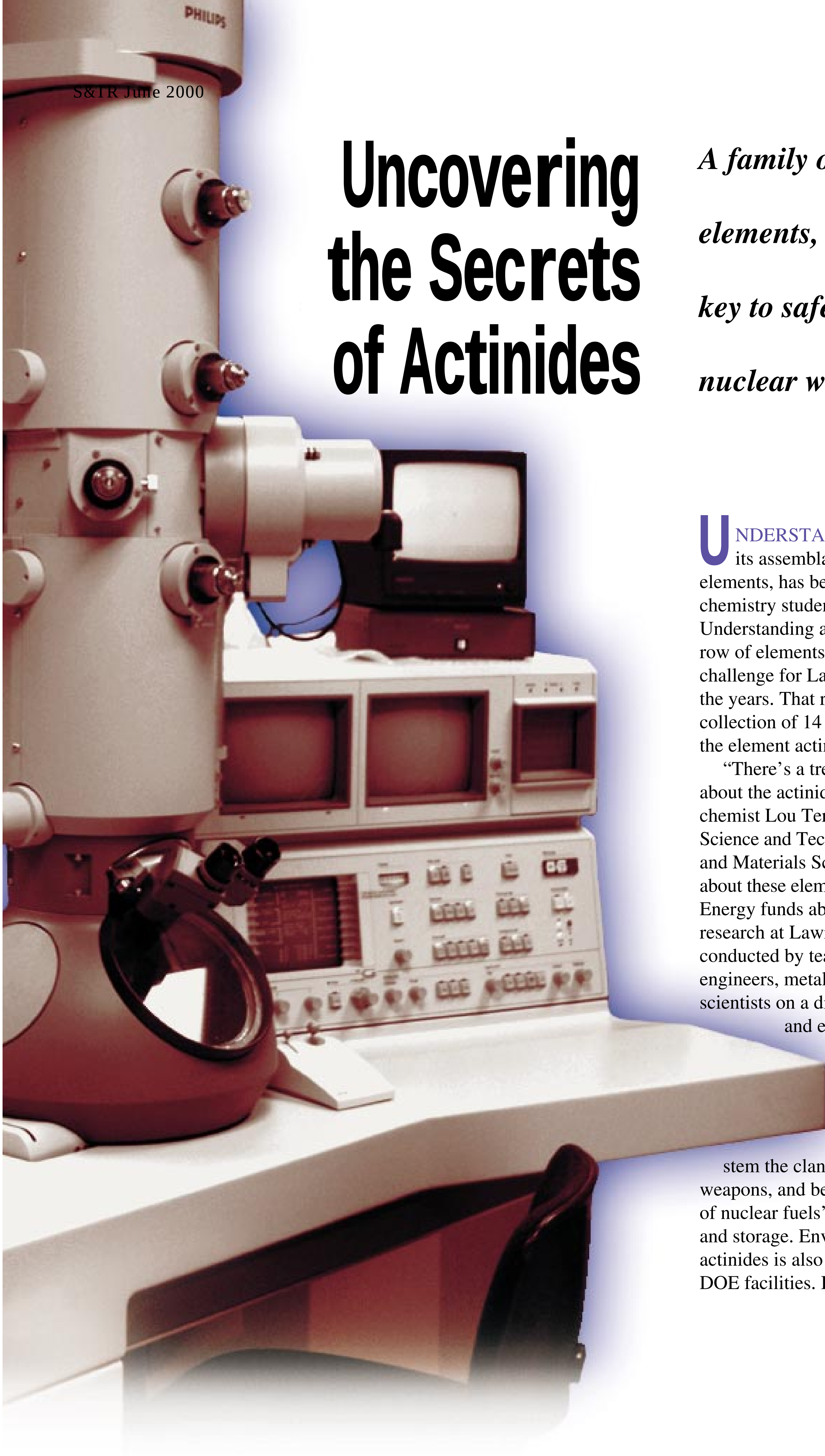


Uncovering the Secrets of Actinides

A family of radioactive elements, the actinides, is key to safe stewardship of nuclear weapons.

UNDERSTANDING the periodic table, with its assemblage of columns and rows of elements, has been a perennial challenge for chemistry students. (See the box on p. 17.) Understanding at the atomic level a remarkable row of elements has been a particular research challenge for Lawrence Livermore scientists over the years. That row is called the actinides, a collection of 14 radioactive elements named after the element actinium.

