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Multitechnique characterization of lapis lazuli for provenance study

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Abstract Lapis lazuli is one of the oldest precious stone, being used for glyptic as early as 7,000 years ago: jewels, amulets, seals, and inlays are examples of objects produced using this material. Only a few sources of lapis lazuli exist in the world due to the low probability of geological conditions in which it can form, so that the possibility to associate the raw material to man-made objects helps to reconstruct trade routes. Since art objects produced using lapis lazuli are valuable, only nondestructive investigations can be carried out to identify the provenance of the raw materials. Ionoluminescence (IL) is a good candidate for this task. Similar to cathodoluminescence (CL), IL consists in the collection of luminescence spectra induced by megaelectronvolt ion (usually protons) irradiation. The main advantage of IL consists in the possibility of working in air while measuring simultaneously the composition of major and trace elements by means of complementary ion beam analysis techniques like particle-induced X-ray emission (PIXE) or particle-induced gamma-ray emission (PIGE). In the present work, a systematic study of the luminescence properties of lapis lazuli under charged particle irradiation is reported. In the first phase, a multi-technique approach was adopted (CL, scanning electron microscopy with microanalysis, micro-Raman) to characterize luminescent minerals. This characterization was propaedeutic for IL/PIXE/PIGE measurements carried out on significant areas selected on the basis of results obtained previously. Criteria to identify provenance of lapis lazuli from four of the main sources (Afghanistan, Pamir Mountains in Tajikistan, Chile, and Siberia) were proposed.

Keywords Lapis lazuli · Provenance · Ionoluminescence · Cathodoluminescence · Archaeometry · Ion beam analysis

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Introduction

Lapis lazuli is one of the oldest precious stones, being used for glyptic as early as 7,000 years ago [1]. It was diffused throughout the Ancient East and Egypt by the end of the fourth millennium B.C. and continued to be used during the following millennia: jewels, amulets, seals, and inlays are examples of objects produced using this material. In more recent times, from the sixth century B.C. until the last centuries, finely grinded lapis lazuli was also used as pigment.

Only few sources of lapis lazuli exist in the world due to the low probability of geological conditions in which it can be formed [2, 3]. Thus the possibility to associate the raw material to man-made objects is helpful to reconstruct trade routes. This is especially true for ancient contexts where there is an absence or scarceness of written evidences [4]. Although the Badakhshan mines in Afghanistan (the more famous being Sar-e-Sang) are now widely considered as the only sources of the lapis lazuli in ancient times [4–7], other

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sources have been taken into consideration: Pamir mountains (Lyadzhuar Dara, Tajikistan) [5, 8, 9], Pakistan (Chagai Hills) [8–10], Siberia (Irkutsk, near Lake Baikal) [5], Iran [5], and Sinai [11]. The last two possibilities are not geologically confirmed, and their interpretations are still debated [6, 9].

A systematic and exhaustive provenance study of the raw material utilized in works of art is still lacking. Results obtained using physicochemical analysis (atomic absorption spectrometry) on limited quantities of cut wastes from Shahr-i-Sokta [8, 9] are in agreement with Pamir mountains and Chagai Hills provenance, other than Badakhshan. Moreover, there is some evidence that also in Renaissance the Chagai Hills deposits could be utilized as source of lapis lazuli to produce ultramarine blue pigments [10]. Nevertheless, lapis lazuli provenance is still an open question, and a systematic study on lapis lazuli objects would be helpful in resolving such problem. Pigments are less suitable for provenance study due to the processes involved in their fabrication that could introduce contaminants or remove minerals, even if good results were already reached [10, 12–14]. Since art objects produced using lapis lazuli are valuable, only nondestructive investigations can be carried out to identify the provenance of the raw materials. For this kind of investigation, prompt gamma activation analysis was proposed, and preliminary studies on rock samples were promising [15].

