Ion Microbeam Analysis in cultural heritage: application to lapis lazuli and ancient coins

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ABSTRACT
Ion Beam Analyses (IBA) techniques, for example PIXE (Particle Induced X-ray Emission) and IL (IonoLuminescence), are a powerful analytical tool used to investigate the composition and structure of materials in cultural heritage. These techniques could be applied both in vacuum, preparing the sample as in electron microscopy, and in air in a non-invasive way allowing to analyse artworks of practically any shape and dimension without sample preparation. Moreover the use of a focused beam (microbeam) permits to reach an analysis resolution of few micrometers in vacuum and ten micrometers in air.
In this work, instruments and methodologies are described and two examples of case study are reported: I) the mapping of elemental distribution in ancient roman coins; II) the trace elements measurement in lapis lazuli for provenance determination.

1. INTRODUCTION

Ion Beam Analyses (IBA) are performed by using a proton beam provided by small accelerators as probe and collecting the products of the interaction between the particles and the atoms of the sample [1]. Depending on the applications and techniques, a broad beam (a few mm²) or a micro-beam (2-20 μm in diameter) could be used as probe; a scanning system permits to map the properties of the material under investigation in an area of about 2×2 mm² when micro-beam is employed. The energy of protons useful for IBA techniques is around 2-3 MeV whereas the current is of the order of few hundreds of pA, low enough to avoid any damage in the majority of the materials. IBA techniques can be carried out both in vacuum, preparing the sample as in electron microscopy, and in atmosphere, allowing the non-invasive analysis of objects such as artworks of practically any shape and dimension without sample preparation. Among the most used

IBA techniques RBS (Rutherford Back-Scattering), PIXE (Proton Induced X-Ray Emission), PIGE (Proton Induced Gamma-ray Emission), ERDA (Elastic Recoil Detection Analysis) and NRA (Nuclear Reaction Analysis) [1], [2] could be used in many scientific fields for elemental analysis, IL/IBIL (IonoLuminescence or Ion Beam Induced Luminescence) [3], [4] for characterization of optical properties of materials and IBIC (Ion Beam Induced Charge) [5] for the characterization of electronic properties of devices. In the cultural heritage field many of these techniques are used, though PIXE has a particular importance for the elemental composition analysis (especially for trace elements).

In this paper an application of micro-PIXE and IL (both micro-IL and broad beam) to solve outstanding archaeological issues is described. In particular two case studies are reported. The first is related to ancient silver-copper alloy coins from Roman and pre-Roman Italian cultures. The coins were studied

by means of micro-PIXE to investigate their composition in function of the depth to obtain information on manufacturing and degradation processes. The second case study is related to provenance study of lapis lazuli, that is a blue semi-precious stone that has been used since Neolithic Era (VII millennium BC) for the manufacturing of precious carved artefacts. The aim was to identify the extraction sites of the rock obtaining information on ancient trade routes.

2. INSTRUMENTS AND METHODS

Ion beam analyses were carried out mainly by means of two scanning proton micro-beam lines at INFN (National Institute for Nuclear Physics) facilities having different acceleration voltages: the 2.5 MV AN2000 accelerator at the Legnaro National Laboratory (INFN-LNL) in Padua (Figure 1) widely used for material characterization/modification and ion implantation [6]-[8] and the 3 MV accelerator of the INFN-LABEC Laboratory in Florence (Figure 2) widely used for multi-disciplinary studies [9]-[11]. In few cases also the in air AGLAE microbeam facility of the C2RMF in Paris was used [12].

Analyses at the micro-beam line in Legnaro are performed in a vacuum chamber. Therefore, the samples need to be prepared in a way similar to Scanning Electron Microscopy (SEM), i.e. a conductive carbon coating is applied (Figure 1). PIXE measurements were carried out both on coins and on lapis lazuli rocks using 2 MeV protons and a current below 500 pA. The beam was below 5 μm in diameter with a 3×3 mm² maximum scanning area.