"There's a tremendous amount we don't know about the actinides," says Lawrence Livermore chemist Lou Terminello, who leads the Materials Science and Technology Division of the Chemistry and Materials Science Directorate. To learn more about these elements, he says, the Department of Energy funds about $100 million per year for research at Lawrence Livermore. The research is conducted by teams of chemists, physicists, engineers, metallurgists, and environmental scientists on a diverse set of national security and environmental issues.

Terminello says that a more fundamental understanding of actinides is needed to better assess the nation's nuclear stockpile, help stem the clandestine proliferation of nuclear weapons, and better understand the implications of nuclear fuels' (such as enriched uranium) use and storage. Environmental contamination by actinides is also a major concern at several major DOE facilities. In addition, actinides such as uranium, neptunium, plutonium, and americium are the major contributors to the long-term radioactivity of nuclear waste currently targeted for the proposed Yucca Mountain repository in Nevada.

Stockpile stewardship, DOE's program for certifying the long-term safety and performance of the enduring stockpile without underground nuclear testing, has heightened the importance of assessing and predicting the long-term behavior of actinides. A major focus is on obtaining a better scientific understanding of the isotopes uranium-235 and, especially, plutonium-239.

Plutonium is the most complex and perplexing element in the periodic table. The element's complexity stems in part from its mercurial nature. Depending on temperature, it assumes one of six different forms or phases, each with a different density and volume. Because of plutonium's enigmatic behavior and the need for stringent safety and environmental procedures when handling the toxic material, much of the extensive characterization work done on other metals has not been performed on plutonium.

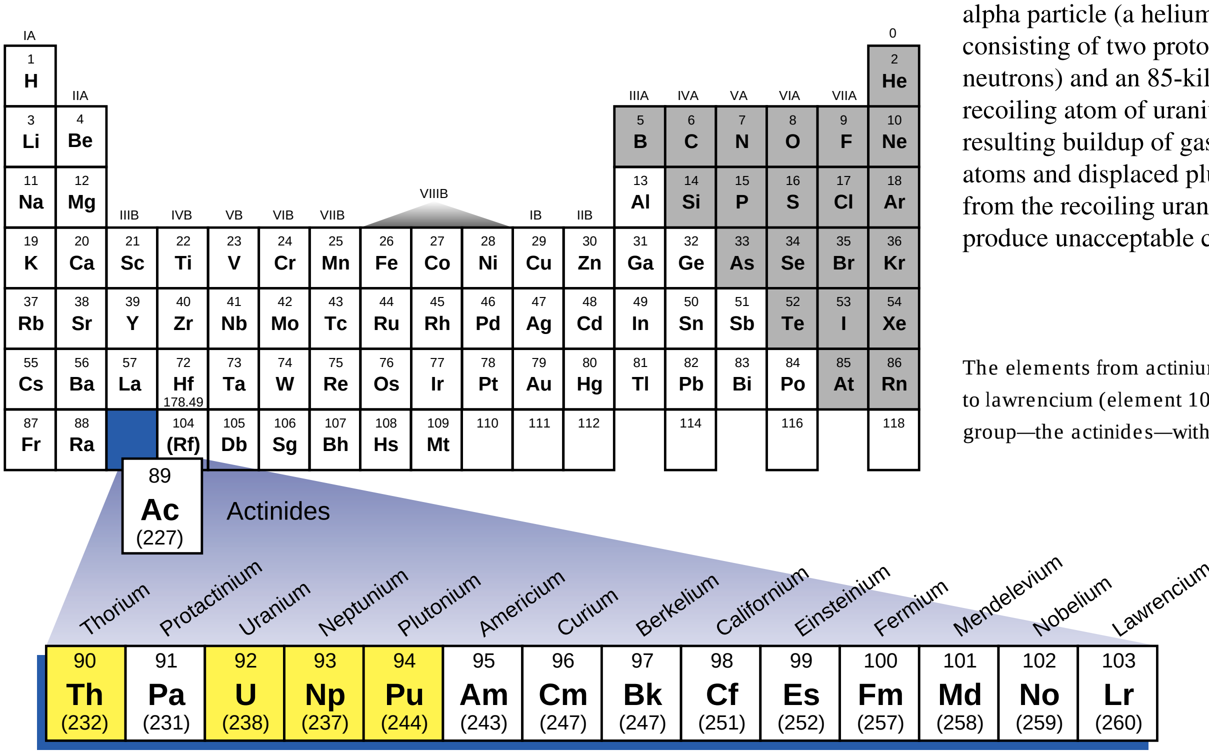
Surrogates Inadequate

Materials scientist Mike Fluss points out that because of plutonium's unpredictability, experimenters prefer not to use surrogate materials. "It's as challenging a material as you can imagine," he says. Even the process of measuring its electrical resistance has proven surprisingly complex because of its unexpected and not fully understood dependency upon temperature.

