

ARCHAEOPHOTONICS:



TV3-Televisió de Catalunya

Pablo Loza-Alvarez (right)
and David Artigas in the lab

Scientists use two-photon absorption fluorescence to recover written

Q FAB

Lasers Unveil the Past

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Excavation in
the Roman city
of Iesso, 2006
campaign

Courtesy of ICAC

information on Roman relics and solve a 2,000-year-old mystery.

When people think of archaeology, they often conjure images of adventurers such as Indiana Jones, who spend most of their time searching for mysterious ancient objects. We forget that the main objective in archaeology is to uncover the history hidden behind the objects, in the hope that they can help us understand a small fraction of the immense puzzle that is the past. Artifacts typically make a long journey from archaeological site to museum show case—with many stops along the way at high-tech research facilities.

In a discipline known as archaeometry, scientists use a number of chemical and physical procedures to obtain information from an archaeological artifact. Probably the most well-known strategy is the use of the radioactive isotope carbon-14 (^{14}C) to date biological samples.

For non-organic objects, more indirect techniques may be used to allocate them to a particular historical context, such as studying the geological substrate where the piece was found or even the artistic style of the piece. Whenever possible, however, scientists opt for more direct techniques that gather qualitative and quantitative information about the chemical composition of the object.

With this information, researchers can trace the evolution of certain fabrication technologies through history. This information not only helps them to date archaeological objects, it enables them to identify the fabrication place and sources of raw material, revealing details about ancient trade and provenance. Analysis of chemical compounds in archaeology has been routinely based on ion beam and X-ray techniques.

Photonics enters the field of archaeometry mainly through the use of spectroscopic techniques, such as Raman spectroscopy, laser-induced fluorescence (LIF) and laser-induced breakdown spectroscopy (LIBS). These technologies allow for the fast, *in situ* identification of the

chemical composition of a great variety of objects.

Researchers are also starting to use photonics for imaging within archaeology. For example, laser scan surveys can detect irregularities on a surface with important archaeological significance, uncovering features that are invisible to the naked eye. It is also used in cases where the topography of the sample is required but contact with the surface is not recommended. Examples of this are the scan-

ning of carved rocks in the Paleolithic site of Cap Blanc, France, or the Stonehenge Scanning project.

Our archaeological problem

In our case, we were looking for a way to uncover information painted on the surface of a wine amphora that could help determine the foundation date of the Roman village of Iesso, which is nowadays the city of Guissona in Catalonia

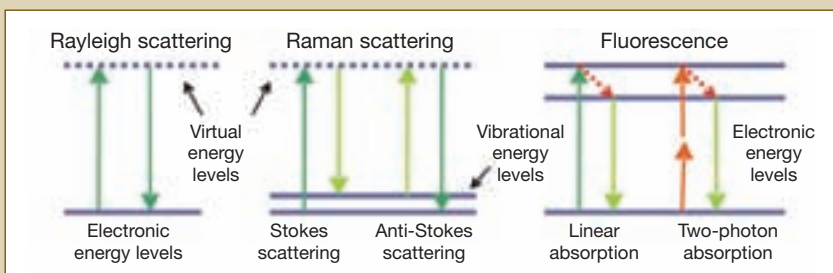
[Laser spectroscopic techniques used in archaeology]

Raman spectroscopy: This form of spectroscopy is based on Raman scattering from laser light. Vibrational energy levels interact with the scattered photons in such a way that the energy of the re-emitted photons is shifted up (anti-Stokes scattering) or down (Stokes scattering). Since the shift is equal to the vibrational energy-level difference, it is characteristic of each molecule, allowing its identification. Raman spectroscopy provides complementary information when compared to near-infrared spectroscopy, a vibrational spectroscopic technique extensively used in art conservation studies.

Laser-induced fluorescence (LIF): In LIF, one absorbed photon induces a transition from the ground state to an upper electronic energy level determined by the photon energy. Then, in the relaxation process to lower energy levels, the energy can be emitted in the form of light (fluorescence). The wavelength and bandwidth of the emitted light therefore characterizes the chemical nature of the sample.