In Florence, the measurements were carried out in air (He-flux) using a 3 MeV proton beam and a current below 200 pA. The beam was of about 10 μm in diameter with a 2×2 mm² maximum scanning area. Only lapis lazuli were analysed both by means of PIXE and IL. In the case of IL also the broad beam ion microscopy [13] was employed. Working in air the samples don't need any preparation and rocks or artworks of almost any shape and dimension can be analysed in a non-
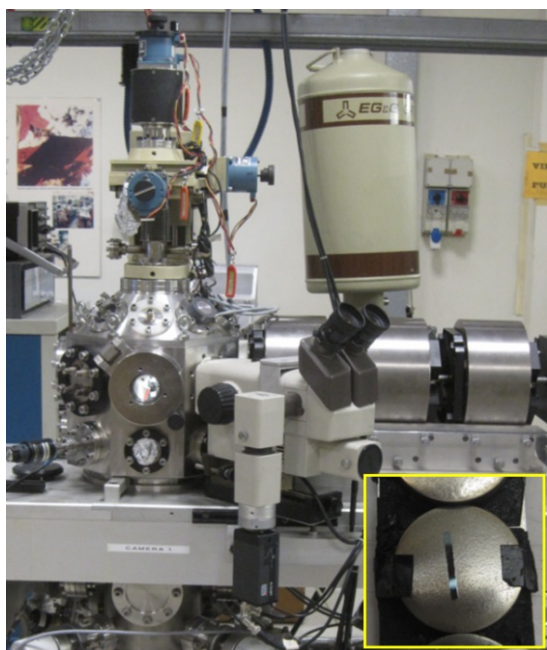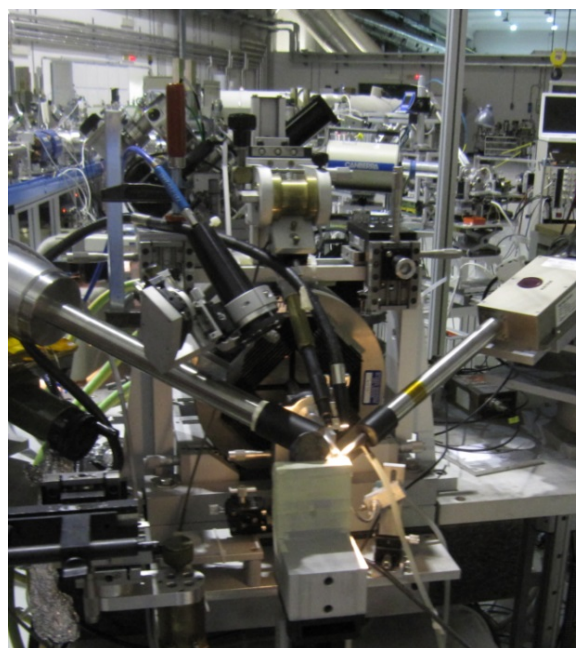

Figure 2. In air micro-beam line at INFN-LABEC laboratory during the analysis of a lapis lazuli artefact.

invasive way.

Both PIXE data acquired in Legnaro and in Florence were quantitatively analysed by means of GUPIXWIN (version 2.1.3) and by the use of a set of reference standards for the determination of the experimental parameters.

3. CASE STUDIES

3.1. Ancient coins

A study to analytically characterise ancient coins has been started in 2010. This topic is particularly interesting for numismatic and archaeometry, because it allows to evaluate commercial exchanges among tribes, to hypothesize relative chronologies, to verify the presence of a debasement along the years and to investigate the exchange ratios among different emissions of coins [14]. Until now the study has been focused on coins made of a silver-copper alloy in the Roman (Figure 3) and pre-Roman period. The main activity was carried out using neutron diffraction, neutron activation analysis and p-XRF, that are non-invasive techniques useful to measure the elements content [15]-[17].

The coins made in this material are often characterised by a surface layer with an Ag content higher than the bulk. To better study this surface silver-enriched layer, corrosion layers or inhomogeneity between surface and bulk, some silver coins have been chosen and prepared using a standard metallographic procedure, to analyse directly their section. At first, they have been cut with a rotating diamond wheel and their sections have

Figure 1. In vacuum analysis chamber at INFN-LNL laboratory and a coin sample cut, embedded in resin and covered with a carbon coating.

Figure 3. Obverse and reverse images of one of the investigated victoriatus JC1 (RRC: 166)

been mounted in resin. Subsequently, surfaces were polished with papers having different grit and also with a diamond crystal paste (with grains 6-3-1 µm). A carbon coating has then been applied to make the surfaces conductive. µ-PIXE measurements were carried out in vacuum on these cross-sections at the AN2000 microbeam facility of INFN-LNL.

