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A provenance study on the lapis lazuli collection from the Regional Museum of Natural Sciences in Turin

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Abstract. Studies on the provenance of raw material used in the production of lapis lazuli artifacts can be particularly useful also in confirming or discarding the attributions given in past times by museum curators. In this work, a case study on five pieces belonging to the 19th century “Savoy Collection” of the Regional Museum of Natural Sciences in Turin is presented. The analysis allowed to assess the correctness of a previous Chilean attribution and to assign a provenance for the whole set of samples.

1. Introduction

Lapis lazuli is a semi-precious blue stone widely used since the antiquity. Due to the restricted compositional and physical constraints in which lapis lazuli can form, only few sources of this rock exist in the world [1]; several are located in Asia (for instance Badakhshan in Afghanistan, Pamir Mountains in Tajikistan or the Siberian deposits), but others can be found also in the American continent, e.g. Chilean quarries. The correct provenance attribution of the raw lapis lazuli used to produce artefacts of archaeological and artistic interest can be fundamental to reconstruct old trade routes [2] and can as well reveal non authentic pieces.

A systematic study of this stone, comparing physico-chemical properties of rocks and historical objects, has been carried out at the Physics Department of the University of Turin since 2007 [1, 3-11]. Over the years it was possible to gather a considerable database, analysing both lapis lazuli rocks and artworks, and to define specific provenance markers for the establishment of an analytical protocol for the provenance determination [1]. In particular, only some of the numerous mineral phases present in lapis lazuli are object of study, namely diopside ($\text{CaMgSi}_2\text{O}_6$), pyrite (FeS_2) and wollastonite (CaSiO_3).



These minerals can be selectively investigated thanks to microanalysis, using different probes such as electrons [3,5,11], protons [3,4,6,8,9], X-rays [7,10].

When the sole information on the provenance of a piece is given by an old label in museum collections, sometimes provided by unidentified scholars, the provenance study can reveal mistakes in attributions: an interesting example is presented in this work.

2. Samples

Five lapis lazuli specimens belonging to the 19th century “Savoy Collection” of the Regional Museum of Natural Sciences in Turin [12] were analysed. This collection is composed by rock samples, decorative elements and polished items. No precise information was available for these objects, with the exception of the details reported in the museum catalogue, that are shown - together with representative pictures - in Table 1. It is relevant to notice that two of the samples were ascribed to a Chilean provenance, whereas the origin of the three remaining objects was completely unknown.

Table 1. Main features of the analysed specimens; in the last column, the attribution reported in the museum catalogue.

	Catalogue number	Description	Dimensions (cm)	Attribution
	<i>M/U6565.1</i>	polished lapis lazuli small plate	4 × 4 × 0.2	Chile
	<i>M/U6565.2</i>	polished lapis lazuli small plate	3 × 3 × 0.3	Chile
	<i>M/U6565.4</i>	polished lapis lazuli plate mounted on slate	8.5 × 8.5 × 0.5	-----
	<i>M/U6565.5</i>	polished lapis lazuli plate	6.4 × 5.2 × 0.5	-----
	<i>M/U15512</i>	polished lapis lazuli oval (cabochon)	3.4 × 1.1 × 0.6	-----

3. Methods

Thanks to the particularly favourable geometry of these objects (with the exception of the sample M/U15512), it was possible to acquire elemental maps of the surfaces by means of micro X-ray fluorescence spectroscopy (μ -XRF), in order to obtain preliminary indications about the distribution of different mineral phases and to better direct further analyses. μ -XRF analyses were performed with an Eagle III-XPL instrument (Roentgenanalytik System GmbH & Co. KG. Taunusstein, Germany) at the Interdepartmental Centre “Giovanni Scansetti”, hosted at the Earth Sciences Department of the University of Turin, that is equipped with a Rh anode (50 kV, 1 mA) and polycapillary lens (variable spot size in the range 30 - 300 μ m). Spectral acquisitions (using single spot acquisition, profiles or mapping) are operated by the EDAX Vision 32 software. For maps acquisition, tube voltage was set at 40 kV, with 1 mA current and a process time of 10 μ s; dwell time on each pixel was set at 150 ms on a matrix of 512 × 400 pixels.