Two-photon fluorescence: When two photons with half the energy between the two electronic levels are used as an excitation mechanism, the approach is referred to as two-photon excitation fluorescence or simply two-photon fluorescence. This process is nonlinear since it requires two photons to be absorbed by the same atom at the same time. Therefore, the probability that this process will occur depends on the photon density (light intensity). This condition is usually reached by the use of ultrashort pulses.

Laser-induced breakdown spectroscopy: This technique is based on the ablation produced by a laser of a small portion of the sample (μg - ng) resulting in a plasma cloud. The emitted spectrum, which is characteristic of each chemical element, is then collected, allowing for its identification.



Light-matter energy diagrams: Solid arrows indicate radiative absorption (up) or emission (down). Dotted arrows indicate non-radiative transitions.

Laser scan surveys can detect irregularities on a surface with important archae

in northeast Spain. Archaeologists from the Institute of Classical Archaeology of Catalonia (ICAC) found this amphora among others near the city walls.

The place and disposition of the amphorae led the archaeologists to conclude that the objects were brought by the first Roman Legions that arrived on Iesso, and that the wine was consumed during a ritual celebration related to the wall building and the city foundation. As was usual at that time, the amphora had written on its neck the consular date—which is the name (initials) of the two Roman consuls ruling in the year of production. This was a signature of good quality wine.

Because the names and time frames for all the Roman consuls are known, this finding would allow us to date the foundation of the Roman city of Iesso. Unfortunately, at the moment of the discovery, the paint used to write the consular date was barely readable. In addition, since its discovery, natural photobleaching had taken its toll, and the archaeologists' initial method for reading the inscription (humidifying the painted area with a water solution) had remarkably further deteriorated the quality of the paint. Using this method, the archaeologists were able to identify only the next group of letters:

Q•FAB•.....•COS

The first letters are the initials for *Quintus Fabius*, the first consul, while the last three letters signify *Consolibus*, a Latin word meaning “being consuls.” The name of the second consul should have been located at the space between these two groups of letters (i.e., the dotted line). However, this area was considerably damaged and most of the paint had disappeared, making it impossible to decipher the second consul name. Unfortunately, the knowledge of the first consul is not enough, since, during the same period, two different consuls owned the same name.

[The importance of the foundation of Iesso]

The Romans arrived on the Iberian Peninsula during the second Punic War against Carthage (218-202 B.C.E.). After they defeated Carthage, their presence in *Hispania Citerior* (northeast of the Iberian Peninsula) was reduced to the colony of Tarraco (nowadays Tarragona), where they remained for nearly a century. At some unknown moment between the second and first century B.C.E., a broad city foundation program was started by Rome to take control of the country.

Among the founded cities was Iesso. It was strategically located to protect the country from northern invasions, as it was the gate of a natural path in the Pyrenees that follows the Segre River. (This path was also followed by Hannibal, who managed to avoid the Roman legions controlling the coastal route on his way to Italy in 218 B.C.E.) Due to its strategic importance, Iesso was thought to be one of the first established cities during this Roman founding program. Thus, discovering the foundation date of Iesso is critical to determining when the Roman expansion in *Hispania Citerior* began.



Map of the western Roman provinces (100 B.C.E.) showing the strategic situation of Iesso.

[Roman amphora]

(Top) Amphora under study; (bottom) zoom of the area to be analyzed with the name of the two consuls.



Iain G. Cormack

archaeological significance, uncovering features that are invisible to the naked eye.

To uncover the missing name, we needed a detection technique that was able to detect and map small amounts of paint or some of its components (pigments or agglutinant). After examining the possible laser techniques, we discarded the use of LIBS and Raman spectroscopy. In the first case, the semi-destructive nature of LIBS could damage the sample. In the second, the Raman signal generated by such a small amount of paint would be hardly distinguishable from the background signal generated by the pottery.

We decided that a technique based on fluorescence appeared to be the best option. Fluorescence from the paint is usually generated by the agglutinant, while the pigment, which is generally composed of metallic elements, inhibits it. This characteristic was quite convenient for our purposes; it helped us to identify previously painted areas where the pigment had disappeared but the agglutinant has persisted.