In this work, the capabilities of ion beam analysis (IBA) to distinguish the provenance of lapis lazuli were investigated. IBA consists in the collection of different signals (visible photons, X-rays, gamma-rays, and others) induced by megaelectronvolt ion (usually protons) irradiation. Such analysis is not destructive; it can be performed in air, and sample pretreatment is not required. Moreover, by using a microbeam, a spatial resolution of about 10 μm can be achieved, which is generally sufficient to distinguish mineral phases inside the samples. Particularly, this work is focused on ionoluminescence (IL) that appears as a good candidate for provenance studies. Similar to the well-known cathodoluminescence (CL) extensively used in geosciences [16–18], IL consists in the collection of luminescence spectra induced by proton irradiation rather than electrons [19]. Besides general peculiarities of IBA techniques, such as the possibility to work in air, other advantages with respect to CL are: greater probing depth (up to 0.1 mm) that allows the overcoming of surface layers on works of art; the possibility of performing simultaneous major and trace element analysis by means of particle-induced X-ray emission (PIXE) and particle-induced gamma-ray emission (PIGE). The IL capabilities to distinguish Chilean lapis lazuli from Afghan and to apply this technique on works of art were already demonstrated in a previous preliminary work [20, 21]. In this paper, an in-depth study of the luminescence properties of lapis lazuli under charged particle irradiation is reported. Twelve stones coming from four of the main sources were systematically analyzed using optical microscopy, cold CL, and scanning electron microscopy (SEM)–energy-dispersive X-ray spectrometry (EDS)–CL techniques; in a few cases, micro-Raman spectroscopy was used to identify ambiguous phases. This characterization work was propaedeutic to IL/PIXE/PIGE measurements. Such articulated use of complementary techniques is motivated by the lesser time required in measurements with respect to IBA techniques. In order to confirm the possibility of extending the results obtained by means of CL to IL characterization, significant areas were selected and analyzed by means of IL on the basis of results obtained using CL measurements.

Experimental

Samples

The lapis lazuli stones analyzed in this work are part of the collection of the Mineralogy and Lithology section of the Museum of Natural History, University of Firenze [22]. In Table 1 the catalog number and a brief description of the starting material, the acquisition conditions, and the provenances of the different samples are reported. As already pointed out by other authors [10, 22], there is a lack of precise geographical information for many specimens. For most of the samples under investigation, only the provenance area is specified, but the exact mines are not known: three samples come from Badakhshan in Afghanistan (probably Sar-e-Sang mine), four samples from America (only two samples are cataloged as Chilean but probably are all from Ovalle), one sample from Irkutsk in Siberia, and four samples from Pamir mountains in Tajikistan (Lyadzhuar Dara lazurite deposit at 4,800 m above sea level and 76 km south of Khorugh in Gorno-Badakhshan).

Instrumentation and operating conditions

Samples were prepared as semithin sections (about 50 μm thick) and mounted on special slides with a 3-mm-diameter hole in the center. The holes were made to avoid any interference from the sample holder during IBA, the penetration depth of the proton probe being about 60–80 μm (SRIM calculation). It is worth stressing that this procedure for sample preparation was adopted only in the first characterization stage to simplify and speed up the measurements but that it will be not necessary when works of art will be analyzed by means of IBA techniques in future investigations.

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**Table 1** Description, acquisition, and provenance of the analyzed samples

Catalog	Description	Acquisition	Provenance
RI 388	Cut and partially polished fragment	Bought in Munich, 1985	Badakhshan (Afghanistan)
12397	Polished thin slice	Ciampi collection n. 3780	Badakhshan (Afghanistan)
47860	Big piece, partially polished	Afghan Gems (Germany) Mineralientage 1999	Badakhshan (Afghanistan)
RI 3063	Rough small piece	Bought from C. Djankoff Global Mining LLC 2007	Ladjvardara (Tajikistan)
RI 3064	Rough medium piece	Bought from C. Djankoff Global Mining LLC 2007	Ladjvardara (Tajikistan)
RI 3065	Rough small piece	Bought from C. Djankoff Global Mining LLC 2007	Ladjvardara (Tajikistan)
RI 3066	Rough big piece	Bought from C. Djankoff Global Mining LLC 2007	Ladjvardara (Tajikistan)
12394	Rough small piece	Magistero collection	America
12403	Rough small piece	Capacci donation	Chile
12405	Partially polished piece	Bought from Brogi, Siena	America
16980	Big piece, partially polished	Acq. Le Pietre, 1980	Chile
RI 390	Cut and partially polished fragment	Mineralientage, Munich, 1985	Irkutsk (Siberia)

All samples under study were observed in reflection mode by means of an optical microscope to evaluate their color (Fig. 1) and to compare them with CL measurements. CL measurements were performed using two different instruments: a broad electron beam "cold cathode" apparatus and an SEM–CL system.

