Physicist glances at cultural heritage [DOI: 10.1051/epn:2007020]

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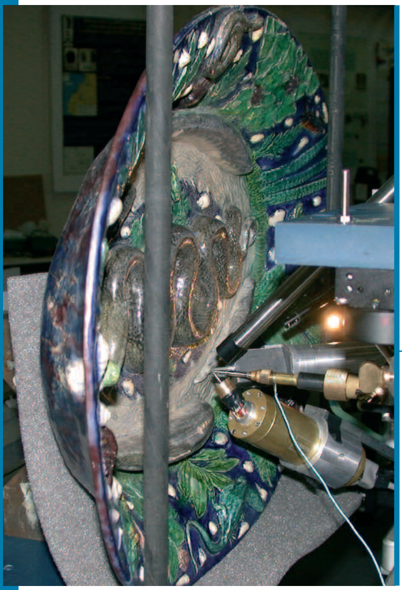
It is nowadays regarded as a necessity to preserve the past production of human activity, as well as to understand the knowledge and the skills associated with the objects; hence the development of many disciplines such as history, archaeology, conservation, life science, physics, chemistry, *etc.* applied to cultural heritage. Multidisciplinary investigations are currently performed by curators, chemists, physicists, geologists, conservators *etc.* that aim at helping the restoration and the conservation of objects as well as improving the understanding of their fabrication by ancient artists or craftsmen, and of their use. Specific analytical techniques have been implemented, of which many derive from physics.

Multidisciplinary and multi-scale examinations of objects are a prerequisite to any detailed analytical investigation. This is the domain of historians and curators. In addition to direct visual observation, these specialists are helped by the use of various electromagnetic radiations such as infra red, ultra violet and X rays. The radiography of paintings has been performed more than 10,000 times since it began in the 1920's. These techniques give information beyond the surface and allow the discovery of details about the fabrication of the objects or about their deterioration or their ancient restoration. An example of such a multidisciplinary research was undertaken recently on the *Mona Lisa* by Leonardo da Vinci. All the partners of the C2RMF, curators from the Louvre Museum associated with specialists of French and Canadian research centres, developed a common study of the famous painting [1].

Resulting from such investigations, many questions are often raised concerning the origin and the processing of the materials, the alteration of the object, the date of manufacture, *etc.* To attempt to bring answers, it is necessary to use various types of analytical techniques dealing with the electrons and the nuclei in order to determine detailed characteristics of the materials, such as chemical compositions, atomic arrangements in molecules or in crystals, lattice imperfections, *etc.*



◀ **Fig. 1:** View of a colourful ceramic platter in position for PIXE/PIGE analysis with AGLAE. The horizontal pipe holds the beam exit window; it is surrounded by various types of detectors and art work monitoring devices.

Dating past events (geological events, evolution of living species, *etc.*) is fascinating ; nuclear physics is involved in most of the dating techniques. Applications to cultural heritage studies are useful mostly for the past 20-30000 years and exceptionally for older times. For such a time span, ^{14}C is particularly suited (the ^{14}C half life is 5730 years) to date organic materials left by living species when they stop being in chemical equilibrium with their environment. The decay of radioactive ^{14}C is directly related to the age of the death of animals or plants. It requires the measurement of $^{14}C/^{12}C$ ratios less than 10^{-12} that is currently carried out by accelerator mass spectroscopy (AMS). AMS gives dates with very small amounts of carbon (1 mg) and has such a sensitivity that ages as old as 50000 years are determined [2]. In a detailed study concerning the disappearance of men from Greenland around 1500, the change of diet composition was tracked from terrestrial to marine food according to the concentrations of the stable carbon isotope ^{13}C [2].

As a complement to the previous technique, thermoluminescence (TL) dating is applied to minerals; it has been used to date ancient ceramics for the last 30-40 years [3]. TL is a universal tool for dosimetry; it applies to heated minerals giving the possibility of measuring the total dose of natural radiation recorded since the last temperature increase ($T>350°C$). In order to calculate the "age", the annual dose rate must be known for the whole life of the artefact after the thermal event. The dose rate is related to the concentrations of radio-elements (uranium, thorium, potassium) inside the object and in the environment [3]. Errors on "age" can be as small as 5-10% in the best cases. Among many sources of uncertainty are the unknown humidity level in the objects during their storage and also the possible application of ionizing radiation, mostly X or g rays, that induces an artificial ageing (laboratory study, airport safety, *etc.*) [3]. In spite of these limitations, TL dating is commonly used, not only in archaeology, but also for museum collections and in the art market where the results should be considered with some caution.

