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Lapis lazuli provenance study by means of micro-PIXE

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Abstract

In this paper we report about the micro-PIXE characterization of lapis lazuli, for a provenance study of this semi-precious stone, used for glyptic as early as 7,000 years ago. The final aim is to find markers permitting to identify the origin of the raw material coming from three quarries in regions of historical importance: Afghanistan, Pamir Mountains and Siberia. This may help to reconstruct trade routes, especially for ancient objects for which written testimonies are scanty or absent at all.

Due to the heterogeneity of lapis lazuli we concentrate our attention on single phases instead of the whole stone; in particular we focused on two of the main phases: lazurite, responsible for the blue colour, and diopside, the most frequent accessory mineral. This study was preceded and completed by means of microanalysis with scanning electron microscopy (SEM-EDX) and cold-cathodoluminescence (cold-CL) analysis.

Despite the limited number of analyzed samples, results are sufficient to exclude/suggest a few features as provenance markers, partly confirming what has been previously published in literature.

Keywords: Lapis lazuli, Provenance, PIXE, Archaeometry, external microbeam

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Introduction

External ion beam analyses have been widely used in cultural heritage investigations owing to the possibility to work in air on large objects without any pre-treatment. IBA techniques, exploiting proton beams, can be used in most materials without damaging. Moreover, the availability of scanning micro-beams allows the investigation of details down to the micrometer scale, which proved to be very useful in many cases [1]. Particle-Induced Gamma ray Emission (PIGE), Backscattering Spectrometry (BS) and especially Particle-Induced X-ray Emission (PIXE) can be considered as the chief IBA techniques, but also Ion Beam Induced Luminescence (IBIL) has been successfully employed in this field [2-4].

The IBA techniques can be applied to the study of the provenance of the raw material used in the object making, which can help to reconstruct ancient trade routes. A promising material in this context is the semi-precious stone lapis lazuli, used for glyptic as early as 7,000 years ago and for painting starting from the Medieval Age. Only few sources of lapis lazuli exist in the world, due to the low probability of geological conditions in which it can form [5]. Historical sources are in very inaccessible places, such as Afghan and Pamir Mountains, and stones were transported for thousand of kilometres, in times for which the knowledge of trade routes is still largely incomplete. Although presently the mines in Afghanistan are widely considered as the only sources of the lapis lazuli in ancient times [6-8], other sources have been proposed [6,7,9,10], so that the provenance of ancient lapis lazuli is still an open question.

Lapis lazuli is a metamorphic rock characterised by the presence of the mineral lazurite (responsible for its blue colour), combined with other types of minerals whose presence and relative amount varies from and within deposits. Lazurite is traversed by gray-white or yellowish veins, due to the presence of various accessory minerals such as calcite, wollastonite, phlogopite, plagioclase, diopside and others. There may be also other feldspathoids of the same lazurite family such as haüyne, sodalite or nosean. Furthermore, lapis lazuli of all deposits contains small inclusions of pyrite, mistaken in the past for gold inclusions. Due to the rocks heterogeneity, it is very difficult to identify provenance markers by analysing elemental composition of the whole rocks or works of art. Hence, a campaign to individually analyse mineral phases in lapis lazuli stone by means of ion beam techniques was started. Samples from four quarries of historical importance were analysed: three samples from Afghanistan, four samples from Pamir Mountains, one sample from Siberia and four samples from Chile. A description of the analysed samples and the details of their acquisition and provenance are presented in [11]. To accurately characterize lapis lazuli phases, ion beam analyses were preceded and completed by systematic measurements using cold-cathodoluminescence (cold-CL), SEM-EDX and SEM-CL. These vacuum-operating techniques are normally not suitable to art objects, but proved to be useful at this stage of the work, in which rocks are being characterized. For example, cold-CL is a very rapid method to identify mineralogical phases distribution. Concerning ion beam analysis, encouraging results were obtained by means of micro-IBIL [11]. Luminescence spectra were collected on lazurite, diopside, wollastonite, calcite and k-feldspar mineralogical phases. The capability to distinguish Chilean lapis lazuli by other provenances was demonstrated and some criteria for Pamir Mountains origin identification were also proposed. Nevertheless, IBIL features in analysed mineralogical phases were not sufficient to provide criteria for distinguishing Siberian from Afghan lapis lazuli.

