CHEMMATTERS

OCTOBER 1995

As Riverside General Hospital declared a state of disaster and evacuated the emergency room, the body was sealed in a bag, transferred to an airtight casket, and rushed to the morgue.

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THE TOXIC PATIENT

by Robin Meadows

February 19, 1994, started out like just any other Saturday night in the emergency room of Riverside General Hospital, which lies east of Los Angeles. But then Gloria Ramirez was rushed to the emergency room in an ambulance. The first nurse to treat her fainted. Then the doctor who took over also fainted and had muscle spasms and trouble breathing as well. Other members of the emergency room staff were stricken shortly thereafter, and the head doctor ordered the emergency room evacuated. Most of the staff and all of the patients—except Ramirez—moved out to the hospital parking lot. Altogether 23 out of the 37 staff members on duty that night had adverse symptoms, and five were so severely afflicted that they were taken to other hospitals for treatment. All this happened a mere 15 minutes after Ramirez's arrival.

This story dominated the news a year and a half ago, but no one could figure out what had happened. Recently, however, chemists found a possible chemical explanation for these bizarre events. To determine what may have happened, we need to go back to the beginning of the story. Early in the evening of February 19, Gloria Ramirez's boyfriend called an ambulance because she had an irregular heartbeat and was having difficulty breathing.

She also had been vomiting for several days and suffered from advanced cervical cancer. However, she had not yet started radiation treatment or chemotherapy.

The ambulance arrived at about 7:50 p.m., and the paramedics followed the standard procedure of putting Ramirez on a heart monitor, giving her oxygen through a mask, and starting her on an IV. The ambulance reached the Riverside General Hospital emergency room at about 8:15 p.m. Although Ramirez was breathing shallowly and her heart was beating too rapidly, she was alert enough to talk to the emergency room staff. In an attempt to return her heartbeat to normal, the staff defibrillated her by applying high-voltage shocks via padded electrodes on the bare skin directly above her heart. At that point, several staff members noted that her skin had an oily sheen and that she smelled fruity or garlicky.

Then nurse Susan Kane drew blood, which is usually a routine procedure. But what happened next was far from routine: Kane smelled an ammonia-like odor and gave the blood-filled syringe to respiratory therapist Maureen Welch, who sniffed it and also smelled the odor. Welch then gave the syringe to Dr. Julie Gorchynski, who smelled the odor and also saw white crystals floating in it (normal blood contains no crystals). Dr. Humberto Ochoa, chair of the Department of Emergency Medicine, saw these crystals too. In short order, Kane, Gorchynski, and then Welch fainted. Gorchynski was also shaking and breathing irregularly, and Kane's arms and legs were flailing around uncontrollably.

When several other emergency room staff members said they felt ill, Ochoa ordered the emergency room evacuated while he and a few staff members stayed to continue caring for Ramirez. Their attempts to save her life were to no avail, however, and Ochoa pronounced her dead at 8:50 p.m., only 35 minutes after her arrival.

Riverside General Hospital declared itself to be in a state of internal disaster, and all ambulances were directed to other hospitals. Ramirez's body was placed first in a sealed bag and then in an airtight casket, and moved to the hospital morgue.

Two hours later (at about 11:00 p.m.), a Hazardous Materials



team arrived and tested the emergency room air for common hazardous gases including ammonia, hydrogen cyanide, and phosgene, the latter a gas that bursts capillaries in the lungs and effectively drowns victims in their own blood. The results were negative. Later the California Division of Occupational Safety and Health and three other organizations studied the hospital's ventilation and plumbing systems to determine whether they could have made the emergency room staff ill. Again the results were negative.

Likewise, the autopsy of Ramirez's body—which the pathologists performed in an airtight chamber while wearing airtight suits with external air supplies— revealed nothing more remarkable than that she had died of cardiac dysrhythmia. Next, several analytical laboratories analyzed samples of Ramirez's blood and tissue for toxicants including common organic solvents, carbamate pesticides, and organophosphate pesticides. These laboratories included the Riverside Coroner's Office and the Lawrence Livermore National Laboratory's Forensic Science Center, which is about 60 miles east of San Francisco. These particular toxicants were chosen because they could have caused some of the symptoms reported by the emergency room staff members. But once again, the results were negative.

It all happened a mere 15 minutes after Ramirez's arrival

The Riverside Coroner's Office then turned to the California Department of Health Services for an answer to what could have caused the "Ramirez incident." In September 1994, the Department of Health Services issued a report attributing the incident to mass hysteria. The Department of Health Services based this conclusion in part on the facts that no poison had been found, that mass hysteria strikes people under stress, and that the emergency room staff members with the worst symptoms were all women, who are supposedly more likely to succumb to mass hysteria.

The afflicted emergency room staff members were not happy with the Department of Health Services hypothesis. Indeed, victims of mass hysteria typically recover very quickly—and this was definitely not the case in the Ramirez incident. Several people on the emergency room staff continued to experience symptoms long after the night Ramirez came to the emergency room, notably Julie Gorchynski, the first doctor who had treated her. To this day Gorchynski suffers from a wide range of debilitating symptoms including knee damage, hepatitis, and flashbacks.

Dissatisfied with the mass hysteria hypothesis, Maureen Welch (who had been the second person to smell the syringe of Ramirez's blood) sent her extensive file on the incident to the Forensic Science Center and asked them to try again. Welch's request "stimulated an in-depth analysis of the mystery, and led to the [following] proposed scenario," said Forensic Science Center chemists Patrick Grant, Jeffrey Haas, Richard Whipple, and Brian Andresen in their November 1994 report "A Possible Chemical Explanation for the Events Associated with the Death of Gloria Ramirez at Riverside General Hospital." The Forensic Science Center chemists prefaced their scenario with a disclaimer to the effect that there is no easy explanation for the events in the Riverside General Hospital emergency room on that February 19. That said, they have proposed an ingenious solution to the mystery of why Gloria Ramirez felled the emergency room staff.

"In typical forensic fashion, [we made our] best attempt at correlating observations and data with known physical and biologic parameters," wrote Grant and his colleagues. One of their key assumptions was that the emer-



The ambulance arrived at Riverside General Hospital at 8:15 pm carrying a gravely sick woman. About 15 minutes later, with doctors and nurses falling ill, the order was given to evacuate the emergency room. For the rest of the night, the emergency room staff was forced to work on patients in the parking lot.

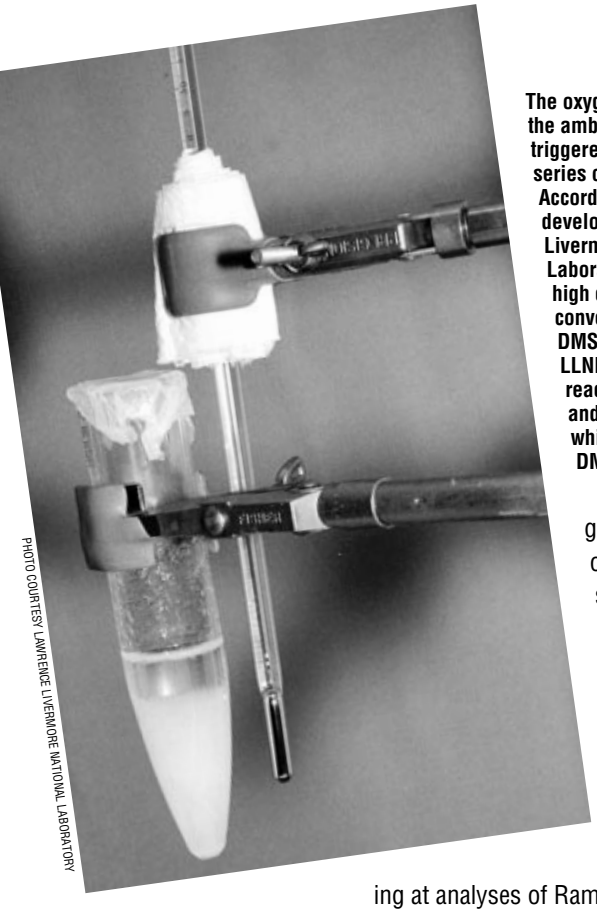


PHOTO COURTESY LAWRENCE LIVERMORE NATIONAL LABORATORY

The oxygen administered in the ambulance may have triggered an extraordinary series of reactions. According to the hypothesis developed at the Lawrence Livermore National Laboratory (LLNL), the high concentration of O_2 converted DMSO to $DMSO_2$. Chemists at LLNL duplicated the reaction in the test tube and produced these white crystals of $DMSO_2$.

gency room staff's observations and symptoms were accurate. "The staff were, after all, trained and experienced personnel in healthcare emergencies."

