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A provenance study of lapis lazuli: The "Collezione Medicea" case study

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Summary. — Lapis lazuli is a semi-precious blue stone widely used for different purposes since the antiquity but, at present, there are still some lacking information about both its trade in ancient times and the quarries exploited from different civilisations. Although the Afghan mines are widely considered as now as the only sources of lapis lazuli in ancient times, other sources have been taken in consideration, even if an exhaustive provenance study of the raw material utilised in artworks is still lacking. In this work a systematic study of this fascinating stone comparing physico-chemical properties of rocks and historical objects is presented, to contribute in the solving of the lapis lazuli provenance problem. Since often it is impossible to take a sample from the object under analysis due of its extreme value, it is fundamental to use only non-invasive techniques: for this reason Ion Beam Analysis has been selected, complemented by some invasive techniques, like electron microscopy, just to speed up the characterisation of geological samples and to gain experience with the material. Some preliminary but encouraging results relating to a "Collezione Medicea" artwork from the "Museo di Storia Naturale" in Firenze are also presented.

PACS 91.65.Rg – Minerals, occurrences and deposits.
PACS 91.67.Pq – Minerals, major and trace element composition.
PACS 29.30.Kv – X-ray spectroscopy, nuclear physics.
PACS 78.60.Hk – Luminescence, cathodoluminescence, ionoluminescence.

1. – Introduction

Semi-precious stones have been used since Neolithic Age for the manufacture of jewels, objects of social prestige and veneration articles. The few fragments of Sumer cuneiform script, survived till now through clay tablets, exalt not only the beauty of the semi-precious stones but also their meaning in connecting the people with the divinity [1]. Some of these stones are very rare, because they can be found in very few places on

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the Earth, and so they were procured through complex networks of exchanges and trade routes and transported thousand kilometres away from their origin. This has been proved by archaeological findings, mostly coming from rich graves, among which there were also many lapis lazuli, one of the first semi-precious stones used in Middle East, Asia and Europe. In Mesopotamia the earliest archaeological evidence of the use of lapis lazuli was traced back to the 5th millennium BC [2] with the discovery of beads at a cemetery outside the temple walls of Eridu (Sumer) in southern Babylonia. Artworks containing lapis lazuli used between 2700 and 2500 BC were recovered in the 1920s during excavations of the ancient Chaldean city of Ur. The most famous of these were recovered from the royal tomb of Queen Pu-abi (2500 BC), including three gold headdresses, and two bead necklaces [3, 4], as well as two statues of male goats with shoulders, eyes and horns of lapis lazuli [5]. There were many other applications of lapis lazuli, some of them discovered only in recent periods: small objects (such as seals, amulets and jewels), larger objects (such as vessels, votive cylinders, dagger handles, etc.) and fragments of inlays are just some examples [6, 7].

In Egypt, prior to 3100 BC, lapis lazuli was used for scarabs, pendants, beads and inlaid jewels [3]. The tombs of Ramses II (about 1279 BC) and Tutankhamon (1361–1352 BC) revealed rings and other jewels made of lapis lazuli. In fact, the golden mask over the head and shoulders of Tutankhamon's mummy has eyebrows and areas around the eyes inlaid with lapis lazuli [8].

Also in Asia lapis lazuli has been known and used for a long time: the Indus Valley Civilisation used it together with other stones to manufacture beads from the 3300 BC, as proved by some findings in the archaeological sites of Harappa, Pakistan [9]. In China the use of lapis lazuli was mentioned the first time in Chinese annuals of the 6th and 8th centuries BC, as the stone was a favourite of Chinese carvers [10]. Some Chinese hair and belt ornaments carved from lapis lazuli have been dated between 551 and 479 BC [3].