In this work we report on micro-PIXE characterization of lapis lazuli rocks from three quarries: Afghanistan, Pamir Mountains and Siberia. Although available, Chilean samples were not taken into account for micro-PIXE investigation due to an already well established identification method based on the massive presence of wollastonite, absent in all other samples, and the associated characteristic strong luminescence [11-13]. Only SEM-EDX measurements were carried out on lazurite in Chilean samples.

Investigation was focused on two mineral phases, i.e. the main phase lazurite and the accessory phase diopside, present in all the three Asian lapis lazuli under investigation.

Lazurite is a mineral belonging to the feldspathoids family; more specifically, it is a poor silica tectosilicate in the sodalite group. This group consists of eight minerals, among which the main ones are: sodalite, nosean, haüyne and lazurite. The chemical formula of lazurite is $Na_6Ca_2Al_6Si_6O_{24}[(SO_4), S, Cl, (OH)]_2$ and the blue colour is due to the S_3^- chromophore in the sodalite cage. Diopside is a mineral belonging to the pyroxene family, in particular it is an inosilicate with a single calcium and magnesium chain, whose chemical formula is $CaMgSi_2O_6$. A common practice to evaluate the composition of a pyroxene from the chemical analysis of the mineral consists in calculating the end members (pure terms) percentage and to report the results on a triangular diagram [14].

Experimental

External micro-PIXE and micro-IBIL were proven to be applicable on rocks and work of art having various shapes [12], but to facilitate the characterization of the rocks at this stage of the work, samples were prepared as free-standing semi-thin (i.e. about 50 μm) sections. A more accurate description of the twelve samples under investigation together with 15 keV cold-CL images that were used to rapidly identify areas to be analysed by means of SEM-EDX and micro-PIXE is reported in [11]. Preliminary SEM-EDX measurements for major elements evaluation were carried out using a Leica Stereoscan 420 equipped with an Oxford Pentafet EDX and operating with a beam energy of 20 keV. Quantitative results were obtained from analysing data by means of the INCA Microanalysis Suite software package (version 4.08) and by the use of a set of reference standards.

As for the scanning microbeam analyses, two facilities have been used: the in-vacuum beam facility of the 2.5 MV Van der Graaff accelerator at the INFN Laboratory in Legnaro (Padova) [15] and the external beam facility of the 3 MV Tandetron accelerator at the INFN LABEC Laboratory in Firenze [16]. In the first case a 600 keV proton beam with a lateral resolution of about 2 μm and a current of about 1 nA was used to analyse diopside by means of micro-PIXE. Despite the low cross section for characteristic X-ray generation, the relatively low ion energy was selected in order to investigate a volume close to that analysed by means of SEM-EDX and CL, for a more reliable comparison among major element contents and to attempt a correlation between trace element presence and luminescence peaks. CASINO (version 2.42) and SRIM (version 2008.04) codes were employed to calculate the probed volume for electrons and protons, respectively. In a few samples diopside crystals with dimensions below 50 μm were observed. In this case high energy ions cannot be used, because they would probe also minerals beneath the investigated crystals due to the high penetration depth. In diopside (density of 3.3 $g \cdot cm^{-3}$) a 20 keV electron beam has a penetration depth of 3 μm and a lateral straggling of about 4 μm, whereas a 15 keV electron beam has a penetration depth of 2 μm and a lateral straggling of about 2.5 μm. On the other hand, a 600 keV proton beam has a penetration depth of 5 μm and a lateral straggling below 2 μm. Such characteristics represent a good compromise between the reduction of cross section associated with the employment of low-energy ions and the proximity to the electron probed volume.

At the external facility of Firenze, micro-PIXE measurements were carried out on lazurite minerals using a 3 MeV proton beam with a current of about 200 pA and a lateral resolution of about 10 μm. The penetration depth in lazurite (density of 2.4 $g \cdot cm^{-3}$) is about 85 μm so that the samples were probed along all their thickness, while the dimensions of the analysed lazurite crystals were sufficiently large to avoid the presence of other minerals beneath the investigated ones.