The strategy of analysis depends on many parameters such as the questions to be answered, the nature of the materials (organic, mineral), their alteration with time, the necessity of non-destructive analysis, *etc.* This approach is at the encounter of humanities, earth sciences, chemistry and physics. A large variety of materials are currently studied, from metals, ceramics, stones to organic materials. The present article gives examples related to inorganic materials. The techniques used for the analysis of materials (X ray fluorescence, electron microscopy, X ray diffraction, infra-red absorption, *etc.* in the laboratory or at synchrotron radiation facilities) all derive from physics. Several important techniques used at the C2RMF involve ion beam analysis (IBA); the C2RMF has been pioneering in IBA of art works thanks to the design and construction of an attachment for non-destructive analyses at atmospheric pressure [4].

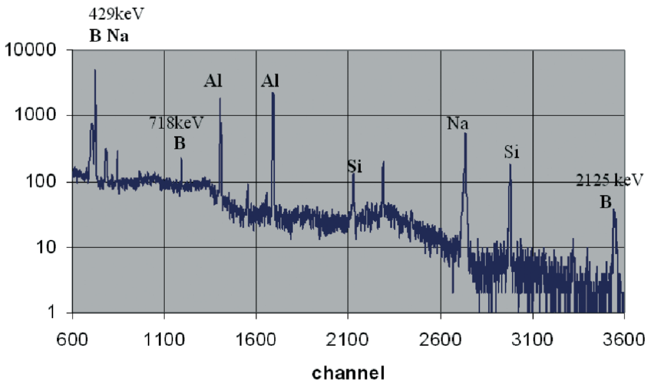
Ion beam analysis of chemical elements

Materials are fully characterized once the chemical composition, the crystal lattice and the microstructure (grains, lattice imperfections, *etc.*) of the various phases are determined. This requires extensive investigations. Chemical element analysis is the most common because it is done by the spectrometry of X rays emitted under the impact of X rays (fluorescence; XRF), of electrons in a scanning electron microscope (SEM-EDX) or of particles (Particle Induced X-ray Emission, PIXE) in an accelerator such as AGLAE (Accélérateur Grand Louvre d'Analyse Elémentaire located at the C2RMF). XRF and PIXE are performed directly at atmospheric pressure without taking specimens from the objects; they are non-destructive and give information on the superficial layers (10-50 µm from the surface). SEM-EDX is routinely used because it combines imaging and analysis; small samples (usually less than 1 mm) have to be taken from the art works when the whole object cannot be inserted in the vacuum chamber of the SEM.

AGLAE and its applications have been described in many publications [4 - 6]. The equipment is based on a 2 MV NEC tandem accelerator 5SDH-2 that is used with beams of protons, deuterons and α-particles, and less frequently of heavier ions such as O or N. The beam exits to the atmosphere through a 0.1 µm thick window made of silicon nitride. This external beam allows the analysis to be performed, usually in a flow of helium, at atmospheric pressure (figure 1), thus avoiding the need to introduce the objects into a vacuum chamber with the risk of damaging fragile art works. With this system, beam diameters as small as 20 µm are currently achieved.

All the ion beam analysis (IBA) techniques are available at **AGLAE**. PIXE is the most common analysis because it readily gives quantitative compositions and it has limits of detection (typically 5-10 ppm) much lower than SEM-EDX (0.1%) because of the reduced "brehmstrahlung" for heavy particles. PIXE, SEM-EDX and XRF have the same limitations for the analysis of light elements, i.e. below sodium in the periodic table. This difficulty is overcome with **AGLAE** by using nucleus transitions associated with γ ray emission (Particle Induced Gamma Emission, PIGE) or nuclear reaction analysis (NRA), thus giving access to fluorine, boron, nitrogen, *etc.* in art works.

Depth profiling near the surface can be obtained by these techniques, for instance using beams inclined at various angles in PIXE/PIGE or using resonant NRA. However, such profiling is usually made at **AGLAE** by Rutherford back-scattering (RBS), most often with incident α-particle beams [5]. Hydrogen profiling has also been performed by elastic recoil detection analysis (ERDA) with α-particles [7].