"We're rebuilding plutonium metals science at Lawrence Livermore," says metallurgist Adam Schwartz. He points to a growing number of experiments measuring the structural, electrical, and chemical properties of plutonium and its alloys and determining how they change over time as a result of the cumulative effects of radioactive decay and consequential damage. These measurements will enable scientists to better model and predict the material's long-term behavior in the nation's aging nuclear stockpile.

Schwartz also cites the recent acquisition of advanced instruments such as a transmission electron microscope capable of nearly perfect resolution at the atomic scale. Additionally, Livermore experts are taking advantage of one-of-a-kind facilities at Lawrence Berkeley and Argonne national laboratories, the Stanford Linear Accelerator Center, and other DOE sites to more completely characterize the electronic and atomic structure of plutonium alloys and compounds.

One line of research is studying the evolution of damage to plutonium metal's crystalline structure on scales as small as a billionth of a meter. This so-called microstructure is always changing because when plutonium-239 decays, it emits a 4-megaelectronvolt alpha particle (a helium nucleus consisting of two protons and two neutrons) and an 85-kiloelectronvolt recoiling atom of uranium-235. The resulting buildup of gaseous helium atoms and displaced plutonium atoms from the recoiling uranium could produce unacceptable changes in the



The elements from actinium (element 89) to lawrencium (element 103) form a distinct group—the actinides—within the periodic table.

plutonium metal. Fluss notes that after 10 years, every plutonium atom has been displaced at least once from its lattice site, but most atoms eventually return there. The plutonium decay itself is slow; in about 24,000 years, only half the plutonium-239 has changed to uranium-235.

The concern, says Fluss, is that atoms of helium and the actinides americium and uranium, also present in the weapon environment, might slowly change the chemistry of the plutonium metal. At the same time, the accumulation of small-scale radiation damage to plutonium alloys over several decades could affect a weapon's safety or its performance. Like other solids, plutonium metal is made of many crystals (or grains) with different orientations. If vacancies or defects coalesce, they may cause changes in properties, with possible unwanted effects to a warhead. By better understanding the nature of the changes, scientists can refine their predictive codes.

100-Year Predictions Needed

"We need to know how plutonium in our stockpile will react over 100 years," says Fluss. "We're asking harder questions today because nuclear weapons must last a lot longer than their designers ever intended." The answer, he says, lies in obtaining fundamental understanding at the atomic level.

Schwartz and colleague Mark Wall are using the transmission electron microscope to document the differences between plutonium from old, disassembled nuclear warheads and newly cast plutonium. By using electrons instead of light waves, the transmission electron microscope can image features at near-atomic resolution. They start with plutonium samples measuring less than 3 millimeters in diameter and 120 micrometers thick. The center of each sample is thinned to create a region only 100 nanometers

Actinides Can Mean Nuclear Chemistry

The group of elements known as the actinides are the elements from actinium (element 89) to lawrencium (element 103). All members of the series can resemble actinium in their chemical and electronic properties, and so they form a separate group within the periodic table. (An element's atomic number is the sum of the protons and neutrons in the nuclei of its atoms.)

All actinides are metals and all are radioactive. As a result, they dominate the study of nuclear chemistry. The elements emit energy in the form of alpha particles, beta particles, or gamma rays. By emitting these particles, the atoms lose protons and therefore become another element with a lower atomic number. If the immediate product of radioactive decay is radioactive, it also decays to form another element. This process continues until a stable element is formed.

Actinides undergo radioactive decay at different rates; that is, they have different half-lives. Elements with higher atomic numbers have short half-lives and rapid radioactive decay. Some actinides with lower atomic numbers, however, have half-lives ranging between thousands to millions of years.

The two actinides of most interest to Livermore scientists are uranium and plutonium. Uranium, a silver and lustrous metal, has four main isotopes. Because uranium-235 is fissionable, it is used to fuel nuclear power plants and as a component in nuclear weapons.

Plutonium is a silver-gray metal that has 16 isotopes. The isotope of chief interest is plutonium-239, which, like uranium-235, is fissionable. Most nuclear weapons are based on plutonium-239, while plutonium-238 is used as a power source in long-mission space probes.