The amphora has been preserved in a dark area. Thus, an obvious requirement of our experiment was to avoid, at any price, laser-induced photodamage. This immediately prevented us from using high-energy photons for exciting the fluorescence. Unfortunately, it is known that the agglutinant used by the Romans (casein or albumin) fluoresces in the visible. This would require green-to-UV excitation sources, increasing the risk for photodamage. An alternative that was available in our lab was the use of femtosecond laser pulses to produce two-photon excitation fluorescence (TPEF), which allowed us to use near-infrared light as the excitation source, thereby greatly reducing the probability of producing photodamage.

Two-photon fluorescence imaging

The best known use for the non-damaging properties of TPEF is in nonlinear microscopy for biological applications. Nonlinear microscopy uses infrared light

to help ensure cell viability and is the technique of choice for imaging *in vivo* over extended observation periods. Our experimental set-up, shown in the figure below, reproduces a typical nonlinear microscope scheme, except for the fact that, for our purposes, high resolution was not required.

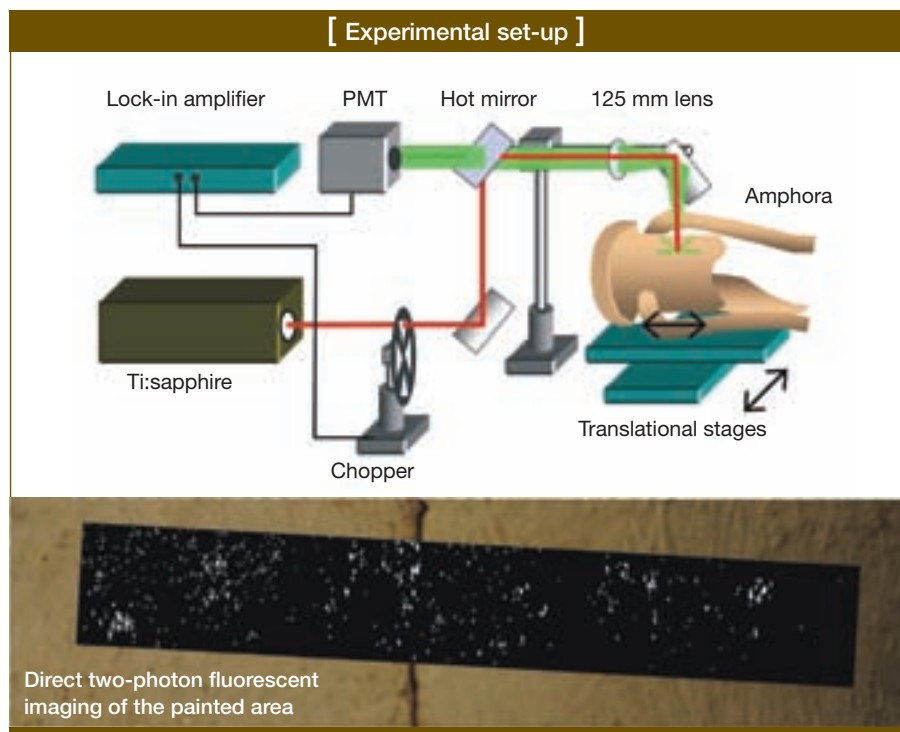
In fact, the beam of a titanium:sapphire mode-locked laser was gently focused on the painted area on the amphora. The fluorescence signal was captured by a lens and directed through a hot mirror to the detection system, which was composed of a photomultiplier tube and a lock-in amplifier; this increased the sensitivity of the detection system. Two translation stages supporting the amphora composed the scanning system.

Previous experiments on amphora fragments found in the same archaeological site allowed us to test our system and determine the photodamage threshold, optimal focusing and scanning parameters. These preliminary experiments also showed that the measured fluorescence was generated only from painted areas.

After these experiments, we scanned the painted area of the amphora, shown in the bottom of the figure on p. 23. In order to adapt to the amphora's curvature and maximize the excitation of fluorescence, we divided the painted area into three regions, and scanned each region at three different focusing positions. The scanning of one zone was performed in 100 min in complete darkness.

The fluorescence image is shown in the inset image of the figure below. At first glance, the fragment may seem to show little evidence of any writing. However, as we previously mentioned, two vital pieces of information had to be considered. First, the generated fluorescence corresponded to regions where agglutinant was present, and, second, regions that contain pigment in fact inhibit the fluorescence. In our scanned image, this resulted in large dark areas.

