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New markers to identify the provenance of lapis lazuli: trace elements in pyrite by means of micro-PIXE

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Abstract

Lapis lazuli has been used for glyptics and carving since the fifth millennium BC to produce jewels, amulets, seals, inlays, etc; the identification of the origin of the stone used for carving artworks may be valuable for reconstructing old trade routes. Since ancient lapis lazuli art objects are precious, only non-destructive techniques can be used to identify their provenance, and ion beam analyses (IBA) techniques allow us to characterise this stone in a fully non-invasive way. In addition, by using an ion microprobe, we have been able to focus the analysis on single crystals, as their typical dimensions may range from a few microns to hundreds of microns.

Provenance markers, identified in previous IBA studies and already presented elsewhere, were based on the presence/absence of mineral phases, on the presence/quantity of trace elements inside a phase and on characteristic features of the luminescence spectra. In this work, a systematic study on pyrite crystals, a common accessory mineral in lapis lazuli,

was carried out, following a multi-technique approach: optical microscopy and SEM-EDX to select crystals for successive trace element micro-PIXE measurements at two Italian facilities, the INFN Laboratori Nazionali di Legnaro and the INFN LABEC laboratory in Firenze. The results of this work allowed us to obtain new markers for the lapis lazuli provenance identification.

Introduction

Lapis lazuli is a blue semi-precious stone used for glyptics and carving by different civilizations as early as 7000 years ago. The identification of the provenance of raw material used for man-made objects can provide valuable help in the reconstruction of ancient trade routes. This task is simplified by the fact that only a few sources of lapis lazuli exist in the world, due to the low probability of geological conditions in which it can form. In recent years, there has been an increasing interest in the study of the provenance of this stone, both in artefacts and in lapis lazuli blue pigment, and results have been obtained using different analytical techniques and approaches [1-5]. We started to work in this field in 2007 [6,7] and we have been developing a fully non-invasive analysis procedure, exploiting ex-vacuo ion beam analysis (IBA) techniques [8]. Due to the paragenetic mineralogical heterogeneity of lapis lazuli stone, we have concentrated our attention on the trace element contents of different mineral phases in stones from known origins. In previous works we focused our attention on lazurite, the main phase of lapis lazuli, and on diopside, one of the most frequent mineral phases associated with lazurite [9,10]. Here, we report on the micro-PIXE (proton induced X-ray emission) characterisation of pyrite, an important accessory mineral present in almost all the petrologic varieties of lapis lazuli.

Pyrite (FeS_2) is the most common sulphide mineral, occurring in various types of rock; in lapis lazuli it develops only during the final stages of rock formation with crystals usually scattered in the stones. The range in variability of natural pyrite with regard to chemical composition is reported in [11], a useful reference for the pyrite composition, based on the data obtained by several authors by means of electron probe microanalysis (EPMA), PIXE [12], secondary ion mass spectroscopy (SIMS, often employing an ion microprobe) and laser ablation inductively coupled plasma mass spectroscopy (LAICP-MS) [13,14].

Experimental setup

Micro-PIXE measurements were carried out at two Italian laboratories, the INFN-LNL AN2000 in-vacuum microbeam facility [15] (2 MeV proton beam) and the INFN LABEC external microbeam facility in Firenze (3 MeV proton beam ex-vacuo [16,17]), see Fig.1 Details on the two setups are summarised in Table 1, which also shows the beam penetration depths in pyrite calculated with SRIM software (version 2008.04). For both the in-vacuum and in-atmosphere measurements, reference standards (minerals from SPI Supplies and oxides from 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) were used for the spectra analysis through the GUPIXWIN software (version 2.1.3).

