UNIT 3: ATOMIC THEORY

LAB	ARTICLE
#8: FLAME TESTS	FIREWORKS
#9: ATOMIC BULLS-EYE-MODERN THEORY OF THE ATOM	A CHEMIST COMES VERY CLOSE TO A MIDAS TOUCH
#10: BEANIUM-AVERAGE ATOMIC MASS	REAL OR FAKE? THE JAMES OSSUARY CASE

FIRE

By Kathy De Antonis

Fireworks are one of the most spectacular outdoor shows. They produce amazing bursts of colors that take a variety of shapes. But how do they work? How do they burn into so many colors and patterns? And why, if not handled properly, can they cause serious injuries or even death?

What's inside a firework?

The source of most fireworks is a small tube called an aerial shell that contains explosive chemicals. All the lights, colors, and sounds of a firework come from these chemicals.

An aerial shell is made of gunpowder, which is a well-known explosive, and small globs of explosive materials called stars (Fig. 1) The stars give fireworks their color when they explode. When we watch fireworks, we actually see the explosion of the stars. They are formed into spheres, cubes, or cylinders that are usually 3–4 centimeters (1–1½ inch) in diameter.

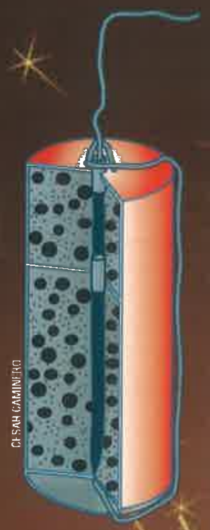

CESAR CAMINERO

Figure 1. Structure of an aerial shell. The black balls are the stars, and the gray area is gunpowder. The stars and the powder are surrounding a bursting charge, which also contains black powder.

Each star contains four chemical ingredients: an oxidizing agent, a fuel, a metal-containing colorant, and a binder. In the presence of a flame or a spark, the oxidizing agent and the fuel are involved in chemical reactions that create intense heat and gas. The metal-containing colorant produces the color, and the binder holds together the oxidizing agent, fuel, and colorants.

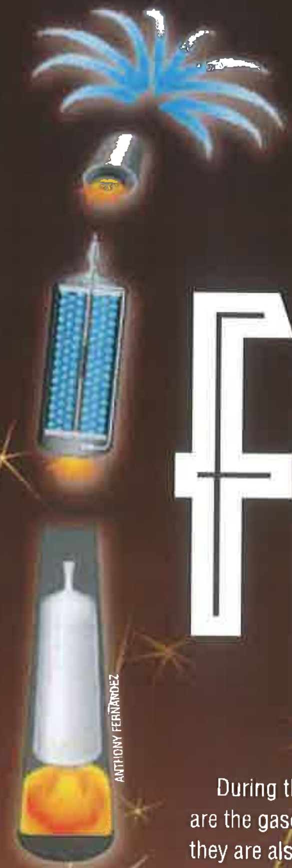
At the center of the shell is a bursting charge with a fuse on top. Igniting the fuse with a flame or a spark triggers the explosion of the bursting charge and of the entire aerial shell.

How fireworks explode

The explosion of a firework happens in two steps: The aerial shell is shot into the air, and then it explodes in the air, many feet above the ground.

To propel the aerial shell into the air, the shell is placed inside a tube, called a mortar, which is often partially buried in sand or dirt. A lifting charge of gunpowder is present below the shell with a fuse attached to it. When this fuse, called a fast-acting fuse, is ignited with a flame or a spark, the gunpowder explodes, creating lots of heat and gas that cause a buildup of pressure beneath the shell. Then, when the pressure is great enough, the shell shoots up into the sky.

After a few seconds, when the aerial shell is high above the ground, another fuse inside the aerial shell, called a time-delay fuse, ignites, causing the bursting charge to explode. This, in turn, ignites the black powder and the stars, which rapidly produce lots of gas and heat, causing the shell to burst open, propelling the stars in every direction.

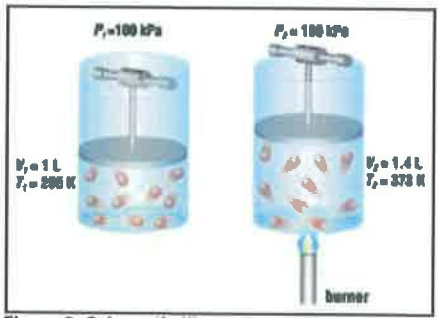

ANTHONY FERNANDEZ

During the explosion, not only are the gases produced quickly, but they are also hot, and they expand rapidly, according to Charles' Law, which states that as the temperature of enclosed gas increases, the volume increases, if the pressure is constant (Fig. 1). The loud boom that accompanies fireworks is actually a sonic boom produced by the expansion of the gases at a rate faster than the speed of sound!

