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Ion Beam Analysis for the provenance attribution of lapis lazuli used in glyptic art: The case of the “Collezione Medicea”

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ABSTRACT

The first part of this study reports on the wide campaign for the extension of the database of both trace and minor elements concentration in diopside by means of μ -PIXE measurements and of luminescence spectra in diopside and wollastonite by means of μ -IL measurements. Diopside and wollastonite are actually two of the most common lapis lazuli-forming minerals. For this former part of the study, we analysed rocks of known provenance at the microbeam line of the LNL laboratories in Legnaro (PD) of the Istituto Nazionale di Fisica Nucleare (INFN).

The latter part of the paper is dedicated to the non-invasive Ion Beam Analyses (IBA) characterisation of six pieces of the “Collezione Medicea”. The collection is exhibited at the Museum of Natural History (University of Firenze) and belonged to the Medici family. It includes artworks made of lapis lazuli manufactured in the 16th and 17th centuries but there is not precise information about the provenance of the used raw material.

Results on the artworks show, as expected, that the Chilean provenance of the material used for the analysed artworks has to be excluded. Lapis lazuli used for five of the analysed artworks can be ascribed to the Afghan quarry district, while one object cannot be attributed only on the base of diopside and wollastonite analysis.

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1. Introduction

Lapis lazuli is a blue semi-precious stone that requires peculiar conditions to be formed, and for this reason it occurs in few places in the world [1]. Even so, it has been widely used in glyptic since the antiquity and by different civilizations. Although the Badakhshan mines in Afghanistan (the most famous being Sar-e-Sang) are now widely considered as the only source of lapis lazuli in ancient times, other sources have been taken into account [2,3]. A systematic and exhaustive provenance study of the raw material employed for artworks is still lacking, even if over the last few years different approaches, all exploiting non-invasive techniques,

have been used to discriminate among different geological sources [4–6].

In previous works we have already analysed samples of rocks of known provenances by means of focalized ion beam techniques, in particular μ -PIXE (Particle-Induced X-ray Emission) and μ -IL (Iono-Luminescence). These techniques were chosen because they allow to analyse single crystals of different minerals, a fundamental aspect in a heterogeneous material as lapis lazuli, and also because of their non-invasivity, being often impossible to take samples from artworks or to work in vacuum. Some markers were found and proposed to distinguish among the four different provenances: Afghanistan (Badakhshan), Tajikistan (Pamir Mountains), Siberia (near Lake Baikal) and Chile (Ovalle) [7–10].

In this work we focused on two among the several mineral phases of lapis lazuli proposed as markers: diopside ($\text{CaMgSi}_2\text{O}_6$) and wollastonite (CaSiO_3). Twelve samples were already analysed

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in previous works [8,9]. Chilean rocks can be easily distinguished from the others: in fact, as reported in previous studies [7,11–13], we confirmed the high contents of wollastonite in all the analyzed Chilean samples (absent in all other analyzed samples). About diopside, in many Afghan samples we observed a high quantity of one or more of the following trace elements not observed in the other Asian samples: Ti (up to about 5000 ppm), V (up to about 600 ppm) and Cr (up to about 900 ppm). However, due to the limited number of characterized samples, the validity of the markers had to be confirmed increasing the amount of analysed rocks prior to use them to attribute the provenance of lapis lazuli in artworks. Therefore, in this paper, a total of 28 samples from 4 different provenances were characterised (8 from Afghanistan, 4 from Tajikistan, 12 from Siberia and 4 from Chile). They belong to different collections: the Mineralogy and Lithology section of the Museum of Natural History (University of Firenze), the Mineralogical, Petrographical and Geological section of the Regional Museum of Natural Sciences of Torino and some were bought by the University of Torino at International Mineral Shows since 2010.

Simultaneously a campaign on artworks and archaeological finds was started to verify the applicability of the method on objects. In this work six precious artworks of the “Collezione Medicea” made of lapis lazuli were analysed to find some indication about the provenance of the raw material. This collection includes both rock samples and artworks, made of precious and semi-precious stones, belonged to the famous Medici family in Firenze and now conserved at the Museum of Natural History (University of Firenze). For many of these objects there is not precise information, especially about the provenance of the raw material used for their manufacturing. In the original catalogue, for some of the analysed artworks an historical provenance such as “Levant” or “Persia” is reported, thus suggesting a generic Asian origin of the raw material, not sufficient to distinguish among the different possible locations.

A first chemical characterisation by means of invasive techniques (XRD and SEM), mainly focused on lazurite, was performed in the past [12] on the rock samples of the collection, but the provenance of the raw material used for artworks has not been investigated yet.

2. The artworks

The Museum of Natural History (University of Firenze) hosts the “Collezione Medicea di pietre lavorate”: a collection of great historical value composed by precious stones both polished and carved, collected from the members of the Medici family since the 15th century.