To fully recover the information on the amphora, we then performed a processing imaging technique based on histogram equalization that took these features into account. Histogram



To fully recover the information on the amphora, we performed a

[Equalization histogram image processing technique]



(a) Recovered information from using an equalization histogram image processing technique; (b) result after Gaussian blurring and binarization; and (c) the two options for the Roman consul written using *Capitalis Rustica* calligraphy.

equalization adjusts for the total distribution of the signal, modifying the scale to better determine regions with similar intensity level. Moreover, we applied it on small zones corresponding to the position where presumably each of the letters for the second consul was.

The area corresponding to the first name initial was affected by a crack and therefore impossible to analyze. The resulting images for the remaining letters (the surname) are shown in part (a) of the figure above, where some dark and brighter areas can be observed. To help the eye, we performed some additional basic image processing techniques (Gaussian blurring and binarization), which enabled us to obtain a clear image of the areas where the paint was (part b of the figure). This result, by itself, was not conclusive enough to determine the missing letters. As a consequence, we needed to delve deeper by making use of historical information.

Solution to the puzzle

As we mentioned earlier, there were two possible occasions in which a consul could have been named *Quintus Fabius*. In the year 121 B.C.E., the consul *Quintus Fabius Maximus Allobrogicus* was ruling together with the consul *Lucius Opimius*. Later, in the year 116 B.C.E., *Quintus Fabius Maximus Eburnus* was the consul in conjunction with *Caius Licinius*

Geta. Therefore, one of the possibilities for the lost writing corresponded to the surname “OPI” (for *Opimus*) and the other one to “LIC” (for *Licinius*).

To make the final analysis, we proceeded to compare our results with the two possible consul names using the Roman calligraphy *Capitalis Rustica*; see part (c) of the figure above. This calligraphy was the informal cursive capital letterform used in that time for painted inscriptions. Examining the two options, it is clear that the first letter could be an “O” and the last can be an “I.” In addition, there is a certain resemblance between the top part of the letter “P” in *Capitalis Rustica* and the central panel in (b).

We therefore could confidently conclude that the missing name was *Lucius Opimius*, and the wine contained in the amphora was from the 121 B.C.E. harvest. This result provides what in archaeology is named a “terminus post quem” for the foundation of Iesso—in other words, the earliest point in time when the city could have been founded. Now, archaeologists must deduce the wine’s age to provide a more precise foundation date of Iesso. ▲

The authors want to thank Professors Josep Guitart and Josep Ros from the ICAC-Institut Català d'Arqueologia Clàssica in Tarragona, the Patronat d'Arqueologia de Gissona for their contribution to the archaeological aspects of the work, and Emilià

Pola from the Generalitat of Catalunya, who initially encouraged the collaboration between the two research institutions.

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[References and Resources]

- >> K.A. Robson Brown et al. “An Automated Laser Scan Survey of the Upper Palaeolithic Rock Shelter of Cap Blanc,” *J. Archaeol. Sci.* **28**, 283 (2001).
- >> P. Weibring et al. “Fluorescence lidar imaging of historical monuments,” *Appl. Opt.* **40**, 6111 (2001).
- >> D. Damiani et al. “Pigments and plasters discovered in the house of Diana (Cosa, Grosseto, Italy): An integrated study between art history, archaeology and scientific analyses,” *Archaeometry* **45**, 341 (2003).
- >> T. Goskar et al. “The Stonehenge Laser Show,” *British Archaeology* **73**, 8 (2003), and www.stonehengelaserscan.org.
- >> G. D. Smith and R. J.H. Clark. “Raman microscopy in archaeological science,” *J. Archaeol. Sci.* **31**, 1137 (2004).
- >> D. Comelli et al. “Fluorescence lifetime imaging and spectroscopy as tools for nondestructive analysis of works of art.” *Appl. Opt.* **43**, 2175 (2004).
- >> A. Giakoumaki et al. “Laser-induced breakdown spectroscopy (LIBS) in archaeological science—applications and prospects,” *Anal. Bioanal. Chem.* **387**, 749 (2007).
- >> I.G. Cormack et al. “Lost writing uncovered by laser two-photon fluorescence provides a terminus post quem for Roman colonization of Hispania Citerior,” *J. Archaeol. Sci.* **34**, to be published (2007).

processing imaging technique based on histogram equalization.