When looking at analyses of Ramirez's blood and bile *(see Box: Blood and Bile Analysis)*, the Forensic Science Center chemists noted the presence of several compounds not usually found in blood. While most of these compounds were metabolites of the medications Ramirez had taken, one was not: dimethyl sulfone, abbreviated $DMSO_2$ *(see Table 1)*. Could this be part of the puzzle? If so, where did it fit in? The chemists reasoned that a likely source of the $DMSO_2$ in Ramirez's body was dimethyl sulfoxide, DMSO. This compound has long been used as a folk remedy for muscle and joint pain as well as for a variety of other ailments including cervical cancer. When DMSO enters the body, the liver metabolizes it primarily into $DMSO_2$. Although not sold as an over-the-counter medication, DMSO is widely used as an industrial solvent and for treating animals.

The second key step was when nurse Kane drew Ramirez's blood

There is a caveat to the DMSO theory: As the Forensic Science Center chemists freely acknowledge, no one knows for certain whether Ramirez had been using DMSO. However, that would explain both the oily sheen of her skin and the garlicky smell of her breath that the emergency room staff noticed when they defibrillated her. DMSO can make skin shiny because the colorless, oily liquid passes freely through cell membranes; and the compound makes people smell like garlic because about 3% of it is metabolized to dimethyl sulfide, a garlicky-smelling compound that is eliminated through the lungs and skin.

Assuming that Ramirez had been using DMSO, the rest of the scenario proposed by Grant and his colleagues falls neatly into place. The first key step was that Ramirez was given oxygen in the ambulance and hospital. The mixture of gases given through an oxygen mask is about 80% oxygen—four times the amount found in air. According to the scenario, the elevated oxygen level in Ramirez's blood drove the reaction of DMSO to $DMSO_2$.

The second key step was when nurse Kane drew Ramirez's blood. After the blood entered the syringe, its temperature fell from the normal body temperature of about 37 °C (98.6 °F) to the emergency room temperature of about 18 °C (about 64 °F). According to the scenario, this temperature drop made some of the $DMSO_2$ crystalize, forming the white crystals that doctors Gorchynski and Ochoa observed in the blood-filled syringe. $DMSO_2$ is a white crystalline solid at room temperature and is freely soluble in aqueous solutions.

The next event in the scenario was the one blamed for all the trouble. Grant and his colleagues propose that the $DMSO_2$ in the syringe was further oxidized to dimethyl sulfate, $DMSO_4$. $DMSO_4$ vapor is so hazardous that the Merck Index classifies it as a war gas. "It can cause severe inflammation, cerebral edema, and pulmonary damage," says Grant. $DMSO_4$ can be inhaled or absorbed directly through the skin.

Because the reaction converting $DMSO_2$ to $DMSO_4$ has not been specifically reported in the chemical literature, this step is the weakest in the scenario. However, the Forensic Science Center chemists believe the reaction is possible because they found previous reports of reactions that could have contributed to converting $DMSO_2$ to $DMSO_4$.

Moreover, the DMSO-to-$DMSO_2$-to-$DMSO_4$ theory gains considerable credence because there is a near-perfect match of the symptoms reported by the emergency room staff with those known to be caused by $DMSO_4$. The emergency room staff reported nine of the short-term symptoms characteristic of $DMSO_4$ exposure including ammonia-like odor, burning skin, respiratory irritation, and dizziness. The emergency room staff also reported six of the longer term symptoms characteristic of $DMSO_4$ exposure including violent muscle spasms, loss of consciousness, severe memory lapses, and restrictive lung disease. All of Gorchynski's continuing symptoms are consistent with the known effects of $DMSO_4$.

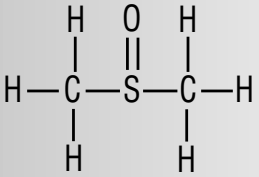
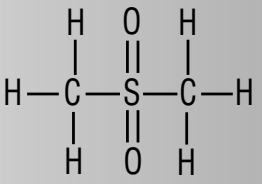
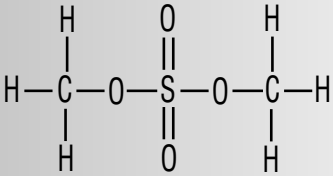
The Forensic Science Center's theory seems straightforward, but how solid is it? Why, for example, was Ramirez's blood toxic when it was in the syringe but apparently not when it was in her body? A possible answer to that, say Grant and his colleagues, is that any $DMSO_4$ that formed in her body would have quickly broken down: at temperatures exceeding 18 °C (64 °F), $DMSO_4$ hydrolyzes to methanol and sulfate.

$$DMSO_4 + 2\ H_2O \longrightarrow 2\ \text{methanol} + 2H^+ + SO_4^{2-}$$

In support of this hypothesis, the level of sulfate in Ramirez's blood was quite high — about 600 micrograms/milliliter, which is 20–80 times the reported normal range.

Why wasn't the $DMSO_4$ that formed in the syringe also hydrolyzed? $DMSO_4$ is not very soluble in water at room temperature and so could have separated from the blood in the syringe, forming a colorless, oily layer. Some of this liquid $DMSO_4$ then "volatilized into the vapor space [in the syringe] to assail the emergency room personnel," wrote Grant and his colleagues.

TABLE 1

Abbreviation	Name	Structure	Formula
DMSO	Dimethyl sulfoxide		$(CH_3)_2SO$
$DMSO_2$	Dimethyl sulfone		$(CH_3)_2SO_2$
$DMSO_4$	Dimethyl sulfate		$(CH_3)_2SO_4$

While not highly volatile, $DMSO_4$ is 10 times more volatile than naphthalene, which gives mothballs their characteristic smell and toxicity.

Why didn't the Hazardous Materials team find any $DMSO_4$ when they tested the emergency room for hazardous gases? $DMSO_4$ does not persist under field conditions, according to the 1987 *U.S. Department of Defense Reference Book on Chemical Warfare Information*. As Grant and his colleagues concluded, it was therefore "not surprising that the only enduring evidence of the chemical attack might be the symptoms of the victims."

And finally, why weren't all of the emergency room staff members affected? That could be explained by the flow of air through the emergency room's vent system, say the Forensic Science Center chemists. Smoke tests after the incident showed that rather than dispersing throughout the emergency room, the air above Ramirez's table flowed toward the ceiling and then out through a vent. One possibility is that the $DMSO_4$ was released from the syringe in a discrete puff that afflicted only those staff members who stood directly in the path the puff took on its way to the ceiling.

Grant and his fellow FSC chemists are the first to acknowledge that the mystery of what happened the night Gloria Ramirez came to the Riverside General Hospital emergency room may never be resolved conclusively. But the FSC has offered the victims a plausible explanation that restores their dignity. As Gorchynski said to the *Los Angeles Times*, "at least it puts the mass hysteria [hypothesis] to rest. That wasn't doing much for my reputation."