If the stars are arranged randomly in the aerial shell, they will spread evenly in the sky after the shell explodes. But if the stars are packed carefully in predetermined patterns, then the firework has a specific shape—such as a willow, a peony, or a spinner—because the stars are sent in specific directions during the explosion.

The timing of the two fuses is important. The fast-acting fuse ignites first, propelling the shell into the air, and then the time-delay fuse ignites to cause the aerial shell to explode when it is high in the sky. If the timing of the fuses is not just right, the shell can explode too close to the ground, injuring people nearby.

WORKS!



ANTHONY FERNANDEZ

Figure 2. Schematic illustration of Charles' Law. When the pressure of a volume of gas is constant, an increase in temperature leads to a proportional increase in the volume of the gas. The gas molecules move faster at higher temperatures.

Where do fireworks' colors come from?

What makes fireworks so special is the beautiful colors they produce. These colors are formed in one of two ways: luminescence and incandescence.

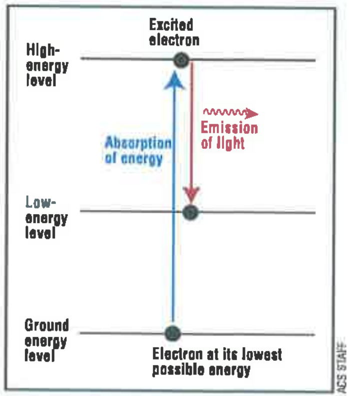
Incandescent light is produced when a substance is heated so much that it begins to glow. Heat causes the substance to become hot and glow, initially emitting infrared, then red, orange, yellow, and white light as it becomes increasingly hotter. When the temperature of a firework is controlled, the glow of its metallic substances can be manipulated to be a desired color at the proper time.

ISTOCK

More often, light from fireworks is produced by luminescence. When fireworks explode in the sky, the gunpowder reactions create a lot of heat, causing the metallic substances present in the stars to absorb energy from the heat and emit light. These metallic substances are actually metal salts, which produce luminescent light of different colors when they are dispersed in the air.

This light is produced by electrons inside the metal atoms (Fig. 3). These electrons absorb energy from the heat, which causes them to move from their original ground-energy state to an excited state. Then, nearly immediately, these electrons go to a lower energy state and emit light with a particular energy and characteristic color.

The color of the light emitted by the electrons varies depending on the type of metal or combination of metals. So, the colors are specific to the metals present in the fireworks. The metal-containing colorants for some common fireworks are listed in Table 1.



ACS STAFF

Figure 3. Principle of luminescence. Heating atoms causes electrons to move from their ground-energy level to a higher energy level (blue arrow). When the excited electrons move to a lower energy level (red arrow), they emit light with a specific energy and characteristic color.

Fireworks' safety

Fireworks are a lot of fun to watch, but they must be handled with great care because they can be dangerous. "When using fireworks, one should follow the label directions very carefully and have an adult in charge," says John Conkling, an adjunct professor of chemistry at Washington College, Chestertown, Md., and former executive director of the American Pyrotechnics Association.

Color	Compound
red	strontium salts, lithium salts lithium carbonate, Li_2CO_3 = red strontium carbonate, $SrCO_3$ = bright red
orange	calcium salts calcium chloride, $CaCl_2$
yellow	sodium salts sodium chloride, NaCl
green	barium compounds + chlorine producer barium chloride, $BaCl_2$
blue	copper compounds + chlorine producer copper(I) chloride, CuCl
purple	mixture of strontium (red) and copper (blue) compounds

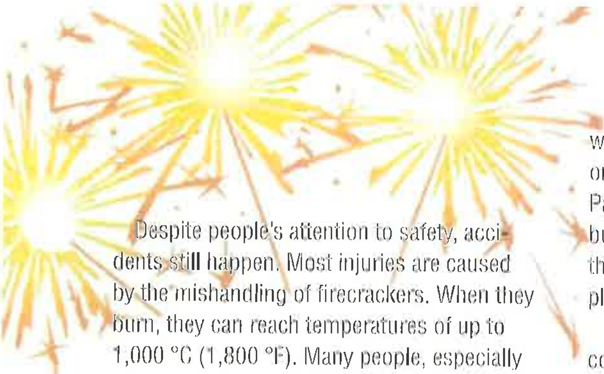
HTTP://WWW.SCIFUN.ORG/ ; PROF. BASSAM Z. SHAKHASHIRI, UNIVERSITY OF WISCONSIN-MADISON

Table 1. Colorant compounds used in fireworks and the colors they produce.