The cold cathode apparatus is a "CITL Cold Cathode Luminescence 8200 mk3" instrument equipped with a polarized optical microscope Olympus BH2 and a CCD camera. The semithin sections were placed in a vacuum chamber with transparent windows, and the pressure was maintained at about 0.8 mbar. At this stage, sample coating was not necessary because the working pressure was high enough to avoid charging effects. During the measurements, the accelerating voltage and current were 15 kV and 500 μA, respectively. Since the electron beam was about 1 cm^2 broad, the current density was approximately 5 μA/mm^2. The

penetration depth of the 15-keV electron beam probe is about 5–7 μm, depending on material density and composition. Lapis lazuli showed an intense luminescence in the visible wavelengths so that acquisition time using standard camera conditions ranged from only 1 to 20 s.
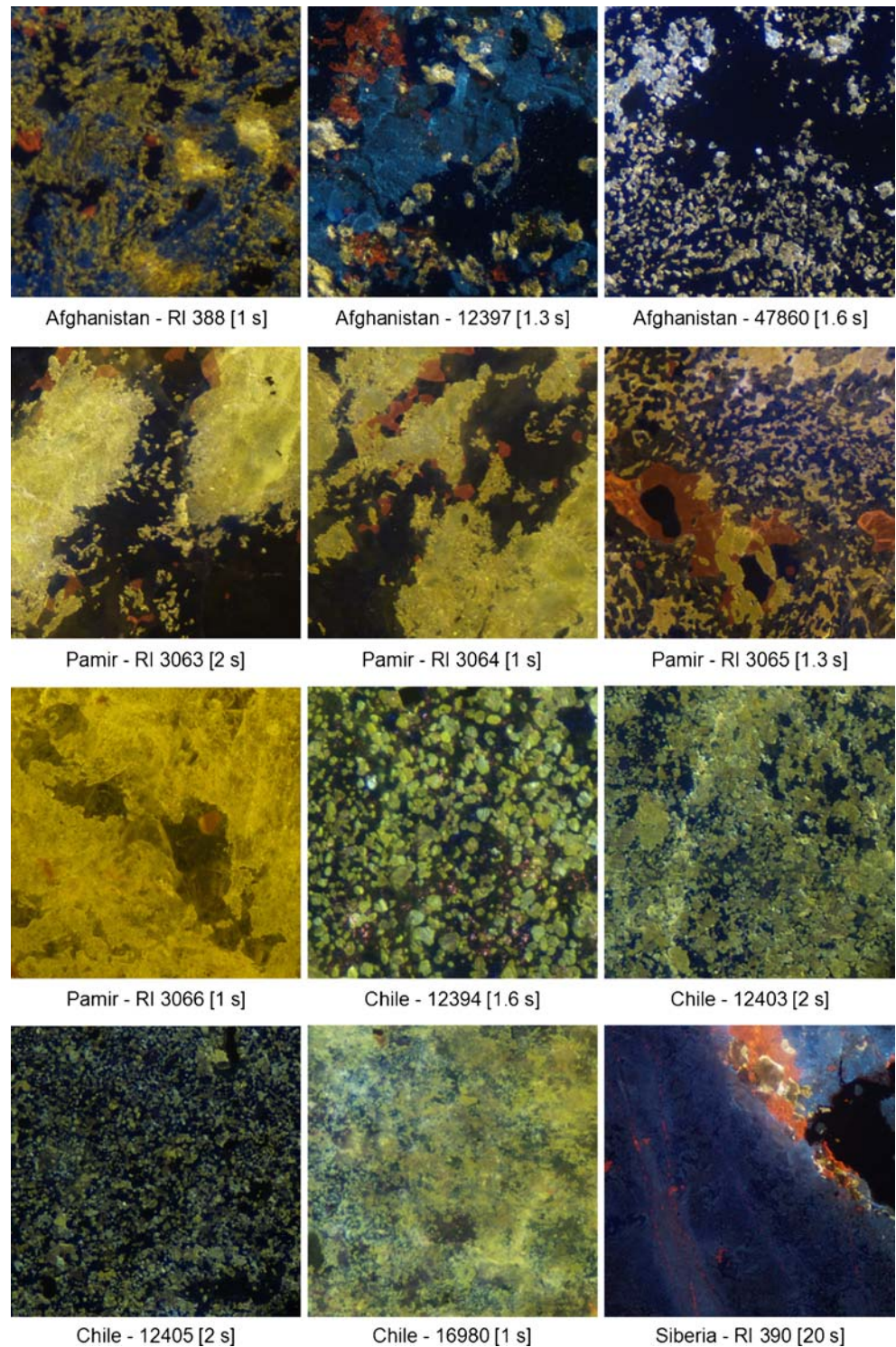
