In-air broad beam ionoluminescence microscopy as a tool for rocks and stone artworks characterisation

The in-air broad beam ionoluminescence microscopy as a tool for rocks and stone artworks characterisation

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ABSTRACT

Broad beam ionoluminescence (IL) microscopy is a promising technique for the non-destructive characterisation of rocks and stone objects. Luminescence imaging by means of broad ion beams has been sporadically used by other authors but, in our knowledge, its potential has not yet been fully investigated, neither in geological science nor in other fields.

The in-air broad beam IL microscopy was developed and installed at the INFN-LABEC external microbeam in Firenze. Similarly to the cathodoluminescence (CL) microscopy, the apparatus exploits a CCD colour camera collecting images (few mm^2 wide, with ~10 μm spatial resolution) of the luminescence emitted by the sample hit by a defocused MeV proton beam. The main differences with the well established and widespread CL are the possibility of working in air (no sampling or conductive coatings required) and the possibility of combining the analysis with micro-beam analysis, such as, for example, μ-IL and μ-PIXE (Particle Induced X-ray Emission).

To show the potential of the technique, IL images of thin sections of lapis lazuli are compared with those obtained by means of a in-vacuum cold-CL. An application to the study of stone artworks is also reported.

This technique and apparatus will provide a valuable help for interdisciplinary applications, e.g. in geological sciences and in the cultural heritage field.

Keywords: ion microprobe, ionoluminescence microscopy, cathodoluminescence, PIXE, lapis lazuli, archaeometry

INTRODUCTION

Ionoluminescence (IL) is the name given to photon emission in the IR/VIS/UV range from a material during irradiation with ions. To minimize damaging effects and to investigate a deeper region in the material (some tens of microns), protons are the most widely used particles. As other luminescence techniques, IL does not provide information about the composition of the sample, but only about the presence of luminescence centres activated by lattice defects or impurity ions. For this reason, the best results are obtained when it is used in conjunction with quantitative IBA (Ion Beam Analyses) techniques, such as e.g. PIXE (Particle Induced X-ray Emission) [1].

Geological science is one of the many fields in which IL has been giving significant contributions [2, 3]. IL analysis provides a material characterisation similar to that of the more well-established and widespread cathodoluminescence (CL), where an in-vacuum electron beam probe is used [4, 5]. By means of the collection of spectra and maps, both techniques are able to identify minerals, to quantify the phase distribution in rocks and to analyze the structure of solids (defects, zonal growth, trace elements and their valence, etc.). The main differences of IL with respect to CL are:

- a greater probing depth, due to the higher penetration of protons with respect to electrons;
- the possibility of combining the analysis with other ion beam techniques, such as PIXE (by far more sensitive than EDX), PIGE (Particle Induced Gamma-ray Emission) and BS (Backscattering Spectrometry);

- the possibility of working in air maintaining high spatial resolution (external microbeams) [6].

Above all, the last feature makes IL very attractive in artworks study, due to the non-invasivity of the method (no sampling or conductive coatings required).

The most important information achievable with CL microscopy is constituted by the luminescence colour images obtained by means of a defocused electron beam hitting the sample in a vacuum chamber equipped with a transparent window and an optical microscope. Nevertheless, up to now, IL maps have been obtained practically always by raster scanning a microbeam over the sample [7-9]: in this mode, maps are related to a range of wavelength selected by means of filters or monochromators. Sensitivity is high but the valuable colour information of the whole area hit by the beam is lost or difficult to reconstruct. Wide area IL imaging, by means of broad ion beam coupled with an optical microscope and a camera, was sporadically used, for example in vacuum on geological thin samples in transmission mode [1, 10], or in-air for biological application [11], but, in our knowledge, the potential of in-air broad beam IL imaging has not yet fully investigated, neither in geological science nor in other fields.

