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XRF

Characterization of Pyrite Inclusions in Lapis Lazuli Using X-ray Fluorescence Micro-imaging

Application Note

Geology XGT19

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Abstract: Lapis lazuli is a blue semi-precious gem of the sodalite group. These rocks are characterized by the presence of clusters of golden colored pyrite, the size of which can vary and making attractive patterns on the gems. Thanks to its XY stage, XGT-9000 can provide a wide range of information concerning the elemental distribution in geological samples. Regions of interest can be identified and with the high resolution X-ray guide tube, detailed mapping and point analysis can be performed. In this application note we study pyrite impurities and major elements distribution in a commercial lapis lazuli pendant.

Keywords: X-ray Fluorescence (XRF), Micro-imaging, elemental analysis, Geology, Inclusions

Introduction

Lapis lazuli is a deep-blue metamorphic rock used as a semi-precious stone that has been prized since antiquity for its intense color. The most important mineral component of lapis lazuli is the “lazurite”. However, most lapis lazuli also contains calcite (white), sodalite (blue) and pyrite (metallic yellow-gold) inclusions which can impact the value of the stone. It is worth noting that if the flecks are small and sprinkled “attractively” throughout the gem, their presence doesn’t necessarily lower lapis lazuli’s value.

Lapis Lazuli Ore

The degree of purity or inhomogeneity of such minerals can be analyzed using micro X-ray fluorescence (µ-XRF). With its micrometer spot size, µ-XRF offers good spatial resolution combined with high sensitivity for low elemental concentrations. µ-XRF mappings results in detailed elemental images which highlight both the distribution of mineral phases, such as pyrite inclusions, and the inhomogeneities of the lazurite mineral. In addition, the possibility to perform point analysis allows for rapid identification of mineral species.

The instrument

The HORIBA **XGT-9000** instrument (Figure 1) is an Energy Dispersive X-ray Fluorescence (EDXRF) microscope, relying on an X-ray source to excite all the elements in the sample, and on an energy dispersive detector for the collection of the emitted fluorescence radiation.

With recent developments in X-ray optics, narrow X-ray beams ranging from several mm down to just 10 µm can be generated, thus providing the necessary high spatial resolution for the analysis of geological inclusions.

Figure 1. Picture of the XGT-9000 microscope

Mapping of inclusions

Figure 2a shows a pendant made of 16 lapis lazuli mounted together to form a geometric pattern. The image shows that the pendant is characterized by a high degree of heterogeneities, not only concerning the distribution of the metallic inclusions, which are spread in various areas of the pendant, but also for the inhomogeneity of the blue color. These features can be easily studied using the new **XGT-9000**. The advantage of this instrument is the large mapping area (maximum size, 10x10 cm), which enables imaging of the whole pendant, and an XY stage providing the possibility to acquire a pixel-by-pixel X-ray spectrum from which elemental images can be reconstructed.

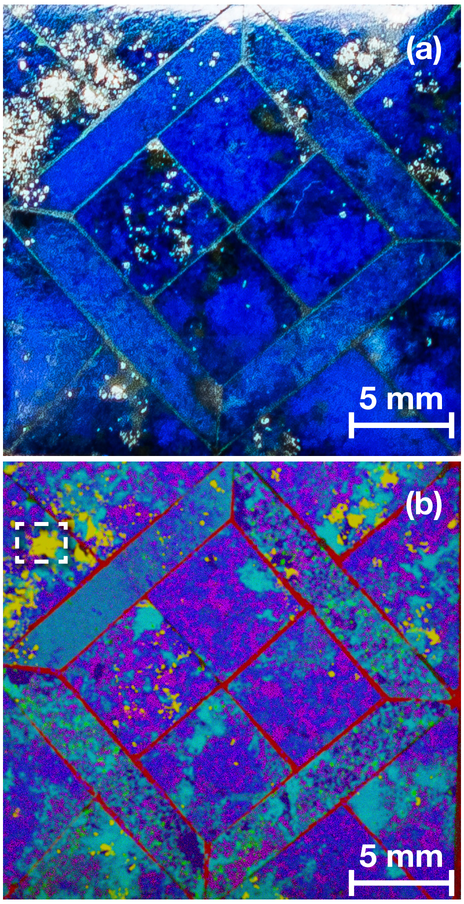

Figure 2. (a) Optical image of the lapis lazuli pendant and (b) secondary X-ray image showing Fe (yellow), Si (blue), Ca (green), Al (pink) and Ba (red) elements.