Blood and Bile Analysis

The FSC chemists used a technique called gas chromatography–mass spectrometry (GCMS) to analyze Gloria Ramirez's blood and bile samples. GCMS involves heating a drop of sample to 320 °C and moving it through a separation column packed with methyl silicone. Each compound in the vaporized sample moves through a column at a different rate depending on its volatility and affinity to the methyl silicone. As each compound comes off the separation column, it goes into a mass spectrometer. There, a beam of electrons bombards the vaporized compound and ionizes it. The resulting ions are then separated according to their mass-to-charge ratio, and the relative amount of each ion is plotted as a series of peaks. A unique pattern of peaks for each compound allows chemists to identify many of the components of an unknown mixture.

Robin Meadows *is a science writer living in Fairfield, CA. One of her recent contributions to* Chem Matters *magazine ("Buried in Ice," April 1994) received the Distinguished Achievement Award from the Educational Press Association.*

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Ice That Burns

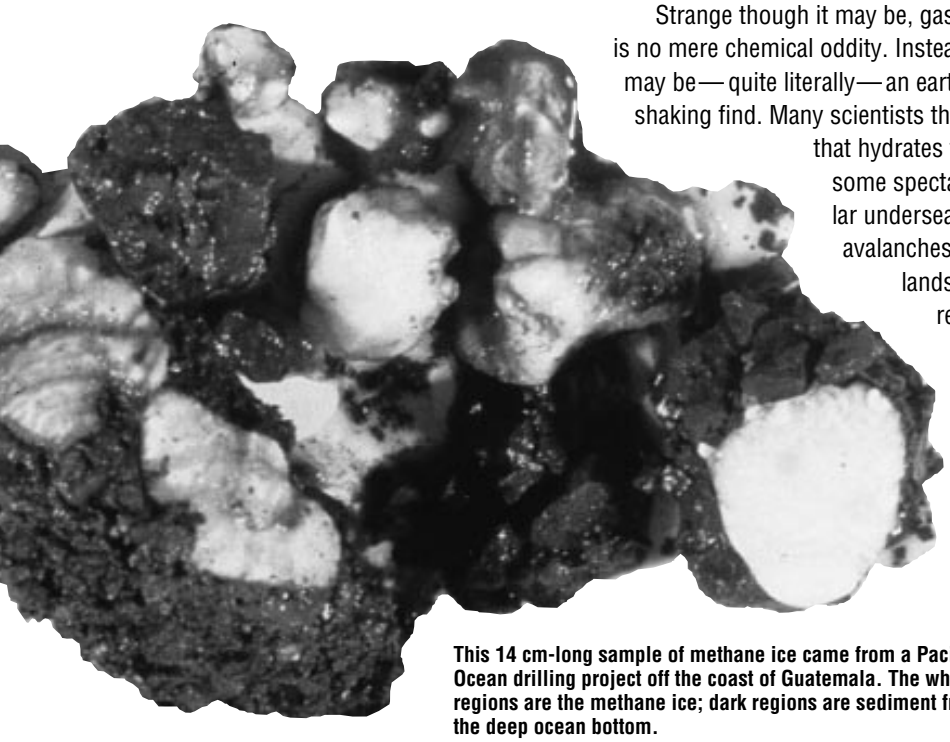
by Peter Banks



Undersea explorers usually quest after the exotic: sunken ships, strange new species, or the dramatic trenches and canyons of the ocean floor. But when an international team of ocean researchers sets sail off the Carolinas in October 1995, they'll be probing the seabed for something that looks like nothing more than dirty ice.

Yet this ice, a mixture of water and natural gas called gas hydrate, is nothing like ice you might pull from the freezer. Exposed to atmospheric conditions, it fizzes away in minutes, leaving behind a puddle of water and a few bubbles of gas. Strike a match to an icy gas hydrate chunk, and it actually burns like a charcoal briquette.

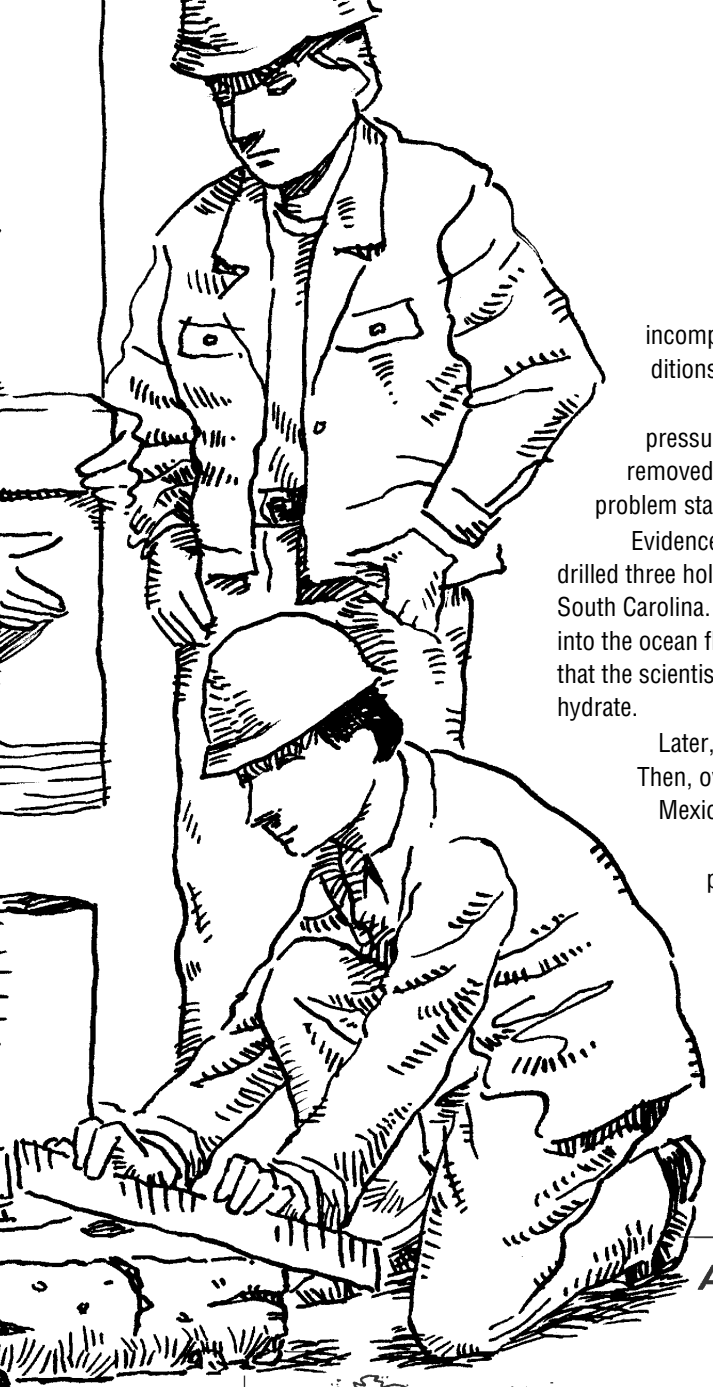
Strange though it may be, gas hydrate is no mere chemical oddity. Instead, it may be—quite literally—an earth-shaking find. Many scientists think that hydrates trigger some spectacular undersea avalanches and landslides that release clouds of methane, the main component of natural gas. Because methane in the atmosphere traps heat, these ocean eruptions may lead to global warming and may have helped end ice ages in the past (see Figure 1). What's more, gas hydrate deposits worldwide may contain vast quantities of natural gas for energy—if a way can be found to pipe it up from the ocean bottom.



This 14 cm-long sample of methane ice came from a Pacific Ocean drilling project off the coast of Guatemala. The white regions are the methane ice; dark regions are sediment from the deep ocean bottom.

PHOTO COURTESY KEITH A. KVENVOLDEN, U.S. GEOLOGICAL SURVEY.

