ION BEAM ANALYSIS TECHNIQUES: A POWERFUL SET OF TOOLS FOR THE IDENTIFICATION AND SOURCING OF ANCIENT GEMS

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1. INTRODUCTION

Gemstones are defined as rare minerals having a high clarity, a high hardness and showing a bright colour and a nice shining. The most important gems are diamond, ruby, sapphire and emerald. These gems are called precious stones.

Gems have fascinated man since the earliest times. They have always been sought out by man for their aesthetic and symbolic value. Due to their scarceness and high value, gems were appreciated by the mighty ones as a sign of their power (emperors and kings, dignitaries of religions ...). Their high hardness and hence strong resistance to deterioration symbolised the everlastingness of their reign. This last property is interesting from an archaeological point of view: gemstones travel through time without noticeable alteration, even buried in aggressive environment. On the other hand, gems may be used several times on different jewels, possibly cut and polished again. Like spices and other precious and sought-after items, gems were brought back from long distance. Accordingly, they are good tracers for ancient trading routes and influence of civilisations. Each civilisation had its own favourite gemstones: lapis lazuli in Egypt; amber and emerald in the Roman Empire; garnet in early Middle Ages western civilisations; jade, ruby and sapphire in Far-East cultures. Moreover, the provenance of some ancient gems such as emeralds or garnets is still debated. For all these reasons, the study of gems kept in museum collections is a promising research field.

2. ANALYSIS OF GEMSTONES

Usually, the identification of gems relies on the measurement of optical and mechanical properties: refractive index n, birefringence, visible optical spectrum, specific gravity ρ [1]. When gemstones are set on a jewel, these measurements are not always

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readily carried out. Dismounting them from the setting or sampling is of course prohibited. The provenance of gems, that means the geographical location of the deposit, is often inferred by identifying specific inclusions. Another possibility is the chemical characterisation of gemstones. In this case, gems are directly identified by means of their major chemical constituents. For instance, diamond is a pure carbon crystal; ruby is an Al_2O_3 crystal coloured by less than 1% Cr; sapphire is also an Al_2O_3 crystal but its blue colour is due to trace amount of Ti and Fe; emerald is a beryl of formula $Be_3Al_2(SiO_3)_6$ coloured by a small amount of Cr. The trace element content of gems also carries valuable information. Indeed, some of these trace elements come from the surrounding rocks, being incorporated during the genesis of the crystal. Being linked to the geological context (type of terrain and rock-forming history) trace element content may act as a fingerprint of the occurrence of a gemstone. A wide range of techniques have been applied in view to perform chemical analysis: EMPA, XRF, NAA, ICP/MS, SIMS. Table 1 summarises some features of these analytical techniques. Of course, careful observation of the gems and their internal features using conventional gemmological means has to be performed prior to proceeding to these chemical analysis. Moreover, several analytical techniques have often to be combined for inferring unambiguously the provenance of a gem.

Table 1. Features of several analytical techniques used for the chemical characterisation of gems

	EMPA	*EDXRF*	*NAA*	*LA-ICP/MS*	*SIMS*	*IBA*
Element range	> Na	> Na	Selected	all	all	all
LOD	> 1.000 ppm	1-1.000 ppm	< 1 ppm	< 1 ppm	< 1 ppm	1-1.000 ppm
Probe size	μm	mm	whole sample	10-μm	μm	10-μm
Destructive	no	no	activation	μ-destructive	μ-destructive	no
Preparation	yes / coating	no	no	no	yes / coating	no
Isotopic info	no	no	no	possible	yes	no
Sample size	cm	any	cm	any	cm	any

EMPA: electron microprobe analysis. EDXRF: energy-dispersive X-ray fluorescence.
NAA: neutron activation analysis. LA-ICP/MS: laser-ablation Ion-coupled-plasma mass spectrometry.
SIMS: secondary ion mass spectrometry. IBA: ion beam analysis.

