Oak Ridge National Laboratory

REVIEW

Vol. 23, No. 4, 1990

DISORDER IN CRYSTAL SURFACES

VERDICT ON ACID RAIN

ORNL AND ANTARCTICA

ON THE COVER

The lead phosphate glasses developed by ORNL's Solid State Division represent a new class of phosphate-based materials that can be used for optical applications such as lenses, prisms, and windows. ORNL scientists Brian Sales and Lynn Boatner have doped phosphate glasses with various impurities from the iron and rare-earth groups to alter their optical properties—for example, color—as shown in the photograph. Glasses of different colors have potential applications as optical filters, selective absorbers, and radiation-resistant window materials. Basic research carried out on these materials in the Solid State Division has also led to a new level of understanding of the structural properties of the glass and amorphous state of matter, as discussed by Brian Sales and Lynn Boatner in their article on p. 19. Photo by Bill Norris

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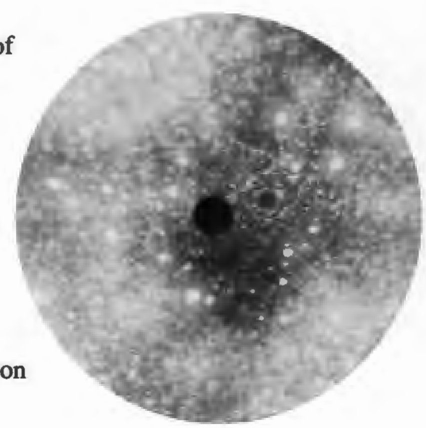
FEATURES

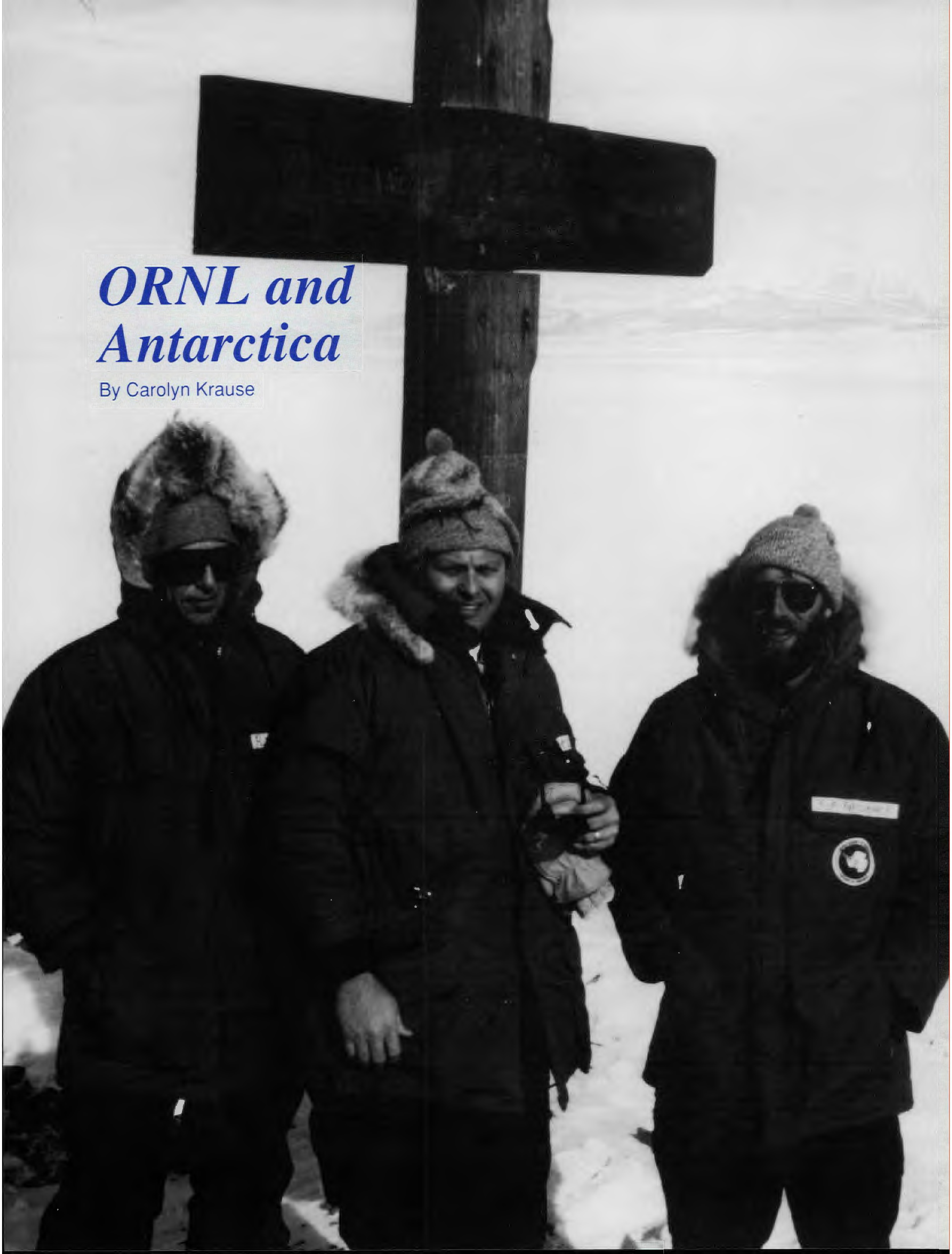
DEPARTMENTS



Oak Ridge National Laboratory is a multiprogram, multipurpose laboratory that conducts research in the physical, chemical, and life sciences; in fusion, fission, and fossil energy; and in energy conservation and other energy-related technologies.

ORNL and Antarctica

By Carolyn Krause



Bob Reed, Rich McLean, and Steve Railsback view McMurdo Station (a U.S. research base in Antarctica) from the top of Observation Hill. The cross was erected in 1913 as a memorial to British explorer Robert Falcon Scott and his four companions who died returning from the South Pole.

Penguins, seals, and subzero temperatures were on the minds of three ORNL researchers in November 1989. They were on a three-week work assignment in Antarctica to gather information about the environmental impacts of U.S. research activities there. This unique opportunity arose because of ORNL's extensive experience in preparing environmental impact statements for many kinds of projects in many different geographic areas.

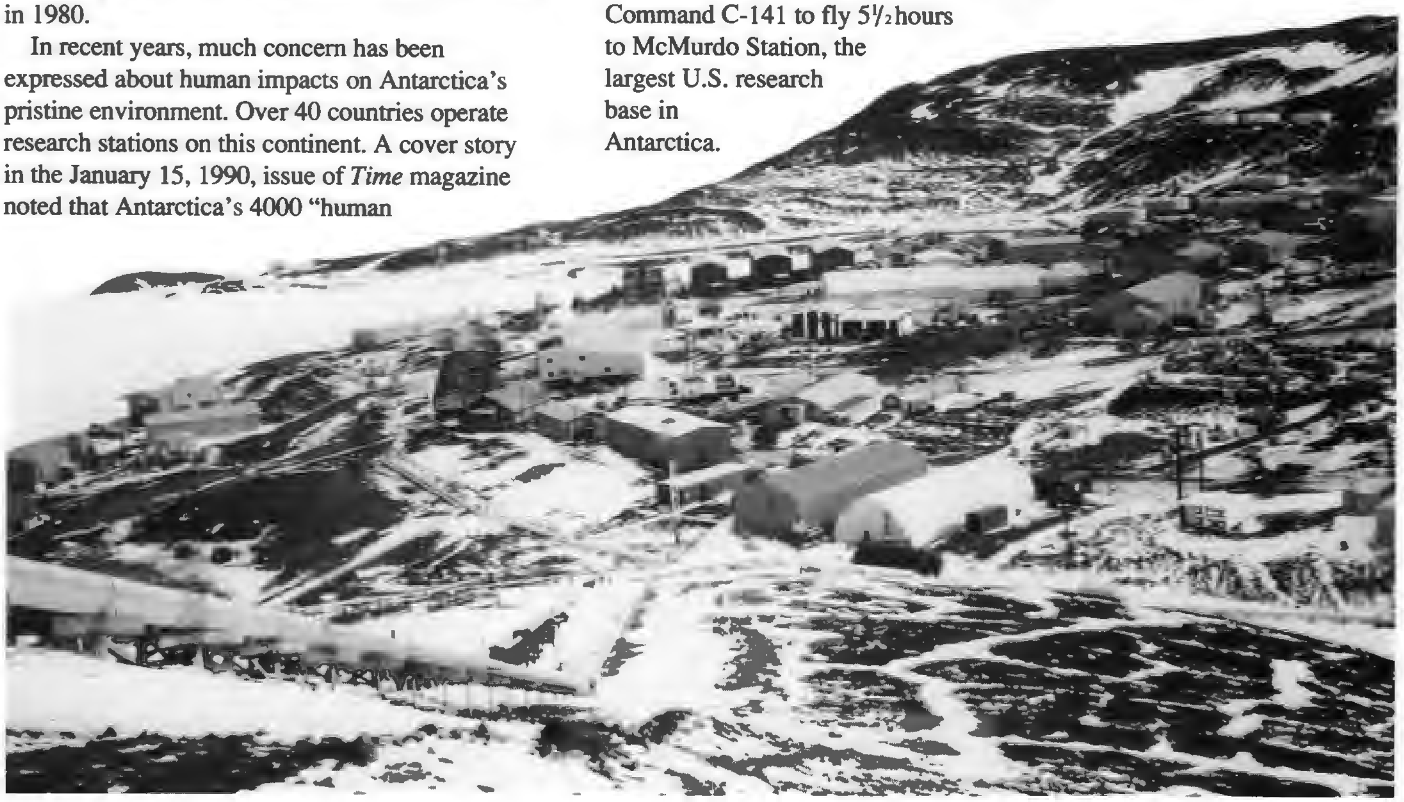
The ORNL researchers who made the trip were Rich McLean, project leader, of the Energy Division; and Bob Reed and Steve Railsback, both of the Environmental Sciences Division. McLean and Reed are principal investigators for the project.

The information is being used to help the National Science Foundation (NSF) draft a supplemental programmatic environmental impact statement for the U.S. Antarctic Program. This comprehensive supplemental statement will update a programmatic impact statement published in 1980.

In recent years, much concern has been expressed about human impacts on Antarctica's pristine environment. Over 40 countries operate research stations on this continent. A cover story in the January 15, 1990, issue of *Time* magazine noted that Antarctica's 4000 "human residents have endangered natural habitats by spilling oil into the seas, dumping untreated sewage off the coasts, burning garbage in open pits, and letting huge piles of discarded machinery slowly rust on the frozen turf." Antarctica has been in the news lately because of recent proposals to restrict oil and mineral exploration and to establish a world park to preserve the continent's unspoiled environment.

Living with the Chill Factor

In November the ORNL researchers visited two U.S. research stations in Antarctica—the McMurdo Station and the Amundsen-Scott South Pole Station—to gather data on the environmental impacts on Antarctica of all American activities related to research. On November 1, 1989, they flew from Knoxville to the west coast, and then on through Honolulu to Christchurch, New Zealand, where they were outfitted with cold-weather clothing. After a few day's delay because of weather, they boarded a Military Airlift Command C-141 to fly $5\frac{1}{2}$ hours to McMurdo Station, the largest U.S. research base in Antarctica.



The three ORNL researchers spent much of November 1989 at McMurdo Station, viewed here from the side of Observation Hill. In the left background is Hut Point, site of Scott's *Discovery* Hut, and the frozen McMurdo Sound.

Elephant seals abound on a small island near the Palmer Station, another U.S. research base.

Supplies of food abandoned in 1909 in the hut built for British explorer Ernest Shackelton's polar expedition are still well preserved because of Antarctica's cold climate. The hut is located at Cape Royds, near McMurdo Station.

November is early summer in Antarctica, and the researchers found that daily temperatures rose as high as –18 to –5°C (0 to 22°F), but the coastal wind lowered the chill factor to well below zero. "At times my face became numb in 30 seconds when I walked outside," said McLean, "and I found it hard to get used to the cold and the winds—perhaps because I was raised in Daytona Beach." The ORNL researchers were impressed by how well the Antarctic cold preserves, leaving few signs of deterioration: on their visits to two huts built in the early 1900s for the Scott and Shackelton expeditions, they saw well-preserved hay, a seal carcass, spilled beans, and food left in a frying pan.

To survive the outdoors, the ORNL researchers wore boots, wool socks, thermal underwear, wind pants, wool shirts, vests, parkas, hats, gloves, and mittens—all issued by the NSF before they left New Zealand. They also wore special sunglasses to protect their eyes from the glare of the snow.

The *Discovery* Hut was built in 1902 for Robert F. Scott's expedition to the South Pole.

"I felt dwarfed by the environment," said McLean. "When you look down, you see human communities, but when you look up, you see awesome mountains and 7-foot-thick sea ice of incredible beauty as well as vast stretches of ice that seem to go nowhere.

"Even though in most parts of Antarctica there is not much precipitation, there is a lot of accumulation because of the cold. The average thickness of ice, which is really packed snow, is over 7000 feet. Not surprisingly, we saw T-shirts saying, 'Ski South Pole—Two Miles Base, One-Half Inch Powder.' "

The McMurdo Environment

The ORNL researchers spent most of their time at McMurdo Station, which has an average summer population of about 1100. This station serves as a staging area for field parties studying geology, volcanology, meteorology, glaciology, atmospheric physics, biology, and astronomy. For example, some researchers are studying the ecological effects of the thinning ozone layer, and one group is studying the Antarctic cod to determine the type of "antifreeze" the fish uses to survive subfreezing temperatures.

The ice and the extremely cold temperatures of Antarctica limit waste disposal practices. Burial of wastes, for example, is not desirable because organic material does not decompose at subzero temperatures. Current practices, such as burning combustible garbage and recycling metals, comply with international guidelines developed under the Antarctic Treaty. However, the NSF is conducting a major study of waste disposal alternatives to reduce the risk of environmental impacts.

While at McMurdo, the ORNL researchers observed the construction of a new deepwater wastewater outfall. Care is taken not to use the ocean to dispose of chlorinated sewage and

Metal scrap at McMurdo Station awaits shipment back to the United States for recycling.

sewage containing chemical wastes because, unlike raw sewage, these can be toxic to marine life.

Most supplies for the program are brought to Antarctica by ship once a year, including heavy equipment, which is unloaded at McMurdo Station and transported to other research bases by sled, tractor, or airplane. The barrels in which some materials are packed are emptied and reloaded with waste materials to be returned, or "retrograded," for final disposal in the United States.

Electrical power is supplied to McMurdo Station by a power plant fired by cold-weather diesel fuel, called Diesel Fuel–Arctic. At one time a small nuclear power plant generated electricity at McMurdo, but it has since been dismantled and shipped back to the United States. Fuel oil is brought in by tanker vessel and stored in tanks and fuel bladders. Minor oil leaks and major oil spills have occurred in the past, and leaking fuel bladders remain a potential environmental problem.

Most residents of McMurdo Station are conscious of the need to reduce their impact on the environment. For example, efforts are made there to collect beverage cans and glass bottles for recycling. Whenever machines are worn out, they are stripped of their usable parts, with the remaining skeletons being shipped back to the United States. Much of the refuse left from the earlier "expeditionary days" has been collected and returned to the United States for disposal. Great effort goes into reducing the amount of unnecessary materials, such as packaging, that reach McMurdo. Hazardous and radioactive wastes are carefully packaged and returned to the United States.

Model Research Base

Scott Base, the recently rebuilt research station operated by New Zealand—one of more than 30 nations conducting research in Antarctica—is generally considered a model facility from the standpoint of environmental protection. Most of

The entrance to the South Pole Station, a U.S. research base housed in an aluminum dome, is partly buried by drifting snow.

the station's human and research activity wastes (except wastewater, which is discharged into the ocean) are collected, contained, and shipped back to New Zealand for final disposal—"a good policy," says McLean. This base houses a maximum of 80 persons, so it has less than one-tenth the summer work population of McMurdo Station, making waste management less burdensome. According to Reed, the New Zealand base "depends heavily on the logistics support provided through the neighboring McMurdo Station." Its approach is given good marks by the environmental activist organization Greenpeace, which has an Antarctic base for monitoring the environmental impact of other research stations' activities.

McLean, Railsback, and Reed had the opportunity to fly for a short visit to the U.S. Amundsen-Scott South Pole Station, whose thickly insulated buildings are covered by a geodesic dome. Some scientists are suggesting that solar energy be used at this base because the sun shines at the South Pole 24 hours a day

The Ceremonial South Pole is surrounded by the flags of the Antarctic Treaty nations. The location of the actual pole appears to change because the ice sheet is moving. A marker (far right) is placed at the actual pole every year.

A worker helps clean up a science camp in Taylor Valley, one of the Dry Valleys (so called because they are one of the rare areas in Antarctica not covered by glaciers).

The fence around McMurdo Station's landfill area prevents some of the wind-blown debris from reaching the frozen McMurdo Sound.

during the summer, and its light is intensified by reflection from the snow.

The Antarctic Peninsula

In late March 1990, Reed and Railsback returned to Antarctica to visit the third U.S. base. Palmer Station is located on the Antarctic Peninsula, about 1400 km south of the tip of South America. Because of its moderate weather, abundant wildlife (especially penguins, seals, seabirds, and whales), and spectacular scenery, the peninsula is the site for a majority of research stations and for tourism in Antarctica.

The researchers traveled to Palmer Station on the U.S. Antarctic Program's research ship, the R/V *Polar Duke*. Because the availability of travel is restricted, Reed and Railsback made their trips to the base at different times. They both took commercial flights to Punta Arenas, Chile, and then flew by a U.S. military transport airplane to the Chilean base on King George Island in Antarctica, where they boarded the *Polar Duke*.

Railsback spent 10 days aboard the ship as it conducted oceanographic studies in the pack ice of the Weddell Sea before traveling to Palmer Station. Reed's trip included several days of

This is one of the National Science Foundation's ski-equipped LC-130 transports used to fly personnel and supplies to Antarctic stations and remote field sites.

trawling for Antarctic fish to be used in research at Palmer Station. Palmer Station sits on a rocky spit at the foot of a receding glacier on Anvers Island, houses about 40 staff members, and supports biological and atmospheric research. The ORNL researchers were able to visit several areas of ecological interest; observe the remains of the Argentine ship Bahia Paraiso, which sank near the station in 1989; visit the site of the Old Palmer Station; and travel to the British base at Faraday.

Following their fact-finding missions, Reed, Railsback, and McLean, along with other ORNL staff, prepared a draft impact statement that was published in December 1990. This statement evaluates the environmental impacts of several alternatives the NSF is considering for continuing its research program over the next ten years. Major issues being evaluated include potential impacts of materials and solid waste management, wastewater discharges, use of fuel, fuel spills, atmospheric emissions, and scientific research. This impact statement, which is being revised to take into account public comment on NSF plans, concludes that current activities are localized and can continue at current or increased levels with minimal risk to the environment. ornl

Reducing Friction To Save Energy

By Peter J. Blau

"The cost of friction and wear problems in the United States has been estimated at well over $70 billion per year."

The relationship between friction and energy consumption is complex. In a mechanical device, friction from components rubbing together robs the device of some of its useful kinetic energy, converting it to heat and vibration. However, friction makes it possible for us to safely use the mechanical energy of automobiles and trucks; without it, brakes would not stop vehicles, tires would not prevent them from sliding out of control, and clutches would not transmit the rotation of the engine crankshaft to the gearbox and then to the wheels. Wear, a consequence of friction, is also important for fueling our cars: crude oil, which is needed to make gasoline, is obtained by rock drilling, an extreme form of abrasive wear.

