Luminescence Properties of Lapis Lazuli Investigated by means of a Proton Micro-Beam

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INTRODUCTION

Lapis lazuli is a blue semi-precious stone that has been used since the Neolithic Era (VII millennium BC) for the manufacturing of precious carved artefacts. Our group is studying this rocks since 2008, mainly for a provenance study purpose [1]. In fact a systematic study of rock samples coming from different known sources could allow finding some markers discriminating various provenances. The possibility to identify the extraction sites of the rock in a non-invasive way, can give information on artefacts and consequently on ancient trade routes [2].

Lapis lazuli is an aggregate of several different minerals, in the form of crystals ranging from sub-micrometric to millimetric sizes. The possibility to analyse a single crystal is one of the main features to use a proton micro-beam to probe the samples. The main markers we found until now are related to trace elements present in some mineralogical phases, mainly in diopside and pyrite, and to luminescence properties of diopside and wollastonite [1-6]. Luminescence is a promising technique to discriminate lapis lazuli provenances also in a non-invasive way: using an in-air extracted microbeam, luminescence has been acquired both on precious artefacts [4,6] and archaeological samples [2]. For these reasons we decided to investigate the luminescent properties of other different minerals forming lapis lazuli, analyzing the semi-thin sections obtained from lapis lazuli samples from the Museo di Storia Naturale of the Università di Firenze.

EXPERIMENTAL

Ion beam analysis were carried out at the microbeam line of the AN2000 accelerator, using 2 MeV protons with a current below 500 pA and a beam size around 5 µm.

The micro-IonoLuminescence (µ-IL) apparatus has been expressly developed for this beamline and installed consequently (Figure 1). It consists in a collecting lens, sensitive from UV to IR, fixed inside the chamber and connected to a spectrometer through two optical-fibres, one inside and one outside the chamber, and a vacuum feed-through. The lens can be manually aligned, so to acquire the light coming from the point hit by the ion beam, allowing for simultaneous IL and PIXE measurements. The spectrometer is an Ocean Optics USB4000 with 3648 pixels, fitted with a 600 l/mm grating blazed at 500 nm. The whole system has a sensitive bandwidth between 350 and 900 nm. The spectra acquired with this setup are then corrected for the spectral response of the instrument, obtained using an intensity calibrated lamp.

RESULTS AND DISCUSSION

Combining µ-PIXE and µ-IL, different crystals can be easily identified: the first step of the analysis is the raster-scanning of the beam on the sample, acquiring µ-PIXE elemental maps. They are useful to find the crystals to be analysed, looking for homogeneous areas of at least 50×50 µm^2. The second step is the simultaneous acquisition of µ-
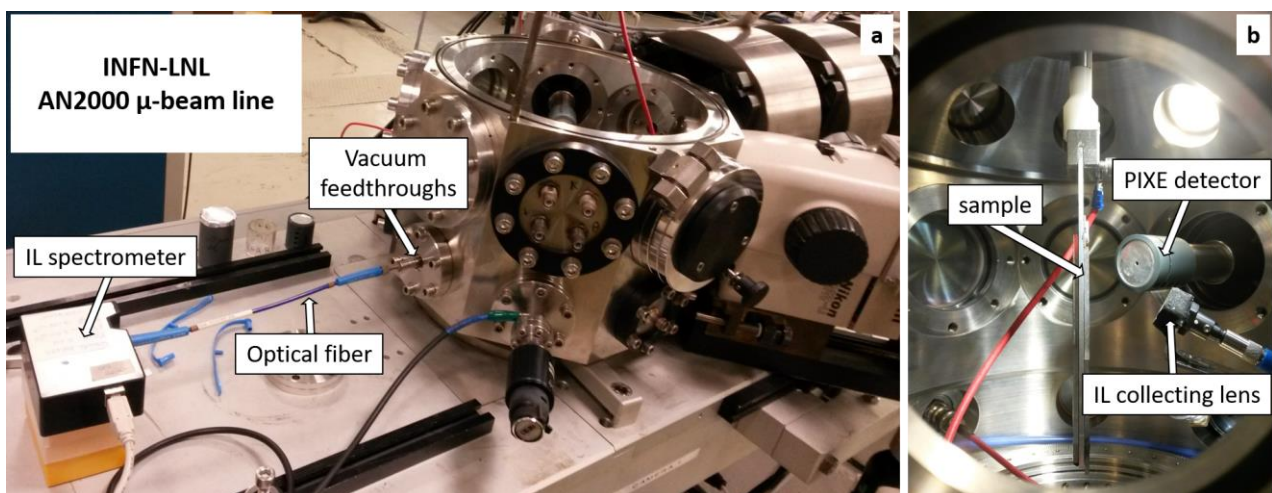