In Europe, from the eleventh century AD [6] until last centuries, lapis lazuli was crushed to be used as a blue pigment called "ultramarine". During the Renaissance, lapis lazuli was used for cups, bowls and urns and was inlaid into clock faces and tables. An example of application of lapis lazuli is visible in Italy with the popular mosaics in Florence [11]. More recently, at the beginning of the 20th century, French jewellery and the artist Peter Carl Fabergè (1846–1920 AD) used lapis lazuli in many of his major works, among which there was one of his 58 Imperial Easter Eggs, a gift from Czar Nicholas II of Russia to Czarina Alexandria in 1912 [5]. In Russia, lapis lazuli was used as a decorative stone, as at the Winter Palace in St. Petersburg and the Palace of Catherine the Great in the city of Pushkin [12].

In more recent times, during the 20th century, lapis lazuli was used also in North and South America primarily for local ornamental use. In South America, there have been several recent references to the use of lapis lazuli by the Moche (800–100 BC) and the Inca (1100–1537 AD) cultures, which occupied present day Peru, Ecuador, Bolivia, Northern Chile and north-western Argentina [3] although the Columbian artefacts studied at the University of La Serena have been found to contain sodalite or other blue minerals, but not lapis lazuli [13]. However, evidences of ancient human activity near the lapis lazuli mining area suggest that the deposit could have been known to early inhabitants of the region, but further research is needed to determine if the Chilean deposit was exploited in ancient time [14, 15].

1˙1. *The quarries of lapis lazuli*. – Only few sources of lapis lazuli exist in the world due to the low probability of geological conditions in which it can form [16], so that the

possibility to associate the raw material to man-made objects is plausible and would help to reconstruct trade routes. Historical sources were located in very inaccessible places, such as Afghan and Pamir Mountains, and stones were transported for thousands of kilometres. The knowledge of trade routes used in ancient times is still largely incomplete: this is especially true for ancient contexts where there is an absence or scarceness of written evidences [17]. Although the Badakhshan mines in Afghanistan (the most famous being Sar-e-Sang) are widely considered till now as the only sources of the lapis lazuli in ancient times [1, 6, 17-19], other sources have been considered: Tajikistan (Lyadzhuar Dara, Pamir Mountains), Pakistan (Chagai Hills), Siberia (Irkutsk, near Lake Baikal), Iran [18] and Egypt (Sinai) [20]. The last two possibilities are not geologically confirmed and their interpretations are still debated [6, 21-23], so that the provenance of ancient lapis lazuli is still an open question. Other sources [24] are: Mazanderan (but there are many doubts about it and it seems quite unlikely [18]), Dizmar in Azerbaijan and Kerman (there are doubts about the presence of metamorphic rocks and there are no evidences of lapis lazuli [10, 18]). Moreover there are references to other sources [21], in particular to northern China and Tibet, but nor in these cases neither in the previous ones there is any geological confirmation.

2. – Petrography of lapis lazuli

Lapis lazuli is generically classified as a metamorphic rock, even if this definition could not be considered exhaustive, due to the complexity of mechanism involved in its genesis. It is characterised by the presence of the mineral lazurite ($Na_6Ca_2Al_6Si_6O_{24}$ $[(SO_4)$,S,Cl,$(OH)]_2$), combined with other types of minerals whose presence and relative amount varies from and within deposits [25]. The typical blue colour of the rock is due to the mineral lazurite, that seldom presents well-formed crystals, since usually is an aggregate of quite small crystals. Lazurite is traversed by gray-white or yellowish veins, due to the presence of various accessory minerals such as calcite ($CaCO_3$), wollastonite ($CaSiO_3$), phlogopite ($KMg_3Si_3AlO_{10}(F, OH)_2$), feldspars ($(Ca, Na, K)(Al, Si)_4O_8$), diopside ($CaMgSi_2O_6$) and others. Grains of pyrite (FeS_2) are often present in lapis lazuli and there may be also feldspathoids of the same lazurite family such as haüyne ($(Na, Ca)_{4-8}Al_6Si_6(O, S)_{24}(SO_4, Cl)_{1-2}$), sodalite ($Na_8Al_6Si_6O_{24}Cl_2$) or nosean ($Na_8Al_6$ $Si_6O_{24}(SO_4)$).