Metallurgists are probing the microstructure of actinides with a transmission electron microscope capable of near-atomic resolution.

(100 billionths of a meter) thick for the electron beam to pass through. The resulting electron micrographs reveal the nature and extent of defects in unprecedented detail.

Researchers are also doing a variety of accelerated aging studies in which plutonium samples are exposed to higher than normal levels of radiation so that the aging process is significantly accelerated. Such experiments provide an important basis for validating computer models. Other aspects of the physics of radiation effects are being studied by ion irradiation using various light and heavy ions to investigate the predictions of the models.

Lawrence Livermore scientists are also benefiting from fundamental work on plutonium performed by their colleagues in Russia. One study, done over the past 25 years and announced last year, claims to have produced plutonium's correct phase diagram, the roadmap between its six different phases or structural forms. The Russian study, says Schwartz, clarifies certain details about how delta-phase plutonium transforms to a less desired alpha state.

Fluss, Schwartz, and others are planning research that will tap the Laboratory's resources to review the Russian work and test its conclusions. The likely outcome, says Schwartz, is a refinement of current computer codes to more realistically simulate the nature of plutonium.

New Look at Old Data

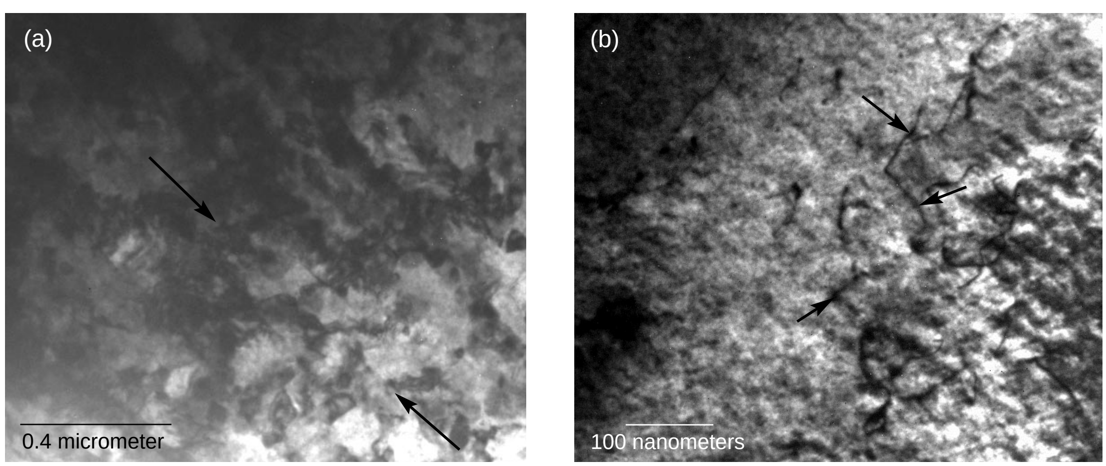
Other Lawrence Livermore researchers are taking a different approach to strengthening the ability of scientists to predict the likely performance and safety of aging weapons. The scientists are looking at results from years of underground nuclear detonations at DOE's Nevada Test Site.

According to nuclear chemist Ken Moody, new measuring techniques and instruments, along with improved understanding of actinide chemistry, warrant revisiting test data that are decades old. Moody is one of a dwindling number of nuclear chemists who did the original chemical separation of actinides from underground tests before they ceased in 1992. He notes that stored actinide samples and even debris from tests could be a treasure-trove of data, despite their reduced radioactivity due to age. The reanalysis could give stockpile stewards a clearer idea of how the nuclear devices performed when they were detonated and how those same designs would perform today.

Livermore researchers are applying their actinide know-how and a suite of sensitive instruments to nuclear forensics work. Chemists like Moody are working with Lawrence Livermore's Forensic Science Center to help America's intelligence agencies stem the proliferation of nuclear materials, especially those from the former Soviet Union. Experts have raised concern about the security of large amounts of weapons-grade nuclear materials in Russia and neighboring states that inherited the materials as a result of the breakup of the Soviet Union. In particular, the dismantlement of thousands of old Soviet nuclear weapons has resulted in large quantities of surplus nuclear materials.

Some actinides, such as uranium-235 (used in nuclear fuel rods) and plutonium-239, have shown up in small quantities in unauthorized hands and on black markets in Western Europe. The concern, of course, is that such materials might make their way to a terrorist group or a nation that supports terrorist activities.