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

Results and discussion

In Fig.1 typical micro-PIXE elemental maps of lapis lazuli obtained at the external microbeam line at LABEC are shown. Due to the good spatial resolution, the capability to distinguish and then individually analyse mineral phases in lapis lazuli is evident. The lazurite crystals can be identified from the correlation of both sodium and sulphur distributions. The upper lazurite crystal is embedded in a calcite formation, while one of the lower crystals is surrounded by diopside (characterised by a high magnesium content). All around, many veins of K-feldspars are visible that obviously show a high potassium content. Finally, the iron map shows few small pyrite grains. A comparison with a BS electron microscopy map and a cold-CL map is also shown. As described in [11], cold-CL maps can be obtained with an exposure time of a few seconds using a commercial camera mounted on a microscope and they are very useful to rapidly identify mineral phases in the samples. At the present time, we are upgrading the LABEC microbeam apparatus with a high sensitivity CCD camera and appropriate optics to obtain similar results using ionoluminescence. This system will be used on archaeological objects for which the cold-CL is not to be used.

From the examination of cold-CL maps, about fifty points of interest in lazurite on all the samples were identified for quantitative SEM-EDX analysis. In lazurite only major elements were observed, with a percentage varying slightly inside the same samples and within samples of the same provenance. In Fig. 2 the potassium vs. sulphur content, normalized to the sum of aluminium and silicon contents, is reported in a logarithmic graph; these features represent the most interesting elements in terms of provenance markers. In fact, despite an overlapping of points relevant to Pamir Mountains and Siberia samples, the low concentration of potassium in Chilean stones and the practically linear correlation in Afghan samples are evident. In particular, it seems that Afghan samples are the only ones characterised by lazurite crystals with both high potassium and low sulphur contents. About ten points of interest investigated by means of SEM-EDX were also analysed using the micro-PIXE at the external beam facility of LABEC obtaining comparable results. In Fig. 3 the results regarding trace elements in lazurite are shown; the coloured column indicates the average elemental content and the dark points represent the individual measurements. The higher quantity of strontium and barium in the Siberian sample compared with other samples, is the most interesting result and is in accordance with previous studies [9,17] and can, therefore, be considered as the main criterion for identifying Siberian lapis lazuli. It is important to note that barium and strontium are not incorporated in lazurite but are present in small grains of mineral not yet determined (whose dimensions are below the resolution capabilities of the employed microbeam facilities), as observed by means of SEM analysis. Similar grains were observed also in other lapis lazuli phases.

Further results consist in the higher quantity of arsenic in samples from Pamir Mountains, as well as of zirconium in Afghan samples, even if the latter seems to be present in small inclusions of a phase not yet determined.

Diopside is the second analysed phase. About eighty points of interest were analysed by means of quantitative SEM-EDX. In Fig. 4 the compositional diagram of piroxenes is shown; the complete overlapping of the composition of the samples from different origin is clear. It can be concluded that the concentration of major elements in diopside cannot be used as a useful criterion for provenance attribution. Micro-PIXE analysis was carried out at Legnaro laboratory on about twenty points of interest. As expected, due to the similar probing volume, there was a very good accordance with SEM-EDX analysis about major element contents. Results about trace elements are shown in Fig. 5. The trace elements identified are common in all diopsides, but there are many differences in quantity, if we compare samples from Pamir Mountains and from Afghanistan. In fact, all the samples coming from Pamir Mountains show average contents in titanium, vanadium and chromium lower than those found in Afghan samples, but on the other hand a higher quantity of iron is observed. Siberian sample seems to have more features in common with the lapis lazuli coming from Pamir with respect to the Afghan one.

At last, no evident correlations between ionoluminescence peaks and trace elements content were found. Ti, Mn and Fe are the mainly responsible for luminescence in diopside [18-20], 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 summary of the markers found in this work and in the previous ones on micro-IBIL [11,12] is shown in Tab. I, where results from literature are also reported. It is worth noting that in a complex material like lapis lazuli it is unlikely that only one marker or one technique can be sufficient to unequivocally distinguish among different provenances.