The SEM apparatus is a "Cambridge Stereoscan S360" equipped with Oxford PentaFET EDS and MONO-CL light collection system that can operate both in monochromatic (MC) or panchromatic mode. In MC mode, the light from the sample is focused into a spectrometer consisting of a monochromator and a photomultiplier tube. The spectral range is about 300–800 nm, and the wavelength resolution is of the order of few nanometers depending on monochromator slit aperture. The measured spectra were corrected for the spectral response of the instrument. In order to compare the relevant photon emissions, spectra were collected using the same operating conditions: working distance,
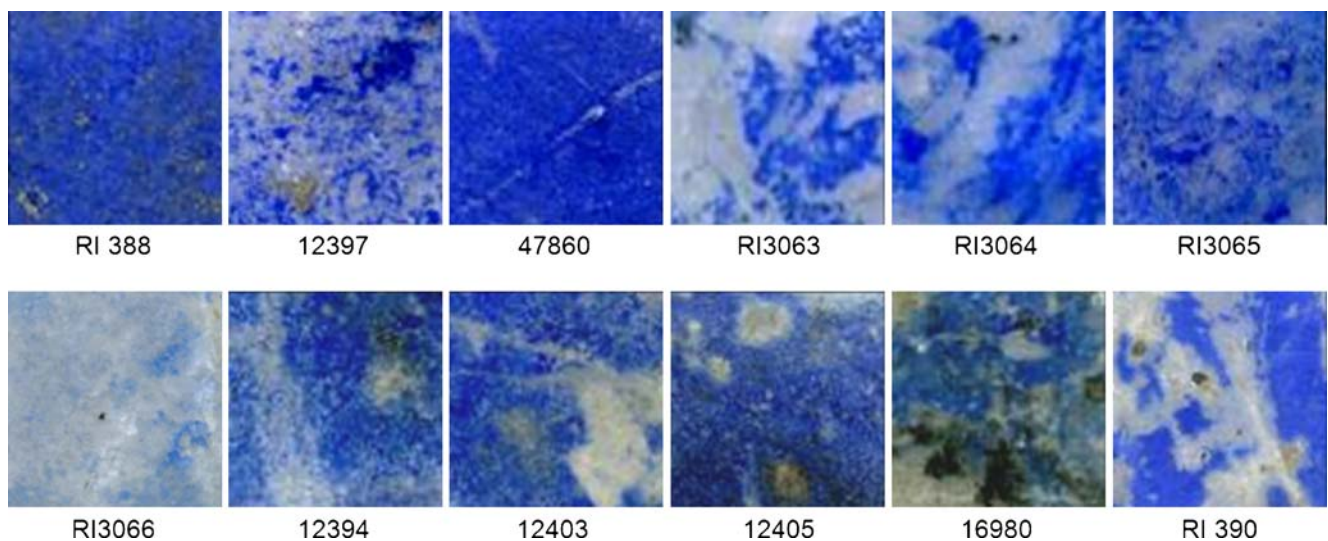
Fig. 1 Optical reflection images of the samples: each square is 6 mm wide and is representative of the semithin section

limits in the analyzed object dimensions. Samples were characterized by means of IL, PIXE, and PIGE. IL apparatus was developed in the last 2 years mainly for cultural heritage applications. The spectral range is 200–900 nm, and the resolution is 2 nm. The measured spectra were corrected for the spectral response of the instrument. More details on experimental setup are reported in previous works [20, 21].