3. – The samples

All the lapis lazuli analysed in this work are part of the collections of the "Museo di Storia Naturale" of the University of Firenze. This museum conserves about fifty pieces of lapis lazuli: half of them are blocks of rock, rough or partially polished, but the other half consists of carved objects of exquisite workmanship and fragments or whole tessera for inlays. Some of them have already been studied in the 1980s [26, 27]. The lapis lazuli stones of the section "Mineralogy and Lithology" of the museum are fragments, thin slices or pieces of different sizes, some rough and other polished or partially polished. As already pointed out by other authors [27, 28], there is a lack of precise geographical information for some specimens. In this case, for most of the samples studied only the provenance area is specified, but the exact mines are not known: 3 samples come from Badakhshan in Afghanistan (probably Sar-e-Sang mine), 4 samples from Chile (only 2 samples are catalogued as Chilean, but probably are all from Ovalle), 1 sample from Irkutsk in Siberia, and 4 samples from Pamir mountains in Tajikistan (Lyadzhuar Dara lazurite deposit

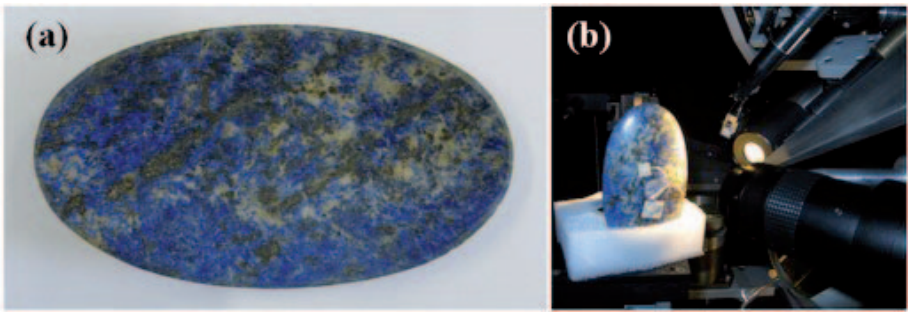

Fig. 1. – (a) "Coppetta ovale" in lapis lazuli of the "Collezione Medicea" (catalogue number 13688; dimensions: $9 \times 5 \times 1\,\mathrm{cm}^3$); (b) the same artwork during IBA measurements at LABEC.

at 4800 m above sea level and 76 km south of Khorugh in Gorno-Badakhshan). More information about the samples have already been reported elsewhere [29]. Samples were prepared as semi-thin sections and mounted on special slides with a 3 mm diameter hole in the centre. The holes were made to avoid any interference from the sample-holder during ion beam analysis, being the penetration depth of the proton probe up to about 60–80 μm, depending on the mineral (SRIM calculation). The choice to have thicker sections (from 60 to 100 μm) compared to classical thin sections (about 30 μm) is necessary because of the hole, that makes samples more fragile. Obviously this fact, essential for our purpose, makes it impossible to do an accurate petrographical analysis by means of transmitted light, but it is important to remember that this kind of measurements has to be excluded when analysing artworks and so it is not among the main techniques of this work. It is worth stressing that this procedure for samples preparation was useful only in the first characterisation stage, to allow the use of invasive techniques, simplifying and speeding up the measurements on rocks. The same semi-thin sections has been characterised also by means of non-invasive techniques, but just for convenience; it will not be necessary to perform this sample preparation when artworks are analysed.

3˙1. *Artwork of the "Collezione Medicea di pietre lavorate"*. – This collection has a great historical value: in fact almost all the objects have been described in the catalogues since the end of the 18th century. It is composed of precious stones, both polished and carved: part of them were manufactured in the ancient glyptic school in the gardens of "S. Marco" in the middle of the 16th century and are present in the inventories of the same century [27]. To test the analytical method we analysed one of these precious objects made in lapis lazuli, and in particular the "Coppetta ovale" (catalogue number 13688), shown in fig. 1.