The force of friction resists relative motion. In the moving parts of engines, friction results when one surface rubs against another. When surfaces are frequently in contact with each other, the engine components wear so that they eventually must be replaced; thus, the problems of friction and wear often go hand in hand. In engines, friction can also result when components move through liquid or gas, such as water or air.

Because friction wastes energy and contributes to rapid wear and early failure of engine parts, designers seek ways to reduce it. Less friction reduces fuel consumption and increases engine efficiency. The obvious ways to reduce frictional contact in automotive vehicles are through increased streamlining of the vehicles (to reduce aerodynamic friction), better engine bearings, and improved lubricants.

The U.S. Department of Energy has been supporting research on ways to decrease friction, slow wear, and improve lubrication because of their potential for reducing the demand for imported oil and other fuels. The science and technology of friction, wear, and lubrication are collectively called tribology.

One focus of tribology is the rolling-element bearing, which was invented in Europe about 1000 B.C. to reduce sliding friction. A ball bearing contains balls, and a roller bearing contains rollers, but both work by the same principle. In a ball bearing, friction is kept low because the area of contact between the balls and the moving parts is very small.

Why Is Tribology Needed?

In a major survey conducted in 1980 by the American Society of Mechanical Engineers and published in the Society's *Strategy for Energy Conservation Through Tribology*, it was estimated that improvements made in machinery as a result of tribology could potentially save the nation $8.9 billion a year in the cost of oil needed for road transportation. (This converts to $13.1 billion in

Peter Blau uses the friction microprobe designed and built at ORNL to study variations in the friction of microscopic surface features of composite materials. This work may guide the development of "self-lubricating" materials tailored to minimize friction.

1989 dollars, and since the oil-price shock resulting from Iraq's invasion of Kuwait on August 2, 1990, that amount may grow much higher.) The 1980 survey also predicted potential energy savings for all types of fuel through applications of tribology research results: $0.9 billion for power generation, $4.4 billion for turbomachinery, and $7.2 billion for industrial machinery and processes. (In 1989 dollars, the amounts saved would have been $1.3 billion, $6.5 billion, and $10.6 billion, respectively.)

Similar surveys conducted in other countries have provided a strong motivation for research and development (R&D) aimed at better lubricants, new wear-surface modification technologies, and more reliable "tribomaterials"—materials for use in critical components subjected to friction and wear. Emerging designs for higher-performance and reduced-emissions engines have placed additional demands on materials and lubricants.

The cost of friction and wear problems in the United States has been estimated at well over $70 billion per year. This figure includes the cost of new parts to replace the worn ones as well as the labor to repair worn parts and install new ones. When only a few grams of material are worn from the surface of a bearing, a mechanical face seal, or gear, these engine parts can fail to function in the intended way. Thus, repair or replacement of worn parts is essential for reliable and safe engine operation.

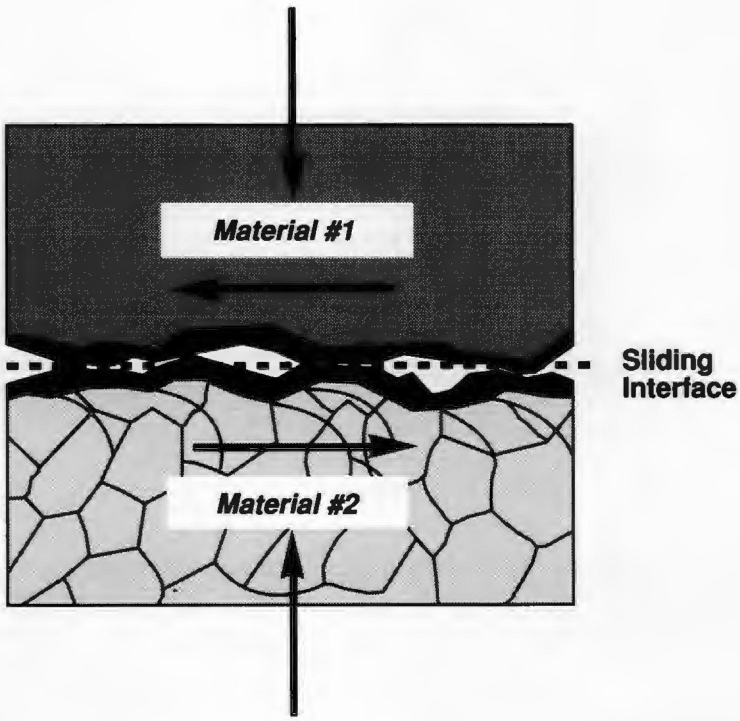
Several trends indicate that tribology research is increasingly needed. Because of concerns about depletion of mineral resources and the growing cost of materials, it is no longer justifiable to discard a large mechanical component simply because a tiny amount of material is worn from its outside surface. In addition, consumers are increasingly demanding improved product quality, energy efficiency, and reliability in the vehicles and appliances they buy. The oil-price shock of August 1990 has focused renewed attention on the need to use methanol, ethanol, and other alternative fuels for road transportation; yet the substitution of such fuels for petroleum fuels will create new friction and wear problems in cars and trucks.

Tribology at ORNL

Tribology research at ORNL began in 1982 in response to the need to develop concepts for high-temperature, high-efficiency ceramic heat engines. Charlie Yust , a principal investigator on our tribology staff, led the initial effort, which established ORNL as an early leader in the field of friction and wear in ceramics.

Some of the nation's best tribology test systems are located in ORNL's High Temperature Materials Laboratory (see photo below). The equipment is configured to study friction and wear at various temperatures and in various gaseous environments. The four side-by-side units in the foreground are used for sliding

This bank of custom-built machines permits controlled-atmosphere sliding friction and wear tests to be performed. At the right rear is a high-temperature machine capable of testing at up to 1000°C.



Relative motion in the sliding interface can result in near-surface deformation and shearing in one or both materials, especially if lubrication is absent or ineffective. A highly deformed layer may be created just below the surfaces of both materials.

friction and wear testing at room temperature, and the tall unit behind them is used for experiments on advanced materials at temperatures up to 1000°C.

Most of our studies are in solid friction—the result of contact between two solid bodies. In the 17th century, solids were seen as having serrated surfaces, and friction was explained in terms of ratcheting, or interlocking, sawteeth. Later, it was believed that high friction between surfaces was the result of atomic-level adhesion. More recently, solid friction has been explained as "material deformation by localized shearing." (See drawing above.) In other words, when two materials come into very close contact, the surface features interlock, resulting in shear (a stress that results from applied forces in which two contiguous parts of a body slide relative to each other in a direction parallel to their plane of contact).

When the force pressing two moving surfaces together is relatively small, the friction may be governed by the characteristics of thin films placed between those surfaces. Use of an effective lubricant to separate two moving bodies is a good example. When large forces press the surfaces together, a lubricant may fail to keep them separated or the lubricant may be squeezed out. In that case, the shearing strength of the interlocking solid materials themselves may be the major contributor to the measured friction force. Friction in machinery may, therefore, arise from a combination of phenomena, which must be analyzed on a case-by-case basis.

In the early 1980s our group in the Metals and Ceramics Division critically evaluated the high-temperature wear of a number of monolithic, polycrystalline ceramics, such as alumina, silicon nitride, silicon carbide, and zirconia. Then in the mid-1980s our research interests shifted toward evaluating the new generation of high-toughness, whisker-reinforced ceramic composites, such as alumina reinforced with silicon carbide whiskers. Our more recent work has also involved whisker-reinforced silicon nitride matrix composites, in both lubricated and unlubricated conditions. The aim of the new work is to identify the contact conditions that can lead to transitions between acceptable and unacceptably high, or catastrophic, friction coefficients or wear rates. Three-dimensional representations of the relationships among several variables—the pressures that parts of bearings exert on each other, the velocity with which components in contact (sliding partners) slide past each other, and the time of sliding—are being developed to help set design limitations to prevent catastrophic wear in advanced ceramic materials used in heat engines.

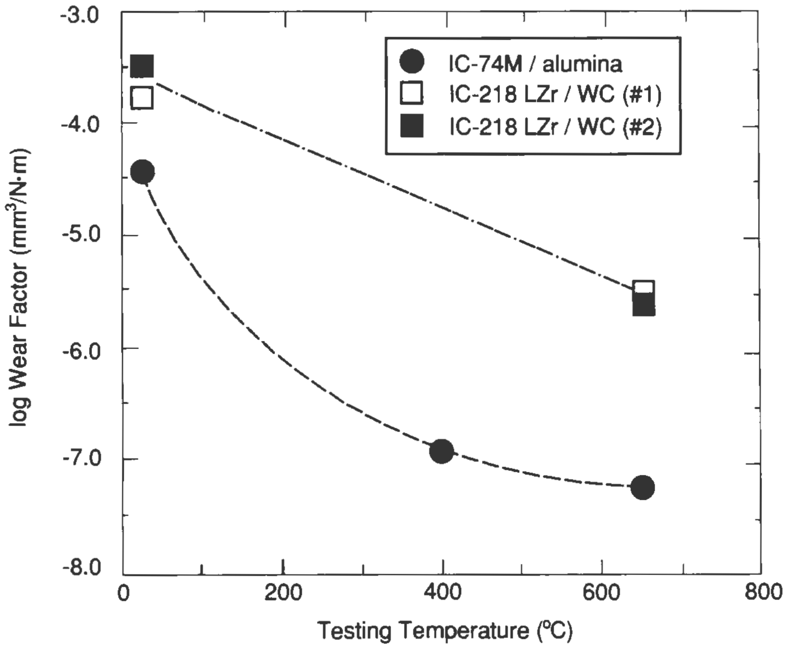
Performing wear and friction tests is only the first step in our investigations. To understand frictional behavior, we may subsequently require detailed studies of contact surface morphology—the shapes of the features of rubbing surfaces—and of the structure and chemistry of various thin layers that can form during repeated surface contact. To understand the manner in which wear manifests itself in different materials, we use both optical and electron microscopy, sometimes looking at the contact surfaces from above, and sometimes in cross section. X-ray analysis and transmission electron microscopy of the wear products (debris) provide additional clues to answering the fundamental question: How does the combination of the structure and physical properties of given materials lead to their wear and friction behavior in specific situations? We observed that tangled dislocations—linear defects in crystal perfection—formed a few millionths of a meter below the sliding contact surface of a ceramic composite of alumina and silicon carbide whiskers (see photo on this page). Such features indicate that material damage gradually accumulates below a worn surface, leading to catastrophic wear.

In 1987, we began evaluating the potential for using ORNL-developed nickel aluminide alloys (unique alloys with ordered crystal structures, based on the compound Ni_3Al) for components subjected to friction and wear at elevated temperatures. Because the strength of these unusual materials rises with increasing temperature (up to about 650 to 750°C), we became curious about whether the wear resistance would also improve as the temperature increased. Sure enough, our tests showed that the wear rates of two of the nickel aluminide alloys (designated as IC-50 and IC-218 LZr) against ceramic sliding partners dropped significantly—as much as 1000 times—as the temperature of testing was increased from room temperature to 650°C (see figure on p. 14). Although the unlubricated sliding wear rates of these alloys at room temperature are not impressive, their wear rates at elevated temperatures rival those of many ceramics tested under similar conditions. Because they are more easily fabricated by conventional methods than are ceramics, we believe that nickel aluminide alloys may be an attractive alternative for certain high-temperature wear applications. Commercial licensees of these unique alloys are watching our work with interest.

Fine dislocation tangles begin to form as more and more damage accumulates below a wear surface. This transmission electron micrograph shows subsurface dislocation tangles in a composite of silicon carbide whiskers in an alumina matrix. The cross section of a hexagonal whisker 0.5 µm in diameter is visible at the top left. (Photo by C.S. Yust)

"The aim of the new work is to identify the contact conditions that can lead to transitions to catastrophic friction coefficients or wear rates."

During the past year, we have studied the differences and similarities between a nickel aluminide alloy's tribological behavior and its machining characteristics. Using different cutting tools, fluids, and lathe turning speeds, we observed such characteristics of the cut surfaces as their resulting surface finishes and the extent to which the material below the surface was



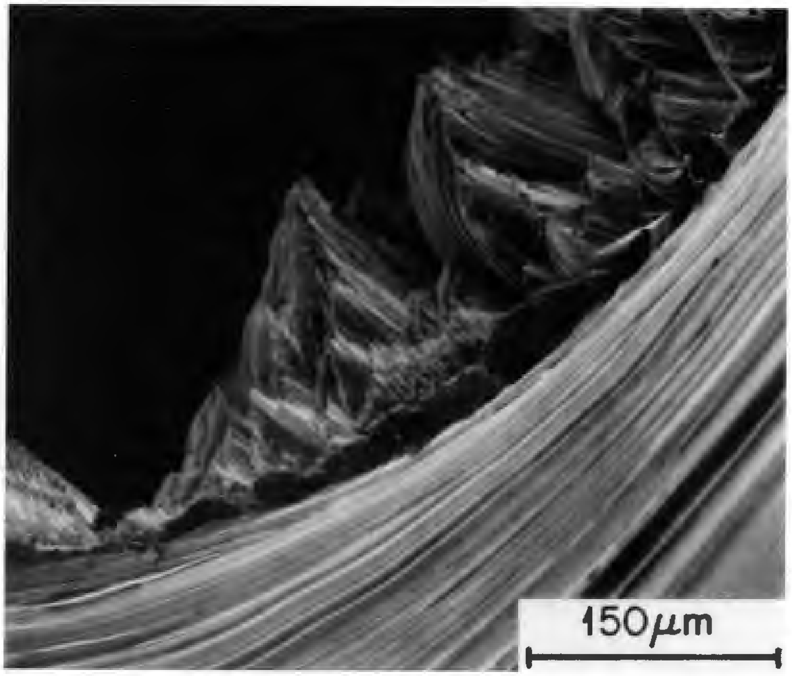
Unlike many materials whose wear rates increase as temperature increases, the wear rates of several nickel aluminide alloys actually decrease with rising temperatures. Tests were done in the high-temperature machine shown in the background of the photo on p. 11. The top curve was generated with tungsten carbide sliders on nickel aluminide, and the bottom with alumina sliders on nickel aluminide of a different composition.

damaged as the cutting tool passed over it. One interesting feature of the machining process is the manner in which the "cutting chips" (chips produced by cutting) are generated. If the chips form long and continuous strands, they can snarl the machine tools. We found that higher cutting speeds produce much shorter chips, which do not tangle on the tooling. In a scanning electron microscope view of the edge of a small cutting chip (see photo on p. 15), we observed both the long scratches on the nickel aluminide surface that slid against the cutting tool and the sawtooth-like features that formed on the opposite side of the chip as the alloy changed its shape during the chip-forming process. Understanding the origins of such severe deformation aids our efforts in modeling wear processes in materials subjected to machining.

Within recent years it has become possible to grow diamond films on a variety of substrate materials by elevated-temperature decomposition of methane gas in hydrogen environments. Because diamond is very hard, chemically inert, highly conductive, and naturally low in friction, it has evoked considerable interest for tribological applications. To determine how crystal growth facets can affect the magnitude of sliding friction, we investigated three diamond films with different microgeometric surface features that Bob Clausing and Lee Heatherly, also of the M&C Division, grew by hot-filament-assisted chemical vapor deposition. Friction experiments using both sapphire and bearing steel sliders confirmed that square, flat diamond crystal facets, grown with silicon substrate temperatures of about 1273 K, were lower in friction (a friction coefficient of ~0.15–0.20) than either the finely grained surfaces grown at about 1200 K (~0.3–0.4) or the sharper, pyramidal facets grown at about 1323 K (~0.40–0.50). These and related experiments are guiding the optimization of processes that grow diamond films that achieve the best frictional performance in a variety of applications, ranging from computer hard disks to surgical knives and cutting tools.

Some recent tribology research highlights are:

- We determined that the leading candidate ceramics for high-temperature rubbing parts of advanced heat engines are unsuitable for use under unlubricated conditions.



This "moonscape" is actually the side view of a machining chip produced by lathe turning the nickel aluminide alloy IC-218 LZr. This view was taken by the scanning electron microscope at the High Temperature Materials Laboratory. The grooves at the bottom were caused when the back of the chip slid up the forward face of the cutting tool, and the "mountains" were produced by upheavals of material on the opposite face of the chip as it was deformed during cutting.

- We determined that nickel aluminide alloys have significant potential for uses in sliding or rolling element bearings that operate in a temperature range of 400 to 600°C.

- We published the first studies of the friction and wear of high-temperature superconducting ceramics, reporting them to be generally unsuitable for applications such as electrical contacts, which involve significant rubbing under pressure.

- As mentioned previously, we established a direct relationship between the surface topography of chemical vapor-deposited diamond films and their frictional behavior.

- We identified the fundamental mechanism by which two-phase zirconia particles influence the wear of silicon carbide whisker-reinforced alumina composites.

- We developed a new friction research instrument (described in the following section) for studying the details of microscopic sliding interactions.

- We hosted the first international conference devoted to the tribology of composite materials (May 1990).

ORNL's Tribology Tools

Applications-oriented research and fundamental research in tribology often require different tools. In applications-oriented research, a concerted effort is made to duplicate the surface contact stresses, sliding velocities, temperatures, type of motion, and chemical environments present in a specific machine component. Fundamental studies isolate the effects of specific testing parameters or materials variables in controlled friction and wear experiments, which may not necessarily mimic a specific application. ORNL has tools for performing both types of research.

Applications-oriented research is performed on two machines, one commercially manufactured, and one designed and built at ORNL. The former machine is used for testing components subjected to oscillating motion, such as that of an engine piston moving up and down. It can run either dry or lubricated tests in which the lubricant is heated by a programmable temperature controller that simulates the thermal cycles of engines. The ORNL-designed rolling contact machine was constructed in 1990 and placed in operation in January 1991. This device

"The ORNL-designed rolling contact machine was placed in operation in January 1991."

makes possible studies of combined surface fatigue and sliding contact damage in gear teeth, rolling-element bearings, or various internal combustion engine components.

Fundamental studies are conducted with the "pin-on-disk" sliding wear machines (shown on p. 11) and on two specialized instruments designed and built at ORNL—a friction microprobe (FMP) and a scanning microsclerometer (SMS). The FMP is used to explore detailed, point-to-point variations in the sliding friction coefficient, a measure of the manner in which a material's constituents having different crystal structures affect the instantaneous friction force. It has a tiny stylus that moves across a surface, touching a surface area as small as 0.001 cm in diameter. As the contact point passes between individual crystal grains, microscopic surface features, or microcomponents of a composite material, frictional variations may occur. The FMP will help us understand which surface structures in contact are high in friction and which ones keep it low. This work may eventually permit the evolution of "rules of mixture" for developing "self-lubricating" composites and other materials tailored to minimize friction.

A self-lubricating material can be loosely compared to a blueberry muffin. The cake in the muffin represents the material's structural constituents, and the blueberries may be thought of as the material's pockets of lubricant. When the surface of this self-lubricating body slides on another, the juice from the "blueberries" spreads out and lubricates the entire surface while the "cake" bears the load.

The SMS is being developed at ORNL to map variations in the hardness of microscratches on small, sub-millimeter-square areas of heterogenous solid surfaces. We plan to use the SMS to conduct basic studies of localized abrasion resistance, assess the durability of thin films and coatings for use in bearings, and identify the fine-scale response of materials during micromachining (e.g., cutting out microchips from silicon wafers).