Knowing the rules and regulations is important, too. According to Conkling, fireworks that are publicly available in stores are legally allowed in 41 of the 50 U.S. states. So, you may not be able to purchase fireworks if your state does not allow it.

Also, regulations require that consumer fireworks should have no more than 50 milligrams (about 1/500th of an ounce) of gunpowder. This may seem like a relatively small amount. But don't be fooled. Even 50 milligrams of gunpowder or less can cause serious injuries. "You would be surprised by how powerful fireworks can be," says Doug Taylor, president of Zambelli Fireworks, one of the largest fireworks companies in the United States.

Some fireworks contain more than the limited amount of 50 milligrams. Although they are illegal, such fireworks—which include the "cherry bombs" and "M-80s"—can be found in some stores or on the black market and cause even more damage.



Despite people's attention to safety, accidents still happen. Most injuries are caused by the mishandling of firecrackers. When they burn, they can reach temperatures of up to 1,000 °C (1,800 °F). Many people, especially children, are burned by them.

Accidents involving fireworks occur every year. They cause field and house fires and result in injuries and deaths. Many of the accidents involve young people. For instance, in 2009, a 17-year-old boy in Latrobe, Pa., lost his right hand and leg after an M-80 firework exploded in his lap.

Another case involved teenagers who were playing with fountain fireworks—aerial fireworks that shoot up tall fountains of sparks—on the front porch of a duplex home in St. Paul, Minn., when a fire broke out. The flames burned through the second floor and reached the roof, resulting in nine people being displaced from their homes.

Because of the danger associated with consumer fireworks, the American Academy of Pediatrics recommends that children and young adults avoid them altogether and attend local aerial fireworks demonstrations instead. Taylor says watching aerial fireworks can be very moving. "One of the grandchildren of the founder of Zambelli Fireworks was known for saying, 'Grandpa, I like your fireworks because I can feel them in my heart,'" he says. "That's so true! It's really an emotional experience." ▲

SELECTED REFERENCES

Chemistry of Firework Colors: http://chemistry.about.com/od/fireworkspyrotechnics/a/fireworkcolors.htm [accessed June 2010].

Fireworks! NOVA Online/Public Broadcasting Service (PBS): http://www.pbs.org/wgbh/nova/fireworks/ [accessed June 2010].

Fireworks Safety: http://pediatrics.about.com/od/safety/a/0607_fireworks.htm?p=1 [accessed June 2010].

Finn, R. The Island; Finding Refuge in the Family Fireworks. *The New York Times,* July 2, 2006: http://query.nytimes.com/gst/fullpage.html?res=9A0DE4DE1430F931A35754C0A9609C8B63 [accessed June 2010].

Kathy De Antonis is a science writer who lives in Old Saybrook, Conn. Her latest *ChemMatters* article, "Space Food," appeared in the December 2009 issue.

INTERVIEW WITH PYROTECHNIC CHEMIST JOHN CONKLING

JOHN CONKLING

During the past 30 years, John Conkling, a fireworks expert at Washington College, Chestertown, Md., has made more than 40 trips to China—the world's major producer of fireworks—to meet with officials from the Chinese fireworks industry. He is the author of *The Chemistry of Pyrotechnics—Basic Principles and Theory*, which many consider the most definitive reference on pyrotechnics, and he holds nine patents dealing with energetic chemical systems. Conkling explains what pyrotechnic chemists do.

What do pyrotechnic chemists do?

They combine compounds to make a mixture that can explode to produce color, light, and audible effects, such as the sizzles, pops, and booms of fireworks. When these compounds are lit by a spark or a flame, explosive chemical reactions occur, creating the light and sound effects seen in fireworks.

The mixtures made by pyrotechnic chemists are used not only for entertainment, but also for emergency signaling–such as pink flares that people put on the road next to car accidents—and military applications, such as mixtures that produce effects visible only with night vision goggles.

How did you become a pyrotechnic chemist?

I was interested in all kinds of science as a child, and eventually, chemistry became my focus. I went to graduate school at Johns Hopkins University, Baltimore, Md., to pursue a Ph.D. in physical organic chemistry. The topic of my thesis (unusual reaction mechanisms involving "nonclassical" pathways) doesn't have much to do with what I do now, but it taught me the discipline of doing research and recording observations.

In 1969, I went on to teach undergraduate chemistry at Washington College, Chestertown, Md., which is where I pursued my undergraduate studies. Soon after that, I was approached by a fireworks company that wanted to hire me for a side project on developing chemical compositions for fireworks that are safe to carry and store. I became really interested in the chemistry of fireworks.