4. – Experimental set-up

Nowadays there are many instruments that allow not to damage the sample under analysis; Ion Beam Analyses (IBA) allow to obtain information about the trace elements concentration in the samples, very useful to perform provenance studies. In this work also Scanning Electron Microscopy (SEM) has been used, both coupled with Energy Dispersive X-ray Spectrometry (EDX) detector and Cathodo Luminescence (CL) detector, but these techniques are not necessary for the study of precious objects. The description and the experimental details of these instruments are reported elsewhere [29, 30]. The

TABLE I. – *The mean penetration depth (p.d.) and lateral straggling (l.s.) of different probes used in this work in some of the main phases of lapis lazuli; the values are obtained by means of CASINO* [33] *for electrons and SRIM* [34] *for protons.*

Technique		CL		SEM-EDX		μ-PIXE			
Probe		15 keV electrons		20 keV electrons		600 keV protons		3 MeV protons	
Mineral phase	Density (g/cm^3)	p.d. (μm)	l.s. (μm)	p.d. (μm)	l.s. (μm)	p.d. (μm)	l.s. (μm)	p.d. (μm)	l.s. (μm)
lazurite	2.41	1.34	0.79	2.24	1.30	6.87	0.40	83.2	3.35
diopside	3.29	0.96	0.56	1.59	0.95	5.18	0.32	60.6	2.54
pyrite	5.02	0.61	0.36	1.00	0.61	3.84	0.31	47.6	2.86

measurements involving the use of an ion microprobe have been performed at two Italian nuclear laboratories of INFN (the Italian National Institute of Nuclear Physics): the in-vacuum ion-beam facility of the 2.5 MV Van der Graaff accelerator AN2000 at LNL (Legnaro National Laboratories, Padova) [31], and the external beam facility of the 3 MV Tandetron accelerator at the LABEC Laboratory (Firenze) [32].

4˙1. *Simulations.* – Two simulation codes (one for electrons and one for protons) have been used to choose the proper probe energy in order to analyse only one crystal and not beneath it. The codes used are: CASINO (version 2.42) [33] for electrons and SRIM (version 2008.04) [34] for protons. They have been used mainly to obtain the dimensions of the probed volume in different minerals, evaluating the penetration depth and the lateral straggling of particles of different energies in different mineral phases. In table I the mean values (not the maximum) of both penetration depth and lateral straggling are reported: the energy values both for electrons and protons are the ones selected for this work. In fact, before choosing the experimental conditions, other parameters to be evaluated besides the probed volume are the maximum and minimum energies obtainable with the facility and the intensity of signal coming out from the sample at the selected energy, mainly depending on the cross-section and the geometry. In this work, at the external facility of Firenze, μ-PIXE measurements were carried out on lazurite using a 3 MeV proton beam, that means a mean penetration depth of about 85 μm. In this way the samples were probed along all their thickness, but the dimensions of analysed lazurite crystals were sufficiently large to avoid the presence of other minerals beneath the investigated ones.

A different approach was followed to study diopside: for a more reliable comparison the probed volume is the closest as possible of that analysed by means of CL (using a 15 keV electron beam), that has a mean penetration depth of about 1 μm and a mean lateral straggling below 1 μm. For this reason the minimum energy achievable at the in-vacuum facilities of LNL (600 keV proton beam) has been used: it has a mean penetration depth of about 5 μm in diopside and a lateral straggling below 1 μm. Such characteristics represent a good compromise between the reduction of cross-section associated with the use of low-energy ions and the proximity to electron probed volume.

5. – Results

Due to the heterogeneity of lapis lazuli it is very difficult to identify provenance markers analysing elemental composition of the whole rocks or artworks. At the same time it

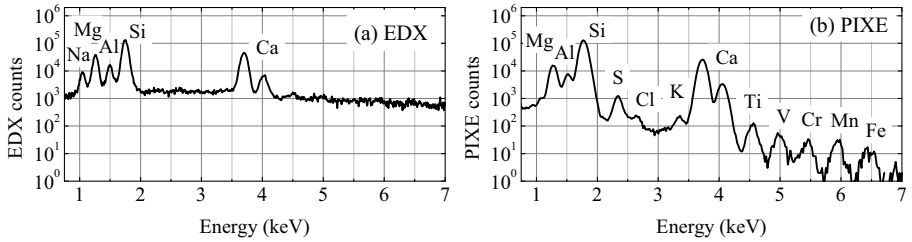

Fig. 2. – Comparison of X-ray spectra of diopside measured using: (a) EDX with 20 keV electrons probe; (b) PIXE with 600 keV protons probe.