Addressing both fundamental issues and applications-related issues in tribology broadens our perspective and helps us to become more familiar with a wide variety of friction and wear problems. Because tribology is largely an enabling technology, much of our work is motivated by the need to make more efficient engines for road transportation and to convert energy more economically to drive industrial machinery and generate power. Evolving needs of the energy supply and conservation community present us with a continuing challenge for applying state-of-the-art materials and surface engineering technology in ways that provide useful services to our energy-intensive society. ORNL's research on friction and wear is focused on achieving greater energy conservation to reduce our nation's needs for imported oil. ornl

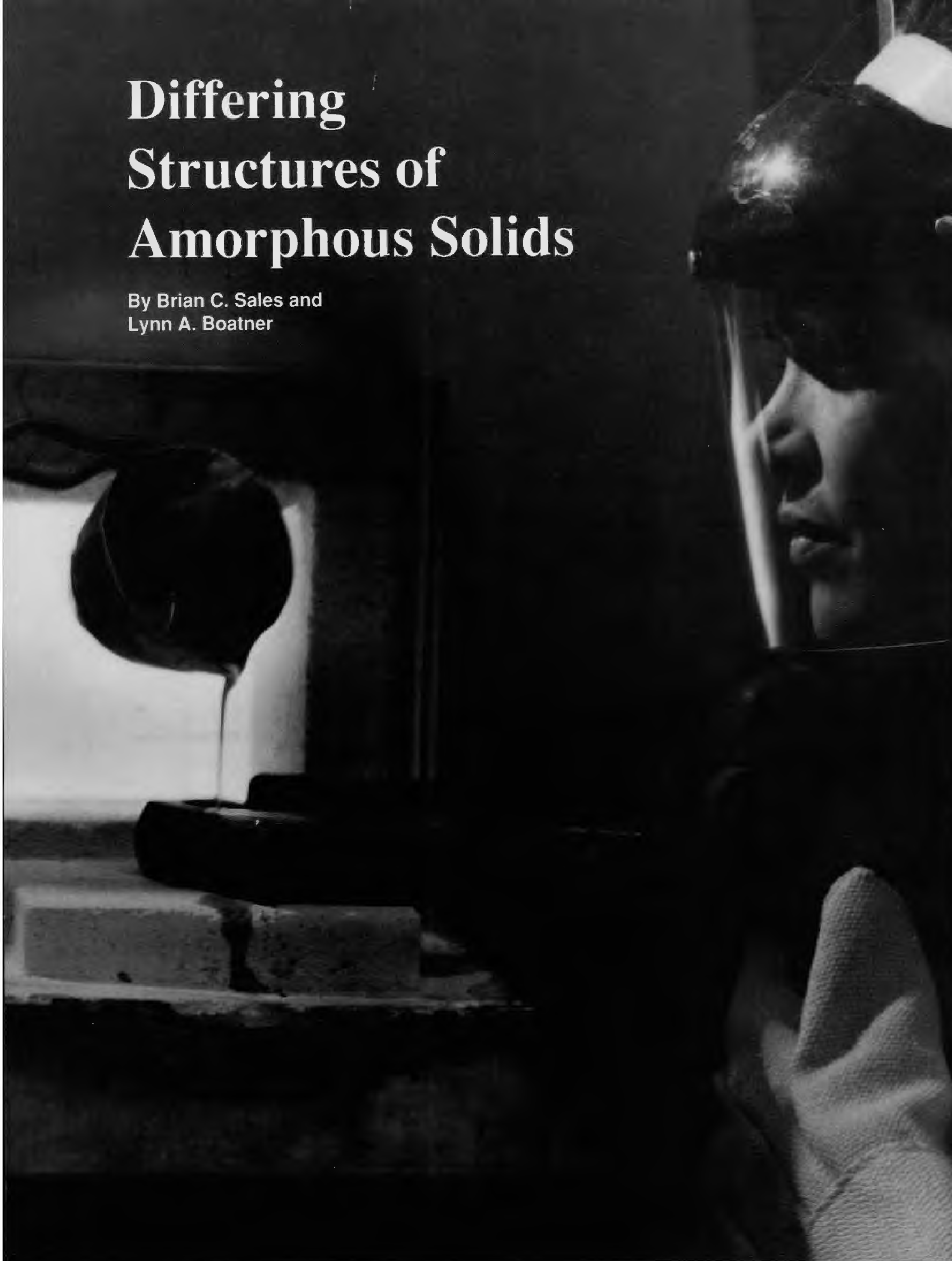
Blau conducts fundamental studies of friction and wear at a "pin-on-disk" sliding wear machine.

Biographical Sketch

Peter J. Blau is leader of the Friction and Wear Task Group in ORNL's Metals and Ceramics Division and author of the book *Friction and Wear Transitions of Materials.* He received his B.S. and M.S. degrees in metallurgy and materials science from Lehigh University and his Ph.D. degree in metallurgical engineering from Ohio State University. He served three years at the Air Force Materials Laboratory in Dayton, Ohio, and eight years doing tribology research at the National Bureau of Standards (now National Institute of Standards and Technology) before coming to ORNL in 1987. He is past chairman of the ASM International™ Wear-Resistant Materials Group and a member of the ASME Research Committee on Tribology. Recently, he was appointed volume chairman of the upcoming ASM Metals Handbook volume on *Friction, Lubrication, and Wear Technology*, to be published in early 1992.

Differing Structures of Amorphous Solids

By Brian C. Sales and
Lynn A. Boatner



Joanne Ramey casts a lead phosphate glass. The molten glass is poured from a platinum crucible into a graphite mold.

Although glass is undoubtedly the most common example of a noncrystalline solid, the term glass actually refers to only one special case of a larger generic family of "amorphous," or highly disordered, materials. In general, all glasses are produced in the same way. A solid is heated to form a liquid, which is then cooled so rapidly that the ordered repetitive lattice characteristic of crystalline materials does not have time to form. Glass can be thought of as a quickly frozen or quenched liquid in which the random positions of the elements are locked in place before they can arrange themselves into ordered cells.

Most of the glasses we encounter in everyday life (such as window glass, bottles, and camera lenses) are silicate glasses in which the basic structural building block is an SiO_4 tetrahedron (a solid having four faces). However, many other types of glasses exist, including the phosphate glasses investigated at ORNL, for which the basic structural unit is a PO_4 tetrahedron. In fact, almost all crystalline solids (metals, semiconductors, ceramics, alloys, etc.) can be made into a glass by cooling the molten liquid at a sufficiently high rate. (For metals, the cooling rate necessary to bypass crystallization can be as high as 10^7 °C/s.) On the other hand, some materials, such as quartz, do not "like to crystallize" on cooling the melt, and they will form a glass even when cooled at very slow rates.

Is It Amorphous or Glass?

Glass, as we have noted, is only one type of amorphous solid. Solids can also be made amorphous, for example, by placing them in a beam of high-energy ions. In this process, the particles in the beam interact with and displace the atoms in the solid. If enough of these displacements occur, then the ordered structure of the original crystal lattice will be destroyed, and the solid will become amorphous.

In nature, a similar process occurs in some minerals that contain sufficiently high concentrations of the radioactive elements uranium or thorium. In these minerals, most of the damage is done by the recoil of the uranium or thorium nucleus following alpha particle decay—i.e., emission of a helium nucleus. If a mineral is made amorphous through this process it is said to be "metamict." In nature, metamict minerals can be found whose exterior appearance is that of a faceted crystal but whose X-ray diffraction pattern shows that they are, in fact, totally amorphous (see photos on this page).

These naturally occurring samples of the mineral zircon are called metamict minerals because their crystalline structure was destroyed by internal radiation. The damage resulted from alpha particle decay of trace amounts of uranium and thorium contained within these samples.

Because a solid can be made amorphous by different synthesis routes (e.g., by the melting and quenching route to form a glass or by the ion-damage process), several basic questions arise concerning the nature of the underlying structure of the amorphous state. For a given material, does the structure of the amorphous state depend on the synthesis route? In the case of damage by collisions in which atoms are displaced, does the final structure depend on the initial structural state of the solid? What detailed structural path is followed during the crystallization of an amorphous material to form a crystalline solid? For most amorphous materials, it has not been possible to obtain the answer to even these most basic questions about the structure of the disordered solid.

Recent work by Brian C. Sales, Lynn A. Boatner, Joanne O. Ramey, and Jeffrey C.

McCallum, all of ORNL's Solid State Division, has provided significant new answers to these fundamental questions. Through the novel application of a high-performance chromatographic method (originally introduced to the Solid State group by Rose Ramsey of ORNL's Analytical Chemistry Division), it has been possible to determine experimentally some basic properties of amorphous phosphate solids. First, we have shown that the glass state and the amorphous, ion-damaged (i.e., ion-implanted) state of a phosphate solid are structurally different—regardless of the implant dose. Second, final-state amorphous structures created by heavy-ion damage depend on the initial state (i.e., crystalline or glass) of the bombarded solid. Third, the structural path that a solid follows as it transforms from a glass to a crystalline solid has been determined in detail. Finally, we have established a structural basis that accounts for the corrosion properties of phosphate glasses.

"We have shown that the glass state and the amorphous, ion-damaged state of a phosphate solid are structurally different."

Phosphate "Chains" and Metal Cation "Glue"

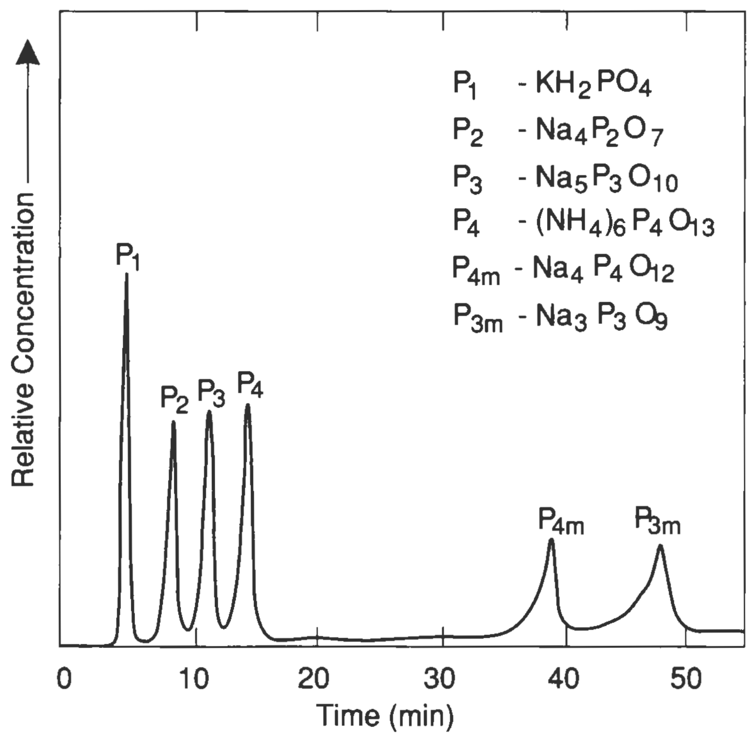
To understand how these results were obtained requires some qualitative understanding of the structural properties of metal-phosphates. In these materials, the basic building block of the structure is the PO_4 tetrahedron (i.e., phosphorus covalently bonded to four oxygen atoms lying at the corners of a tetrahedron). The PO_4 tetrahedra are corner-linked together to form chains of varying size. These chains form the "backbone" structure of the solid. The metal cations (positively charged ions of metal, such as lead in lead pyrophosphate) in the material are usually rather weakly bound to the nonbridging oxygen of the tetrahedral units so as to "cross-link" the neighboring polyphosphate chains made of anions (negatively charged molecules of phosphorus and oxygen). A crystalline phosphate solid has only one type of phosphate anion, and all of the phosphate chains have the same length. However, an amorphous phosphate solid having the same chemical composition as the crystalline phosphate consists of longer and shorter phosphate chains. An amorphous phosphate can be thought of as being made up of varying-length chains of PO_4 tetrahedra that are effectively "glued" together by the metal cations. The trick in determining the distribution of phosphate chains in the solid can then be viewed as one of finding a solvent that dissolves away the "glue" and allows the chains to separate intact from the solid.

Liquid Chromatography Probes Amorphous Solids

Can liquid chromatography provide information about the structure of a solid? For most amorphous solids, such as silicate or borosilicate glasses, high-performance liquid chromatography (HPLC) is of very limited use in probing the structure of the solid state. However, for a large class of amorphous metal-phosphates, this technique provides unique information about the type and distribution of phosphate anions in the solid. Although this kind of detailed information about the structure of the amorphous state cannot be obtained using any other technique of which we are aware, the chromatographic data are consistent with results obtained by more traditional solid-state techniques that directly probe the solid, such as Raman, infrared, electron paramagnetic resonance (EPR), and magic-angle nuclear magnetic resonance (NMR) spectroscopies.

Perhaps the best evidence for the validity of the HPLC technique in probing the structure of an amorphous solid comes from applying the method to various crystalline phosphates. For crystalline phosphate compounds, we know which phosphate anions are present from a detailed analysis of the crystal structure using X-ray diffraction. For a large number of crystalline phosphate compounds in which the structural units are either linked PO_4 chains or ring structures, the results of liquid chromatography and X-ray diffraction are in perfect agreement! The reason that the HPLC technique works so well for phosphate materials hinges on the relatively unique dissolution mechanisms of phosphate solids in neutral or high pH solutions. As the phosphate solid dissolves in these solutions, the bonds between the metal cations and the phosphate chains are broken. The chains are, therefore, transported into solution intact and can then be separated and "counted" using a modern HPLC system equipped with an anion exchange column.

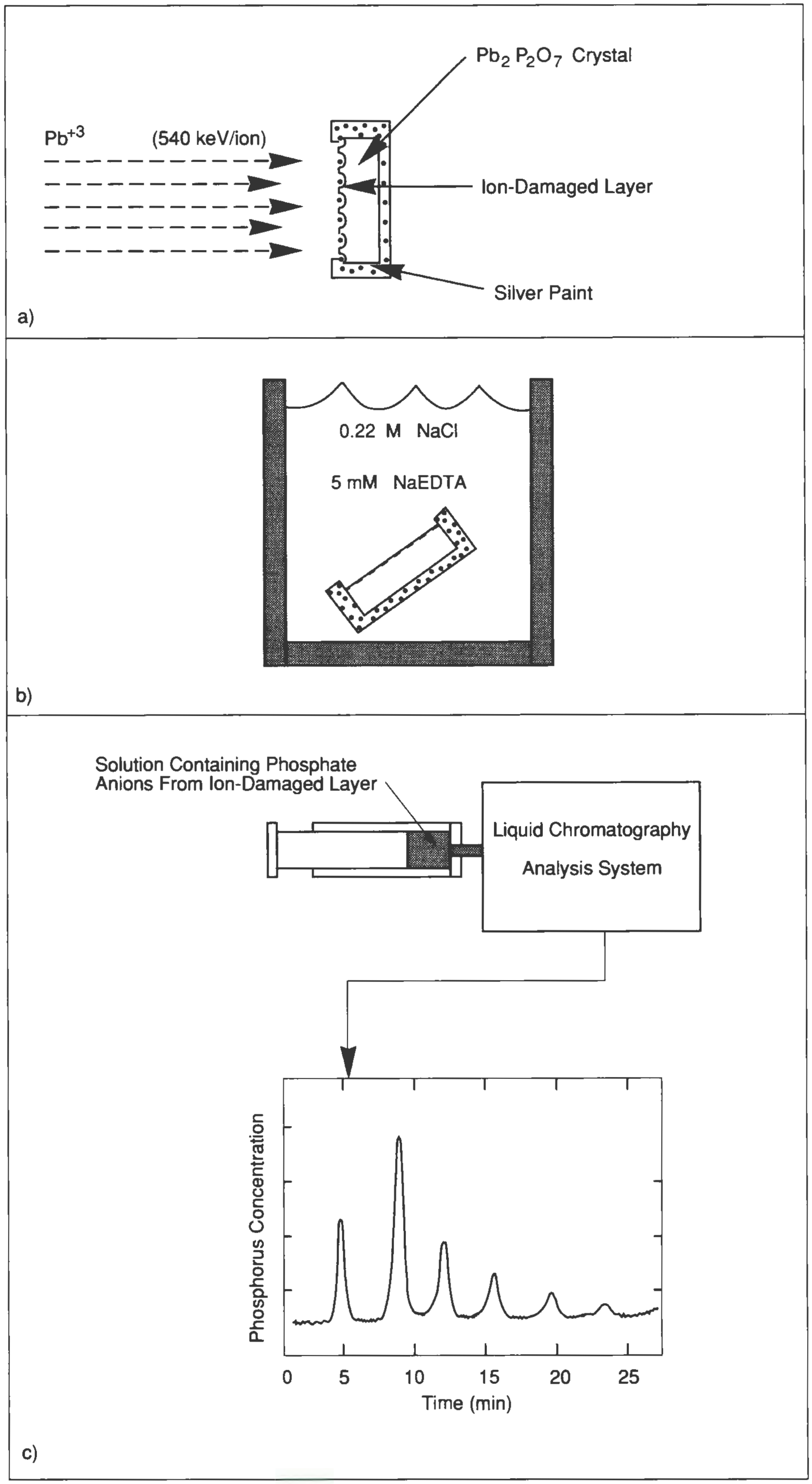
A chromatogram from the output of the HPLC system consists of a series of peaks with each peak corresponding to a phosphate chain of a given length (or to ring structures, if they are present). The area under each peak is proportional to the amount of phosphorus present in chains of that length. Crystalline phosphate compounds are used to calibrate the HPLC system. A liquid chromatogram from a "standard solution" of crystalline phosphate compounds is shown in the illustration on this page. The structures of the phosphate chains (or cyclic phosphate structural units such as those in trimetaphosphate or tetrametaphosphate) in the crystalline material are known from single-crystal X-ray structural refinements. Each of the phosphate compounds listed in the upper right portion of the illustration contributes only one phosphate anion and is, therefore, responsible for only one of the peaks in the chromatogram. Such compounds may be individually analyzed by HPLC methods or they may be combined in predetermined ratios to produce chromatography "standards." Based on this type of calibration, a chromatogram from the HPLC apparatus will consist of peaks starting at the left with the orthophosphate anion, which consists of isolated PO_4 tetrahedra (designated as P_1), followed by pyrophosphate anions (i.e., two corner-linked PO_4 tetrahedra designated as P_2), and continuing with longer chains (going from left to right in the chromatogram) that are released as the NaCl molarity at the ion exchange column is increased as a function of time.



This chromatogram of a "standard" was prepared by dissolving several crystalline phosphate compounds in an aqueous solution. The structures of the phosphate chains (or of cyclic phosphate structural units such as those in trimetaphosphate or tetrametaphosphate) in the crystalline material are known from single-crystal X-ray structural refinements. Each of the phosphate compounds shown here contributes only one phosphate anion and is responsible for only one of the peaks in the chromatogram.

Why Lead Pyrophosphate?

The study of some of the most basic questions regarding the structure of an amorphous solid requires a material that can be made amorphous by several different routes and that can also be prepared in the crystalline state. To fully use the HPLC technique to analyze the



Steps involved in the determination of the structure of an ion-damaged layer on lead pyrophosphate single crystals.

(a) A $Pb_2P_2O_7$ crystal is bombarded with 540-keV Pb^{3+} ions to produce a damaged layer approximately 200 nm thick. The other surfaces of the crystal are masked with silver paint.

(b) The implanted crystal is placed in the sodium chloride plus EDTA solution. Dissolution occurs only on the implanted face because the remaining faces are protected by silver paint.

(c) The solution containing the phosphate anions from the implanted layer is injected into the HPLC system, and a chromatogram is obtained as the sodium chloride molarity at the ion exchange column is ramped as a function of time. This chromatogram represents the amount of phosphorus contained in chains of differing lengths and starts at the left-hand side of the chromatogram with the orthophosphate group (designated as P_1 and consisting of one PO_4 tetrahedron) and continues to longer chain lengths (from left to right).