The X-ray tube settings used for the whole mapping allowed for high-energy secondary X-rays (e.g. Ba Kα at 32.194 keV) to be generated. Step size and integration time per pixel were set to 15 µm and 15 ms, respectively. The obtained elemental distribution is presented in Figure 2b, showing some of the major elements.

The X-ray image reflects the heterogeneity of the 16 lapis lazuli. The main elemental contribution comes from Si (in blue in the Figure), while other areas are enriched in Ca (green in the Figure, and giving the light blue contribution, when summed with the Si signal) and in Al (pink). The Ba signal (red), which is observed at the joints of the different stones, comes from the resin used to compose the pendant.

The impurities that characterize the different minerals, can be easily attributed to the presence of Fe (yellow). The resolution of this mapping is more than enough to spot the mineralogical features in the sample and to identify regions of particular interest for detailed analysis. For instance, an area rich in large Fe inclusions, highlighted by a white rectangle in the Figure, was identified and selected for additional detailed analysis.

Elemental mappings were acquired using the high-resolution capillary (step size and integration time per pixel size were set at 4 µm and 30 ms), on a small area, selected for its rich concentration of inclusions.

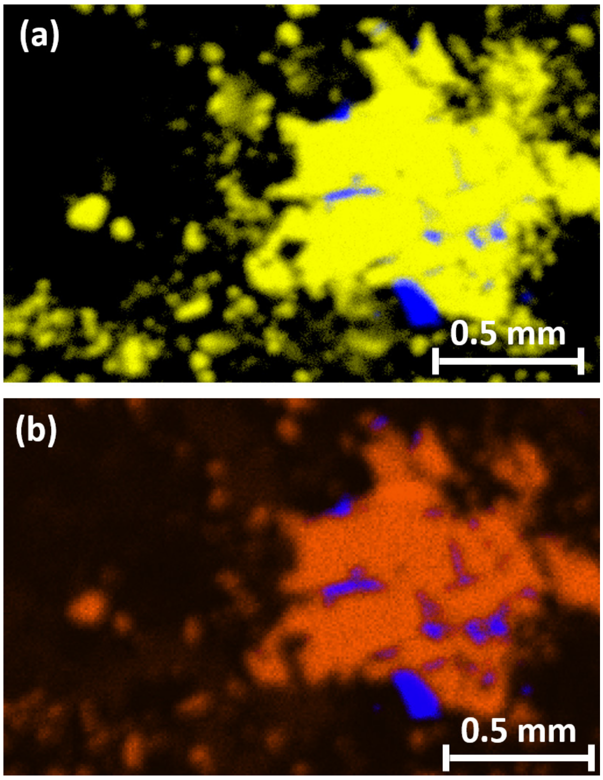

Figure 3. Close-up secondary X-ray images corresponding to the inset in Fig.2b, showing (a) Fe (yellow) and Cr (blue) and (b) S (orange) and Cr (blue) elements.

In Figure 3 we show the secondary X-ray maps of Fe and Cr (Figure 3a) as well as S and Cr (Figure 3b). The correspondence of the Fe and S signals is characteristic of pyrite, also known as fool's gold due to its metallic luster and brass-yellow hue, which is an iron sulfide with the chemical formula FeS_2. Cr rich areas can be identified and might be residuals of the Cr oxide used by jewelers to polish the stones.

Spectra shown in Figure 4 were acquired in FeS_2 areas and in Cr-rich ones. The green spectrum corresponds to a FeS_2 mineral, whereas in the blue one we see the appearance of the secondary X-ray Cr lines. The presence of Fe and S in the Cr-rich areas might be linked to the high penetration depth of the primary X-rays.