Many of the lapis lazuli stones analysed in this work belong to collections of three museums: 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 the Geological section of the Natural History Museum of the Accademia dei Fisiocritici of Siena; the others were bought at the Turin International Mineral Show since 2010. The 38 studied samples (Table 2) have Afghan (19), Tajik (Pamir Mountains) (4), Siberian (5), Chilean (9) and unknown (1) provenances. Some of them were prepared as semi-thin sections (of the order of one hundred microns, enough to stop the proton beams) and carbon coated to make the in-vacuum analyses possible. The lapis lazuli specimens not allowed to be sampled were studied only at the LABEC external microbeam. For each sample, we selected typically four crystals of pyrite with area above $50 \times 50 \mu\text{m}^2$, much wider than the maximum dimensions of the beams used for the analysis ($\sim 10 \mu\text{m}$ maximum spot size, see Table 1). The size of the chosen crystals was also compatible with the maximum penetration depth and the lateral straggling of protons in pyrite ($\sim 25 \mu\text{m}$ and $48 \mu\text{m}$ ranges for 2 and 3 MeV protons respectively; less than $2 \mu\text{m}$ straggling for the beams of both energies).

A preliminary characterisation of the samples was carried out by means of optical microscopy (OM), on semi-thin sections, and macro-photography, for massive samples, to individuate those crystals with optical properties similar to pyrite, i.e. appearing darker and shinier with respect to other phases.

Then, after a control of the absence of the induced luminescence signal in these crystals (by means of cold-CL in vacuum for the semi-thin sections and by in-air broad-beam ionoluminescence microscopy [18] for massive samples), we focused on their elemental composition. For the semi-thin sections, scanning electron microscopy-energy-dispersive

X-ray spectroscopy (SEM-EDX) was preliminarily used, to obtain the high-quality SEM-back-scattered electron (BSE) images and the concentrations of the major elements. For the SEM characterisation we used 20 keV electron beams (1 μm mean penetration depth in pyrite, CASINO version 2.42) of the Leica Stereoscan 420, equipped with an Oxford Pentafet EDX. Quantitative results were obtained by the INCA Microanalysis Suite software package (version 4.08) and a set of reference standards (the same used for the in-vacuum PIXE measurements). Then for both massive samples and semi-thin sections, the possible crystals for major and trace element quantitative analyses were chosen by micro-PIXE elemental distribution maps.

Results and discussion

As already mentioned, the crystals of interest were identified by OM (crystals show as opaque), cold-CL (no light emitted) and SEM-BSE images (lighter aspect) on the semi-thin sections, and by macro-photography (darker and shinier) and in-air broad-beam ionoluminescence microscopy (no light emitted) on massive samples.

More than 90 regions were studied: as expected, the major elements of most of the analysed crystals were Fe and S, with concentration ratios compatible with the pyrite stoichiometry (an example of the characteristic spatial correlation of Fe and S in pyrite crystals is shown in Fig.2a). Unexpectedly, in the spectra collected on crystals of some Siberian samples, there was no correlation between the sulphur and the iron spatial distributions (Fig.2b). The lack of sulphur clearly points out that this iron-based mineral cannot be pyrite; it could be an iron oxide-hydroxide, probably an alteration product of pyrite. Since the sulphur-lacking iron mineral was detected only in the Siberian samples (both in semi-thin sections and massive samples), its presence is a good candidate to act as a marker of the Siberian provenance.

Focusing only on pyrite crystals, we looked for elements whose concentration variations were in correlation with the different provenances. The best candidates as provenance markers were nickel, copper and selenium; their concentrations are reported in Fig. 3. Ni was detected in all the Afghan (400 - 2800 ppm) and Siberian (500 - 1700 ppm) samples, and in some Chilean samples (< 800 ppm), while in the samples from Pamir, the Ni content was always close to or within the detection limit (about 100 ppm). Consequently, a Ni concentration higher than 250 ppm could possibly exclude the Pamir provenance and, if higher than 2000 ppm, could even be a marker of the Afghan provenance. The Pamir and Afghan distributions are clearly separated.

Copper was detected in all the samples from the Pamir Mountains (200 - 350 ppm), well above the limit of detection; rather lower copper contents were found in the Afghan (<

180 ppm), Chilean (< 70 ppm) and Siberian pyrites (< LOD, that is about 50 ppm), thus suggesting that the abundance of this element could be a good indicator for the Pamir provenance. The copper distribution of the Pamir samples is actually well separated from that of the Afghan pyrites and even more clearly from those from Chile and Siberia.