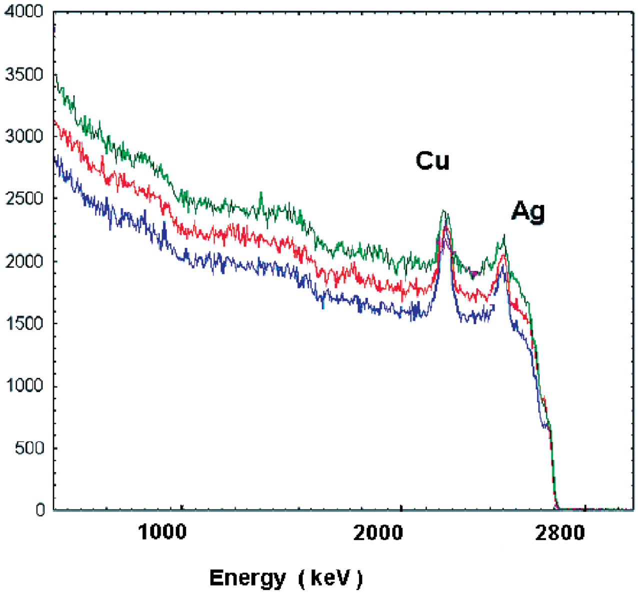
▲ **Fig. 2:** PIGE spectrum of the glaze of a ceramic platter possibly made by Bernard Palissy. The glaze is on a snake (figure 1) and is grey; its B_2O_3 concentration is 1.1%.

In the following, we give two examples to illustrate these techniques applied to ceramics, with first a PIGE analysis of boron in glazes of wares fabricated between the middle age and the 19th century and second a PIXE / RBS study of lustre on Hispanic ceramics.

Boron has appeared in glasses in the 17th-18th century with a massive presence in the 19th century due to a decrease of its price after the discovery of large quantities of borax in Death Valley (California) [8]. Boron cannot be detected by PIXE, then, we use PIGE induced by 3 MeV protons. The emission of γ rays corresponds to the reactions displayed in table 1; a spectrum for an ancient ceramic glaze (figure 1) is shown in figure 2. The concentrations for the three emissions of boron are used to verify that there is no coincidence in γ emission energy with other nuclei, giving thus reliable results. The concentration c is determined from the ratio of the peak areas of the art work (figure 2) to a standard for boron.

We have examined 33 ceramic objects covered with glaze produced between the Middle Ages and the 19th century to check for the presence of boron. Each object was submitted to one or two PIGE measurements. In the example of figure 2, the presence of boron confirms that the ceramic platter is not from the renaissance, but very likely a 17th century fabrication.

Indeed, among the 33 objects, there were medieval tiles from the "châteaux de Vincennes" and objects from Arras. From the Renaissance, PIGE was performed on fragments of objects from the Della Robbia's activities between 1450 and 1550, tiles made by Masséot Abaquesne who died in 1564, and shards of Palissy (1510 - 1590) wares found at the time of excavations made near the Louvre museum in the 1980's. In none of these objects, the concentration of B_2O_3 is above the detection limit that is around 0.05 % (weight percent). A number of glazes on ceramic wares from followers of Palissy contains B_2O_3 concentrations between 0.2% and 0.75%. Finally, PIGE was performed on various colours of two glaze palettes made by Avisseau (19th century); B_2O_3 concentrations between 3% and 15% have been found in 7 cases out of 35 PIGE •••



▲ **Fig. 3:** Rutherford backscattering spectra (RBS) obtained at one helium atmosphere taking three different points on a lustre ceramic ware (RFM 3) from Seville. A 50µm diameter 3 MeV α-particle beam was used. The spectra were simulated with SIMNRA [11] to obtain the concentration profiles of the various elements; they correspond to atomic concentrations of 4% Ag and 18% Cu in a 110 nm thick glaze layer at the surface.

••• measurements. The present results on glazes are in agreement with those found for glass [8].