µ-PIXE elemental maps allow to analyse the distribution of major elements in few minutes, as shown for example in Figure 4. Thanks to this feature, the presence of a very thick surface silver-enriched layer (up to 250 µm) has been confirmed, for example, on a specific Roman coin emission: the Victoriati (4 samples analysed). All these coins are characterised by a silver content clearly higher in the surface layer and by peculiarities, such as for example the presence of voids, that suggest a probable intentional depletion occurred with acid chemicals before minting operations, as reported in other works [18]-[20]. This is a different process in respect of the production of suberatus coins where a copper core is wrapped with a silver foil.

Anyway, the added value of µ-PIXE is the possibility to detect minor and trace elements inside the sample with a resolution of few micrometers. Similar techniques that make use of electron and X-ray beams show for some aspects lower performances than µ-PIXE. Using SEM-EDS only Cu and Ag elements are detected due to the low sensitivity to trace elements, whereas µ-XRF has a beam diameter greater than 10 µm and then a lower spatial resolution than µ-PIXE. Moreover, although not used in this work, using proton beam, it is possible to carry out RBS analysis at the same time, which in some cases is capable of resolve the distribution of chemical elements in depth [21]. In Figure 5 typical PIXE spectra of the
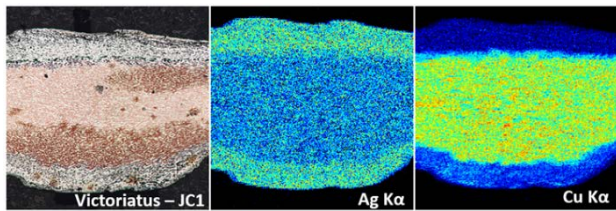
external and internal regions of the coin are shown. The distribution of the elements along the section was measured, analysing small areas of about 40×40 µm², recreating a profile of all the detected elements along the coin section, as shown e.g. in Figure 6b for silver and copper in the same Victoriatus
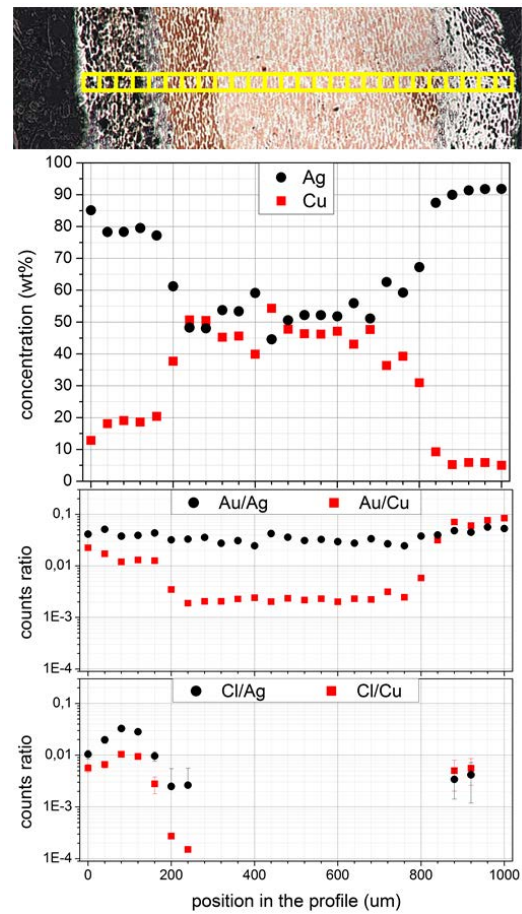
Figure 6. µ-PIXE results of a profile of the same Victoriatus shown in Figure 3 and Figure 5; a) optical microscopy section showing the analysed areas (each yellow square is about 40×40 µm²); b) concentration profiles of the main elements (Ag and Cu); c) ratio of peak areas Au/Ag and Au/Cu; d) ratio of peak areas Cl/Ag and Cl/Cu.

Figure 4. Optical microscopy section of a Victoriatus compared to µ-PIXE maps (area ~ 1.5 × 1.5 mm²).

Figure 5. Example of PIXE spectra (in linear and in logarithmic scale) of internal and external regions of the Victoriatus shown in Figure 3 and Figure 4.