In Firenze, the passion of the Medici for importing precious stones led to Ferdinando I de' Medici's foundation, in 1588, of the Grand-ducal workshops “Gallerie dei Lavori”, a court manufactory, located in a wing of the Uffizi that fabricated precious artworks with polychrome stones. The Grand Duke created this special hard-stone workshop and elevated it to a level of importance above artisanal studios and actually the “Galleria dei Lavori” quickly gained international acclaim for its magnificent products. With time the “Galleria dei Lavori” changed its name into “Opificio delle Pietre Dure”, nowadays one of the most important restoration centres in Italy.

Among the 700 specimens of the “Collezione Medicea” there are carved ornaments, panel and tesserae used for the *pietra dura* decorative technique and some precious stone objects carved and decorated, remarkable high quality examples of craftsmanship and artistry of the Florentine artists during the Renaissance. Some information about the objects is already present in the inventories of the 16th century and, since the end of the 18th century, almost all

the items are described in the catalogues, which provide historical information and in some cases indications about the raw materials provenance.

Six of these precious objects, made of lapis lazuli and manufactured in the Grand-ducal workshops “Galleria dei Lavori”, were analysed in this work. The main characteristics and pictures of the artworks are shown in Fig. 1.

The largest and more precious of them is an oval bowl (catalogue number: 13682), decorated with a carved palmette and the outline of a big leaf. Two carvings on the rear, the Grand-Ducal crown and the monogram “FM 1600”, indicate that the object was manufactured in 1600 during the reign of Ferdinando I de' Medici and it originally belonged to the Grand Duke. According to the catalogue description, the bowl was supported by a well-rounded foot also decorated with a band of lapis lazuli, nowadays lost. The bowl is in the list of objects delivered to the Grand Duke's Private Secretariat in 1782 and then moved to the “Real Gabinetto di Fisica e Storia Naturale” in 1789.

The second object is a small rectangular case (catalogue number: 13684), with carved faces of lapis lazuli and borders, base and feet made of gilded metal. The interior of the case is divided in six spaces and, according to the catalogue description, this object was used as a container for teeth. It was made in the Grand-ducal workshops between the end of the 16th century and the beginning of 17th century and it arrived at the “Imperial Regio Museo di Fisica e Storia Naturale” in 1787.

The third object is a disc of lapis lazuli (catalogue number: 13148), decorated with a star made of citrine, a yellow variety of quartz. It was manufactured in the last 20 years of the 16th century and it was part of the ornament of the *mezzanino* in Palazzo Pitti, from where it was removed in 1771.

Historical information on the last three objects is less exhaustive: the small vase with screw cap and golden metal hinge (catalogue number: 13685), the saltcellar (catalogue number: 13687) and the oval panel (catalogue number: 13688) were manufactured in the Grand-ducal workshop between the end of the 16th century and the beginning of 17th century and belonged to the Grand Duke's collections.

3. Instrumentation and operating conditions

About lapis lazuli rock samples for which there are no problems in performing invasive analysis, IBA measurements on graphite-covered thick petrographic sections (ca. 100 μm) were carried out at the in-vacuum microbeam line [14] at the AN2000 accelerator of the INFN-LNL Laboratory in Legnaro (PD). A 2 MeV proton beam was used, with an ion current of about 200 pA and a spot dimension of about 5–10 μm ; the analysis chamber is shown in Fig. 2. From SRIM 2013 [15] simulations, the penetration depth in diopside (density 3.278 g/cm³) and wollastonite (density 2.9 g/cm³) was evaluated to be about 31 μm and 36 μm , respectively. $\mu\text{-PIXE}$ measurements were performed using an Ortec IGLET-X HP-Ge detector with an Al funny filter. The $\mu\text{-IL}$ setup has been recently installed: it consists in a collecting lens fixed inside the chamber and connected to a spectrometer through two optical-fibres, one inside and one outside the chamber, and a vacuum feed-through. The spectrometer is an Ocean Optics USB4000 with 3648 pixels, fitted with a 600 l/mm grating blazed at 500 nm (bandwidth 350–1000 nm, spectral resolution of 2 nm). The measured spectra were corrected for the spectral response of the instrument.

The analysed diopside and wollastonite crystals were previously selected on the basis of optical images and cold-CL maps acquired before the carbon-coating, following a protocol explained elsewhere [8], which exploits the strong white-yellowish luminescence

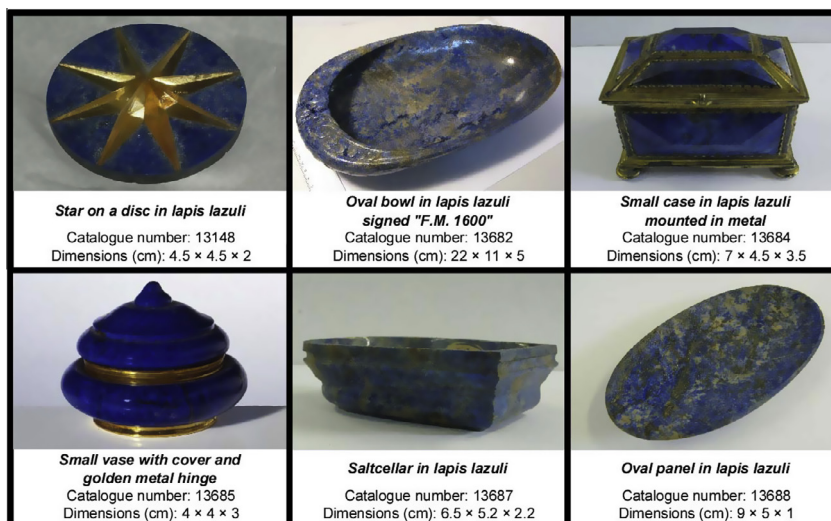


Fig. 1. The objects of the “Collezione Medicea” analysed in this work: description, catalogue number and dimensions are taken from the museum catalogue.