Ion beam analysis was then carried out at the new external microbeam line of the NewAGLAE facility at the C2RMF in Paris [13]. μ -PIXE (Proton Induced X-ray Emission) was performed on selected diopside and pyrite crystals; μ -IBIL (Ion Beam Induced Luminescence) spectra were also collected for luminescent phases. The 3-MeV proton beam was focused to 50 μ m on the target with an average beam current of 500 pA. PIXE data was acquired with five SDD detectors: one flushed with helium gas was dedicated to measure low-Z (major) elements and the other four, shielded by 100 μ m Mylar filters, for trace elements detection. The scanning system combining a vertical magnetic scan of

the beam with a horizontal target translation allows to quickly acquire elemental maps. From the maps, spectra of regions of interest can be extracted with AGLAEMap software [14]. Quantitative results for elemental concentrations are then obtained via TRAUPIXE [14], a software based on GUPIXWIN package [15] after a calibration with reference mineral standards. IBIL signal was collected with an optical fibre (1 mm diameter) and brought to an Ocean Optics QE65000 spectrometer with a bandwidth of 200-1000 nm, to provide an additional fingerprint for the luminescent mineral phases.

4. Results and discussion

μ -XRF for the very flat samples allowed to identify at a glance some of the mineral phases of interest: the simultaneous presence of S and Fe indicates the occurrence of a pyrite crystal, whereas Si and Ca together with Mg identify diopside phases (Figure 1).

As previously mentioned, two specimens (M/U6565.1 and M/U6565.2) were ascribed to a Chilean provenance. This attribution was disproved due to the absence of wollastonite [1] in these specimens, undetected also in all the other artefacts, that was verified by quickly scanning the whitish areas of the samples with μ -IBIL. Excluding the Chilean origin, μ -PIXE analyses on diopside and pyrite crystals were performed to move forward in the provenance attribution and the detected trace elements were compared with the μ -PIXE databases obtained on rock samples from the Asian provenances published in [1].

