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REVIEW

Vol. 33, No. 2, 2000

Carbon Management

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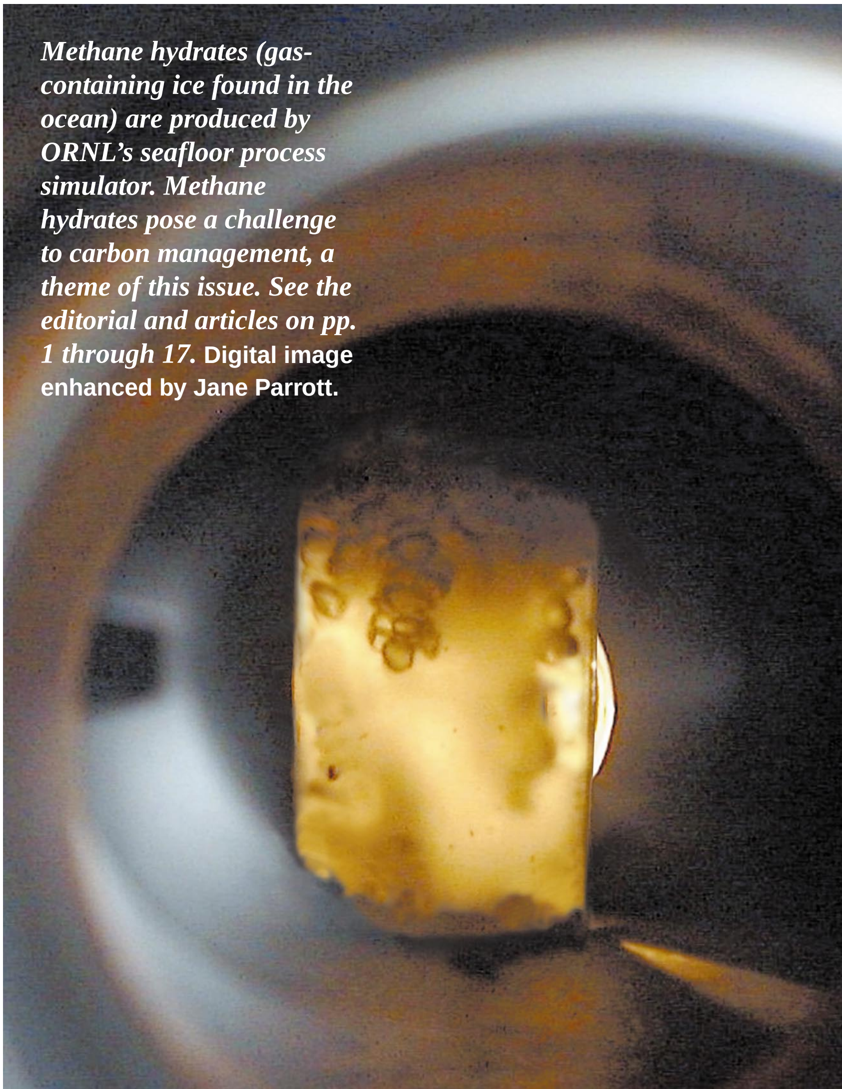

Methane hydrates (gas-containing ice found in the ocean) are produced by ORNL's seafloor process simulator. Methane hydrates pose a challenge to carbon management, a theme of this issue. See the editorial and articles on pp. 1 through 17. Digital image enhanced by Jane Parrott.

Editorial: ORNL Could Be DOE Leader in Carbon Management

R. G. Gilliland

W. F. Harris

More and more scientists agree that the world is experiencing a warming trend. Scientists who once asked whether global warming is occurring are now trying to predict its effects. In the *U.S. National Assessment of Potential Consequences of Climate Variability and Change*, which was officially released to the public June 12, 2000, the U.S. government made its first thorough assessment of the potential consequences to our nation of global warming. The report mentions steaming northern cities in the summer, eroding coastlines, increased drought in some regions, changes in rain and snowfall patterns that could affect the availability of fresh water, and bumper crops in the heartland.

Will intensified global warming increase the variability in our weather patterns and bring about longer droughts, bigger floods, and more violent storms? Will ocean levels rise enough to flood coastal states? Can these climatic impacts be delayed? Researchers working in the field of carbon management are developing technologies and strategies to slow the growth in atmospheric levels of greenhouse gases, especially carbon dioxide (CO_2), in the hope of avoiding climate changes. Carbon management is defined as "the full range of science and technology opportunities (including policy options) to stabilize atmospheric CO_2 concentrations by decreasing the carbon-production potential of the energy system and by reducing CO_2 emissions, including the capture and sequestration of atmospheric CO_2 and modification of the carbon biogeochemical cycle."

Researchers at Oak Ridge National Laboratory are studying three approaches to retarding the growth in atmospheric CO_2 emissions from human activities (including burning forests to clear land for agriculture). One approach is to develop and implement energy-efficient technologies to decrease the need to burn CO_2-emitting fossil fuels. Another plan is to switch from fossil-fuel combustion to lower-carbon and carbon-free fuels and technologies for power production. A third proposal is to capture carbon emissions from energy production facilities and securely store, or sequester, the carbon in plants, geological formations, and the oceans.

In this issue of the *ORNL Review*, Mike Farrell, director of the Global Environmental Studies Program at ORNL and leader of ORNL's carbon management program, and other ORNL leaders discuss issues of carbon management and the reasons why ORNL is well positioned to play a leading role in carbon management research. This issue also features highlights on ORNL work in the carbon management field: energy-efficient appliances and cooling systems for buildings that reduce the need to burn coal; new ways to produce and detect hydrogen for use in fuel cells that make electricity; a design of a highly efficient power plant that combines a solid-oxide fuel cell with a gas turbine and incorporates ORNL's novel heat-exchange and separation technologies; a new carbon capture and separation technique of great interest to industry; the potential use of genetic technology to create trees and grasses that sequester more carbon and provide more energy when harvested; sequestration of carbon in geological formations and in biologically active ponds; and improvement of degraded lands to make them store more carbon.

We are studying methane hydrates in the ocean and Arctic permafrost because they hold a tremendous natural gas resource that could affect climate change favorably or adversely, depending on how the hydrates are harvested. We are also evaluating strategies for adapting to any climate change that will probably occur even if all the greenhouse gas controls recommended at the Kyoto conference were implemented.

J. W. Nave

ORNL is also practicing carbon management in its operations. For example, we are participating in the Tennessee Valley Authority's Green Power Switch Program. We will buy 56,250 kilowatt hours a month of electric power generated from renewable resources, such as solar collectors, wind turbines, and landfill gas.

Because of the range of expertise and experience at ORNL, we believe we are well positioned to be a leading Department of Energy laboratory in carbon management. As one of the four Battelle labs in the DOE system—the others are the Brookhaven and Pacific Northwest national laboratories and the National Renewable Energy Laboratory, we at ORNL are proud to be part of the Battelle-DOE Carbon Management Network. We hope this issue of the *Review* will provide the world with a window on an important part of DOE's research capabilities in carbon management.

R. G. Gilliland, *Associate Director for Energy and Engineering Sciences*

W. F. Harris, *Associate Director for Biological and Environmental Sciences*

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Oak Ridge National Laboratory is a multiprogram, multipurpose laboratory that conducts research in energy production and end-use technologies; biological and environmental science and technology; advanced materials synthesis, processing, and characterization; and the physical sciences, including neutron-based science and technology.

Managing Carbon: ORNL's Research Roles

ORNL is well positioned to be a national leader in carbon management research.

In 1968 Jerry Olson, an ORNL ecologist, began studying how trees take carbon from the atmosphere, incorporate it into their leaves and wood, and return it as carbon dioxide after they die. Ever since, studies of the global carbon cycle have been under way at ORNL.

In 1975, a former ORNL director and nuclear power enthusiast, Alvin Weinberg, met with a number of government officials. He reiterated the scientific concern expressed by Roger Revelle of Harvard University in 1965. Weinberg told them that the carbon dioxide buildup in the atmosphere as a result of increased fossil fuel combustion for power production could lead to climate change. He reminded them that nuclear power plants do not produce carbon dioxide, a greenhouse gas that traps excess heat from the sun, warming the earth's surface. As a result, the effect of human activities on atmospheric carbon dioxide levels began to receive government attention; a carbon dioxide effects office was established in the Energy Research and Development Administration, the predecessor of the Department of Energy.

Also in 1975, a program of carbon dioxide research was started at the Laboratory, which for years had focused on the development of nuclear reactors as power sources. During the same decade, because of the rising price of imported oil and concerns about nuclear reactor safety, ORNL researchers received funding to develop ways to use energy more efficiently and explore alternative, non-nuclear energy sources such as solar power, hydrogen, and fuels from biomass. As a result, ORNL researchers have developed insulation standards and more efficient refrigerators and heat pumps (for cooling homes and heating water) and have led a program that could bring large-scale production of biofuels from hybrid poplar trees and switchgrass.

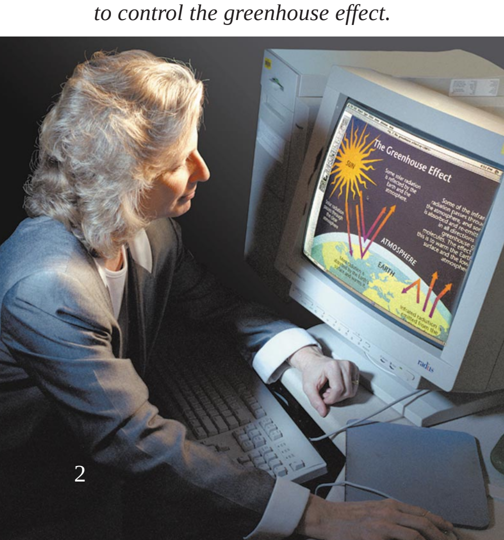
From 1976 to 1984, Weinberg's Institute for Energy Analysis (IEA) in Oak Ridge was the nation's center for issues related to carbon dioxide. Then emerging studies of carbon dioxide and global climate at ORNL and other labs began receiving increased support from DOE, and IEA researchers such as Gregg Marland and David Reister came to ORNL. In 1989 ORNL Director Alvin Trivelpiece established the Center for Global Environmental Studies at the Laboratory.

Covers of Technology Opportunities to Reduce U.S. Greenhouse Gas Emissions *and* Carbon Sequestration Research and Development, *two DOE reports that ORNL played a major role in writing, editing, and publishing.*

In 1997 a group co-led by Marilyn Brown, deputy director of the Energy Efficiency and Renewable Energy Program at ORNL, completed a report entitled *Scenarios of U.S. Carbon Reductions*, which involved contributions from five Department of Energy national laboratories. This report identified a portfolio of energy-efficient and low-carbon technologies that could provide a low-cost path for reducing carbon emissions in the United States to their 1990 levels by the year 2010. In 1999 the same five labs were asked to extend their analysis to 2020 and to identify specific policies and programs that could produce the technological advances and market penetration levels needed to address a range of energy and environmental challenges facing the nation. This follow-on study, *Scenarios for a Clean Energy Future*, is expected to be published later this year.

On Earth Day, April 24, 1998, DOE released a two-volume report entitled *Technology Opportuni-*

Marilyn Brown has studied ways to control the greenhouse effect.

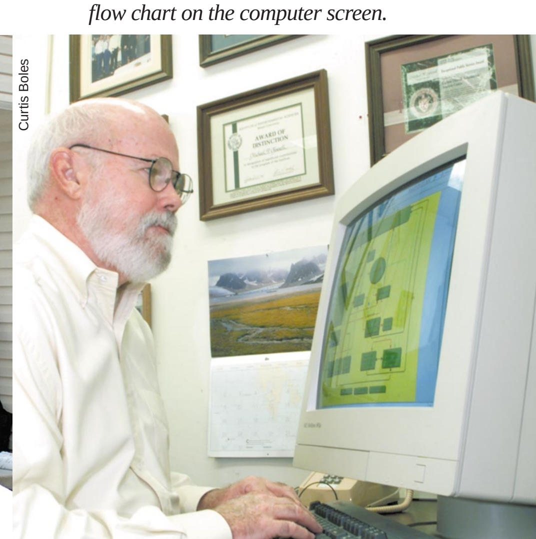


Jeff Christian, director of DOE's Buildings Technology Center User Facility, shows a sample of polystyrene wall insulation that cuts energy use in a new Habitat for Humanity home.

Curtis Boles

Mike Farrell examines a carbon management flow chart on the computer screen.

Curtis Boles



ties to Reduce U.S. Greenhouse Gas Emissions. ORNL's David Reichle, Marilyn Brown, John Sheffield, and Mike Farrell were the technical co-leaders for the planning and drafting of the DOE report. The same year DOE organized a workshop to devise a roadmap for doing research on carbon sequestration, methods for capturing and securely storing carbon dioxide from fossil fuel plants. In December 1999 another DOE report, *Carbon Sequestration Research and Development*, was released; its technical co-leaders included ORNL's Reichle, Rod Judkins, and Gary Jacobs.

Mike Karnitz (left) and David Stinton chat in the High Temperature Materials Laboratory exhibit area during the Distributed Generation Showcase held June 19 and 20, 2000, at ORNL.

ORNL Emerging as Leader

"For 25 years ORNL has been conducting research that positions us well to be a leader among DOE labs in carbon management," says Mike Farrell, director of ORNL's Global Environmental Studies Program and leader of the Laboratory's carbon management programs. "We have explored energy efficiency, clean energy, carbon sources and sinks, the global carbon cycle, biomass, and climate modeling.

"Because of our historically broad background in these areas, we were asked to co-lead the development of the greenhouse gas emission reduction and carbon sequestration reports. Doing this suite of reports allowed us to look at our own skills, other labs' capabilities, and available technologies related to carbon management."

Farrell defines carbon management as "the full range of science and technology opportunities (including policy options) to stabilize atmospheric CO_2 concentrations by decreasing the carbon-production potential of the energy system and by reducing CO_2 emissions, including the capture and sequestration of atmospheric CO_2 and modification of the carbon biogeochemical cycle." The term "carbon management" has been adopted by the business community (e.g., electric utilities, coal mining firms, etc.) as preferable to "development of climate change technologies."

The carbon- and energy-related research being conducted at ORNL today is certainly no carbon copy of the type of research performed here in the past two-and-a-half decades. "What is new," says Farrell, "is research on carbon capture, emission reduction technologies, and sequestration."

One way to manage carbon is to use energy more efficiently to reduce our need for a major energy and carbon source—fossil fuel combustion. Another way is to increase our use of low-carbon fuels (natural gas and ethanol give off 40% as much carbon dioxide as coal when burned), and carbon-free fuels and technologies (nuclear power; hydrogen fuel cells; and renewable sources such as solar energy, wind power, and biomass fuels). Both approaches have long been studied by ORNL researchers and other DOE national laboratories.

Today, for example, ORNL is studying distributed generation—electricity produced on site using fuel cells and microturbines (which operate on natural gas) and renewable energy systems such as wind turbines and solar electric cells to meet specific energy needs for factories, hospitals, and office and commercial buildings. ORNL researchers are devising better ways to combine microturbines with fuel cells, which provide waste heat that help run the turbines. According to Tony Schaffhauser, manager of ORNL's Energy Efficiency and Renewable Energy Program, microturbines could be combined with ORNL-developed heat pump chillers that may be marketed as air conditioners. If ORNL-developed desiccant systems are used to pull out the excess humidity, less air conditioning will be needed, decreasing energy use 15 to 20% and reducing carbon emissions. The desiccant material that absorbs moisture from the inside air before it is chilled will give it off to the outside air when the material is warmed by waste heat from a microturbine.

Solomon Labinov prepares to measure air flow in a microturbine at ORNL's Buildings Technology Center while Jeff Christian looks on. The velometer Labinov is studying is next to the turbine, which drives the generator at right.

The third and newest way to manage carbon is carbon sequestration. In this proposed approach, carbon will be captured from the atmosphere and from stack emissions of fossil-fuel combustion facilities. Some of the carbon may be transformed into useful products. The rest will be transferred to aboveground terrestrial ecosystems such as forests, to belowground terrestrial ecosystems such as underground coal seams, and to the ocean.

DOE has established two carbon sequestration centers, one of which is co-led by ORNL researchers. It is the DOE Center for Research on Enhancing Carbon Sequestration in Terrestrial Ecosystems (CSiTE), and its co-manager is Gary Jacobs of ORNL's Environmental Sciences Division (ESD). (For details, see the article in the *Review*, Vol. 32, No. 3, 1999, pp. 21–23.) The other is the DOE Center for Research on Ocean Carbon Sequestration (DOCS). ORNL researchers David Cole (Chemical and Analytical Sciences Division) and Gerry Moline (ESD) participate in one of DOE's geologic sequestration projects.

In evaluating ORNL's emerging role as a leader in carbon management research, Farrell says, "We found that ORNL's missing pieces included analytical capabilities to determine the potential of geological and ocean systems to store pumped-in carbon, to predict how long it would be stored, and to assess if the sequestration methods are safe. We also need to determine the best mix of energy-producing technologies in terms of cost, energy production, and carbon dioxide emissions."

Carbon Management Model

Farrell and his colleagues see the need for a carbon management model, and they recently won internal funding to develop one. "We plan to build a carbon management model to evaluate different carbon management strategies and options," Farrell says. The team of ORNL researchers who have received funding to build the model are Tony King of ESD, Kathy Yuracko of the Life Sciences Division (LSD), Paul Leiby of the Energy Division, Mike Taylor of the Computational Physics and Engineering Division (CPED), and Brian

Worley of the Computer Sciences and Mathematics Division (CSMD). They are conducting the research in collaboration with Pacific Northwest National Laboratory.

"We will be doing cost-benefit analyses of a mix of energy and sequestration technologies and predict their impacts on atmospheric carbon dioxide levels," says King, an expert in the global carbon cycle who will analyze natural impacts on carbon dioxide levels such as volcanoes, forest fires, and El Niño. "For example, we will compare terrestrial and ocean sequestration in terms of cost and the expected carbon storage time. We will analyze the risks of sequestration options and other carbon management strategies. We will do life cycle analysis and uncertainty analysis.

"Our model will update and combine existing global carbon cycle models, energy technology models, and economic models. The model will be modernized so that it can use different programming languages across platforms and make complex calculations on parallel supercomputers such as the IBM SP at ORNL."

"The model will be used to ask 'what if' questions," Farrell says. "For example, what if it was decided to introduce hydrogen fuel cell cars in the United States to greatly reduce carbon dioxide emissions from the transportation sector, which represents about one-third of total U.S. carbon emissions? What are the risks and uncertainties with respect to building an infrastructure to support these vehicles?"

In building such a model, the developers are following DOE assumptions, as explained by Farrell.

"We can reduce energy intensity through energy efficiency improvements between now and 2010," he says. "We can reduce carbon intensity by substituting clean energy sources for coal combustion by 2020.

Because we have abundant supplies of coal, we can once again burn it in large quantities to produce energy by introducing carbon capture and sequestration technologies by 2030. Right now we can enhance carbon sequestration naturally by planting trees and grasses on marginal farmlands that can be converted to biomass fuel."

Why Sequester Carbon?