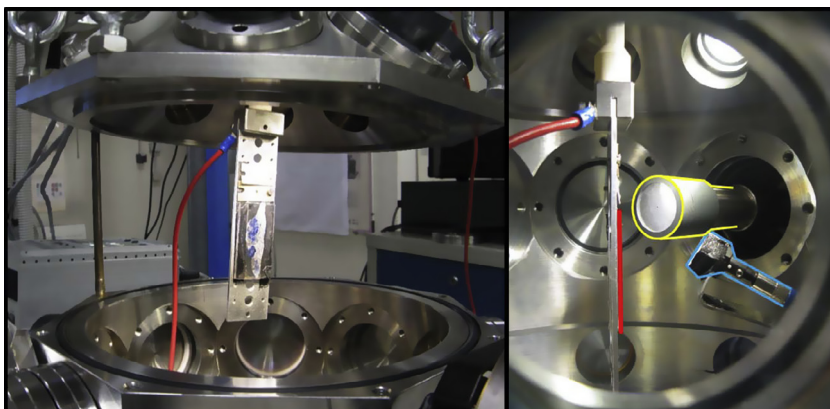


Fig. 2. The microbeam analysis chamber of the LNL-AN2000 accelerator with PIXE detector and IL collecting lens (yellow and blue outlined, respectively) before the analysis of a petrographic section of lapis lazuli (red outlined). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of both phases. Moreover, to avoid contributions from close mineralogical phases, only relatively big crystals, greater than the resolution capabilities of the employed microbeam facility and greater than the penetration depth of the beam, were selected. During IBA analysis they have been identified thanks to the optical microscope direct on the sample outside the microbeam chamber and an accurate selection of the homogeneous area has been carried out using μ -PIXE elemental mapping.

The measurements on artworks were performed at the external scanning microbeam facility of the Tandatron accelerator of the INFN LABEC Laboratory in Firenze [16], using a 3 MeV proton beam (Fig. 3). For this energy the penetration depth in diopside and wollastonite was evaluated to be about 60 μ m and 70 μ m, respectively, from SRIM 2013 [15] simulations. Considering the impossibility to perform preliminary invasive analysis on artworks, the first step of the measurement method was a survey of all the samples by means of the broad beam IL microscopy apparatus [17]. Due to the different luminescent properties of the mineralogical phases, this technique allows to recognize their distribution very rapidly and to save a lot of time searching the point of interest, i.e. in our case a particular mineralogical phase on an unknown and heterogeneous sample. In fact, due to the texture of lapis lazuli, it is difficult to find a specific mineralogical phase using only μ -PIXE and μ -IL, since the time required to have significant statistics to identify it

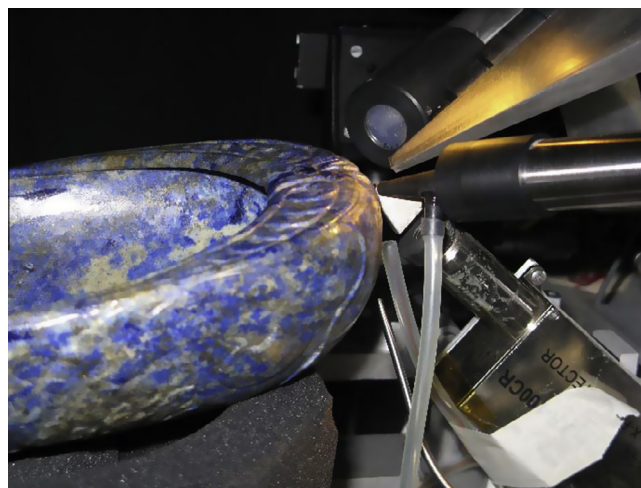


Fig. 3. Experimental set-up of the external microbeam line at INFN-LABEC in Firenze during the analysis of the Oval Bowl (“Collezione Medicea”).

is high. In Fig. 4 the broad beam IL microscopy and the optical images of two areas (about 1.5 × 1.5 mm² wide) on artworks obtained in few seconds are shown. In this case the points of interest