Lawrence Livermore's actinide forensics capabilities are formidable, Moody says. Radiochemical methods can reveal, for example, when a sample of plutonium was manufactured and even the chemical techniques used in its



Images of plutonium metal taken with the transmission electron microscope reveal changes to the plutonium's microstructure. At the 0.4-micrometer scale, diagonal bands in (a) are typical of accumulations of a deformed microstructure. Dark lines in (b) at the 100-nanometer scale are individual dislocations.

Educating Future Actinide Scientists

The Department of Energy national laboratories have long been the stewards of expertise in actinides in the United States. However, many actinide experts are retired or in the process of retiring, and they are not being replaced in adequate numbers.

The situation largely results from a sharp downturn in the number of students graduating with specialties in nuclear chemistry. Across the nation, only a few colleges and universities still provide facilities for actinide research, and professors teaching actinide science have mostly retired. Also, fewer undergraduates are expressing an interest in pursuing careers in nuclear chemistry.

Whatever the expense of improving education, it is an investment in the future we must make. Excellence costs. But in the long run mediocrity costs much more.

—Glenn T. Seaborg

According to Livermore actinide experts, U.S. leadership in heavy-element science will fast erode unless the national laboratories address this issue, which is vital to DOE stockpile stewardship and other missions such as nuclear waste disposition. "One of the most important challenges facing stockpile stewardship is the successful passing of the torch in actinide science," says Lawrence Livermore chemist Lou Terminello.

The University of California's Glenn T. Seaborg Institute for Transactinium Science is attempting to remedy the labor shortage by attracting and training the next generation of actinide scientists. The institute was established in 1991 with facilities at both Lawrence Livermore and Lawrence Berkeley national laboratories. (A third chapter was added in 1997 at Los Alamos National Laboratory.)

The institute is named for the late UC Berkeley professor in recognition of his enormous contributions to the field, including the discovery of 10 elements, among them plutonium. The institute advances fundamental and applied science and technology of transactinium elements (actinides and beyond). Workshops, conferences, lectures, and research projects focus on national security, nuclear energy, environmental protection and remediation, and nuclear waste isolation and disposition.

The institute emphases training at the undergraduate through postgraduate levels. In this way, says Terminello, who serves as institute director, Lawrence Livermore is making a long-term investment in its future. To that end, the institute's Livermore facility operates a summer school for undergraduates who have shown an interest in nuclear chemistry. "We want to capture the imagination of young people by giving them hands-on experience in nuclear science. We want them to go to graduate school and return to Livermore, where they will form our next generation of actinide scientists," Terminello says.

Performing research on actinides for stockpile stewardship often requires training beyond that which is available from universities. As a result, the institute also trains chemists who have recently obtained a Ph.D. For example, young scientists are learning the techniques of x-ray absorption that were refined for actinides by Livermore chemists such as Patrick Allen, deputy director of the institute.

The researchers use the facilities of the Stanford Synchrotron Radiation Laboratory, a part of the Stanford Linear Accelerator Center. The laboratory generates synchrotron radiation, a name given to x rays produced by electrons circulating in a storage ring at nearly the speed of light. The extremely bright x rays excite electrons closest to the nucleus, yielding detailed information about the chemical nature, molecular structure, and electron distribution of actinide-containing materials.

Lawrence Livermore researchers use x-ray absorption to probe samples of uranium and plutonium alloys and compare the results to current computer models. The results are useful in addressing stockpile stewardship issues as well as understanding the behavior of actinides in contaminated soils and potential radioactive waste storage facilities.

Professor Glenn T. Seaborg poses with college students participating in the first summer session (1998) at the Glenn T. Seaborg Institute for Transactinium Science at Lawrence Livermore.