Results and discussion

Cold CL images of the whole sample surface were acquired from all samples using the above-mentioned experimental conditions; only camera integration time was modified during the measurements. In Fig. 2a, representative collection of the obtained images is shown. Average luminescence intensity is similar in all samples except for the Siberian sample, which is more than five times less luminescent. From cold CL images, the distribution and intensity of luminescent mineral phases are clear. Minerals were identified mainly by means of EDS analysis, but micro-Raman was also used. Moreover, PIXE analysis was performed in point of interest to evaluate trace elements.

With the exception of the Siberian sample, CL images are dominated by white–yellow luminescent phase that was identified as wollastonite in Chilean lapis lazuli and as diopside in the other samples. Another abundant common mineral phase shows a blue–azure luminescence; it was attributed to K-feldspars, and it is the main feature of the Siberian sample. All the K-feldspars observed in lapis lazuli under investigation exhibit a lower luminescence with respect to diopside; this is the reason for the poor luminescence of this sample. Another significant feature is the orange–red color that was associated to calcite crystals. Lazurite, which is responsible for the blue color of lapis lazuli, shows a very weak luminescence and can be recognized as dark blue; for example, in RI3065, the three regularly shaped dark regions are well-formed lazurite crystals. The latter phase is dominant in Afghanistan samples. Lastly, pyrite do not exhibit any luminescence and therefore appears as black. Crystal dimensions vary from a few micrometers to hundred of micrometers but do not seem to be related to different provenances. Apart from wollastonite founded only in Chilean samples, all the above-mentioned phases were found in different proportions in all the samples.

In order to acquire data with significant statistics, spectra for each luminescent phase were collected in all the samples by means of CL–SEM, for a total of more than a hundred acquisitions. Many spectra exhibit a strong dependence on beam current density and therefore such parameter was kept at about 2–40 $\mu A/mm^2$, similar to the value adopted in cold CL analysis.

Spectra from calcite and K-feldspar (not reported here) exhibit the same features in all the samples. Calcite spectra are characterized by two broad bands at 625 and 350 nm. These bands are due to Mn^{2+} substituting Ca^{2+} and to intrinsic luminescence, respectively [24]. In K-feldspar spectra, the only band observed was at 455 nm; such emission is very common in this mineral due to $Al–O^{-}–Al$ defects [25].

In all the samples, lazurite has a very weak luminescence, and spectra show the same bands of the main luminescent phases, i.e., wollastonite in Chilean, K-feldspar in Siberian, and diopside in the other samples. This can be attributed to the contaminations of these phases inside the lazurite or to luminescence generated by multiple scattering during measurements (i.e., electrons hit strong luminescent phases after backscattering from the detectors). In any case, such luminescence is too weak to be useful for any provenance study.

Wollastonite ($CaSiO_3$) is one of the strongest luminescent phases, and it is common to all Chilean samples. Spectra are characterized by three bands (Fig. 2) at about 450, 560, and 620 nm. The first band is characteristic of silicate matrix and is common to other phases such as diopside [26]. The other two closed bands (more evident in Fig. 5, where the corresponding IL spectra are shown) are related to α-$CaSiO_3$:Mn and β-$CaSiO_3$:Mn polymorphic structures [27]. Such manganese-related bands were not observed in any other samples and therefore represent a significant fingerprint for Chilean provenance, as already observed in [20, 21].