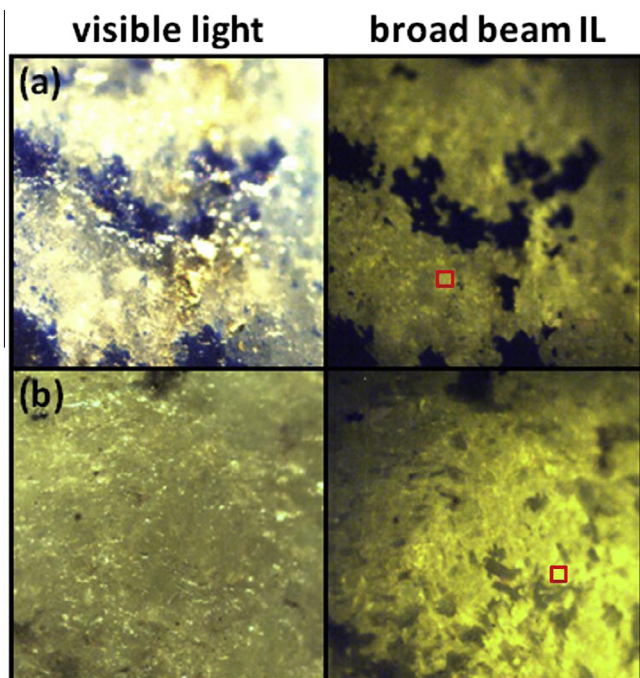


Fig. 4. Pictures in visible light (left) and broad beam ionoluminescence microscopy (right) of two different areas (a and b) of the Oval Bowl of the “Collezione Medicea” (each square is 1.5 mm wide). To study diopside, points of interests can be selected in bright yellow areas (shown as red squares) avoiding inhomogeneous regions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

were selected in bright yellow areas (diopside). In the second step of the above-mentioned measurement procedure, the areas, selected thanks to the broad beam IL microscopy, were analysed by means

of μ -IL and μ -PIXE. Measurements were performed with a spot dimensions of about 15–20 μ m and ion current of about 500 pA. The μ -IL apparatus at LABEC was developed for Cultural Heritage and material science applications. More details on the experimental set-up are reported in previous works [7,18]. For some of the analysed objects the same Ocean Optics spectrometer employed at the LNL laboratory was used.

The μ -PIXE spectra were quantitatively analysed by means of GUPIXWIN (version 2.2.3) [19] using a set of reference standards for the determination of the experimental parameters: minerals from SPI Supplies and Polaron Equipment Ltd. for the in-vacuum measurements, a soda-lime container from NIST and thick pure elements from Goodfellow Cambridge Ltd. for the ex-vacuo measurements.

4. Results and discussion

The first step of this work was related to the extension of the database of trace and minor elements concentration in diopside by means of μ -PIXE measurements and of luminescence spectra in diopside and wollastonite by means of μ -IL measurements. A total of 28 rocks from 4 different provenances were characterised. Analysis were carried out on 111 crystals (99 diopside and 12 wollastonite).

As already stated, the selection of points of interest was done on the basis of cold-CL maps, looking for crystals showing white-yellowish luminescence typical of diopside or wollastonite. Quantification of major elements contents was used to confirm the recognition of one of these mineral phases. As previously observed, the widespread presence of wollastonite discriminates Chilean rocks from others, so that trace and minor elements data analysis was implemented only on diopside.