Rose Ramsey of ORNL's Analytical Chemistry Division uses a high-performance liquid chromatograph system. A similar system was used by the Solid State Division group to determine experimentally some basic properties of amorphous phosphate solids.

"Lead pyrophosphate can be prepared in the form of large single crystals or as a glass simply by varying the cooling rate of the melt."

structure of the disordered solid, the material must be a metal-phosphate. Lead pyrophosphate ($Pb_2P_2O_7$) satisfies all of these requirements.

Lead pyrophosphate can be prepared in the form of large single crystals or as a glass simply by varying the cooling rate of the melt, so this material is ideally suited for studies of the structural characteristics of the amorphous state. In addition, when lead pyrophosphate undergoes a glass-to-crystalline transition, only one crystalline structure is formed. HPLC analysis of crystalline lead pyrophosphate shows that only one type of phosphate anion is present, corresponding to a chain that is two PO_4 tetrahedra in length. This result is in perfect agreement with the results of single-crystal X-ray diffraction analysis. Amorphous lead pyrophosphates were prepared either by thermally quenching the molten phosphate to produce a glass, by implanting oxygen or lead ions into lead pyrophosphate single crystals, or by implanting oxygen ions into lead pyrophosphate glass. The structures of the amorphous phases produced by these methods were then determined using the HPLC technique.

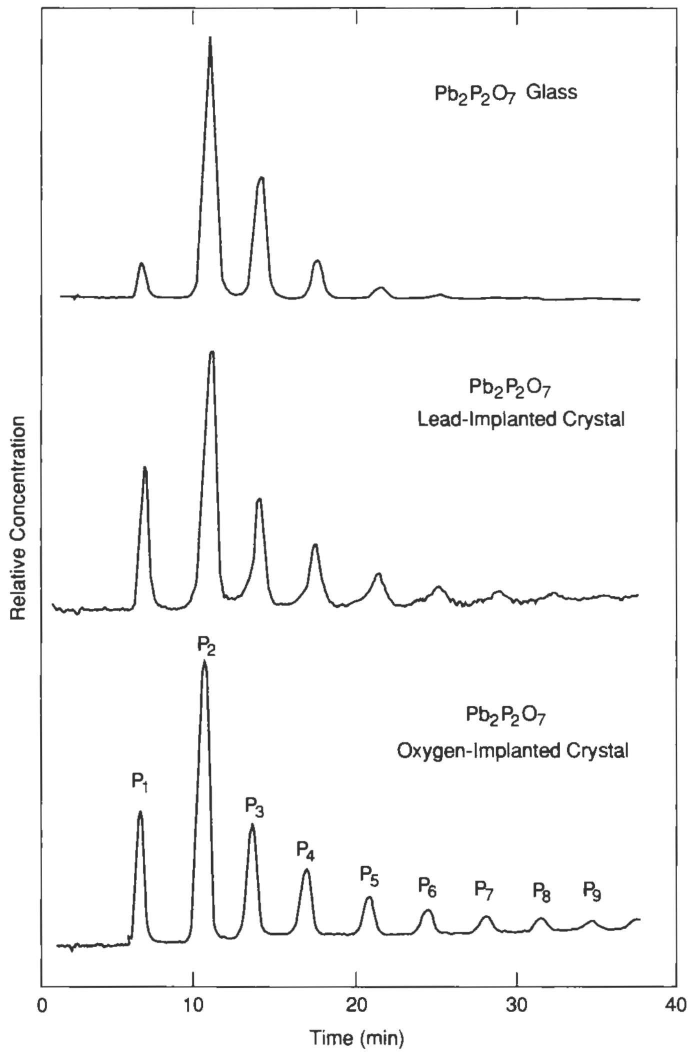
A schematic diagram of the procedure used to make the HPLC measurements for the ion-damaged surfaces is shown in the illustration on p. 22. Only the large faces (i.e., faces perpendicular to the **c** axis) of the lead pyrophosphate single crystals were ion-implanted, and the remaining surfaces (i.e., the sides and back of the crystal) were covered with silver paint so that only the implanted surface was analyzed by the HPLC technique. The lead or oxygen ions implanted into lead pyrophosphate penetrate only a short distance below the surface (about 1000 Å), but the displacement damage extends somewhat beyond this depth. To analyze the structure of this relatively thin ion-damaged layer, the crystal was removed from the chromatography solution when the amount of phosphorus in solution corresponded to the loss of a layer from the surface of about 1000 Å. The implant doses were kept sufficiently low so that the chemical composition (i.e., metal-to-phosphorus ratio) of the ion-damaged layer was not altered to any significant degree.

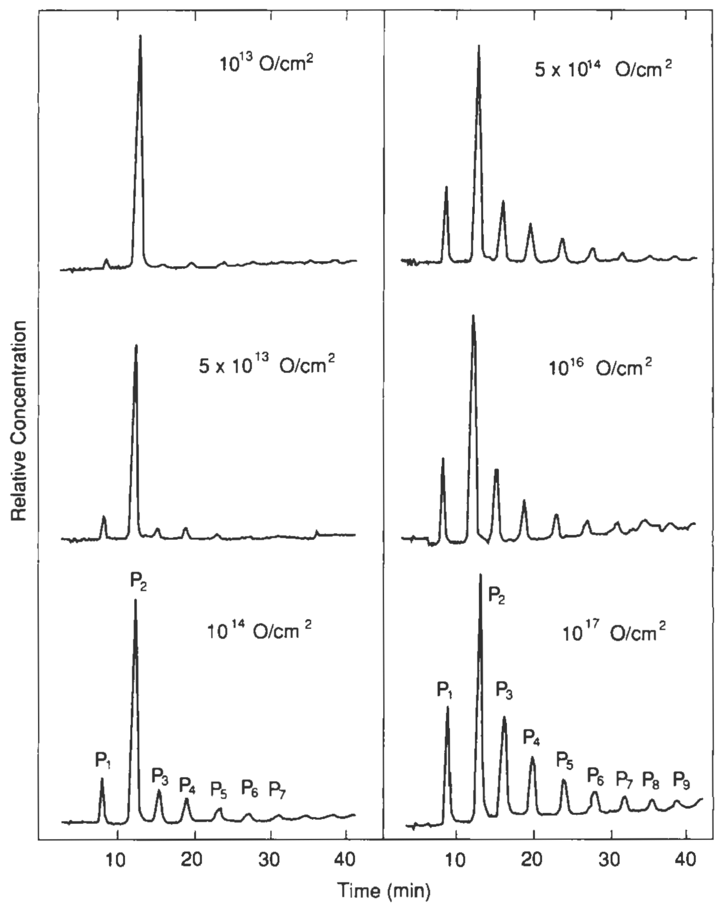
Varying Amorphous Structures of Lead Pyrophosphate

Does the structure of the amorphous state depend on the way in which the material became amorphous, and if so, how are the structures different? A comparison between the chromatograms for lead pyrophosphate glass prepared by thermal quenching and those from the amorphous layers formed by ion damage shows significant differences between the structures (see figure on p. 25). Compared with the glass, the percentage of P_2 (i.e., chains that are two PO_4 tetrahedra in length) is much lower for the ion-damaged layers. This finding indicates that these layers are effectively "more amorphous" in the sense that, because crystalline lead pyrophosphate consists only of P_2 chains, the ion-damaged material's deviation from the crystalline state is larger than that of glass. In addition, the glass has a much larger percentage of P_3 chains (i.e., three PO_4 tetrahedra in length), whereas the amorphous layers formed by ion implantation have significantly higher concentrations of P_1, P_4, P_5, P_6, P_7, and P_8 chains. Somewhat surprisingly, the structures of the two amorphous layers produced by ion implantation with either oxygen or lead ions are very similar despite the fact that the damage cascades in the two cases are different.

The chromatographic results clearly show that the structure of phosphate glasses produced by conventional melting and cooling through the glass transition is different from the amorphous state produced by high-energy bombardment of a crystalline material, even though both substances have an identical chemical composition. In fact, even when crystalline material was bombarded by ions to the point that structural changes no longer occurred, the structure of the glass state could not be duplicated (see figure on p. 25). This experimental finding is significant because of its implications for ion-beam modification of materials, displacive radiation damage effects, and the basic theory of the structural properties of disordered materials. From the theoretical point of view, the distribution of phosphate chains (predicted by a model developed by Parks and Van Wazer) was in excellent agreement with the experimental results obtained for phosphate glasses, but the distribution did not agree with that obtained for amorphous phosphates produced by ion bombardment. This result indicates that the distribution of phosphate chains in an ion-damaged solid arises from a fundamentally different process than that occurring during the formation of a glass. The results indicate that, contrary to some previously advanced concepts, the ion-damage process generally should not be viewed as a mechanism that is equivalent to melting the material and then rapidly cooling it. In other words, ion bombardment cannot be used to accurately simulate melting and quenching of lead pyrophosphate to produce a glass state.

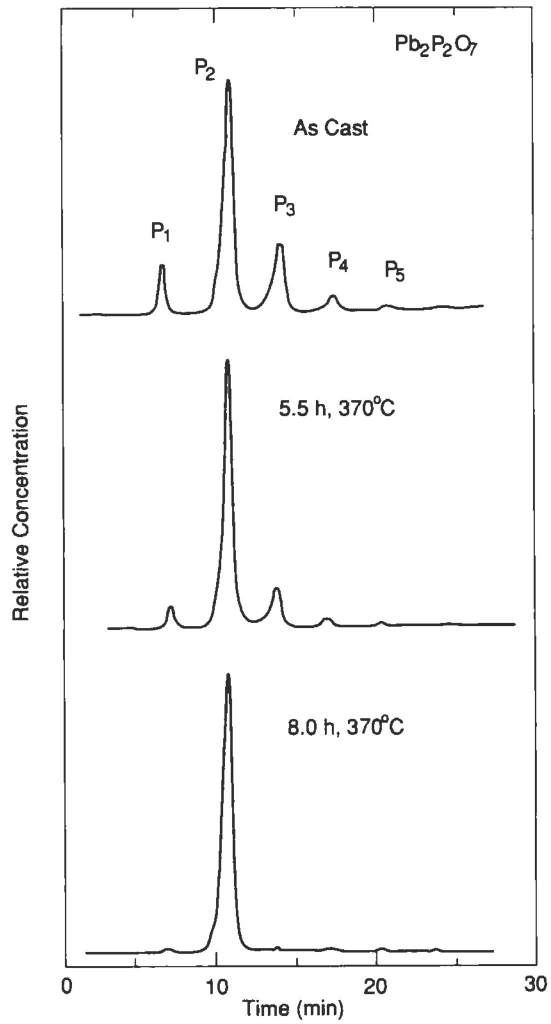
Does the final structural state of an ion-damaged amorphized solid depend on the initial structure of the material? To answer this question, we implanted a piece of lead pyrophosphate glass with an ion dose that would





A comparison of the HPLC chromatograms from amorphous lead pyrophosphates produced by quenching a melt to form a conventional phosphate glass (top), ion bombardment of the crystal surface with 10^{15} Pb^{3+} ions/cm^2 at 540 keV/ion (middle), and by ion bombardment of the crystal with 10^{17} O^{2+} ions/cm^2 at 55 keV/ion (bottom). The labels P_1, P_2, P_3, . . .denote chains of phosphate tetrahedra that are, respectively, 1, 2, 3 . . .tetrahedra in length. A comparison of the ratios of the areas under each peak (representing the total amount of phosphorus contained in chains of that length) for the three chromatograms shows that the structure of the pyrophosphate glass is significantly different from that of either of the ion-beam–amorphized layers, whose structures are the same within the limits of accuracy of the analysis.

HPLC results for 100-nm-thick layers on the surface of lead pyrophosphate single crystals that were implanted with various doses of oxygen ranging from 10^{13} to 10^{17} ions/cm^2 with an energy of 55 keV/O ion. The threshold dose for detectable alteration of the phosphate chain structure is shown to be slightly less than 10^{13} O/cm^2.



Liquid chromatograms for lead pyrophosphate glass as prepared (top); material at an intermediate state of the devitrification transition at 370°C (middle); and almost fully recrystallized $Pb_2P_2O_7$ after 8 h at 370°C. By using HPLC methods, the structural path followed by the material in transforming from the glass to the crystalline state can be mapped out.

have made crystalline lead pryophosphate completely amorphous. The resulting structure was compared with that of a piece of ion-implanted lead pyrophosphate that was initially in the crystalline state. The results of this experiment revealed that the final amorphous structure of the material does, indeed, depend on the initial structural arrangement!

From Glass to Crystal

All glasses can, at least in principle, be converted back to the crystalline state by heating the glass to a suitable temperature and then simply waiting for crystals to form. Knowing the temperature at which the process, called "devitrification," occurs is important for determining the useful operating temperature range for a glass. Understanding the structural changes that occur during devitrification is also important for fundamental and practical reasons. Using the technique of HPLC, it has been possible to map out in detail the structural changes that take place during the isothermal transition from a glass to a single-phase crystalline solid (see figure on this page). These detailed quantitative experimental results have provided the basis for the formulation of a more specific microscopic theory of the devitrification process than currently exists. In particular, measurable changes in the distribution of phosphate chains have been observed during the time required for crystals to nucleate and, therefore, this observation should be considered in any devitrification model.

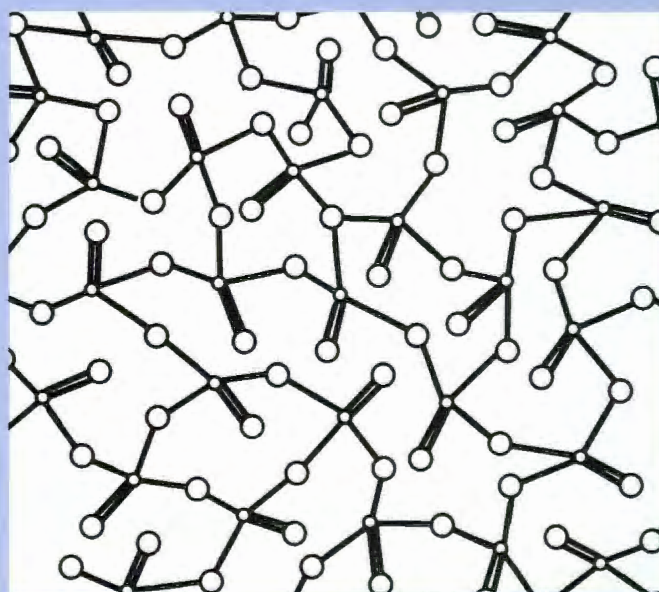
Three-Dimensional Model of Amorphous Solids?

Through a novel application of the HPLC technique, we have been able to answer some basic questions concerning the structural properties of the amorphous state. We have demonstrated that lead pyrophosphate has at least three distinct amorphous structures even though the chemical composition of each of its amorphous states is the same. We also have learned that the final amorphous structure depends not only on the technique used to make the material amorphous, but on the starting structure as well.

Using the HPLC technique, we have been able to obtain a detailed structural "map" of the isothermal glass-to-crystalline transition of lead pyrophosphate. As is normally the case in science, however, these initial answers have generated a large number of unanswered questions that will guide future research. These questions include: How are long phosphate chains generated during the bombardment of the solid with high-energy ions? and, What is the relative role of ion-electron vs ion-nuclei collisions in the generation of longer phosphate chains?

The determination of the structural properties of amorphous solids has been and continues to be one of the baffling problems of solid-state science. The intrinsic nature of these materials greatly reduces the utility of the standard diffraction-based techniques that have proven to be so powerful in accurately determining the structures

Limitations in Understanding Structure in Amorphous Solids



What is an amorphous solid? The word "amorphous" has its roots in the Greek word "amorphos," defined as "having no determinate form and shape." In modern usage, however, the term "amorphous solid" generally refers to a material formed by atoms that are "disordered"—not arranged as a repetitive structural unit on an ordered "lattice" as in a crystalline material.

Although this general definition of an amorphous solid is correct, it is much too vague to be useful. For instance, using this definition it is not possible to distinguish between a crystalline material that simply has a large number of defects and a material having no remnant of the crystalline lattice.

Experimentally, a more precise definition of an amorphous solid is "a material that has no evidence of long-range order (i.e., a repetitive crystal lattice) as detected in a diffraction experiment." X-ray diffraction is normally used to search for the characteristic diffraction patterns of a crystalline lattice, but neutron and electron diffraction techniques can also be employed. If no crystalline diffraction peaks are found, the material is said to be amorphous.

When applied to highly ordered crystalline materials, diffraction analysis can precisely locate the positions of all of the atoms in the solid, whereas for amorphous materials, by definition, this type of result is not possible. The limitations of X-ray, neutron, or electron diffraction techniques in determining the structure of amorphous solids have severely restricted our level of understanding of disordered materials. Fortunately, the use of high-performance liquid chromatography, described in the main article, may greatly increase our knowledge about the structures of a very large class of scientifically and technologically important materials.

of crystalline materials. In the case of disordered phosphates, however, we have been able to shed new light on the structural features of the amorphous state by applying a chemical rather than physical approach to the problem.

It is convenient to divide the problem of solving the structure of amorphous materials into two parts—namely, the number and type of each basic structural unit that is present in the solid must be determined, and, second, the spatial arrangements of these units must be fixed. By applying HPLC methods to phosphate solids, the first half of this problem can be solved. The question that now remains is, can we combine the HPLC results with other information (e.g., from neutron scattering, NMR, EPR, Raman, infrared, etc.) and thereby construct a complete three-dimensional model of the structure of amorphous phosphates? If the future holds a positive answer to this question, then we can enter a new era in our understanding of disordered solids.