Selenium was detected in some Chilean samples in quantities up to 100 ppm, well above the limit of detection (around 30 ppm); in some Afghan samples a presence of selenium comparable to the limit of detection was found. This element, if present in “high quantities”, could be a good candidate to act as a marker for the Chilean provenance.

All this information is condensed in Fig.4, which shows the correlations between copper, nickel and selenium concentrations; the combined use of these markers allows us to better cluster data referring to different origins.

The above reported conclusions are the most significant. Further hints, e.g. the presence of arsenic (up to 180 ppm) and cobalt (up to 2000 ppm), are currently under study but more data are required for statistical significance. The amount of all the trace elements found in pyrite crystals in lapis lazuli is within the range of variability found by other authors in different kinds of pyrite [11].

Calcium, although not an element occurring in pyrites [19], was present almost everywhere with a concentration up to 0.4 wt%, but, since its spatial distribution was not correlated with those of iron and sulphur, its origin was attributed to other Ca-rich phases present in the rocks (for example, calcite and diopside) over and inside the studied pyrites and not considered in this study.

To test the effectiveness of the above-reported possible markers, a sample of unknown origin was analysed. The discriminating parameters collected in previous studies on other phases (mainly lazurite and diopside) were already tested on this sample [10] suggesting an Afghan provenance. New measurements were carried out on two pyrite crystals of this sample; the Ni content was of the order of 1000 ppm (760 ± 100 and 1320 ± 110 ppm) and both copper and selenium were within the limit of detection (LOD). From the above conclusions, it seems reasonable to exclude both the Pamir and the Chilean provenance for this lapis lazuli, and the hypothesis of the Afghan provenance, as proposed on the basis of the previously identified markers, is strengthened.

Conclusions

The elemental analysis of the pyrite crystals in lapis lazuli by means of micro-PIXE was useful for the provenance study of this stone. In fact some new markers were found in

stones from known origins (Afghanistan, Pamir, Siberia and Chile) which could allow us to distinguish among the four provenances. The major element composition can give information to indicate the Siberian provenance because of the presence of a sulphur-lacking iron mineral instead of pyrite. The analysis of trace elements permits indications that are useful to distinguish among the other provenances: high values of the nickel concentration, above 2000 ppm, could be a hint of the Afghan provenance; Pamir samples could be identified by a quantity of copper much higher than that in lapis lazuli of all the other origins; some of the Chilean samples are characterised by the presence of selenium inside pyrite crystals; among the trace elements allowing provenance discrimination, Siberian pyrite contains only nickel.

These markers were used to characterise the provenance of an unknown lapis lazuli sample and the new clues strengthen the Afghan provenance indication by markers found in our previous works.