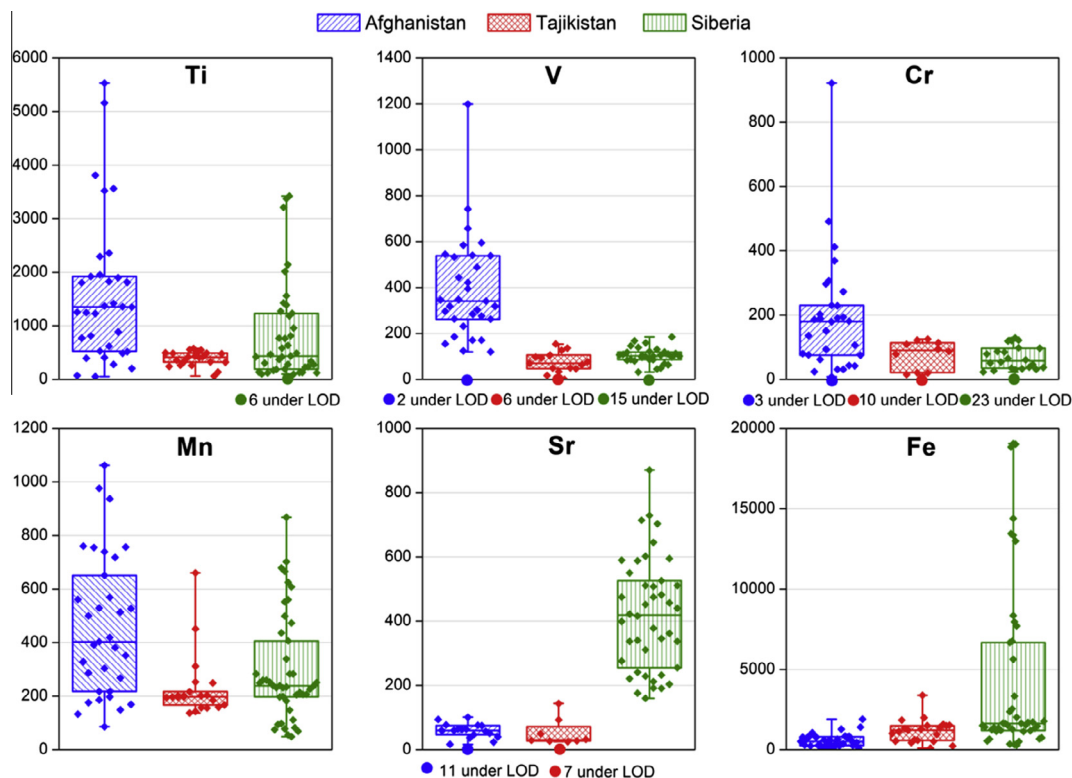


Fig. 5. μ -PIXE results (in ppm) on diopside crystals in lapis lazuli from different provenances: the boxes include 50% of analysed points (from 25 to 75%), while the bars contain all the other points (from 0% to 25% and from 75% to 100%). Each box is separated in two parts by a line dividing the points in two identical groups (50 and 50%).

4.1. Analysis of rocks: μ -PIXE

Results on trace (Ti, V, Cr, Mn, Sr) and minor (Fe) element contents in diopside are shown in Fig. 5, where new data were added to the ones obtained in [9], thus noticeably increasing the existing database. Iron is considered a minor element because diopside ($\text{CaMgSi}_2\text{O}_6$) belongs to the monoclinic pyroxene series forming a complete solid solution with hedenbergite ($\text{CaFeSi}_2\text{O}_6$) [20]. Each point in Fig. 5 represents the analysis of a crystal and the samples are grouped on a provenance basis. The boxes include 50% of analysed points (from 25% to 75%), while the bars contain all the other points (from 0% to 25% and from 75% to 100%). Each box is separated in two parts by a line dividing the points in two identical groups (50 and 50%). Only the elements found in many samples, which are thus possible candidates for provenance discrimination, are reported. The elements found only in few samples or not useful for a provenance discrimination at now (such as, for example, Cu, Zn, Ar, Y, Zr and Pb) are not represented in the graphs.

Most of the results obtained in [9] were confirmed and new markers observed. In particular, the high quantity of Ti (up to 5500 ppm), V (up to 1200 ppm) or Cr (up to 900 ppm) in Afghan diopside and not observed in other Asian provenances was confirmed with a raising of the upper limits. For comparison, the higher values of these trace elements in Tajik samples are respectively 560 ppm for Ti, 160 ppm for V and 120 ppm for Cr, so that a high value of these elements can exclude the Tajik provenance. A similar result was obtained for Siberian samples where V is also lower than 200 ppm and Cr is lower than 150 ppm; in this case

Ti is a usable but weaker marker than for Tajikistan rocks because it can reach a value of 3500 ppm.

Moreover new markers were added, in particular on Siberian rocks, that are the only samples in which Fe content is higher than 3500 ppm and Sr content is higher than 160 ppm. It is important to notice that the high quantity of Fe observed in [9] was not considered as a marker due to the low number of Siberian samples analyzed and Sr was not detected in diopside from all provenances due to the lower energy of the employed proton beam probe respect to the one employed in this work (600 keV in [9]; 2 MeV and 3 MeV in this work). At now this last marker seems to be the strongest one since there is no overlapping among the Siberian samples and others provenances, i.e. all the samples from Tajikistan and Afghanistan have Sr contents lower than the minimum quantity measured in Siberian samples. All these results have been confirmed by analogous measurements carried out by means of μ -XRF (X-Ray Fluorescence) [21].

4.2. Analysis of rocks: μ -IL

The μ -IL spectra on rocks are presented in Fig. 6, subdivided by provenance. The first set of spectra refers to Chilean samples, showing the typical wollastonite features (double broad bands at 560 nm and 620 nm, merged in a single asymmetric peak) already observed in [7,8], while all the rocks from Asian provenances are characterised by the main band due to diopside at 580 nm, as already shown in [8]. These results confirm, with higher confidence thanks to the increased number of analysed samples, that due both