Farrell says that if the Kyoto conference recommendations for controlling greenhouse gas emissions are followed, the United States can continue major use of fossil fuels only if we can capture, transport, and dispose of carbon in an economical way. "Right now the technologies are there," he says, "but studies suggest that it would double the cost of electricity from fossil fuel plants." For most Americans, that's too many greenbacks to reduce greenhouse gases.

People will sequester carbon only if a value is placed on this action, Farrell says. "Let's suppose that the government imposed a carbon tax of $50 per ton of carbon discharged. Then it might be economical to capture the carbon and convert it to useful products or dispose of it permanently by injecting it into a geological formation or the ocean. The higher the carbon tax, the more capture and sequestration technologies will be valued."

It will be costly to build a fossil plant, a capture plant, and a natural gas-like infrastructure to pipe half a gigaton of captured carbon gas to special facilities for injection into geological formations or the ocean.

The most economical approach, Farrell says, is to delay the mitigation response for coal-fired power plants because new technology should allow us to capture and sequester carbon emissions more economically in the next three decades. In the meantime, we can switch from high-carbon to lower-carbon or carbon-free fuels and introduce energy efficiency technologies.

Challenges to Carbon Management

One challenge to carbon management is plant and animal biomass. Schaffhauser calls plant biomass "carbon neutral" because, while they give off carbon dioxide when burned, plants absorbed and sequestered the same amount of the greenhouse gas before they were harvested. "Green plants are a gift," Schaffhauser says, "because they provide us with food, fuel, chemicals, building products, and a way to sequester carbon." But biomass can be a large source of carbon dioxide to the atmosphere if large tracts of forest are burned because of drought and demands to clear the land for agriculture and development.

Biomass and other materials disposed of in landfills decay to form landfill gas, which is mostly methane. The release of landfill methane to the air boosts greenhouse gas levels. But landfill gas can be captured and run through gas turbines to produce electricity, turning trash into treasure.

Animal waste is also a challenge to carbon management. According to ORNL's John Sheffield, who is also director of the Joint Institute for Energy and Environment at the University of Tennessee, U.S. farms for raising cattle, poultry, and swine to help feed the world have 1.4 billion tons of wet manure, which annually emits almost 3 million metric tons of methane, a greenhouse gas. Because the United States has about 15% of the world's manure, it is apparent that animal waste worldwide is a significant contributor to greenhouse gas levels.

Landfills are rich sources of methane.

"Manure is commonly used as a fertilizer," Sheffield says, "but it also is a large, generally untapped, source of energy. Cleverly applied technological solutions could allow farmers to sell manure as a feedstock for producing methane for energy and for making other products. Income from the animal waste feedstock will help farmers offset the costs of controlling pollution from farm chemicals such as fertilizers, pesticides, pathogens, antibiotics, and hormones."

Another challenge to carbon management is methane hydrates, which harbor a huge amount of natural gas in the ocean and Arctic permafrost. The problem is that harvesting these hydrates for energy might result in the release of the methane to the atmosphere, raising the greenhouse gas levels enough to change the climate (see article on p. 14).

U.S. Geological Survey

Burning gas from methane hydrate ice.

"As a key resource for science and technology, we hope to support DOE's mission of fostering a secure and reliable energy system that is environmentally and economically sustainable," Farrell says. "Our goal is to be DOE's major resource of carbon management science and technology.

"We hope to expand our leadership in energy efficiency R&D by increasing our R&D on distributed energy power, buildings, and transportation. We plan to expand our clean power R&D by increasing our R&D on fuel cells, gas turbines, reciprocating engines, hydrogen production and storage, agricultural biomass genetics, and methane hydrates. Through CSiTE we hope to increase our ability to estimate the potential for terrestrial carbon sequestration. We want to invest in fundamental R&D to advance the development of chemical, biological, and engineering technologies for capturing and sequestering carbon."

David Reichle, who recently retired from ORNL as an associate director, is in charge of helping ORNL leverage its capabilities through partnerships with the other Battelle-managed labs—Brookhaven National Laboratory, Pacific Northwest National Laboratory, and the National Renewable Energy Laboratory. These labs and ORNL have formed a DOE carbon management network. The network will work with core universities and industrial firms to form an R&D consortium. By broadening the network's skill base, its R&D proposals for funding in the area of carbon management should be increasingly competitive.

With such a plan, ORNL hopes to capture a leading role in DOE's research program for managing carbon. ornl

Building Energy Use and Carbon Management

Americans can significantly reduce carbon emissions and their electricity bills by buying more efficient appliances.

If we build one, they will buy it. That's the dream of Jeff Christian, director of the Buildings Technology Center (BTC) User Facility at ORNL. BTC has been involved in developing, evaluating, and promoting household appliances and heating and air-conditioning equipment that are far more energy efficient than what Americans are using today. If most Americans replace their washing machines, refrigerators, water heaters, and air conditioners with new, highly efficient ones by 2010, they will save energy and money in the long run. Most important, from a carbon management point of view, they will reduce power plant emissions of carbon to the air by almost 95 million metric tons per year (MMT/yr). That's the amount of carbon emitted annually by nearly 20 million people (5 MMT/yr per person) or by 56 1000-megawatt coal-fired power plants.

"Buildings and their appliances use 36% of the nation's energy," Christian says. "Buildings are also responsible for 36% of U.S. emissions of carbon dioxide produced by human activities. We have an opportunity to cut our energy consumption and carbon emissions significantly through use of energy-efficient technologies."

One way to help clean up our carbon emissions act is to buy and use new water-saving, tumble-action clothes washers that incorporate a "horizontal-axis" design rather than the conventional vertical agitator. Because this design requires less water and, thus, has less water to heat, it saves energy. In addition, its improved spin cycle cuts down time in the dryer, further reducing energy use.

In 1997, the Department of Energy and Maytag Corporation, the efficient machine's manufacturer, selected 100 residents of Bern, Kansas (population: 200), to test the new washer. Bern has an unreliable supply of well water when the weather is dry.

John Tomlinson and his BTC colleagues in ORNL's Energy Division made measurements that confirmed a reduction in water and energy use when the 100 residents switched from old washers to the new, high-efficiency washers. The ORNL researchers found that the residents used 56% less energy and 38% less water, saving the town of Bern 640,000 gallons annually.

"If most U.S. households change over to high-efficiency clothes washers by 2010," Christian says. "U.S. carbon emissions will be reduced by 28 million metric tons of carbon per year."

In collaboration with Whirlpool, General Electric, Frigidaire, Amana, and Maytag through cooperative research and development agreements, ORNL researchers led by Ed Vineyard have been designing the next generation of popular refrigerator models, to cut their energy use in half. By adding insulation and using more efficient motors and compressors, the ORNL-industry partnership has designed a 20-cubic-foot refrigerator that operates on only 0.93 kilowatt hours per day, using 53% less energy than the maximum allowed by new DOE standards.

"If Americans replaced their aging refrigerators with these new, efficient ones by 2010," Christian says, "they would use 58% less energy to chill their foods and beverages and reduce carbon dioxide emissions by 48 million metric tons per year."

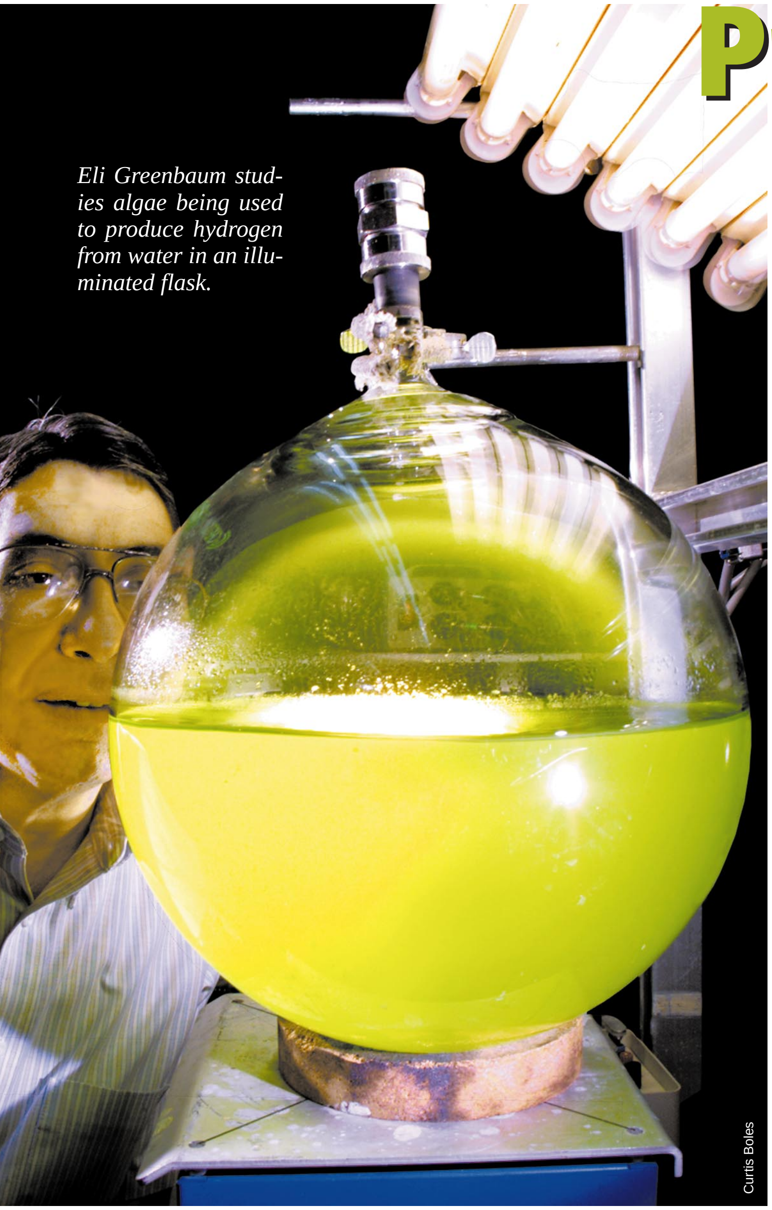
In collaboration with Enviromaster International, Inc., Tomlinson and his ORNL colleagues have developed a drop-in residential heat pump water heater. This highly reliable device is more energy efficient than the conventional water heater, which uses resistive heating. The new water heater, which will soon be on the market, can be installed by a plumber at a low cost.

"If half of American households replace their old water heaters with heat pump water heaters by 2010," Christian says, "the energy used nationwide for home water heating will be reduced by 0.6 quad and the amount of carbon emitted will be decreased by 9 million metric tons per year."

Additional energy savings can be made by replacing home air conditioners with a generator-absorber heat exchanger (GAX) chiller (developed by private industry under the guidance of ORNL researchers) and by insulating and sealing leaks in heating and air-conditioning ducts to eliminate energy losses. The total reduction in carbon emissions by 2010 if most households make these changes will be 95 MMT/yr.

It is hoped that Americans will buy into new energy-saving and money-saving technologies that will reduce carbon emissions from buildings.

ORNL research has stimulated the development of more efficient washing machines, refrigerators, water heaters, and air conditioners.



Eli Greenbaum studies algae being used to produce hydrogen from water in an illuminated flask.

Producing and Detecting Hydrogen

ORNL researchers have come up with new ways to produce and detect an energy-rich gas.

Hydrogen is a clean-burning, carbon-free gas that is becoming more attractive in an era of concern about climate change. Hydrogen could be used in fuel cells to provide electricity for homes, businesses, and hybrid electric cars. The only waste product from hydrogen fuel cells is water.

Hydrogen, however, is costly to produce. It is commonly stripped from natural gas, but that process leaves carbon dioxide, which must be disposed of in an environmentally acceptable way. The conventional way to produce hydrogen without generating carbon dioxide is to separate hydrogen from oxygen in water using electrolysis. Of course, it is quite possible that the source of electricity for this separation process is a coal-fired power plant, which, itself, produces lots of carbon dioxide.

Today's electrolytically produced hydrogen costs around $30 per million British thermal units (Btu); by comparison, natural gas costs about $3 per million Btu, and gasoline costs about $9 per million Btu. So the economic barriers to hydrogen production are formidable.

ORNL researchers are studying biological ways to produce hydrogen that might prove to be economically competitive someday. The research is being funded by the Hydrogen Research Program of the Department of Energy's Office of Energy Efficiency and Renewable Energy.

Water molecules can be split into hydrogen and oxygen atoms using algae, one-celled organisms that thrive in water. ORNL researchers Eli Greenbaum (an ORNL corporate fellow), James Lee, and Steve Blankinship—all in the Chemical Technology Division (CTD)—have discovered that the green alga *Chlamydomonas reinhardtii* can produce hydrogen and oxygen from water under certain conditions. "It's the biological version of electrolysis," Greenbaum says. "The goal of the research is to replace conventional electrolysis with a renewable biological process for hydrogen production."

These algae normally grow new cells by photosynthesis, using carbon dioxide from the air in the presence of sunlight. But after placing the aquatic organisms in a large flask of water illuminated by lamps, the ORNL researchers "trick" the algae by depriving them of carbon dioxide and oxygen. As a result, a normally dormant gene becomes activated, leading to the synthesis of the enzyme hydrogenase. The algae use this enzyme to produce both hydrogen and oxygen from water. The relative amounts of oxygen and hydrogen that evolve in the flask are measured by sweeping the gases over hydrogen and oxygen sensors, whose electrical conductivity increases with rising gas concentration.

Greenbaum says that several research projects are exploring ways to optimize the process. Membrane separation technologies are being developed that will separate the hydrogen from the oxygen more efficiently. Because the algal hydrogenase eventually shuts down from exposure to oxygen, Michael Seibert and Maria Ghirardi, researchers at the National Renewable Energy Laboratory, are working to create

ers at the National Renewable Energy Laboratory, are working to create a mutant organism that makes a hydrogen-producing enzyme that is less sensitive to oxygen. The third challenge is to optimize the ability of the algae to use light.

Algae naturally survive under a variety of light intensities, ranging from bright sunlight to shade. Because of the algae's chlorophyll antenna size, increasing the light intensity beyond natural levels will overwhelm the electron transport processes of the algae rather than boost photosynthesis. The ORNL scientists want the antennae of the algae redesigned to maximize hydrogen production. Laurens Metz, a molecular biologist at the University of Chicago, has genetically engineered the algae to produce mutants with an altered antenna size. "Eventually," Greenbaum says, "we hope to have mutant algae that will produce 10 times more hydrogen if we increase the light intensity 10 times."

Jonathan Woodward and his associates in CTD are trying to use enzymes to make hydrogen from the cellulose present in old newspapers, grass clippings, and other waste products of renewable resources. The first step is to transform cellulose into glucose sugar, and the second step is to convert the glucose product and its byproduct, gluconic acid, into hydrogen. The second step has proved easier.

In 1996 Woodward and his colleagues reported an important advance. They learned how to produce a molecule of hydrogen from a molecule of glucose using two enzymes (called extremozymes) produced by microorganisms that grow under extreme temperatures.

In October 1999, CTD researchers Woodward, Mark Orr, Kimberley Cordray, and Greenbaum reported producing 11.6 hydrogen molecules for every glucose molecule in the substrate. The researchers achieved 97% of the maximum stoichiometric yield possible—12 hydrogen molecules for each glucose molecule. This is the highest yield of hydrogen ever obtained from glucose by a biological process. The results are to be published in an upcoming issue of *Nature*.

This high stoichiometric yield of hydrogen from glucose was attained through an "oxidative pentose phosphate cycle" using 11 enzymes. In this cycle, glucose is oxidized completely to the compound NADPH and carbon dioxide. In the presence of the extremozyme hydrogenase, hydrogen is released. This extremozyme produced by the bacterium *Pyrococcus furiosus* is also one of only two such enzymes known to accept electrons from NADPH to produce hydrogen.

The downside to the renewed interest in hydrogen is that widespread use of the energy-rich gas will raise safety issues that must be addressed. For example, if an aerospace worker lights a match in air with a concentration of more than 4% hydrogen, an explosion could result. If the United States decides to build a national infrastructure devoted to hydrogen as an energy source, reliable methods for detecting hydrogen in the air will be needed.

Robert Lauf of the Metals and Ceramics Division and Barbara Hoffheins of the Instrumentation and Controls Division have developed a low-cost, solid-state hydrogen sensor that can be easily mass produced by conventional manufacturing processes. The patented sensor, which has been licensed to DCH Technology in Valencia, California, is selective for hydrogen and is relatively insensitive to other common gases. The sensor measures the change in the electrical resistance of palladium as it absorbs hydrogen. The sensor could be used to detect hydrogen leaking from a hydrogen-fueled car or from hydrogen filling stations. It could be used at a battery-charging station for electric buses and cars, to detect a potentially dangerous buildup of hydrogen in the air when lead-acid batteries are overcharged and ventilation around the charger is inadequate.

Hydrogen is a promising fuel for carbon management, but its long-term acceptance by both consumers and regulators will depend on their ~~confidence that it can~~ be generated, stored, and used safely.

Bob Lauf and Barbara Hoffheins show the hydrogen sensor they developed.

New Hydrogen-Producing Reaction Could Lead to Micropower Sources

A new method for the sustained production of hydrogen has been discovered by researchers in ORNL's Chemical Technology Division (CTD). The discovery could lead to the development of palm-sized fuel cells that cost only a few cents apiece. The fuel cells could be used to power compact environmental sensors for the U.S. military, as well as cell phones, cameras, and portable audio and video equipment.

Soldiers could easily carry these fuel cells on the battlefield and recharge them by adding iron powder and vinegar and then shaking them. These cells could serve as micropower sources for sensors that can detect the presence of hazardous gases and emissions from nearby chemical and biological warfare weapons.

In the summer of 1998, CTD's Jonathan Woodward and researchers John Getty and Mark Orr tried a new way to make hydrogen from sugar, which involved the deposition of the metal platinum on a glucose-digesting enzyme. The experiment worked.

"After several different experiments," Woodward says, "we then observed that mixing iron powder with water also produced hydrogen at ambient temperatures, but the production was not sustained. Then we discovered that if we add gluconic acid as well as iron powder to the water, we obtained sustained hydrogen production under certain conditions."

Gluconic acid is an organic acid consisting of carbon, hydrogen, and oxygen ($C_6H_{11}O_7$) that is produced from glucose sugar, an abundant and renewable carbon source. Woodward noted that the sustained hydrogen-production reaction works well under three conditions: a temperature of 80°C, neutral pH, and the absence of oxygen.

Although the mechanism of the reaction is not fully understood, Woodward says that iron may be serving as the active catalyst for the production of hydrogen gas from water under anaerobic conditions. During the reaction, the metal iron (Fe) is converted to an iron-oxide compound called magnetite (Fe_3O_4). The magnetite would then be reduced back to iron in the oxygen-free atmosphere containing gluconic acid. Thus, the iron catalyst would be regenerated from the magnetite, enabling the continuing production of hydrogen.

"We found that after 100 hours of the experiment, we lost little metal and got more hydrogen than we expected," Woodward says. "We generated more hydrogen than the typical metal displacement reaction where iron is normally consumed. We believe that some of the hydrogen is produced by the reaction of the iron metal with the organic acid, but more experiments must be done to prove that.