Later, the U.S. Army asked me if I was interested in working on some military pyrotechnic applications involving the production of brightly colored smoke for signaling purposes, and my pyrotechnic chemistry career shot off. Nowadays, I do training seminars for people interested in anything that explodes—from people who design and manufacture fireworks to people who dispose of bombs.

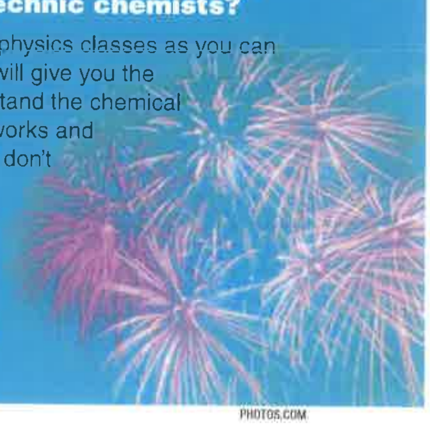
How do you make sure that fireworks are safe?

Mainly, you don't want compounds that explode as they fall on the ground. It's important to develop stable compounds that ignite only in the sky. Fireworks were invented hundreds of years ago, and we have learned through the centuries to avoid certain chemicals and mixtures that are too easy to ignite accidentally. There is also a big push now to make fireworks as environmentally friendly as possible.

Do you have any advice for students who want to become pyrotechnic chemists?

Take as many chemistry and physics classes as you can while in school. These classes will give you the background you need to understand the chemical reactions that take place in fireworks and other pyrotechnic devices. Also, don't experiment on your own with explosive materials! There are many easy ways to make explosives, but that does not mean they are safe.

—*Christen Brownlee*



PHOTOS.COM

The New York Times

October 15, 2012

A Chemist Comes Very Close to a Midas Touch

By HILLARY ROSNER

In a lab in Princeton University's ultra-sleek chemistry building, researchers toil in a modern-day hunt for an elusive power: alchemy.

Throughout the centuries, alchemists tried in vain to transform common metals like iron and lead into precious ones like gold or platinum. Today, Paul Chirik, a professor of chemistry at Princeton, has managed a new twist on the timeworn pursuit.

Dr. Chirik, 39, has learned how to make iron function like platinum, in chemical reactions that are crucial to manufacturing scores of basic materials. While he can't, sadly, transmute a lump of iron ore into a pile of valuable jewelry, his version of alchemy is far more practical, and the implications are wide-ranging.

The process could herald a new era of flexible manufacturing technologies, while enabling companies to steer clear of scarce elements as prices rise or obtaining them becomes environmentally or geopolitically risky.

"No chemist would think lithium was in short supply," Dr. Chirik said, "but what happens if you put a lithium battery in every car? This is why chemistry needs to be ahead of the curve. We need to have adaptable solutions."

Despite the cost and relative scarcity of precious metals — iridium, platinum, rhodium — we rely on them to manufacture products from denim to beer, pharmaceuticals to fuel cells. The elements are used as catalysts, substances that kick off or enable chemical reactions.

Dr. Chirik's work involves dissolved catalysts, which are mixed into the end product. The molecules of the catalyst dissipate during the reaction. For instance, a solution containing platinum is used to make silicone emulsifiers, compounds that in turn feed products like makeup, cookware and glue. Tiny amounts of the expensive metal are scattered in all these things; your jeans, for instance, contain unrecoverable particles of platinum.

"We're not about to run out of platinum," said Matthew Hartings, a chemist at American University in Washington, "but this process spends that platinum in a nonsustainable way."

Dr. Chirik's chemistry essentially wraps an iron molecule in another, organic molecule called a ligand. The ligand alters the number of electrons available to form bonds. It also serves as a scaffold, giving the molecule shape. "Geometry is really important in chemistry," Dr. Hartings said. Dr. Chirik's "ligands help the iron to be in the right geometry to help these reactions along."

In addition to iron, Dr. Chirik's lab also works with cobalt, which sits beside iron on the periodic table. Using cobalt, Dr. Chirik said, the scientists have generated "a whole new reaction that no one has ever seen before." It produces new types of plastics using very inexpensive starting materials.

But the price of cobalt has shot up since the lab first began its research, thanks to the element's use in the flat batteries that power gadgets like iPads and iPhones.

"The iPad has completely changed the price of cobalt," Dr. Chirik said, "so something that once was garbage is now valuable."

While the rising cost may undermine the economic incentive to use Dr. Chirik's cobalt-fueled materials, it seems to perfectly underscore his basic point about the need for flexibility.