The capability to attribute a lapis lazuli to a quarry using the markers in Tab. I was tested on a sample of unknown origin. A Chilean origin was excluded due to the absence of wollastonite phase and the correlated double luminescence band at around 600 nm. Moreover a value of K/(Si+Al) concentration ratio ranging from 0.028 to 0.047 was found by means of the major element analysis. These values are higher than the maximum value found for Chilean samples that is K/(Si+Al)=0.025 (see Fig. 2). Taking into account the values of S/(Si+Al) ranging from 0.25 to 0.33, the unknown rock falls in the main sequence of Afghan samples, but very close to Pamir Mountains and Siberian samples. Nevertheless, a Siberian origin was excluded by means of trace elements analysis, since the lazurite does not contain barium. Other measured trace elements were strontium (240 ppm) and arsenic (160 ppm), at the moment not significant for provenance attribution. Finally, due to the absence of both the UV luminescence characteristic of the cancrinite phase and the 700 nm luminescence in diopside, the Pamir Mountains provenance was excluded. We therefore conclude that the unknown sample probably comes from Afghanistan.

Conclusions

In this work a systematic study by means of micro-PIXE on elemental composition of lazurite and diopside phases in lapis lazuli from different quarries is reported. The aim of the work is the identification of markers useful to attribute the provenance of raw materials used in archaeological finding and works of art. Despite the still limited number of analyzed samples, results are promising and significant differences among different samples are pointed out. All the proposed markers can be identified using external ion microbeam analysis, in particular by means of micro-IBIL and micro-PIXE. These techniques were simultaneously used on rocks and objects by means of the external microbeam facility of LABEC. The capability to attribute a lapis lazuli sample to a quarry using the identified markers was tested on a sample of unknown origin. According to our analysis, the sample was attributed to an Afghan origin. Finally, 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 conclusion is to be confirmed by increasing statistics in future works.