With the exception of Chilean samples, diopside ($CaMgSi_2O_6$) was found in all lapis lazuli and, together with wollastonite, it is the strongest luminescent phase. In Fig. 3, diopside spectra from few samples are shown in comparison with wollastonite spectrum of a Chilean sample. Apart from the 450 nm and the infrared emission (probably due to Fe-related impurities [28]), the spectra are characterized by an intense band at about 580 nm and by a weaker band at 690 nm. These two bands can be attributed
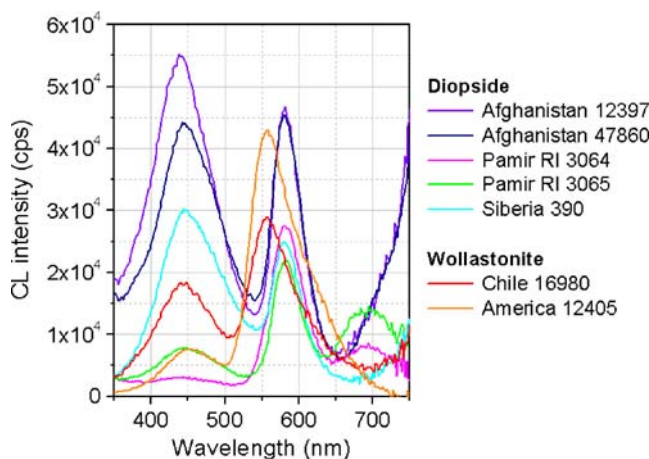

Fig. 3 CL spectra of diopside in different samples (from Afghanistan, Pamir, and Siberia) and wollastonite in a Chilean sample and in an American sample (probably from Chile)
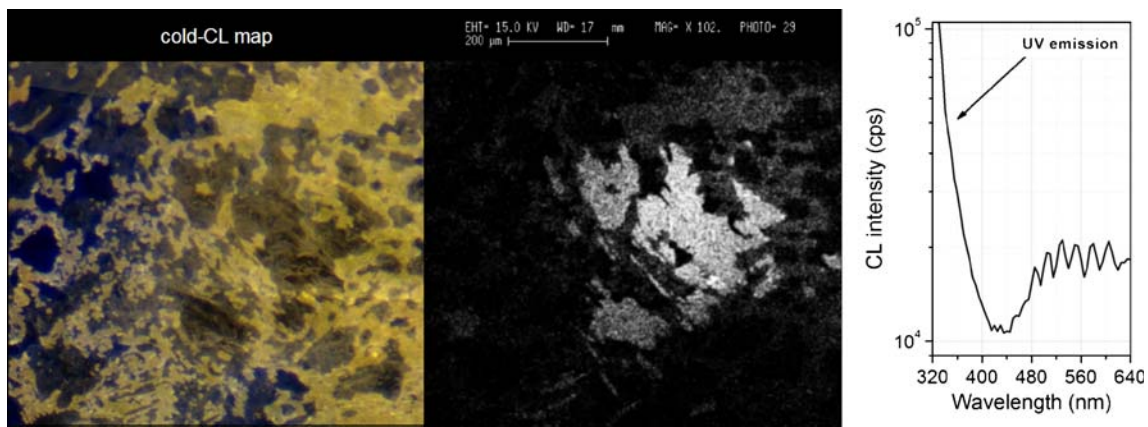
Fig. 4 CL images and spectrum of the sample RI3065 from Pamir: **a** cold CL map; **b** CL map centered at 350 nm (10-nm band pass) showing a cancrinite phase emitting in the UV region; **c** CL spectrum of such phase

to Mn^{2+} ions in M1 sites and in M2 sites [29]. The 690-nm emission was observed only in Pamir samples, and therefore it could represent a good criterion to distinguish this provenance from the others.

Lastly, the UV detection capabilities of the CL–SEM apparatus allowed the observation of a luminescent phase that was not visible in cold CL images due to the low camera sensitivity in this wavelength range. From EDS/PIXE composition and preliminary micro-XRD analysis, this mineral phase is probably related to the cancrinite group. A CL–SEM image obtained at 350 nm (10-nm pass band) is shown in Fig. 4 in comparison with a cold CL image of a 200 μm cancrinite crystal. The CL spectrum (also shown in Fig. 4) is very interesting and can be attributed to the strong UV emission and to a vibronic structure with ZPL at 2.55 eV. This phase was abundantly observed only in Pamir samples, and therefore it could be used to distinguish this provenance from the others.