So far, what we know about gas hydrates comes mainly from indirect measurement, because it is notoriously difficult to capture and study up close. "I've never seen natural gas hydrate," admits Charles Paull, the University of North Carolina geologist who will serve as one of the chief scientists for the expedition this fall. "People and gas hydrates are fundamentally



incompatible: We die under conditions they're stable in, and they decompose under conditions we're comfortable in."

Gas hydrates first came to attention in the 1930s, as a nuisance affecting high-pressure gas pipelines. Gas companies found that, unless all of the water was carefully removed from gas, chunks of gas hydrate would form and clog the pipes. The pipeline problem started scientists asking whether gas hydrate could also form in nature.

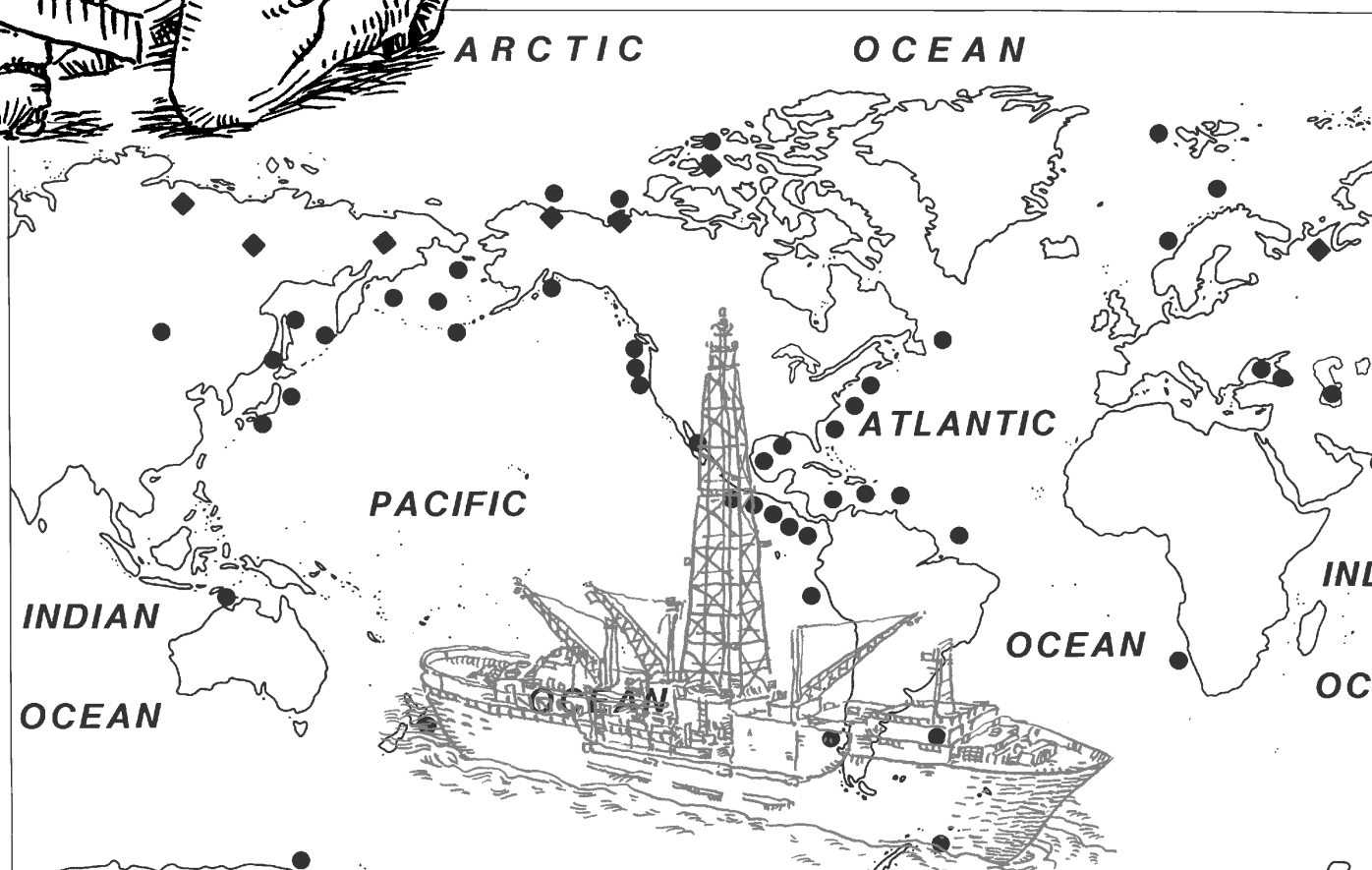
Evidence that it does didn't come for almost 40 years. Then, in May 1970, scientists drilled three holes in the Blake Outer Ridge, a patch of ocean floor off the coast of North and South Carolina. What they found was puzzling. The cylindrical core samples gathered by drilling into the ocean floor fizzed, expanded, and oozed out of their collection tubes. It wasn't until later that the scientists realized that they had witnessed for the first time the breakdown of natural gas hydrate.

Later, in 1974, Soviet scientists pulled some fizzy chunks of hydrate from the Black Sea. Then, over the next few years, drillers found more hydrate deposits in the ocean floor off Mexico and Guatemala.

It soon became apparent that gas hydrates form in abundance under high pressure and low temperature. Such inhospitable conditions exist beneath the permanently frozen soil of the polar regions and in ocean floor sediments where the water is deeper than 300 to 500 meters. At this depth, the pressure is 30 to 50 atmospheres.

All that's needed for gas hydrate is a source of methane. And there's plenty of that, from bacteria that give off methane as a waste product and from gas that leaks upward along fractures in rocks from traps deeper in the earth.

● = ocean gas hydrate deposits
◆ = permafrost gas hydrate deposits



Gas hydrate might be described as a "jailhouse rock" in which water molecules form ice cages to trap methane (see Figure 2). The water molecules array themselves in 12-sided cages. Within each cage, a molecule of methane can vibrate or rotate, but not slip out.

Because the cages pack in methane tightly, gas hydrate efficiently traps large amounts of methane. Each cubic foot of hydrate can lock up gas that, at room conditions, would occupy 160 cubic feet.

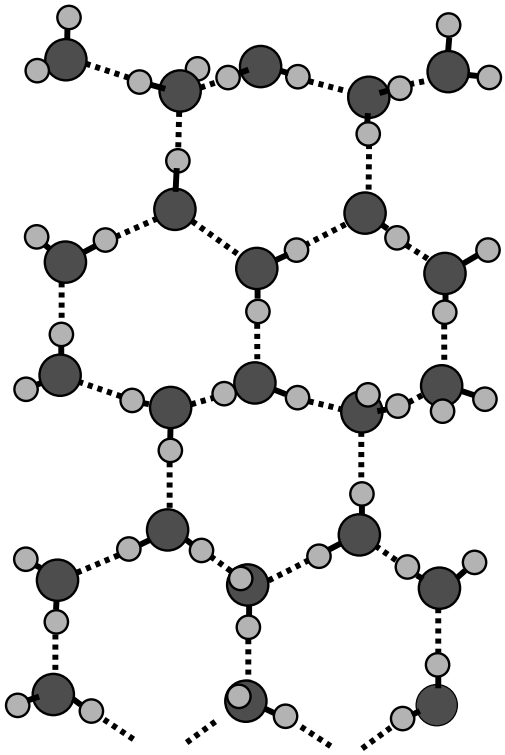
It's no surprise, then, that regions of the ocean floor with rich deposits of gas hydrates contain staggering amounts of methane. Within the Blake Outer Ridge, from 200 to 600 meters beneath the sea floor, there may be more than 100 cubic kilometers of gas hydrate in an area of only 3000 square kilometers, estimates William Dillon of the U.S. Geological Survey (USGS) in Woods Hole, Massachusetts. That amounts to about 630 trillion cubic feet of methane, or more than 30 times the yearly gas consumption in the U.S. "The volumes are immense," says Dillon.

