The Origin of Ancient Gemstones Unveiled by PIXE, PIGE and μ-Raman Spectrometry

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Chapter II-2

The Origin of Ancient Gemstones Unveiled by PIXE, PIGE and μ-Raman Spectrometry

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Abstract

Gemstones set on ancient jewels are invaluable witnesses from the past. To obtain these much appreciated items, Men had established long-distance trade routes, the extension and historical evolution of which represent a major archaeological issue. For these studies, chemical characterisation has proved to be very useful. First, the elemental composition directly provides the nature of the gemstone, like for example, SiO_2 for quartz, Al_2O_3 for ruby and sapphire, $Be_3Al_2Si_3O_{18}$ for emerald. Secondly, the trace element content of a gemstone, when compared to reference gems of known origin, may unveil its provenance. However, to perform the chemical characterisation of these valuable items, suitable analytical methods must be non-invasive (neither sampling nor dismounting of the gems from the jewels) and non-destructive (no damage to the gem). Ion beam techniques such as particle-induced X-ray emission (PIXE) or particle-induced γ-ray emission (PIGE) meet these specific requirements. PIXE permits the measurement of all elements heavier than sodium with a sensitivity reaching the μg/g, while PIGE extends the range of elements to lighter ones (Li, Be, B, F). These totally harmless techniques are directly applied to the gem in air with a 20-μm spatial resolution, allowing selecting specific regions of the crystal. The identification of inclusions, a provenance criterion often used in gemmology, can be complementarily performed by Raman micro-spectrometry. Indeed, the inclusions are often located out of reach of the ion beam in the crystal. This paper presents the benefits of the combined use of external beam PIXE/PIGE and Raman micro-spectrometry. The use of these modern analytical techniques is exemplified by the study of ancient gems: rubies from a Mesopotamian statuette, emeralds and garnets set on Barbarian jewels dating from the Dark Ages.

1. Introduction

Gemstones are defined as precious minerals combining high hardness, bright colour, nice brilliance and good transparency. Among the rare minerals exhibiting these features, the most important ones are diamond, ruby, sapphire and emerald. These gems are called precious stones. Gems have fascinated men since the earliest times and have been sought for their aesthetic and symbolic value. Their superior hardness and hence strong resistance to alteration is interesting from an archaeological point of view as gemstones can travel through time without noticeable weathering, even buried in an aggressive environment. Like spices and other precious and sought-after items, gems used to be recovered from long distance and therefore can be used today as archaeological tracers of ancient trading routes. Each civilisation had its own favourite gemstones: lapis-lazuli and turquoise in Ancient Egypt, amber and emerald in Roman Empire, red garnets for Germanic peoples of the Dark Ages; jade, ruby and sapphire in Far-East cultures. Two major issues concern ancient gems. The first is the identification of the mineral, since its often poor crystal quality (compared to modern ones), rough polish and irregular shape can be misleading. The second issue is the determination of its provenance, often scarcely documented in ancient texts or even completely unknown. For all these reasons, the study of gems conserved in museum collections by modern analytical techniques is a promising research field.

2. Analytical methods suitable for the characterization of gemstones

In gemmology, the identification of gemstones usually relies on the measurement of optical and mechanical properties: refractive index n, birefringence B, visible optical spectrum, and less frequently specific gravity ρ and hardness H [1]. However, since ancient gemstones are frequently mounted in a metallic setting and their surface is seldom flat (often in round shape) and transparent, these simple measurements are often problematic (any dismounting from the setting or sampling being of course prohibited). Under these circumstances, gemstones can still be directly identified by means of their chemical composition. For instance, diamond is a pure carbon crystal; ruby is an aluminium oxide crystal (Al_2O_3) coloured by less than 1% Cr; sapphire is also an Al_2O_3 crystal but its blue colour is due to trace amounts of Ti and Fe; emerald is a beryl of formula $Be_3Al_2Si_6O_{18}$ coloured by traces amounts of Cr. Table 1 summarises the properties of important gems. Note that gems are often composed of light elements (e.g. Be, Li, C, O, F, Al, Si, see for instance the tourmaline); therefore techniques suitable for their chemical analysis must be able to measure a wide range of elements, ideally extending down to hydrogen. The provenance of gems, i.e. the geographical location of their occurrence, is usually determined by the observation of microscopic features inside the crystal such as mineral inclusions, by means of an optical microscope. Raman micro-spectrometry, very effective for the identification of mineral phases, is being increasingly used for this task [2]. Chemical analysis can also be employed to establish the provenance by measuring trace elements present in gems. In fact, trace elements incorporated in the