In this paper, after describing the experimental set-up, to show the capability of the technique we present a comparison between the results on semi-thin sections obtained by means of the in-air IL microscopy and the conventional in-vacuum cold cathode CL microscopy (cold-CL). Moreover we show how the technique can be exploited also for the study of large stone objects and not only of semi-thin sections. Although IL microscopy can be performed on all geological materials, both sections and objects analyzed are made in lapis lazuli, as this work falls in the framework of the provenance study of lapis lazuli used for artworks we are carrying on since 2008 [9, 12, 13]. In this context, the broad beam IL microscopy was developed to drastically reduce the time to find areas of interest to be studied by means of μ-IL and μ-PIXE analysis.

EXPERIMENTAL

Ion Beam Analyses were performed at the external scanning microbeam facility [14] of the 3 MV accelerator of the INFN LABEC Laboratory in Firenze, widely used for studies in cultural heritage and geological problems [15-17].

The new IL microscopy apparatus is composed by a CCD colour camera equipped with a zoom lens at 45° with respect to the beam direction (Fig. 1). The camera is a Prosilica GC2450C and the objective is a TECHSPEC VZM 1000 Zoom Imaging Lens, with magnification from 2.5× to 10× and working distance of 35 mm. The sample is maintained in atmosphere. The instrument characterisations were carried out by using 3 MeV proton beams spread over the whole exit window, (2×2 mm^2 wide and 500 nm thick). In this condition, at the sample position (1 cm from the exit window), the beam area was about 6 mm^2. The ion beam current density was ~ 2 nA/mm^2, sufficiently low not to induce any damage in the stone [6, 18]. This way, in few seconds (1 - 20 s), we acquired the image of all the luminescent phases in the area hit by the beam (~ 6 mm^2) with a spatial resolution of ~ 10 μm. Thanks to the different luminescent properties of the minerals present in the bombarded area, the IL images allowed for the quick identification of regions of interest for the successive IBA analyses (μ-PIXE and μ-IL) with the focused ion beam (spot size of 15÷20 μm).

To check the performances of the apparatus, IL images of lapis lazuli thin sections were compared with those obtained by means of a conventional cold-CL operating in vacuum (0.8 mbar) [12]. The electron beam current density was about 5 $\mu A/mm^2$ on a 1 cm^2 area and the electron energy was 15 keV. Acquisition time from 1 to 20 s was adequate. As mentioned, the cold-CL is unsuitable for artworks because it is carried out in vacuum and this is why the comparison between the two techniques was made only on semi-thin sections.

In the above conditions, depending on the minerals composing lapis lazuli, the penetration depths are 60÷80 μm and 5÷7 μm respectively for protons (SRIM 2008 simulations [19]) and electrons (CASINO simulations [20]).

RESULTS AND DISCUSSION

Broad beam IL microscopy is a powerful instrument which can be used for any study where luminescence mapping is requested or can be of help in successive studies. It is worth stressing that this technique is absolutely non-invasive and can be used in-air on whole objects also of large dimensions. In our case, we used this technique to quickly put into evidence the presence of minerals of interest and to map their distribution on relatively large areas. This is of the utmost interest in our

research on lapis lazuli provenance, as we demonstrated the possibility of distinguishing the origin of lapis lazuli by using trace element concentrations and luminescence spectra of the minerals in the stone [9, 12, 13].

Lapis lazuli semi-thin sections (part of the collection of the Mineralogy and Lithology section of the Museum of Natural History, Università di Firenze) were used to check the performances of the apparatus by comparing IL and cold-CL images. As an example, in Fig. 2 luminescence images of the same area of a lapis lazuli semi-thin section from Pamir mountains (sample RI 3063), obtained by means of the two techniques, are shown. The good agreement is apparent and the slight differences in shape and colour of some crystals can be ascribed to the different probed volumes (some μm using electrons, about ten times greater using protons), as the shape of the crystals normally changes with depth. Luminescence images, obtained in 2 s and 1.5 s for electrons and protons respectively, allow us to distinguish different minerals and to determine their distribution in the examined area. Moreover if the luminescence colour of each mineralogical phase is known, it is also possible to identify directly the minerals, otherwise this task can be accomplished by μ-PIXE analysis (in the very same way in which EDX analysis can be carried on in a SEM coupled with a CL). In the case of the lapis lazuli from Pamir mountains of Fig. 2, main mineralogical phases, identified by their luminescence colours, are diopside (yellow), calcite (orange) and lazurite (dark blue) [12].