And Dillon should know. He and other hydrate-watchers have spent the past several years trying to measure how much gas hydrate exists under the ocean floor. Because it is difficult to take a look at hydrate deposits directly, Dillon and other geologists use seismic waves for measurement. Seismic waves are the kind of earth-traveling shock waves that let a person in Las Vegas feel an earthquake in Los Angeles. By creating such seismic waves, and analyzing what waves are reflected back from the ocean floor sediments, it is possible to tell whether hydrates are really present and to estimate the amounts. Scientists create these seismic waves with "guns" that shoot compressed air at the ocean floor. Signals that echo back from the deep are picked up by a series of underwater microphones—called hydrophones—towed behind the research ship.

Impressive as these methods are, however, their accuracy still needs to be confirmed with direct measurements of hydrate. And that is where ocean drilling comes in. For several years, the National Science Foundation has supported the Ocean Drilling Program (ODP), in part to measure the makeup of hydrate reserves.

At first, says Keith Kvenvolden of the USGS in Menlo Park, California, ODP drillers were not allowed to drill though the base of the hydrate deposits. Scientists feared that there might be a pool of free methane gas under high pressure just below the hydrate, and that puncturing the hydrate could cause methane to spew out. "We thought we might have an uncontrolled blowout," says Kvenvolden. But recent drilling off the coasts of Chile and Canada showed that there was probably little danger of a methane eruption.

The drilling this fall off North Carolina is the latest leg of the ODP research. Paull and the team of scientists on board the research ship plan to start drilling into the hydrate-rich regions of the Blake Outer Ridge. To see how much hydrate is present, the researchers will try to haul up hydrates from the ocean floor sediments in special barrels that maintain samples under the same pressure found under the ocean floor. Contained like this, the hydrate may stick around long enough for tests.



Ordinary Ice

One of the major ways the researchers will measure the amount of gas hydrate is by checking the concentration of seawater ions. When hydrates form their icy cages, they trap methane but push out ions such as chloride. When samples of ocean floor sediment containing gas hydrates are fished up

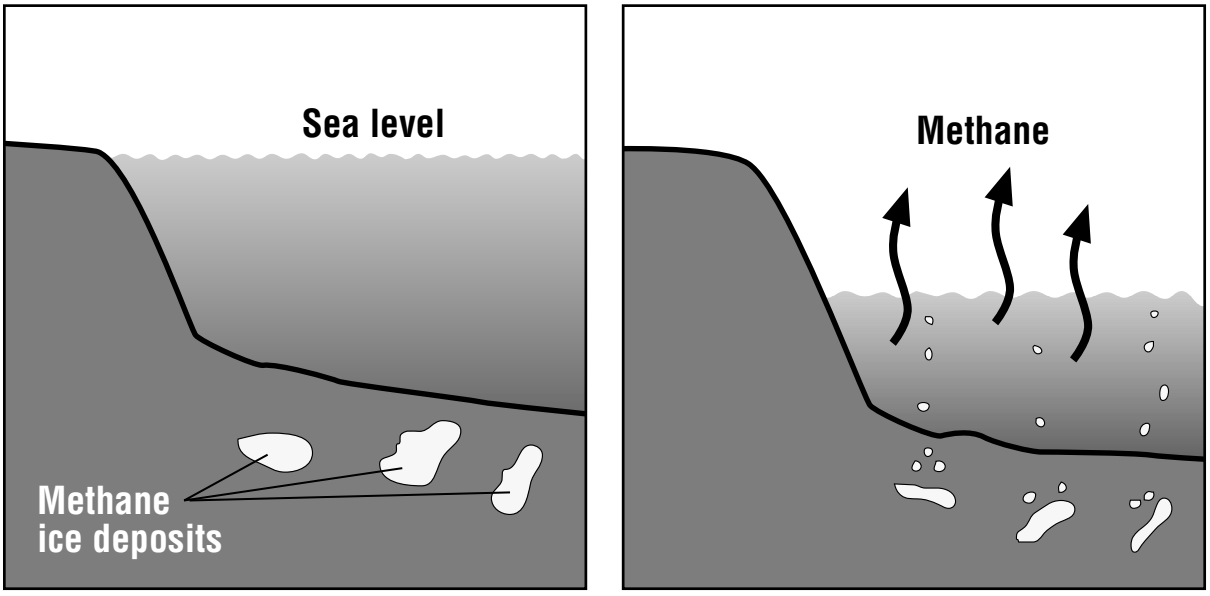


FIGURE 1. Most methane ice deposits are found under the ocean bottom where they are held in the solid state by the cool temperatures and the pressure of the water above. During an ice age, the sea level drops and the reduced pressure can release methane, a greenhouse gas, into the atmosphere. This can warm the earth and reduce the effect of the ice age.

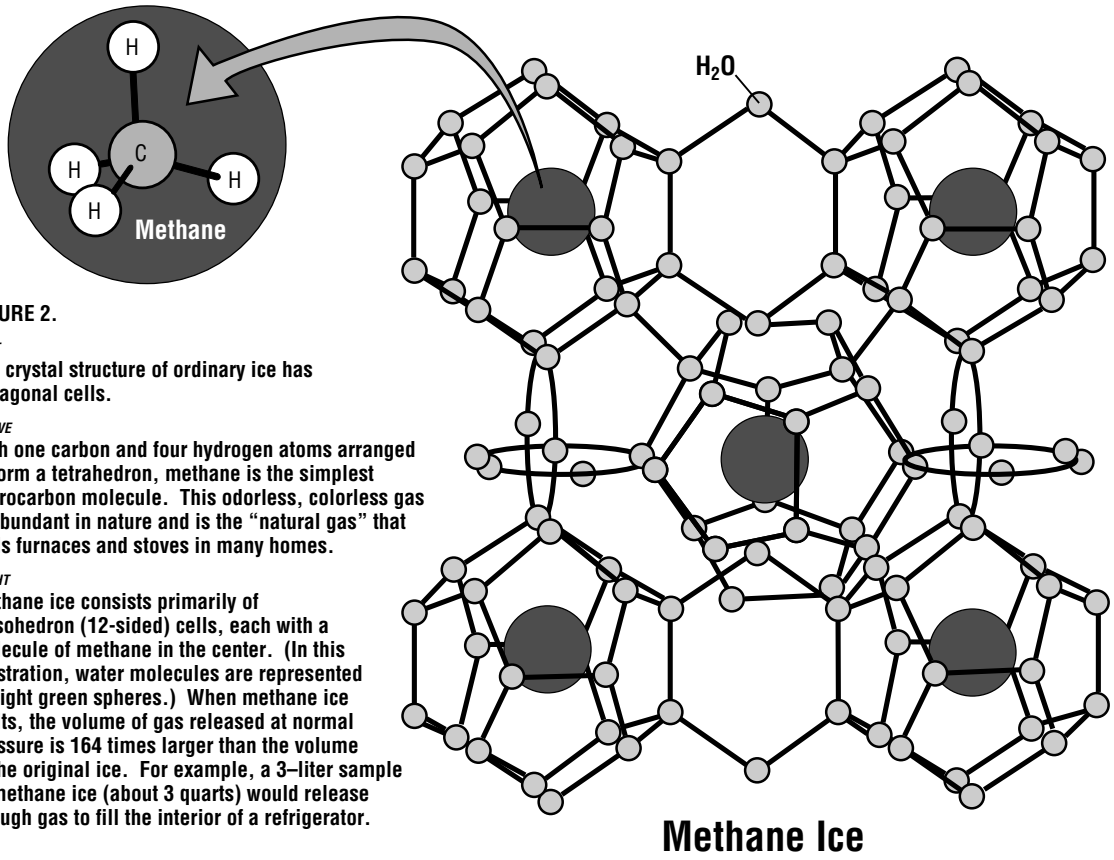


FIGURE 2.