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Figures

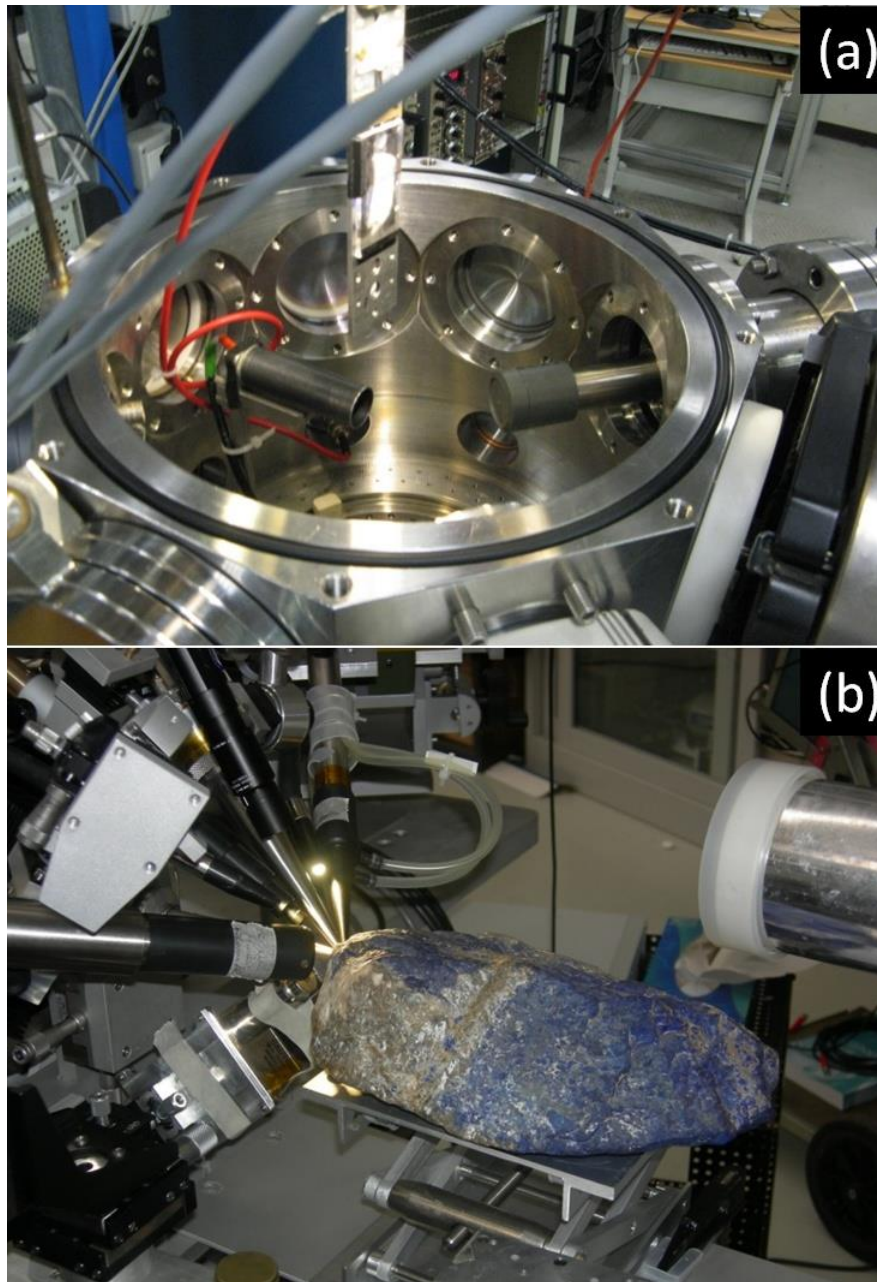


Figure 1. (a) The vacuum chamber of the microbeam line of the AN2000 accelerator at LNL used for μ -PIXE analysis of semi-thin sections of lapis lazuli. (b) The measurement point of the microbeam line at the LABEC laboratory during the analysis of a massive lapis lazuli rock.