"Hydrogen produced this way could be used as a power source for fuel cells that power sensors and cameras requiring very low current in the micro- to milliampere range. Larger-scale applications may also be possible."

Fuel Cells: Clean Power Source for Homes and Cars?

Through materials and technology developments, ORNL researchers are finding ways to improve fuel cells for powering buildings and cars.

Fuel sells if it is cheap, clean, and carbon-free. That may become a maxim of this millennium and an argument in favor of fuel cells. These devices may be used to produce electricity in homes and cars using oxygen from air and hydrogen from natural gas. Their chief waste product is harmless water vapor.

At ORNL, Tim Armstrong of the Metals and Ceramics (M&C) Division is leading the effort to develop solid-oxide fuel cells and components using advanced materials. This type of fuel cell is flexible in the fuels it can use; for example, it can use natural gas in a process to convert chemical energy to electrical energy. How is the system made and how does it work?

Hydrogen from natural gas is passed over an anode (negative electrode) made of nickel and yttria-stabilized zirconia (YSZ). The hydrogen atoms break apart into positively charged ions and electrons. The electrons travel through an external circuit to a cathode (positive electrode) made of the rare-earth oxide lanthanum strontium manganate ($LaSrMnO_3$).

Oxygen from the air or carbon monoxide is collected at the cathode where the gas accepts electrons to form negatively charged oxygen ions, which are passed through a YSZ electrolyte separating the anode and cathode. The electrolyte is heated to 600 to 1000°C by an electric heater to start the electrochemical reaction. On arrival at the anode, each oxygen ion is discharged by reacting with two hydrogen ions to form water. The heat from the electrochemical reaction maintains the cell temperature, allowing the electric heater to be turned off.

Iron aluminide alloys developed in the M&C Division by C. T. Liu, Claudette McKamey, and Vinod Sikka are candidates for solid-oxide fuel cell containment vessels. ORNL Fossil Fuel Energy Program Manager Rod Judkins and Sikka worked with Siemens Westinghouse to confirm the efficacy of iron aluminide in the fuel cell application. Compared with the stainless steels currently used for containment, the iron aluminide alloys are stronger and more resistant to the simultaneous oxidizing and reducing conditions to which containment vessels are exposed. Thus, iron aluminide containments are expected to be more reliable and to last much longer. Mike Santella of the M&C Division is working with industrial partners to develop the technology for fabricating iron aluminide containment vessels.

"This solid-oxide fuel cell can also provide high-quality waste heat that can be used to warm the home or provide refrigeration and air conditioning," Armstrong says. "Its only emissions are steam, trace amounts of nitrogen oxides and sulfur oxides, and a small amount of carbon dioxide."

For powering many homes at once while eliminating carbon dioxide emissions, the M&C group has designed a power plant using a solid-oxide fuel cell and gas turbine and incorporating ORNL's novel activated-carbon and membrane-separation technologies and heat-exchange technologies, such as the carbon foam that rapidly transports heat. The most efficient gas turbines available today produce electricity using 60% of the energy in the fuel gas. Siemens-Westinghouse has designed a solid-oxide fuel cell that is 60% efficient and a hybrid fuel cell–microturbine plant in which waste heat from the fuel cell is used to drive the microturbine. This combined-cycle power plant is 70% efficient.

"Based on the results of our computer model, the ORNL design for a similar combined-cycle power plant is 80% efficient," Armstrong says. "The reason is that we combine our efficient heat-exchange technologies with membrane technologies for separating hydrogen and carbon monoxide from natural gas for use in the fuel cell." In addition, the power plant allows carbon sequestration because ORNL's carbon fiber composite molecular sieve technology (see article on p. 9) can capture the carbon dioxide leaving the fuel cell as a waste product. This gas can then be collected and used for enhanced oil recovery or sequestered in geological formations.

Cars powered by electricity from hydrogen fuel cells are being designed because they will eliminate discharges of carbon dioxide, nitrogen oxides, and particulate emissions. Such a "zero emissions" vehicle is a goal of the Partnership for a New Generation of Vehicles, which involves the automobile industry and the Department of Energy.

A proton exchange membrane (PEM) fuel cell is the technology of choice in the automobile industry for future electric cars because of its low-temperature operation and rapid startup. PEM fuel cells have been plagued with problems, but recent developments at ORNL may make this technology more feasible and affordable.

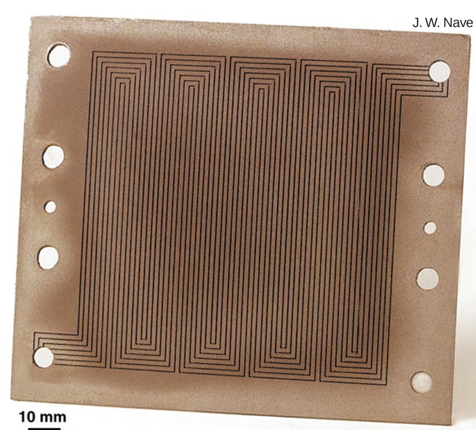
The problem with using today's PEM fuel cells to power cars is that their bipolar plates (positive and negative electrodes), which are made of machined graphite, are too heavy, too brittle, and too costly for use in automobiles. ORNL's solution is to make bipolar plates from a carbon-fiber composite, which is lighter, tougher, and cheaper than machined graphite.

Ted Besmann, James Klett, Tim Burchell, and John J. Henry, Jr., all of the M&C Division, have developed a method for making composite plates that includes chemical vapor infiltration. Basically, carbon fibers are molded to make an electrode, and methane is flowed over the plate at high temperatures to deposit carbon that seals its surface pores. Because a fuel cell is a stack of bipolar plates with electrolytes between, the porous plate surfaces must be sealed to prevent leakage of hydrogen and oxygen from one cell to another—a showstopper for fuel cells.

ORNL researchers have shown that carbon-fiber composite plates not only can be made to perform as well as graphite plates but also are half as heavy, may cost one-fifth as much, are more conductive and corrosion resistant, and are easier to manufacture.

Thanks to ORNL's progress in this area, the fuel-cell car may be just around the bend. ornl

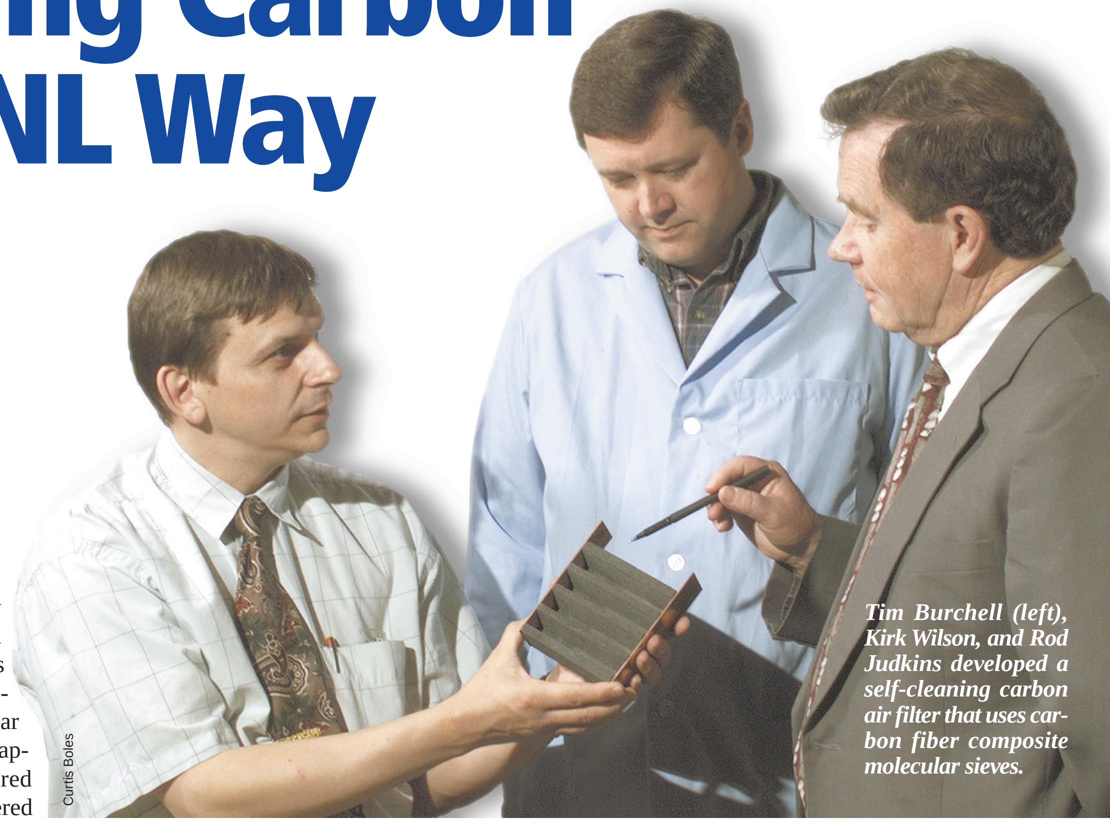
J. W. Nave



ORNL's carbon-composite bipolar plate may be used for fuel cells in electric cars.

Capturing Carbon the ORNL Way

ORNL has developed a new technique for efficiently capturing carbon dioxide from waste gas streams from fossil fuel combustion. The separation technique has stirred industrial interest.


Curtis Boles

Tim Burchell (left), Kirk Wilson, and Rod Judkins developed a self-cleaning carbon air filter that uses carbon fiber composite molecular sieves.

Carbon composites may be the key to capturing carbon dioxide from fossil fuel combustion. ORNL researchers have developed a promising new technology called carbon fiber composite molecular sieves (CFCMS) that can be designed to capture carbon dioxide emitted from coal-fired power plants and gas turbines. The recovered carbon gas could be collected in a vessel for transport to a carbon sequestration site. It could then be injected into an underground coal bed, depleted oil reservoir, or the ocean.

Tim Burchell, Charlie Weaver, and Bill Chilcoat, all of ORNL's Metals and Ceramics Division, developed CFCMS technology in collaboration with researchers at the University of Kentucky. The work was grounded in ORNL's previous experience of developing carbon-bonded, carbon-fiber insulation for thermoelectric cells in space probes.

"Our technology has several advantages over conventional granular activated-carbon beds for removing carbon dioxide from gas streams," says ORNL Fossil Energy Program Manager Rod Judkins. "It not only adsorbs more carbon but it also takes it up 5 to 10 times faster. And 2 to 10 times less energy is required to recover the adsorbed carbon dioxide and regenerate the filter so it can be used again."

Because the CFCMS filter is electrically conductive, carbon can be removed from the saturated sieve by running an electrical current through it at low voltage. "There are several possible explanations of how electrical desorption works," Judkins says. "Maybe it's a surface heating effect." In a conventional activated-carbon bed, the carbon is recovered by a more energy-intensive process, such as heating or depressurizing the bed.

ORNL researchers can make monolithic CFCMS structures in various shapes, such as a rectangular slab or a cylinder. "The structure is very porous and very low in density," Judkins says. "It's 80% void space."

The secret to adsorbing a specific gas is to create a structure with numerous pores of the right size—width and volume—to trap the gas molecules, which are naturally attracted to the carbon. Burchell, Judkins, and their colleagues used chopped-up carbon fibers made from petroleum pitch, bonded them together with phenolic resin, and then "activated" the structure to create micropores as adsorption sites for gas molecules.

"We activate the structure by flowing in steam, oxygen, or carbon dioxide at 850°C to gasify its carbon and carry much of it off," Judkins says. "We control this process to get a large enough surface area and pore volume and width to optimize the capture of carbon dioxide."

The ORNL technology has attracted the interest of many large industrial companies looking for better ways to remove or recover carbon dioxide and other gases from process streams. An international consortium of oil companies and a fuel cell manufacturer want to use the technology to remove carbon dioxide from natural gas. Another fuel cell manufacturer is interested in removing sulfur compounds from natural gas to make it a better hydrogen source. Sulfur compounds are added as odorants so people can smell leaking natural gas and take precautions. The international consortium plans to use the ORNL technology to remove carbon dioxide from the exhaust stream of a gas turbine to mitigate its emissions.

"We are negotiating with a major carbon company to license the CFCMS technology," Judkins says.

Similar technology was used in Burchell, Judkins, and Kirk Wilson's development of a self-cleaning carbon air filter that received an R&D 100 Award in 1999. When this filter becomes dirty, it doesn't have to be replaced like filters containing loose, granular, activated carbon. Instead, it uses an automatic reverse-air-cleaning cycle in which an electric current is passed through the filter, releasing the adsorbed contaminants into a purge air stream that exhausts harmful pollutants outdoors.

The self-cleaning carbon air filter could be used to reduce cooking odors in kitchens, filter formaldehyde and other airborne toxic gases from home and office air, and preserve air quality aboard airplanes and submarines. The British Ministry of Defense and the U.S. Army are testing the ORNL technology for removing chemical agents from air. It is likely that ORNL's gas capture technology will continue to capture industrial and military interest. ornl

Boosting Bioenergy and Carbon Storage in Green Plants

Genetic tools will be used to maximize carbon production in green plants for energy production and carbon sequestration.

Some ORNL researchers don't want some green plants to be carbon copies of their parents. They hope to genetically manipulate these plants to fix more carbon from the air by photosynthesis so they grow faster and hold more carbon in their stems, leaves, and roots. The goal is to grow trees and grasses that can produce more fuel and store more carbon in the soil.

These researchers work for DOE's Bioenergy Feedstock Development Program, which is managed at ORNL. "Our program manages tree and grass crops in experimental systems to maximize carbon production for energy and carbon sequestration," says Lynn Wright, program co-manager. "Our research focuses on developing, cultivating, and harvesting fast-growing plants for energy instead of using fossil fuels. We are trying to increase the production of carbon in hybrid poplar trees and switchgrass aboveground to improve energy production. We also want to use these plants to conserve or add carbon belowground for sequestration."

In the early days of the program, researchers tried to optimize the aboveground growth of plants. They developed fast-growing varieties and hybrids that grew rapidly and used inputs like water and fertilizer efficiently. More recently, genetic manipulation has moved to the front burner. In manipulating plants such as hybrid poplar trees, plant geneticists talk about allocating the carbon between the aboveground stems and leaves and the belowground roots of the plant. They also talk about partitioning (dividing) it among three types of plant cell wall components—cellulose, hemicellulose, and lignin.

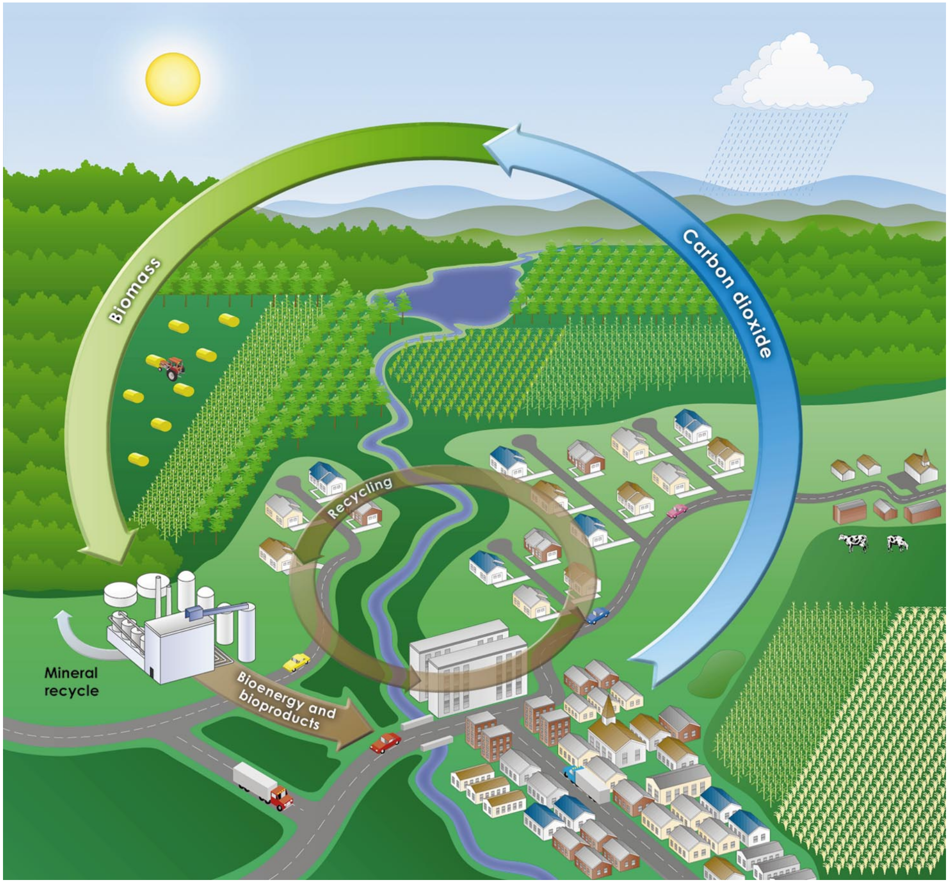
What researchers would like to do is create a plant that is very high in cellulose aboveground, increasing its energy conversion potential. Cellulose is a polysaccharide containing chains of 6-carbon sugars. Enzymes can split cellulose into individual sugar molecules, which can then be converted by microorganisms into ethanol. When used as a fuel, ethanol is cleaner than gasoline. Because the carbon in plants is taken from the air during photosynthesis, burning ethanol from cellulose contributes very little net carbon dioxide to the atmosphere.

This "designer" plant would also be high in lignin in the roots. Lignin consists of carbon-containing phenolics that are amorphous in structure. It resists digestion by enzymes, making it less susceptible to microbial degradation and more effective at sequestering carbon in the soil.

"To customize a plant species genetically to boost its carbon content, we must understand the fundamental biological processes that control carbon allocation and partitioning," says Jerry Tuskan, an ORNL plant geneticist. "We hope to make progress in this area through our wood chemistry and genetic studies using an experimental population of hybrid poplar trees."

Tuskan, Stan Wullschleger, Tim Tschaplinski, and Lee Gunter, all of ORNL's Environmental Sciences Division (ESD), and Brian Davison of the Chemical Technology Division are involved in this study, which is partly funded by the Laboratory Directed Research and Development Program at ORNL. Collaborating in this study are researchers from DOE's National Renewable Energy Laboratory (NREL).

In this population, explains Tuskan, each tree has the same grandparents but its genetic characteristics are unique. "It's like shuffling a deck of cards for each tree," he says. "Each tree



Biomass in forests and fields takes up carbon dioxide. It can be converted to low-carbon fuels, construction wood, and other products. Illustration by Brett Hopwood.

will have a different arrangement of diamonds, clubs, hearts, and spades. The progeny will have characteristics different from those of their grandparents and each other."

At the end of August 2000, the experimental planting was a year old. Each tree will be lifted, roots and all, and ORNL and NREL researchers will measure the trees to determine their energy content and the relative amounts of cellulose and lignin aboveground and belowground. The trees that contain the most carbon in their trunks or roots will be further analyzed biochemically by the project's plant physiologists to identify specific compounds in the cell wall.