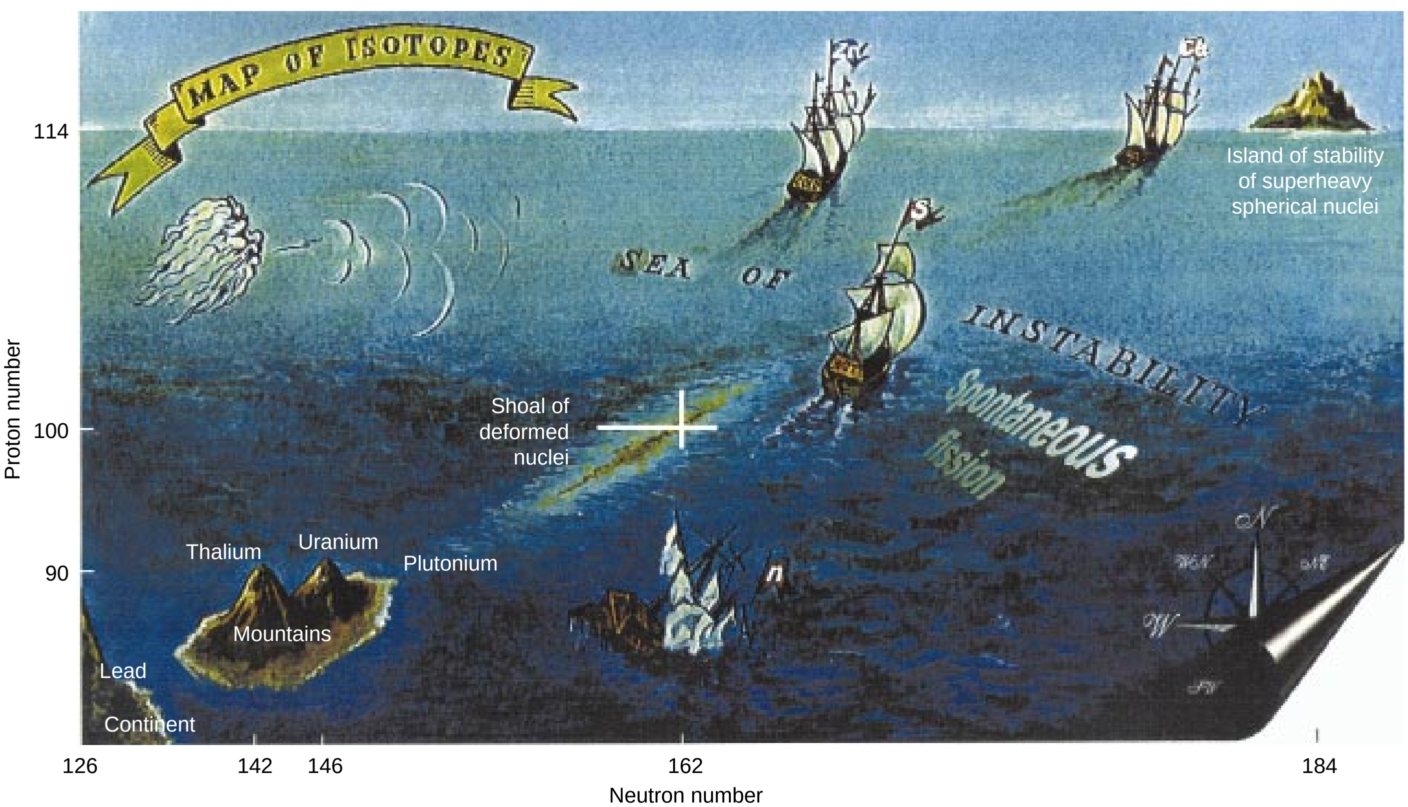
creation. They can also readily show if a suspect material is a hoax rather than a real threat.

Creating Element 114

The accumulated knowledge of actinides' nuclear structure has helped Lawrence Livermore scientists create entirely new elements. In 1989, a Livermore team led by nuclear chemist Ken Hulet (now retired) began a collaboration with scientists at the Joint Institute for Nuclear Research in Dubna, Russia. Over the past decade, the international team discovered isotopes of elements 106, 108, and 110 at the Russian institute.

The researchers' goal in 1998 was far more challenging: to create element 114 and demonstrate a long-postulated region of enhanced nuclear stability against

For more than a decade, Russian and Lawrence Livermore collaborators have used the facilities of the Joint Institute for Nuclear Research in Dubna, Russia.



A Russian artist depicts the modern nuclear theory of the heaviest elements. At the upper far right is the island of stability, which was demonstrated by the production of long-lived element 114 in 1998 by a Russian–Livermore team.

spontaneous fission. This region, considered by some impossible to reach, was theorized to lie amidst a "sea" of extremely short-lived, super-heavy nuclei.

The most recent experiment, led by Moody, involved a team of five Livermore scientists and 17 Russian researchers. The team bombarded ions of the rare isotope calcium-48 onto a target of plutonium-244 (the heaviest long-lived plutonium isotope) supplied by Livermore. It took the team 40 days of irradiation to create one atom of the new super-heavy element 114 in December 1998. The new element lasted 30 seconds, some 100,000 times longer than if there were no enhanced stability in that area of the periodic table.