gem crystal during its growth are linked to its geological context (type of terrain and rock-forming history) and can therefore be used as a fingerprint of its occurrence. Recently a new method to determine provenance has been introduced based on the slight variation of isotopic composition, which also depends on the formation conditions of the gem crystal. For example, the concentration of isotope 18 of oxygen ($^{18}O/^{16}O$ ratio) has been successfully applied to determine the origin of ancient emeralds [3]. The isotopic ratio is measured using secondary ion mass spectrometry, a micro-destructive method performed in vacuum that can only be applied to small objects.

Table II-2-1. Properties of a few gems: n is the refractive index, B birefringence, ρ specific gravity, H hardness. In the colour column are indicated the trace elements responsible for the colour of the gems.

	Formula	n	B	ρ	H	Structure	Colour
diamond	C	2.42	0.000	3.52	10	cubic	/
ruby	Al_2O_3	1.77	0.008	4.00	9	rhomboedric	Cr
sapphire	Al_2O_3	1.77	0.008	4.00	9	rhomboedric	Fe, Ti
emerald	$Be_3Al_2(SiO_3)_6$	1.58	0.006	2.71	7.5	hexagonal	Cr, V
topaz	$Al_2(F,OH)_2SiO_4$	1.63	0.010	3.54	8	orthorhombic	Fe, Cr
tourmaline	$Na(Li,Al)_3Al_6(BO_3)Si_6O_{18}(OH)_4$	1.63	0.018	3.06	7.5	rhomboedric	Mn, Fe
quartz	SiO_2	1.55	0.009	2.65	7	rhomboedric	/
amethyst	SiO_2	1.55	0.009	2.65	7	rhomboedric	Fe
garnet	$X_3Al_2(SiO_4)_3$, X=Fe,Mg, Mn	~ 1.8	0.000	4.00	7.5	cubic	Fe, Cr

Table 2 summarises the main features of several analytical techniques used to characterise gems: XRF, scanning electron microprobe, neutron activation, mass spectrometry using ICP/MS and SIMS, Raman micro-spectrometry. Ion Beam Analytical methods have the advantage to combine non-destructiveness, a wide range of measured elements together with a good sensitivity and accuracy. The chemical analysis by IBA can usefully be combined with the structural information delivered for instance by Raman spectrometry. In any case, a careful observation of the gems and their internal features by conventional gemmological means has to be performed prior to proceeding to chemical analysis. However, IBA techniques cannot be used for isotope determination nor does it give information on chemical environment (valence, bonds).

Table II-2-2. Features of several analytical techniques that have been applied for the chemical characterisation of gems. [1] X-ray fluorescence in air, [2] Scanning electron microscope with energy-dispersive microanalysis, [3] Inductively coupled plasma with mass spectrometry and laser ablation, [4] Secondary ion mass spectrometry, [5] μ-Raman spectrometry, [6] Neutron activation analysis, [7] Ion beam analysis.

	any size	non-destructive	no samp preparat.	sensitivity μg/g	lateral resol μm	depth μm	Z range	isotopic analysis	accuracy %
XRF [1]	√	√	√	> 100	~ 1000	1 - 100	> 11	no	10-20
SEM [2]	no	√	coating	> 1000	~ 1	~ 1	> 5	no	5-10
ICP/MS [3]	ν	no micro	√	< 1	~ 10	< 10	all	possible	10-20
SIMS [4]	no	no micro	√	< 1	~ 1	< 1	all	√	10-20
μ-Raman [5]	√	√	√	identificat.	~ 1	> 1000	n/a	no	n/a
NAA [6]	no	activation	√	< 1	none	> 1000	selective	no	< 5
IBA [7]	ν	ν	√	> 1	~ 10	1 - 50	all	no	< 5

