

Analysis of Diopside in Lapis Lazuli for Provenance Study by Means of Micro-PIXE

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INTRODUCTION

Lapis lazuli is one of the oldest semi-precious stone, being used for glyptic as early as 7000 years ago. 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 sixth century B.C. until last centuries, finely grinded lapis lazuli was also used as pigment. Only few sources of this stone exist in the world due to the low probability of geological conditions in which it can be formed [1,2], so that 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. Although the Badakhshan mines in Afghanistan (the more famous being Sar-e-Sang) are widely considered as now as the only sources of the lapis lazuli in ancient times, other sources have been taken in consideration: Pamir mountains (Lyadzhuar Dara, Tajikistan) [3,4,5], Pakistan (Chagai Hills) [4,5,6], Siberia (Irkutsk, near Lake Baikal) [3], Iran [3] and Sinai [7]. The last two possibilities are not geologically confirmed and their interpretations are still debated. However a systematic and exhaustive provenance study of the raw material utilized in works of art is still lacking.

In this work we report about the micro-PIXE characterization of lapis lazuli rocks, for a provenance study. 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. Due to the heterogeneity of lapis lazuli we concentrate our attention on single phases instead of the whole stone; in particular we focused on the diopside, the more frequent accessory mineral of lazurite, the main phase of lapis lazuli.

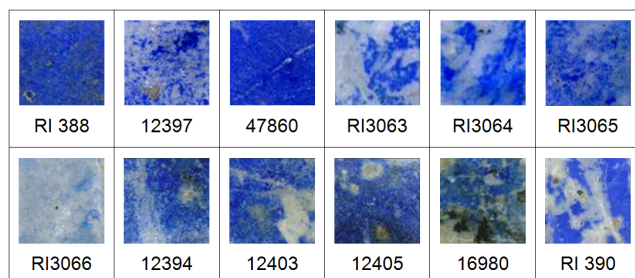


Fig. 1. Optical reflection images of the samples: each square is 6 mm wide and is representative of the semi-thin section scale.

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 $\text{CaMg}(\text{SiO}_3)_2$.

EXPERIMENTAL

The lapis lazuli stones analysed in this work are part of the collection of the Mineralogy and Lithology section of the Museum of Natural History, University of Firenze. They come from Afghanistan, Pamir, and Siberia. Samples were prepared as semi-thin sections (about 80 μm thick) and mounted on special slides with a 3 mm diameter hole in the centre. The holes were made to avoid any interference from the sample-holder during ion beam analysis. All samples were observed in reflection mode by means of an optical microscope to evaluate their colour (figure 1). A more accurate description of the 12 samples under investigation is reported in [8].

Micro-PIXE measurements were carried out at the AN2000 microbeam facility by using 600 keV protons. The beam was focused to a spot size of $\sim 5 \mu\text{m}$ and raster-scanned over the samples. The current was about 1 nA. To simultaneously analyse light and heavy elements with the same detector we used an Aluminium funny filter [9], that is a filter with a hole drilled at its centre and placed in front of the detector window. 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 (results not shown here [8,10]), for a more reliable comparison among major element contents and to attempt a correlation between trace element presence and luminescence peaks.

A set of reference mineral standards has been acquired and spectra analysis has been carried out through the Gupixwin software (version 2.1.3). To test the validity of the quantitative analyses a standard of diopside has been analysed.

RESULTS AND DISCUSSION

μ -PIXE analysis was carried out on about twenty points inside diopside crystals on all the samples, except for Chilean samples where diopside was not found. Points were selected by means of μ -PIXE elemental maps, BS Electron Microscopy and cold-cathodoluminescence images, as shown in figure 2. The major elements content

is compatible with SEM-EDX measurements [10], but does not show any useful indication for a provenance study.

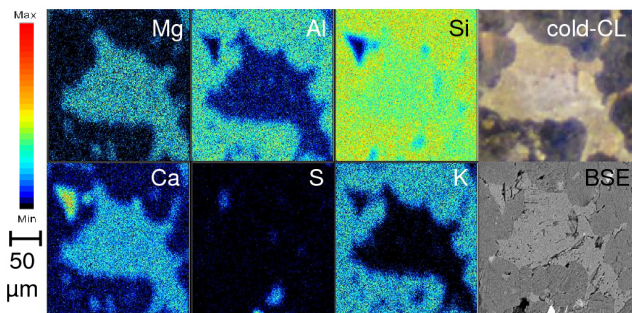


Fig. 2. μ -PIXE elemental maps (the inclusion in the map is composed by calcium, magnesium and silicon that are the main elements of diopside), BS Electron Microscopy and cold-cathodoluminescence images.

In figure 3 the trace elements detected and their content are presented. Identified trace elements are common in almost all diopside crystals, 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 contents in titanium, vanadium and chromium lower than those found in Afghan samples, but on the other hand a higher mean quantity of iron is observed. The Siberian sample does not show any evident difference with respect to the other samples.

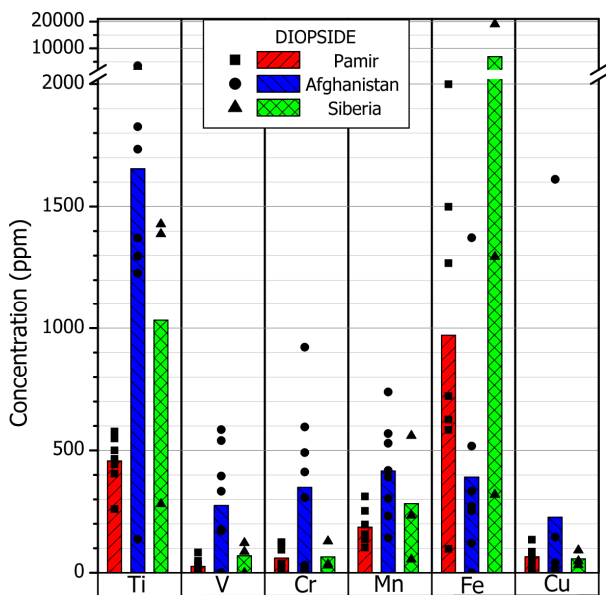


Fig. 3. Minor and trace elements in diopside. The columns indicates the average elemental content and the points represent the individual measurements [10].

Comparing these results with luminescence spectra, no evident correlations between luminescence peaks and trace elements were found. Ti, Mn and Fe are the main responsible for luminescence in diopside 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.

CONCLUSIONS

The elemental analysis of the single crystals of diopside in lapis lazuli by means of μ -PIXE showed to be useful for a provenance study of this stone. Even though the main elements do not give any information about the origin of a sample, the analysis of trace elements content permits to have some indication useful to distinguish among three Asian provenances of lapis lazuli.

ACKNOWLEDGMENTS

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