Moody believes the discovery of element 114 has strengthened interest in heavy-element science. Since the discovery, Lawrence Berkeley researchers have found two new elements—116 and 118. The continuing discoveries are providing important insights into the arrangement of electrons in atoms and chemical bonding.

The Livermore–Russia connection is still going strong. Since the December 1998 discovery, the U.S.–Russian team has found a different isotope of element 114, one with a decay time of one second. The team is currently working on finding another isotope of element 116, this time with a curium isotope target, so they can continue mapping the region of enhanced stability.

Plutonium Moves Differently

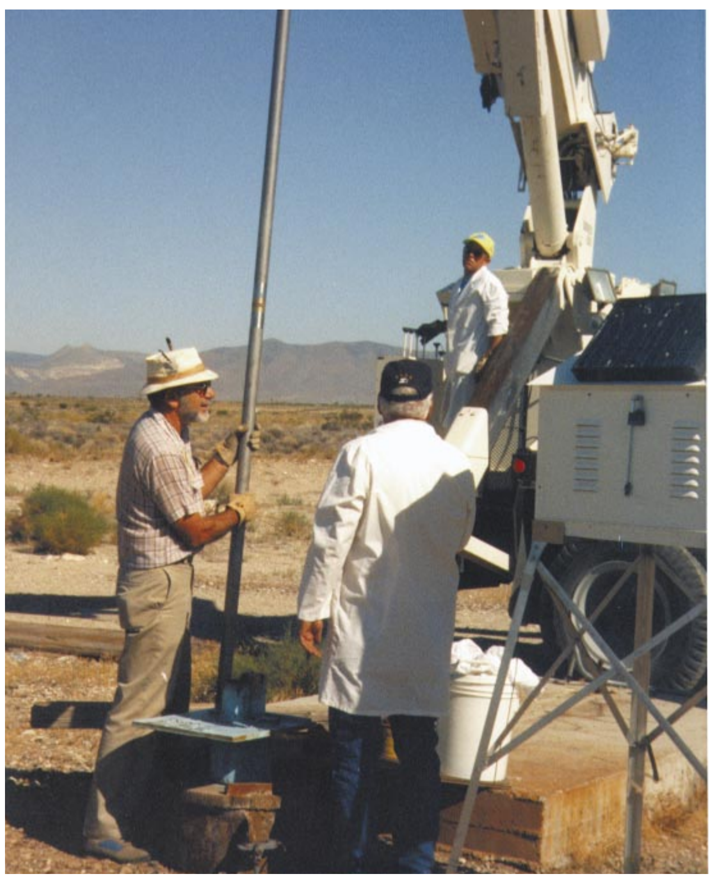
An important aspect of Lawrence Livermore actinide research is studying how these elements behave in the environment, particularly how they migrate underground in solution. The research results have challenged some long-established scientific assumptions.

For example, scientists assumed that plutonium, because of its low solubility in water and its strong tendency to sorb (adhere) to clumps of dirt and rocks, does not travel far in groundwater. A Lawrence Livermore–Los Alamos team led by Livermore geochemist Annie Kersting has shown, however, that plutonium can adhere to colloids, which are naturally occurring particles of rock smaller than a micrometer in diameter. In this way, small amounts of plutonium can be transported considerable distances by groundwater.

The team studied the distances plutonium ions had traveled from the Pahute Mesa region of DOE's Nevada Test Site. The group analyzed some of the groundwater pumped from two deep sampling wells dug near the sites where four underground nuclear tests had been conducted. The researchers discovered that colloids filtered from the water contained more than 99 percent of the small amount of plutonium found in the well-water samples. (In contrast, 99 percent of the tritium was found in solution, and virtually none was found in the filtrates.) The team proposed that small amounts of plutonium had adhered to mineral colloids that were transported by groundwater away from the test location.

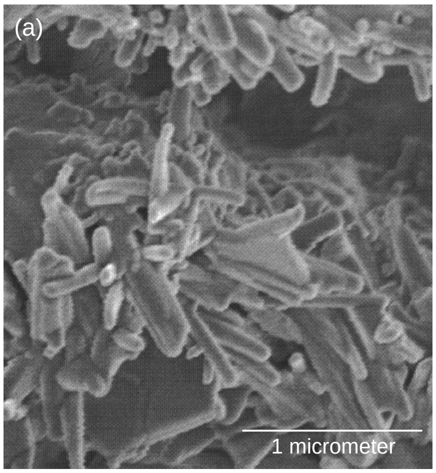
The team ascertained which of the four tests conducted in the area had produced the plutonium by measuring the ratio of the plutonium-240 isotope to the plutonium-239 isotope. (Every nuclear test can produce a unique ratio of the two plutonium isotopes.) The isotopic ratio measured on the groundwater colloids matched that of the 1968 Benham underground test, which was conducted 1.3 kilometers from one of the wells.