"There's a broad appeal and logic to focusing on more abundant elements in designing catalysts," said Roderick Eggert, a professor of economics and business at the Colorado School of Mines.

A vast majority of the chemicals we manufacture and then use to make other products require catalysts. And a lot of catalysts use so-called noble metals like platinum, palladium and rhodium, which are expensive. A pound of platinum costs about $22,000. A pound of iron, meanwhile, costs about 50 cents.

As an undergraduate chemistry major, Dr. Chirik worked on reactions that used iridium as a catalyst. A pound of iridium costs about $16,000. Dr. Chirik's boss kept the iridium-based compound locked in a desk drawer.

"You had to walk from his office to the lab holding it with two hands, and not talk to anyone," Dr. Chirik recalled. The experience left him with the seed of an idea, he said. "Why can't we do this with something cheaper?"

On a spring afternoon at the Princeton lab, a graduate student toiled away at a glovebox, a vacuum chamber that prevents the iron from rusting. Rust is a potential downside of using iron in manufacturing, and controlling it could prove challenging and expensive. "We're not talking about making a dish of spaghetti at home," Dr. Chirik said, referring to the volume of chemicals involved when doing reactions on an industrial scale. It remains to be seen, he said, whether concerns about the use of an "air sensitive" substance outweigh concerns about the costs and environmental impact of precious metals.

There have been other hurdles. Dr. Chirik showed two small dishes of silicone flakes, used to make envelope glue. One he made using iron, the other platinum. They were indistinguishable. Getting them that way, however, was no easy task — it's taken nearly a decade of work.

"One of the reasons most of us got involved in this type of chemistry is that compounds that have metals in them turn really cool colors and it's fun to watch," Dr. Chirik said. "But if you're making something that's going to go in a consumer product, the glue on an envelope, the bottom of a shoe, an ingredient in shampoo, you really don't want it to be black."

Chevron and Momentive, a silicone manufacturer, are financing Dr. Chirik's work. Merck is also a partner in the research. (Many drugmaking processes rely on rhodium or palladium.) One product in development is a fuel-efficient tire that employs a new, cleaner process, with no byproducts, by using iron instead of platinum.

Dr. Hartings, of American University, believes that using abundant materials where possible could free up the scarcer materials for applications that truly require them. "There's less of an argument to do crazy mining when you've got something else that works just as well," he said.

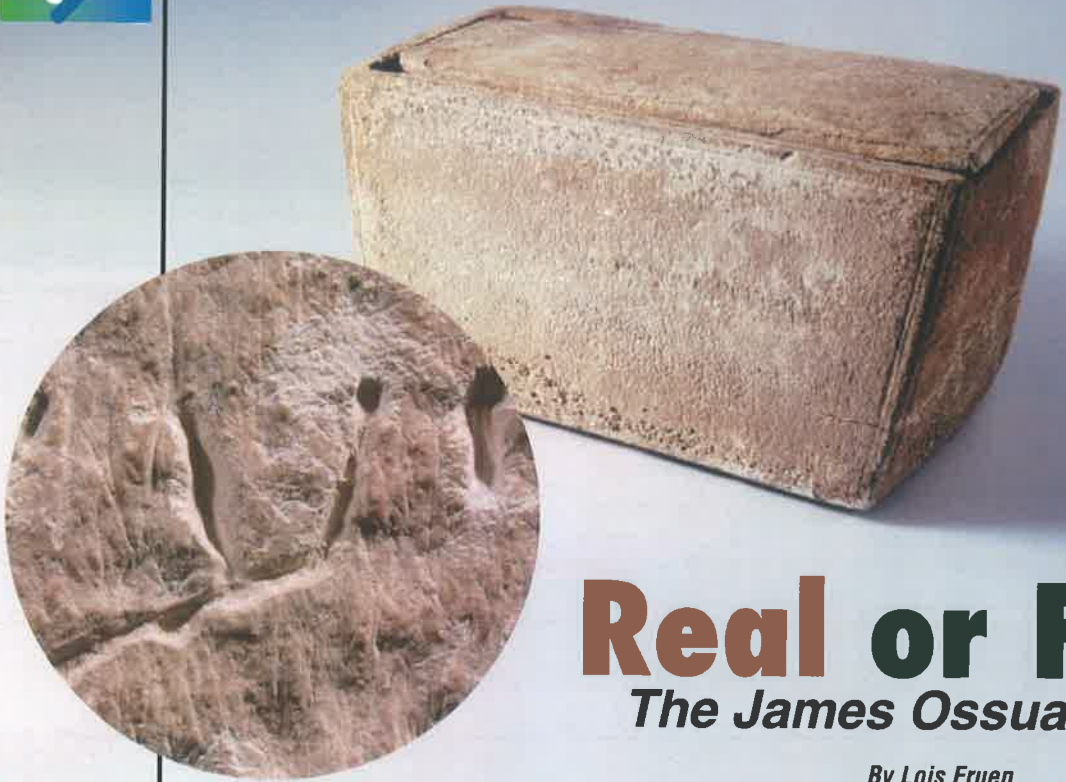
Researchers in Dr. Chirik's lab are also hunting for ways to use catalysts to convert nitrogen from the air into forms used in various products, from fertilizer to carpet fiber. The current method, the Haber-Bosch process, is so energy-intensive it accounts for 1 percent of all global energy use.