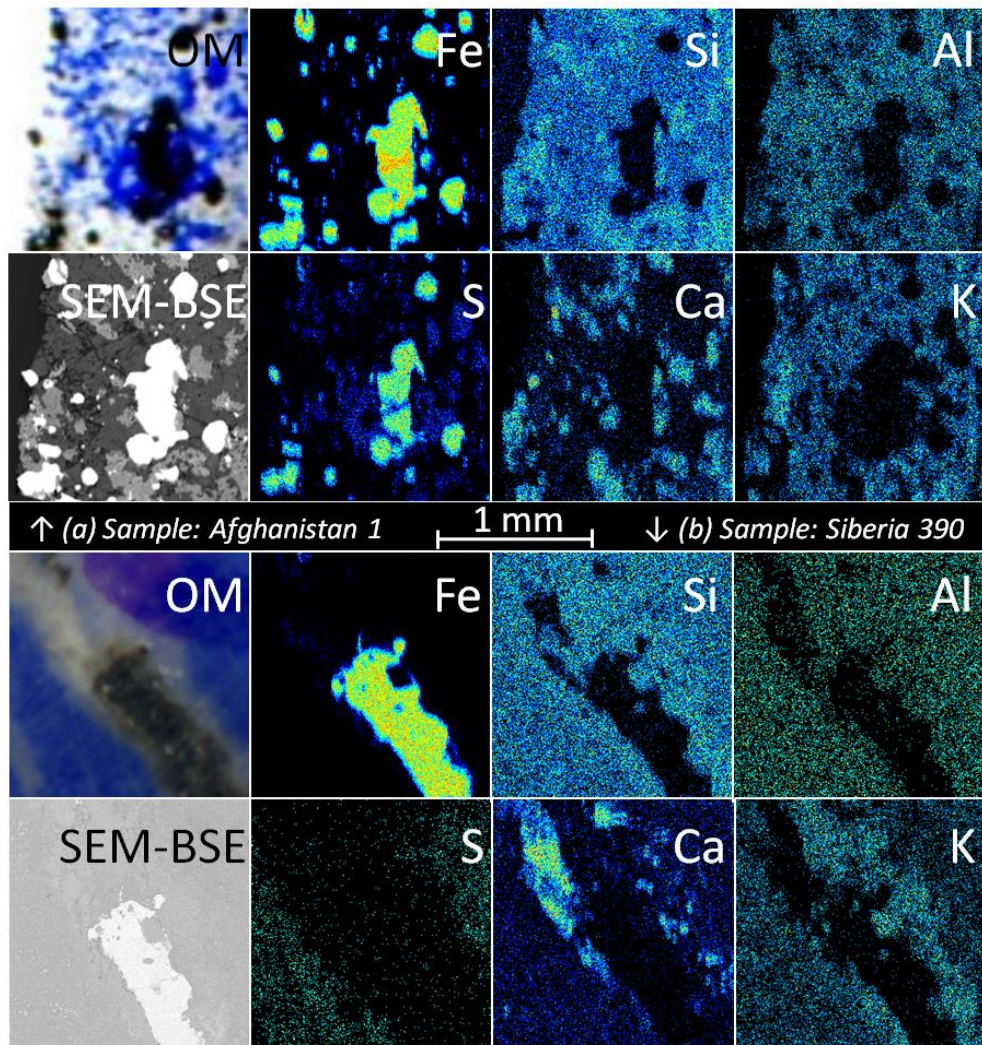


Figure 2. Optical microscopy (OM), BS electron microscopy (SEM-BSE) and μ -PIXE elemental maps (acquired at the in vacuum LNL facility) of a representative area of the samples: (a) Afghanistan 1 (the opaque minerals in the map are composed by iron and sulphur, the main elements of pyrite); (b) Siberia 390 (the opaque minerals in the map are composed mainly of iron, the only detectable element of iron oxide-hydroxide).

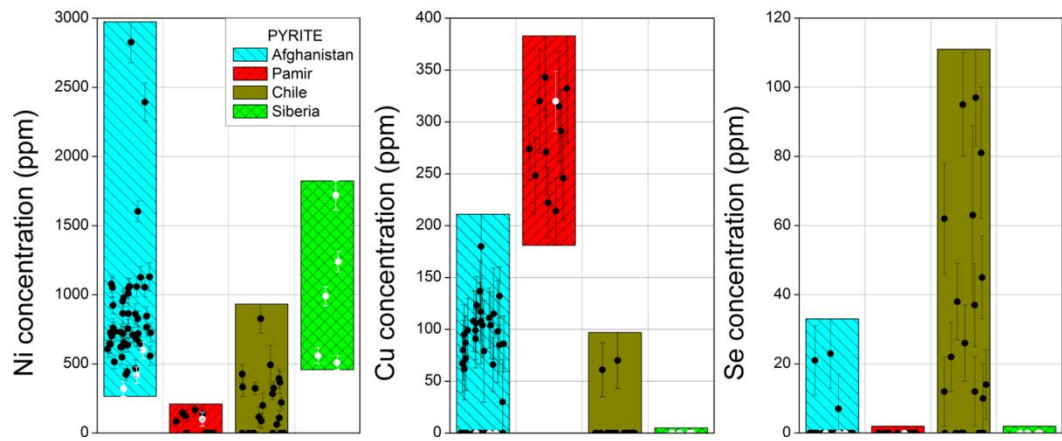


Figure 3. Trace element contents in pyrite from micro-PIXE measurements performed at the in-vacuum microbeam line of the AN2000 accelerator at the LNL laboratory (in black) and at the extracted microbeam line of the LABEC laboratory (in white). The points represent the individual measurements (± 1 standard deviation); the coloured floating columns simply give an idea of the dispersion of the experimental points.

