Micro-PIXE Analysis of Pyrite in Lapis Lazuli for a Provenance Study

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INTRODUCTION

In this work we report about the micro-PIXE characterization of lapis lazuli rocks. These measurements have been carried out in the framework of a wider provenance study of lapis lazuli we are carrying on since 2008 [1,2]. An introduction to this study has already been explained in the last Annual Report of LNL [3].

Due to the heterogeneity of lapis lazuli we concentrate our attention on single phases instead of the whole stone and this is one of the main motivations to use the micro-PIXE technique. In previous works we focused on lazurite, the main phase of lapis lazuli and on diopside, one of the most frequent accessory mineral of lazurite. In this work we focused on pyrite, another accessory mineral present in almost all the samples. Pyrite is an iron disulfide with chemical formula FeS_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 are 13 samples coming from Afghanistan (3), Pamir (4), Siberia (1), Chile (4) and from an unknown provenance (1). 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. An accurate description of the 13 samples under investigation is reported elsewhere [1].

Micro-PIXE measurements were carried out at the AN2000 microbeam facility by using 2 MeV protons. The beam was focused to a spot size of ~5 μm and raster−scanned over the samples. The current was about 500 pA. To simultaneously analyse light and heavy elements with the same detector we used an aluminium funny filter [4], that is a filter with a hole drilled at its centre and placed in front of the detector window.

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 marcasite (FeS_2) has been analysed.

RESULTS AND DISCUSSION

Micro-PIXE analysis was carried out on 21 points inside pyrite crystals on all the samples, except for Siberian sample where pyrite was not found. Points were selected by means of μ-PIXE elemental maps, BS Electron Microscopy and cold-cathodoluminescence (CL) images [1], as shown in figure 1. The major elements content is compatible with SEM-EDX measurements and Fe and S maps are very useful to identify the point of analysis, but does not show any indication for a provenance study.

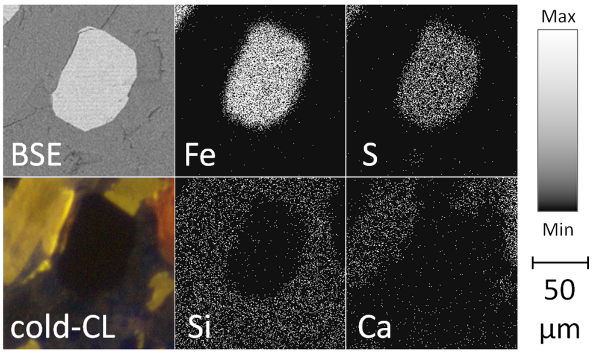

Fig. 1. μ-PIXE elemental maps (the inclusion in the map is composed by iron and sulfur that are the main elements of pyrite), BS Electron Microscopy and cold-cathodoluminescence images.

In figure 2 the trace elements detected and their concentration are presented. Identified trace elements varies in pyrite crystals of different provenances and there are also many differences in quantity. Nickel has been detected (in quantities above the limit of detection) in all the samples from Afghanistan (more than 500 ppm) and in some samples coming from Chile (less than 1000 ppm), so a high quantity of nickel can be a good marker for an Afghan provenance. Copper have been detected over the limit of detection (150 ppm) in all the samples coming from Pamir Mountains, so the presence of this element can be a good indicator for this provenance. Arsenic has been detected only in some crystals coming from Pamir Mountains, so its presence can suggest this provenance. Finally selenium has been detected above the limit of detection only in some samples coming from Chile, so this element can be a good indicator for this provenance.

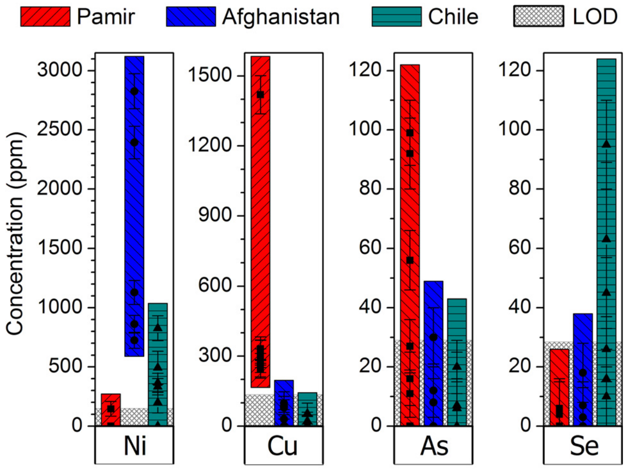

Fig. 2. Trace elements contents in pyrite from micro-PIXE measurements performed at the in-vacuum microbeam line of AN2000 accelerator with 2 MeV protons. The points represent the individual measurements (±1 standard deviation) and the floating columns indicate the range ± 2 standard deviation of the extreme values.

To test these markers a sample of unknown provenance has been analysed. Two pyrite crystals have been measured and the only trace element detected has been nickel, with concentration (760 ± 100) ppm and (1320 ± 110) ppm.

These values suggest Afghanistan as a provenance for this sample, but alone they are not significant enough. Other analysis, carried out on the same sample but testing other markers, gave the same indication [2].

CONCLUSIONS

The elemental analysis of the single crystals of pyrite in lapis lazuli by means of micro-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 four provenances of lapis lazuli.

[1] A. Lo Giudice et al., Analyt. and Bioanalyt. Chem. 395 (2009) 2211.
[2] A. Re et al., Nucl. Instr. and Meth. B 269 (2011) 2373.
[3] A. Re et al., INFN-LNL Report 234 (2011), 169-170.
[4] S. Gama et al., Nucl. Instr. and Meth. B 181 (2001) 150.