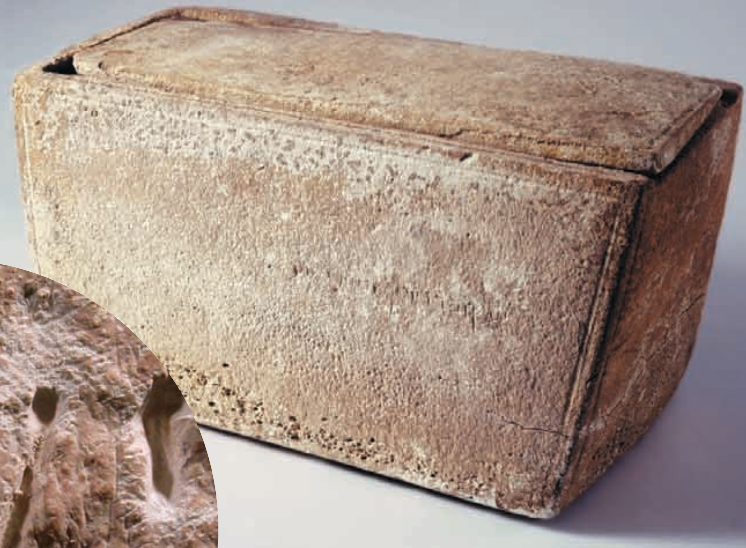
ChemMystery



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?

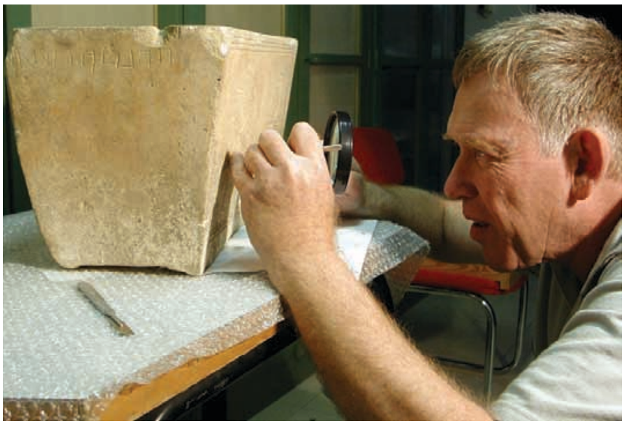
Dr. Elizabetta Boaretto at the Weizmann Institute radiocarbon ^{14}C–dated the tablet, using samples of patina from the inscription. Patina is the coating that builds up on ancient objects over long periods of time. The main component of the patina in the inscription is calcium carbonate ($CaCO_3$), 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:

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

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.

$$\underset{\text{calcite}}{3CaCO_3} + \underset{\text{phosphoric acid}}{2H_3PO_4} \rightarrow 3CO_2\,(g) + 3H_2O + Ca_3(PO_4)_2$$

$$CO_2\,(g) + H_2O\,(1)$$

$$\downarrow\uparrow$$

$$\underset{\text{calcite}}{CaCO_3\,(s)} + \underset{\text{dissolved }CO_2}{CO_{2\,(aq)}} + H_2O\,(1) \rightarrow Ca^{2+}\,(aq) + 2HCO_3^-\,(aq)$$

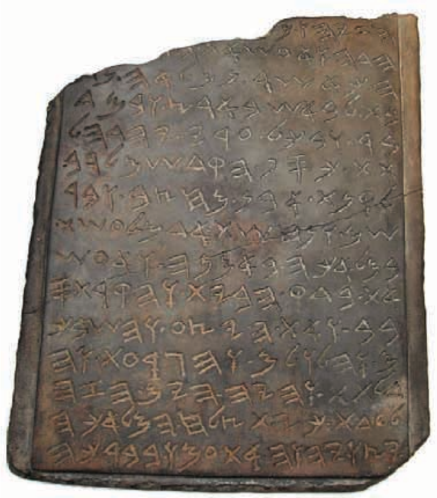
Dr. Ayalon compared $\delta^{18}O$ for patinas on the bone box to $\delta^{18}O$ of patinas from 1st century AD bone boxes that he knew were authentic. He found $\delta^{18}O$ of authentic boxes were between –4.1 and –6.7 per mil $\delta^{18}O$. These matched results for surface patina on the bone box 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.

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.

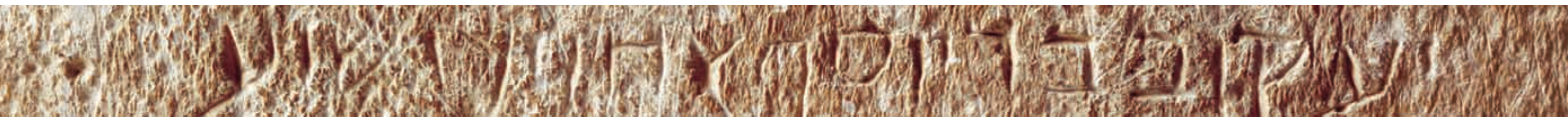
When calcite-rich groundwater is exposed to air in a burial cave, the equilibrium shifts back, releasing CO_2 gas into the cave and precipitating calcite.

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



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

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 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.

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*.