IL microscopy was also successfully used on valuable stone art objects without any pre-treatment or sampling. The analysed objects are part of the "Collezione Medicea", a collection of artworks, carved in precious and semi-precious stones, belonged to the famous Medici family of Firenze and now housed in the Museum of Natural History (University of Firenze) [21]. Visible-light and luminescence images of the same areas were acquired looking for big and homogeneous crystals, where it was possible to carry on μ-IL and μ-PIXE analyses avoiding the risk of mixing information corresponding to different minerals.

As an example of this application, in Fig.3a and Fig. 3b visible-light and luminescence images (2 s acquisition time) of an area on the sample "coppetta ovale" (cat. 13688) of the "Collezione Medicea" are shown. In the IL image the black, non-luminescent area corresponds to a pyrite crystal (brass-yellow in visible light), while the regions appearing whitish in visible light correspond to

two different minerals, showing a yellow luminescence and greyish/light-blue emission respectively. Focusing the ion beam into regions of interest (~ 1000 μm^2) selected respectively inside the yellow luminescent and the greyish/light blue zones, μ-IL and μ-PIXE results allowed confirming the identification of the former mineral as diopside ($CaMgSi_2O_6$) and the latter as k-feldspar. In Fig. 3c and Fig 3d we report μ-IL spectrum and μ-PIXE element contents (evaluated by means of GUPIXWIN 2.1.3) of the yellow-luminescence area, as these are the feature playing a significant role in provenance attribution [12, 13]. Ionoluminescence spectrum shows a strong 580 nm band that is a characteristic of diopside and it is due to Mn^{2+} activator [12]. Major elements measured by means of μ-PIXE are typical of diopside and also the low quantities of Al, Na and Fe are quite common in this mineral [13]. An extensive study of the artworks of the "Collezione Medicea" will be presented in a future work.

CONCLUSIONS

In this work, the new in-air broad beam IL microscopy apparatus and technique are described. Broad beam IL microscopy was exploited for the characterisation of both semi-thin sections and stone objects. Imaging of semi-thin sections showed the capability of the technique to obtain information similar to those provided by the in-vacuum CL microscopy; differences are the higher penetration depth and the capability to work in air without sample pre-treatment, fundamental feature to analyse artworks. When used for mineral characterisation, regions of interest identified by means of broad beam IL microscopy can be successively analysed by means of μ-PIXE for trace elements quantification and μ-IL for luminescence properties determination.

It is worth stressing that the analytical method developed in this work allows to study many other materials (e.g. glass, gems, pigments, etc.) providing a valuable help for interdisciplinary applications, e.g. in geological sciences and in the cultural heritage field.

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Figure captions

Fig.1

Experimental setup of the broad beam IL microscopy apparatus (cyan outlined) on the external microbeam line of the INFN-LABEC in Firenze during the analysis of “coppetta azzurra” (cat. 13687).

Fig. 2

Cold-CL (a) and IL (b) microscopy images of the same area in a lapis lazuli semi-thin section (sample Pamir RI3063). The integration time was 2s and 1.5s respectively.

Fig. 3

Visible light (a) and IL microscopy images (b) of the same area on the “coppetta ovale” (cat. 13688) of the “Collezione Medicea”. μ-IL spectrum (c) and μ-PIXE elemental analysis (d) were carried out in a region of interest (red square).