Left
The crystal structure of ordinary ice has hexagonal cells.

Above
With one carbon and four hydrogen atoms arranged to form a tetrahedron, methane is the simplest hydrocarbon molecule. This odorless, colorless gas is abundant in nature and is the "natural gas" that fuels furnaces and stoves in many homes.

Right
Methane ice consists primarily of icosohedron (12-sided) cells, each with a molecule of methane in the center. (In this illustration, water molecules are represented as light green spheres.) When methane ice melts, the volume of gas released at normal pressure is 164 times larger than the volume of the original ice. For example, a 3–liter sample of methane ice (about 3 quarts) would release enough gas to fill the interior of a refrigerator.

and melted, the water has much less chloride than ordinary seawater. The more hydrate, the less chloride there will be. Thus the water in the pores of the sample gives an indication of the concentration of gas hydrate.

If the drilling off the Carolina coasts does prove the presence of high concentrations of methane in hydrate form, it will mean that a source of untapped energy awaits not far offshore. But recovering the methane won't be easy. Releasing the gas would mean creating conditions in which hydrate breaks down and releases its free methane so it can be piped to the ocean surface. Scientists have proposed pumping warmer fluid into the hydrate to melt it or reducing the deepwater pressures hydrates need to survive. So far, the technology to accomplish either feat on a large scale has not been perfected. "Wide-scale recovery of methane… probably will not take place until sometime in the 21st century," says Kvenvolden.

Even if hydrates could be enticed to give up their methane, there are some potential dangers in doing so. Gas hydrate acts as a kind of cement to keep ocean floor sediments together. Some scientists think that tampering with gas hydrate deposits could lead to underwater landslides that would expose veins of hydrates and possibly lead to large amounts of methane bubbling up. This could have serious consequences for the environment, because methane is a "greenhouse gas." Just as the glass windows of a greenhouse let in light but don't let heat escape, gases in the atmosphere let in sunlight but don't allow heat to escape. Compared with the most common greenhouse gas, carbon dioxide, methane is up to 50 times more effective at trapping heat.

There are some clues that underwater landslides do take place in nature, and another of the objectives of the October drilling project will be to see whether hydrates play a role in this slipping and sliding. Paull speculates that within the hydrate deposits, hydrate cements the ocean floor sediments together and keeps them mechanically strong. Deeper down, however, the warmth from deeper in the earth prevents the formation of hydrates. Instead of hydrate, methane exists in what Paull calls "water–gas mush." Where the sea floor slopes down, as it does in the Blake Outer Ridge, that layer of mush may act like a layer of "grease" to let the heavier sediment on top of it go sliding down the slope. This explanation, though not proven, could account for the landslide scars that dot the sea floor off the East Coast.

Paull and other scientists think that gas hydrates also may have had something to do with ending the last ice age. When the last ice age peaked about 17,000 years ago, ice sheets pulled enough water from the oceans to lower the sea level about 120 meters. The fall in sea level would have reduced the pressure on hydrates, causing them to become unstable and possibly to burp up methane. If enough methane was released to produce a greenhouse effect, ice would begin to melt and the sea level would rise again; that, in turn, would flood frozen ground in the Arctic regions, melting more hydrate and releasing even more methane. The new ODP drilling project should shed some light on whether methane hydrate appears likely to play this kind of climate control function. Whatever the results from the ODP drilling off the Carolinas, hydrate researchers are almost certain to be treated to some final answers about the fuel potential of hydrates by the year 2000. Japan, which has far greater need for methane than does the United States, is set to start a five-year project that will end in exploratory drilling to see whether methane can in fact be recovered from hydrates.

"This is very exciting," says USGS's Kvenvolden, who has spent 20 years in hydrate research. "It means we'll know the answer in my lifetime."

***Peter Banks** is a freelance writer living in Fairfax, VA. This article is his first contribution to* Chem Matters *magazine.*

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Chemiluminescence, the Cold Light

by Gail B.C. Marsella



Imagine yourself on vacation at an ocean resort. On the boardwalk you buy a tubelike necklace that lights up—without batteries. Leaving the boardwalk at dusk, you notice the random flashing of the evening's first fireflies. At the dock, an old sailor tells about the wake of a ship lighting up at night—looking almost on fire.

The lights in the necklace, fireflies, and glowing ocean are all caused by *chemiluminescence*—light made by a chemical reaction that produces light but no heat, cold light.

Any source of light—whether luminescent or incandescent (the glow emitted by a very hot object)—can be traced back to the absorption of energy and its release as light. To understand the process of absorbing energy and emitting light, imagine an electron on a roller coaster ride. Ordinarily the electron is on the ground. When it gets on the ride, energy pushes it up. The electron can only go as high as the tallest hill of the roller coaster and no farther. It's not stable up there, either, and must come back down. As it returns to the ground, at great speed, it emits its version of a scream—light of a single wavelength. As long as energy is available to push more electrons up, they line up for the roller coaster, and the light continues to shine.

Light on a stick

You have probably seen a Light Stick, a plastic tube that is often stored in an emergency survival kit instead of a flashlight. Once activated, the Light Stick glows brightly for many hours. How can it do this?

The light stick is actually a tube inside a tube. The large outer tube is made of flexible, translucent plastic. Inside is a solution of an oxalate ester and a fluorescent dye, as well as a smaller glass tube that contains hydrogen peroxide. When you bend the stick, a thin glass tube breaks inside the larger plastic tube, and the chemicals can mix and react (see Figure 1 on p. 14). The chemical reaction provides the energy to excite the electrons.



Glowing bacteria. This dish was swabbed with the saliva of a TB patient. Later luciferin—discovered in fireflies—was added and the TB bacteria glowed. This new technique helps doctors select the most effective anitbiotic.

Living light

The chemiluminescent reactions found in living organisms are called *bioluminescence*. Living things have found many charming ways to use cold light. Certain mosses glow in the dark. Rotting tree stumps give off an eerie light that has been called foxfire. In the nighttime ocean, invertebrates send a wide variety of luminous messages: Go away! Look out! Come up and see me sometime!

A small ocean crustacean called the fireflea can generate a tremendous amount of light and communicates with others of its own species and with predators. Groups of male firefleas attract females by emitting patterns of light, flashing synchronously. A group of firefleas can emit a single large flash, probably as an alarm.

Fireflies and firefleas make their own bioluminescent chemicals, but most bioluminescence depends on bacteria. Sometimes the bacteria live with another larger organism, which uses the bacteria's light to hunt food and frighten predators. The flashlight fish, for example, has sacs of luminous bacteria near its eyes. The bacteria glow continuously, but the fish can cover and uncover the sacs with flaps of skin, like putting a Light Stick in your pocket and taking it out again. They search for food with their lights, blink to attract other members of their species, and confuse their predators by flashing and changing direction rapidly. Flashlight fish live very deep in the ocean, where the dark is complete.

The black dragon fish is even more sophisticated. It gives off a red light that most other species cannot see. The dragon fish can see red, so it can see its prey, but the prey can't see it!

Scientists have discovered that bacteria and fireflies produce light by mixing luciferin and luciferase in the presence of oxygen and energy-rich ATP (adenosine 5´-triphosphate). Luciferase is an enzyme, or biological catalyst, that makes the reaction go faster. ATP provides the energy to excite the electrons, and luciferin, shown in Figure 2, is one of the relatively rare molecules that gives off energy as light rather than heat.