3. IBA TECHNIQUES: PIXE AND PIGE APPLIED TO THE STUDY OF GEMS

It is not the place here to give a complete description of Ion Beam Analysis (IBA) techniques; numerous books and review papers will fulfil this requirement [2 and 3]. Let us just recall that IBA techniques rely on the same process: identification of elemental constituents by detecting products of interaction of the ion beam and the target (i.e. gemstone). Among them, PIXE (*particle induced X-ray emission*) is quite similar to XRF, being based on the detection of X-ray emitted by the target atoms, subsequent to an inner-shell ionisation. The only difference stems from the excitation source which is a charged particle beam instead of a X-ray beam. For the PIGE technique, acronym for *particle induced γ-ray emission*, there is no counterpart. PIGE relies on a nuclear reaction subsequent to the collision between an incident particle and a target nucleus. Following this reaction, the nucleus might emit a γ-ray having a specific energy. On the other hand, IBA techniques cannot be used for isotopic ratio determination nor does it give information on chemical bonds.

From the point of view of gemmology, the IBA techniques exhibit several interesting features. First, in-air IBA techniques allow *in situ* and non-destructive analysis of gems without sample preparation. This harmlessness is a must for the study of valuable objets such as historical jewels. Using simultaneously the PIXE and PIGE methods it is possible to determine a wide range of elements. PIXE gives the composition for elements ranging from Na to U, while PIGE usefully extends the range to lighter ones: F, Be, Li, B. Secondly, the high sensitivity of these techniques permits measurement of elements down to a low level of concentration (e.g. ~ ppm wt level for transition metals in corundum). Finally, the use of a microbeam with a size of less than 20-μm allows selection of inclusions for their identification. Such a small spot is also useful for analysing a region free of inclusions. Indeed, when using a broader spot size, there is always the risk of including an inclusion in the analysed area that may bias the trace composition of the crystal (e.g. an Fe-containing inclusion might lead to a wrong Fe trace content in a ruby).

From the point of view of the IBA techniques, gemstones are ideal samples when compared to other objects of cultural heritage such as paintings or ceramics. They have a simple, homogeneous composition. The sample has a polished and often flat surface. Owing to their very stable crystal structure, gems are nearly insensitive to beam effects (no alteration). Charging of these usually non-conductive targets is avoided when using an external beam setup.

4. EXPERIMENTAL SETUP

The experimental setup and its successive improvements have been thoroughly described [4]. Only the striking features will be recalled here.

The analytical system is based on an external beam line of the AGLAE accelerator facility (figure 1). The usual 3-MeV proton beam is focused down to 30 μm size using magnetic lenses (3 MeV is proved to be an optimum energy for analysing geological samples). This beam is brought on the sample by passing through a very thin Si_3N_4 foil. The detection of X-rays is achieved using two detectors. A first one is dedicated to light elements, which are the major constituents of the gems (from Na to Fe). It has a low solid angle, and a minimal filtering using an ultra thin window combined

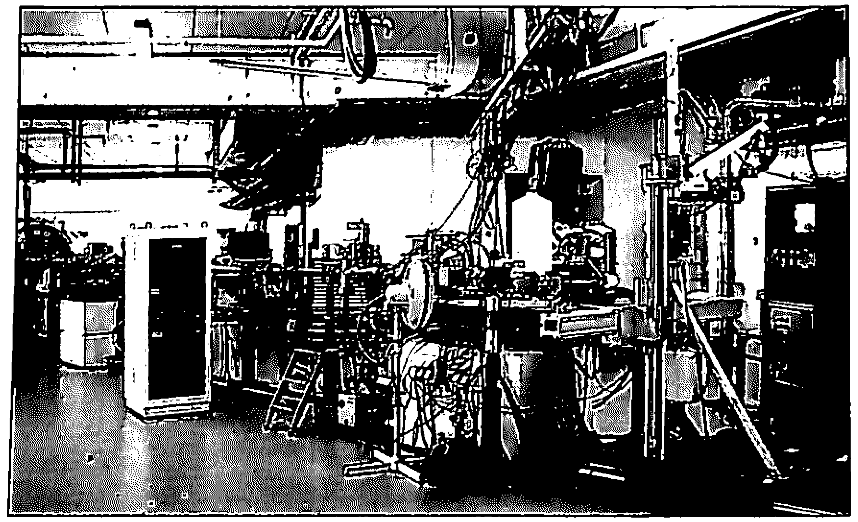

Figure 1. View of the external beam line of the AGLAE accelerator-based IBA facility.