Acknowledgements

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Figures

Fig. 1

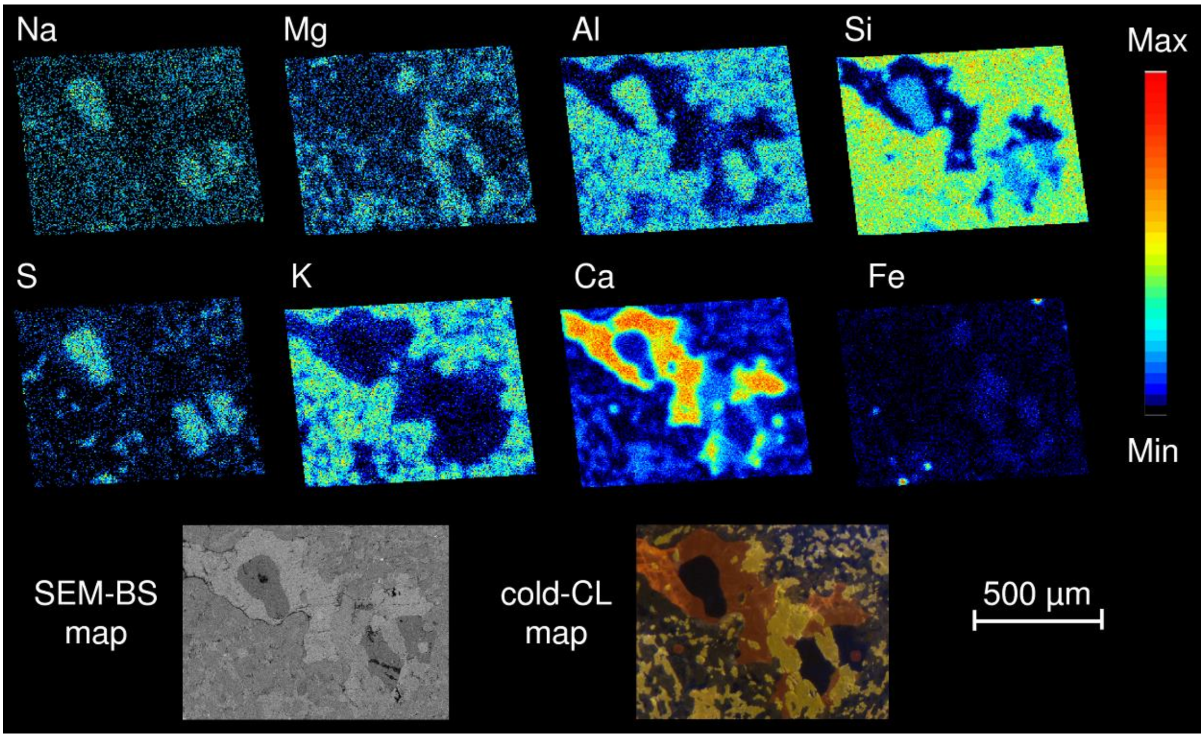