"Using genetic techniques, we will identify genetic markers, or the DNA sequences flanking the genes, that are responsible for desirable cell wall traits, such as high carbon content in lignin in the roots," Tuskan says. "These markers will allow us to identify regulatory regions that control carbon allocation and other genes that control partitioning either aboveground or belowground. We will provide our findings to the energy and forest products industry to help them customize crops to get a desired product."

Janet Cushman of ESD, who co-manages the DOE bioenergy feedstock program, says that switchgrass is also ideal for producing ethanol and sequestering carbon, largely because its roots can go 7 m (20 ft) deep. The same genetic manipulations proposed for tree crops can be applied to this perennial grass of North America. If concerns about increasing concentrations of carbon dioxide in the atmosphere lead to policies to promote carbon storage and encourage use of renewable energy, there will be even more incentives to switch from fossil fuels to biomass. ornl

Carolyn Krause

Hybrid poplar trees may be genetically modified to store more carbon in the soil.

Carolyn Krause

Switchgrass, a perennial grass that grows deep roots, can be converted to ethanol.

Land Use and Climate Change

Forests and the way we manage them provide significant opportunities to help control climate. A climate control effort that includes forests should account for both the release and absorption of carbon dioxide and reward only those activities that help slow the buildup of atmospheric carbon dioxide.

These are conclusions of "Land Use and Global Climate Change: Forests, Land Management, and the Kyoto Protocol," a report prepared for the Pew Center on Global Climate Change in June 2000. The authors are Bernhard Schlamadinger of Joanneum Research in Austria and Gregg Marland of ORNL's Environmental Sciences Division. Schlamadinger recently completed an 18-month postdoctoral fellowship at ORNL.

The Kyoto Protocol, negotiated in Japan in 1997, sets forth binding targets for emissions of greenhouse gases from developed countries. Kyoto Protocol commitments include land use, land-use change, and forestry, but, according to Schlamadinger and Marland, lack the effective implementation details required to realize the potential benefits from land management. Land management can retard the buildup of carbon dioxide by (1) slowing the loss of carbon from plants and soils through reduced rates of deforestation and (2) encouraging the return of carbon from the atmosphere to the terrestrial biosphere by planting trees or improving management of forests or agricultural soils.

The Kyoto Protocol provides that planting new forests and clearing forested land will be accounted for in determining compliance with national commitments to reduce greenhouse gas emissions. Schlamadinger and Marland raise the question whether it is possible under the Kyoto Protocol to protect existing forests, plant forests where there are not now forests, and protect or increase the carbon in agricultural soils.

The report notes that the Kyoto Protocol recognizes that greenhouse gas emissions will be reduced by the use of sustainably produced biomass products. "Biomass fuels," states the report, "can be used in place of fossil fuels, and construction wood can be used in place of other, often more energy-intensive, materials such as steel or concrete."

Building up biomass on the earth offers several benefits in addition to slowing the buildup of carbon dioxide in the atmosphere. According to the report, "Increasing carbon in the terrestrial biosphere appears to be a low-cost way to help mitigate the increasing concentration of atmospheric carbon dioxide while providing ancillary benefits in terms of protecting forests, biodiversity, water quality, and soil fertility. Many land management activities are attractive because they can be pursued now, without technological innovation. Increasing carbon storage cannot by itself solve the problem of increasing atmospheric carbon dioxide, but can help, especially in the short term."

Plunging into Carbon Sequestration Research

This strip mine site is a source of acid mine drainage (note the amber color) to the environment.

Reclamation in progress is turning this degraded land into a site that could reduce soil erosion and sequester more carbon.

ORNL is conducting studies on sequestering carbon in geological formations and biologically active ponds and on improving degraded lands to enhance carbon storage.

Sometime in 2001, probably at a one-hectare site on a depleted oil reservoir in Texas or California, a slug of carbon dioxide (CO_2) will be injected some 600 m (2000 ft) into the ground. But it won't be pure CO_2. It may be tagged with helium, argon, and other noble-gas tracers introduced into the injected stream at various known concentrations in a regular pattern, providing a "chemical wave" signature. It may also contain intentionally introduced isotopes of carbon, hydrogen, nitrogen, and oxygen whose ratios could shed light on the effects of the injected CO_2 on the site's geochemistry and on the ability of the underground formation to trap the CO_2.

Gerry Moline, a hydrologist in ORNL's Environmental Sciences Division (ESD) who developed the concept of tagging CO_2 with a chemical wave, and David Cole, a geochemist in ORNL's Chemical and Analytical Sciences Division, will use noble gas and isotopic tracers in injected CO_2 to help determine whether and how long the site will securely store, or sequester, the CO_2. The tagged CO_2 will be introduced at injection wells and sampled as it migrates through return wells, a hundred or so meters away. Moline will measure the chemical wave signal in the sampled gas using a portable gas chromatograph. Cole will measure isotope ratios in gas and fluid samples using mass spectrometry.

These measurements should help answer these questions about injected CO_2: Where did it go? How fast does it move? How long will it stay? Could it leak back into the atmosphere, thereby contributing to greenhouse gas levels?

The ORNL results should also help address these questions about the selected site for CO_2 injection: Is this a suitable or unsuitable site for carbon sequestration? What are the optimal depths, temperatures, and pressures for carbon sequestration in this reservoir? How much injected CO_2 is dissolved in underground fluid, trapped in pores, or adsorbed on rock? How much CO_2 can be stored at this site?

Moline says that the noble-gas tracers should provide useful information because they are inert, so they do not interact with subsurface rock and fluids in the same way as the isotopic tracers do. She will be looking for an attenuation of the chemical wave signature when she samples for CO_2 and noble gases. A diminished signal for CO_2 relative to the noble gases will indicate how much of the injected CO_2 has been "lost" during transport—that is, sequestered.

Cole says that analysis of the isotope tracers should help scientists better understand the interactions between the injected CO_2 and the site geochemistry. "When a bubble of carbon gas is injected into the formation," he says, "it may displace the water there. Some of the CO_2 will be dissolved in the fluid, and the CO_2-bearing fluid will interact with the underground rock. Our tracer studies may show whether minerals are precipitated from the CO_2-bearing fluid to the rock, whether minerals in the rock are dissolved in the fluid, and whether the fluid affects the permeability or porosity of the rock in the formation."

These ORNL scientists are participating in the geological sequestration (GEO-SEQ) project sponsored by DOE's Office of Fossil Energy. They are helping to study the effects of injecting CO_2 into depleted oil reservoirs, brine formations, and coal beds. Participants in this three-year project on geologic sequestration of CO_2 include Lawrence Berkeley, Lawrence Livermore, and Oak Ridge national laboratories, in cooperation with Chevron, Texaco, Pan Canadian Resources, Shell CO_2 Co., BP-Amoco, Statoil, the Alberta Research Council Consortium, Stanford University, and the Texas Bureau of Economic Geology. One goal of the work is to determine whether CO_2 injection can result in economic benefits—enhanced oil recovery and production of methane from coal beds—as well as sequestration.

"In these studies, we will be studying whether the injection of CO_2 changes the formation," Cole says. "For example, CO_2 interacting with brine, which is mineral-rich saltwater, may lead to changes in the fluid chemistry that could either increase or decrease the porosity-permeability characteristics of the saline aquifer, depending on its mineral composition."

ORNL's role in GEO-SEQ is to evaluate and demonstrate monitoring technologies, with a goal of selecting ones that are safe and that work best in verifying that carbon has been sequestered. GEO-SEQ's other tasks are to (1) develop methods to sequester CO_2 in enhanced oil recovery, sites, depleted gas reservoirs, and saline aquifers; (2) enhance and compare computer simulation models for predicting, assessing, and optimizing geologic sequestration in brine, oil, gas, and coal-bed methane formations; and (3) improve the methodology and information available to assess the sequestration capacity of different sites.

Another approach to slowing the buildup of greenhouse gases in the atmosphere is to minimize losses of carbon and nitrogen from disturbed lands. ORNL and Pacific Northwest National Laboratory have joined Ohio State University and Virginia Polytechnic Institute and State University in a two-year project funded by DOE's Office of Fossil Energy to find ways to improve the natural carbon uptake of lands disturbed by mining, highway construction, or poor management practices. For this purpose, they are studying the use of soil enhancers made from the wastes of coal-fired power plants and sewage treatment facilities. The research is being done at sites in Kentucky, Ohio, and West Virginia. Tony Palumbo, John McCarthy, Gary Jacobs, Jizhong Zhou, Jeff Amthor, and Patrick Mulholland, all of ESD, will study the impact on soil carbon of reclaiming disturbed lands by planting them with grasses and trees (e.g., pines and poplars) and fertilizing them with coal fly ash and sewage waste.

"Because adding fly ash to clay soil makes it friendlier for plant growth, we hope that more carbon will be built up in the soil," Palumbo says. "We will measure soil organic carbon before and after each site is planted. We may plant grass first because it will remove boron and other toxins from the fly ash so they don't adversely affect tree growth. On the other hand, we may find that toxic fly-ash metals will get tied up with organic compounds in the sewage sludge, making them less of a threat to the trees."

If carbon tax credits are granted in the United States, landowners will have more of an economic incentive to exercise stewardship over lands they must reclaim to comply with state and federal laws. They will want their reclaimed sites to receive credit for sequestering carbon.

"We will also measure nitrogen releases from the soil to determine whether ammonia in sewage sludge is being converted to nitrous oxide, a greenhouse gas," Palumbo says. "We will study ways to manipulate the soil, perhaps by wetting it and introducing specific microorganisms, to minimize nitrous oxide emissions."

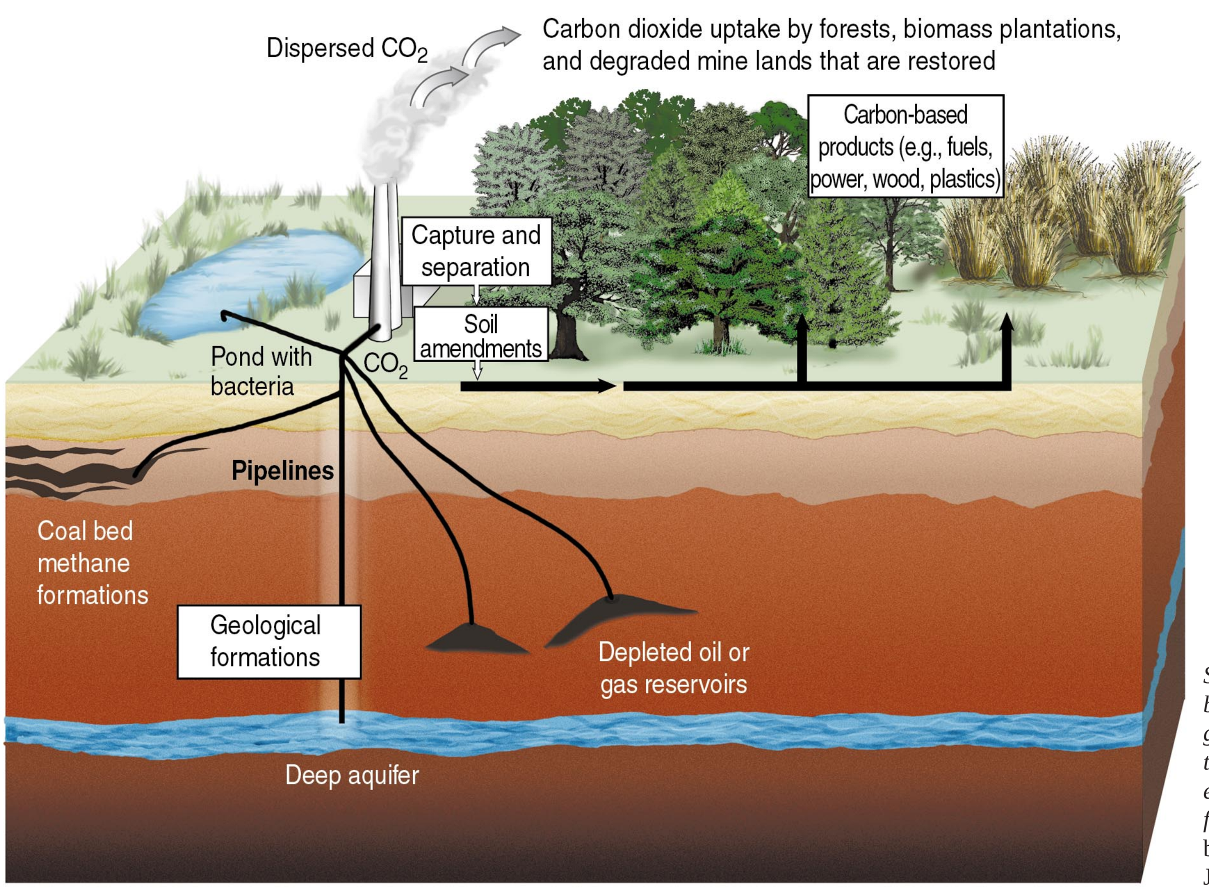
The project's findings as to what works and what doesn't in reclaiming land to increase carbon storage will be transferred to mine reclamation firms and other interested industrial companies. This effort is part of the activities of DOE's Center for Research on Enhancing Carbon Sequestration in Terrestrial Ecosystems (CSiTE), which is co-managed by Jacobs.

In a project funded by DOE's Office of Fossil Energy, Tommy Phelps, an ESD microbiologist, proposes to build a football-field-sized pond 30 m (100 ft) deep next to a coal-fired power plant. The object of his research is to see if carbon captured from the coal plant and injected into the pond will be successfully sequestered. To sequester carbon in the pond, Phelps plans to introduce the TOR-39 bacteria that he discovered in 1993 in Virginia. The pond will also receive iron leached from coal fly-ash waste.

"These bacteria feed on carbon and respire iron, converting it to magnetite," Phelps says. "They also do not need oxygen or light, so they thrive anywhere in the pond."

Experiments at ESD show that TOR-39 bacteria in water can also make micron-sized particles of iron carbonate (siderite) from iron hydroxide and carbon dioxide introduced into the test tube. "We believe that these bacteria can combine carbon dioxide from the coal plant with iron in the water to produce iron carbonate," Phelps says. "The iron carbonate will sink into the pond sediments, sequestering the carbon."

ORNL researchers are sinking their talents into interesting approaches to carbon sequestration in the hope of delaying climate change. ornl



Schematic showing both terrestrial and geological sequestration of carbon dioxide emissions from a coal-fired plant. Rendering by LeJean Hardin and Jamie Payne.

Methane Hydrates: A Carbon Management Challenge

ORNL is conducting research on methane hydrates, a huge source of an energy-rich greenhouse gas.

An enormous natural gas resource locked in ice lies untapped in ocean sediments and the Arctic permafrost. If this resource could be harvested safely and economically by the United States, we could possibly enjoy long-term energy security. Known as methane hydrates, this resource also may have important implications for climate change. When released to the air, methane is a greenhouse gas that traps 20 times more heat than carbon dioxide (another greenhouse gas). When burned, methane releases up to 25% less carbon dioxide than the combustion of the same mass of coal and does not emit the nitrogen and sulfur oxides known to damage the environment.

Methane hydrates contain methane in a highly concentrated form. Hydrates are a type of ice in which water molecules form cages (clathrates) around properly sized guest molecules. Gas hydrates form when water and gas (e.g., methane, ethane, and propane) come together at the right temperatures and pressures.

Thanks to the recent passage of the authorization bill, *The Methane Hydrate Research and Development Act of 1999*, the Department of Energy's Office of Fossil Energy is planning a national research and development (R&D) program on methane hydrates. ORNL researchers are doing research in this area using internal funding from the Laboratory Directed R&D (LDRD) Program and are proposing projects for DOE funding.

"The driver of DOE's gas hydrates program is the need for a new, abundant source of relatively clean energy, yet concerns about climate change are being addressed, considering that methane is a greenhouse gas," says Lorie Langley, leader of ORNL's Natural Gas Infrastructure, Methane Hydrates, and Carbon Dioxide Sequestration programs. "Methane can be used as an inexpensive source of hydrogen, a carbon-free fuel that could help slow climate change, providing that methods are developed to sequester the carbon dioxide that results from hydrogen production."

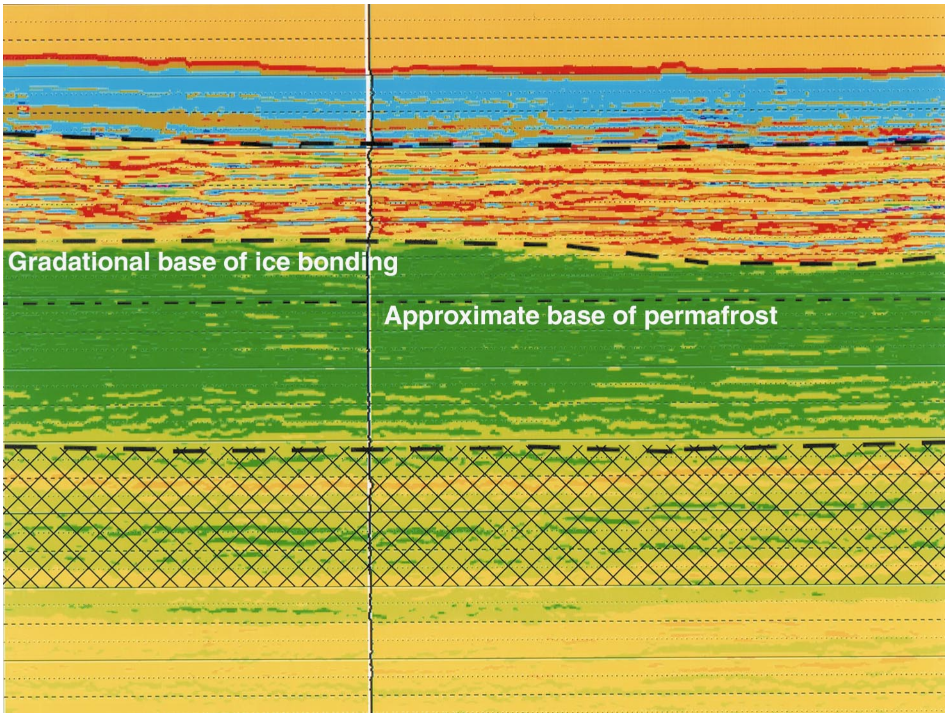
Among the questions the DOE program will address are these: How much natural gas actually is present in the world's methane hydrates? (Estimates range as high as 700,000 trillion cubic feet, many times the estimated total of worldwide conventional resources of natural gas and oil.) Are the hydrates stable enough to sequester carbon dioxide injected into them? Which production methods could safely harvest methane from the hydrates?

What are the risks of recovering methane from ocean hydrates? Could the release of methane make the sediments unstable enough to cause the collapse of seafloor foundations for conventional oil and gas drilling rigs? Could the melting, or dissociation, of methane hydrate ice lead to releases of large volumes of methane to the atmosphere, raising greenhouse gas levels and exacerbating global warming?

To help answer questions about the formation and dissociation of methane hydrates in ocean sediments, ORNL is operating a new seafloor process simulator (SPS), which is the largest, most highly instrumented pressure vessel in the world for methane hydrate studies. This 72-liter vessel, which is more than 30 times larger than the typical vessel used for methane hydrate research, is the product of an LDRD project led by Gary Jacobs and Tommy Phelps, both of ORNL's Environmental Sciences Division (ESD).