2.1. CHEMICAL ANALYSIS BY ION BEAM METHODS

We shall not give a complete description of Ion Beam Analysis (IBA) techniques, as comprehensive reviews are available in textbooks [4,5]. Let us just recall that the principle of IBA techniques relies upon the detection of the products of interaction of an ion beam of a few MeV with the target, that is the gem. Among these techniques, PIXE (*particle induced X-ray emission*) is similar to XRF as it is 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 an X-ray beam. Because in PIXE the X-ray emission occurs almost without background, this method has a very good sensitivity (reaching the μg/g level for the transition elements, which are implied in the colouring mechanism of gems). The lightest measurable element depends on the ability to detect low energy X-rays. With a minimum X-ray energy set to 1 keV, PIXE can measure all elements starting from sodium. For the PIGE technique, acronym for *particle induced γ-ray emission*, there is no such conventional counterpart as for PIXE. PIGE is based on a nuclear reaction between the incident particle and the nucleus of a target atom. Following this reaction, the nucleus emits a γ-ray with a specific energy. This reaction occurs when the incident particle is able to surmount the Coulomb repulsive barrier of the nucleus, a situation mainly met for light target atoms (more specifically Be, Li, B, F when using a proton beam). Therefore, PIGE usefully extends the range of PIXE (from Na to U) to these elements. For the measurement of hydrogen in gems, specific experimental arrangements have been developed to carry out ERDA [6] (*elastic recoil detection analysis*) with a He beam or resonant nuclear reaction with a ^{15}N beam [7].

From the point of view of gemmology, the IBA methods present several interesting advantages. First, in-air IBA techniques performed with an external beam allow *in situ* and non-destructive analysis of gems without any target preparation. This harmlessness is necessary for the study of valuable objects such as historical jewels. Moreover, the availability of a micro-beam with a size of less than 20-μm permits to select inclusions for their identification. Such a small probe is also useful to select an inclusion-free region of the crystal. Indeed, with a broader spot size, there is always the risk that an inclusion incorporated in the analysed area may bias the mean trace element concentration of the crystal (e.g. an ilmenite $FeTiO_3$ inclusion in a ruby might lead to a wrong Fe and Ti mean concentrations).

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. Moreover, gems exhibit a polished and often flat surface at the scale of the beam spot. Owing to their very stable crystalline structure, gemstones are almost always insensitive to beam damage (no alteration) and charge build-up on these usually non-conductive targets is avoided when IBA are carried out in air.

The experimental set-up used in this study and its successive improvements have been thoroughly described [8], consequently, only the striking features will be recalled here. The PIXE/PIGE system is built upon the external nuclear microprobe line of the AGLAE accelerator facility. In this beam line, the 3-MeV proton beam is

focused down to a diameter of 20 µm using magnetic lenses (3 MeV is an optimum energy for analysing geological samples). The beam is impinging on the gem placed in air 2 mm downstream a very thin Si_3N_4 exit foil, which insures the air/vacuum interface. The detection of X-rays is achieved by two Si(Li) detectors located at 45° from the beam in the horizontal and vertical planes. The first one is dedicated to the measurement of light elements, which are often the major constituents of gems (from Na to Fe). With a 10-mm^2 active area, it has a low solid angle, and a minimal filtering using an ultra thin window combined with a helium flow. A magnetic deflector prevents backscattered protons of the beam from entering the silicon crystal. The second detector is dedicated to the measurement of heavy elements (from Ca to U) at the trace level. Its 50-mm^2 active area yields a large solid angle and the absorber is chosen to attenuate X-rays emitted by major elements (typically a 50-µm aluminium foil in case of Si-containing samples). The distance of the two detectors can be adjusted to optimise and balance their counting rates. Gamma-rays are collected using a third detector (high purity germanium with a 20% efficiency). The beam is monitored using the silicon X-ray line emitted by the Si_3N_4 exit foil by means of a compact Silicon-drift detector. Spectra are collected in 1000 seconds with a beam current of the order of 1 nA, yielding an integrated charge of about 1µC.