Fig. 2

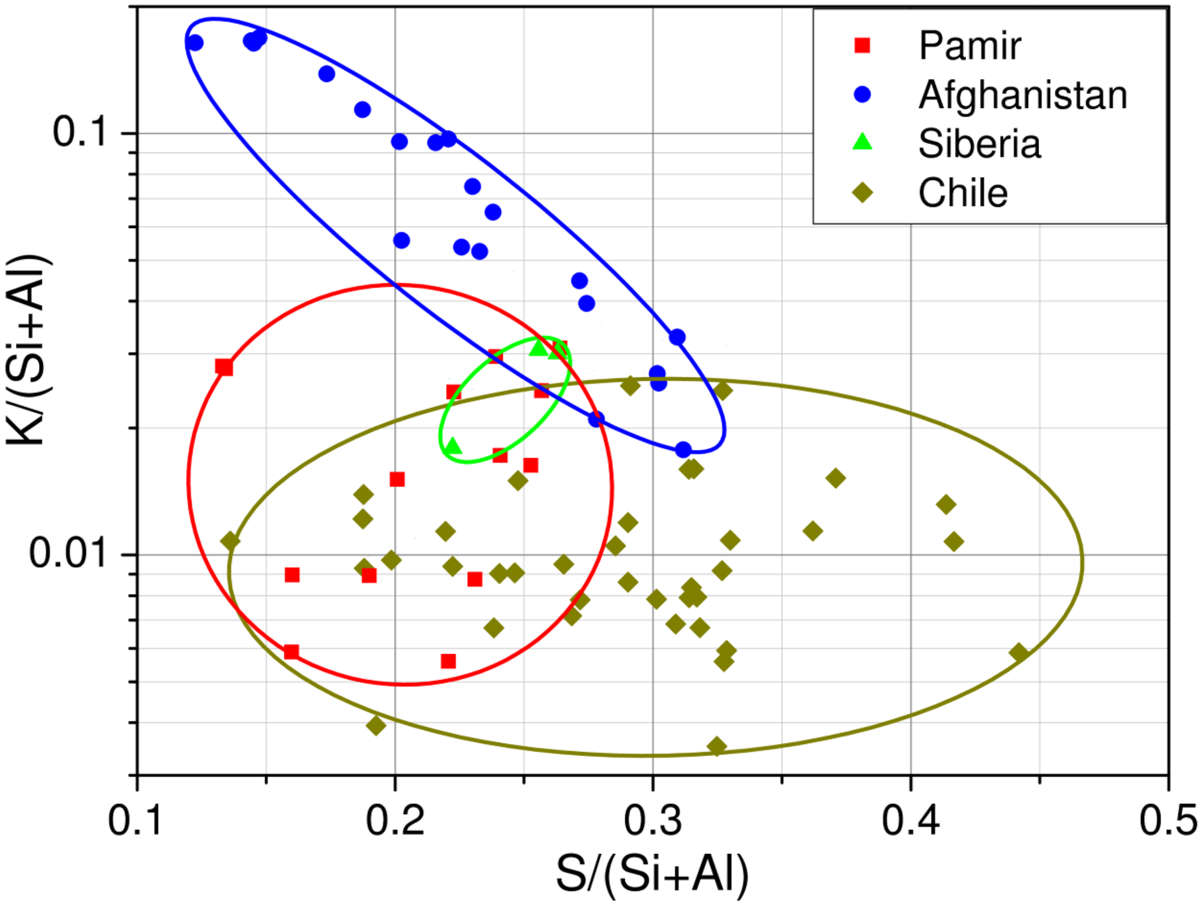
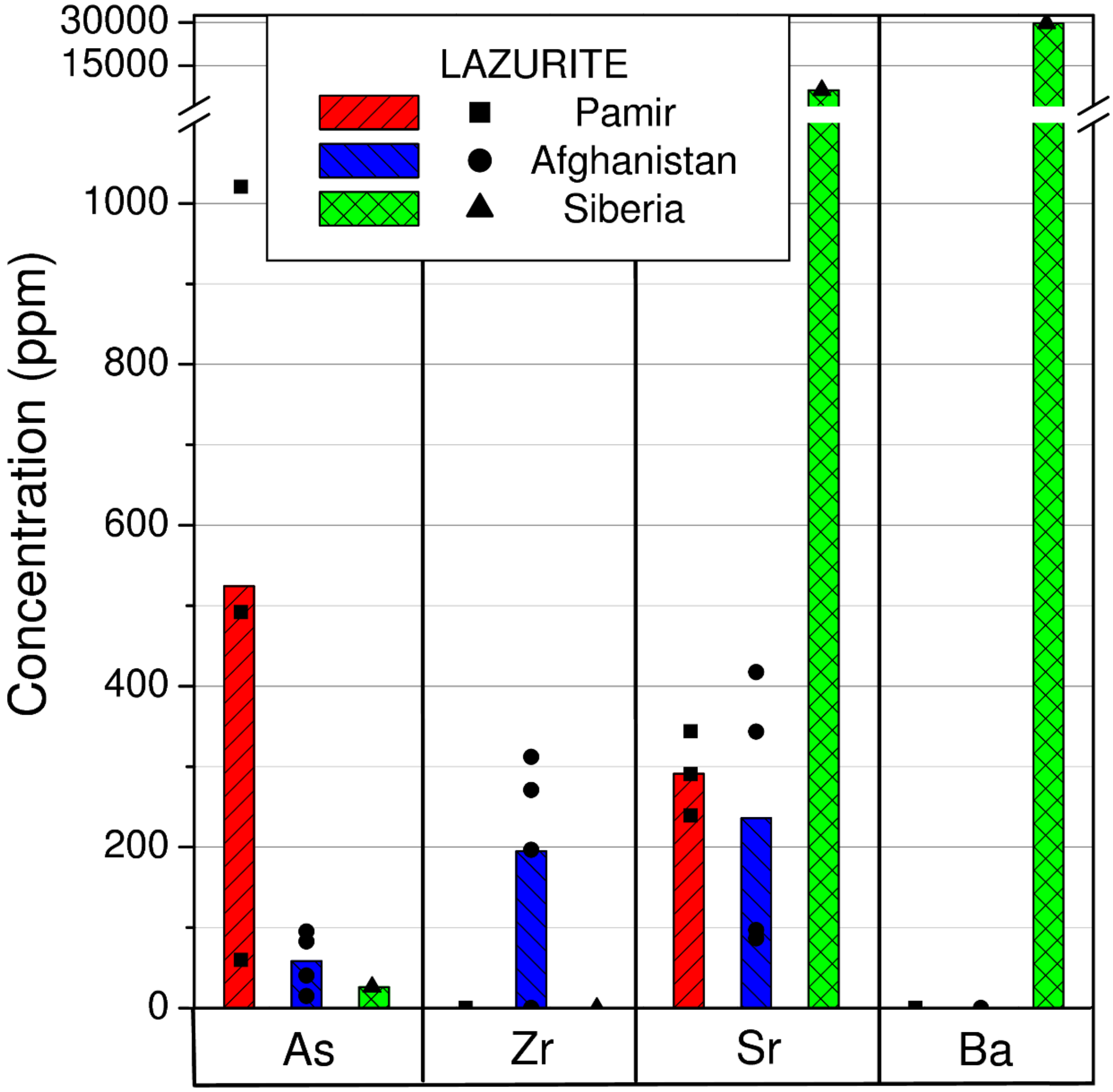