In the SPS, methane is bubbled into the seawater-containing vessel. The fluid is cooled to ~4°C and pressurized between 50 and 100 atmospheres to form methane hydrates. Methane hydrate samples are produced for analysis by instruments at numerous ports around the vessel, and their formation is captured by a video camera.

"Because of the size of our vessel, we have found a way to make methane hydrates easily and predictably," Phelps says. "Our large pressure vessel is also more suitable for research on the interactions between heterogeneous sediments and hydrates during their formation and dissociation. We can mimic actual heterogeneous conditions such as ocean water and sediments mixed with microorganisms, organic matter, carbonate particles, sand, silt, clay, and sulfides. Our data will be used to test and verify computer models of heterogeneous hydrate formation."



The dissociation of methane hydrates is a major concern for oil companies, Phelps says, noting that five oil firms have expressed interest in conducting research at SPS. “When the temperature rises or the pressure drops, one cubic foot of methane hydrate ice can release 160 cubic feet of gas,” he explains. “Forces from methane hydrate dissociation have been blamed for a damaging shift in a drilling rig’s foundation, causing a loss of $100 million. Oil and gas drilling companies are more interested in protecting their drilling equipment than harvesting the hydrates as an energy resource, at least for the next 10 years.”

At the SPS, hydrates could be grown in intact sediment cores filled with particles of controlled size to determine the effects of decomposing hydrates on sediment structure. Experiments at the SPS might also help determine which conditions could lead to a “burp” of methane from ocean hydrates that might enter the atmosphere and cause climate change. Some evidence suggests that a catastrophic release of frozen methane from the ocean 55 million years ago was responsible for an abrupt warming of the earth. As a result, ocean temperatures rose by 7 to 14 degrees over 1000 years, causing the die-off of more than half of some deep-sea species.

“Eventually, we could do dynamic production simulations at the SPS,” Phelps says. “We may test ideas for harvesting methane hydrates, such as depressurization, stimulating them with sound waves to melt them gently, or injecting solvents to extract the methane into gas recovery wells.”

What other research is being done at ORNL on methane hydrates? In 1999, Bill Doll, an ESD geophysicist, in collaboration with scientists from Kansas and Canada, used high-resolution seismic reflection methods developed for solving environmental problems to obtain very sharp images of hydrate-bearing zones 1000 m deep and of an overlying permafrost zone. The work was conducted in Canada’s MacKenzie Delta, along the Arctic Ocean.

“We are developing tools to precisely locate methane hydrate layers, assess whether the hydrate is distributed uniformly or in pockets within the sediments, and ultimately determine how much methane is there,” Doll says. “Our high-resolution measurements have impressed oil exploration companies.”

Libby West, who is in charge of day-to-day operations of the seafloor process simulator, and David Peters prepare the pressure vessel for new methane hydrate production experiments. The device, which was designed by Jack Heck, an engineer at the Oak Ridge Y-12 Plant, is operated at 4°C in the cold room in the background.

This line of geophones on the Arctic snow receives sound waves produced by a vibrating truck (inset) and reflected back from boundaries marking a change in the type of sediment or rock or in the material filling rock pores. The pattern of velocity differences (see figure on p. 14) provides images of the sand and silt layers and the effects of permafrost (high velocities in the top 400 m) and the underlying methane hydrate layer.

In a collaboration with the U.S. Geological Survey (USGS), David Reister and N. S. V. Rao, both of ORNL’s Computer Science and Mathematics Division, have been developing an improved method to determine how much methane is present in gas hydrates on the ocean floor. “Hydrates occupy pores of rocks,” Reister says. “To determine how much methane is present in the ocean, we must accurately estimate porosity and hydrate concentration in the pores for all ocean sediments.”

They are developing mathematical models based on rock physics to predict the locations and concentrations of methane hydrates in oceans and Arctic permafrost in the MacKenzie Delta. They use well log data obtained by oil and gas drilling companies, which provide a variety of measurements, including density, velocity, and electrical resistivity of sediments and the contents of their pores.

Peter T. Cummings, an ORNL-University of Tennessee (UT) Distinguished Scientist, Ariel A. Chialvo, an ORNL-UT collaborating scientist, and Mohammed Houssa of UT are using sophisticated models of methane, carbon dioxide, and water to better understand methane hydrates. “We are doing molecular simulations of methane hydrates at different temperatures, such as 270 K and 170 K,” says Cummings. “Methane doesn’t like water, so it pushes the surrounding water molecules away in clathrates, forcing them into a structure that is more stable than the normal arrangement of water molecules.”

The scientists’ goal is to predict the stability of methane hydrates in the real environment. Methane hydrates are trapped in pores of sandstone sediments that are contaminated with bacteria, algae, sand, and ions from saltwater. “We will eventually simulate the effects of impurities on the stability of methane hydrates,” Cummings says. “Our models may show that confinement in pores enhances methane hydrate stability.”

Claudia Rawn of the Metals and Ceramics Division, Bryan Chakoumakos of the Solid State Division, and Simon Marshall of ESD are interested in using neutrons to measure the effects of temperature and pressure changes on methane hydrate stability. “We measured the expansion of a unit cell of a USGS methane hydrate sample as temperature rises,” Rawn says. They hope to determine the effects of different gases on hydrate stability and compare the movements of water molecules and the strengths of hydrogen bonds in hydrates and normal ice.

The DOE National Methane Hydrate Program Plan has four research goals: resource characterization, production technology, global climate change, and safety and seafloor stability. “ORNL has the opportunity and capability to contribute to all of these goals,” says Langley. ornl

Adapting to Climate Change

ORNL researchers will compare the costs and benefits of investing in strategies to adapt to climate change and investing in ways to avoid it.

As a result of the drought in July and August 1999, part of the streambed of Bear Creek at Forest Park, Maryland, was dry.

The unusual weather in 1998 brought a flood to Clear Lake, California.

Since 1965 the scientific world has issued grim warnings, and now we're actually experiencing global warming. Evidence of this warming trend appears in reports issued by the widely recognized Intergovernmental Panel on Climate Change. The *U.S. National Assessment of Potential Consequences of Climate Variability and Change*, which was released for public review on June 12, 2000, discusses the likely impacts of climate change in the United States. This report notes that the warming has already had an impact in Alaska. Because the Arctic permafrost there is thawing, roads and airstrips are buckling, requiring constant and costly repairs. As the ice melts, Alaskans who hunt ice-dwelling seals for food are struggling to adjust to a more uncertain future.

Adapting to climate change has never been easy for humans, but now that there is a consensus that global warming is occurring, three ORNL researchers are focusing on adaptation to climate change and to increased variability in weather patterns.

"We are among the first to do a study that will compare the costs and benefits of investing in methods to adapt to climate change with investing in ways to avoid it," says Tom Wilbanks. Wilbanks, who leads the Global Change and Developing Country Programs in ORNL's Energy Division, is an ORNL corporate fellow and a contributor to the national assessment report.

"In the 1980s and 1990s, the emphasis had been on using increased energy efficiency and fuel switching to avoid climate change. But now it is accepted that the global average surface temperature could rise 2.5°F in 100 years even if the controls recommended at the Kyoto conference are put into place. So, adaptation is likely to be required regardless how successful we are with mitigation."

Wilbanks, Marilyn Brown, deputy director of ORNL's Energy Efficiency and Renewable Energy Program, and Russell Lee, director of the Energy Division's Center for Energy and Environmental Analysis, are developing an analytical approach to compare the costs and benefits of adaptation versus avoidance. This project is a three-year study funded internally by the Laboratory Directed Research and Development Program. They note that reducing greenhouse gas levels to avoid climate change has national and international impacts, whereas adaptation approaches and their payoffs may vary from region to region.

For example, large cities such as Chicago are likely to have hotter summers. One adaptation strategy might be to ensure that all homes in the city have air conditioning to prevent severe, even lethal, health risks to the elderly poor. (Some have died from stifling heat because they wouldn't open their windows for fear of break-ins by burglars.)

Coastal areas in the southeastern United States may face more hurricanes and tropical storms such as Hurricane Floyd, which caused such devastating flooding of hog farms in eastern North Carolina in 1999. Adaptation strategies to reduce the population's vulnerability to the effects of future hurricanes might include better management of river systems, protection of municipal water supplies, changes in building codes to make houses more flood-resistant, and improved management of animal wastes (which could be used as a relatively clean energy source).

Franklin, Virginia, was flooded in 1999 as a result of Hurricane Floyd, which caused 40 deaths.

If the ocean rises and the coast of Florida is in danger of being perpetually flooded, people may have to evacuate their houses permanently or replace them with flood-resistant houses that may be called for by building codes. "Better warning systems will be needed," Brown says. "Dikes may have to be built. But building a seawall can be a problem ecologically because some species inland thrive on the influx of saline water."

Farmers in the Midwest may face more and longer droughts. Adaptation strategies could include improved water resource management and planning, such as transporting water to the region from long distances or drilling deeper wells. Farmers could switch from one crop to a variety of crops, including newly developed drought-resistant grains. Another option would be to shift agricultural production to areas less prone to drought.

"The sugar maple industry is already moving from Maine to Canada," Wilbanks notes, "and commercial forestry is switching from hardwoods to pulpwoods."

"States may put political pressure on Washington to provide funding to their regions for adaptation," Lee says. "Regions may want to make investments in anticipation of relatively high-probability changes such as drying and lower-probability but higher-impact changes such as increases in the frequency and severity of storms."

Global warming could also have an impact on health and health-care facilities. For example, tropical diseases such as dengue fever might spread to northern climes. "The U.S. government may have to strengthen its public health care system to make sure physicians know how to treat diseases they are not used to seeing," Wilbanks says.

"A key challenge in our project," says Lee, "is to develop an analytical approach that assesses the costs and benefits of such varied adaptation options and increases our knowledge about how much they can help reduce impacts of climate change." ornl

The high growth rate of an Oak Ridge tree plantation exposed to carbon dioxide–enriched air declined significantly in the FACE experiment's second year.

High-Carbon Tree Growth Rate Falls

In 1998, an experimental 10-year-old sweetgum plantation in Oak Ridge National Laboratory's Environmental Research Park showed a 35% increase in growth over a nearby control stand of trees. More wood was produced in the test forest's tree trunks and more fine roots grew in the soil. The 15-m-tall sweetgum trees in the plantation's 25-m-diameter plots grew more because they were being exposed to air containing 50% more carbon dioxide (CO_2) than is in the atmosphere, thanks to free-air CO_2 enrichment (FACE) technology.

In 1999, the second year of the FACE experiment funded by the Department of Energy, some of the data surprised Richard Norby and his ORNL collaborators Stan Wullschleger, Carla Gunderson, Gerry O'Neill, Paul Hanson, Nelson Edwards, Tim Tschaplinski, Mac Post, Don Todd, and Tony King. The growth rate increase of the experimental plantation was reduced to 15% over that of the control stand. These results differ from those at a Duke University plantation dominated by loblolly pine trees with sweetgum trees in the understory. In the past three years, Duke researchers have observed a sustained growth rate increase of 25% per year in the trunks of high-CO_2 pine trees over that of control trees in a normal atmosphere.

"The dramatic growth response we saw in the first year in Oak Ridge disappeared in the second," says Norby, leader of the collaboration at the FACE facility and a researcher in ORNL's Environmental Sciences Division (ESD). "It could be year-to-year variability or a blip in the first year's data because of the sudden increase in CO_2 concentration. It could be a short-term response that is not indicative of the long-term response. Some of our data indicate that the growth increase was actually maintained but the extra carbon was not stored in the tree trunks."

Many of the physiological responses observed in the second year were similar to those in the first year of the FACE experiment. "We observed that photosynthesis remained enhanced," Norby says, referring to the process by which plants use the energy from sunlight to convert CO_2 and water into sugars needed for growth. "The leaf area stayed the same, and the trees conserved water just as well in the second year as the first."

In both years, ORNL scientists observed that the tree leaf pores (stomata), which allow CO_2 to enter and water vapor to escape, were not open as wide in plots receiving the extra CO_2. "Trees use more water on sunny days and less on overcast or rainy days," says Norby. "Because of high CO_2 in air, they can close their stomata a little on days of high water use and get the CO_2 they need while letting out less water. Thus, they draw less water from the ground, allowing soil moisture levels to be higher. Higher soil moisture could result in more activity by microbes that may make more nitrogen available to plants, fertilizing them and promoting their growth."

In addition to the tree growth rate difference in 1998 and 1999 at the FACE facility, ORNL scientists also observed that the leaves of the high-CO_2 trees became heavier in 1999, probably because more of the extra carbon was used to produce leaves than increase trunk growth. They also found that the nitrogen concentration of leaves and litter (fallen leaves on the forest floor) was lower, which could retard the cycling of nitrogen and carbon in the ecosystem.

ORNL researchers also observed an increase in production and mortality of fine roots in the second year, resulting in a change in the belowground allocation of carbon. "We saw an increase in carbon cycling because of high root turnover," Norby says. "The fine roots took in more carbon and then rapidly died, releasing more carbon to the soil than usual."

Because ORNL and Duke scientists are doing similar experiments on plantations of equivalent size and age in the same climate zone, they propose to collaborate on a study of nutrient cycling and carbon sequestration in these test forests if DOE funding is available. They will also try to help each other understand the variability in the results from the Oak Ridge and Duke experiments. ornl

Curtis Boles

Standing in a hydraulic lift, Rich Norby collects leaves in the high-carbon sweetgum forest for measurements of leaf mass, nitrogen concentrations, and rates of photosynthesis.

Reshaping the Bottle for Fusion Energy

The National Spherical Torus Experiment at Princeton, New Jersey, which was conceived by an ORNL physicist, may provide data that will help revolutionize the development of a clean, safe energy source. ORNL fusion researchers are helping the NSTX achieve its scientific mission.

The new centerpiece fusion experiment, called the National Spherical Torus Experiment (NSTX), at the Princeton Plasma Physics Laboratory (PPPL) in New Jersey might provide the answer to the question fusion researchers are asking in an age of rising oil prices and greenhouse-gas levels: Can practical fusion energy be developed at reduced cost?

The new experiment will not break world records for plasma temperature and the amount of carbon-free fusion energy produced, as did its predecessor at PPPL, the Tokamak Fusion Test Reactor (TFTR). (TFTR produced a world-record 10.7 megawatts of fusion power in 1994.) But the much smaller NSTX aims to provide new data for determining whether a subsequent, next-generation spherical torus device could produce three times the power of TFTR at one-third the cost.

NSTX passed its first plasma test in February 1999 and resumed operation in September 1999. This machine fulfilled an important milestone in December 1999, nine months ahead of schedule, by inducing an electric current of one million amperes in its plasma. The plasma is an extremely hot state of matter consisting of charged heavy hydrogen nuclei and free electrons swirling around at very high velocities. This level of current was a world record for a device of NSTX's design.

In January 2000, a series of experiments on NSTX validated an idea about how to produce and control its current. In one test, a current of 130,000 amps was generated in the plasma by injecting current directly into the chamber, thanks to a new technique developed in cooperation with the University of Washington at Seattle.

The spherical torus concept, which was proposed in 1985 by Martin Peng, an ORNL scientist now on assignment to PPPL, does not have a doughnut shape like TFTR. Instead it is shaped like a cored apple, a more compact design. It was generally believed in 1985 that a large hole in the doughnut was needed to accommodate large magnets to confine the plasma and keep it from crashing against the vessel wall, where it would lose its energy. But Peng showed theoretically that only small magnets would be needed to confine the spherical torus plasma. The spherical shape may overcome the problem that has been prevalent in tokamaks: turbulence—and other instabilities—that cause energy to leak from the hot plasma and undermine fusion reactions unless a very strong magnetic field is applied.

"In the spherical torus," Peng says, "the same plasma pressure can be maintained with a much lower magnetic field, significantly reducing the size and cost of the fusion device."

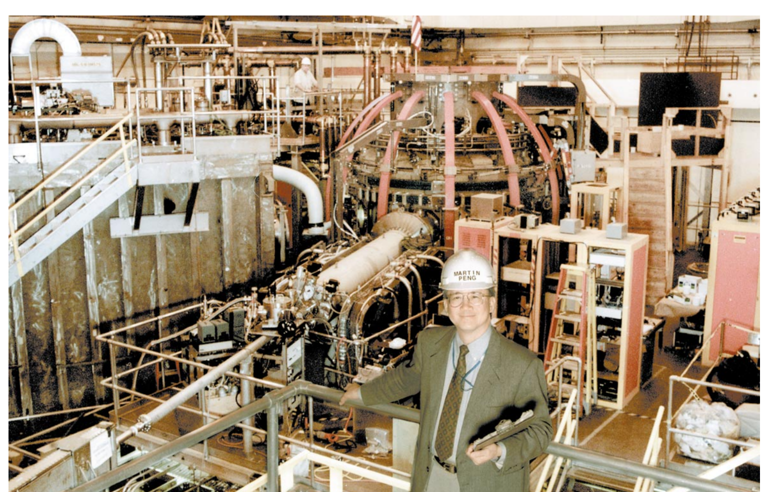
ORNL, Columbia University, and the University of Washington joined PPPL in building the NSTX. ORNL made major and key contributions in plasma design, including the plasma shape (Dennis Strickler), plasma edge (Peter Mioduszewski et al.), radiofrequency systems, and engineering design of the first wall components (Brad Nelson et al.). Some of these and other ORNL researchers have since joined the NSTX National Team of researchers from 15 national laboratories, universities, and industries and contributed much to the success of the initial experiments.

NSTX was built for $24 million two months ahead of schedule and within cost. "The equipment already available at PPPL was used effectively to reduce much of the construction cost of the NSTX facility," Peng says. "By using much smaller electromagnets to confine the plasma, we have also reduced power requirements, keeping operating costs down." Peng, who is the NSTX program director, co-directs the spherical torus facility with PPPL physicist Masa Ono, the NSTX project director.

In the next couple of years, the NSTX team will apply powerful radiofrequency waves and neutral particle beams to heat the plasma to very high temperatures (it is hoped to more than 20 million degrees Celsius). Both of these techniques have been areas of major strength for ORNL's Fusion Energy and Instrumentation and Control divisions. In a recent test, Dave Swain and Phil Ryan of ORNL, together with researchers from PPPL and General Atomics, coupled—for the first time—two of what will eventually be six radiofrequency devices to heat the plasma in a new way, using a technique similar to that employed in a kitchen microwave oven. John Wilgen and Greg Hanson built and installed a radio wave interferometer system, which has already produced high-quality measurements of plasma density near these new radiofrequency devices.

Another radiofrequency system from ORNL was brought to NSTX by Tim Bigelow to preionize the fuel and ensure reliable plasma operation. Also, ORNL's Rajesh Maingi was selected to serve as the deputy run coordinator, beginning in October 2000.

"We hope to achieve high plasma performance in NSTX," Peng says. "The scientific knowledge we will gain could pave the way for affordable development of economical fusion power in the future." ornl



ORNL researcher Martin Peng (shown here) conceived the National Spherical Torus Experiment now in operation at Princeton Plasma Physics Laboratory.