with a helium flow. The second one is dedicated to heavy elements (from Ca to U) at a low level content. It has a high solid angle and a filter chosen in order to remove matrix X-rays. Gamma-rays are collected using a High Purity Germanium detector. The beam is monitored using a signal emitted by the exit foil: backscattered protons or X-ray line of Si, according to experimental requirements.

5. APPLICATION TO GEMSTONES

We will describe some recent applications of the PIXE and PIGE techniques to ancient gems from museums performed with the AGLAE setup of the *Centre de Recherche et de Restauration des musées de France*. It should be emphasised that all gemstones studied here are well documented and have traceable history. So we are confident that these gems are the original ones.

5.1. RUBY: ISHTAR'S STATUETTE

This statuette which may represent Ishtar, a goddess equivalent to Aphrodite, is a perfect illustration of a IBA study of gemstones (figure 2). The sculpture is a naked woman carved in alabaster, her eyes and navel inlaid with rubies. This remarkable piece, which joined the Louvre collections in 1866, was excavated in the vincinity of Babylon in Mesopotamia [5]. For stylistic and typological reasons it is attributed to the Parthian period (2nd century B.C. to the late 2nd century A.D.).

We were able to confirm that the cabochons were indeed natural rubies and not coloured glass, as had been believed even quite recently, as the two main constituents of rubies were revealed: 99% alumina (Al_2O_3), associated with less than 1% chromium, the element responsible for the characteristic red colour of ruby. Several trace elements were also measured, including titanium, vanadium, iron, copper, gallium, all being characteristic of natural stones (figure 3). The similar aspect and chemical composition of the three inlays suggest the use of a single batch of stones for the statuette.

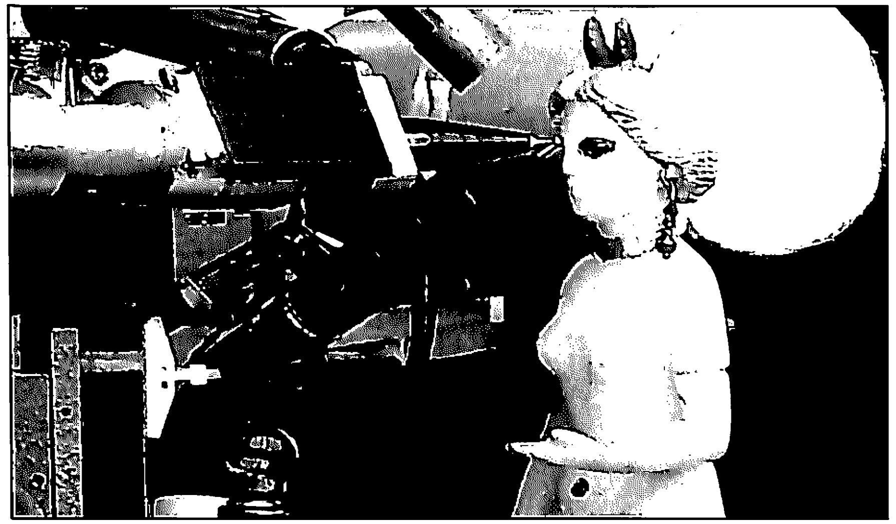

Figure 2. Ishtar in being analysed using the external beam system (ver cuadernillo a color, pág. v).