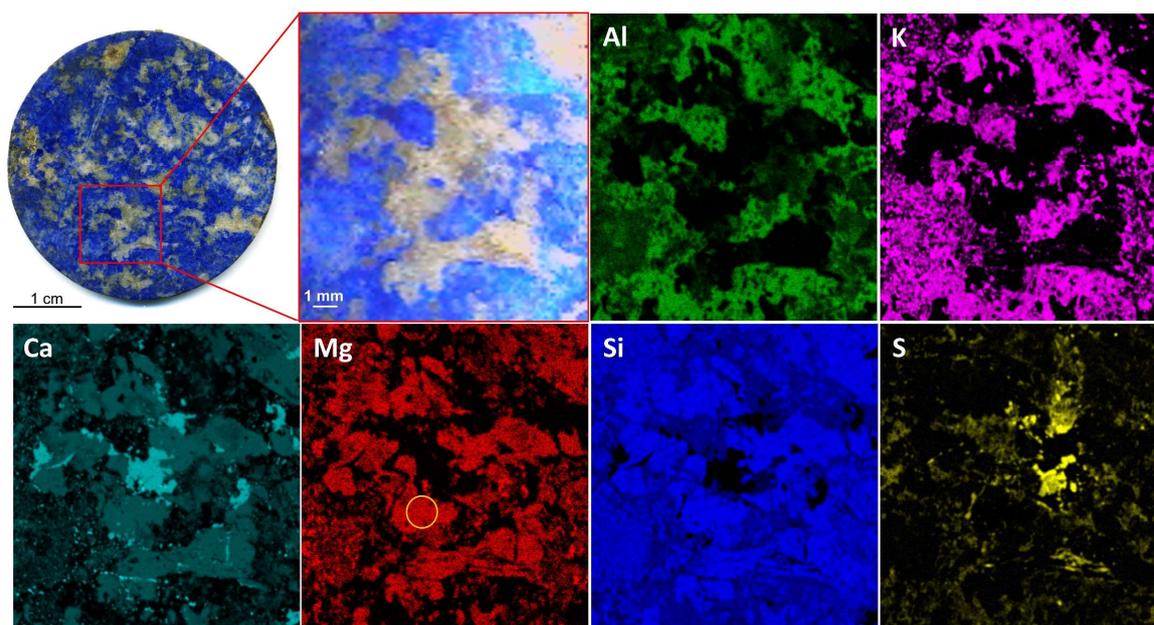


Figure 1. μ -XRF elemental maps of a representative area for sample M/U6565.1. The orange circle indicates one of the diopside crystals identified for further analysis.

4.1. Diopside

μ -PIXE results obtained for diopside, useful for the provenance discrimination, are reported in Table 2 and graphically represented in Figure 2. With the exception of only two experimental points, characterised by a very high limit of detection (LOD) values, Sr content detected in all the artefacts is lower than the minimum value measured in Siberian samples (180 ppm).

Weaker markers for Afghan provenance were found for three artefacts, M/U6565.2, M/U6565.4 and M/U15512, that present some analysed areas with high V and Cr content (higher than 200 ppm for both elements); moreover, sample M/U6565.2 also shows high Mn content (>990 ppm).

Table 2. Trace elements concentrations (ppm) in diopside crystals for the “Savoy Collection” samples from in air μ -PIXE measurements; each line is one point of analysis and when an element is below the limit of detection is indicated with < LOD.

Artefacts	Ti	V	Cr	Mn	Sr
M/U6565.1	260 ± 10	30 ± 10	< 10	380 ± 10	50 ± 10
	210 ± 10	50 ± 10	< 10	400 ± 10	60 ± 10
	330 ± 10	90 ± 10	< 10	370 ± 10	90 ± 10
	1780 ± 100	< 160	< 70	350 ± 40	< 140
	2060 ± 100	< 90	< 60	700 ± 40	< 140
	2900 ± 120	< 90	< 50	610 ± 40	< 110
	1220 ± 80	< 120	< 70	600 ± 40	< 150
M/U6565.2	1040 ± 110	< 90	< 90	520 ± 50	< 670
	1370 ± 30	230 ± 20	100 ± 10	1010 ± 20	100 ± 20
	2970 ± 60	320 ± 20	110 ± 10	990 ± 20	70 ± 20
	2110 ± 180	450 ± 80	< 70	1180 ± 100	< 330
M/U6565.4	2250 ± 150	320 ± 60	230 ± 30	1030 ± 70	< 160
	1280 ± 20	1270 ± 10	520 ± 10	310 ± 10	50 ± 10
M/U6565.5	940 ± 20	270 ± 10	150 ± 10	200 ± 10	70 ± 10
	220 ± 10	90 ± 10	< 10	370 ± 10	50 ± 10
	250 ± 10	100 ± 10	< 10	360 ± 10	50 ± 10
	140 ± 10	100 ± 10	< 10	350 ± 10	40 ± 10
	160 ± 40	< 40	< 30	510 ± 30	< 70
	210 ± 30	< 30	< 20	470 ± 20	< 40
	210 ± 20	60 ± 10	< 20	400 ± 20	< 20
	210 ± 30	< 30	< 40	330 ± 20	< 60
M/U15512	770 ± 20	330 ± 10	240 ± 10	320 ± 10	30 ± 10

The representative μ -IBIL spectra collected on diopside crystals for each specimen are shown in Figure 2. The main luminescence band at 585 nm, characteristic of diopside, is present in all the spectra. Samples M/U6565.4 and M/U15512 also show a second broad band centred around 770 nm, comparable to the one found only in many Afghan samples. The band centred around 690 nm that seems to be present in two artworks (M/U6565.1 and M/U6565.5) should not be taken into account because of its low intensity.