2.2. RAMAN SPECTROMETRY

Chemical data alone is sometimes insufficient to define the nature of the crystal. Actually a gem is defined by a chemical formula arranged in a specific crystal structure and thus chemical data must sometimes be combined with structural information delivered by complementary techniques, such as XRD (X-ray diffraction) or Raman spectrometry. Raman spectrometry is an optical method similar to infrared spectrometry measuring vibrational bands of structural groups in the crystal like Si-O or O-H. Its probe, a laser beam, allows the direct and non-destructive identification of gems in reflection geometry. The two following examples show how complementary chemical and structural analytical techniques can be for the study of gems. Calcite and aragonite, constituents of coral, shells and pearls have an identical $CaCO_3$ formula, but the two minerals are well separated by their markedly different Raman spectra. Conversely, all pyralspite garnets (gems of formula $X_3Al_2(SiO_4)_3$, X being a divalent element like Mg, Fe, or Mn) have almost undistinguishable Raman spectra whereas they are easily differentiated by their chemical composition.

The Raman measurements have been carried out with a Jobin-Yvon Labram infinity spectrometer, a semi-transportable equipment weighting about 100 kgs. The laser source is a 532-nm green YAG delivering 3.5 mW on the sample. In confocal mode with a 50X objective the analysed volume is approximately 5 µm in diameter by 10 µm in depth. The detector was a Peltier-cooled CCD detector with 1024 channels and the resolution achieved is about 1cm^{-1} in the 100-4000 cm^{-1} Stokes range. The precise positioning of the laser on microscopic inclusions located at any depth inside the gems is performed by a motorized microscope stage. Typical acquisition time is 100 seconds.

3. Application to ancient gems

We describe here three applications of the PIXE, PIGE and Raman techniques to ancient gems from museums performed at the *Centre de Recherche et de Restauration des Musées de France*. It should be emphasised that all jewels studied here are well documented and have traceable history, and there is no doubt about their authenticity.

3.1 RUBY: ISTAR'S EYES

The first illustration of an application of PIXE to gemstones concerns a statuette representing Ishtar, the famous Mesopotamian goddess of Love and Fertility as well as War. The cult of Ishtar was widespread in ancient Babylon and she became under various names the most important Goddess of the Near-East and Western Asia. [fig.1] This remarkable small-sized sculpture carved in alabaster (23-cm high) figuring a naked woman was excavated in the vicinity of Babylon and entered the Louvre collections in 1866 [9]. According to its merged Greek and Mesopotamian style and typology, this representation of Ishtar dates from the Parthian period (2nd c. BC - 2nd c. AD).
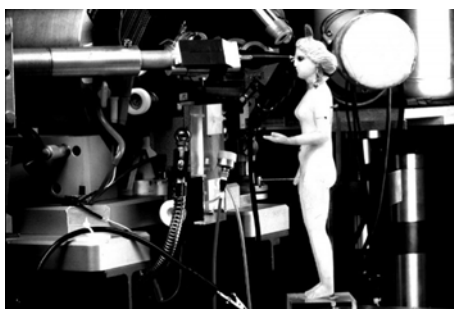

Figure II-2-1. Ishtar statuette being analysed using the external beam system.

The issue is to determine the nature of three intriguing red cabochons (rounded shape) inlaid in the eyes and the navel.

The PIXE spectrum shows the lines of the main constituents: 99% alumina (Al_2O_3) associated with less than 1% chromium (fig 2). This confirmed our impression that they are rubies, and not coloured glass or red garnets as previously reported. As shown in the PIXE spectrum of trace elements, slight amounts of titanium, vanadium, iron, copper, gallium concentrations are also measured, all being characteristic of natural rubies.