Building a Transistor That Doesn’t Forget

By depositing a barium titanate film on germanium, ORNL researchers are building a “smart” transistor that doesn’t lose data when the power is turned off.

It will use almost no power and take up almost no space. But it will store lots of data permanently, even when power is interrupted. It’s a smart transistor, and the first version was built and demonstrated recently at ORNL.

ORNL researchers Rodney McKee and Matt Chisholm and University of Tennessee researcher Fred Walker are building an even better prototype of a smart transistor by taking advantage of their recent materials breakthrough in depositing a high-quality, crystalline film of barium titanate on germanium. This powerful transistor is “smart” because barium titanate’s crystal structure gives it desirable ferroelectric properties, such that in certain regions of the film, positive and negative ions separate, setting up a semi-permanent internal field. As a result, the transistor “remembers” information even when the power is turned off.

“Smart transistors could be used in smart cards because they can cram in more information and need much less power to get information in and out,” McKee says. “Because one smart transistor can retain as much information as two silicon transistors and two power-hungry capacitors, a chip with germanium–barium titanate transistors will hold one million bytes of data compared with 256,000 bytes for a silicon chip of the same size. A smart, low-power chip could serve as the hard disk drive of a laptop computer and extend the lifetime of laptop batteries.”

The researchers built a field-effect transistor (FET) by depositing barium titanate as a dielectric film on a germanium substrate. Three electrodes were also placed on the germanium transistor.

FETs, which are used as common switching devices in modern electronic equipment, are normally made of silicon. When a conventional FET is turned on, electrons injected from a source electrode flow as a current through the silicon base and are collected at a drain electrode. To turn the transistor off, a gate electrode between the other electrodes applies an electrical voltage to a silicon dioxide dielectric film, causing it to “pinch off” the current by raising resistance in the silicon base. In this way, a transistor can function as an on-and-off switch or as a repository for a bit of information (e.g., an “on” transistor stores a 1 and an “off” transistor stores a 0).

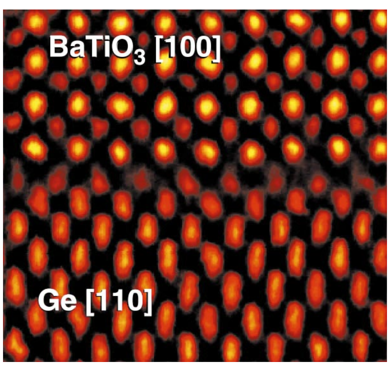
Depending on whether the direction of the field of the barium titanate dielectric film is up or down, it either pulls up or pushes away electrical charges in the germanium substrate, facilitating or resisting the flow of electrical current (and making an “on” or “off” transistor). Unlike the case with a silicon transistor, the direction of the field on the new transistor stays up or down all the time, so no external power is needed unless the field must be flipped. All information in the “on” and “off” transistors is retained despite loss of power.

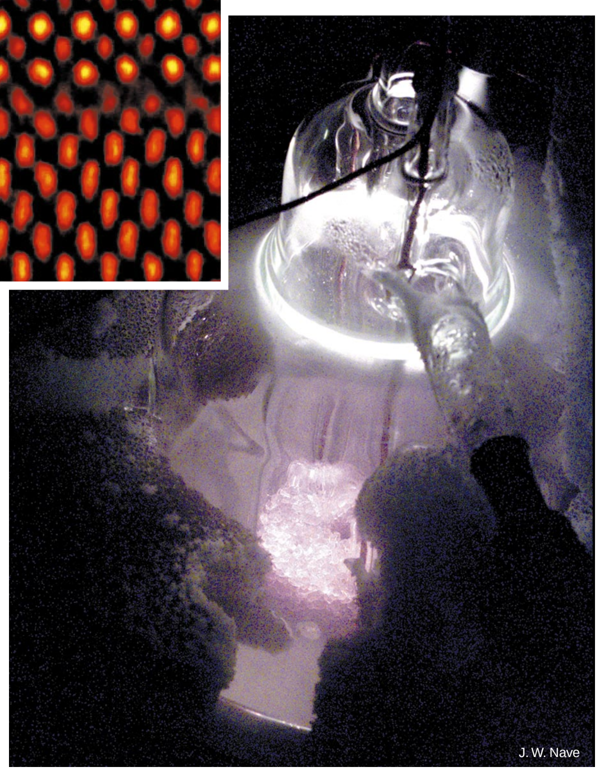
To deposit a barium titanate film on germanium, McKee and Walker used molecular beam epitaxy (MBE), a precisely controlled process for growing thin films under an ultrahigh vacuum. McKee knew that to make a smart transistor, the barium titanate had to be put into the right oxidation state on germanium. The correct state gives the film the insulating properties needed to make it work effectively. The only way to get the proper oxidation state is to use the most reactive form of oxygen—ozone. But the ozone must be made quickly and released at the proper rate.

To solve this problem, Alex Gabbard and Charles Malone, both of ORNL’s Metals and Ceramics Division, developed an ozone-dispensing device. In this device, a column of silica gel beads is placed in a small lab vessel cooled to cryogenic temperatures. An oxygen-ozone mixture from a standard ozone generator flows into the vessel and up through the gel. At the right temperature, ozone, unlike oxygen, adsorbs onto the gel surface. After 20 minutes, as ozone adsorption on the gel reaches full saturation, the translucent gel turns deep purple.

To retain the ozone, the gel is cooled to a constant temperature of –100°C using liquid nitrogen, which is at –192°C. The temperature of the gel, which affects the rate at which ozone is collected or exhausted, is controlled by the flow of nitrogen gas in a jacket surrounding the gel. A vacuum chamber enclosing this jacket and the silica gel chamber inside it isolates the jacket and inner column of gel from the extreme cold of liquid nitrogen. When the gel is saturated with ozone, the ozone is released at a controlled rate to the MBE equipment by flowing more nitrogen gas into the chamber to heat the gel slightly.

The winning combination of technologies perfected at ORNL to make a smart transistor is attracting the attention of the electronics industry. ornl





A translucent silica gel in a vessel turns deep purple as ozone adsorption on the gel reaches full saturation. Ozone is released at a controlled rate from this vessel to the MBE equipment used to deposit a barium titanate ($BaTiO_3$) film on a germanium (Ge) substrate. Inset: Z-contrast scanning transmission microscope image of the $BaTiO_3$-Ge interface structure that promotes the ferroelectric field effect needed for transistor action.

Nuclear physicists at ORNL have identified a novel form of radioactivity predicted by theory—simultaneous emission of two protons from a decaying atomic nucleus.

New Type of Radioactivity Discovered at ORNL

Based on preliminary experiments at ORNL's Holifield Radioactive Ion Beam Facility (HRIBF), nuclear physicists have identified a new form of radioactivity—simultaneous emission of two protons from the decaying nucleus of an atom. The discovery of the protons, which may have been initially bound together in an ephemeral helium-2 nucleus as they were emitted from a neon-18 nucleus, is significant. It will allow physicists to better understand the strong nuclear force that holds protons and neutrons together in the nucleus, countering the repulsive Coulomb force that drives protons apart because of their like charges. Information about the energy levels and other properties of the emitted pair of protons will help scientists determine how protons are bound together in the nucleus and how they interact with each other and with neutrons.

"The nucleus is sending us a message about how it is put together," says Jim Beene, director of HRIBF, the only two-accelerator facility for producing radioactive ion beams in the United States.

"This is the first time that two-proton emission has been observed," says Witold Nazarewicz, deputy director of science at HRIBF, a leading theorist in nuclear structure physics, and a professor of nuclear physics at the University of Tennessee at Knoxville (UTK). "Experimenters at the Holifield facility have already discovered five radionuclides that emit single protons through decay." Nazarewicz makes calculations to describe the decay of one-proton emitters and is developing theory to describe two-proton emitters.

Led by George Gomez del Campo of ORNL's Physics Division, a group of ORNL and UTK physicists discovered two-proton emission from the decay of neon-18 nuclei formed in an experiment at HRIBF. Fluorine-17 ions in an intense, difficult-to-produce HRIBF beam bombarded hydrogen atoms (protons) in a polypropylene target. For the most part, protons were scattered from the bombarded target. Once in a billion encounters, a fluorine ion captured a proton in the target, forming neon-18.

One particular quantum state of neon-18, with an energy just over 6 million electron volts (MeV), was found to decay about one time out of 3000 by emitting two protons simultaneously to form oxygen-16. The remaining 2999 times it decayed by emitting a single proton to form fluorine-17.

"We still have to answer a key question," Nazarewicz says. "Were the two protons leaving the neon-18 nucleus closely coupled together to form helium-2, or were they emitted almost independently in a direct three-body breakup into oxygen-16 and two protons, sometimes called 'democratic' decay? Even if the protons were emitted as a helium-2 nucleus, they would fly apart almost instantly. Our data favor the helium-2 emission, but a further experiment will be required to definitively distinguish between the two possibilities."

Two-proton (helium-2) decay was predicted in 1960 by the Russian theorist V. I. Goldanski. In the succeeding 40 years many efforts have been made to identify this elusive process definitively, but none have succeeded. These searches have invariably found sequential emission of single protons, through an intermediate state, instead of simultaneous two-proton emission (either as helium-2 or "democratically").

"For states of neon-18 up to 6.4 MeV," Nazarewicz says, "two protons can be emitted along with oxygen-16 only if they are emitted simultaneously. The sequential one-proton emission process is not possible, because no appropriate intermediate state exists."

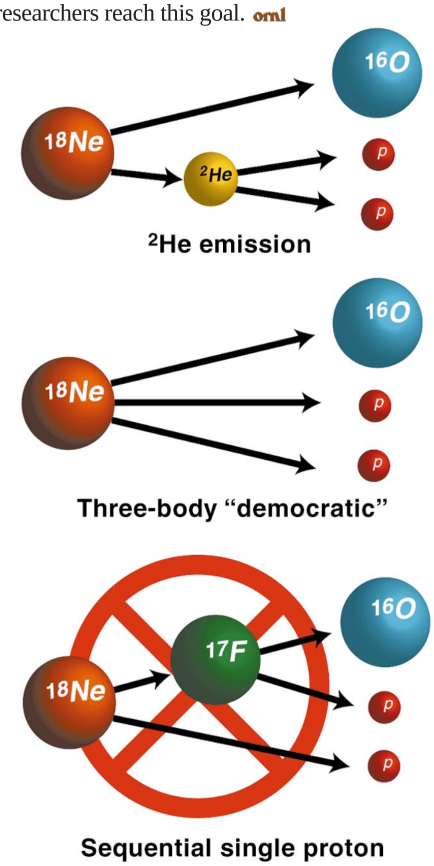
The identification of two-proton emissions is important, but it will be especially significant if the emitted protons come out bound together and then separate, providing information on how they are entangled in their original state inside the neon-18 nucleus.

At HRIBF five single-proton emitters have been discovered by researchers led by ORNL's Krzysztof Rykaczewski. The proton-rich nuclides are holmium-140 (^{140}Ho), holmium-141*m* (^{141m}Ho), thulium-145 (^{145}Tm), lutetium-150*m* (^{150m}Lu), and lutetium-151*m* (^{151m}Lu).

"Of the single-proton emitters, we found that thulium-145 has the shortest half-life yet measured for proton radioactivity," Rykaczewski says. "It decays in 3.5 microseconds to form another radionuclide, erbium-144."

Nuclear physicists at HRIBF also discovered that thulium-146 breaks down into erbium-145 (^{145}Er), releasing protons of different energies. In this case, Rykaczewski says, the observed proton fine structure offers a tool for studying neutron states in exotic nuclei.

Rykaczewski is looking forward this year to HRIBF's first radioactive ion beams for nuclear structure physics research—a proton-rich, nickel-56 beam, as well as neutron-rich beams. These beams will help nuclear physicists explore uncharted territory as these scientists create and discover some of the 3000 neutron-rich and proton-rich radioactive nuclides believed to exist when conditions are right. Recently commissioned digital signal processing electronics should help researchers reach this goal.



Future experiments at the HRIBF could determine whether the neon-18 nucleus can decay by forming an oxygen-16 nucleus and helium-2 nucleus that breaks apart instantly into two protons, or whether the neon-18 undergoes a direct, three-body breakup into oxygen-16 and two protons, sometimes called democratic decay.

Forecasting Epileptic Seizures

ORNL researchers have devised a computer-based method to warn an epileptic that a seizure might occur in the next 20 minutes, allowing time to get medical help.

Travis, 19, is eager to drive, swim, and climb mountains. His doctor, however, has warned him against undertaking these activities, because they could injure or kill him. Travis is one of almost 3 million epileptics in America. During a seizure, his muscles contract violently, and he briefly loses bladder control and consciousness, often embarrassing and sometimes hurting himself. His condition has not responded to drug therapy (which causes many epileptics to be drowsy, uncoordinated, and disoriented), so Travis risks sudden death from an accident, interrupted breathing, or heart failure. He avoids social situations and has trouble holding a job. His medical bills are huge.

ORNL researchers are developing new technology that could someday improve life for epileptics like Travis. Indeed, they have devised a computer-based method that will warn an epileptic that a seizure might occur in the next 20 minutes or so, giving him time to stop hazardous activities and get medical help to prevent or reduce the severity of the seizure.

This ORNL work could eventually lead to a portable, noninvasive monitor, allowing Travis more freedom. A wearable monitor is greatly preferable to a wall-powered electroencephalograph (EEG) that records brain activity from a “subdural” electrode under the skin of his skull. Instead, Travis might wear dime-sized electrodes—one to replace the earring he currently wears and the other attached by conductive glue to his scalp covered by his baseball cap. The electrodes would relay EEG signals to a pocket computer that looks for pattern changes in his brain waves and alerts him that a seizure is imminent.

The seizure alerting system—dubbed SeizAlert—detects the change from nonseizure brain waves to patterns that forecast a seizure. SeizAlert was developed by Lee Hively and Ned Clapp, Jr., both of ORNL’s Engineering Technology Division; Vladimir Protopopescu of the Computer Science and Mathematics Division; and Paul Gailey, an adjunct staff member in the Energy Division and a professor at Ohio University. Using DOE funding, the group is working with Nicolet Biomedical Inc., in Madison, Wisconsin, to develop a commercial version of the system under a cooperative research and development agreement.

SeizAlert is a nonlinear technology that converts continuous time-serial data to a distribution function for the baseline brain-wave activity. “We then compare nonseizure activity with pre-seizure and seizure activity,” Hively explains. “We measure the dissimilarity between the base case and test case distribution functions to detect pre-seizure conditions.”

SeizAlert is sensitive to many seizure types, according to Hively. Unlike other such systems, it has a filter that removes confounding signals such as eye blinks—something physicians have been trying to do for nearly a century. The ORNL approach obtains seizure forewarning from a single-channel scalp EEG, rather than relying on subdural EEG used by other monitoring methods. It has highly discriminating dissimilarity measures that detect small differences in a patient’s EEG data that are not recognizable by visually scanning typical EEG charts. SeizAlert provides a warning if these differences exceed a predetermined threshold.

To fine tune the algorithm and establish a database for reference, the ORNL researchers analyzed 19 sets of time-serial EEG data, each from a different patient who suffered an epileptic seizure. “We saw forewarnings of a seizure as much as three hours before the event, with a typical forewarning of 20 to 30 minutes,” Hively says. “Also, the algorithm correctly reported no warnings when tested with EEG data that contained no pre-seizure or seizure activity.”

Once perfected, the SeizAlert technology would help epileptics like Travis have lots more fun with much less fear. ornl

Ned Clapp, Jr., Vladimir Protopopescu, and Lee Hively developed the SeizAlert method to detect the onset of a brain seizure.

Curtis Boles

Lynne Parker's Cooperative Robots

For her pioneering contributions to the new field of cooperative robotics, ORNL's Lynne Parker received the prestigious Presidential Early Career Award for Scientists and Engineers.

In 1989, when Lynne E. Parker left ORNL's Center for Engineering Science Advanced Research (CESAR) to pursue a Ph.D. degree in computer science at the Artificial Intelligence (AI) Laboratory of the Massachusetts Institute of Technology (MIT), she planned to focus on a new field—cooperative robotics.

"CESAR had only one robot but a second one was under construction," she says, noting that she had been offered a job at CESAR after taking a University of Tennessee course in AI from Chuck Weisbin, then CESAR director. "Because I was thinking of returning to CESAR, I was interested in finding ways to get two robots to work together. At that time, people thought that getting one robot to perform a task was all you could hope for. But it became clear that the advantage of two or more robots working together on a complex task is redundancy and fault tolerance—one can take over for another if it fails."

The subject of her Ph.D. thesis was heterogeneous multirobot cooperation. Based on her MIT research and her work after she returned in 1994 to ORNL's Computer Science and Mathematics Division (where CESAR resides), she wrote the computer program ALLIANCE, which enables several robots to jointly perform a task. The achievement has made Parker a pioneer in the infant field of cooperative robotics.

On April 12, 2000, Lynne Parker received a Presidential Early Career Award for Scientists and Engineers and a DOE Office of Science Early Career Scientist Award. The second award was presented to her by Secretary of Energy Bill Richardson.

Because of her groundbreaking research, this East Tennessee native who graduated from Powell High School in Knox County and earned a B.S. degree in computer science from Tennessee Technological University, received a prestigious award on April 12, 2000, at the White House. Parker was one of five scientists from DOE's national laboratories and among 60 university and government researchers to be honored with a Presidential Early Career Award for Scientists and Engineers. Parker, who received her award from Neal Lane, the President's science adviser, was recognized "as a shining example to future generations of researchers—the best of the group of scientists and engineers who will be responsible for America's 21st century greatness." On the same day she also received a DOE Office of Science Early Career Scientist Award from Secretary of Energy Bill Richardson in a ceremony at Washington's Forrestal Building.

Most operating robots today are stand-alone industrial robots that carry out single tasks such as cutting, bending, or welding metal for automobiles. But future intelligent machines in factories and other environments are likely to include cooperative robots.

"In cooperative robotics," Parker says, "more than one robot performs a task that cannot be done by one robot alone." Through use of onboard software written in C and C++ and attached sensors and effectors, Parker has "trained" small, mobile robots to work together to manipulate objects. For example, Ada, Alexandra, Edith, and Grace, CESAR's four "Nomad technology" robots named after female pioneers in computer science, recently passed a baton over a series of barriers to reach a goal. The four robots, she says, can get the job done faster than one robot can.

"We have demonstrated that robots can move in formation," Parker says. This capability could be useful for mowing a sports field, sweeping a gym floor, or scraping an ice rink.

"The ALLIANCE program coordinates the movement of robots so they don't interfere with each other," Parker says. "It also allows them to cooperate through communication. They share information about their intentions so the other robots can adapt as they work to achieve a common goal."

Parker cites several advantages for cooperative robotics. A team of robots can accomplish more complex tasks than a single robot can working alone. The team is more reliable and robust; if one robot fails, the other robots can take over and continue the mission. By working in parallel, the team can complete the task much faster than one robot. Because the individual robots will have a simpler design, a team of robots may cost less to construct and maintain than one robot built to carry out a complex task.