Biographical Sketches

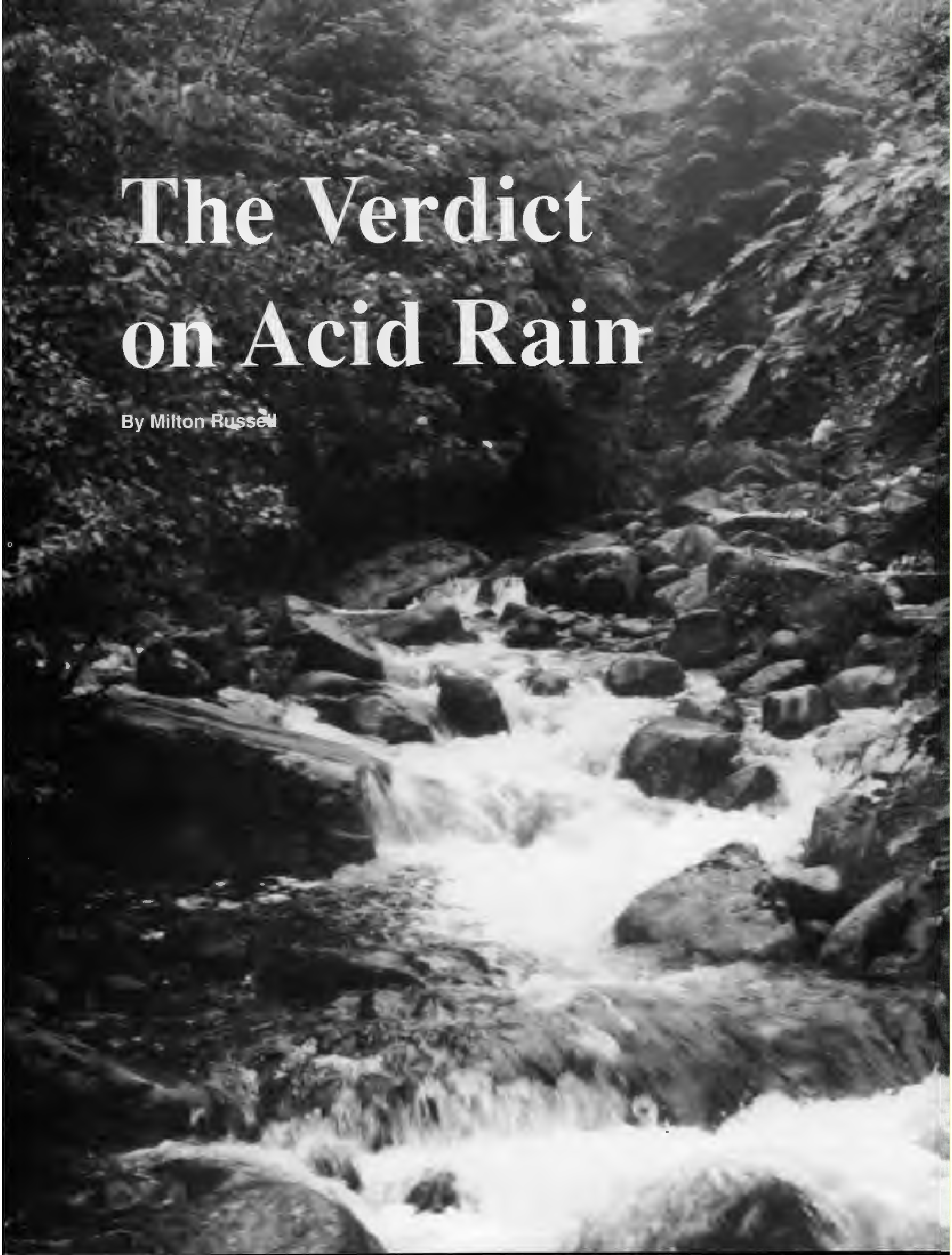
Lynn Boatner (left) and Brian Sales adjust the controls for a particle accelerator at ORNL's Surface Modification and Characterization Collaborative Research Laboratory. The accelerator is used to implant lead phosphate crystals with high-energy ions to produce a material that has a higher degree of disorder than glass of the same composition.

Brian C. Sales is co-leader of the Novel Materials Research Group in ORNL's Solid State Division. He joined the division in 1981 after conducting research for several years at the University of Cologne in the Federal Republic of Germany and at the University of California at San Diego, from which he earned his Ph.D. degree in solid-state physics. At ORNL he has developed new phosphate materials for nuclear waste disposal, optical components, and glass-to-metal seals. For the development of a lead-iron phosphate nuclear-waste glass, he received an I•R 100 Award from *Industrial Research* magazine and awards from the Department of Energy and *Science Digest*, and he was named 1985 Inventor of the Year by Martin Marietta Energy Systems, Inc. He has also conducted research on high-temperature superconductivity. He holds four patents.

Lynn Boatner is head of the Ceramics and Interfaces Section in ORNL's Solid State Division. He joined the ORNL staff in 1977 after a two-year appointment at the Ecole Polytechnique Federale de Lausanne in Switzerland. He holds a Ph.D. degree in solid-state physics from Vanderbilt University. He is a fellow of the American Physical Society and the American Association for the Advancement of Science. He has received two I•R 100 awards (in 1982 with Marvin Abraham and in 1985 with Sales). Along with Sales, he was recognized as one of *Science Digest*'s 100 Top Innovators in 1985. He also received the DOE Research Competition Award for "Significant Implications for Energy Technology in Solid State Physics" in 1984, The Francis F. Lucas Award of the International Metallographic Society in 1988, and a First in Class Award in the 1990 International Metallographic Contest. In 1989 he was named a Distinguished Alumnus in Physics by Texas Tech University. He holds five patents.

The Verdict on Acid Rain

By Milton Russell



Only about 4% (by length) of the upper reaches of streams in targeted U.S. areas where acidic deposition was thought to be of potential concern were actually found to be acidic; in turn, only about half of these were attributed to atmospheric deposition.

The verdict is in on acid rain: a problem exists, but it is not as serious or urgent as many had feared. Acid deposition from human activities has had some harmful effects on a limited number of lakes, streams, forests, and some structural materials. Precursor emissions lower visibility and contribute to regional haze. There are no negative effects on agriculture and only speculative effects on human health. Current levels of acid precipitation are not likely to increase greatly the size or extent of damage for several decades. Early reductions are possible at added costs, especially to electricity users; those reductions would reverse many, but not all, of the effects of past higher levels of acid deposition, and the water quality of some lakes and streams would begin to improve in about two decades. Ozone and other related atmospheric pollutants remain a significant source of ecological damage and may be more difficult to control.

This verdict was formally released in the fall of 1990 by the National Acid Precipitation Assessment Program (NAPAP), a decade-long, $0.5-billion research and assessment effort involving about 2000 scientists in the United States and abroad. Initiated by President Carter and the U.S. Congress in 1980, NAPAP was designed to provide the scientific and engineering basis for understanding the causes, effects, and possibilities for management of acid deposition. It was also to assess the significance of the effects and costs of control and to provide the interpretations and "wisdom" that policymakers need to decide which actions to take. What follows is a policy-oriented overview of this huge scientific, technological, and assessment effort.

Extreme Views Invalid

NAPAP was started at a time when concern about the effects of acid rain was mounting, but the understanding and facts on which to act were sparse. An impressionistic reading of the public—and scientific—perceptions in 1980 suggests strong polarization. Some people believed that damage was already significant and that an ecological disruption of major proportions would soon be evident. In this view, immediate action, even taken at great expense, was in the country's best interest. Conversely, others believed that little damage was evident and that a business-as-usual reduction in sulfur emissions, such as that already under way, would overtake any possible negative effects long before they occurred. This view rejected early action on the grounds that the cost would grossly outweigh any possible benefits and harm the U.S. economy.

As previously suggested, both extreme views have been rejected as a result of 10 years of research and assessment. Acid deposition has caused damage, and more will occur without further reductions in both sulfur and nitrogen emissions, but the damage is limited in geographical extent, in severity, and in the types of resources affected. Even without further action we should not expect an aquatic version of Rachel Carson's *Silent Spring* or mass destruction of forests. At the same time, the United States has lakes and streams whose fish populations have been destroyed or stressed, others which, without further reductions, may have problems over the next half century, and some tree species that have been damaged. Visibility has been impaired. Other, more speculative, damage is possible in the longer term.

"Acid deposition has caused damage . . . but the damage is limited."

These findings were produced by an interagency effort of unprecedented scope and duration. The program was organized, directed, and coordinated through a small office headed by a director who reported to a task force headed by six "joint chairs"—from the Environmental Protection Agency, the National Oceanic and Atmospheric Administration, the Council on Environmental Quality, and the departments of Agriculture, Energy, and the Interior. The actual work of research and assessment was conducted by professionals at government agencies, the national laboratories, private firms, universities, and foreign institutions.

Products of Research

The products of the research have been published in the peer-reviewed literature, but NAPAP undertook the task of bringing it together in a series of 27 summary State of Science/

Chantale Wong, a staff assistant in the NAPAP office in Washington, D.C., hugs the stack of manuscripts of the 27-volume NAPAP report.

Technology reports that are to be published this winter. This monumental collection of authored documents (approximately 7,000 typescript pages) is a textbook example of intensive peer review and provides the basic reference source on the subjects covered. One element of the review was a week-long final review conference in February 1990 at Hilton Head, South Carolina, attended by some 700 researchers from 30 countries.

The essence of NAPAP's mission was to bring all available information together to assist in the decision process. Therefore, in addition to research, an "integrated assessment" was performed, organized around five key questions:

1. What are the effects of concern and what are the relationships between acidic deposition/air pollutant concentrations and effects?
2. What is the relationship between emissions and acidic deposition/air pollutant concentrations?
3. What is the sensitivity to change?
4. What are the estimates of future conditions based on illustrative future scenarios?
5. What do comparative evaluations of illustrative future scenarios indicate?

The results of this integrated assessment are also to be published in early 1991.

Obviously, the verdict proffered by NAPAP includes numerous uncertainties, and some conclusions must be considered tentative, as is the case with much science. In this case the problem is compounded. The effects of most concern relate to broad ecosystems where experimentation is difficult and to processes (e.g., forest growth/decline, changes in soils) where response times to perturbations are measured in decades. Therefore, a lack of observed effects may reflect the limitations of the analyses rather than a lack of ecosystem sensitivity. Continuing research is needed to tease out the subtle and slow reactions that could make major differences far in the future.

Even though the final results of the integrated assessment have not yet been published, its conclusions were foretold in NAPAP's *1989 Annual Report and Findings Update to the President and the Congress* (NAPAP, June 1990).

ORNL researchers found that acidic cloudwater combined with other stresses is associated with the reduced growth rate of trees in high-elevation spruce forests in the eastern United States, about 0.1% of the total.

A few of those findings of particular interest can be summarized here.

The NAPAP research has demonstrated that emissions from human activities are a major contributor to acidification, though natural sources of atmospheric pollutants are significant, especially to ozone formation. Median sulfate deposition decreased 27% at monitoring stations between 1979 and 1987, consistent with the reduction in national emissions resulting from compliance with existing pollution regulations. Thus, it can be concluded for policy purposes, to a first approximation, that what goes up *does* come down. And when it comes down, emissions from human activities affect the acidity of rain, clouds, fog, and particles carried in the wind that are later deposited.

Aquatic Effects

Depending on the soils, vegetation, and land use patterns, added acidity in precipitation can contribute to changing the acidity level (pH) of streams and lakes. In a national survey, about 4% of the lakes and 8% of the upper end of streams in targeted U.S. areas where acidic deposition was thought to be of potential concern were found to be acidic. (These numbers are cut in half when lake area or stream miles are considered.) Of these, about 75% of the acidified lakes and 47% of the acidified streams are thought to be primarily affected by atmospheric deposition—in other words, about 3% of the lakes and 4% of the upper reaches of streams, and substantially less by area or miles—and the rest by natural causes or other conditions.

It is projected that the number of acidified lakes would not increase significantly in the Northeast under current acid loads and that it would shrink slightly in a decade or so if deposition were decreased by 30%. In contrast, in the Southern Blue Ridge, where few lakes are now acidified, current deposition loads will bring some lakes to an acidified state over the next 50 years. Although generally similar effects are expected on the much larger number of Canadian lakes and streams, uncertainties in the analysis are greater in Canada than in the United States. The definition of acidity ($pH \leq 5.0$) adopted here is somewhat arbitrary and is a point indicator for a

". . . the number of acidified lakes would not increase significantly in the Northeast under current acid loads."

continuum that must be carefully interpreted when specific implications are drawn.

The significance of all this lies mostly in the effects of lower pH (higher acidity levels) on aquatic systems, and in these, fish are an important marker. Again there is a continuum of effects, some of which depend on other aspects of water chemistry. Also, fish species display a substantial range of tolerance. As stress mounts, species diversity and population regeneration can suffer.

The NAPAP *Annual Report* concludes that

> The proportion of lakes and streams whose chemistry suggests high levels of stress is zero in most regions for tolerant fish species, whereas for the most sensitive species, high levels of stress might occur in approximately 25% of the lakes in the Northeast and Midwest and approximately 40% of the upper stream sites in the Mid-Atlantic Coastal Plain region. Such results are not meant to imply that sensitive fish would be present in these waters if the stress imposed by acidic deposition were removed. (*Annual Report*, p. F-13)

Effects on Forests

The concern for aquatic resources has been matched by fears that acid precipitation may be seriously harming forests. Compared with the intense concerns of a few years ago, the news here is good, though it must be tempered as always with the realization that some subtle effects not yet discerned may have long-term consequences. The NAPAP *Annual Report* summarized forest effects from air pollution in the following way:

> (1) acidic deposition and ozone appear to intensify the effects of natural stresses upon red spruce at eastern mountain-top locations; . . . (2) soil process models show that cumulative effects of acidic deposition at current levels may change the chemistry of some sensitive forest soils in the lower mid-western and southeastern United States within a period of approximately 50 to 100 years; . . . (3) ozone adversely affects forest health in regions of southern and central California, and possibly in some regions in the Southeast. . . . Extensive surveys of forest conditions in North America have indicated that the majority of the forests are healthy. (*Annual Report*, p. F-17)

The high-elevation spruce-fir stands known to be stressed by acid deposition occupy less than 0.1% of the forests of the eastern United States, but their position on ridge tops makes any damage to them of particular concern in recreation areas because of their visual prominence. In general, the concern that current or prospective U.S. acid deposition loadings could lead to the large-scale forest destruction now visible in much more polluted Eastern Europe was shown to be unfounded.

Other Effects

NAPAP researchers have discovered no negative effects on agriculture from acidic deposition except, rarely, in the Los Angeles Basin for a few sensitive crops. Indeed, the added input of sulfur and nitrogen may improve soil fertility in some locations. In contrast, reductions in crop yields from ozone have been well documented.

NAPAP also examined the effects of acid precipitation on structural materials, such as galvanized steel and masonry, and on stone and bronze in monuments, gravestones, and other culturally significant artifacts. As expected, somewhat greater physical deterioration was found to be associated with higher acidity. The significance of this relationship is not so clear, however, because other factors are much more important in weathering, especially in urban areas. Further, the added rate of deterioration is unlikely to affect the timing or extent of maintenance, reconstruction, or replacement. Economically, the damage may be zero or negligible, though incremental damage to cultural items must be considered. Again, this situation contrasts with areas of Europe where much higher loadings of pollution have severely damaged fragile monuments such as those found in the cities of Athens, Greece, and Kracow, Poland.

As for health, existing regulations already hold atmospheric concentrations of sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) below levels judged to cause direct harm even to sensitive groups ("with an adequate margin of safety") except at a very few U.S. locations. Investigation continues on whether sulfuric acid aerosols, resulting from a chemical transformation of SO_2 in the atmosphere, may have

Damage to these high-elevation spruce-fir stands is caused primarily by insects, but acid deposition may be an additional stressor. Although these stands occupy less than 0.1% of the forests of the eastern United States, their position on ridge tops makes any damage to them of particular concern in recreation areas because of their visual prominence. These trees are on the top of Mount Mitchell in the North Carolina part of Great Smoky Mountains National Park.

harmful effects at levels observed. Suggestive evidence has linked acid aerosols (at higher concentrations than those observed) with increased likelihood of respiratory symptoms among sensitive individuals, such as those with asthma or bronchitis, but this linkage has not been demonstrated. An indirect risk pathway has been suggested for another possible connection between acid deposition and human health. The hypothesis is that additional exposure to harmful metals such as lead, mercury, or aluminum could occur because increased acidity could make them more bioavailable in soils for plant uptake or increase the rate at which they are leached out to drinking water sources.

To summarize what is now known about health effects, the reasonable conclusion would be that further decreases in sulfur emissions may be desirable as a precautionary measure against unknown health effects, but there is no evidence that reduced emissions would lessen human health risks. Further research, however, is clearly indicated. In contrast, the harmful effects from ozone are well documented, and about 100 urban areas in the United States each have at least one monitoring station indicating that health standards are being violated.

The types of emissions that ultimately increase precipitation acidity also decrease visibility. The average visual range estimated for the East in the

The New Clean Air Act, NAPAP, and the Consumer

Acid rain is a product of burning fossil fuels for purposes such as generating electricity or powering automobiles. It is formed when emissions of sulfur and nitrogen oxides react with moisture and other chemicals in the atmosphere. Although the NAPAP study concluded that acid rain has caused only limited damage to the health of forests and water bodies in the United States, Congress included major provisions to reduce emissions of sulfur and nitrogen oxides in the revised Clean Air Act, which was signed into law by the President on November 15, 1990. The 748-page act also provides for the reauthorization of NAPAP.

The new Clean Air Act calls for sulfur dioxide emissions (at 1980 levels) to be cut about in half by 2000, to 10 million tons annually, and nitrogen oxide emissions to be reduced by one-third, to 4 million tons annually, with both reductions phased in beginning in 1992. Economists say this provision will require coal-burning utilities to spend up to $3 billion a year to burn low-sulfur fuel or natural gas or to install scrubbers to remove sulfur and nitrogen oxides from emissions. Consumers will pay this cost through higher electricity bills.

The new act also requires that passenger cars emit 60% less

"Consumers will pay the extra costs of the new products that oil and automobile companies must develop."

nitrogen oxide by 2003 using pollution control equipment that must last 10 years. This reduction can be accomplished by use of cleaner-burning gasolines and special emission-reducing equipment in exhaust systems. Consumers will pay the extra costs of the new products that oil and automobile companies must develop: by 2000 gasoline costs can be expected to rise 6 to 10 cents per gallon, and by 2003 a new car will cost an average of $600 more.

The new act incorporates a favorite prescription of economists: to cushion the economic impacts, allow "emission trading" whereby utilities able to keep their sulfur dioxide emissions below the legal limit can sell credits to utilities that find it more costly to hold emissions at or below the limit. The added efficiency in holding pollution down would prevent large increases in electricity costs, plant shutdowns, and loss of U.S. competitiveness in world trade.

The total cost of implementing the new Clean Air Act, which also calls for reductions of toxic, carcinogenic, and ozone-depleting emissions, is calculated to be $25 billion to $35 billion a year when it is fully effective. Meeting the growing public desire for a better environment carries a hefty price tag.—*Carolyn Krause* absence of anthropogenic degradation is 150 $\pm$ 45 km, but the actual measured value is in the range of 20 to 35 km. Sulfate is estimated to account for about half of the degradation in the East and 10 to 20% in the urban West. The benefit to be ascribed to improved visibility is less certain, both because changes may be below the perceptual threshold and because it is difficult to convert any changes recognized to reasonably accepted economic measures.

"National emissions, in fact, would be roughly the same by 2030 with or without the special controls debated in Congress during 1990."

Implication for Policy

NAPAP as originally envisioned was to bring the results of the research into a rough cost-and-benefit framework, and from that come to some conclusions on the wisdom of alternative policies. This did not occur, but the basis for making comparisons was established through the creation of policy scenarios that marry possible future emission patterns with regional changes in deposition. From these, physical effects can be projected.

The findings of NAPAP are such that a wide range of policy actions could be supported depending on the values ascribed to these physical effects, and especially on how risk-averse the decision maker was to different uncertainties. Clearly, decreases in acid deposition would have benefits, and the earlier those emission reductions were made, the greater the total benefits (and the total costs) would be. At the same time, ultimate levels of damage avoided (e.g., the number of lakes acidified) do not appear particularly sensitive to when reductions occur over the next few decades; in contrast to what many believed a decade ago, urgent action is *not* required to avoid major, irreversible ecological changes. In any event, national sulfur emissions have fallen about 20% since their peak, and though they edged up in the late 1980s, the levels are expected to decline again as existing regulations take effect. (In the southern United States, by contrast, emissions of SO_2 and NO_2 are still increasing.) Because of these built-in reductions, national emissions, in fact, would be roughly the same by 2030 with or without the special controls debated in Congress during 1990. The judgment Congress had to make was whether the benefits in the interim warranted the extra cost of earlier reductions—a cost estimated at about $100 billion over the next 40 years. On this matter, even after taking into account the information produced by NAPAP, opinions will differ.

A major debate over acid rain policy occurred in 1989–1990. With the passage of the sweeping revisions of the Clean Air Act in late 1990, the decision to cut SO_2 emissions by 10 million tons and NO_2 emissions by 2 million tons was made before the final NAPAP report was published. Many of its interim findings were available to inform deliberations, however. So it cannot be said that this work was not used. Moreover, implementation of the legislation will be more efficient and effective because of what has been learned. Furthermore, another debate on how best to revise the new Clean Air Act will likely occur within this decade. When that time comes, NAPAP's contribution will be available. Returns from NAPAP—even in narrow terms—will be flowing in for years to come.