In the last few years, there has been a strong interest for ancient lustre ceramics that have been investigated using SEM, transmission electron microscopy (TEM), X-ray diffraction, IBA, *etc*. [9 - 11]. Lustre is a ceramic decoration that appeared in the 9th century in the Middle East and spread around the Mediterranean basin in the following centuries. Lustre gives a metallic aspect which is due to copper and silver nano-particles distributed into a thin layer under the glaze surface. These particles can be visualized by TEM [9]. RBS provides a fast and universal technique to obtain concentration profiles of copper and silver in art works; it is non-destructive and is currently performed on valuable lustre ceramic wares from museum collections [10]. A study has been recently performed on shards excavated from a workshop in Seville that was unknown for any production of lustre ceramics [11]. The chemical composition of the glazes, determined by PIXE is typical of the Iberian production with 50% SiO_2, 35% PbO, 7% SnO_2. Concentration profiles have been determined by RBS. In places, the profiles show a loss of lead due to surface weathering during the underground storage over centuries [11]. The lustre layers are revealed by the Ag and Cu peaks (figure 3), both elements being present in all the lustre objects from Seville. Quantitative profiles are obtained with the SIMNRA simulation code. The layers containing the metallic particles are particularly thin (100-200 nm) and generally not covered by a 20-100 nm glass layer commonly found in other productions; they are rich in Cu. The ratio of Ag to Cu concentrations is found to vary considerably with the origin of the wares, lustre ceramics rich in Ag being yellow and those rich in Cu being red. External beam RBS is a very convenient non-destructive technique to obtain characteristics of art work sub-surface layers, as in the case of lustre ceramics [11].

Potters making lustre ceramics can be considered as early "nanotechnologists". However, nanoparticles were produced even earlier in dyeing hair and wool black [12]. It is important that the dyeing treatment leaves unchanged the mechanical properties of the fibres; this is achieved by 5 nm size PbS grains aligned along the axis of the hair, produced according to a recipe applied during the last 2000 years to darken hair. These ancient formulas included $PbO+Ca(OH)_2$ [12], lead acetate being present now in a popular men's hair colouring available in the market. This opens a possible inexpensive way to produce semiconductor quantum dots!

Synchrotron radiation

Synchrotron radiation methods find increasing number of applications in the field of cultural heritage. This has prompted the creation of dedicated committees at synchrotron facilities (for example, "Environmental and Cultural Heritage matters" at the European Synchrotron Radiation Facility; ESRF). Similar to **AGLAE**, synchrotrons offer powerful techniques combining high lateral resolution, high sensitivity, and, in addition, access to other physical and chemical information. Examples of application are various, going from "hard matter", studying corrosion in ancient metals or decoration of jades, glass or bronzes, to "soft matter", such as paper, textile, wood and passing through hybrid materials such as cosmetics or paintings.

In cosmetics from ancient Egypt, lead compounds are ubiquitous, with mostly black lead sulphide (PbS) and white lead carbonate ($PbCO_3$) in eye make-up [13]. Unexpected white constituents (laurionite PbOHCl; phosgenite $Pb_2Cl_2CO_3$) have been identified by X-ray diffraction; these compounds are not found in nature and have been synthesized in ancient Egypt by wet chemistry [13]. Laurionite and phosgenite were added because of their pharmaceutical properties. The microstructure of lead compound grains was evaluated by analysing the diffraction peak broadening and by TEM to identify the powder processing (grinding, thermal treatments, wet chemistry) for the cosmetic manufacture [14,15].

High energy X-ray radiations could be particularly suited for painting analyzes. Studies can be performed directly on the entire painting such as, for example, by K-edge imaging (radiography with X-rays of energy below and above the absorption edge), which will offer a direct visualization of the elemental distributions at the painting scale. But, analyses are generally carried out on micro-samples taken from the art work. The success of synchrotron techniques for such studies is linked to the intrinsic characteristics of the paintings that make classical analyses very hard. First, the amount of matter is usually tiny (less than 1 mm thickness), hence requiring sensitive techniques. Second, paintings always exhibit multi-layered structures, with layer thicknesses of ~10 µm; this leads to the favouring of micro-imaging techniques, with a good lateral resolution (about one micrometer). Third, painting fragments are very complex in term of chemistry, as they are made of mineral and organic matters, amorphous and crystallized phases, major and minor elements. Accordingly, a multi-modal approach is usually essential to solve the chemical complexity of such hybrid materials. In particular, the combination of micro X-ray fluorescence, micro X-ray absorption near edge spectroscopy (XANES), micro X-ray diffraction and micro-FTIR (infrared) spectroscopy is a key tool for the complete elucidation of painting compositions in order to derive information on its history (painter techniques, pigment synthesis, authentication…) and on its preservation for the future (mechanisms of degradation, processes of restoration…).