Pamir
Afghanistan
Siberia
Chile
0.1
0.01
K/(Si+Al)
0.1
0.2
0.3
0.4
0.5
S/(Si+Al)

Fig. 3



LAZURITE
Pamir
Afghanistan
Siberia
Concentration (ppm)
30000
15000
1000
800
600
400
200
0
As
Zr
Sr
Ba

Fig. 4

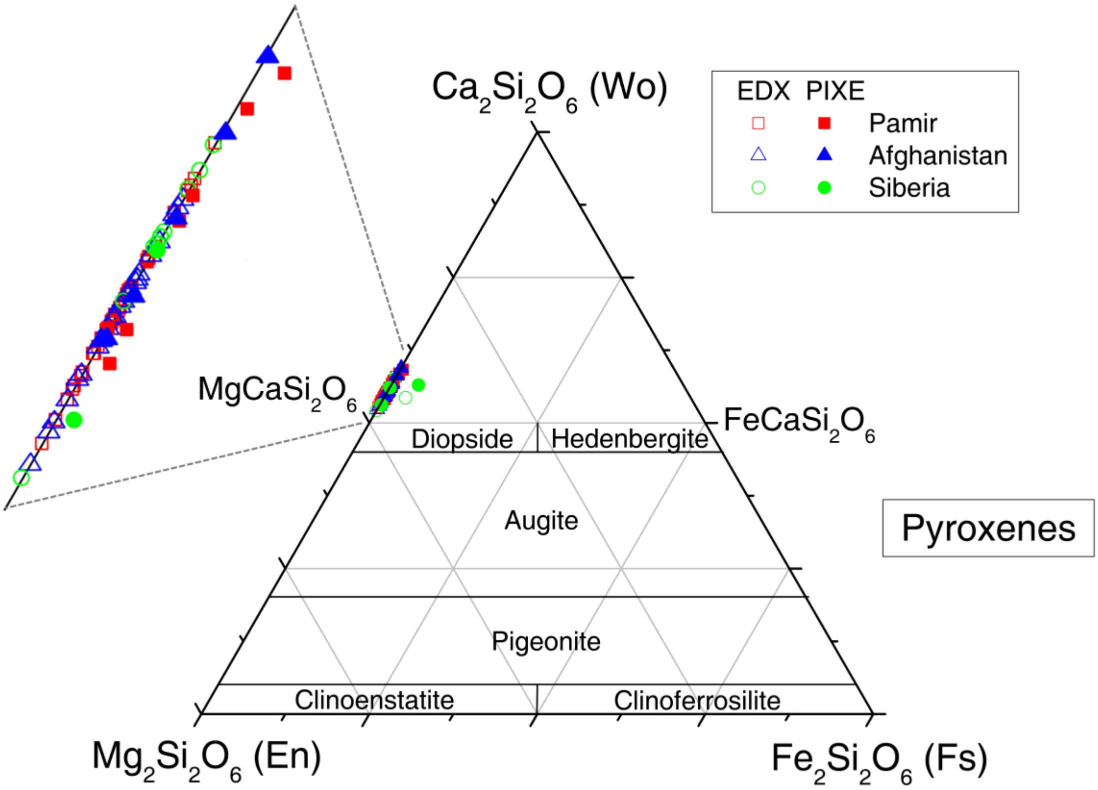

Ca$_2$Si$_2$O$_6$ (Wo)
EDX PIXE
□ ■ Pamir
△ ▲ Afghanistan
○ ● Siberia
MgCaSi$_2$O$_6$
FeCaSi$_2$O$_6$
Diopside
Hedenbergite
Augite
Pigeonite
Clinoenstatite
Clinoferrosilite
Pyroxenes
Mg$_2$Si$_2$O$_6$ (En)
Fe$_2$Si$_2$O$_6$ (Fs)