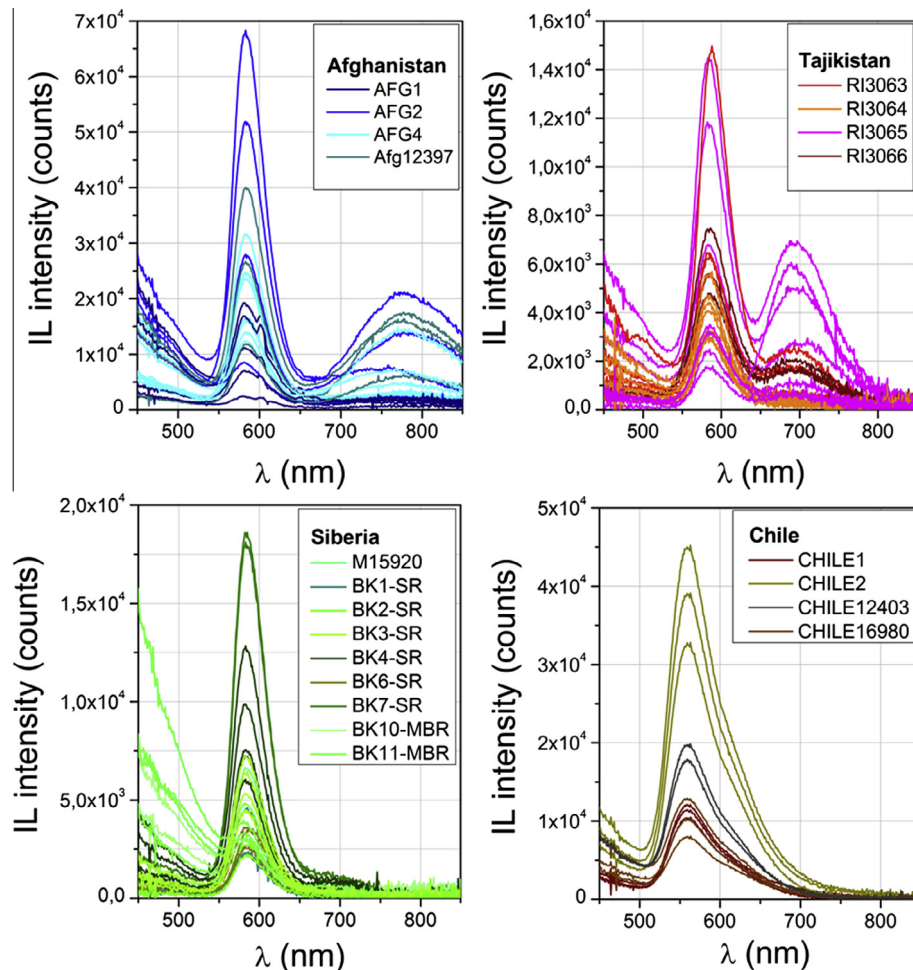


Fig. 6. Selection of representative IL spectra of diopside crystals in different samples (from Afghanistan, Tajikistan and Siberia) and wollastonite crystals (from Chile).

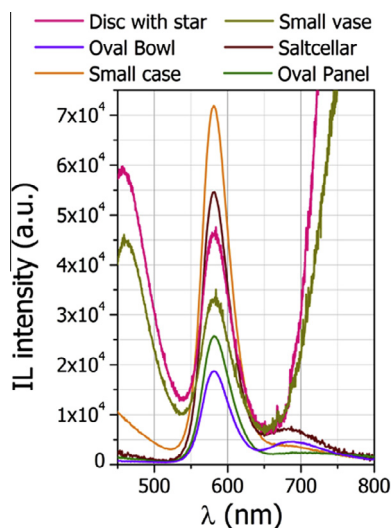


Fig. 7. IL spectra of diopside in the samples of the "Collezione Medicea": each spectrum is the mean of a sequence of spectra.

to the quickness in acquiring IL spectra and to the high intensity of wollastonite and diopside luminescence signal, dominating over all other luminescence emission in lapis lazuli, IL analysis is the best way to distinguish Chilean from Asian samples.

Also for diopside, results obtained in [7,8] were confirmed with a significant statistics and more exhaustive consideration about luminescence markers for provenance discrimination can be carried out. In particular, only the diopside crystals from Tajikistan show in many cases an additional band centred around 690 nm, relatively strong respect to other samples. Similarly only some samples from Afghanistan show a relatively strong band around 770 nm, while all the studied Siberian spectra are almost flat at wavelengths above 700 nm.

As already stated elsewhere [9], no evident correlations between ionoluminescence peaks and trace elements content were at now found by means of IBA analysis. Usually Ti, Mn and Fe are the main responsible for luminescence in diopside [22,23], but due to a competition process between activators and quenchers a direct proportionality does not always exist between the intensity of a luminescence peak and element contents. A more detailed analysis about this topic will be carried out and presented in a future work.

4.3. Analysis of artworks: broad beam IL microscopy, μ -PIXE and μ -IL

The first step for the provenance study of the artworks was the screening of their surface by means of the broad beam IL microscopy

setup. As already stated, visible light and luminescence images of the same area were acquired, looking for homogeneous crystals with white-yellowish luminescence typical of diopside or wollastonite. The luminescence images permit to have a preliminary indication of the distribution of different mineralogical phases, to select the biggest crystals and to evaluate their homogeneity (thus reducing the possibility of analysing non homogeneous crystals). Even though the broad beam IL microscopy makes easier to search suitable crystals, the irregular shape of the objects slow down these operations, which, by their nature, are extremely time consuming so that only one to three areas were selected for each artwork. After the identification of a homogeneous white-yellow luminescent crystal with dimensions of at least 100 μ m in each area, the ion microbeam analysis (μ -IL and μ -PIXE) was performed on it. For each of the artworks a representative luminescence spectrum collected (1s acquisition time) in the analysed white-yellow luminescent area is shown in Fig. 7. In all the cases the typical main band of the diopside at 580 nm was observed, immediately excluding, as expected due to the historical context, the Chilean provenance for the lapis lazuli utilized in the realization of all these artworks. Moreover two artworks ("Disc with star" and "Small vase") show a second broad band after 700 nm, analogous to the one found only in many Afghan samples. The band centred around 690 nm that seems to be present in two artworks ("Oval bowl" and "Saltcellar") should not be taken into account because of its low intensity: as reported before, this is a Tajik marker only if its intensity is high.