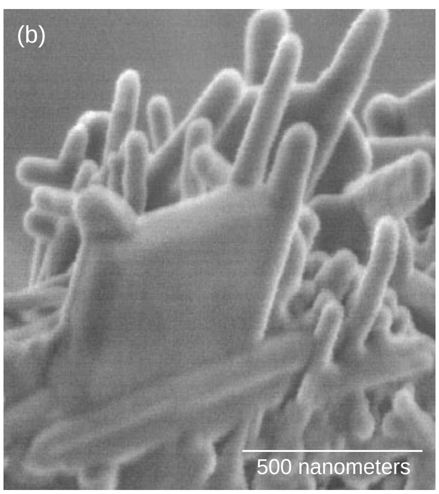
"We were surprised to find that the plutonium in the wells was from the Benham test because 1.3 kilometers is a long distance for plutonium to migrate," says Kersting. She adds, however, that the detected plutonium concentration was extremely small and did not pose a health risk.



Groundwater pumped from wells drilled in Pahute Mesa at the Nevada Test Site showed that small amounts of plutonium traveled surprising distances underground.

The team's findings have important implications for the proposed Yucca Mountain nuclear waste repository in Nevada (see *S&TR*, March 2000, pp. 13–20.) The findings may also be applicable to other DOE sites such as Rocky Flats in Colorado and the Hanford Nuclear Reservation in Washington, although their underground geology differs from the Nevada Test Site's.





Two scanning electron microscope images of mineral colloids (tiny rock particles) containing plutonium filtered from groundwater at (a) the 1-mircrometer scale and (b) the 500-nanometer scale. Mineral colloids consist of clay and zeolites, common secondary minerals found in rocks at the Nevada Test Site. Research by a Lawrence Livermore team suggests that small amounts of plutonium can be transported considerable distances by groundwater by adhering to colloids.

In light of the team's research, Kersting says that models that do not allow for transport of plutonium by colloids may significantly underestimate how far and fast the element can travel. She also notes that colloids may be important in the transport of other actinides. "We want to know how other actinides such as neptunium, americium, and uranium move underground," she says.

Kersting is collaborating with other Livermore geochemists to determine experimentally how actinides are associated with mineral colloids. In addition, she is investigating the importance of colloid-assisted transport of actinides in the vadose zone, or unsaturated subsurface, which is located between the ground surface and the water table. Two-thirds of the underground nuclear tests were detonated in the vadose zone at the Nevada Test Site. The research is taking place in tunnels that have been dug at the site's Rainier Mesa, whose vadose zone was previously studied by Livermore scientists.

The colloid discovery, she says, emphasizes the importance of linking precisely controlled laboratory experiments with field studies. "If you only look at results from experiments in the laboratory, you won't necessarily understand what's happening in the field."

From the arid stretches of the Nevada Test Site to physics research laboratories of Russia, Lawrence Livermore researchers are pursuing wide-ranging aspects of actinide science. They are combining theory, fieldwork, laboratory experiments, and computer simulations on scales ranging from atoms to kilometers, all with the aim of uncovering the secrets of the actinides.

—*Arnie Heller*

Key Words: actinides, colloids, Forensic Science Center, Glenn T. Seaborg Institute for Transactinium Science, Nevada Test Site, plutonium, Stanford Linear Accelerator Center, Stanford Synchrotron Radiation Laboratory, stockpile stewardship, uranium.

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About the Scientist

LOUIS J. TERMINELLO is currently leader of the Materials Science and Technology Division in the Chemistry and Materials Science Directorate at Lawrence Livermore National Laboratory. He is also director of the Glenn T. Seaborg Institute for Transactinium Science at Livermore. He earned his Ph.D. in physical science from the University of California at Berkeley in 1988 and is an adjunct associate professor there. His research interests include solid-state physics, atomic and electronic structure determination of novel materials using synchotron radiation photoemission and absorption, and photoelectron holography and valence-band imaging studies of electronic material surfaces and interfaces.