requires very long time to study in detail all the phases inside this stone. For this reason differences inside single phases instead of the whole stone have been analysed, mainly focusing on two of the main phases: lazurite, the main phase of lapis lazuli responsible for the blue colour, and diopside, one of the more frequent accessory mineral characteristics of all the Asian samples. This study was performed by means of IBA techniques, both Particle Induced X-ray Emission (PIXE) and Ion Beam Induced Luminescence (IBIL), but was preceded and completed by means of cold-CL, SEM-EDX, SEM-CL (both spectra and maps) and μ-Raman Spectroscopy measurements. As can be seen from fig. 2 the results obtained by means of PIXE confirm SEM-EDX analyses, providing more information about trace elements; analogously IL spectra are very similar to CL spectra (fig. 3). This is the reason to choose electron probe techniques for a preliminary characterisation and ion probe techniques for a confirmation of the results and to study artworks. Despite the limited number of analysed samples, results are sufficient to exclude/suggest few features as provenance markers, partly confirming what previously published in the literature. Most of the results obtained in this work have already been published [29,30]; here an explanation of the method and a list of the markers are presented.

5˙1. *Method.* – The first step of the characterisation has been the observation of all the samples in reflection mode by means of an optical microscope, to have some optical maps to use as a reference during the analyses and as a comparison with other mapping techniques. After this, even if it was not the aim of this work and the samples were not prepared for this kind of measurements, the semi-thin sections have been observed

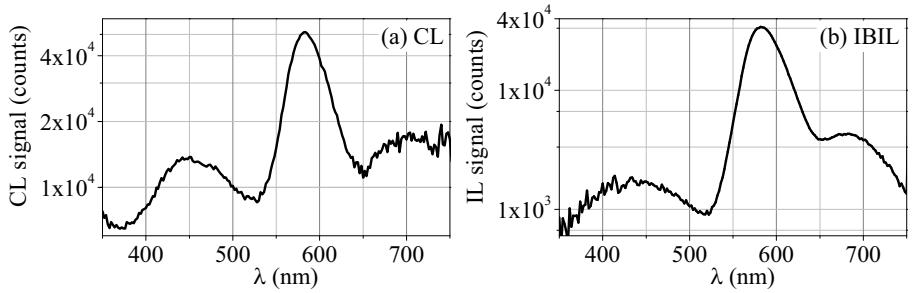

Fig. 3. – Comparison of luminescence spectra (corrected for detector efficiency) of diopside measured using: (a) CL with 15 keV electrons probe; (b) IBIL with 3 MeV protons probe.

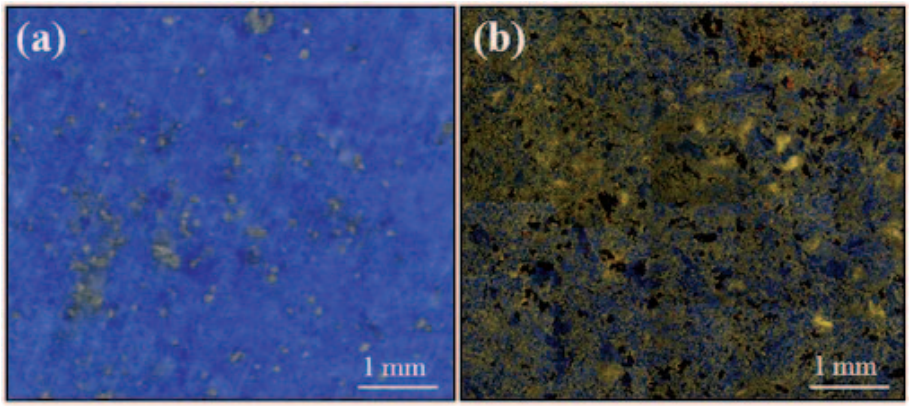

Fig. 4. – Lapis lazuli sample from Afghanistan (RI388): (a) optical image in reflection mode; (b) cold-CL image of the same area (the CL image results from many pictures).

in transmitted light, to have some basic petrographical information. Because of their thickness, more than double respect to ordinary thin sections, just one polarizer could be used and not all the samples give information; in particular the Chilean ones were too thick (about 100 μm) to obtain significant images.