During the μ -IL measurements, μ -PIXE analyses on the same crystals were performed. The concentrations of major elements confirmed the composition of diopside ($\text{CaMgSi}_2\text{O}_6$). The trace elements detected in diopside were used to discriminate among the three considered Asian provenances on the basis of the results previously obtained on rocks. In Table 1 the μ -PIXE results useful for provenance discrimination of the artworks under investigation are shown. Cu, Zn, As, Zr, Rb, Ag and Pb were also detected in some analysed crystals but they were not reported as, sic stantibus rebus, they do not seem to be useful for provenance attribution.

The Sr content is below 100 ppm in all the objects: it is lower than the minimum value measured in Siberian samples, that is 150 ppm, and this feature potentially excludes this provenance. Moreover other Afghanistan markers were found. In particular, four objects ("Disc with star", "Small case", "Small vase" and "Oval panel") show at least one analysed area with a high content of vanadium (higher than 300 ppm), two objects ("Disc with star" and "Small vase") show at least one analysed area with a high content of chromium (higher than 200 ppm) and two objects ("Disc with star" and the "Oval Bowl") show at least one analysed area with a high content of titanium (higher than 5000 ppm).

The summary of the identified markers and suggested provenances for the analysed objects is presented in Table 2. All the lapis lazuli used for artworks, and in particular "Disc with star" (five

Table 1

Trace elements and iron concentrations (ppm) in diopside crystals in lapis lazuli objects of the "Collezione Medicea" from in air μ -PIXE measurements at INFN-LABEC; each line is one point of analysis and when an element is under the limit of detection is indicated with <LOD.

Artworks		Ti	V	Cr	Mn	Sr	Fe
13,148	Disc with star	6000 \pm 300	<30	200 \pm 20	170 \pm 20	60 \pm 10	1270 \pm 60
		3100 \pm 400	500 \pm 100	<20	260 \pm 30	60 \pm 20	850 \pm 60
13,682	Oval bowl	5200 \pm 300	<30	90 \pm 40	820 \pm 60	<10	240 \pm 30
		4800 \pm 300	<30	60 \pm 40	780 \pm 90	<10	230 \pm 40
13,684	Small case	360 \pm 100	300 \pm 60	90 \pm 20	310 \pm 20	30 \pm 5	1130 \pm 60
		520 \pm 90	100 \pm 50	<20	260 \pm 20	<10	360 \pm 20
		520 \pm 100	240 \pm 50	<20	230 \pm 30	<10	430 \pm 30
13,685	Small vase	3400 \pm 400	460 \pm 90	230 \pm 50	220 \pm 30	<10	1000 \pm 50
13,687	Saltcellar	<200	<30	<20	420 \pm 60	<10	1200 \pm 90
		<200	<30	<20	490 \pm 80	<10	1700 \pm 100
		<200	<30	<20	190 \pm 20	<10	280 \pm 20
13,688	Oval panel	1000 \pm 200	400 \pm 80	90 \pm 50	330 \pm 40	<10	1090 \pm 60

Table 2

Summary of the obtained results on diopside in the objects of the “Collezione Medicea”, with the indication of the suggested provenance. Chilean provenance has been excluded by the absence of wollastonite in all the artworks. Samples with more than three identified markers are written in bold.

Artworks	Identified markers	Suggested provenance
13,148	Disc with star Ti, V, Cr, Sr IL band after 700 nm	Afghanistan
13,682	Oval bowl Ti, Sr	Afghanistan
13,684	Small case V, Sr	Afghanistan
13,685	Small vase V, Cr, Sr IL band after 700 nm	Afghanistan
13,687	Saltcellar Sr	Afghanistan or Tajikistan
13,688	Oval panel V, Sr	Afghanistan

markers found) and “Small vase” (four markers found), can be attributed to an Afghan provenance even if for the “Saltcellar” also the Tajikistan provenance cannot be excluded and then further analysis will be needed to confirm the attribution for this object.

5. Conclusions

In this work a full characterisation of wollastonite and diopside crystals inside lapis lazuli from four different geological provenances has been carried out. Thanks to μ -PIXE and μ -IL some markers to distinguish among samples coming from Chile, Afghanistan, Tajikistan and Siberia have been found. The widespread presence of wollastonite as a clear indication of the Chilean provenance was confirmed, quickly distinguishable even only by means of luminescence. The presence of high content of titanium, vanadium or chromium revealed to be a discriminator for the Afghan provenance, while high content of iron or strontium are peculiar of the Siberian one.