NAPAP's Legacy

In a broader sense the legacy of NAPAP goes beyond its contributions to acid rain decisions and scientific understanding. For one thing, NAPAP pioneered in developing a model for an institution that may have considerable usefulness in addressing other major social problems. It is always difficult to mobilize science to inform public decisions, but in this case it was successfully done in a process that melded numerous government agencies in pursuit of a common goal. Much was learned about how to do the job better in the future.

The NAPAP experience also had a more direct effect on the persons involved. Because of the interdisciplinary assessments that were required and the large number of institutions involved, NAPAP brought numerous scientists into productive, continuing networks that otherwise probably would not have been formed. The cross-fertilization went beyond the usual sharing of disciplinary insight to include different modes of work, institutional settings, and ways of thinking. In particular, the necessity for scientists to be involved in assessment—asking what the results mean—enriched research agendas, honed skills of communication, and sharpened understanding of what was required of them to make maximum contributions to science and to public policy.

NAPAP represents an occasion when, as a nation, we decided to draw on our collective scientific resources before launching a major effort to solve an ill-defined problem. We gave the process time—a decade—and the money—$537 million—to get better answers before acting. The answers turned out to be different in many ways from the conceptions held a decade ago. Based on those answers, a range of credible options was opened. This is a notable achievement.

On November 12, 1990, James Mahoney, director of the National Acid Precipitation Assessment Program (NAPAP), gave a talk summarizing NAPAP findings and expressing appreciation for ORNL's help in providing answers to questions about the effects of acid rain. Here, he shakes hands with David Shriner (left), who conducted and later coordinated acid precipitation studies for ten years at ORNL's Environmental Sciences Division. Looking on is Milton Russell, chairman of the Oversight Review Board for NAPAP and author of the article.

Biographical Sketch

Milton Russell is chairman of the National Acid Precipitation Assessment Program Oversight Review Board appointed by the Joint Chairs Council, headed by William Reilly, administrator of the Environmental Protection Agency (EPA). The board's task has been "to provide advice to NAPAP management and the Joint Chairs Council regarding the quality, scientific integrity, credibility, and practicality . . ." of the processes and products of NAPAP. Russell is a collaborating scientist with ORNL's Energy Division and with the University of Tennessee's Energy, Environment and Resources Center and its Economics Department. From 1983 through 1987, he served as an assistant administrator of EPA.

A Heinz Walz gas exchange analyzer is used to measure physiological responses of plant leaves to environmental variables, such as light and temperature following chronic exposure of plants to air pollutants (including acid rain).

ORNL's Technical Contributions to NAPAP

The story of ORNL's technical contributions to the National Acid Precipitation Assessment Program (NAPAP) really begins in the late 1960s and early 1970s when ecologists at the Laboratory began long-term experiments to study nutrient cycling in streams, soils, and forests. These biogeochemical cycling experiments were conducted on forested watersheds on the Oak Ridge Reservation. Studies begun for the Atomic Energy Commission in 1967 on Walker Branch Watershed have provided key long-term data on precipitation chemistry, surface water chemistry, and biological cycling—the movements of sulfur and nitrogen compounds from acid precipitation through soils, vegetation, trees, and stream organisms. Later ORNL research conducted for the Energy Research and Development Administration, the Department of Energy, the Environmental Protection Agency, and the Electric Power Research Institute has built upon that foundation.

ORNL research on the ecological effects of acid rain began in 1975, and in 1978 the Laboratory became a charter participant in the National Atmospheric Deposition Program (NADP). This was the first U.S. program to monitor and study ecological effects related to acidic deposition.

Because of its early participation in such programs, ORNL was well positioned to step into active roles in program planning, research, and assessment when NAPAP was created by passage of the Energy Security Act of 1980. The scope and direction of ORNL participation in NAPAP during the early years were outlined in an article in the Number Four, 1984, issue of the *Review* ("Acid Rain and Dry Deposition of Atmospheric Pollutants: ORNL Studies the Effects" by David Shriner), and information on some of the results was presented in the Number Two and Three, 1989, issue ("Complexities of Acidic Deposition" by S. B. McLaughlin et al.). In this article, I list the ORNL findings that had an impact on the final NAPAP Assessment report to the President and Congress.

More than 15 years ago, acid rain was not generally considered responsible for the acidification of lakes. However, as results of various studies became known in the late 1970s, doomsayers began to say that acid rain—formed from sulfur and nitrogen compounds injected into the atmosphere from fossil fuel combustion—would kill many fish and green plants.

Since then, evidence collected by the $537-million, 10-year NAPAP shows that neither position is right. For example, NAPAP scientists have found that acid precipitation has been responsible for the acidification of surface waters but that less than 5% of the lakes and 10% of the streams sampled in the National Surface Water Survey are chronically acidic.

Several of the conclusions of the NAPAP study were influenced by work done at ORNL. Fifteen staff members of ORNL's Environmental Sciences Division (ESD) contributed to seven of NAPAP's 27 State of Science/Technology reports. Key ESD researchers in this effort over the years have been Bob Cook, Sig Christensen, Jerry Elwood, Chuck Garten, Dale Johnson, Paul Kanciruk, Steve Lindberg, Sandy McLaughlin, Dick Olson, Mike Sale, David Shriner, Glenn Suter, Robert Turner, Helga Van Miegroet, and the late Ernie Bondietti, who died in an automobile accident on his return from the NAPAP conference in February 1990 at Hilton Head, South Carolina. In addition to these principal investigators, nearly 100 ORNL staff members have made significant contributions to the NAPAP program over its lifetime.

"Several of the conclusions of the NAPAP study were influenced by work done at ORNL."

ORNL studies of atmospheric processes show that (1) atmospheric deposition of sulfur and nitrogen oxides is twice as great in the Great Smoky Mountains as that at White Face Mountain in New Hampshire, which is typical of high-elevation sites in the Northeast; (2) increases in sulfur compounds below the forest canopy are the result of throughfall enrichment by atmospheric deposition (dry particles and precipitation passing down through the leaves to the forest soils) rather than to natural internal sources; and (3) the forest canopy appears to absorb and retain nitrogen compounds from both the air and precipitation. The surface analysis techniques developed in ESD have been widely used in the United States and Europe to quantify atmospheric deposition of sulfur oxides, nitrogen oxides, and trace metals to forest ecosystems.

The ORNL study of data on past Canadian surface water acid-base chemistry revealed that the

Dave Shriner (left), Rob Turner, and Dick Olson review output from ORNL's geographic information system. Here it provides analyses of spatial patterns used as a tool in the NAPAP assessment of sensitive ecological resources.

lakes having the highest concentrations of sulfate ions were those in Southern Ontario, close to major Canadian sources of sulfur oxides. Other acidic lakes also in areas of high sulfur deposition, however, were found to be dominated by organic acids.

These analyses confirmed that simple spatial correlation between deposition and acidity alone is insufficient to prove that air pollution causes acidification. Nevertheless, Canada's vocal concerns that industrial emissions carried across the northern U.S. border are responsible for its acidified lakes and streams probably speeded the development of acid rain control legislation in the United States, which was recently passed as part of the amended Clean Air Act.

ORNL's assessment of the biological effects of acidic precipitation on fish populations was limited by the available information on fish distribution. As a result, ORNL researchers helped develop an acidic stress index (ASI) for fish. This approach allows results from laboratory toxicity response experiments and biologically relevant chemical information from field surveys of surface waters to be combined to provide relative frequency distributions of stress levels—that is, indications of where fish are most likely to be exposed to toxic substances as a result of acidic precipitation. The ASI technique has proven useful for regional comparisons as well as for future projections in the absence of field data on fish distribution. Using this technique, ESD researchers found that the greatest stress to fish in eastern streams occurs in the mid-Atlantic Coastal Plain.

ORNL researchers studying the responses of vegetation to atmospheric deposition and pollution have found that acidic precipitation at ambient levels in the United States has not decreased crop yields, that ozone is more damaging than acid rain to U.S. agricultural production, and that acidic cloudwater combined with other stresses is associated with the reduced growth rate of trees in high-elevation spruce forests in the eastern United States.

ORNL will continue work started by Bondietti, who showed that acidic precipitation can alter forest soil chemistry, possibly enough to affect forest growth. He and his colleagues have found that iron and aluminum in the soil (mobilized as a result of acid input) competitively inhibit the uptake of calcium and magnesium by trees. Calcium and magnesium are soil nutrients that help trees grow.

ORNL studies of the Walker Branch Watershed indicate that mechanisms controlling acidification in a watershed can be identified. However, understanding the regional effects of acid precipitation remains very difficult. ORNL scientists, nevertheless, continue to try to better understand multiple stress interactions in ecosystems and relate atmospheric and landscape interactions to global changes. These results will be useful for continuing studies by NAPAP, which has been reauthorized by the new Clean Air Act.—*David S. Shriner, head of the Environmental Analyses Section of ORNL's Environmental Sciences Division.*

Measurements of plant physiological responses to air pollution stresses under field conditions have been important indicators of pollutant effects on plant growth. Here, Marion Cockrill, a summer student from Kalamazoo College in Michigan, measures rates of leaf photosynthesis with a field portable gas analyzer system.

ORNL Contributed 7 of NAPAP's 27 Volumes

Listed below are the seven State of Science/Technology reports authored or coauthored by ORNL scientists and incorporated into the 27-volume NAPAP report recently submitted to the President and to Congress.

Atmospheric Processes Research and Process Model Development, by S. E. Lindberg (primary coauthor)

Current Status of Surface Water Acid-Base Chemistry, by R. J. Olson, R. B. Cook, B. M. Ross-Todd, and J. J. Beauchamp (contributing coauthors)

Watershed and Lake Processes Affecting Chronic Surface Water Acid-Base Chemistry, by R. S. Turner, R. B. Cook, H. Van Miegroet, J. W. Elwood, S. E. Lindberg, M. K. Lyday, and L. J. Allison (principal author, primary coauthors, and contributing coauthors)

Biological Effects of Changes in Surface Water Acid-Base Chemistry, by S. W. Christensen, M. J. Sale, G. W. Suter, and J. J. Beauchamp (of ORNL's Engineering Physics and Mathematics Division) (primary coauthors)

Historical Changes in Surface Water Acid-Base Chemistry, by R. B. Cook, R. J. Olson, J. J. Beauchamp, and B. M. Ross-Todd (primary coauthors)

Methods for Forecasting Future Changes in Surface Water Acid-Base Chemistry, P. F. Ryan (contributing coauthor)

Responses of Vegetation to Atmospheric Deposition and Air Pollution, by D. S. Shriner, S. B. McLaughlin, J. D. Joslin, and M. K. Lyday (principal author, primary coauthors and contributing coauthor)

RE: Awards & Appointments

Beverly Wilkes has been named director of ORNL's Office of Planning and Management, replacing **Truman Anderson**, who heads the office's new Technology Assessment Program.

James B. Roberto has been named director of ORNL's Solid State Division, replacing **Fred W. Young, Jr.,** who has retired.

Robert C. Ward has been appointed director of ORNL's Engineering Physics and Mathematics Division, replacing **Fred C. Maienschein,** who has retired.

Michelle V. Buchanan has been appointed to the editorial advisory board of the journal *Analytical Chemistry*.

Martin Marietta Energy Systems, Inc., in 1990 was named "Employer of the Year" by the city of Knoxville and the Knoxville Advisory Council for the Handicapped.

John Sheffield received the Outstanding Achievement Award from the Fusion Energy Division of the American Nuclear Society.

James Corum has been named a fellow of the American Society of Mechanical Engineers.

Elizabeth Peelle has been awarded the honorary doctor of laws degree from Miami University in Oxford, Ohio, during its 20th Anniversary Symposium of Environmental Sciences.

Multiple divisions involved in designing and constructing ORNL's **Nonradiological Wastewater Treatment Project** were named the Project Team of the Year for 1990 by the national Project Management Institute.

Jane L. Eggers has been elected to the Executive Committee of the American Nuclear Society.

Vinod Sikka has received the Distinguished Alumni Award of the University of Cincinnati.

S. M. Gibson has been appointed newsletter editor for the American Institute of Chemical Engineers.

I. W. Osborne-Lee has been named chairman of the Minority Affairs Committee and the Committee for New Technology and Development of the American Institute of Chemical Engineers.

A. E. Osborne-Lee has been elected secretary of the National Organization of Black Chemists and Chemical Engineers.

Susan Sherrow has been named technical assistant to **William Fulkerson,** ORNL associate director for Advanced Energy Systems.

Donald B. Hunsaker, Jr., has been elected to a three-

Beverly Wilkes

John Sheffield

James Corum

Vinod Sikka

year term on the Board of Directors of the National Association of Environmental Professionals. He will serve as its vice president for one year.

Tuan Vo-Dinh has been selected to serve on the Senior Research Associate Board of the Environmental Research Center, University of Nevada, Las Vegas, and on the Tennessee Department of Education's Committee on the Curriculum for Biomedical Technology.

Mike Terry has been appointed Affirmative Action Program site manager at ORNL.

Richard H. Busey (retired) received the James J. Christensen Memorial Award at the 1990 Calorimetry Conference in Ann Arbor, Michigan.

I. W. Osborne-Lee

John Hayter has been appointed scientific director of the Advanced Neutron Source project.

Tom Rosseel, A. P. Baddorf, and **G. R. Gruzalski** have been elected president, vice president, and program manager, respectively, of the Tennessee Valley Chapter of the American Vacuum Society.

Vivian M. Baylor has been elected chairman of the Technology Transfer Committee of the American Society for Metals International.

Robin A. Cantor received a "Tribute to Women" in the business and industry category from the Young Women's Christian Association of Knoxville.

John Hayter

Scott L. Painter received the 1990 Fusion Engineering Division Student Award from the American Nuclear Society for his paper entitled "Alpha-Particle Losses in Compact Torsatron Reactors."

D. L. Kibby has been elected to the Board of Directors of the National Asbestos Council.

Paul S. Rohwer has been named president-elect of the American Academy of Health Physics.

Roy Fenstermaker, Jr., has been named head of the ORNL Quality Department.

Nancy Norton has been named director of Human Resource Management and Administration, and **Charles Emery** has been appointed director of Training and Development in the Human Resources Organization of Martin Marietta Energy Systems, Inc.

Vivian Baylor

Charles E. Childress has been named to represent the United States on Commissions V and XI of the International Institute of Welding.

M. A. (Mike) Kuliasha headed ORNL's effort to develop a plan for taking corrective actions in reponse to environmental, health, and safety concerns and findings of the DOE Tiger Team.

Nermin Uckan has been elected a fellow of the American Nuclear Society. ornl

Paul Rohwer

RE: Educational Activities

Encouraging Outstanding Teachers

Courtesy of Martin Marietta Corporation

Fred Holtzclaw, biology teacher at Oak Ridge High School, is featured in a Martin Marietta Corporation advertisement that has appeared in *The Atlantic*, *Fortune*, and other national publications. The theme is the corporation's commitment to education through support of such endeavors as the new Academy for Teachers of Science and Mathematics, a program of the University of Tennessee's Summer School of the South. As the ad says, "If we want to fire up the masterminds of tomorrow, the best thing we can do is keep our outstanding teachers energized today." Holtzclaw has been a leader in developing field environmental study and research experiences for his students. Last summer, he was a teacher research participant at ORNL.

Martin Marietta Corporation added its support to Secretary of Energy Admiral Watkins' drive for better education by pledging $1 million for a new regional Academy for Teachers of Science and Mathematics. The Department of Energy and the state of Tennessee have also pledged $1 million each to the University of Tennessee–ORNL program that will provide advanced training for selected outstanding middle and high school teachers.

"This should be an exciting, hands-on study—one that inspires the teachers through their own thinking, questioning, and participation in the project, and one that translates to the classroom so that the participants can similarly inspire their own students," said Ed Aebischer, project administrator of Graduate and Outreach Programs. Selected staff members from the University of Tennessee at Knoxville and ORNL will serve as faculty for the academy.

Invitations have gone out to school superintendents in Tennessee, Kentucky, North Carolina, and Florida to nominate candidates for the program's first four-week session, which will be June 23 through July 19, 1991. About 80 teachers are expected to participate in this first session. In the future, the program will be expanded to include lower-grade and kindergarten teachers and teachers from other states neighboring Tennessee.

Each participant in the program becomes a Martin Marietta Fellow, and as such receives a $1200 tax-exempt stipend, travel expenses, lodging in the apartment dormitory, a meal allowance, and books and materials.

SACAM Redefines Saturdays

For many teenagers, Saturday is their only chance to sleep until noon. For SACAM participants, though, it's a chance to get their hands on advanced equipment and their minds on research problems.

The Saturday Academy for Computing and Mathematics began in October, and for eight weeks groups of one teacher and four or five students from each of six high schools in the area (Bearden, Farragut, Karns, Oak Ridge, Oliver Springs, and Webb) spent their Saturday mornings at ORNL working with computing and mathematics to solve problems in various areas of research. Sessions have dealt with subjects such as advanced materials, particle physics, and modeling the global climate.

On one Saturday, for instance, Mike Strayer, Chris Bottcher, Ted Barnes, Jim Beene, Soren Sorensen, and Robert Varner from the Physics Division set up seven identical Macintosh IIs with identical software for the groups. According to Bottcher, "We wanted to provide a hands-on experience—a tutorial-type session. We first introduced a couple of problems having to do with the physics of an accelerator like the Holifield Heavy Ion Research Facility accelerator, which they were going to see later in their tour. Then we moved on to problems involving algebraic, numerical, and graphical information and techniques. The students typed the problems, ran them on the VAX, and then checked their output. We were also able to log in through the National Energy Research Supercomputing Center to the Cray computer at Lawrence Livermore National Laboratory and to run some problems on it."

The students were delighted to have experience with the supercomputers. They were also amazed at the ease with which they moved from something they already knew, the Macintosh, to supercomputers. "The students were especially intrigued with some of the high-resolution graphics software, which was provided with a selection of other software as a sampler," said Bottcher. In fact, they were so impressed with the equipment and techniques they were using that some stayed three hours "after school" for more study.

Bottcher found his work with SACAM "very worthwhile and rewarding," and he certainly plans to participate again. "Eventually, it would be nice to have a permanent room set up for this purpose with our own hardware. We would have our tutorial packages in place, so there wouldn't be as much preparation required for each Saturday session."

The very successful pilot program has led to a winter session that will be expanded to include about 40 participants from a total of nine or ten high schools. Even more students will now find Saturday mornings worth waking up for.

Mobile Robot Surveys ORNL Waste Site

"The location and quantities of contaminated materials must be determined before initiating site remediation."

In September 1990, a mobile, remotely operated robot outfitted with electronic systems, sensors, and computers, including an ORNL-developed automated data acquisition system, surveyed an Oak Ridge radioactive landfill waste storage site. The local news media covered the automated remote survey by the eight-wheeled all-terrain vehicle at ORNL's Solid Waste Storage Area No. 3 (SWSA-3).

The purpose of this demonstration was to show the feasibility of using remotely operated robots to locate and measure radioactivity from contaminated materials in trenches covered with soil nearly 20 years ago. The location and quantities of contaminated materials must be determined before initiating site remediation. Because of the potential hazard to human health, a remotely operated vehicle that carries equipment for recording and transmitting information on trench boundaries and radiation levels at waste sites is desirable.