The similar appearance and chemical composition of the three cabochons suggest the use of a single batch of gems. A very important outcome of the age of the statuette is that these rubies are, up to our knowledge, the oldest ruby found in Middle-East. The fact that Mesopotamia has no source of gems raises the problem of provenance of these rubies, therefore a comparison with contemporary rubies of known provenance has to be undertaken to determine their geographical origins.
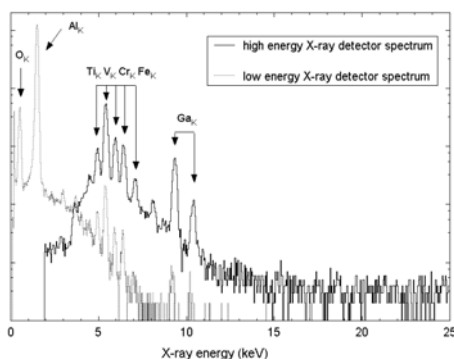
Figure II-2-2. X-ray spectra of major and trace elements recorded on the right eye of the statuette.

Over 500 PIXE analyses have been carried out on rubies from the most important occurrences: Afghanistan, Myanmar (Burma), Cambodia, India, Kenya, Madagascar, Sri Lanka, Thailand and Vietnam [10]. The trace element content of these reference gems appears markedly different for each occurrence and homogeneous within a given deposit, a criterion necessary to use the geochemical data for provenance. Three compositional groups corresponding to three different geological contexts can be identified. As shown in the Fe/Cr plot [fig. 3], Ishtar's gems fall into group I, which has the lowest Fe content and corresponds to deposits from Burma and Vietnam.
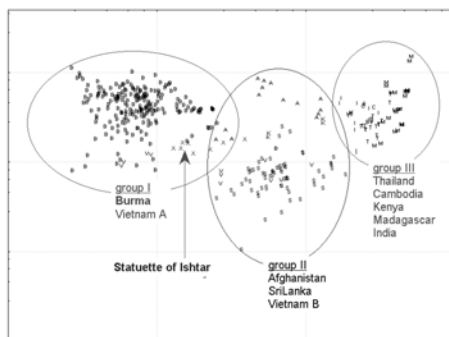

Figure 3. Plot of Cr vs Fe content for the rubies of the statuette and reference rubies.

As Vietnam rubies have only been mined since the 20th century, we can deduce that the eyes of Ishtar were extracted from the deposits of Burma. This result is confirmed by multivariate statistical processing (principal component analysis, hierarchical clustering) involving the entire set of trace elements (Ti, V, Cr, Fe, Ga) and by the observation of mineral inclusions specific to Burmese rubies (aggregates of short rutile needles). The three rubies therefore represent an evidence of a trade over several thousand kilometres between Mesopotamia and Southeast Asia twenty centuries ago.

3.2. EMERALDS: THE BARBARIAN TREASURE OF THE VISIGOTHS

The second example deals with emeralds set on barbarian jewels from the Dark Ages period. These votive royal crowns and crosses were unearthed in 1858 in the small village of Guarrazar, near Toledo, the capital of the Visigoth kingdom located in the Iberic peninsula. It constitutes one of the most important archaeological remains of the Visigoth period (7th-8th c. AD). The treasure is nowadays divided between the National Archaeological museum in Madrid, Spain and the National Middle-Ages museum in Paris, France [11].

The jewels are made of gold inlaid with gemstones such as sapphire, amethyst, quartz, pearls and emeralds. The archaeological question concerns the provenance of the emeralds, because whereas the origin of emeralds employed during the Roman Empire are well discussed by Pliny the Elder's in the 37th book of *Natural History*, little is known about the origin of emeralds of the early Middle-Ages period.

Figure II-2-4. Royal votive crown inlaid with gems positioned in front of the external beam set-up. Note the two Si(Li) detectors and HPGe in the back.

This work aims at comparing these "Barbarian" emeralds to those from various occurrences (Egypt, Austria, Afghanistan, Pakistan, Ural, India, Colombia, Madagascar, Zambia, Zimbabwe, Brazil), on the basis of chemical composition. As shown in fig. 4, the combination of PIXE and PIGE techniques performed with an external beam was used to measure their major constituents (Be, Al, Si) and to determine their trace elements.

In comparison to the rubies in the study presented above, emeralds show a much-extended set of discriminating trace elements (Na, Mg, Ca, Ti, V, Fe, Rb, Ni, Cu, Zn and Cs) including also light ones (Li, F), as illustrated in fig 5.