Non invasive IBA measurements on six objects of the “Collezione Medicea” carved in lapis lazuli were performed in order to obtain some indications about the provenance of the raw material used for their realization. The broad-beam IL microscopy apparatus proved to be extremely useful to help in individuating crystals sufficiently big and homogeneous to be studied by means of micro-beam techniques (μ -PIXE and μ -IL) without contributions from adjacent minerals. The absence of wollastonite excludes the Chilean provenance for all the lapis lazuli utilized in the realization of these artworks. The trace elements detected in diopside crystals and collected IL spectra ascribe to Afghanistan the material used for all but one of the objects; actually for the “Saltcellar”, also the Tajikistan provenance cannot be excluded and further analysis are needed to confirm/reject the attribution to the Afghan provenance.

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References

- [1] L. Von Rosen, L., Lapis lazuli in geological contexts and in ancient written source, in: *Studies in Mediterranean Archaeology and Literature*, 65 ed., Paul Aströms förlag, Partille, Sweden, 1988.
- [2] G. Herrmann, *Iraq* 30 (1968) 21–57.
- [3] A.B. Delmas, M. Casanova, South Asian archaeology, in: *Proceedings of the ninth International conference of the Association of South Asian archaeologists in Western Europe*, 493–505, 1987.
- [4] J. Zöldföldi, S. Richter, Zs. Kasztovszky, J. Mihály J, in: *Proceeding of the 34th International Symposium on Archaeometry, Zaragoza – Spain*, 353–360, 2004.
- [5] T. Calligaro, Y. Coquinot, L. Pichon, B. Moignard, *Nucl. Instrum. Meth. B* 269 (20) (2011) 2364–2372.
- [6] T. Calligaro, Y. Coquinot, L. Pichon, G. Pierrat-Bonnefois, P. de Campos, A. Re, D. Angelici, *Nucl. Instrum. Meth. B* 318 (A) (2014) 139–144.
- [7] S. Calusi, E. Colombo, L. Giuntini, A. Lo Giudice, C. Manfredotti, M. Massi, G. Pratesi, E. Vittone, *Nucl. Instrum. Meth. B* 266 (2008) 2306–2310.
- [8] A. Lo Giudice, A. Re, S. Calusi, L. Giuntini, M. Massi, P. Olivero, G. Pratesi, M. Albonico, E. Conz, *Anal. Bioanal. Chem.* 395 (7) (2009) 2211–2217.
- [9] A. Re, A. Lo Giudice, D. Angelici, S. Calusi, L. Giuntini, M. Massi, G. Pratesi, *Nucl. Instrum. Meth. B* 269 (20) (2011) 2373–2377.
- [10] A. Re, D. Angelici, A. Lo Giudice, E. Maupas, L. Giuntini, S. Calusi, N. Gelli, M. Massi, A. Borghi, L.M. Gallo, G. Pratesi, P.A. Mandò, *Appl. Phys. A* 111 (1) (2013) 69–74.
- [11] A. Borelli, C. Cipriani, C. Innocenti, R. Trosti R, *La Gemmologia* XI, 24–27, 2003 (in Italian).
- [12] C. Cipriani, C. Innocenti, R. Trosti-Ferroni, *Museol. Sci.* V (1–2) (1988) 17–30 (in Italian).
- [13] M. Favaro, A. Guastoni, F. Marini, S. Bianchin, A. Gambirasi, *Anal. Bioanal. Chem.* 402 (2012) 2195–2208.
- [14] D. Bollini et al., *Nucl. Instrum. Meth. A* 328 (1993) 173–176.
- [15] J.F. Ziegler, M.D. Ziegler, J.P. Biersack, *Nucl. Instrum. Meth. B* 268 (2010) 1818–1823.
- [16] L. Giuntini, M. Massi, S. Calusi, *Nucl. Instrum. Meth. A* 576 (2007) 266–273.
- [17] A. Lo Giudice, A. Re, D. Angelici, S. Calusi, N. Gelli, L. Giuntini, M. Massi, G. Pratesi, *Anal. Bioanal. Chem.* 404 (1) (2012) 277–281.
- [18] E. Colombo, S. Calusi, R. Cossio, L. Giuntini, A. Lo Giudice, P.A. Mandò, C. Manfredotti, M. Massi, M.A. Mirto, E. Vittone, *Nucl. Instrum. Meth. B* 266 (2008) 1527–1532.
- [19] J.L. Campbell, N.I. Boyd, N. Grassi, P. Bonnick, J.A. Maxwell, *Nucl. Instrum. Meth. B* 268 (2010) 3356–3363.
- [20] N. Morimoto, *Miner. Petrol* 39 (1988) 55–76.
- [21] D. Angelici, et al, *Microscopy and microanalysis*, (in press).
- [22] A.L. Smith, *J. Electrochem. Soc.* 96 (5) (1949) 287–296.
- [23] G. Walker, *Chemical bonding and spectroscopy*, in: F.L. Berry, D.J. Vaughan (Eds.), *Mineral Chemistry*, Chapman and Hall, London, 1983, pp. 103–140.