Fig. 5

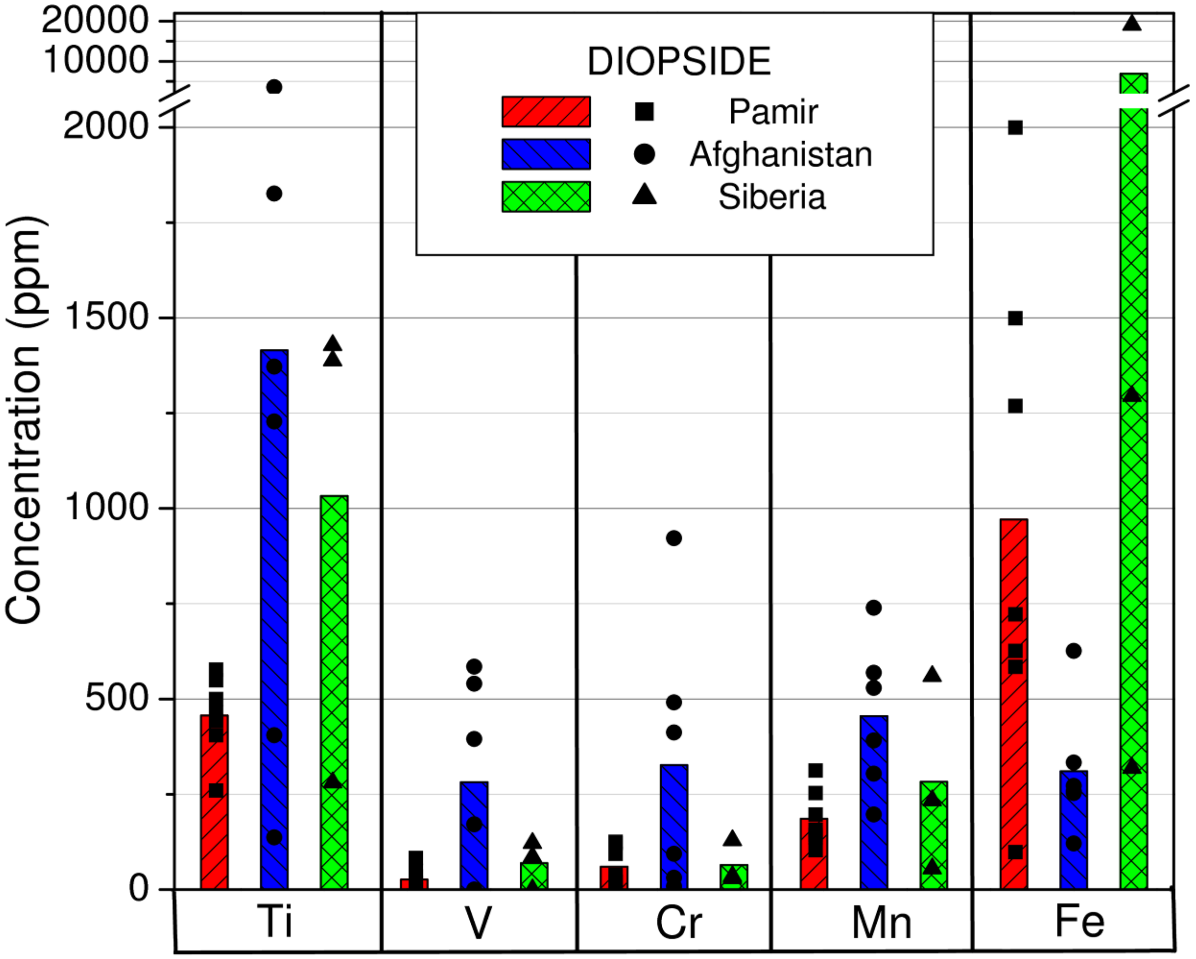

DIOPSIDE
Pamir
Afghanistan
Siberia
Concentration (ppm)
20000
10000
2000
1500
1000
500
0
Ti
V
Cr
Mn
Fe

Figure captions

Fig. 1: Micro-PIXE elemental maps complemented by SEM-BS and cold-CL maps of the same area. The PIXE measurements were performed at the external microbeam line of LABEC in Firenze. It’s easy to recognize the different phases of the lapis lazuli.

Fig. 2: SEM-EDX analysis of elemental contents in lazurite: potassium vs. sulphur, normalized to the sum of aluminium and silicon.

Fig. 3: Minor and trace elements in lazurite of different provenance from micro-PIXE measurements performed at the external microbeam line of LABEC in Firenze. The coloured column indicates the average elemental content and the dark points represent the individual measurements.

Fig. 4: Analysis of major element contents in diopside using SEM-EDX and micro-PIXE measurements in vacuum, displayed in the diagram of piroxenes.

Fig. 5: Minor and trace elements in diopside of different provenance from micro-PIXE measurements performed at the ion microbeam line of the INFN Laboratory in Legnaro. The coloured column indicates the average elemental content and the dark points represent the individual measurements.

Tables

TAB. I: Markers for provenance recognition of lapis lazuli with ion beam analysis techniques; the results obtained in this work are in bold type.

Chile:

a) double broad bands of luminescence at 560 nm and 620 nm due to wollastonite [11,12]
b) large amount of wollastonite instead of diopside [11]
c) **lower quantity of K in lazurite**

Afghanistan:

a) **higher quantity of Ti, V, Cr in diopside**
b) **contemporaneous higher quantity of K and lower quantity of S in lazurite**
c) **presence of Zr in some inclusions**

Pamir:

a) UV luminescence emission due to a cancrinite phase [11]
b) broad bands of luminescence at about 690 nm in diopside [11]
c) **higher quantity of As in lazurite**

Siberia:

a) **presence of Ba in some inclusions** (confirming what was observed by other authors [9,17])
b) **higher quantity of Sr** (confirming what was observed by other authors [9,17])