Sustainability often focuses on "recycling cans and better gas mileage," Dr. Chirik said. While important, those efforts are only part of the picture. There's also the way products are made.

"When you buy jeans, some weird element on the periodic table was used to make them," Dr. Chirik said. "Or you think you're doing something good by buying a Prius, but it's got all this neodymium in it that comes out of a pit mine in Mongolia.

"If you can transition to a completely earth-abundant world," he said, "you can have a huge impact."

ChemMystery



Real or Fake?

The James Ossuary Case

By Lois Fruen

CSI (criminal scene investigation) is not limited to murder. Recently, a crime team was assembled to examine a controversial and potentially priceless bone box and black stone tablet. Although the bone box may have once held skeletal remains, the team was not interested in DNA or fingerprint evidence. They focused on a grimy buildup, called patina, on the surface and in the inscriptions of the box and tablet. If proven to be fake, the patina could expose a forgery ring that has faked inscriptions on ancient objects found in museums all around the world.

The inscription on the bone box claims that it once held the bones of the brother of Jesus, while the tablet reports ancient repairs to Solomon's Temple in Jerusalem. Too good to be true? The Israel Antiquities Authority thinks so. But what did the crime team find?

Dr. Elizabetta Boaretto at the Weizmann Institute radiocarbon ^{14}C–dated the tablet, using samples of patina from the inscription. Patina is the coating that builds up on ancient objects over long periods of time. The main component of the patina in the inscription is calcium carbonate ($CaCO_3$), called calcite by geochemists. Calcite contains carbon, which can be ^{14}C tested. Dr. Boaretto reported that the patina dates to 390–200 BC. This makes it tempting to declare the tablet authentic, but ^{14}C dating is not enough to prove it is real. Expert forgers know that scientists use ^{14}C dating to authenticate pieces, so they concoct patinas using ancient carbon (charcoal) found at archaeological digs. Dr. Boaretto reported that ^{14}C-dating the bone box would not provide any better proof of authenticity than she obtained for the tablet.

Carbon Dating

Plants and animals take in small amounts the radioactive isotope ^{14}C when alive. When an organism dies, replenishment of ^{14}C stops and ^{14}C steadily decreases at a known rate. The longer the organism is dead, the less ^{14}C remains. One important fakery note—a pencil made yesterday from a tree cut down 2000 years ago will appear to be 2000 years old. But a tree cut down last year will not!

Above: Bone box that may have held the bones of the brother of Jesus.

Next, Professor Yuval Goren at Tel Aviv University examined the tablet and the bone box. He tested hardness and density and did microscopic analysis of the mineral composition. He determined that the tablet is greywacke, a stone found in western Cyprus and northern Syria, not Israel. Because the tablet is supposed to be from the 9th century BC, it seems less likely that imported stone would have been used instead of local stone. With further investigation, Professor Goren found that the surface patina is a silicate that firmly adheres to the surface. He pointed out that it was unlikely that a silicate patina formed in the calcite environment of Jerusalem. Even more suspicious, the patina in the inscription is different from the surface patina. It is calcite and soft enough to be easily removed with a toothpick. This softness is a hallmark of recent patina formation. He concluded that the inscription was added in recent times.


GEOLOGICAL SURVEY OF ISRAEL

Dr. Avner Ayalon from the Geological Survey of Israel examines the controversial bone box.

Professor Goren also analyzed the bone box and determined that it was made of native limestone ($CaCO_3$)—a stone that was commonly used to make bone boxes in the 1st century AD. That finding and his analysis of the surface patina convinced him that the box is genuine. It was the patina in the inscription that concerned him. On close inspection, he found the inscription cut through the surface patina, so he was suspicious that it had been faked in modern times.