The application of robotic technology to hazardous waste problems is a major element of DOE's Environmental Restoration and Waste Management Program five-year plan for applied research, development, demonstration, testing, and evaluation. Robotic systems offer the opportunity to reduce human exposure to hazardous substances and conditions during waste site characterization, cleanup, repackaging, and storage or disposal activities. In addition to the safety benefits, automation of some of the survey tasks can lead to productivity improvements, including more effective record keeping because robotic systems can automatically generate computer records.

The remotely operated robot was loaned to ORNL by the U.S. Army, and ORNL outfitted it with the appropriate detectors and electronic systems to conduct a remote waste site survey. This instrumented "testbed" was developed as an element of the U.S. Army Human Engineering Laboratory's (HEL) Soldier Robot Interface Project (SRIP), which addresses human factors issues in military applications of robotics. Initial development of the SRIP testbed was performed by a team including ORNL, Tooele Army Depot, HEL, and Odetics, Inc. This DOE-DOD cooperative effort will be continued in 1991 with a similar landfill survey demonstration at the Idaho DOE complex, where the major buried-waste remediation projects are located.

The eight-wheeled all-terrain vehicle can be driven by a human teleoperator seated at a remote control console. The operator also can control the vehicle's high payload-to-weight ratio manipulator arm developed through an Army Small Business Innovative Research contract with Odetics, Inc. The vehicle and all-onboard computer and electronic systems are powered by a 15-horsepower diesel engine.

For the ORNL demonstration, several environmental sensors were mounted to the vehicle, including a terrain conductivity meter for detecting anomalous subsurface features, a gamma radiation detector, and a gas analyzer/detector. ORNL engineers modified the control system for the vehicle steering and drive motors to permit the vehicle to follow a predetermined survey path autonomously when not controlled by the teleoperator. Similarly, the manipulator arm controls were modified to permit an autonomous sweep of the arm during the survey.

As a result, the arm automatically swept the gamma detector back and forth across the path of the vehicle in a regulated motion and the vehicle automatically drove across the survey area, turned around, and returned in the opposite direction along a parallel path separated by a distance specified by the operator.

The Ultrasonic Ranging and Data System (USRADS), developed at ORNL's Instrumentation and Controls (I&C) Division and marketed commercially by the Chemrad Tennessee Corporation of Oak Ridge, was used to determine the precise position of the vehicle and to record measurements every second from the three environmental sensors. Data from these sensors were mapped and analyzed to determine the location, radioactivity levels, and other characteristics of the underground trenches.

Although a more complete characterization would be required before the radioactive wastes could be

This mobile, remotely operated robot outfitted with electronic systems, sensors, and computers, including an ORNL-developed automated data acquisition system, recently surveyed an Oak Ridge site for storage of radioactive waste. Inset: Representatives of the local news media cover the event.

retrieved, the three sensors selected demonstrated the feasibility of using a remotely controlled robot to perform a remote survey. Data generated from this survey demonstration will be used to help determine the role of robotic technology in providing accurate characterization of waste sites—the first step in developing safer, faster, and more cost-effective methods for remediation of contaminated areas.

The team of ORNL researchers who developed the instrumented mobile robot for the remote survey includes Bill Hamel, Barry Burks, Brad Richardson, Steve Killough, Dave Thompson, John Jansen, Marion Dinkins, Gary Armstrong, Mark Noakes, and Todd Appleton, all of ORNL's new Robotics and Process Systems Division (formerly the Fuel Recycle Division), and Mike Emery of the I&C Division.

"The new test greatly expands the universe of hazardous wastes."

ORNL Toxic Waste Test Adopted by EPA

A real-world test developed largely at ORNL has been adopted by the U.S. Environmental Protection Agency (EPA) as a standard procedure for identifying leachable landfill wastes that pose a toxic hazard.

The new procedure has been used at Superfund sites—abandoned waste sites selected by EPA for cleanup—to determine if the removed material must be managed as hazardous waste. The test is being used on the Oak Ridge Reservation, one of 1200 Superfund sites, to identify which of its 500 or more hazardous waste sites have the potential to release toxic materials to the environment.

The test, called the Toxicity Characteristic Leaching Procedure (TCLP), replaces the Extraction Procedure Toxicity Test, which was used by EPA in the 1980s. Most of the development work was done by Chet Francis of ORNL's Environmental Sciences Division and Mike Maskarinec of the Analytical Chemistry Division.

Wastes buried in municipal landfills include materials having organic constituents that can break down and form carboxylic acids. These acids, in combination with water flowing through the landfill, have the potential to dissolve, or leach out, many toxic metals and chemicals, including herbicides, pesticides, and other waste constituents, making them available for transport into groundwater.

"The toxicity characteristic," says Maskarinec, "indicates how toxic a waste is by measuring the potential for its toxic constituents to leach from the waste and contaminate groundwater at levels that may threaten human health and the environment."

Wastes already listed as "hazardous wastes" are not affected by or subject to TCLP, unless they are candidates for "delisting." Wastes classified as hazardous are so listed because of their known hazardous characteristics, which include toxicity, ignitability, corrosivity, and reactivity. Toxic wastes in landfills must be managed in compliance with the Resource Conservation and Recovery Act to prevent damage to health and the environment.

The TCLP is more accurate and reliable than the previously used procedure because it simulates the actual leaching behavior of industrial wastes under municipal landfill conditions and also because it adds 25 organic constituents to the toxicity list. In addition, the test determines whether each constituent meets or exceeds regulatory limits. Maskarinec and Francis demonstrated several years ago that the TCLP simulated disposal leaching conditions more accurately than the previously used procedure.

"The promulgation of the new test," said Maskarinec, "greatly expands the universe of hazardous wastes."

ORNL Materials Aboard *Ulysses* Space Probe

When the U.S. space shuttle *Discovery* rocketed into orbit on October 6, 1990, several ORNL researchers once again realized that another piece of their alloy had found its destiny in space.

One of the goals of the five-man *Discovery* crew (including William M. Shepherd, a native of Oak Ridge) was to release the space probe *Ulysses* so that it could automatically rocket itself out of

Earth orbit and fly to Jupiter. The giant planet's gravity pull will then act like a slingshot to accelerate the probe to an even higher speed in the direction of its goal, the sun. In 1994 *Ulysses* will explore the sun's north and south poles, which have never been examined before.

Ulysses contains the same ORNL-made cladding that was used in other spacecraft—*Voyager I*, *Voyager II*, and *Galileo*. The cladding is an iridium alloy containing 0.3% tungsten and minor additions of aluminum and thorium. It was developed in the 1970s chiefly by C. T. Liu, Henry Inouye, and Tony Schaffhauser, all of ORNL's Metals and Ceramics Division.

The cladding is used to encapsulate the plutonium fuel for the radioisotope thermoelectric generator (RTG) that powers *Ulysses*. Because iridium is extremely tough and has a high melting point, it can withstand continued contact with the radioisotopic fuel, the searing heat of possible reentry into the atmosphere, and the impact of landing on Earth.

During all anticipated operating conditions, *Ulysses*'s RTG cladding is protected by another ORNL development—an extremely light, efficient, thermal insulation composed of bonded mattes of carbon fiber. The carbon-bonded carbon-fiber insulation maintains a cladding temperature within a preferred range during normal operations.

Chief developers of the insulation were Walt Eatherly and J M (Robbie) Robbins, both of the Metals and Ceramics Division. The insulation and iridium materials for *Ulysses* were assembled into RTGs at DOE's EG&G Mound Applied Technologies, Inc., laboratory in Miamisburg, Ohio.

Bill Chilcoat, a Metals and Ceramics Division technician, operates a molding machine for making carbon-bonded carbon-fiber billets from which sleeves are machined. Such sleeves are used to protect cladded fuel in the recently launched *Ulysses* spacecraft.

ORNL Clones Gene Making Fruit Fly Insecticide Resistant

A group in ORNL's Biology Division has cloned essential parts of a gene involved in making fruit flies resistant to commonly used insecticides. The achievement may provide insights into how to prevent insects from becoming resistant and how to protect beneficial insects from pesticides.

Larry Waters begins the process of cloning a fruit fly gene. He has led a group in ORNL's Biology Division in cloning essential parts of a gene involved in making fruit flies resistant to commonly used insecticides.

The ORNL work is helping researchers better understand the molecular mechanisms by which insects become resistant to chemicals commonly used to kill them. The results are potentially important because losses of forest and agricultural products, combined with the cost of insect control, add up to billions of dollars annually in the United States alone. These huge costs can be attributed to increasing insect resistance to available pesticides.

The Biology Division has conducted research on the fruit fly (*Drosophila melanogaster*) for many years to determine the effects of radiation and chemicals on fruit fly genes. Part of this research has included the determination of the biochemical makeup of a specific class of proteins, collectively called P450s.

The ORNL group has confirmed that these enzymes not only can convert harmless chemicals into toxins and mutagens but also can degrade insecticides. Larry Waters, who leads the group that cloned the fruit fly gene, says, "This enzyme system is a double-edged sword because it can both endanger and protect the fruit fly."

Waters and his colleagues previously showed that fruit fly P450 proteins can consist of two smaller sets of proteins—P450-A, which is found in all fruit fly strains, and P450-B, which is present in insecticide-resistant flies in amounts 50 to 100 times greater than what exists in susceptible flies.

A goal of the research is to determine how the P450-B genes in resistant and susceptible flies differ so that P450-B proteins are produced in greater amounts in resistant flies. To achieve this goal, the ORNL group generated molecular probes, or markers, to detect and determine the makeup of the P450 genes.

Waters and his colleagues purified the proteins and made monoclonal antibodies that target a single protein in each of the two P450 sets. These antibodies are special proteins that provide a specific, sensitive method for detecting both a resistance-related protein (P450-B1) and a resistance-unrelated protein (P450-A1). The P450-B1–specific antibody has been used in collaborative studies with researchers at other institutions to show that related proteins exist in other resistant insects, such as the Colorado potato beetle, Southern army worm, tobacco budworm, and house flies.

Using recombinant DNA techniques and the antibodies as a specific selection system, the ORNL group made copies of important segments of the genes responsible for the production of the P450-A1 and P450-B1 proteins. "The importance of the P450-B1 cDNA clone," says Waters, "is that it provides a specific probe to study the organization and the function of a gene responsible for insecticide resistance."

Recently, the ORNL researchers used the special clone to show that the genes involved in making one strain of fruit fly resistant to insecticides differs in structure from the counterpart gene in fruit flies susceptible to the insecticides.

"This is an important finding," said Waters, "because the scientific community has long thought that *gene amplification*—the production of extra copies of genes that code for the proteins that break down insecticides—is responsible for insecticide resistance. Our research results suggest that *gene rearrangement*—a change in a gene's structure that promotes the production of large amounts of insecticide-degrading proteins—may be the actual mechanism for P450-dependent insect resistance to toxic chemicals."

The group is currently attempting to clone the entire P450-B1 gene from both susceptible and resistant flies. With these genomic clones, they can determine the particular structural change that accounts for the greater gene activity in resistant flies.

"Because our antibodies cross-react with proteins in other insects, they along with the cDNA clones might be developed into diagnostic probes that could be used to monitor developing resistance in insects in the field," Waters said. "Other, more speculative uses of the DNA clones might be to make resistant insects more susceptible by site-directed insertion of DNA fragments that would inactivate the genes responsible for making insects resistant. Another possibility is to transfer resistance genes to beneficial but susceptible insects, such as ladybugs, and make them more resistant to insecticides and other toxic chemicals in the environment."

In August 1990 Waters presented the ORNL research results at the International Congress of Pesticide Chemistry in Hamburg, Germany. A number of researchers from throughout the world have requested ORNL's antibodies and DNA clones to use as probes in studies of the molecular mechanisms of resistance in other insects.

Support for the ORNL research has come from the Department of Energy and the Department of Agriculture. Besides Waters, the researchers included Lan-Yang Ch'ang and Steve Kennel, both staff members of the Biology Division; Scott Sundseth, a graduate of the University of Tennessee–Oak Ridge School of Biomedical Sciences; Andy Zelhof, an undergraduate student at Bucknell University who was here for an Oak Ridge Science and Engineering Research Semester; Judy Moyer, a graduate student with the UT–Oak Ridge School of Biomedical Sciences; and Wendy Tipton, an undergraduate student in DOE's Student Research Participation Program.

"Researchers from throughout the world have requested ORNL's antibodies and DNA clones to use as probes in studies of the molecular mechanisms of resistance in other insects."

Immunoliposomes Carry Anticancer Drugs to Mouse Lungs

An improved technique for delivering anticancer drugs to the lungs of mice has been developed by researchers at the University of Tennessee at Knoxville (UTK) and ORNL's Biology Division. Through further development, this drug delivery system may be useful for treating human lung cancer and other diseases.

Leaf Huang, a professor at UTK, Kazuo Maruyama, a postdoctoral researcher who is now working in Japan, and UTK graduate student Atsuhide Mori have developed liposomes—empty spheres made of fatty membranes—filled with anticancer drugs. They coated the liposomes with monoclonal antibodies made by Steve Kennel of ORNL's Biology Division and injected them into mice.

These ORNL monoclonal antibodies are proteins that seek out and attach specifically to endothelial cells, which line lung blood vessels. By making composition changes, the researchers at UTK designed the immunoliposomes to find and cling to these same cells.

"Our experiments with mice showed that our immunoliposomes achieve a high level of lung binding and retention," said Huang. "We also demonstrated that in mice with injected tumor cells in their lungs, our immunoliposomes destroyed the tumor cells located near the endothelial cells. Of the mice injected with tumor cells, those that received immunoliposome treatment lived longer than those that did not."

The research at UTK was funded by the National Institutes of Health, and the ORNL research was supported by DOE.

ORNL Technique Rapidly Identifies Toxins, Drugs

"ORNL researchers have developed a method to determine quickly if organic pollutants are present in indoor and outdoor air."

ORNL researchers have developed a method to determine quickly if organic pollutants are present in indoor and outdoor air. Simple variations of this analytical technique can also rapidly identify and quantify traces of pollutants in water and soil samples and drugs in body fluids.

Marc Wise, Michelle Buchanan, and Mike Guerin, all of ORNL's Analytical Chemistry Division, are developing new sample-handling equipment and computer software for use with an ion-trap mass spectrometer for direct air monitoring. But they have recently found other applications for this powerful and sensitive "direct sampling" method.

The ORNL researchers have used it to detect trace amounts of the tobacco ingredient nicotine in air. They have also used it to detect nicotine and its major metabolites (products of body chemistry) in the urine of active smokers. Nicotine and its metabolites in body fluids are commonly used to determine an individual's exposure to tobacco smoke.

The researchers believe that this analytical method could be further developed to measure nicotine and its metabolites in the urine of nonsmokers who have been exposed to passive smoke. Early ORNL experiments have also shown the technology can rapidly detect trace levels of commonly abused drugs in urine, including cocaine and codeine, suggesting that the methods could eventually be used in drug screening programs.

The ORNL system has been used to detect and identify airborne traces of organophosphonate compounds, which simulate deadly nerve agents and some types of pesticides. Additional compounds in air and water that have been detected directly by this technology include benzene, toluene, and common chlorine-containing solvents such as methylene chloride, chloroform, and perchloroethylene. The ORNL researchers also analyzed soil samples for fuel spills and common volatile organic compounds such as benzene.

"Our technology can be used to analyze samples for the presence of targeted organic compounds much faster than conventional methods using gas chromatography," says Wise. "In 2 or 3 minutes we can analyze air, water, soil, or body fluids for target substances at the part-per-billion level—for example, 50 trillionths of a gram of nicotine in 1 microliter of urine. Since our methods offer increased analytical speed compared with other currently used techniques, a greater number of samples can be analyzed in a day, decreasing the cost per sample."

Federal agencies that have provided funding or shown considerable interest in the development of the technology are the U.S. Army, Department of Energy, the National Cancer Institute, the Food and Drug Administration, and the Environmental Protection Agency. ORNL's initial work on the project received support from the Army and involved the development of an important part of the ORNL system—the automated thermal desorption sample-handling device—for measuring airborne organophosphonates.

This thermal desorber allows air samples to be collected remotely in a 7-cm-long glass tube containing a resin. These traps can be brought into

Mike Guerin (left) and Mark Wise discuss results from ORNL's ion-trap mass spectrometer (shown here). ORNL researchers developed new sample-handling equipment and computer software for use with this instrument for direct monitoring of air for organic pollutants. The technique can also be used to rapidly identify and quantify traces of pollutants in water and soil samples and drugs in body fluids.

the laboratory and analyzed using the automated thermal desorber, which can handle up to 16 samples. Inside the desorber, helium is blown through the resin traps while they are rapidly heated. As a result, the air pollutants are vaporized so they can be introduced to the mass spectrometer system.

The thermal desorber also is used for the analysis of urine samples and can be used to analyze water samples for the presence of target semivolatile organic compounds.

ORNL researchers are now performing experiments needed to validate and ultimately certify these analytical methods for routine use by interested governmental agencies.

For analyses requiring identification of specific compounds, the ORNL researchers use a quadrupole ion-trap mass spectrometer manufactured by Finnigan MAT Corporation. This instrument was selected because of its ability to perform chemical ionization, selective ion storage, and collision-induced dissociation tandem mass spectrometry.

A specific compound can be detected by reacting it with specific chemicals that form ions, which can then be broken down by collisions into

Bob Hettich points out a reading at ORNL's Fourier transform mass spectrometer. Combined with laser desorption, this technique permits the structures of DNA modifications to be characterized at the molecular level.

characteristic fragments. The number of ions produced from a specific compound indicates the compound's concentration in a sample.

"The features of the ion-trap mass spectrometer and the versatility of ORNL's sample-introduction devices," said Wise, "make possible the analysis of many types of samples for targeted compounds without extensive sample preparation or prior chromatographic separation."

For analyses of samples having only a few components, a conventional quadrupole mass spectrometer can be used to identify and quantify volatile organic compounds in air, water, and soil.

New Way To Detect Changes in DNA

Two ORNL researchers are developing a sensitive, instrumental technique for determining structural and chemical changes in the building blocks of DNA. DNA is the blueprint for all life, and any chemical modifications of its normal structure can have adverse effects, often resulting in mutations and cancer.

Bob Hettich and Michelle Buchanan, both of ORNL's Analytical Chemistry Division, are developing laser desorption Fourier transform mass spectrometry (FTMS) for characterizing the structure of DNA modifications at the molecular level. Because DNA is an extremely large molecule, it must be cut into smaller fragments (oligonucleotides) before being examined by mass spectrometry.

The research is designed to determine the structures of unknown modified DNA fragments, called DNA adducts, using nanograms (billionths of a gram) or less material.

DNA adducts are formed by the chemical attachment of a foreign molecule to the DNA molecule. In most cases, the foreign molecule attaches to the DNA's nucleic bases, altering the normal hydrogen bonding between these building blocks of the double helix structure. This change in DNA structure interferes with the normal duplication of genetic material, possibly leading to cancer or mutations.

In collaboration with Sankar Mitra of ORNL's Biology Division, the ORNL chemists have studied alkyl DNA adducts. They have found that the laser desorption FTMS technique could be used to detect, identify, and determine the position of individual methyl and ethyl adducts on DNA bases. This detailed information is needed to determine biological activity and ease of repair of each DNA adduct.

Polycyclic aromatic hydrocarbon (PAH) adducts have also been examined by the ORNL chemists. This class includes compounds such as the benzo(a) pyrene adduct of deoxyguanosine phosphate. Benzo(a)pyrene, commonly found in tobacco smoke and industrial emissions, is converted biologically to the diol-epoxide, which reacts very readily with DNA to form adducts. Other PAH-DNA adducts, such as those formed with DNA and para-aminobiphenyl, beta-aminonaphthalene, or ortho-toluidine, were also studied at ORNL.