The next step for the characterisation has been the cold-CL measurements: images of the whole surface were acquired from all the samples. To map all the sample surface many pictures were necessary, since the area of each picture is just $1.3 \times 1.7\,\mathrm{mm}^2$. After the acquisition all the images have been joined to form a complete map of the samples (an example is shown in fig. 4). From cold-CL images the distribution and intensity of luminescent mineral phases are clear.

After this preliminary mapping the analysis on single crystals using a SEM started; to avoid charging effects during the measurements it was necessary to carbon-coat the samples. The crystals to be analysed have been selected among the biggest for each colour on the base of cold-CL maps. Both SEM-CL, to obtain a luminescence spectrum for each colour in cold-CL maps, and SEM-EDX, to have a quantitative analysis of the main elements in each phase, have been used. In order to acquire data with significant statistics, CL and EDX spectra for each luminescent phase were collected in all the samples, for a total of about 450 acquisitions for each technique. The quantitative analysis allowed to associate a chemical composition to each phase, obtaining in many cases a univocal correspondence between a certain composition and a colour of luminescence. It has often been possible to recognise the phase thanks to the chemical composition, comparing it to the phases already found in lapis lazuli by other authors and acquiring a Raman spectrum of the biggest crystals to confirm the identification of the phase. After this step, for the most important and diffused phases, also the trace elements composition have been investigated, by means of PIXE. In parallel IBIL measurements have been performed, always confirming the results obtained by means of CL; combining PIXE and IBIL measurements sometimes it is possible to find a correlation between the presence (or absence) of an element and a certain peak of luminescence, confirming that an element is an activator (or a quencher) for the luminescence. To analyse the same crystal by means of all the techniques, a map was always collected to select the point to be analysed. For SEM-EDX measurement the point was selected using mainly back-scattered electrons

images, while for SEM-CL measurement the monochromatic CL maps centred on the wavelength emission of the main mineral (diopside or wollastonite) has been used. The μ-PIXE maps have been obtained both at the external microbeam line at LABEC and in-vacuum at LNL: due to the good spatial resolution it is possible to distinguish and then individually analyse mineral phases in lapis lazuli. The lazurite crystals can be identified thanks to the correlation of both sodium and sulphur distributions, diopside is characterised by a high magnesium content, K-feldspars show a high potassium content while from the iron map the pyrite grains can be recognised.

5˙2. *Markers*. – The main distinctive mineral phase in Chilean lapis lazuli is wollastonite, which can be distinguished by an intense luminescence at 560 nm and 620 nm. This behaviour was observed in all 4 samples analysed and confirms what was obtained in previous works [35, 36]. Lapis lazuli from Pamir exhibits a luminescence band at 690 nm in the emission spectra of diopside and it is also characterised by a cancrinite phase with a strong UV emission [29]. Moreover a higher quantity of arsenic in the lazurite from this provenance is a good indication to distinguish it from others [30, 37]. The samples from Afghanistan show a mean value of some trace elements (titanium, vanadium and chromium) in diopside higher than other provenances [30]. Moreover the presence of zirconium in some inclusions seems to be a peculiarity of these samples [30]. Siberian lapis lazuli is characterised by a high content of barium and strontium and therefore the PIXE analysis allows to discriminate this provenance [22, 37, 38].

5˙3. *Results on the artwork of the "Collezione Medicea di pietre lavorate"*. – A first characterisation of the "Coppetta ovale" by means of ionluminescence suggests that diopside is present among accessory minerals, while the characteristic luminescence of wollastonite is lacking, so it is possible to exclude the Chilean provenance for the material utilised for this object. μ-PIXE results obtained for a diopside crystal of this sample shows that the titanium (1000 ± 200 ppm), vanadium (400 ± 80 ppm) and chromium (90 ± 50 ppm) amount are comparable with that in the Afghan rock samples of certain provenance [30], and also the presence of zirconium (1000 ± 140 ppm) suggests the same provenance for the material used for this artwork [30]. Despite this information a Siberian provenance cannot be completely excluded, so further analyses are required to give a more precise indication.