Emeralds being a hydrated mineral, the OH content was measured by forward elastic recoil technique with an alpha beam (ERDA), so as to give a possible additional provenance criterion. The statistical processing of the entire set of trace elements with discriminant method concluded that ten of the eleven emeralds set on the Visigoth jewels are mined from the Alpine deposits (near Habachtal, in Austria), an occurrence not mentioned in Greek and Roman ancient texts [12].
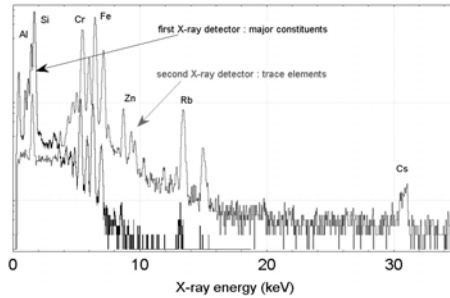
Figure II-2-5. PIXE spectra of an emerald showing the major and trace elements.

By stating that Visigoths had different sources of emeralds than the Romans, this work provides new insights into the trade routes of gemstones at the time of the Great Invasions. Moreover, it reveals that the Alpine deposits were worked much earlier than expected (the most ancient text mentioning these mines was written in 13th century by the Archbishop of Salzburg).

3.3. GARNETS: THE GEMS OF THE FIRST KINGS OF FRANCE

The Germanic tribes, who settled in Western Europe at the fall of the Roman Empire, introduced a very specific type of jewels called *"Cloisonné"*. The main gems used in these jewels are red garnets cut in thin slices (<1mm) and inserted in a honeycomb metallic structure, as shown in fig. 6. Once again, the archaeological issue is the provenance of the garnets used by these nomadic peoples, particularly if we consider the huge quantity of garnets necessary to make these jewels, which were buried in tombs according to the Barbarian custom and not re-used.
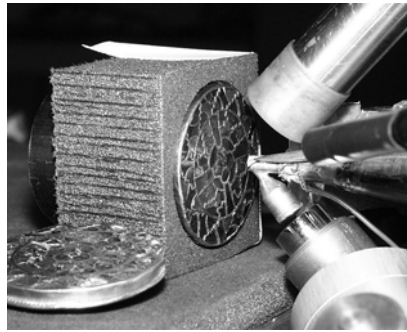

Figure II-2-6. Brooch of Frankish queen *Aregonde* with garnets set in "cloisonné" style.

To solve this problem, over 500 garnets set on the jewels discovered in tombs of members of the Frankish court from the necropolis of the Saint-Denis basilica near Paris were studied. The artefacts span the entire Merovingian period (5th-7th c. AD.) and comprise the famous jewels of the Frankish queen *Aregonde* [13]. From

the mineralogical point of view, garnets present a highly variable composition. The most common type of garnet is the pyraldine family of chemical formula $X_3Al_2(SiO_4)_3$, where X can be a divalent ion like Fe (almandine), Mg (pyrope) or Mn (spessartite), each combination being called an *end-member*. The situation is actually more complex as natural garnets are a solid solution of end-members in any proportion. Because garnets are relatively widespread and their composition highly variable, it was necessary to cross many criteria to determine their origin [14]. The first criterion is the composition; it was determined by external beam PIXE for major constituents (Mg, Al, Si, Ca, Mn, Fe) and trace elements (Ti, V, Cr, Y). As shown in fig. 7, three groups of garnets were identified. Most garnets belong to the first group (almandine, Fe-rich). The second group (one jewel) consists of intermediate almandine-pyrope garnets sometimes called "rhodolite". The third group comprises pyrope garnets (Mg-rich).
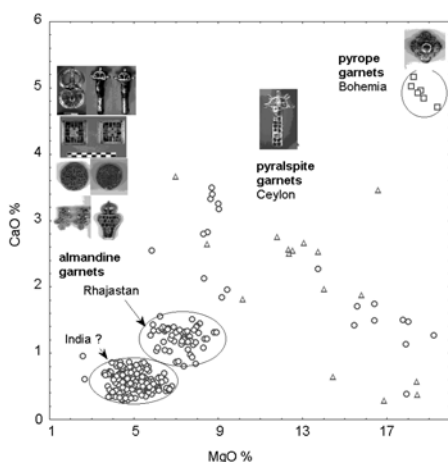

Figure II-2-7. The CaO vs MgO plot for garnets from various jewels shows 4 provenances: *pyropes* from Bohemia, *rhodolites* from Ceylon and two sources of *almandine* in India.