Finally, the spectrum related to the sample M/U6565.2 shows a quite intense band around 720 nm. Further analyses are necessary to verify this peculiar behaviour and the contingent presence of other elements as luminescence activators.

4.2. Pyrite

All pyrite crystals identified on the surfaces of lapis lazuli objects were well preserved, with the exception of sample M/U6565.5 that presented alterations on the whole surface, also involving other mineral phases. However it did not show pyrite transformations to iron oxide-hydroxide: this characteristic, together with the low Sr content in diopside (see Figure 2), allowed to exclude a Siberian provenance for all samples.

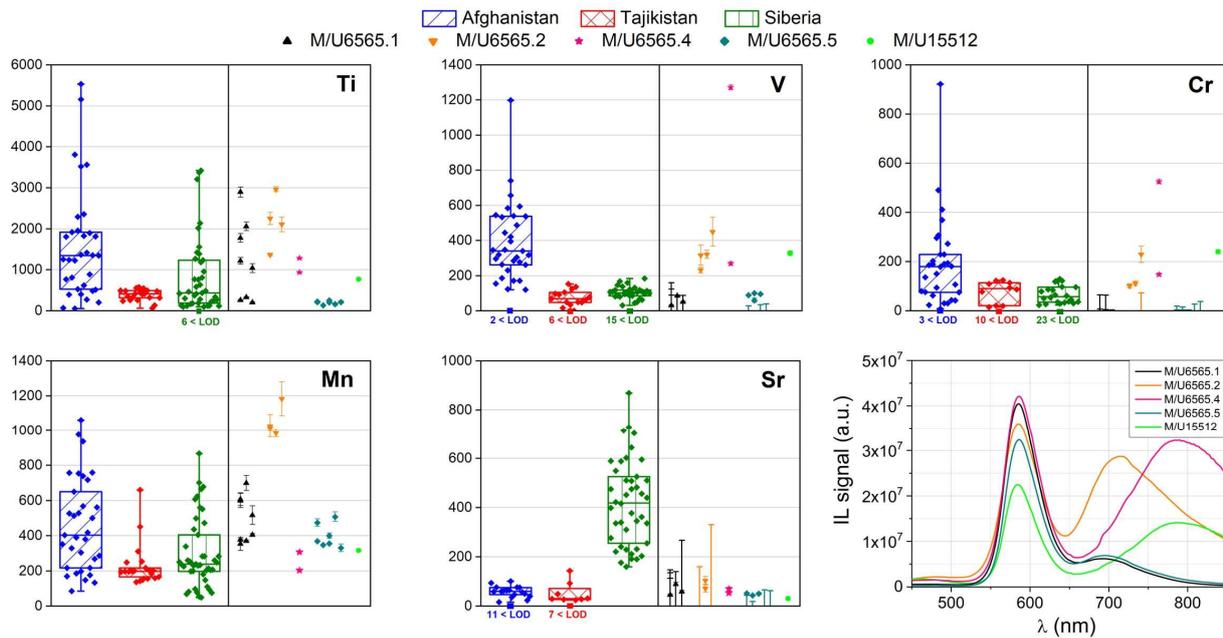


Figure 2. Results of the “Savoy Collection” compared with μ -PIXE database of trace elements content in diopside (expressed in ppm) and representative μ -IBIL spectra. Each point is an individual μ -PIXE measurement and the bars in correspondence to zero value represent the LOD value for that measurement.