6. – Conclusion

In this work a systematic study by means of SEM and IBA techniques on lapis lazuli is reported, allowing for a characterisation of both the elemental composition and the luminescent properties of some of the phases present in this stone. Its final aim is to identify some markers related to different provenances, analysing samples of known origin coming from four of the main lapis lazuli sources. These markers can give indication about where the raw material used in archaeological findings and artworks comes from. Despite the limited number of analysed samples, results are promising and the experimental differences among various samples are significant. All the proposed markers can be identified using an external micro ion beam, in particular by means of μ-IBIL and μ-PIXE.

Spectra obtained by means of CL and IBIL were compared showing a good correlation so that the possibility of extending the results obtained by means of CL to IBIL was confirmed. Differences in luminescence spectra arise from the presence of peculiar mineral

phases associated with lapis lazuli sources and can be used to distinguish the provenance of the stones. The elemental analysis of single phases is also useful to distinguish among provenances: in fact the main elements of lazurite allow in some cases to have a clear indication of the provenance of a sample, while in diopside the analysis of only the main elements does not give any information about the origin of a sample. Moreover the analysis of trace elements in the samples by means of μ-PIXE allows to have more markers to distinguish among provenances.

It is worth stressing that all the results in this work are related to a limited quantity of samples, and that the reliability of the present conclusions is to be confirmed investigating more samples in future works. However the capability to assign a lapis lazuli sample to a quarry using the identified markers has been tested on a sample of unknown origin and according to analyses the sample has been attributed to an Afghan origin [30].

Moreover, after some preliminary measurements, the method can be successfully applied also on artworks, allowing to obtain useful information about the provenance of a lapis lazuli object only by means of non-invasive techniques.

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REFERENCES

[1] Bulgarelli G. M. and Tosi M., in *Geo-Archeologia*, Vol. **1-2** (Japadre Editore, L'Aquila) 1977, pp. 37-50 (in Italian).
[2] Von Rosen L., *Studies in Mediterranean Archaeology and Literature*, edited by Paul Aströms Förlag, Vol. **93** (Partille, Sweden) 1990.
[3] Sofianides A. S. and Harlow G. E., *Gems and Crystals from the American Museum of Natural History* (Simon and Schuster, New York) 1990.
[4] Sutherland L., *Gemstones of the Southern Continents* (Reed Books, Sydney, Australia) 1991.
[5] Coenraads R. R. and Canut de Bon C., *Gems & Gemology*, **36** (2000) 28.
[6] Herrmann G. and Moorey P. R. S., in *Reallexikon der Assyriologie und Vorderasiatischen Archäologisch*, Vol. **6** (W. de Gruyter, Berlin) 1983, pp. 489-492.
[7] Moorey P. R. S., *Ancient mesopotamian materials and industries: the archaeological evidence* (Clarendon press, Oxford) 1994, pp. 85-92.
[8] Silverman D. P., *50 Wonders of Tutankhamun* (Crown Publishers, New York) 1978.
[9] Kenoyer J. M., *World Archaeology*, **29** (1997) 262.
[10] Bowersox G. W. and Chamberlin B. E., *Gemstones of Afghanistan* (Geoscience Press, Tucson, Arizona) 1995.
[11] Hinks P., *Nineteenth Century Jewellery* (Faber and Faber, London) 1975, pp. 56.
[12] Bauer M., *Precious stones: a popular account of their characters, occurrence and applications* (Charles Griffin & Co, London) 1904.
[13] Canut de Bon C., *Apreciaciones sobre las reservas de lapislazzuli de yacimientos chilenos [Reserve estimates for the Chilean lapis lazuli deposits]* (Unpublished report for El Servicio Nacional de Geología y Minería) December 9, 1991.
[14] Rivano S., *Proceedings of 6º Congreso Geologico Argentino*, Vol. **3**, 1975, pp. 165-177.