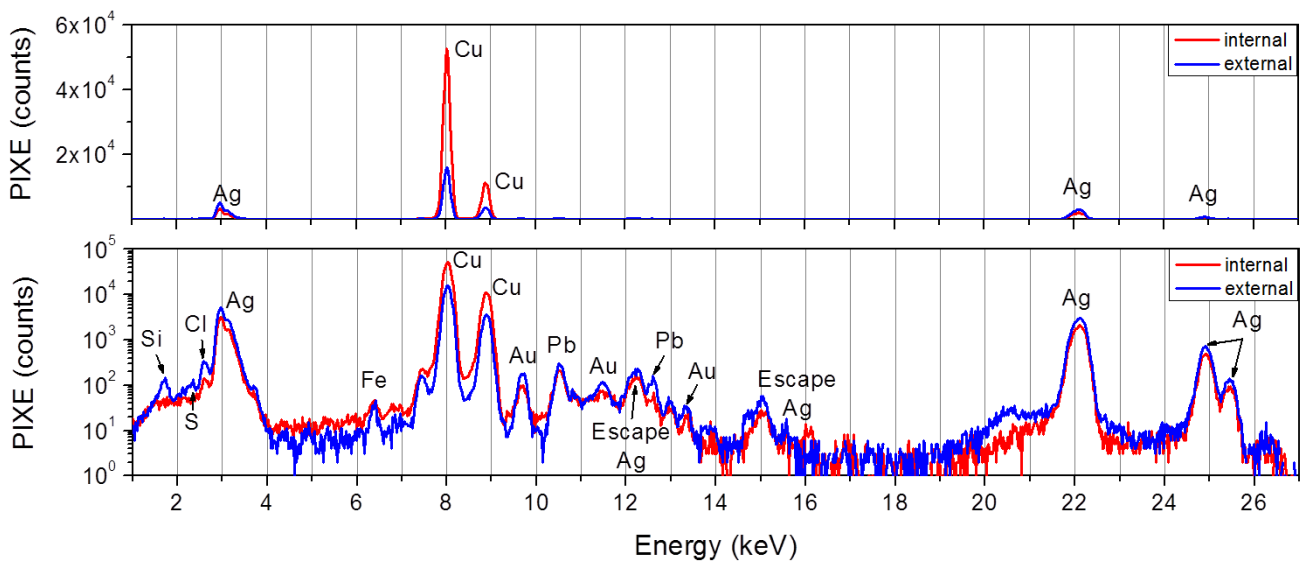Figure 3. The ratio minor element / main element (using the area of one of the main characteristic peaks) has been used to evaluate the correlation of each minor and trace element with the main ones (silver and copper). Some examples of the results are shown in Figure 6c and Figure 6d. In this way it is possible to understand where each element comes from: if the ratio on the main element is constant along the profile, one can suppose that the trace/minor element was present in the related raw material (for example gold in silver, Figure 6c). If both the ratios (on Cu and on Ag) vary along the profile, the element is not correlated to the raw material (for example Chlorine in Figure 6d) but it could be entered in the coin during its burial time or during chemical treatments.

In this way important information was obtained on the analysed coins about the raw material used to mint them. In particular bromine, silicon, chlorine and iron were mainly detected close to the surface but not necessarily in strict correlation with the silver-enriched layer. This means that these elements, commonly present in soil and water, probably entered in the coin during its burial time and are not related to copper or silver ores. For example, in Figure 6d, it can be observed that in one side of the coin (right) chlorine is present only in two of the six areas related to the silver-enriched layer, whereas it is present in all the other side (left).

On the other hand, as expected, gold and lead were clearly linked to silver in all the coins we analysed but not to copper for which a correlation with nickel and zinc was observed. In Table 1 the values measured for two of the four Victoriati studied are shown; in this case Zn was under LOD (Limit Of Detection). Increasing the number of analysed samples, ratios can be used as a semi-quantitative way for provenance study of the raw material or as distinctive elements to identify production places and mints. In our case, for example, Pb/Ag was observed to be up to 0.3 (one order of magnitude higher than observed in the two Victoriati of Table 1) in coins from other regions.