As an example, the combination of micro X-ray fluorescence (µ-XRF) and micro X-ray spectroscopy (µ-XANES) was successfully employed to explain the blackening processes damaging red Pompeian paintings [16]. The conservation of Pompeii and surrounding cities is crucial because these cities are unique snapshot of the every-day life in the Roman Empire at the beginning of the 1st century. Unfortunately, some of the beautiful red wall paintings, which contributed to the Pompeii reputation, are suffering from degradation following their excavation. Many paintings are covered with a deep red pigment, mercury sulphide (HgS), commonly named cinnabar. Since Antiquity, this pigment is known to be potentially unstable. Indeed, in certain circumstances, it can turn into sad grey-black shades (Figure 4, left).

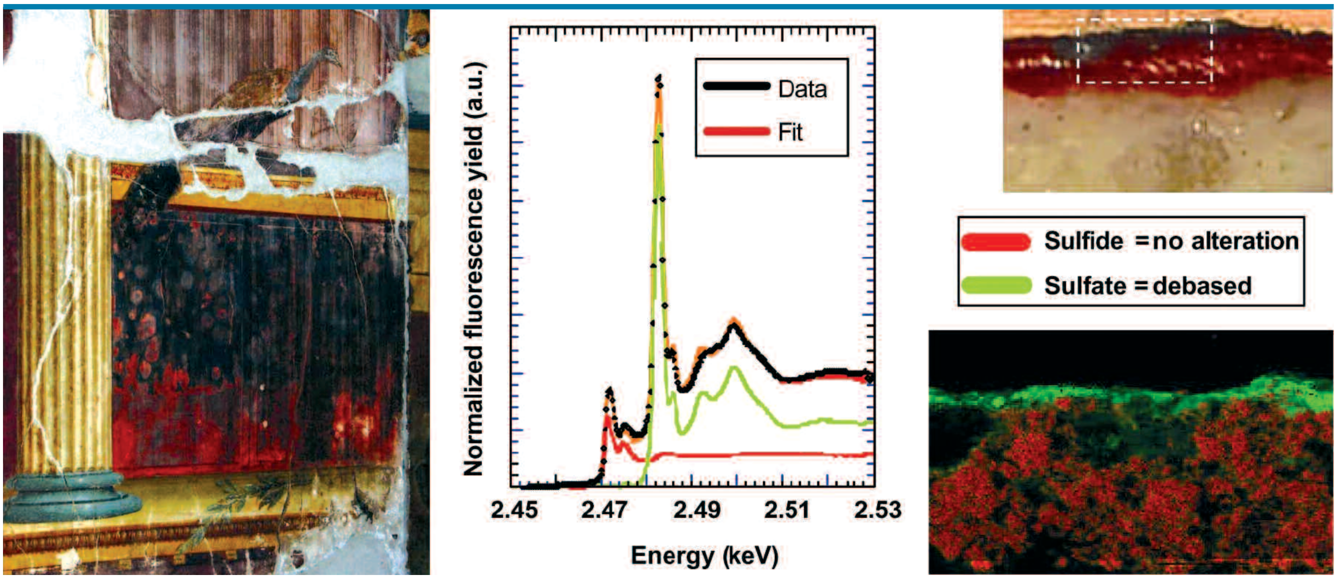
The common assumption proposed to explain this phenomenon is the phase transformation of red cinnabar (hexagonal phase) into black meta-cinnabar (cubic phase) under light. Different analyses were performed at the ID21-beamline (ESRF) to tackle this problem [16].