In order to determine the geographical origin of this statuette's rubies, we undertook a comparative study with contemporary rubies of known provenance [6]. A total of over 500 analyses was carried out on rubies from the main existing deposits: Afghanistan, Myanmar (Burma), Cambodia, India, Kenya, Madagascar, Sri Lanka, Thailand and Vietnam. The trace element contents of the stones are quite different depending on their provenance and are homogeneous within a given deposit, a feature absolutely needed for a provenance study based on geochemistry. Multivariate statis-

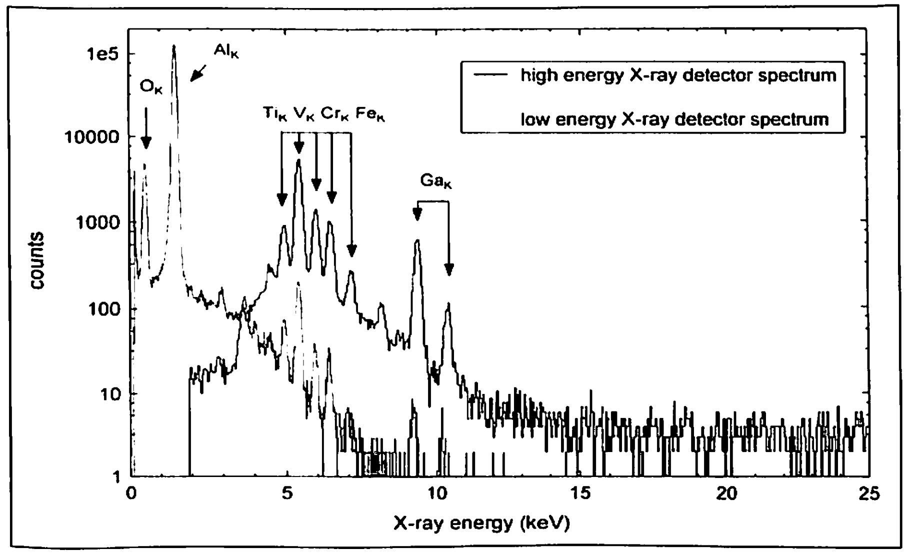

Figure 3. X-ray spectra of major and trace elements recorded on a red eye of the statuette.

tical methods were used (factor analysis, hierarchical classification and discriminant analysis), incorporating all the chemical tracer elements (Ti, V, Cr, Fe, Ga). All these analyses converge and show that the statuette's rubies have a composition very close to that of rubies from Burma (figure 4).

The results of the geochemical study were confirmed by classical gemmological observations conducted concurrently; in particular, the rutile inclusions observed in the eyes and the navel are consistent with a Burmese origin.

Research carried out on the rubies of the Parthian statuette from the Louvre combining observation of the gems and their geochemical characterisation by the PIXE method has led to a better insight into this work of art by identifying its constituent materials. In addition, it has provided the opportunity to establish a data base on the compositions of the main ruby deposits. Finally, thanks to statistical analysis, a provenance for the statuette's rubies could be proposed: Burma. It can thus be concluded that the gems from the Parthian statuette are evidence for trade or exchange over several thousand kilometres between Mesopotamia and South-East Asia during the Parthian period. As far as we know, this is the earliest use of rubies identified to date in this region. This figure of Ishtar is remarkable for it combines influences deriving from three civilisations: Mesopotamia (the image of the naked woman as a fertility symbol), Greece (the Hellenistic realism of the body), and finally Asia (the presence of the rubies).