Diagnosing TB—light work

The luciferin and luciferase reaction of fireflies has emerged as an important tool for diagnosing tuberculosis (TB), a serious lung disease. In the 1930s, TB was a lethal plague and people infected by the contagious bacterium were isolated in TB sanitariums—far from any city. In the 1940s, antibiotics that could kill the bacteria were discovered, and the sanitariums began to close. By 1960, doctors believed that the disease had been practically eliminated from the United States, although it still flourished in less developed countries. Recently, however, tuberculosis has made a comeback in developed countries because some strains of the bacteria are resistant to antibiotics. TB is increasing among our homeless population; in

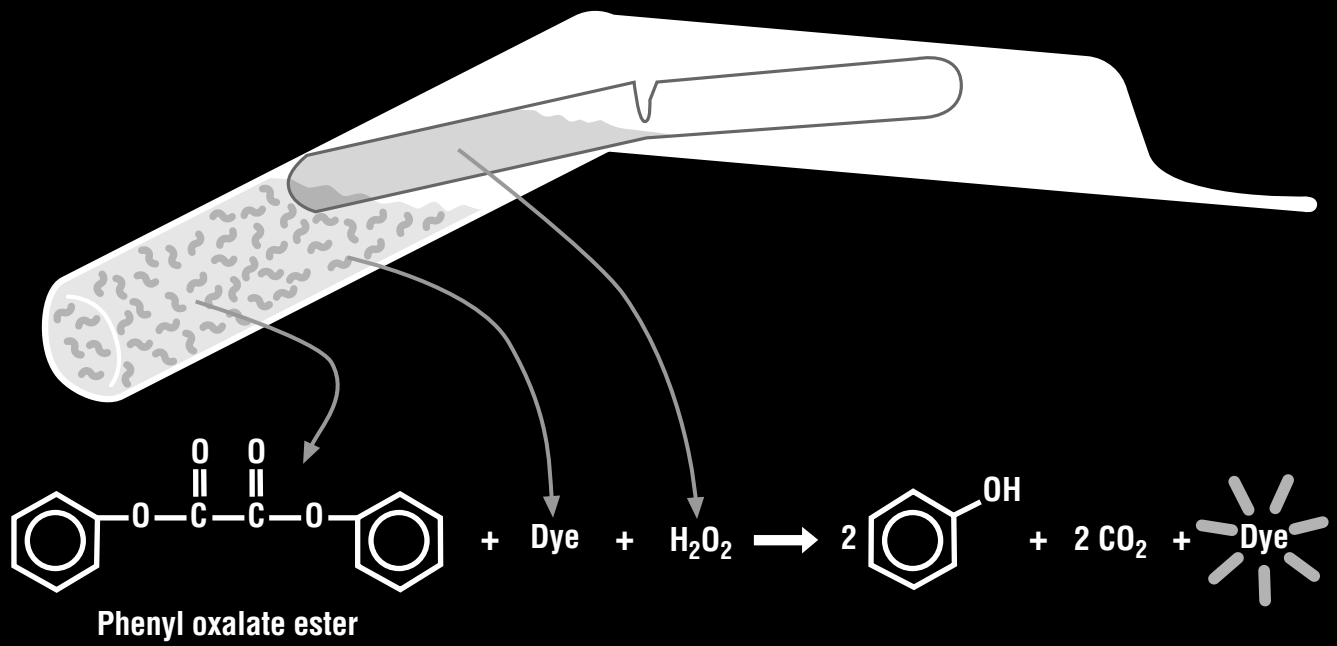


FIGURE 1. The Light Stick is actually a tube inside a tube. When you activate it by bending the flexible outer tube, the inner glass tube breaks, which releases hydrogen peroxide into the solution in the larger tube and starts the chemical reaction. The oxalate ester and hydrogen peroxide react to form carbon dioxide, phenol, and energy; another chemical transfers the energy to the dye molecules. Some of the electrons in the dye molecule are raised to an excited state; when the electrons fall to their original state, they give off light.

1992, 28,000 cases were reported in the United States.

When a new case of TB is discovered, the doctor wants to begin treatment with antibiotics immediately—but which antibiotic? The question can be answered by taking a saliva sample from the patient, plating it on a growth medium in a Petri dish, and waiting for the bacteria to multiply until the colony grows to visible size and can be tested. However, the TB bacterium grows so slowly that a couple of months may go by before a lab has any idea which of several drugs would work best for the patient. Recently, a new chemiluminescent test has been devised that gives results in just a couple of days. The key was moving a gene from a firefly to a virus.

The test, developed in the laboratories of microbiologists William Jacobs and Barry Bloom (Albert Einstein College of Medicine) and Graham Hatfull (University of Pittsburgh), is simple in theory. Several saliva samples are taken from the TB patient and are placed in separate Petri dishes for a day or two. This allows the bacteria to multiply briefly, but the bacterial colony is still too small to be seen. Each dish is then treated with a different set of antibiotics and, after a waiting period, all the samples are inoculated with the modified virus.

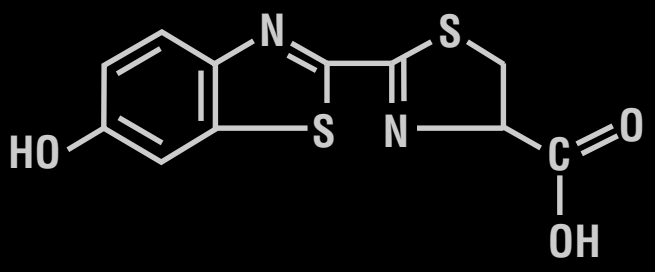


FIGURE 2. Luciferin is a generic term for a wide variety of compounds that emit light when oxidized by the enzyme luciferase. Many of the luciferins isolated from different species vary greatly in structure, although identical structures have been found in widely diverse animals. Firefly luciferin, shown above, has been isolated from the American firefly and the Japanese firefly. Researchers were forced to collect 17,000 active fireflies to obtain 10 milligrams of luciferin.

Researchers altered the genetic material of the virus so that it carries a firefly gene for making the luciferase enzyme. The virus infects the tuberculosis bacteria and thereby implants the luciferase gene into the bacteria's genetic material. This causes the bacteria to begin making luciferase. Finally, luciferin is added to all the samples. The live bacteria that contain luciferase begin to glow. This small number of bacteria would normally be undetectable, but when they light up, it is like switching on a flashlight in a dark room to signal "Here I am!" The bacteria samples that give off light are still alive and thus resistant to the drugs. The bacteria that were sensitive to the antibiotics do not glow because they were killed before they were exposed to the virus. The doctor can select the best antibiotic and administer it to the patient immediately.

"This is a very important breakthrough," says Lee Reichman, president of the American Lung Association and director of the New Jersey Medical School National Tuberculosis Center. "When it takes 13 weeks to make a decision as to whether someone has resistant organisms, you run the risk of having some people not respond [because they are being treated with the wrong drugs] and give resistant TB to others. If [a patient] is treated appropriately, he very rapidly becomes noninfectious."



For decades, chemiluminescence was a scientific novelty and researchers pursued the firefly simply to understand how it worked. Today, the firefly gene is at the center of an extraordinarily sensitive medical test. And the test comes none too soon. Worldwide, TB still kills 3 million people each year.