Dr. Avner Ayalon from the Geological Survey of Israel took the investigation further. Using mass spectroscopy, he analyzed the oxygen isotope composition ($\delta^{18}O$) of patina from both the bone box and the tablet. Oxygen isotope analysis measures the ratio of ^{18}O to ^{16}O in a sample, compares the ratio to a standard, and then expresses the finding as per mil $\delta^{18}O$. In this notation, the lower case Greek letter delta (δ) signifies the relationship between the measured ^{18}O and the ^{18}O found in a standard. You can think of the delta value as the number of atoms per 1000 that the heavy isotope in the sample differs from the heavy isotope in the standard. To calculate a value, investigators use this formula:

$$\delta^{18}O = \left[\left(\frac{\left(^{18}O/^{16}O\right)_{sample}}{\left(^{18}O/^{16}O\right)_{standard}}\right)-1\right]\cdot 1000$$

To find the $\delta^{18}O$, Dr. Ayalon reacted samples of patina with phosphoric acid (H_3PO_4). This reaction produces CO_2 gas, seen in the reaction below. The CO_2 gas was ionized in the mass spectrometer, and then the oxygen isotopes were separated by mass by a strong magnetic field.

$$3CaCO_3 + 2H_3PO_4 \rightarrow 3CO_2\,(g) + 3H_2O + Ca_3(PO_4)_2$$

calcite phosphoric acid

$$CO_2\,(g) + H_2O\,(1) \rightleftarrows CaCO_3\,(s) + CO_{2\,(aq)} + H_2O\,(1) \rightarrow Ca^{2+}\,(aq) + 2HCO_3^-\,(aq)$$

calcite dissolved CO_2

Dr. Ayalon compared $\delta^{18}O$ for patinas on the bone box to $\delta^{18}O$ of patinas from 1st century AD bone boxes that he knew were authentic. He found $\delta^{18}O$ of authentic boxes were between –4.1 and –6.7 per mil $\delta^{18}O$. These matched results for surface patina on the bone box in question. But, $\delta^{18}O$ readings of patina from the inscription were between –5.8 and –10.2 per mil $\delta^{18}O$, with all but one of the readings falling outside of the acceptable range. He concluded that the box itself was real, but the inscription was forged.

Oxygen isotope analysis was the nail in the coffin for the bone box. It convinced Dr. Ayalon that the inscription was forged. The reason had to do with the temperature at which the patina in the inscription formed, which he determined from $\delta^{18}O$ values. Natural calcite patina forms in much the same way crusty scale slowly builds up in hot-water pipes and inside kettles, sealing oxygen isotopes in as the patina dries. The process of calcite patination starts when groundwater picks up CO_2 from air trapped in soil. When this CO_2-rich groundwater comes in contact with calcite, it dissolves it. Although calcite is not very soluble in pure water, the higher the concentration of dissolved CO_2 in water, the more calcite will dissolve, shifting the equilibrium to the right.

When calcite-rich groundwater is exposed to air in a burial cave, the equilibrium shifts back, releasing CO_2 gas into the cave and precipitating calcite.

If the patina on the bone box is authentic, the patina could have formed in one of two ways. First, it could have recrystallized from water that seeped into the burial cave. Water entering the burial cave would have absorbed CO_2 gas from the cave environment, formed a thin film of water on the bone box, and reacted with the surface. (This reaction is the same as above because the box is made of limestone, $CaCO_3$). When the film of water evaporated, it would have left behind a white film of calcite patina on the surface of the box. However, if the bone

The Reason ^{18}O is concentrated in the calcium carbonate relative to water is because of quantum mechanical effects: The carbonate has more vibrations whose energies depend on the mass of the oxygen atoms, and the carbonate with the ^{18}O isotope has lower-energy vibrations and overall energy. ^{18}O prefers to be in the carbonate. The importance of this energy difference is lessened at higher temperature because it's an exothermic reaction—the reaction becomes less favorable as the temperature increases.

Stone tablet that reports ancient repairs to Solomon's Temple in Jerusalem.

The inscription on the bone box reads, "Ya'akov bar Yosef ahui d'Yeshua," which translates "James, son of Joseph, brother of Jesus".

box had been buried in a shallow grave, the patina would have precipitated directly from the groundwater water onto the surface of the box by CO_2 degassing from the groundwater.

In either case, if groundwater or seepage water were cold, the patina would have contained more ^{18}O than ^{16}O isotopes, giving higher $\delta^{18}O$ readings.