Micro X-ray fluorescence signals were mapped over pink, grey or black surfaces. Thus, elemental distributions and colours were directly correlated. Two main elements revealed a clear correlation with alterations. Chlorine was found to be associated with a grey alteration. Chlorine K-edge spectroscopy (XANES) demonstrated that it was involved in various species: NaCl and lilac-grey mercury-chalcogen-halide/oxide phases. Analyses performed on darker parts of the painting, showed a high accumulation of sulphur without chlorine. X-ray absorption spectroscopy (XANES) at the sulphur K-edge revealed the speciation of sulphur and refuted the hypothesis of a phase transformation into meta-cinnabar. Amazingly, instead of this suspected phase, another compound was identified: calcium sulphate, namely gypsum (Figure 4, middle). So, instead of a "simple" phase transition, sulphur was subjected to oxidation going from a reduced sulphide (S(-II)) to an oxidized sulphate (S(+VI)) state. Most presumably, this gypsum ($CaSO_4$, $2H_2O$) results from the reaction of SO_2 with the calcite ($CaCO_3$) present in the mortar. This assumption is supported by the fact that chlorine can catalyse the linkage reaction $HgS \rightarrow Hg + S$, thus providing a source of sulphur for further reactions with the oxygen of air and the final formation of SO_2.

Taking benefit from the clear difference of oxidation between original cinnabar (reduced sulphur, S(-II)) and debased sulphur (sulphates, S(+VI)), it was possible to map the distribution of the different species, by tuning the excitation energy at 2.472 and 2.482keV respectively. In this way, maps of the two kinds of sulphurs were obtained on the surface of different fragments [16]. In addition, an in–depth analysis was also performed. The question was how to image the diffusion of the alteration process inside the pigment layer. A sample was embedded in resin and polished perpendicular to the surface. Therefore, all the layers were accessible from the mortar to the surface. The pigment layer was 100 µm thick (figure 4, right, upper) rendering the use of micro-probe essential (0.7µm horizontal by 0.3µm vertical). Figure 4 (right, lower) shows that debased sulphates (in green) are present in a very thin superficial layer of about 5µm. Below, a thick layer of intact cinnabar (in red) is still present.

This work refuted the classical explanation proposed for cinnabar blackening. Instead, a complex pathway involving the reaction of both chlorine and sulphur dioxide was identified [16]. This study exploits the high spatial resolution, low •••

▼ **Fig. 4:** Darkening of cinnabar (HgS) mural paintings from Pompei. Left; photograph of a damaged zone (provided by M. Pagano). Middle; micro-XANES at the sulphur K-edge. The experimental data (black) are fitted by a combination of cinnabar (red) and gypsum (green). Right; cross-section of a painting sample observed in optical microscopy (upper), a detail being mapped by micro-XANES (lower), showing the distribution of the various sulphur species.



••• detection limit and high chemical sensitivity provided at the ESRF – ID21 X-ray microscope, in particular in the XANES mode. A complete elucidation of this phenomenon will require the analysis of a wider variety of samples originating from various environmental contexts (inside or outside buildings; in various climates; with or without protecting overlayer…).

A similar set-up was recently and successfully used to identify uncommon pigments in 16th century paintings. The aim of the study was the elucidation of the Grünewald technique to render metallic aspects in several of its masterpieces (the *Isenheim Altarpiece* and the *Basel's crucifixion*). The same combination of micro-fluorescence and micro-X-ray absorption provided images of micrometer grains of grey stibnite (Sb_2S_3) dispersed in a lead white matrix [17].

Yet, paintings are not made only of minerals. They can also be composed of organic matter, which can vary depending on the layer (gluing layer, ground layer, priming layer, coloured layers, glazes, varnishes, restoration layer). FTIR spectroscopy has already demonstrated its ability for the identification of the various organic material used in paintings (oil, resin, gum, protein…). The combination of a microscope with FTIR spectroscopy was a decisive step for the study of painting as it was possible to see and to choose the location of the spectrum acquisition. An even more decisive step was achieved thanks to the synchrotron sources which provide a much brighter source compared to usual thermal sources. With such equipment, the beam size can be easily lowered below $10 \times 10\ \mu m^2$ without significant lost of flux [18-19]. This latter possibility is essential for the discriminative analysis of each layer of the painting. Recent analyses of paintings from various times and various places should be published soon.