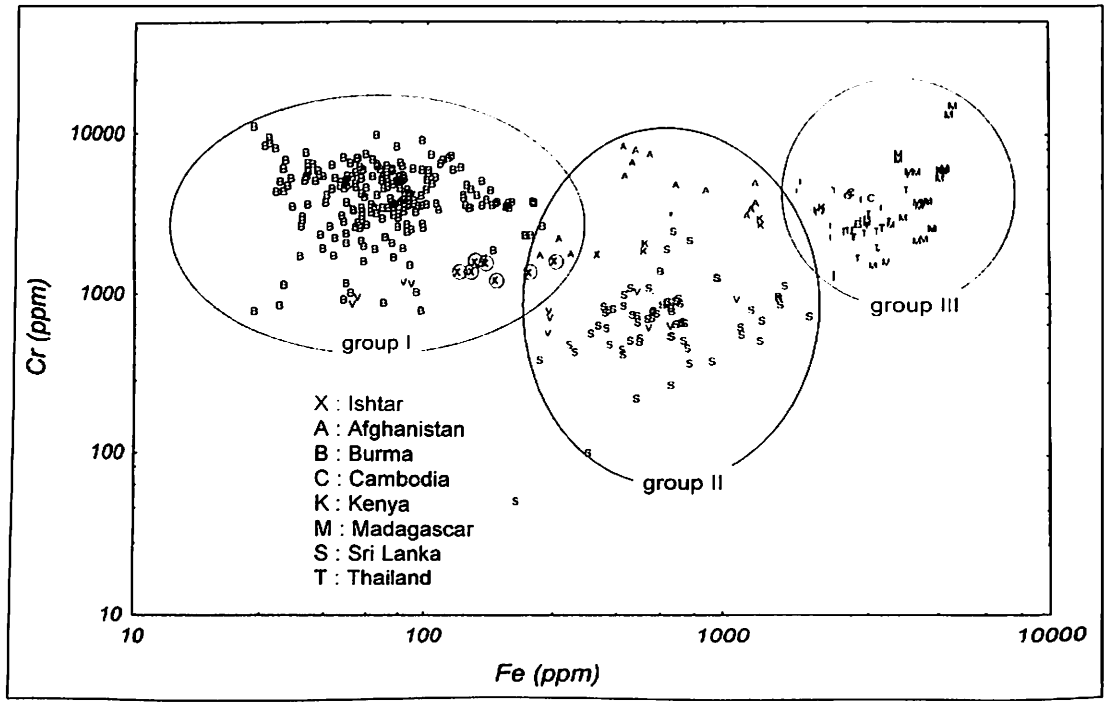

Figure 4. Plot of Cr vs Fe content for the rubies of the statuette and reference rubies.

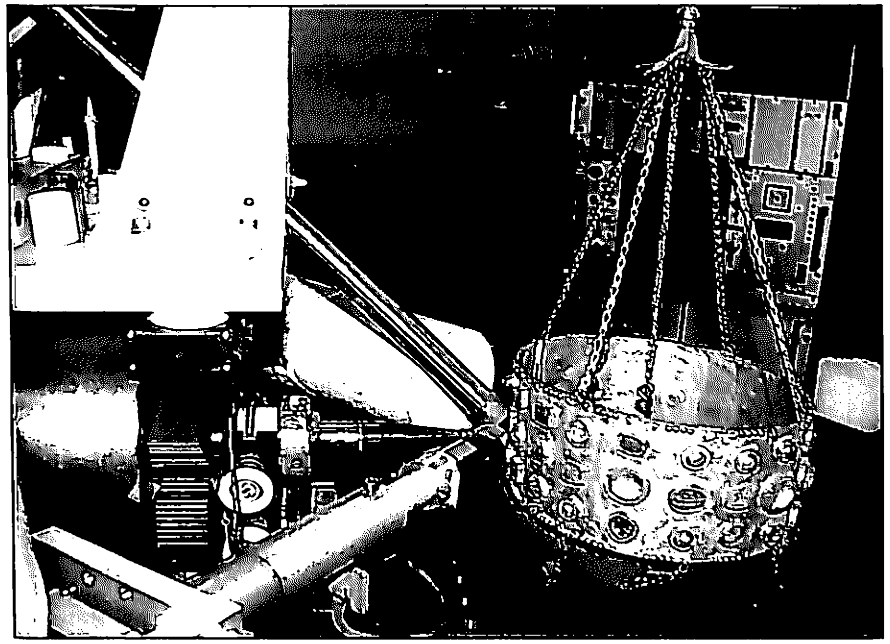

Figure 5. Royal votive crown being analysed with the external beam (ver cuadernillo a color, pág. vi).