3.2. Lapis lazuli

Lapis Lazuli is a blue semi-precious stone that has been used since Neolithic Era (VII millennium BC) for the manufacturing of precious carved artefacts [22], [23]. The possibility to associate the raw material to man-made objects could help historians and archaeologists to reconstruct trade routes, especially for the ancient time when written testimonies are scanty or absent at all. To solve the issue we started in 2008 a long-term research, involving an interdisciplinary team. Due to the low probability of geological conditions in which it can be formed, only few sources of lapis lazuli exist in the world [24]. Until now, 45 lapis lazuli rocks from 4 quarry districts (Afghanistan, Tajikistan, Siberia and Chile) have been analysed, creating a database on this rock. The research has been focused in searching markers on single mineral phases using

microscopic techniques, which allow to observe and to analyse single crystals in a non-invasive way. On the basis of the markers found, a protocol was established [25] in which the luminescence properties and the quantification of trace elements in pyrite and diopside crystals play a crucial role in the provenance determination of lapis lazuli. The protocol was successfully applied on historical and archaeological objects from Medici's Collection (16th-18th century) and from Ancient Egypt (first millennium BC) [25], [26]. It is not the aim of this paper to report all the markers of the protocol, but as an example diopside crystals of the Afghanistan rocks show higher quantity of titanium (> 710 ppm) or vanadium (>210 ppm) or chromium (>220 ppm) than Tajik samples or a strong ionoluminescence band at about 770 nm. Otherwise only Siberian samples have a strontium content in diopside crystals higher than about 180 ppm.

In particular it was verified that all the markers found (presence of a mineralogical phase, peculiar trace elements inside pyrite or diopside crystals, luminescence bands) are simultaneously detectable by means of ion beam analysis techniques, in particular μ-PIXE [18] and IL. Moreover, IBA techniques are very suitable techniques because if applied in air are non-invasive methods usable on precious archaeological objects, contrarily to other techniques used in provenance studies that need a sampling and are destructive [28], [29].

Also μ-XRF have produced good results [30], but limited to elemental analysis because X-ray luminescence (XRL) is normally not present in benchtop instruments. Moreover XRF allows to analyse only relatively large crystals (more than about 100-150 μm in diameter, not always available in archaeological objects) due to the beam dimension and to the higher depth of analysis with respect to IBA techniques that are able to analyse crystals down to 20-50 μm in diameter. For example, in Figure 7 the PIXE map of a portion (about 125×125 μm²) of lapis lazuli is shown in which a pyrite crystal (FeS_2) is visible, that is characterized by the presence of selenium and the absence of copper (under the limit of detection). A content of selenium in pyrite crystals higher than 40 ppm is a marker for a Chilean provenance of lapis lazuli [27]. Such result cannot be obtained neither by means of μ-XRF due to the small dimension of the crystal, nor by means of SEM-EDS because the nickel and selenium contents are too low to be detected.

Table 2 shows another typical result in element quantification, obtained by means of SEM-EDS and μ-PIXE on the diopside crystal shown in Figure 8. All the trace elements, that are the only usable for provenance
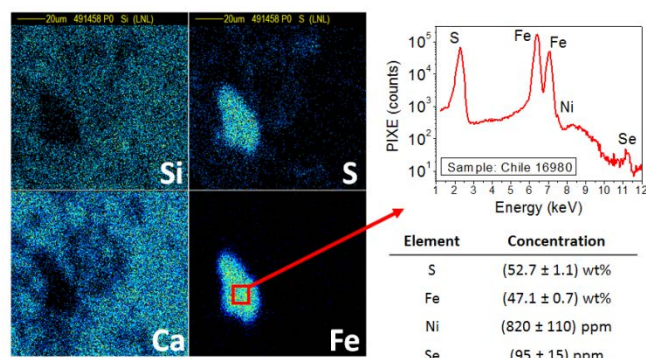
Table 1. Ratio of minor/trace elements with main elements for two Victoriati coins. Victoriatus 1 is the same of Figures 3-6. For these coins Zn was under LOD (Limit Of Detection).

Elements ratio	Victoriatus 1 (JC1)	Victoriatus 2 (JC13)
Au/Ag	$(37 \pm 9) \times 10^{-3}$	$(25 \pm 3) \times 10^{-3}$
Pb/Ag	$(23 \pm 3) \times 10^{-3}$	$(29 \pm 5) \times 10^{-3}$
Ni/Cu	$(2.6 \pm 0.3) \times 10^{-3}$	$(1.8 \pm 0.3) \times 10^{-3}$
Zn/Cu	Under LOD	Under LOD

Element	Concentration
S	(52.7 ± 1.1) wt%
Fe	(47.1 ± 0.7) wt%
Ni	(820 ± 110) ppm
Se	(95 ± 15) ppm

Figure 7. μ-PIXE map of some elements in a lapis lazuli from Chile (sample Chile 16980), μ-PIXE spectrum of a pyrite crystal and elements content.

