's most powerful computers. The Gordon Bell Prize is awarded each year to recognize outstanding achievement in high-performance computing, with particular emphasis on innovation in applications in science, engineering, and large-scale data analytics.

A project titled **Collaboration of Oak Ridge, Argonne, and Lawrence Livermore** (CORAL), which will bring the Sierra supercomputer to the Laboratory in 2018, was recognized by **HPCWire** with an **Editor's Choice Award** for Best HPC Collaboration Between Government and Industry. CORAL represents an innovative procurement strategy—pioneered by Livermore—that couples acquisition contracts with nonrecurring engineering contracts in a way that enables vendors to assume greater risks in their proposals than they would otherwise be able to for a computational system that is several years out. An IBM system, Sierra is expected to achieve performance exceeding 120 petaflops and will serve the National Nuclear Security Administration's Advanced Simulation and Computing Program, which is an integral part of stockpile stewardship. CORAL's industry partners also include NVIDIA and Mellanox.

Materials scientist **Troy Barbee, Jr.**, was inducted into **Stanford University's Multicultural Alumni Hall of Fame** (MAHF) in recognition for his work mentoring Stanford students over the years and for his achievements throughout his long career as a Native American researcher. "I feel honored to be selected for the MAHF, and I'm in some good company," says Barbee.

After earning his Ph.D. at Stanford in 1965, Barbee began work there as a materials scientist—while serving as a freshman academic adviser—including becoming the associate director of the Center for Materials Research, where he established a capability to produce multilayer materials comprised of extremely thin layers only a few atoms thick using the then new technology of magnetron sputtering. Barbee joined Lawrence Livermore in 1985 and has continued developing multilayer materials using magnetron sputtering, producing multilayers of 78 of the 92 naturally occurring elements. According to Johns Hopkins University professor of materials science Timothy Weihs, who worked as a postdoctoral researcher for Barbee, "He was and remains a wonderful inspiration to many postdocs and collaborators. He constantly is thinking of new materials and applications." Barbee has won three R&D 100 awards, and one of his top honors is his 2000 election to Uppsala University's Royal Academy of Arts and Sciences—the oldest royal academy in Sweden—after being nominated by Nobel laureate Kai Siegbahn.

Kenneth Turteltaub was named a **fellow** of the **American Association for the Advancement of Science** (AAAS) in recognition of his development of ultraprecise accelerator mass spectrometry (AMS) methods for biomedicine and for his work on carcinogenesis, macromolecule formation, and low-dose pharmacokinetics. "I'm very excited to have been selected, and I feel lucky to have been able to work with such a great and talented group of people over the years to make AMS useful for biomedicine," says Turteltaub. Election as an AAAS fellow is an honor bestowed upon AAAS members by their peers in recognition of scientifically or socially distinguished efforts to advance science or its applications. Turteltaub was one of 347 AAAS members to receive the honor in 2015 out of over 120,000 members worldwide.

Abstract

Understanding Materials at the Nanoscale

Livermore researchers design and develop new materials with novel structures, functions, and properties. Current research thrusts include validated predictive models, atomic-scale characterization, materials synthesis and assembly, and advanced manufacturing, including three-dimensional additive manufacturing. A portfolio of six materials research projects at Livermore is funded by the Department of Energy's Office of Basic Energy Sciences. The six projects fall under three thematic areas: time-, space-, or energy-resolved investigations of materials; the control of functional materials at the nanoscale (billionth of a meter); and predictive modeling and simulations. All six are strongly aligned with Livermore's "Science on a Mission" motto and research supported by Livermore's Laboratory Directed Research and Development Program. By probing, manipulating, and simulating single atoms and molecules, discrete clusters of atoms and molecules, and large systems containing nanoscale components, the research is producing new scientific understanding and technologies.

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When Certain Substances Become Critical

Livermore researchers work with the Critical Materials Institute to reduce the need for rare-earth elements in America's clean-energy industry.

Coming Next Issue

Also in April/May

- *Researchers are rapidly approaching the conditions needed to experimentally study the relativistic shock waves driving gamma ray bursts.*
- *Using two cutting-edge imaging technologies, a Livermore-led team uncovered mechanisms of soil carbon cycling that are crucial for modeling and managing soil resources.*
- *A decade-long simulation effort will help perfect experimental efforts for imaging single biomolecules using x-ray free-electron lasers.*

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