The obtained results on trace elements contents in pyrite are reported in Table 3 and shown in Figure 3, comparing them with μ -PIXE database related to the rock samples from Afghanistan and Tajikistan [1]. All the analysed crystals present Ni and Cu contents in agreement with the Afghan provenance. The integration of such results with the data obtained from the analysis of diopside allows to confirm the attribution of the samples M/U6565.1, M/U6565.2, M/U6565.4 and M/U15512 to the Afghan origin, taking into account all the markers foreseen by the provenance protocol.

No further indication has been obtained instead for the sample M/U6565.5, because the only two crystals of pyrite present are rather altered, also showing relevant amount of Zn and Pb, respectively in the range 400-500 ppm and 5000-6000 ppm, in addition to Ni and Cu (both in the range 300-400 ppm).

The summary of the identified markers and suggested provenances for the analysed objects is presented in Table 4. For four artefacts the Afghan provenance was suggested, whereas for the sample M/U6565.5 further analyses are necessary to confirm its attribution and to understand if the alteration present in the surface of the object prevents to obtain correct results.

Table 3. Trace elements concentrations (ppm) in pyrite crystals in lapis lazuli objects of the “Savoy Collection” from in air μ -PIXE measurements.

Artefacts	Ni	Cu
M/U6565.1	400 ± 10	50 ± 10
	380 ± 20	50 ± 10
M/U6565.2	730 ± 50	140 ± 30
	630 ± 10	70 ± 10
	680 ± 40	80 ± 20
M/U6565.4	720 ± 10	70 ± 10
	560 ± 20	60 ± 10
M/U15512	650 ± 10	70 ± 10

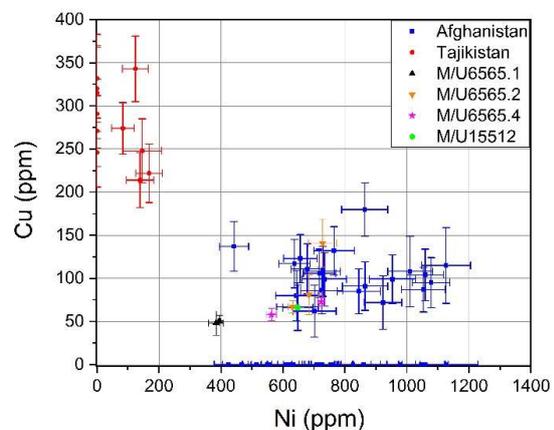


Figure 3. Comparison with database for Cu vs Ni contents in pyrite from μ -PIXE measurements. The individual errors associated to each measurement are plotted, whereas the values below the LOD are represented on the axes.

Table 4. Summary of the obtained results for the objects of the “Savoy Collection”, with the indication of the suggested provenance. The asterisk for Sr represents that this element is present in low quantity or below the LOD; provenance of samples with more than three identified markers is written in bold.

<i>Artefacts</i>	M/U6565.1	M/U6565.2	M/U6565.4	M/U6565.5	M/U15512
<i>Identified markers</i>	Sr* in diopside Ni in pyrite	Sr*, V, Mn in diopside Ni in pyrite	Sr*, V, Cr in diopside IL band at 770 nm Ni in pyrite	Sr* in diopside	Sr*, V, Cr in diopside IL band at 770 nm Ni in pyrite
<i>Suggested provenance</i>	Afghanistan	Afghanistan	Afghanistan	Afghanistan or Tajikistan	Afghanistan

5. Conclusion

The analysis of the lapis lazuli pieces belonging to the “Savoy Collection” of the Regional Museum of Natural Sciences in Turin brings to light a case of misleading catalogue attribution for the material provenance of artefacts, that scientific investigations can rapidly solve when an established provenance protocol exists. In the specific case study, an erroneous Chilean attribution was discovered for two samples (M/U6565.1 and M/U6565.2) and the correct Afghan provenance was assigned after the analysis. Same provenance was attested for two other samples, while the last piece (M/U6565.5) still presents an uncertainty between Afghan and Tajik origin, requiring additional analysis to solve the issue.

Acknowledgments

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