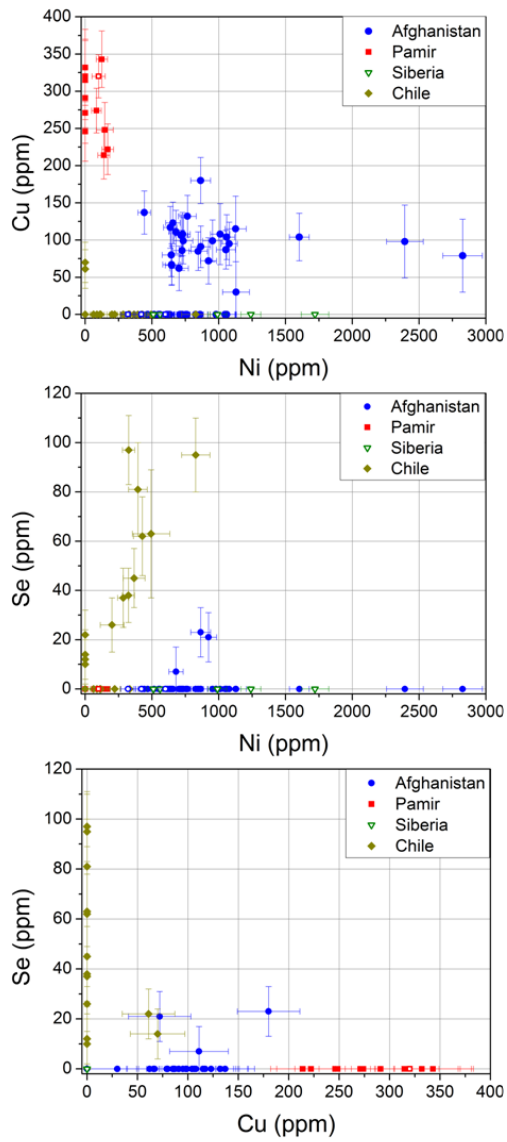


Figure 4. Nickel, copper and selenium contents in pyrite from micro-PIXE measurements performed at the in-vacuum microbeam line of the AN2000 accelerator at the LNL laboratory (filled points) and at the extracted microbeam line of the LABC laboratory (open points)

Tables

Table 1. Characteristics of the ion beams used for the measurements at the two microbeam lines of the INFN facilities (LNL in Padova and LABEC in Firenze). The penetration depths were evaluated with SRIM, assuming a FeS₂ matrix in both cases.

	LNL (Padova)	LABEC (Firenze)
Measurement	In vacuum	He atmosphere
Ion	Protons	Protons
Beam energy (MeV)	2	3
Beam current (pA)	300	150
Beam size (μm)	~ 5	~ 10
Max scanned area (mm ²)	3 × 3	2 × 2
Penetration depth (μm)	25	48
PIXE detection setup	1 detector with Al funny filter	2 detectors, 1 for low energy and 1 for high energy X rays

Table 2. List and provenances of the lapis lazuli samples analysed. The abbreviations are: MSN_FI (Museum of Natural History, University of Firenze); MRSN_TO (Regional Museum of Natural Sciences of Torino); AF_SI (Natural History Museum of the Accademia dei Fisiocritici of Siena); UniTO (University of Torino).

	Afghanistan	Tajikistan	Siberia	Chile	Unknown	Catalogue numbers
MSN_FI	4	4	1	4	1	RI388, 12397, 47860, AFG_P from RI3063 to RI3066 RI390 12394, 12403, 12405, 16980 RI571
AF_SI			3			1359, 1361, 1362
MRSN_TO			1			M15920
UniTO	15			5		from AFG_1 to AFG_15 from CHILE_1 to CHILE_5