The trace elements content and slight differences in major composition permit to split these three groups in five different sources: two sources of pyrope garnets (with and without chromium) and two sources for almandine garnets (distinctive calcium, magnesium and yttrium contents).

Comparison with published data on garnets suggests that almandine garnets have been mined from India while the "rhodolite" garnets may have been imported from Sri Lanka. The sources of pyrope garnets correspond to the Bohemian deposits (Czech republic).

The second provenance criterion is the inclusions. Micro-Raman spectrometry was used to identify mineral inclusions in almandine garnets: apatite, zircon, monazite, calcite, and quartz. Among these inclusions, two of them were specifically found in archaeological garnets: curved needles of sillimanite (Al_2SiO_5) and small (10 µm) metamict radioactive crystals. Fig. 8 shows the Raman spectra of sillimanite, which is a mineral formed under a high temperature and high-pressure metamorphism.
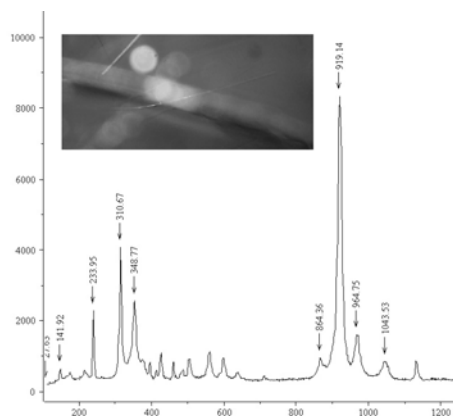
Figure II-2-8. Raman spectra of a *sillimanite* elongated and curved inclusion indicating a high P-T metamorphism of the crystal.

The radioactive crystal was analysed with the microbeam in PIXE mode. Uranium and lead were found as the major constituents of this inclusion. The Pb content being attributed to the radioactive decay of ^{235}U and ^{238}U (0.7 and 4.46 Gy half live, respectively), the Pb/U ratio gives a crystal formation age ranging between 1 to 1.5 billion years. To sum it up, the almandine composition of the garnets, the presence of sillimanite and the very ancient age of the crystal converge towards highly metamorphosed rocks of the Precambrian period. One of the rare parts of earth's crust remaining from that period that has corresponding mineralogical features is the metamorphic belt located in India, a region presenting garnets deposits of gem quality.

The presence of pyrope garnets from Bohemia might also have a historical significance. The pyropes only appear in jewels dated after the end of the 7th century; this indicates that starting from that period Merovingians had to use European garnets instead of Indian ones. This major change in supply is likely a consequence of the closing of the garnet route to India, due to the invasion of the Arabic peninsula by the Sassanids at the end of the 6th century.

4. Conclusions

IBA methods and specially the PIXE and PIGE techniques performed in air appear as tools well suited to the analysis of gemstones mounted on historical jewels, in complement to classical gemmological investigations. This combination usefully provides: 1) a completely non-invasive and non-destructive analysis, 2) the detection of a wide range of elements, 3) the analysis of 10-µm size details, 4) a high sensitivity attaining the µg/g level and 5) highly quantitative results. The identification of mineral inclusions is complementarily achieved by µ-Raman spectrometry. These modern analytical methods were successfully applied to the determination of the nature and provenance of ancient gems, providing new insights

into their trade routes. New developments are being undertaken in several directions. One important field is the investigation of the colouring mechanism of gems in relation with geochemistry. For instance, the detailed distribution of cations in complex stones such as jade may provide the understanding of its colour and provenance. The application of X-ray absorption methods (XANES, EXAFS) with a synchrotron facility is being used for study the chemical environment of chromophoric elements in ruby or emeralds. Finally, the measurement of the hydrated layer diffusion building-up with time at the surface of gems by ion beams (ERDA and resonant nuclear reaction with ^{15}N ions) opens new perspectives for relative dating or at least authentication of gems such as quartz.

5. References

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