In order to confirm the possibility of extending the CL results to IL, a number of crystals were selected to be analyzed by means of IBA techniques. Spectra obtained using CL and IL were compared, exhibiting a good correlation. As an example, Fig. 5 reports the spectra collected from wollastonite in an American sample and from diopside and cancrinite in a Pamir sample.

A systematic PIXE study was not performed even if trace elements inside phases could be useful for provenance. Arsenic in Pamir lazurite and zirconium in Afghanistan lazurite could be good candidates for this purpose. At present, significant PIXE information come from barium and strontium contents. In fact, all the lapis lazuli samples show a barium content that is below the instrument sensitivity, with the exception of the Siberian sample, in which the average content is higher than 1%. Also, strontium concentration is more than ten times higher in Siberian lapis lazuli (6,000 ppm) in comparison with other provenances.

Fig. 5 IL spectra: **a** diopside (sample RI 3064 from Pamir) and wollastonite (sample 12405 from America); **b** cancrinite phase emitting in the UV region (sample RI 3065 from Pamir)
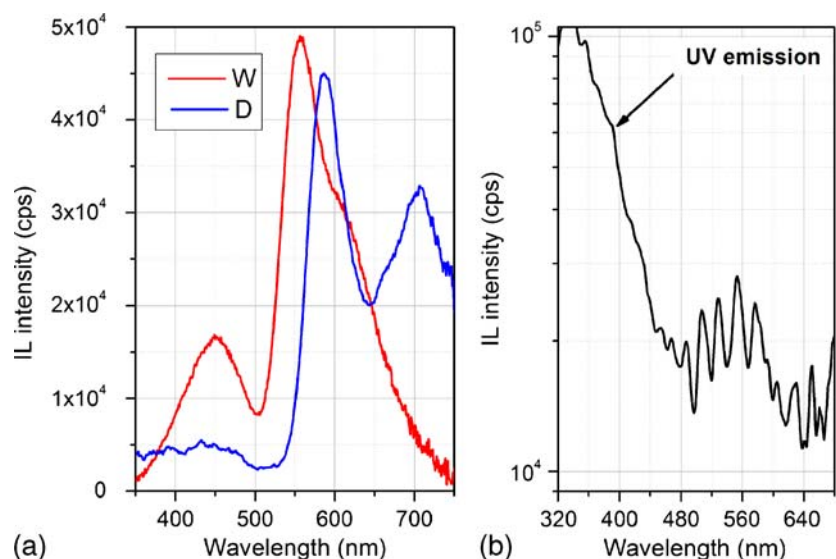
These results confirm previous works on Siberian lapis lazuli [9, 30] and can be used to distinguish this provenance from the others.

Conclusions

In this work, we reported a systematic study on the luminescent properties of lapis lazuli under charged particle irradiation from four of the main sources. Despite the limited number of analyzed samples, preliminary results are promising and the experimental differences among different samples are significant. Spectra obtained by means of CL and IL were compared showing a good correlation so that the possibility of extending the results obtained by means of CL to IL was confirmed.

Differences in luminescence spectra arise from the presence of peculiar mineral phases associated with lapis lazuli sources and may be used to distinguish the provenance of the stones.

The main distinctive mineral phase in Chilean lapis lazuli is wollastonite, which can be distinguished by the intense luminescence at 560 and 620 nm. This behavior was observed in four samples and confirms what was obtained in previous works [20, 21].

Lapis lazuli from Pamir exhibits an additional luminescence band at 690 nm, corresponding to the emission of diopside. It is also characterized by a cancrinite phase with a strong UV emission and a vibronic structure with ZPL at 2.55 eV.

Although differences exist in cold CL images and relevant CL spectra from Afghanistan and Siberian samples, they are weak because they are based only on different mineral phases ratio. However, Siberian lapis lazuli is characterized by a high content of barium as already shown by other authors [9, 30], and therefore the simultaneous PIXE analysis allows the discrimination of this provenance.

It is worth stressing that all results in this work are related to a limited quantity of samples and that the study will be tested with increasing statistics in future works. If the above-mentioned criteria will not be confirmed, new features will be investigated, such as for example the dependence of the spectra from the current density.

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