Negatively charged molecular ions of DNA oligonucleotides are produced by bombarding the solid DNA sample with light from a neodymium-YAG laser. ORNL researchers have determined that mixing the DNA samples with nicotinic acid prior to laser ionization reduces fragmentation so that molecular weights for large oligonucleotides can be determined.

The molecular ions produced by this "soft ionization" technique are then trapped in the FTMS ion cell. Because the cell is surrounded by a magnet, the ions are forced to move in defined orbits and with a frequency of motion characteristic of each type. Electronic detection of this ion motion is used to identify the ions in the cell. Because the ions can be trapped in the FTMS cell for several seconds, their structures and properties can be examined in detail with various ion manipulation techniques.

Theory Explains How To Stabilize Operation of Tokamaks

ORNL researchers have developed a theory explaining why the operation of a tokamak, a


×10

"By understanding why a tokamak shifts from the low mode to the high mode, our theorists are able to predict conditions under which an improved operating mode occurs."

doughnut-shaped fusion device, can suddenly improve.

Fusion is an attractive, clean source of energy production because the fuel it uses will be deuterium, an abundant hydrogen isotope available in water. One way fusion energy is produced is by fusing hydrogen nuclei together by magnetically confining them in a tokamak's superhot, electrically charged, gas consisting of hydrogen ions and electrons, called a plasma. Fusion researchers believe that this heat-producing method could lead to a practical, safe source of electricity by the middle of the next century.

ORNL's theoretical predictions have been verified by experimental results at the CCT tokamak at the University of California at Los Angeles and at General Atomic's DIII-D tokamak in San Diego, California. A report on the theory was published in the June 1990 issue of the American Institute of Physics technical journal *Physics of Fluids B*.

Fusion researchers have observed that a tokamak plasma operating in a state known as the "L," or low, mode suddenly jumps to an improved energy-confining state, called the "H," or high, mode.

John Sheffield, director of ORNL's Fusion Energy Division, says, "By understanding why a tokamak shifts from the low mode to the high mode, our theorists are able to predict conditions under which an improved operating mode occurs. This improvement could help the tokamak be a reliable source of electricity someday."

According to a theory proposed by K. C. Shaing, Charles Crume, and Wayne Houlberg, all of ORNL's Fusion Energy Division, the normal loss of energy confinement typical of the L mode depends on the electric fields generated by the charged particles in the plasma. The ORNL theory suggests that the plasma can be put into the high mode by manipulating electric fields—for example, by removing ions from the plasma. If the ORNL model is deemed correct, it should influence the design and operation of the International Thermonuclear Experimental Reactor (ITER), a proposed fusion test device supported by the European Community, Japan, the Soviet Union, and the United States.

Joe Cunningham adjusts a precision diamond-turning machine used to cut metal and inspect the machined surface. Diamond-turning technologies for metal cutting, which have been used for many years at the Oak Ridge Y-12 Plant, may someday be transferred to small businesses.

ORNL Evaluates Technology for Optical Mirrors

Better optical mirrors are needed by the U.S. Strategic Defense Initiative (SDI) program to direct beams of light and particles toward military targets in space. To help meet this need, a high-technology optics program has been established at ORNL.

The ORNL program is using the concept of "manufacturing operations development and integration laboratories" (MODIL) to develop improved processes for private industry to make optical mirrors of high quality.

MODIL was conceived by Lt. Gen. James A. Abrahamson, retired director of the SDI program. Based on his experiences with the U.S. space shuttle and F-16 fighter aircraft programs, he believed that the question of how to manufacture the final product should be addressed early in the research and development and component-acquisition cycle. He thought this approach would reduce the costs of the final production of complex components and systems.

The mission of the Optics MODIL project at ORNL is to search for and develop new manufacturing technologies that could be used to produce advanced optical components for SDI. The project will integrate the new technologies into the manufacturing process and validate the final system for producing components.

One goal of the ORNL program includes using industry, universities, and federal laboratories to evaluate technologies for their affordability, performance, and production potential before major components are designed. Another goal is to accelerate the transfer of optics technologies for producing highly engineered mirror surfaces to American industry. These technologies also could be used for other optical applications, such as producing baffles and windows.

"The Optics MODIL program focuses on high-risk, high-benefit programs in which private industry might be reluctant to invest," said William R. Martin, project director. "But if the results of the program are successful, industry could easily incorporate these 'leap-frog' technologies."

"If the results of the program are successful, industry could easily incorporate these 'leap-frog' technologies."

According to Martin, researchers search globally for technologies for precision engineering of surfaces and advanced machine control, integrate them into equipment in test facilities at the MODIL, and evaluate them. Through cooperative experiments, U.S. industry can work with the equipment. "Precision machining techniques being developed for the 21st century," says Martin, "will achieve a level as fine as a few layers of atoms."

The program's studies of methods for fabricating precision optical components include an evaluation of extremely accurate single-point diamond machining—using gem-quality diamonds to cut metal at the surface. Slight fluctuations in temperature are among the many factors that can adversely affect machining of these precise components.

In two of the MODIL manufacturing cells in the Productivity and Validation Test Bed (PVTB) at ORNL, temperature profile is controlled through double-walled plastic enclosures to within one-tenth of a degree Fahrenheit using a room-within-a-room concept. According to Arthur C. Miller, manager of the PVTB, if the method can be developed to achieve this level of temperature control economically, then diamond-turning technologies for metal cutting could be transferred to small businesses.

Project managers from ORNL's Engineering Technology and Instrumentation and Controls divisions and from the Development Division at the Oak Ridge Y-12 Plant have been working with industry since the MODIL was established in 1988 to reach a consensus on the best way to achieve the goals. Representatives of private industry, universities, and government are given the opportunity to provide guidance and direction to the Optics MODIL program through workshops and industrial briefings.

Poor Man's Stainless Steel Licensed to Two Firms

On November 17, 1990, for the first time ever, Energy Systems signed two licensing agreements in one day and gave a single company the rights to two different ORNL technologies.

Energy Systems agreed to license both ORNL's iron aluminide and nickel aluminide technologies to Harrison Alloys, Inc., of New Jersey. This marked the second time that ORNL's iron aluminide alloy technology, which received an R&D 100 Award in September 1990, has been licensed to a private company. This was the sixth licensing agreement involving ORNL's nickel aluminides.

Also on November 17, Harrison Alloys expressed interest in locating some of its company operations in the Oak Ridge area. The company's products include resistant heating elements, wire for thermocouples, and spark plug wires.

On November 1, Energy Systems' first licensing agreement involving ORNL's iron aluminides was signed with the Specialty Metals Products Division of Ametek, Inc., of Pennsylvania, which is interested in using iron aluminides to make porous metal gas filters. Harrison Alloys plans to use iron aluminides for heating elements.

The ORNL-developed iron aluminide alloy (Fe_3Al), dubbed the "poor man's stainless steel," is strong to 600°C , ductile, and resistant to corrosion and oxidation at temperatures to at least 800°C. The material could be used in structural components for highly corrosive environments, such as those in advanced fossil-energy conversion systems, chemical-production systems, and engines operated at high temperatures to increase fuel-use efficiency.

Before ORNL's development, Fe_3Al had not been used as a structural material mainly because of its brittleness at room temperature. The material, however, can fill a need because of its excellent resistance to oxidation and corrosion.

To improve the material's properties, Claudette McKamey, C. T. Liu, and Vinod Sikka, all of ORNL's Metals and Ceramics Division, added small amounts of chromium, zirconium, boron, carbon, molybdenum, and niobium for control of microstructure and fracture behavior. The typical composition is Fe-28Al-5Cr-0.1Zr-0.05B, with 0 to 2% Mo and/or 0 to 1% Nb added for specific properties.

The addition of Zr, Mo, or Nb increased the material's strength by solid solution hardening or particle strengthening. The addition of chromium resulted in improved room-temperature ductility because of its effects on the composition or properties of the protective surface oxide. In particular, the chromium minimized the embrittling effects of airborne water vapor, resulting in higher ductilities at ambient temperatures.

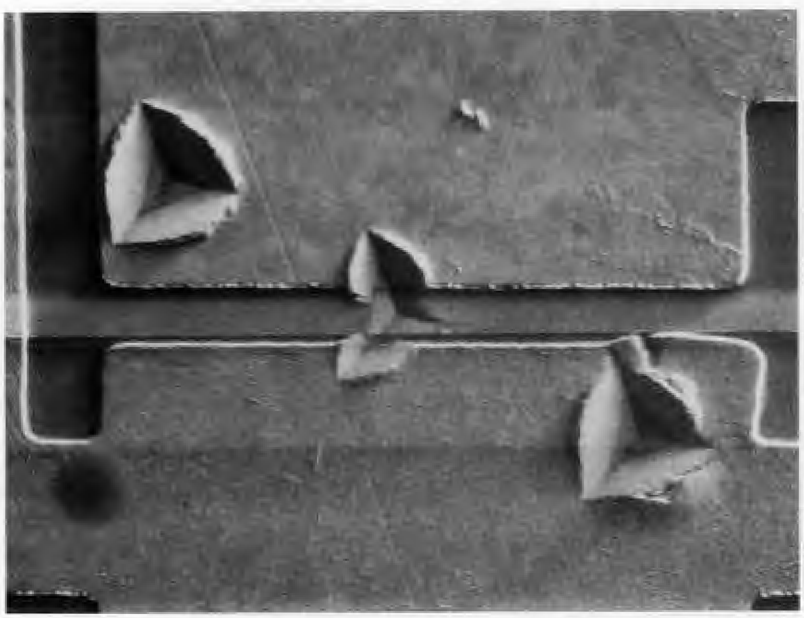
The newly developed iron aluminides exhibit excellent oxidation and corrosion resistance at temperatures up to 1000°C, especially in sulfur-containing atmospheres, because of their ability to form an aluminum oxide coating, which protects the underlying material. Because they possess improved room-temperature tensile ductilities, fabrication of structural components from iron-aluminide-based materials is now easier.

Claudette McKamey inserts an iron aluminide specimen into a furnace at ORNL's Metals and Ceramics Division. Iron aluminide specimens must be heated to help researchers better assess their high-temperature strength and ductility.

Sharing Facilities

Unlike many user facilities, SHaRE isn't a building full of equipment dedicated to the user community. Rather, as the name suggests, it consists of staff members sharing their equipment with outside users to explore scientific questions of mutual interest.

Through the Shared Research Equipment (SHaRE) program, about 25 participants each year use state-of-the-art microanalysis facilities to explore the nature of materials. Examples of SHaRE projects range from characterizing microstructures of advanced austenitic steels, to examining thin films of diamond, to investigating the mechanical behavior of microlaminate materials.



The triangular depressions in this silicon micro-device have been made by a mechanical properties microprobe. These indentations are used here to study the changes in electrical conductivity that occur during indentation.

The program, which was established in 1979, is jointly administered by Oak Ridge Associated Universities (ORAU) and ORNL. Neal Evans of ORAU, who coordinates SHaRE, explains how some of the projects begin.

"Many of the research tasks pursued at ORNL suggest related experiments—but we just don't have the time to pursue them. Or perhaps we'll want to run an experiment again with another material, but we lack that material. On the other hand, there may be someone at a university who already has the material and would like to perform the experiment, but lacks the necessary facilities. We match up these needs and capabilities to create a collaborative team to pursue answers to basic research questions.

"Frequently the projects are initiated at a university. Contacts are established between colleagues—perhaps at a conference or perhaps between researchers who have previously collaborated. Then we start asking questions. Is this good science? How much of a commitment is each party willing to make? Is there someone at the Laboratory who is willing to participate in this project? Although SHaRE is designated as a user facility by DOE, part of its mission is to ensure that each project complements research being performed within the Metals and Ceramics (M&C) Division. Therefore, a research staff member acts as an internal collaborator—as a member of that project."

All but two of the current users are from universities. The internal collaborators often train the participating graduate students to use the equipment so that the work will truly be theirs. Of course, gaining experience with such advanced equipment is exciting and valuable to the students.

Each project is approved for one year by a committee of ORNL and ORAU staff and external SHaRE participants. During that year the outside participant might be at ORNL from a week to three or four weeks. The majority of the projects are renewed by another proposal, which can either continue the studies or permit the investigators to pursue research in another area.

Because the facilities belong to M&C, the projects usually probe issues in materials science. Historically, about 75% of the projects have used analytical electron microscopes (AEMs) or the atom probe field ion microscope.

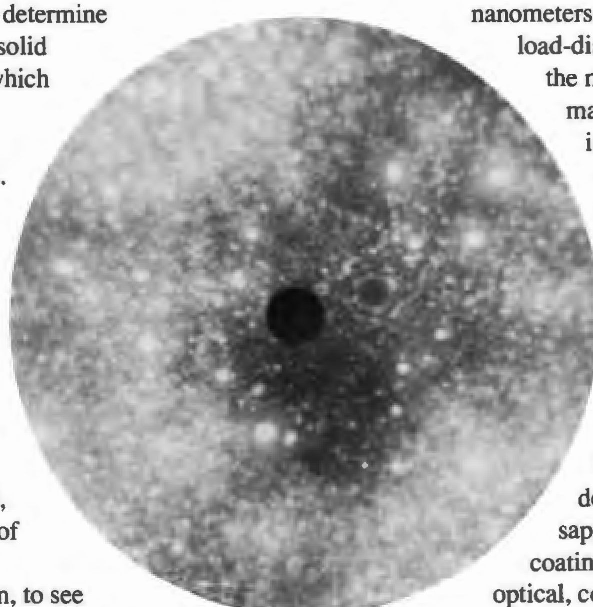
In one such project, Judith Todd of the Illinois Institute of Technology has used an AEM in her microstructural characterizations of advanced austenitic steels. These steels may be used in some replacement components of conventional power plants.

David Paine of Brown University, Rhode Island, has used an AEM to perform in situ annealing experiments to determine the activation energy for solid phase epitaxial growth (which is oriented by the crystal substrate) of amorphized silicon-germanium alloys. Such regrowth can leave the material in a highly strained state, which may give it useful electrical or optical properties.

In other basic research, Jeff Glass and Mike Ma, both of North Carolina State University, are examining thin films of diamond, produced by chemical vapor deposition, to see how the diamond has nucleated and grown. These films have potential as semiconductors that could operate in harsh environments of high temperatures and high electromagnetic frequencies. Glass and Ma are also investigating suitable metal layers that will serve as electrical contacts in diamond-based electronic devices.

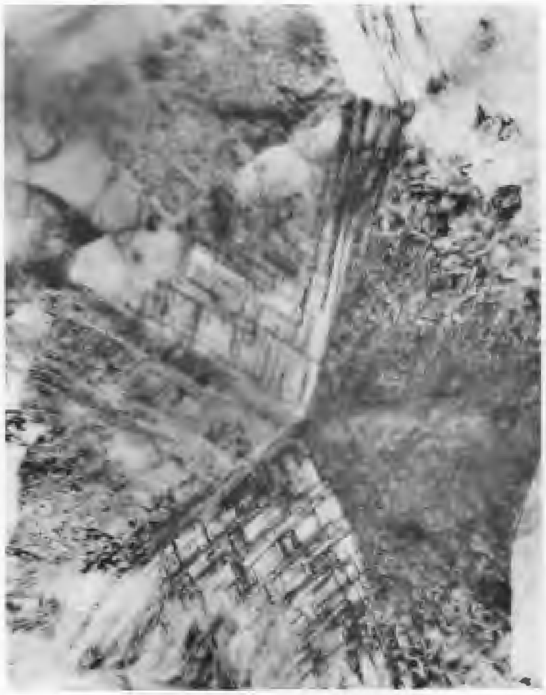
Mike Miller, an M&C researcher, is using the atom probe field ion microscope with Jing Zhang of Lehigh University to determine whether austenitic iron-nickel alloys decompose during long-term heat treatments at modest temperatures in a manner predicted by thermodynamic calculations. This predicted decomposition, which is caused by the magnetic nature of the material, has been observed in iron meteorites that cooled very slowly over millions of years. The results of this project will contribute to the understanding of the iron-nickel alloy system as well as our understanding of the decomposition process and magnetically induced phase separation.

Much of the remaining research involves a mechanical properties microprobe. Differences in mechanical properties of a material in regions less than a micron apart can be resolved from load-displacement data generated by the microprobe. Using programmed loads as small as 5 μN (a unit of force), indentations as shallow as a few nanometers can be made. From the load-displacement information, the mechanical response of the material deformed by the indenter can be determined and then related to the mechanical properties. Using this mechanical microprobe, ORNL researcher Warren Oliver with Brian Fabes from the University of Arizona has characterized the hardness of thin sol–gel derived ceramic coatings on sapphire substrates. These coatings have potentially useful optical, corrosion-resistance, and wear-resistance properties. Oliver and Fabes are currently developing a model to relate the surface areas formed during the indentation process to the substrate hardness, specimen hardness, and the quality of the specimen–substrate interfacial adhesion.



Individual atoms appear as small bright spots in this atom probe/field-ion micrograph of an iron-nickel alloy that was aged 370 days at 300°C. The slightly larger bright spots are 1-nm-diam precipitates. Atom-by-atom identification is possible with time-of-flight mass spectrometry. (magnification 10_6X)

Through SHaRE, Warren Oliver and George Pharr of Rice University have used the mechanical properties microprobe to study the mechanical behavior of microlaminate materials.. These materials consist of alternating layers of two or more dissimilar (metal-metal or metal-ceramic) materials; the laminate spacings can range from a few nanometers to a few microns. The properties of these microlaminates have been shown to be quite sensitive to the thickness of the laminations,



These defect structures, typically found in diamond films grown by chemical vapor deposition, are revealed by transmission electron microscopy. (magnification 45,000X)

Descending from the upper left portion, an advancing crack (the very bright feature) in Ni_3Al has encountered and been stopped by a grain boundary (appearing horizontally). Stresses at the crack top are accommodated by the formation of a slip band which appears near the crack tip and descends to the right. Many factors, such as composition, temperature, and strain rate, affect how a material responds to cracking. (magnification 12,500X)

so the microprobe will be useful in determining the best thicknesses for optimizing mechanical properties.

SHaRE does not have a building of its own, but it offers much of M&C Division's equipment, with the exception of the facilities within the High Temperature Materials Laboratory, which has its own user facility program. SHaRE's principal investigators come not only from universities, but from other government facilities and the private sector. Program funds are available to defray the travel and living expenses of academic participants. Participants working on nonproprietary research, for which the goals are to collaborate with the ORNL researchers and to publish the results, are not charged. "In other words," says Evans, "the users are not buying equipment time. However, those using the SHaRE facilities on a proprietary basis (that is, the results will not be published, so the public sector does not directly benefit from the research) are charged to achieve cost recovery."

Evans is particularly well qualified to evaluate SHaRE because in addition to coordinating the program now, he participated in it as a graduate student. "Outsiders," he says, "are drawn by what SHaRE offers— principally, the expertise of the ORNL research staff, and secondly, the state-of-the-art facilities.

"The program enhances technology transfer and furthers the diffusion of information between national laboratories and universities. The program is a good investment for DOE, too; for the cost of about half a person year, SHaRE annually contributes to about 25 publications, 25 presentations, and 4 dissertations.

"When I was a participant, I thought it was great because it showed me not only what a national lab looked like, but what types of projects were given national importance. SHaRE exposes the students to world-class researchers.

"The program works because the work is collaborative and because everyone who participates in it benefits. The external people gain access to the staff and the facilities, and the internal staff get to work on short-term projects that they would not otherwise get to do."

For the Metals and Ceramics Division, learning to share has been well worth the effort.

—*Cindy Robinson*

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ORNL researchers are helping overcome the barriers to making practical devices from high-temperature superconducting materials.

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