Conclusions and perspectives

The aims of heritage research are to understand the past through the study of objects, establishing detailed information on date, place, technology, materials, *etc.* The efforts in investigating and preserving the heritage are steadily growing in our societies. Through a few examples, we hope to have shown the importance of advanced tools derived from various fields of physics. The laboratory of C2RMF provides an easy access to **AGLAE** for IBA studies of art works that come on a daily basis from nearby museums. **AGLAE** is unique because it is dedicated to non-destructive analyses of art works and has been used in collaboration with curators for more than a decade. Thanks to the support of the European union (EU-ARTECH programme), **AGLAE** is also accessible to researchers from other countries for cultural heritage investigations. New laboratory techniques involving small size beams for 3 dimension analyses are now in development. These take advantage of the progress in sources, optics and detectors, that derive from facilities existing at synchrotron radiation facilities.

Non-destructive analyses are the best approach for art works. However, transportation of valuable or oversize objects is at present a strong limitation on their study at large scale facilities. Portable light weight systems are an alternative and are already available for X-ray fluorescence and diffraction, infra red and Raman spectroscopy, *etc.* Other portable instruments are in development that will extend this approach in the study of cultural heritage objects.

γ energy	429 keV	718 keV	2125 keV
Reaction	$^{10}B\ (p, \alpha_1\ \gamma)\ ^{7}Be$	$^{10}B\ (p, p_1\ \gamma)\ ^{10}B$	$^{11}B\ (p, p_1\ \gamma)\ ^{11}B$
Yields at 3.1 MeV	7.2×10^6	1.3×10^6	4.8×10^6

▲ **Table 1:** PIGE conditions for the analysis of boron

Progress in the knowledge and the conservation of heritage depends not only on the availability of complementary analytical techniques, but also on the close collaboration of many disciplines including physicists, geologists, chemists and curators, art historians, conservators, archaeologists, *etc.* a condition that is not always easy to fulfil. ■

About the authors

The research activity of **J.Castaing** derives from his background in solid state physics and materials science that he applies to the study of heritage objects. After gaining his Ph.D. from the University of Orsay, he joined the CNRS to create a research group on the plasticity of ceramics and spent several years in the USA and in Spain. He has had a number of additional responsibilities, in particular, Head of the laboratory CNRS UPR 1341, Advisor of the "Ministre de la Recherche", *etc.*

After gaining the "agrégation" of chemistry at the "École Normale Supérieure" of Lyon, **M.Cotte** obtained her PhD for her research, at the C2RMF, on lead-based cosmetics and pharmaceutical compounds used in Antiquity. During her post-doc at the ESRF, she has enlarged the application of micro X-ray and FTIR spectroscopies to paintings.

References

[1] J.P.Mohen, M.Menu, B.Mottin, Mona Lisa: *inside the painting by Leonardo*, Harry N. Abrams Incl., 2006.

[2] J. Arneborg *et al.*, *Europhysics News* **33**, 77 (2002)

[3] J. Castaing *et al.*, *J. Cult. Herit.* **5**, 393 (2004)

[4] T. Calligaro *et al.*, *Nucl. Inst. And Meth. B* **161-163**, 328 (2000)

[5] T. Calligaro *et al.*, *Nucl. Instr. and Meth. B* **226**, 29 (2004)

[6] J.C. Dran *et al.*, *Nucl. Instr. and Meth. B* **219-220**, 7 (2004)

[7] I. Reiche *et al.*, *Nucl. Instr. and Meth. B* **249**, 608 (2006)

[8] E. Speel and H. Bronk, *Berliner Beiträge zur Archaeometrie* **18**, 43 (2001)

[9] D. Hélary *et al.*, *J. Amer. Ceram. Soc.* **88**, 3218 (2005)

[10] G. Padeletti *et al.*, *Appl. Phys. A* **83**, 475 (2006)

[11] A. Polvorinos del Rio *et al.*, *Nucl. Instr.and Meth. B* **249**, 596 (2006)

[12] P. Walter *et al.*, *Nano Lett.* **6**, 2215 (2006)

[13] P. Walter *et al.*, *Nature* **397**, 483 (1999)

[14] P. Martinetto *et al.*, *J. Mater. Res.* **17**, 1601 (2002)

[15] C. Deeb *et al.*, *Appl. Phys. A* **79**, 393 (2004)

[16] M. Cotte *et al.*, *Anal. Chem.* **78**, 7484 (2006)

[17] M. Cotte *et al.*, *Anal. Chem.*, in press

[18] M. Cotte *et al.*, *Appl. Phys. A*, in press

[19] A. Luveras *et al.*, *Appl. Phys. A*, in press