5.2. EMERALD: THE VISIGOTHIC TREASURE

We report here an application to the analysis of emeralds of the Guarrazar treasure (figure 5). This famous set of votive royal crowns, made of gold with inlaid gemstones, dates from the Visigothic period (7th-8th centuries). It was excavated in 1858 near Toledo and is now split into two main parts kept at the National Archaeological museum in Madrid, Spain and the National Middle-Ages museum in Paris, France [7]. The sources of emeralds used in ancient Egypt and the Roman Empire are quite well documented; it is not so for the early Middle-Ages. This work aimed at comparing ancient emeralds to those of various origins reported in ancient literature (Egypt, Austria, Afghanistan, Oural), on the basis of chemical analysis [8]. PIXE and PIGE techniques permitted to identify gemstones by means of their composition in major elements (Be, Al, Si) and to determine their trace element contents (figure 6). Provenance determination relies on the comparison of these contents to those of reference emeralds constituting a data base of geochemical composition. The most discriminating elements were Li, Na, V, Rb and Zn. The measured contents in these ancient emeralds are only compatible with Egyptian (Jebel Zabara) or Austrian (Habachtal) deposits (figure 7). Since it permitted to discard alternate assumptions (e.g. Ural, Afghanistan or Pakistan), this work provided a new insight into the trade routes of gemstones at the time of the Great Invasions.

5.3. GARNET: JEWELS OF THE FIRST KINGS OF FRANCE

Garnets belong to a family of gems having variable composition. The most common type is the pyralspite family with the chemical formula $X^{++}{}_3Al^{+++}{}_2(SiO_4)_3$, X be-

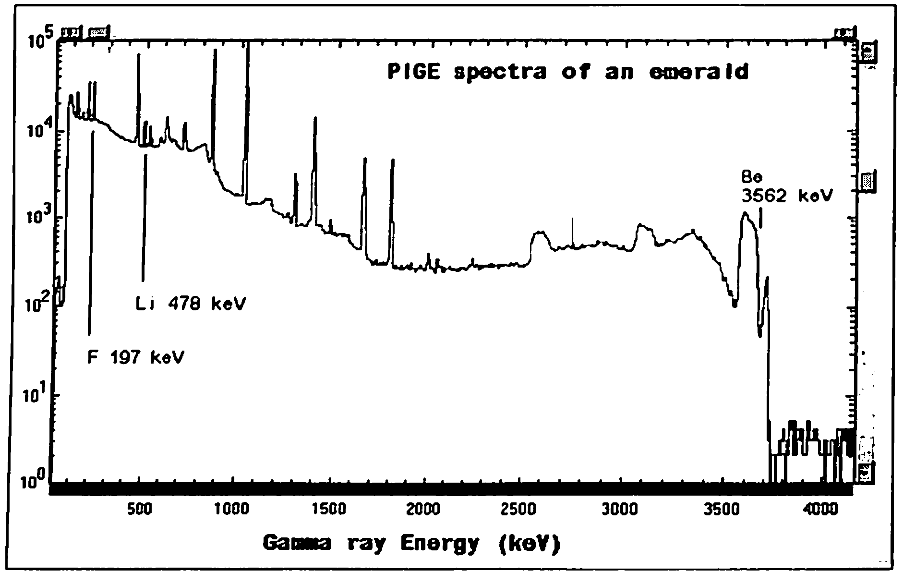

Figure 6. Gamma-ray spectrum of an emerald.