Table 2. Element contents in diopside mineralogical phase shown in Figure 8 obtained by means of SEM-EDS and μ-PIXE analysis.

Element	SEM-EDS (wt%)	μ-PIXE (wt%)
Na	0.4 ± 0.1	Not observable
Mg	10.8 ± 0.1	10.3 ± 0.3
Al	0.4 ± 0.1	0.7 ± 0.1
Si	26.3 ± 0.2	26.1 ± 0.3
Ca	18.2 ± 0.1	17.8 ± 0.2
O	43.9 ± 0.2	44.6 ± 0.4

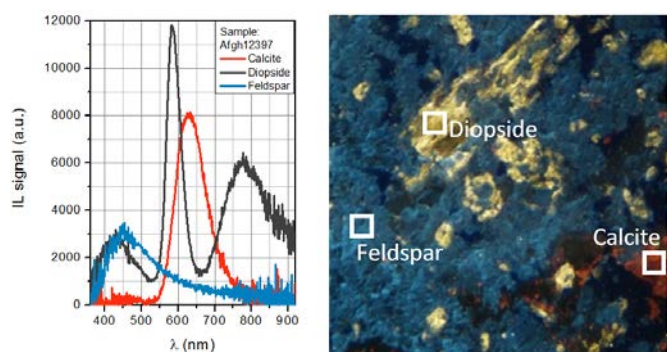| Element	SEM-EDS (ppm)	μ-PIXE (ppm)
S	Under LOD	480 ± 50
Cl	Under LOD	330 ± 40
K	Under LOD	550 ± 30
Ti	Under LOD	1260 ± 50
V	Under LOD	500 ± 40
Cr	Under LOD	170 ± 20
Mn	Under LOD	280 ± 20
Fe	Under LOD	480 ± 20
Sr	Under LOD	28 ± 14
Zr	Under LOD	220 ± 40

Figure 8. Cold-Cathodoluminescence image, about 1.3×1.3mm^2 (right), and μ-IL spectra (left) of an Afghan lapis lazuli (sample Afgh12397). Each mineralogical phase is characterized by a different emission spectrum.

determination, are measurable only by means of μ-PIXE analysis. In this sample, the features of an Afghan provenance of the rock are evident, i.e. the high content in titanium and vanadium and the low quantity of strontium [26].

Recently, to increase the markers, the trace element analysis by means of μ-PIXE was extended to other mineralogical phases in addition to diopside and pyrite, in particular to calcite and feldspar that are easily recognizable in a lapis lazuli by means of their ionoluminescence properties. In fact, as shown in Figure 8, calcite shows a strong red luminescence at about 625 nm whereas feldspar has a characteristic blue luminescence centered at about 450 nm

4. CONCLUSIONS

Thanks to the use of IBA techniques it is possible to measure the elemental composition and luminescence properties of materials in cultural heritage with a micrometric resolution and, if necessary, in a non-invasive way using in-air facilities. This is very useful to answer many of the questions posed by archaeologists, art historians and restorers. Similar techniques that make use of electron and X-ray beams show for some aspects lower performances than IBA and in many cases are not able to solve adequately the issues.

In this paper it was shown how the use of IBA techniques has been suitable to contribute in solving two archaeological issues. μ-PIXE analysis carried out on ancient Roman and pre-Roman coins was useful to know their composition in function of the depth. In particular the profile of the silver-enriched layer has been reconstructed inside the coin obtaining information on manufacturing and degradation processes. Moreover trace elements have been associated to the contaminants of the soil (Br, Si, Cl, Fe) or to the raw minerals (Pb, Au in silver; Ni, Zn in copper). Finally the ratios Pb/Ag, Au/Ag, Ni/Cu and Zn/Cu have been measured and they will be used in future works to identify production places and mints or provenance of raw materials.

About lapis lazuli a protocol to identify the provenance of the stone used for carved artefacts has been carried out. It is based on the measurement of trace elements and luminescence properties of minerals inside lapis lazuli at a micrometric scale. Currently the protocol is completely applicable only by means of IBA techniques, in particular μ-PIXE an IL analysis, also on precious objects. It has been successfully applied on artworks and in particular on precious carved objects from Ancient Egypt (first millennium BC). At now all the analysed objects are ascribable to Afghanistan (Badakhshan Province) that is a further confirmation of trading of this stone up to 4000 km from its extraction site in the first millennium BC.

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