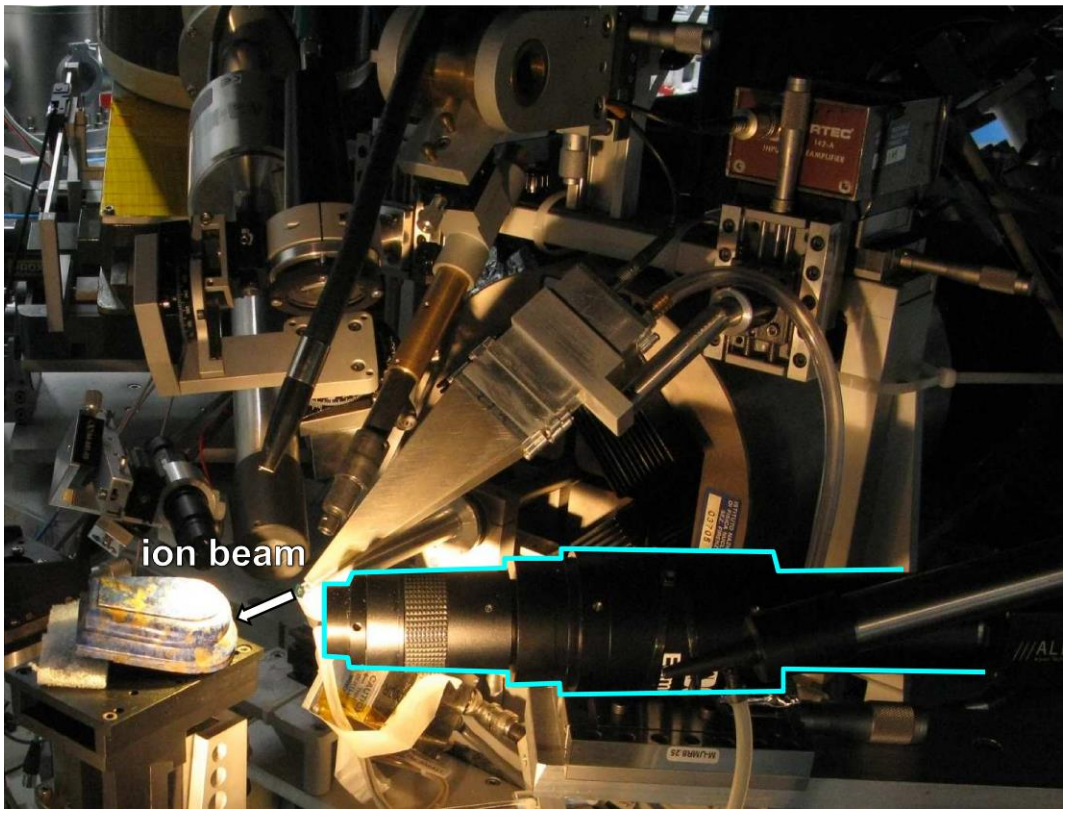


FIG. 1

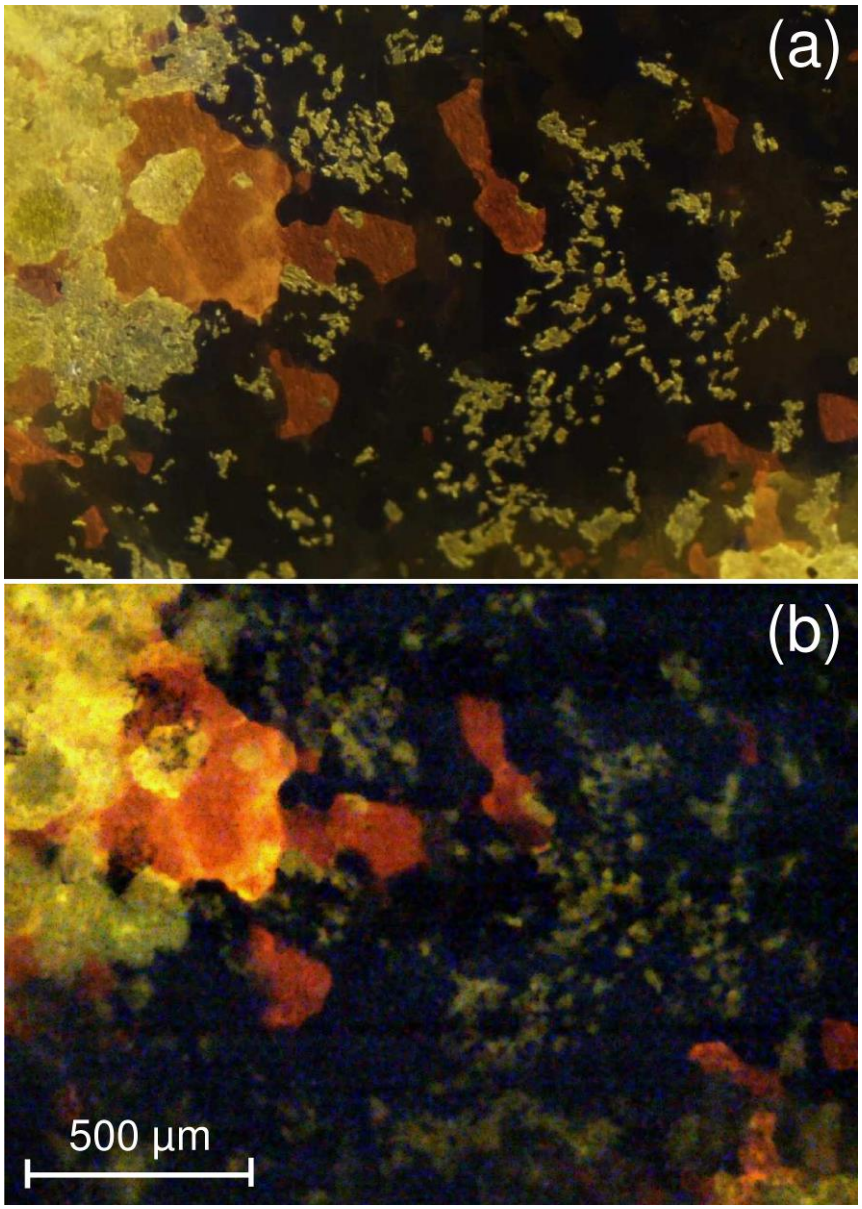
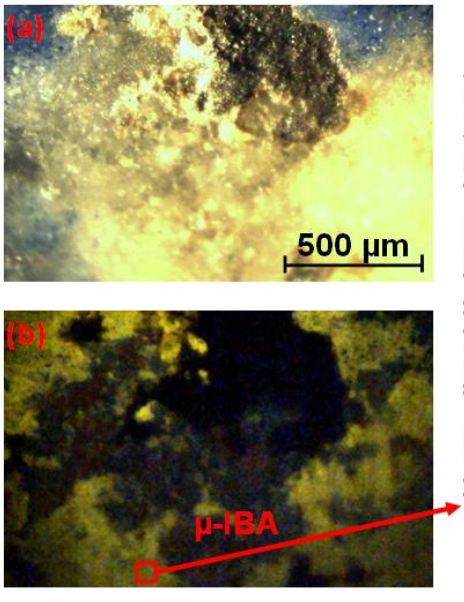
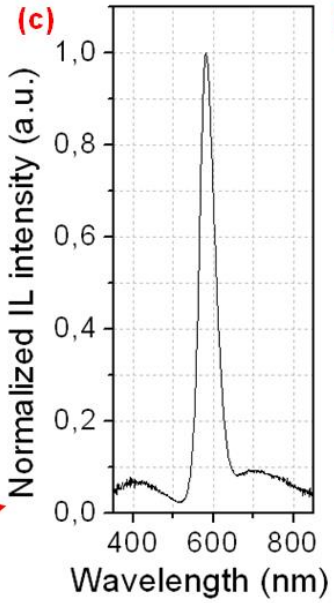


FIG. 2





(d)

Component	[%w]
SiO_2	56,7 ± 2,8
Al_2O_3	3,6 ± 0,2
FeO	0,14 ± 0,01
MgO	12,4 ± 0,6
CaO	24,5 ± 1,2
Na_2O	1,1 ± 0,2

Element	[ppm]
Ti	1000 ± 200
V	400 ± 80
Cr	90 ± 50
Mn	330 ± 40
Cu	110 ± 20
Zn	90 ± 20
Zr	1000 ± 140
Pb	870 ± 150

FIG. 3