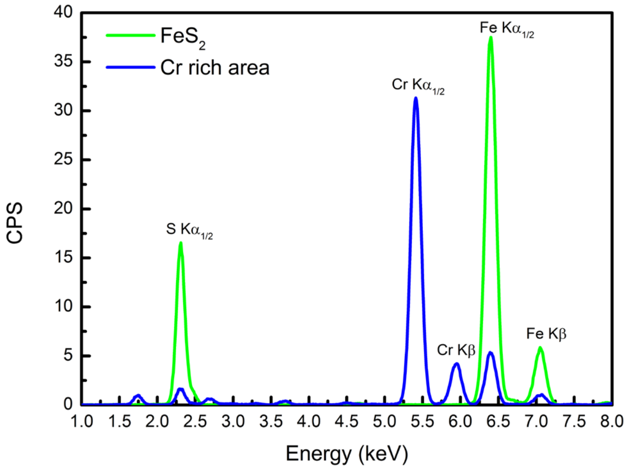

Figure 4. Secondary X-ray spectra acquired in FeS_2 rich area (green) and in a Cr rich area (blue).

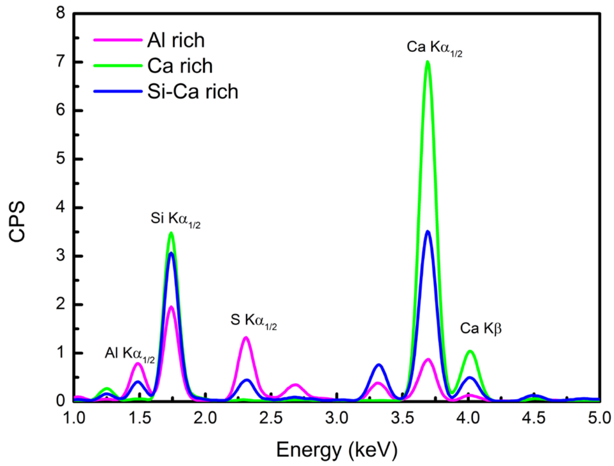

Figure 6. Secondary X-ray spectra acquired in the selected areas presented in Figure 5.

Finally, lapis lazuli are complex silicates. They are rocks and not crystalline minerals such as ruby or diamond. Therefore, they don't have a precise composition. Nevertheless, the pigment responsible for its intense blue color has been identified as ultramarine, with the formula $(Na,Ca)_8(AlSiO_4)_6(S,SO_4,Cl)_2$.

In Figure 5 we show this heterogeneity by mapping, in the same area of the pyrite inclusion, the distribution of the main elements of the ultramarine: Si (blue), Al (pink) and Ca (green).

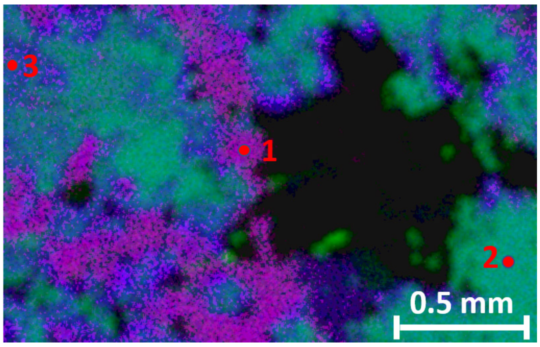

Figure 5. Elemental distribution of Si (blue), Ca (green) and Al (pink). The red dots in the Figure correspond to the positions of single point analysis.

Three spectra were acquired in areas of the sample that can be identified as Al-rich (point 1), Ca-rich (point 2) and Si-rich (point 3). The result is presented in Figure 6.

From these spectra we see that the main elements characterizing the lazurite are well identified, and the variation of the peak's intensities, according to the analyzed area, are non-negligible, showing the high heterogeneity of the minerals. Moreover, the three spectra highlight the presence of S, which is responsible for the blue color of ultramarine. Indeed, the S map presented in Figure 3b is skewed by the high S content of the pyrite, which might lead to the conclusion that no other S contribution can be detected. On the contrary, S is present everywhere in the sample, but at a smaller concentration.

Conclusion

The **XGT-9000** provides a wide variety of information on the structure and composition of geological samples. Thanks to the XY stage and the different size of X-ray guide tubes, the complete distribution of several elements in large mapping areas can be obtained, as well as the sorting of areas of interest for detailed analysis. Lapis lazuli evaluation can benefit from this technique. The large mapping area allows large and thick samples to be easily analyzed and to obtain rapidly the elemental distribution. Then, regions of interest can be identified and detailed mapping, as well as point analysis, can be performed. Using narrow X-ray guide tubes, pyrite impurities were studied, observing the presence not only of pure FeS_2 phases, but also of Cr-rich inclusions. In addition, the heterogeneity of the lazurite mineral was presented, by showing the Si, Ca and Al mapping in a smaller area.

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