Teams of robots could be used to perform complex tasks in areas too dangerous or other-

Lynne Parker prepares to place a baton in the gripper of one robot, which will pass it across the wooden barrier to another robot. These are two of ORNL's four "Nomad technology" robots, which are named Ada, Alexandra, Edith, and Grace after female pioneers in computer science. The two smaller robots are named after Roman emperors Hadrian and Augustus in honor of CESAR—ORNL's Center for Engineering Science Advanced Research.

wise undesirable for humans. Such tasks could include cleaning up hazardous waste sites, exploring planets, mining in unpopulated areas, participating in search and rescue missions, and decommissioning nuclear power plants, as well as taking part in such activities as automated manufacturing, industrial maintenance, and surveillance for threats such as biological and chemical warfare weapons.

For Caterpillar Inc., Parker and her colleagues are performing computer simulations of a cooperative robotics system in which unmanned, automated bulldozers would remove coal from surface mines in remote areas. "Our goal," Parker says, "is to enable a human in one vehicle to direct the actions of the unmanned, robotic vehicles that remove and collect the coal."

For a Defense Applied Research and Development Agency (DARPA) project involving ORNL and Science Applications International Corporation (SAIC) in Littleton, Colorado, Parker is developing software that will coordinate the movements of DARPA's sensor-equipped, tactical mobile robots, which were developed to do surveillance in urban areas. "Military officials want to be able to determine safely whether terrorists are staying in a suspect building," Parker says. "They envision man-portable robots called packbots that toss over a fence several smaller robots, or 'throwbots' that resemble bowling balls with spikes. Such throwbots might crawl through sewage pipes, surreptitiously enter a building, and capture and relay images of people and weapons in the building."

One of Parker's biggest challenges is to enable robots to learn from each other. In one multirobot learning project, the Nomad technology robots were assigned this goal: Using all your capabilities, figure out how to move as a team to keep as many moving targets under view as possible. The robots have vision, compass, infrared, and two-dimensional (2D) laser sensors, as well as odometric, tactile, and sonar sensors. They have an indoor laser-based 2D global positioning system that allows them to locate themselves and each other precisely in the room space. Thanks to a radio ethernet system, they can communicate with each other and with a host computer workstation.

"So far, we've found that the learned approach is better than random movement of the robots, but it's not as effective as my hand-generated computer solution," Parker says. "When I give the robots my force vector field model, which specifies that robots are attracted to targets and repelled by each other, the robots quickly spread out and get close to the targets as a team. This is the fastest solution."

Later this year, Parker will write programs for four smaller, even more mobile, robots, which are named after Roman emperors, in honor of CESAR. She will try to "teach" these robots how to learn by giving them "hints" and "global positive reinforcement" as feedback.

When asked why she chose computer science as a field of study, Parker answered, "I always liked math and science. My father, who is a civil engineer, suggested that I might like computer science because it combines both science and math. Computer science is a relatively new field that presents new challenges. I like to work on and solve new problems, and the field suits my independent nature."

Parker's goal is to make robots more autonomous and independent by giving them the ability to learn. She knows that she and they have a long way to go, but she says, "That's what makes my job fun." ornl

Mercury Beyond Oak Ridge

ORNL Corporate Fellow Steve Lindberg has led efforts to find new ways to measure surface emission and deposition of airborne mercury and determine its interactions with forests and lakes. The results of Oak Ridge studies are influencing global regulations of the toxic metal.

Steve Lindberg measures fluxes of stable mercury isotopes from soils in Canada's Experimental Lakes Area.

In 1989, following a conference on mercury in Sweden, Steve Lindberg was riding on a train from Stockholm when he noticed a familiar face. It was John Huckabee, whom Lindberg had first met in 1974 after he joined ORNL's Environmental Sciences Division (ESD). Huckabee had led an ORNL study of the ecological effects of mercury from the world's largest mercury mine, located in Almadén, Spain.

Lindberg worked with Huckabee and others in the 1970s on a National Science Foundation project that measured mercury concentrations in the North Fork Holston River and Cherokee Reservoir in Virginia and Tennessee. Also in the mid-70s, Huckabee, Lindberg, and Danny Jackson discovered that green plants absorbed mercury from Almadén's mercury-enriched atmosphere through their leaves. (In 1995, Lindberg and ESD's Paul Hanson discovered that plants also emit mercury from their leaves if their internal mercury levels exceed background air concentrations.)

On the train Lindberg struck up a conversation with Huckabee, then head of the Environment Division at the Electric Power Research Institute (EPRI), about atmospheric mercury. Mercury is a heavy liquid metal, but this toxic material can float through the air as a gas. Lindberg was one of the first scientists to suggest that airborne global mercury could be a source of mercury to land and surface water. This hypothesis helped explain why some pristine lakes far from industrial sources of mercury are contaminated with the toxic metal, which can be converted from its elemental form to methylmercury by bacteria. Methylmercury is readily accumulated by fish. Humans exposed to excessive amounts of methylmercury from contaminated fish can develop neurological and other health problems.

At the conference in Sweden, Lindberg had described his computer model for quantifying mercury emissions and deposition, including the two-way flow between the earth's surface (e.g., soils, lakes, and forests) and the atmosphere. Lindberg told Huckabee that he hoped to collect data and develop models that would lead to a better understanding of the exchange of mercury between the atmosphere and forests and lakes.

Huckabee was interested because the energy production sector is the nation's largest point source of mercury. Coal-burning power plants release more than 40 tons of mercury a year, about a third of the total entering the environment. Power plants emit more mercury vapor than either mercury mines or chlor-alkali plants (which produce chlorine). Lindberg had studied all three industrial sources of mercury. In 1980 he and ESD's Jay Story measured mercury emissions from the Tennessee Valley Authority's coal-fired power plant at Cumberland, Tennessee. They found that 99% of the mercury in the feed coal was discharged to the atmosphere as gases (92%) and particles (7%) and that only 1% was captured by pollution control equipment.

On the train Huckabee helped Lindberg outline a proposal to EPRI. EPRI managers knew well that mercury was the next environmental challenge for U.S. coal-fired power plants, which were installing expensive scrubbers to reduce their sulfur emissions to meet new U.S. Environmental Protection Agency (EPA) regulations. As the research arm of U.S. electric utilities, EPRI wanted to know more about the environmental effects of mercury emissions.

As a result of the "train-ride" proposal, Lindberg's group received EPRI funding to make new field measurements, and the Department of Energy supported methodology and instrument development. Collaborators in this work have been Ki Kim, Jim Owens, and Paul Hanson, all of ESD; Ralph Turner, formerly of ESD; and Tilden Meyers of the Atmospheric Turbulence and Diffusion Division of the National Oceanic and Atmospheric Administration (NOAA) in Oak Ridge.

During the 1990s, Lindberg and his colleagues greatly advanced the understanding of atmospheric

Using an approach developed at ORNL, Jim Owens employs an automated mercury sampling system to measure dissolved gaseous mercury concentrations in alligator-filled waters in Florida's Everglades. Mercury vapor is purged from a water sample and is collected in quartz glass tubes that contain metallic gold. When air is drawn through tubes at a prescribed flow rate, mercury vapor amalgamates with the gold. By heating the gold, researchers can precisely measure the amount of mercury vapor released at a level of about a picogram using atomic fluorescence spectroscopy.

mercury in collaboration with internationally known mercury research laboratories, such as the Swedish Environmental Research Institute and the German Hydrophysics Institute (where Lindberg spent two sabbaticals in 1994–1996). Many early tests of his method were performed at East Fork Poplar Creek (EFPC), where tons of elemental mercury were discharged as a result of a lithium separation process at the Oak Ridge Y-12 Plant in support of the development of the hydrogen bomb. This "manipulated backyard" research site proved invaluable for method demonstrations, which have since led to almost 20 new research projects in ESD on mercury cycling. The results were interesting, too: Using their new micrometeorological gradient technique, Lindberg and his colleagues found that more mercury was released to the air from EFPC floodplain soils than to groundwater. After a series of hearings and much scientific evaluation involving many ORNL researchers, the most contaminated floodplain soil was replaced with clean soil.

"While local officials and scientists were focusing on mercury problems at the Y-12 Plant and on the floodplain," Lindberg says, "my colleagues and I were making plans to study mercury beyond Oak Ridge."

Since 1994 the ORNL group has published more than 50 journal articles on the development and application of several new methods for measuring airborne mercury. These ORNL-developed methods are now being used by a dozen other mercury research groups around the world.

The wealth of information obtained by these researchers has prompted EPA to take action. By December 15, 2000, as a result of a July 11 recommendation by a panel of 10 experts convened by the National Research Council, EPA is expected to announce regulations that will require coal-fired power plants to include some level of mercury emission control, which could be costlier than sulfur emission controls. Already EPA has issued guidelines and regulations restricting mercury emissions from municipal incinerators and limiting the use of mercury in fluorescent light bulbs and batteries, to reduce the amount of waste mercury in landfills.

Mercury in Waste

Lindberg was also one of the first scientists to suggest that wastes are a source of mercury to the air. In 1975 he and former ESD geochemist Ralph Turner were involved in a study to help pinpoint the sources of mercury to the contaminated Holston River. In the 1970s there was considerable concern about mercury-contaminated waterways because of the disaster at Minamata City, Japan. From 1953 through 1965, the Chisso Corporation's acetaldehyde factory discharged methylmercury and inorganic mercury into Minamata Bay. As a result, 52 Japanese died and more than 1200 became ill from eating bay fish contaminated with methylmercury. Awareness of this disaster was partly responsible for the passage of the Clean Water Act of 1970.

Lindberg and Turner were asked to study a mercury-contaminated waste storage site at a Saltville, Virginia, chlor-alkali plant on the Holston River. The plant was permanently closed, and the waste site was being considered for a trailer park. The researchers measured the waste site's discharges of mercury to the river as a result of runoff, as well as its emissions of mercury vapor to the air.

For a 1997 EPRI-sponsored intercomparison study of mercury fluxes from natural sources, mercury emissions from geologically enriched soils to the air were measured by various approaches near Steamboat Springs, Nevada. Ten different groups from around the world compared measurements using techniques originally developed by ORNL and NOAA researchers, such as the micrometeorological modified Bowen ratio gradient method illustrated here.

"We were the first to propose that there is an atmospheric route for mercury to get from the waste to the local environment," Lindberg says. "Our measurements showed that atmospheric emissions from the waste site were equal to the direct runoff to the river. We also found that the total amount of mercury lost from the passive waste storage site was higher than that from some active chlor-alkali plants that have emission controls."

In 1977, Lindberg and Turner published their research on chlor-alkali plant waste in *Nature*. The paper concluded that waste storage sites could remain a source of mercury to the air and the environment for hundreds of years. The Saltville site was later remediated at a cost of millions of dollars.

Today Lindberg's group includes several ESD scientists working on projects throughout North America: Hong Zhang, George Southworth, Weijin Dong, Lala Chambers, Todd Kuiken, and Mary Anna Bogle are involved in studies from Florida's Everglades to Point Barrow, Alaska. One project involves measuring mercury emissions from landfills.

"People dump garbage that contains mercury, such as thermometers, batteries, electrical switches, fluorescent light bulbs, and yard waste—mainly leaves and grass," Lindberg says. "Bacteria working on this waste form methane, which is often used to generate 'green power.' Unfortunately, other bacteria also convert the waste mercury into dimethyl mercury, a highly toxic organic compound that is volatile and is released in landfill gas."

The Oak Ridge researchers also have been measuring emissions of airborne mercury from natural sources, such as vegetation in the Everglades National Park; surface waters of a forested lake site in south-central Sweden; soils in hydrothermal areas in California and Nevada; soils at Walker Branch Watershed on the Oak Ridge Reservation; and surfaces in the Arctic regions of Siberia, Alaska, and Canada. Mercury from natural sources must also be measured to predict correctly the effects of pollution controls.

A Sticky Gas

In the early 1980s, Lindberg and others began thinking about the cycling of global mercury. They knew that increasing amounts of mercury vapors were being discharged to the atmosphere from burning fossil fuels, mining, manufacturing, and incinerating waste. They knew that the elemental form of mercury is highly volatile, that its atmospheric residence time is six months to a year, and that it is barely soluble in water.

Lindberg was studying air pollutants and acid rain at the time for the National Acidic Precipitation Assessment Program (NAPAP), so he became interested in their role in promoting the deposition of airborne mercury on the earth's surface. This deposition was evidenced by the increasing number of reports of mercury-contaminated fish in lakes far from industrial sources of mercury.

"We hypothesized that ozone and other pollutant oxidants could react with elemental mercury to form a reactive divalent mercury compound, which is much more soluble in water and more likely to be deposited to the ground and on lakes," Lindberg says. Among the air pollutants Lindberg studied for NAPAP during this period were nitrogen oxides (NO_x), which are present in automobile and coal plant emissions. He found that NO_x emissions when reacted with photo-oxidants resulted in the formation of nitric acid vapor in the atmosphere. "We called it a 'sticky' gas," he says, "because nitric acid was rapidly deposited from the air to vegetation and soil. It 'stuck' to everything."

ESD researchers worked with visiting professor Wil Stratton to develop a mist chamber approach to make the first-ever measurements of reactive gaseous mercury in ambient air. A vacuum pump draws air through the mist chamber from an inlet at the bottom causing a mist to be sprayed into the chamber by aspiration. As the air passes through to the top, the highly soluble reactive mercury in the air is dissolved in the mist. In the field laboratory, the mercury is then reduced to elemental mercury with tin chloride (which adds the two missing electrons). The mercury is stripped from the water droplets by purging with zero gas onto a gold trap, followed by atomic fluorescence spectroscopic analysis.

In 1993 Lindberg proved that airborne mercury also consists partly of a "sticky" gas. He and Wilmer J. Stratton, retired professor of chemistry at Earlham College in Richmond, Indiana, who was conducting research at ORNL at the time, were the first to measure reactive gaseous mercury (RGM) in ambient air. To identify and measure RGM, they developed a method that takes advantage of a "high-flow refluxing mist chamber" previously used in NASA-sponsored, gas-chemistry studies in the Amazon River valley.

"Because RGM is so soluble in water," Lindberg says, "it can be deposited quickly in rain and snow, thus making it a possible source of mercury to lakes far from mercury-discharging industrial plants. During dry weather, RGM would also be rapidly dry deposited to vegetation where it may be washed into soils and nearby streams."

In 1997 Lindberg and Stratton published an article in *Environmental Science and Technology* about their detection of a sticky RGM compound of either mercuric oxide or mercuric chloride. According to their measurements, 2 to 4% of total gaseous mercury in air is the highly water-soluble species of RGM, whereas about 97% is elemental mercury vapor. They discovered that this small fraction of airborne mercury strongly influences the deposition of mercury to the earth's surface.

How does RGM get into the air? It is formed in flue gas when coal or municipal waste is burned. However, Lindberg suspects that it can also be formed in air by chemical reactions with elemental mercury vapor. When inert elemental mercury (Hg°), which has no electrical charge, is oxidized in air, it loses two electrons, forming RGM (Hg^{+2}). Lindberg believes that in the troposphere Hg° is oxidized by reactive halogens, such as bromine, in the presence of ultraviolet light.

In a 1999 paper in *Nature*, Canadian scientist Bill Schroeder observed the disappearance of airborne elemental mercury during his gold-trap measurements of atmospheric mercury at Alert in the Northwest Territories near the North Pole. Most of the year, the mercury levels averaged 1.5 nanograms/m^3, but after the polar sunrise and before snowmelt, elemental mercury levels dropped to levels of 0.2 ng/m^3.

After reading Schroeder's paper, Lindberg's group proposed a companion study at Point Barrow, Alaska, that involved Steve Brooks and others from the Oak Ridge NOAA laboratory. Since 1998, portable Tekran-automated, mercury-speciation units have been used to measure simultaneously near-real-time concentrations of RGM and elemental mercury. Lindberg and Brooks found that when elemental mercury levels fell to 0.5 ng/m^3, their measurements of RGM rose from 0 to 0.9 ng/m^3.

Steve Brooks of NOAA takes a break from mercury measurements at Point Barrow, Alaska, to enjoy the first sunlight in two months.

According to Lindberg, "The evidence suggests that airborne elemental mercury is depleted when conditions are right for converting it chemically to RGM, which is then deposited to the Arctic snow." New analyses by Mary Anna Bogle and George Southworth of snow collected from January through May 2000 confirm for the first time that mercury is accumulating in Arctic snow at record levels.

Mercury Manipulation Study

Lindberg's group is now focused on a multimillion-dollar mercury manipulation study being planned for the Experimental Lakes Area (ELA) in Northwest Ontario. It is called the Mercury Experiment to Assess Atmospheric Loading in Canada and the U.S. (METAALICUS). DOE is supporting the Oak Ridge group in this international collaboration between the United States and Canada, which is designed to answer this central question: "Are atmospheric emissions of mercury largely responsible for the methylmercury contamination of fish in lakes far from industrial sources of mercury?" The ELA has hundreds of remote lakes that can be used safely for environmental experiments; in fact, it was the site of pioneering lake acidification studies in the 1980s.

"We will use aircraft to spray a different stable mercury isotope on a forest, a nearby lake, and a nearby wetland," Lindberg says. "Using inductively coupled plasma mass spectrometry, a University of Toronto lab will analyze the degree to which mercury in the fish comes from the air, the lake, and runoff from the forest and wetland, based on isotopic ratios."

The results of the study will be reported at the October 2001 International Conference on Mercury, which will be co-chaired by Lindberg. It will be held in Minamata City, Japan.

Interestingly, one source of the mercury isotopes for the study is the stockpile of stable mercury at ORNL. Oak Ridge mercury is being sent beyond Oak Ridge to help solve a global problem. ornl

A Disrupted Organic Film: Could Memories Be Made of This?

An ORNL theorist helped Chinese scientists understand on a molecular scale why a physically altered organic film shows potential for high-density data storage.

For the first time, Chinese scientists have shown that nanometer-sized dots of information can be written on a thin film and erased. The work suggests that an organic film, altered electrically to create such dots, could hold a million times more data than a CD-ROM. Calculations by Karl Sohlberg, a theoretical chemist in ORNL's Solid State Division, have enhanced the understanding of the mechanism behind this discovery. The results of the collaborative research, which also involved the University of Chicago, were published in the February 21, 2000, issue of *Physical Review Letters*.

In August 1997, Hongjun Gao, then with the Beijing Laboratory for Vacuum Physics, came to ORNL's Solid State Division (SSD) as a guest scientist. He wanted to both use the division's state-of-the-art microscopes and tap SSD expertise. Gao and his Chinese colleagues had discovered that by exposing an organic film on a graphite substrate to voltage pulses from a scanning tunneling microscope (STM), tiny regions, or "nano-dots," of the non-conductive film become electrically conductive.

Gao told SSD's Steve Pennycook and Sohlberg that when a voltage was applied to a perfect crystalline film on graphite, virtually no electrical current was measured because of the film's high resistivity. But after the film was exposed to positive voltage pulses, it became conductive. Gao was interested in determining the changes at the molecular level that altered the film's electrical properties.