Fig. 1. a) the microbeam line with the installed IL setup; b) the internal part of the vacuum chamber with the IL collecting lens.
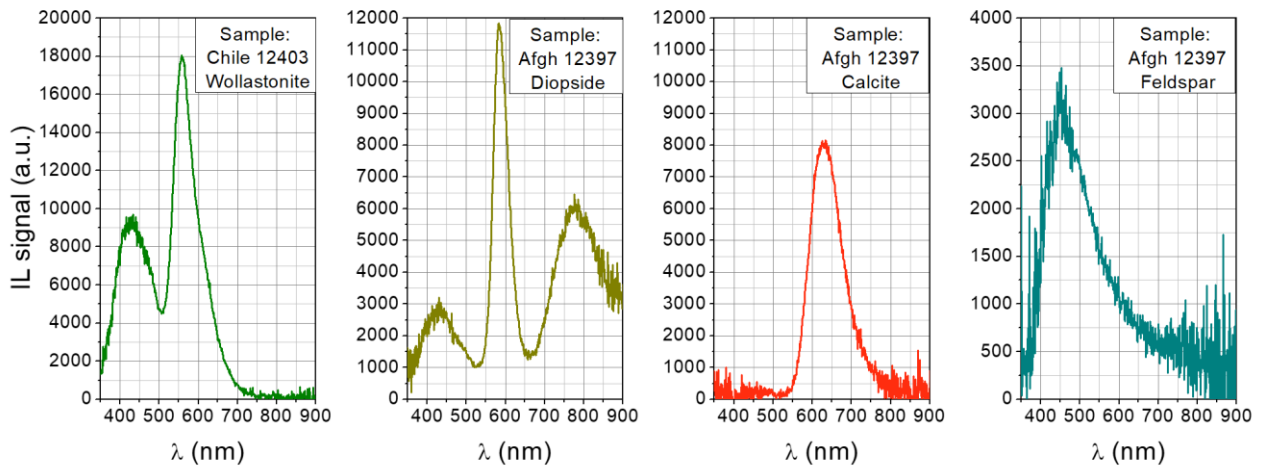
Fig. 2. IL spectra from lapis lazuli (integration time: 5 s for wollastonite and diopside; 10 s for calcite and feldspar); all the spectra are calibrated taking into account the intensity response of the apparatus.

PIXE and μ-IL in the selected points. While IL spectra require few seconds to be acquired, some tenths of minutes are necessary to detect trace elements by means of PIXE. The final result is the elemental composition of the analysed crystal with a detection limit down to some tenth of ppm (depending both on the element and the matrix).

The luminescence spectra obtained for some mineralogical phases are presented in Figure 2: wollastonite and diopside spectra, already presented elsewhere [6], are a specific marker to distinguish Chilean samples, rich in wollastonite, from Asian samples, rich in diopside. The typical feature of wollastonite is the presence of two broad bands at 560 nm and 620 nm, merged in a single asymmetric peak, while diopside is charachterised by a main band centered at 580 nm. In addition to these two phases charachterised by a strong luminescence emission, other phases have been analysed: lazurite, the main phase of lapis lazuli, does not show a detectable luminescence signal; calcite shows a strong red luminescence at about 625 nm; feldspar has a characteristic blue luminescence centered at about 450 nm. This features have been detected on different samples and should be promising for the provenance study purpose.

CONCLUSIONS

The analysis of the luminescence properties of the mineralogical phases in lapis lazuli demonstrated to give indication about the provenance of the rock. The preliminary results obtained has to be extended to all the available samples, to look for common features discriminating one provenance from the others and eventually extended to other luminescent minerals not yet identified.

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