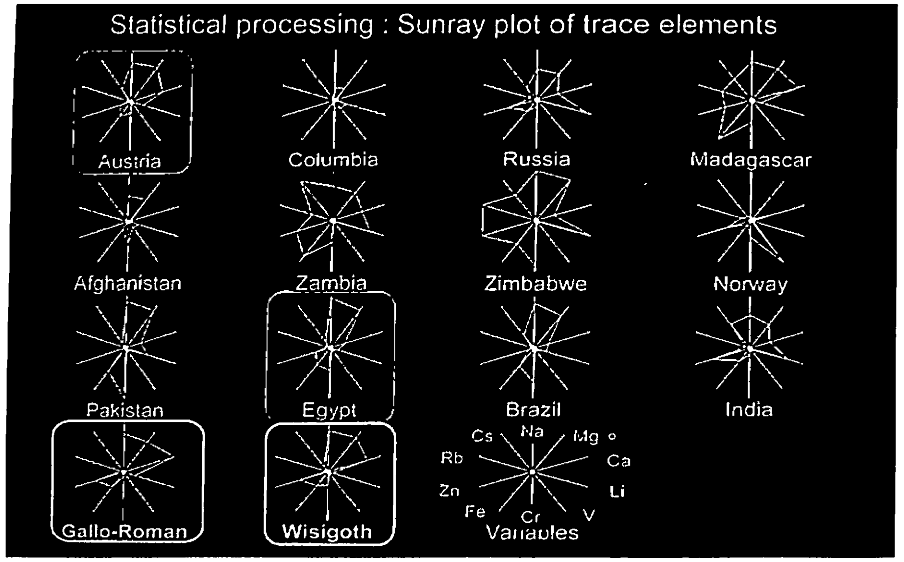

Figure 7. Sunray plot of trace elements content of ancient and reference emeralds.

ing either Fe (almandin garnet), Mg (pyrope garnet) or Mn (spessartite garnet), or a combination of them. The question of the nature, origin, cutting and setting techniques of the garnets used in Europe during the Early Middle Ages is highly debated.

A first attempt to apply IBA techniques to Early Middle Ages garnets has been performed in the C2RMF [9]. This work dealt with the identification of garnets mounted on Merovingian jewellery from Louvres-en-Parisis. The conclusion was that these archaeological garnets had a major composition compatible with garnets from Sri Lanka (almandine-pyrope type).

We are currently developing a new research program on the Merovingian garnets. The aim of this work is to include trace element and near-surface analysis of the gems.

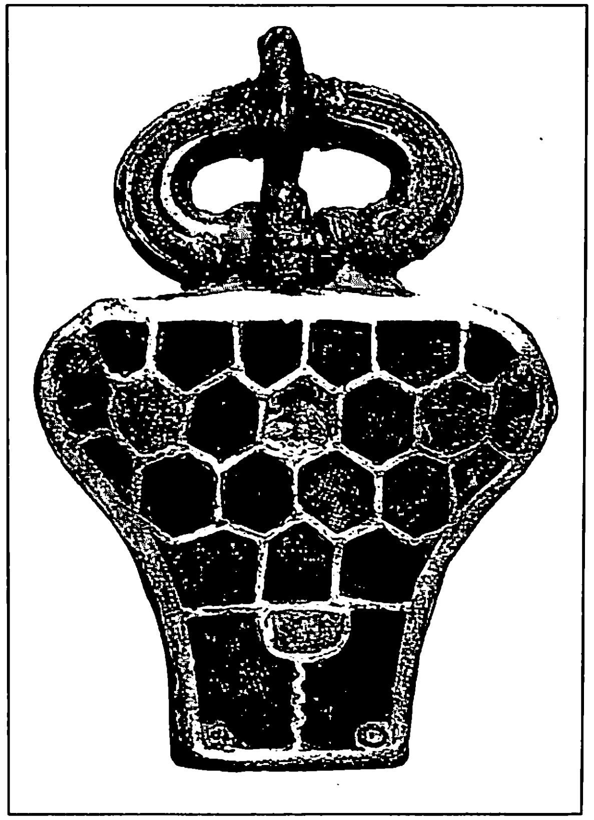

Figure 8. Merovingian jewel with garnets set in cloisonné style (ver cuadernillo a color, pág. vi).

These garnets are set on the *cloisonné* jewels (figure 8) from the royal treasure of Saint Denis, France, comprising the famous jewels of Queen Aregonde [10]. This work will be extended with the analysis of garnets excavated from various archaeological sites in Europe.

6. CONCLUSION

IBA techniques and specifically the PIXE/PIGE combination in air appear as valuable tools for analysing gems mounted on historical jewels. They usefully complement classical gemmological investigations. The main advantages are 1) completely non-destructive analysis, 2) broad range of elements detected, 3) 10-μm size spatial resolution 4) ppm level sensitivity and 5) good accuracy. They were applied to determine the nature and provenance of ancient rubies. For Middle Ages emeralds and garnets, the results already obtained are promising. More reference data are needed and the combination with other analytical techniques has to be tried.

7. REFERENCES

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