Sohlberg, who was Gao's office mate at ORNL, made calculations and used infrared spectra and other data from various experiments conducted on the organic films at the Beijing lab to make this determination. "We were trying to test hypotheses suggested by the experimental results and the scientific literature," he says. "That way we hoped to arrive at the correct explanation."

The researchers ruled out several suggested explanations for the conductivity of the altered film, including the buildup of static electricity and the burning of a hole through the film to the electrically conductive graphite base.

"Then we got an insight from another experiment carried out in the Beijing lab," Sohlberg says. "Occasionally, the Chinese scientists would deposit a film at too fast a rate. When they characterized one such film, they found it was amorphous rather than crystalline like the good film. They also observed that the disordered film was as conductive as the crystalline film altered by voltage pulses."

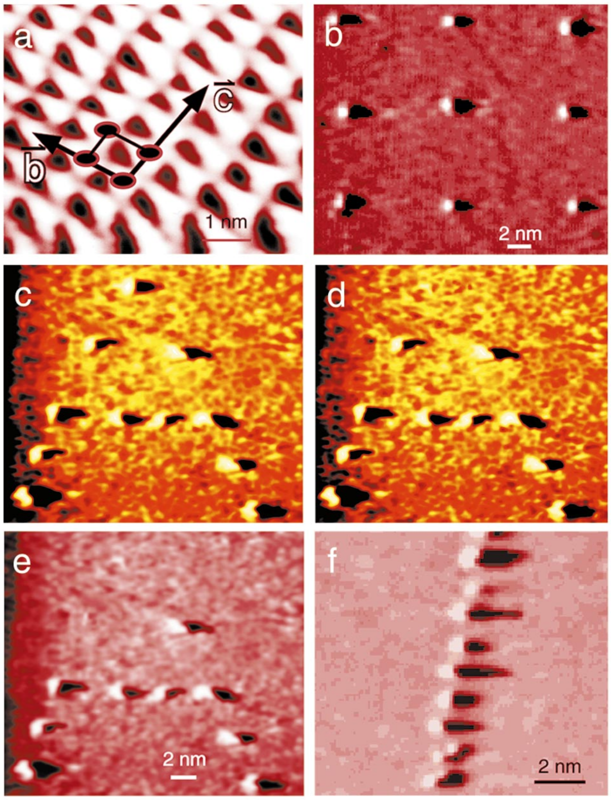
This correlation suggested that the nanodots are actually tiny regions of "local disorder" in the otherwise well-ordered film and that their amorphous nature makes the film conductive. At Beijing, says Sohlberg, the "nail in the coffin" experiment was done to verify this prediction and close the case on why altered crystalline films become conductive.

Pennycook suggested that a thin-film data storage device would be more marketable if data could be erased as well as written on it. So, the Beijing group did some experiments and found that subjecting the nanodots to negative voltage pulses restored them to the nonconductive state. This was the first demonstration of writing and erasing information at or near the single-molecule limit.

In March 2000, Gao left ORNL to become a group leader in the Beijing Laboratory for Vacuum Physics. Sohlberg says that Gao's laboratory will be trying to meet the challenges of making a commercial high-data-density thin-film storage device. In such a device, a conductive nanodot could represent a "1" bit and nonconductive regions could be "0" bits.

"A massively parallel device must be built to read so much stored information at an acceptable speed," Sohlberg says. "In addition, the altered organic materials must be made more stable and durable."

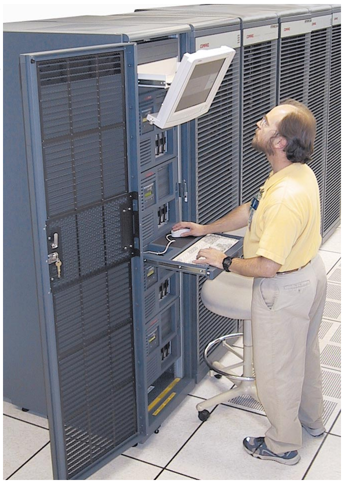
Gao thinks it may be possible to connect the conductive dots, sandwich them in glass, and pack these nanosized circuits in microchips to produce computers that are 10 times smaller and faster. One way or another, because of the growing ability to control their properties on the nanometer scale, organic films may change the big picture for computing technologies. ornl



STM images of an organic film on graphite. (a) An image of the film surface showing crystalline order; (b) an array of nanodots formed by positive voltage pulses; (c) an "A" pattern formed by voltage pulses; (d) and (e) STM images after erasing marks one at a time using negative voltage pulses; (f) resolution test using voltage pulses (the distance between neighboring dots is 1.7 nanometers).

ORNL's Powerful Tools for Scientific Discovery

Because of its two new supercomputers, ORNL is one of the most powerful unclassified scientific computing facilities in the world.



Buddy Bland

Pat Worley works at the Compaq Alphaserver Colt computer.

In April 2000, ORNL became home to the most powerful unclassified computers in the nation, making it one of the most powerful unclassified scientific computing facilities in the world. The IBM RS/6000 SP supercomputer was expanded, and a new Compaq AlphaServer SC system was installed. The two supercomputers can operate at a theoretical speed of 1.5 teraflops, or more than a trillion calculations per second. That's 10 times the computational speed of ORNL's recently dismantled Intel Paragon, which was the fastest supercomputer in the world in early 1995.

The IBM supercomputer (Eagle), which was purchased and installed in 1999, originally operated at 100 gigaflops and then 400 gigaflops, less than half a teraflop. It now can operate at more than 1 teraflop. The recently acquired Compaq Alphaserver supercomputer (Falcon) can operate at half a teraflop; it will soon be upgraded to almost a teraflop. While the IBM supercomputer is dedicated to a range of computational science, the Compaq machine will be used to develop better computational tools for researchers.

The ORNL terascale computing facility was dedicated on June 20, 2000. The keynote speaker was Ernie Moniz, Department of Energy undersecretary, who called ORNL's supercomputers "extraordinary tools for extraordinary science." He noted that "simulation using teraflop computers will be a tool of scientific discovery. Simulation will play an important role in the bridging from the molecular level to engineering systems to get the needed efficiencies" to solve energy and environmental problems. In the ceremony's "virtual ribbon cutting" Moniz sheared a digital ribbon with digital scissors by clicking a mouse.

"This marks a significant milestone for us," said Thomas Zacharia, director of ORNL's Computer Science and Mathematics Division. "These computers allow us the unique opportunity to push forward in our science and technology agenda at the Laboratory."

"The machine can work on many pieces of a problem at once," said David McQueeney, vice president of IBM Communication Technology, who noted that the IBM RS/6000 SP at ORNL ranks 11th among the world's top 500 supercomputers. McQueeney also announced the creation of an IBM postdoctoral fellowship in terascale computing for ORNL.

In addition to its supercomputing capabilities, ORNL also offers 360 terabytes of data storage for the two large parallel computers, using a version of IBM's High-Performance Storage System that ORNL researchers helped develop. The 184-node Eagle has 372 gigabytes of memory and 9.2 terabytes of local storage, and the 80-node Falcon has 160 gigabytes of memory and 5.5 terabytes of local storage.

Computer science will play an increasing role in scientific research, Zacharia believes. The development of new algorithms by ORNL computer scientists will allow the Laboratory's powerful computers to solve more complex scientific problems through simulations of experiments (see the following article). "High-performance computing is needed to meet DOE objectives," he says. "It has become a crucial tool for scientific discovery in climate prediction, bioinformatics, and materials research, as well as many other areas."

One scientific challenge will be to predict changes in the future global climate as greenhouse gas levels rise. Computing at ORNL will be used to predict changes in the regional climate in the Southeast, based on results of global scenarios. For example, scientists will try to predict whether in the next few decades East Tennessee will have more droughts, North Carolina will have more hurricanes, and Florida will have greater coastal flooding than in the recent past.

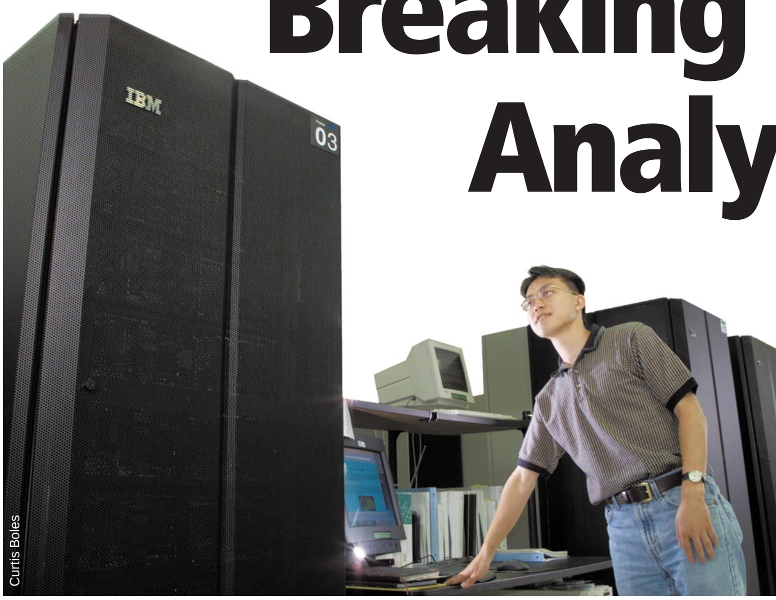
Researchers in the computational biosciences are using ORNL supercomputers for bioinformatics. Relying on information from the Human Genome Project, they are locating and discovering genes in DNA sequences, predicting the structure of proteins encoded by specific genes, and estimating gene functions. The DNA sequences they will be analyzing computationally include human chromosomes 19, 16, and 5. Draft sequences of these chromosomes have already been produced by DOE's Joint Genome Institute, of which ORNL is a part. The new information on genes and gene functions could lead to the development of more effective disease-fighting drugs.

ORNL researchers will use supercomputers to simulate collisions between future cars, which will be made of advanced lightweight materials and designed to burn fuel more efficiently and cleanly. The idea behind these calculations is to determine whether these cars will hold up during crashes as well as do the heavier steel cars of today. These and trillions of other numbers will be crunched at ORNL—one of the world's most powerful unclassified computing facilities. ornl

Leah Dever, manager of DOE's Oak Ridge Operations; Ernie Moniz, DOE undersecretary; Thomas Zacharia, director of ORNL's Computer Science and Mathematics Division, Bill Madia, ORNL director; and Jim Roberto, ORNL associate director for Physical and Computational Sciences, participated in the June 20, 2000, dedication of two new supercomputers at ORNL.

Curtis Boles

Breaking a Record for Analysis of Atoms



Using a new ORNL-developed algorithm on one of the world's fastest supercomputers, researchers can calculate the vibrational modes among 100,000 atoms in a material. Use of the algorithm could lead to a better understanding of vital plant proteins and the virus that causes the common cold.

Refrigerator-sized cabinets house the IBM RS/6000 SP supercomputer on which Chao Yang runs his algorithm.

In a typical solid material, atoms don't just stand still. They tend to vibrate near an equilibrium configuration. Heat the solid and its atoms vibrate even faster. The atoms will move various distances and directions from each other. How fast atoms vibrate (vibrational frequency) and how far and which way they move relative to their neighbors (vibrational mode) are of interest to scientists seeking insights into the structure and behavior of various materials.

Since the 1950s, scientists have used computational methods for normal coordinate analysis (NCA) of systems of atoms. With these methods they have sought to calculate vibrational frequencies and vibrational modes from the known forces between the atoms that determine the strength of the chemical bonds that bind atoms together in a material. But in recent years NCA has hit a brick wall.

Scientists have been unable to model more than a few thousand atoms at a time. For larger systems, the computation becomes enormously expensive. Moreover, some of the computed frequencies often turn out to be negative, suggesting that a system known to be stable is, in fact, unstable. According to an article that appeared in *Annual Review of Physical Chemistry* in 1995, "normal coordinate analysis in Cartesian coordinate space is, with even the most powerful supercomputers, still impossible for proteins larger than roughly 150 residues."

In 1998 Don Noid and Bobby Sumpter, both of ORNL's Chemical and Analytical Sciences Division (CASD), developed an algorithm that allowed them to model 6000 carbon and hydrogen atoms in polyethylene, the simplest polymer in terms of chemical structure. Thanks to their innovative computational procedure, the researchers were able to calculate the forces between each pair of polyethylene atoms about 1000 times faster than had been done before using the traditional NCA algorithm.

But a more computationally challenging task is to extract a set of low-frequency vibrational modes from the force calculation. For the 6000-atom polyethylene model, the traditional method would require more than 2 gigabytes of memory and trillions of calculations per second.

Fortunately, Chao Yang came to ORNL just in time to make the ORNL algorithm even better. Yang was hired as the 1999 Alston Householder Fellow in ORNL's Computer Science and Mathematics Division (CSMD). Householder directed the mathematical activities of ORNL from 1946 until 1969.

While earning his Ph.D. degree in computation and applied mathematics from Rice University, Yang helped develop ARPACK, a popular numerical tool for solving large-scale eigenvalue problems. When he came to ORNL, he adapted the ARPACK program to perform large-scale NCA on parallel processors, such as the new IBM RS/6000 SP supercomputer at the Laboratory, which can now make a trillion calculations per second. Yang also included sparse matrix techniques to improve the efficiency of the calculation. This effort has led to a new "large-scale, time-averaged NCA" algorithm.

"With the traditional algorithm," says Chuck Romine of CSMD, "it takes days to calculate vibrational modes in a 6000-atom system with 18,000 degrees of freedom, which relate to the directions in which an atom can move. With the new ORNL technique, it takes less than an hour to calculate vibrational modes in a 6000-atom system."

To obtain vibrational frequencies and modes between atoms in a large system, researchers calculate an array of numbers and zeroes in rows and columns called a matrix. A zero could represent the force between too widely separated atoms, and a nonzero number represents the magnitude of force between a pair of atoms. Yang's technique does not require the storage of thousands of zeroes in the matrix as does the traditional algorithm, saving time and data storage space.

In 1999, the new algorithm allowed the IBM supercomputer to calculate the forces among 24,000 atoms of polyethylene, a world's record. Currently, 100,000 atoms of the same material are being modeled using the new algorithm.

"Our goal," Yang says, "is to develop a software tool to allow scientists to study more general large-scale molecular systems. The user can input known or conjectured values for the forces and conduct computational experiments. Then, by comparing predicted results with actual experimental measurements, the model can be fine tuned to make it better represent the actual material."

In the past year, Yang and his colleagues have published five papers in technical journals concerning the use of the new algorithm. Because of their paper in *Chemical Physics Letters*, a group at the California Institute of Technology led by Rudolph Marcus, who won the Nobel Prize for chemistry in 1992, is collaborating with Yang, Romine, Noid and Sumpter on studying a vital plant protein that uses light to produce atmospheric oxygen.

Yang will soon apply the new algorithm to calculate vibrational modes of a rhinovirus, which causes the common cold. This information could provide insights into virus structure that could be valuable for development of a cure. ornl

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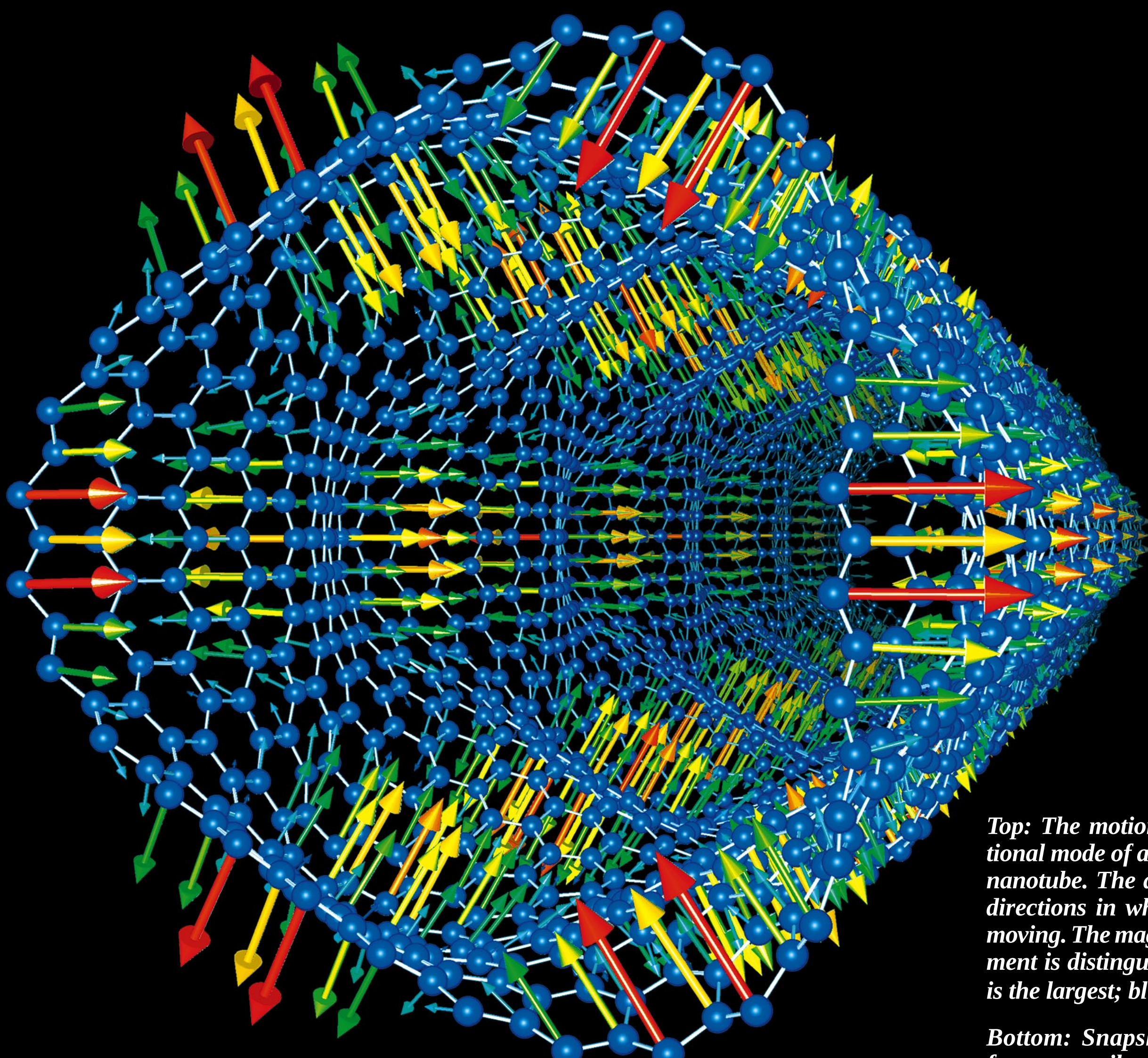
Back cover graphics created by Ross Toedte of Computer Science and Mathematics Division's Visualization Group using calculations from the IBM supercomputer at ORNL. (See articles on pp. 28–29.)



***Top:* The motion of the 7th vibrational mode of a 3000-atom carbon nanotube. The arrows indicate the directions in which the atoms are moving. The magnitude of displacement is distinguished by color (red is the largest; blue, the smallest).**

***Bottom:* Snapshots of three low-frequency vibrational modes of the nanotube.**