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FOR FURTHER INFORMATION:

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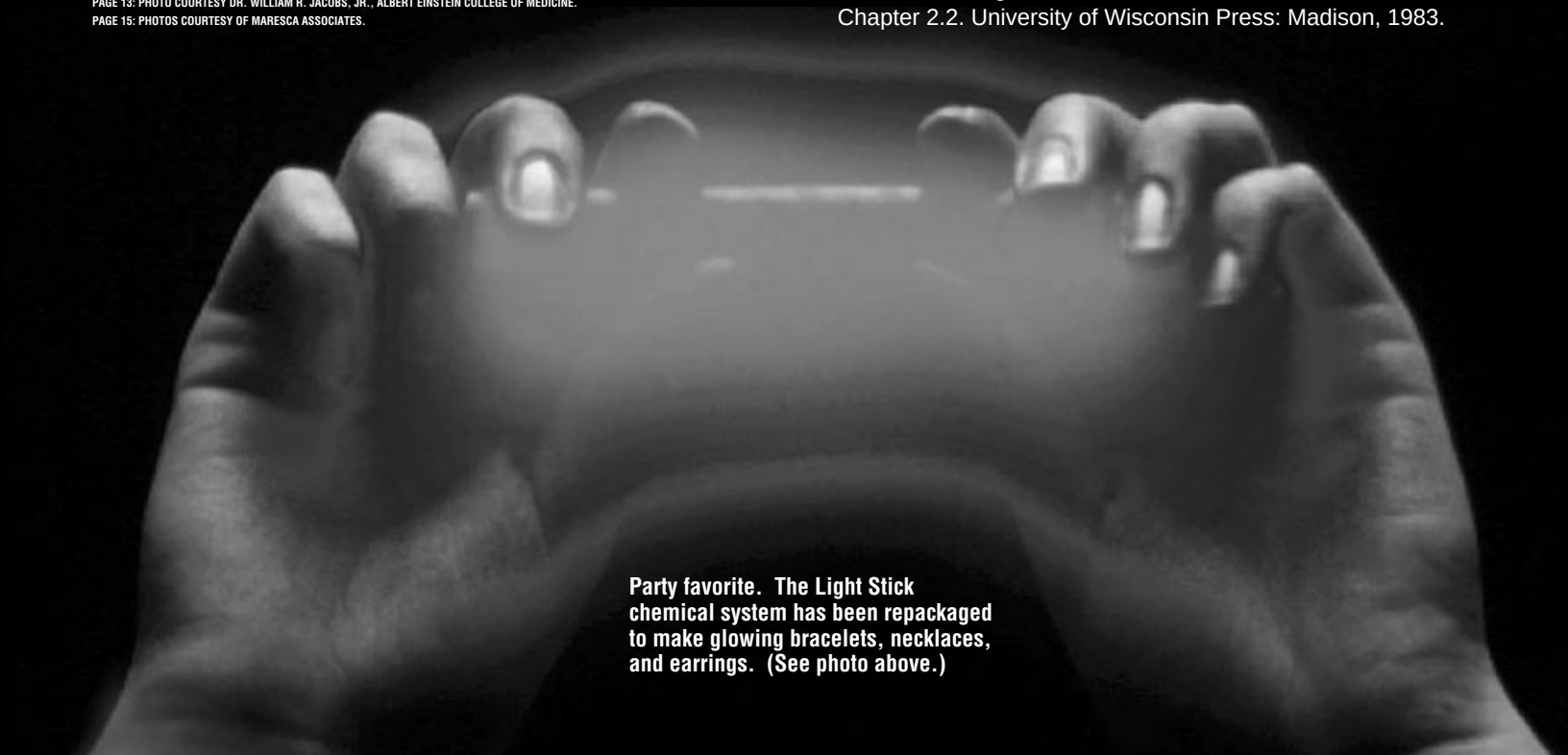
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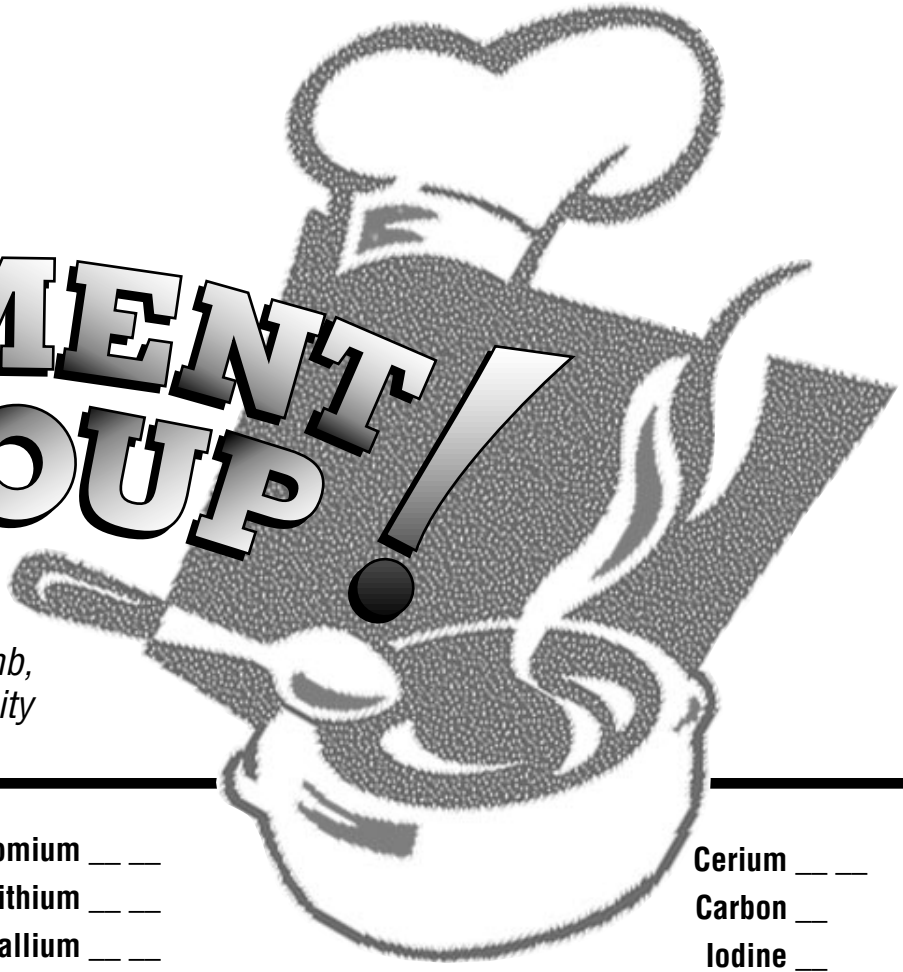
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Party favorite. The Light Stick chemical system has been repackaged to make glowing bracelets, necklaces, and earrings. (See photo above.)

ELEMENT SOUP!

by Dorothy Mann Lamb,
Chicago State University



Write the symbols of the elements and then rearrange their letters in the colored spaces to produce all the ingredients for a delicious element soup.

Chromium __ __
Lithium __ __
Gallium __ __

_ _ _ _ _ _ _

Phosphorus __
Astatine __ __
Osmium __ __
Tellurium __ __
Oxygen __

_ _ _ _ _ _ _ _ _

Argon __ __
Strontium __ __
Oxygen __
Technetium __ __

_ _ _ _ _ _ _ _

Argon __ __
Tellurium __ __
Tungsten __

_ _ _ _ _ _

Einsteinium __ __
Protactinium __ __

_ _ _ _ _

Nickel __ __
Nobelium __ __
Sulfur __
Oxygen __

_ _ _ _ _ _ _

Cerium __ __
Carbon __
Iodine __
Hydrogen __
Nitrogen __
Potassium __

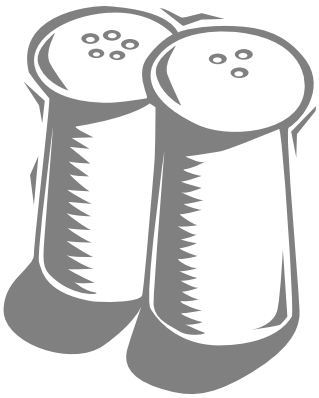
_ _ _ _ _ _ _ _

Yttrium __
Lanthanum __ __
Selenium __ __
Praseodymium __ __

_ _ _ _ _ _ _ _

Thallium __ __
Arsenic __ __

_ _ _ _



Answers on page 3

Answers