[15] Rivano S. and Sepúlveda P., *Illapel 1:250,000 Geological Map Sheet, Chile* (Servicio Nacional de Geología y Minería, Santiago, Chile) 1991.
[16] Wyart J., Bariand P. and Filippi J., *Gems & Gemmology*, **17** (1981) 184.
[17] Tosi M., *Gururājamañjarikā, Studi in onore di G. Tucci* (Istituto Universitario Orientale, Napoli) 1974, pp. 3-22.
[18] Herrmann G., *Iraq*, **30** (1968) 21.
[19] Sarianidi V. I., *Archaeol. Mag.*, **24** (1971) 12.
[20] Nibbi A., *Ancient Egypt and some Eastern Neighbours* (Park Ridge, Noyes Publication) 1981, pp. 33-55.
[21] Von Rosen L., *Studies in Mediterranean Archaeology and Literature*, Vol. **65**, edited by Paul Aströms Förlag (Partille, Sweden) 1988.
[22] Delmas A. B. and Casanova M., *Proceedings of the* 9^{th} *International Conference of South Asian Archaeologists in Western Europe, Venice, 1987* Vol. **66**, edited by Taddei M. (Istituto Italiano per il Medio ed Estremo Oriente, Roma, Serie Orientale) 1990, pp. 493-505.
[23] Nicholson P. T. and Shaw I., *Ancient Egyptian Materials and Technology* (Cambridge University Press) 2000, pp. 39-40.
[24] Hamd-Allah Mustawfi of Qazvin, *The Geographical Part of the Nuzhat-al-Qulub*, translated by Le Strange G., 1919, p. 197.
[25] Deer W. A., Howie R. A. and Zussman J., *Rock-forming minerals* (Longman) 1978.
[26] Borelli A., Cipriani C., Innocenti C. and Trosti R., *La Gemmologia*, **XI** (1986) 24 (in Italian).
[27] Cipriani C., Innocenti C. and Trosti-Ferroni R., *Museologia Scientifica*, **V** (1988) 17 (in Italian).
[28] Ballirano P. and Maras A., *Am. Mineralogist*, **91** (2006) 997.
[29] Lo Giudice A., Re A., Calusi S., Giuntini L., Massi M., Olivero P., Pratesi G., Albonico M. and Conz E., *Anal. Bioanal. Chem.*, **395** (2009) 2211.
[30] Re A., Lo Giudice A., Angelici D., Calusi S., Giuntini L., Massi M. and Pratesi G., *Nucl. Instrum. Methods Phys. Res. B*, **269** (2011) 2373.
[31] Bollini D., Cervellera F., Egeni G. P., Mazzoldi P., Moschini G., Rossi P. and Budello V., *Nucl. Instrum. Methods Phys. Res. A*, **328** (1993) 173.
[32] Giuntini L., Massi M. and Calusi S., *Nucl. Instrum. Methods Phys. Res. A*, **576** (2007) 266.
[33] Drouin D., Réal Couture A., Joly D., Tastet X., Aimez V. and Gauvin R., *Scanning*, **29** (2007) 92.
[34] Ziegler J. F., Ziegler M. D. and Biersack J. P., *Nucl. Instrum. Methods Phys. Res. B*, **268** (2010) 1818.
[35] Calusi S., Colombo E., Giuntini L., Lo Giudice A., Manfredotti C., Massi M., Pratesi G. and Vittone E., *Nucl. Instrum. Methods Phys. Res. B*, **266** (2008) 2306.
[36] Colombo E., Calusi S., Cossio R., Giuntini L., Lo Giudice A., Mandò P. A., Manfredotti C., Massi M., Mirto M. A. and Vittone E., *Nucl. Instrum. Methods Phys. Res. B*, **266** (2008) 1527.
[37] Calligaro T., Coquinot Y., Pichon L. and Moignard B., *Nucl. Instrum. Methods Phys. Res. B*, **269** (2011) 2364.
[38] Ivanov V. G., Samoylov V. S., Petrov L. L. and Yaroshenko S. K., *Dok. Earth Sci. Sect.*, **227** (1976) 200.