Conversely, calcite patinas that form from hot groundwater have lower $\delta^{18}O$ values. The very low $\delta^{18}O$ readings obtained for the patina found in the inscription of the bone box suggest the patina formed from very hot water. In fact, Dr. Ayalon reported that the water temperature had to be between 40 and 50° C. Because groundwater temperatures in caves and shallow graves in the Jerusalem area are between 18 and 20° C, it would have been impossible for a patina with such a low $\delta^{18}O$ values to have precipitated naturally.

On the basis of this evidence, Dr. Uzi Dahri, Deputy Director of the Israel Antiquities Authority, declared that the inscription was a forgery. To further support his case, he reported that fluorine was found in the patina in the same percentage as fluorine added to tap water in Jerusalem to prevent tooth decay. Since drinking water was not fluoridated until modern times, Dr. Dahri concluded that the patina had been faked using modern-day tap water. Things were not looking good for the bone box.

Next, Dr. Ayalon checked the patina on the tablet. From the $\delta^{18}O$, he determined that two different calcite patinas had been used in the inscription. The first gave $\delta^{18}O$ values between −7.3 and −8.4 per mil $\delta^{18}O$, while the second had higher values between −0.9 and −1.7. Dr. Ayalon speculated that the patina was concocted by grinding a carbonate material like chalk with a carbonate that contained fossils. He suggested that the forger then dissolved the mixture in hot water and spread it onto the surface of the inscription. Ms. Orna Cohen, an expert conservator who specializes in identification and restoration of ancient patinas, concurred with him that the patina was forged. She reported that when the patina was removed from the inscription, it appeared freshly cut.

The forgery case seemed airtight. The Israeli police arrested the owner of the bone box, who is an antiquities dealer, on a charge of knowingly conspiring with intent to defraud. And that's when things took a turn.

Muddying the waters

Dr. James Harrell, professor of Archaeological Geology at the University of Toledo, suggested that the low $\delta^{18}O$ readings could have come from a cleanser that was used to clean the bone box. He pointed out that antiquities dealers and collectors often clean artifacts to increase value, and the patina in the inscription "looks and feels exactly like what one would expect from a powdered cleanser". Cleansers contain ground-up limestone ($CaCO_3$) abrasives and baking soda ($NaHCO_3$), which serves as the cleansing agent. Both limestone and baking soda react with H_3PO_4 to produce CO_2 used in $\delta^{18}O$ analysis. Intrigued, Dr. Harrell decided to have an oxygen isotope analysis done on four widely used cleansers from Israel.

The Georgia Center for Applied Isotope Studies tested the four Israeli cleansers with interesting results. Three of the four cleansers produced results lower than the −4.1 to −6.7 per mil $\delta^{18}O$ range set by the Geological Survey of Israel for authentic carbonate patina. And, the most popular cleanser had a $\delta^{18}O$ of −8.5 per mil, consistent with the patina in the inscription of the bone box. The low $\delta^{18}O$ readings, which had convinced the Israel Antiquities Authority that the bone box was forged, could have come from cleanser!

Further doubt was raised by Andre Lemaire of the Sorbonne in France. He suggested that the fluorine found in the inscription of the bone box could have resulted from cleaning with tap water. He also suggested that fluorine might be present in patinas of many authentic antiquities, since the antiquities may have been exposed to groundwater containing modern-day runoff.

Recently, $\delta^{13}C$ data for the bone box patina have been released. $\delta^{13}C$ is a comparison of ^{13}C to ^{12}C isotopes in a sample and is determined using mass spectroscopy. Readings for the surface patina on the bone box varied from −1.2 to −7.7 per mil $\delta^{13}C$. However, unlike the $\delta^{18}O$ results, the $\delta^{13}C$ readings for the inscription patina were almost identical to the values for the surface patina, ranging from −1.1 to −7.4 per mil $\delta^{13}C$.

Are the bone box and stone tablet fakes? If they are, they could expose a forgery conspiracy that has been operating for years. In fact, the Israel Antiquities Authority has warned that many forgeries from this conspiracy could be in museums in Israel and around the world. The forgery trial was scheduled to begin on September 4, 2005. But, even if the defendants are found not guilty or the case is dismissed, doubt will linger about the authenticity of the tablet and bone box. Scientists will continue to disagree about analyses and interpretations of results. Methods to test antiquities will improve, and it is likely that new examinations will be undertaken.

More importantly, even if one day the inscription on the bone box were to be proven authentic, the names James, Joseph, and Jesus were common in the 1st century AD, so the inscription could refer to a family other than the biblical one. You can follow the ongoing controversy on the bone box by clicking on the "Update" section at www.bib-arch.org. ▲

Lois Fruen teaches chemistry at the Breck School in Minneapolis, MN. Her most recent article "Liquid Crystal Displays" appeared in the October 2005 issue of *ChemMatters*.