Characterisation of lapis lazuli for a provenance study by means of SEM-EDX and SEM-cathodoluminescence

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Introduction

Lapis lazuli has been used for more than 7000 years for the manufacture of precious objects and jewellery. The main quarry for this rock in Afghanistan (Badakhshan) is still active (Figure 1), but there are other quarries that could have been exploited in antiquity [1–4]. Sources that have been suggested include: the Pamir mountains (Lyadzhuar Dara, Tajikistan) [1, 5], Pakistan (Chagai Hills) [4, 5], Siberia (Irkutsk, near Lake Baikal) [1], Iran [1, 3] and Sina [6]. The last two are not geologically confirmed and are still debated [2, 5]. For this reason, a provenance study of lapis lazuli could provide answers to some important issues, in particular for in-depth study of its use and distribution through historic commercial routes.

In the present work a systematic study has been performed on lapis lazuli from four quarries in Afghanistan, Chile, Siberia and Tajikistan using energy dispersive X-ray analysis (EDX) and cathodoluminescence (CL) coupled with scanning electron microscopy (SEM). The main goal of this characterisation was to find at least one marker for each provenance. These markers could be the presence or absence of a mineralogical phase, or one or more elements present in a particular mineral, or the different luminescence of the same mineral.

Figure 1 Lapis lazuli from Afghanistan.

Experimental

The analysed lapis lazuli samples are from the Museum of Natural History (Università di Firenze) and have been collected from four sources: Sar-e-Sang Badakhshan (Afghanistan), Ovalle (Chile), Irkutsk near Lake Baikal (Siberia) and the Pamir mountains (Tajikistan). A more detailed description of the samples under investigation has been reported elsewhere [7]. Fifteen semi-thin polished sections were prepared and a preliminary characterisation of the samples, identifying the distribution of the main mineral phases present in the rocks, was carried out by means of optical microscopy (OM) and cold-CL (CL8200 Mk3). After carbon coating (less than 0.5 μm in thickness) selected grains were studied by means of SEM-EDX (Leica Stereoscan 420 with an Oxford PentaFET EDX) and SEM-CL (Oxford MonoCL). All the SEM-CL measurements were performed in the range 350–750 nm at 15 kV energy, with a probe current of 1 nA, an investigated area of 20×25 μm^2 and 16 mm working distance. All the SEM-EDX measurements were performed at 20 kV energy with a probe current of 200 pA, an investigated area of 10×15 μm^2 and 19 mm working distance. To obtain the chemical concentration of each phase we also measured a set of 10 reference standards (calcite, apatite, jadeite, diopside, plagioclase, marcasite, tugtupite, sanidine, wollastonite and titanium oxide).

CL is a powerful technique used to rapidly identify the mineral phase distribution [8]. Luminescence is activated by defects in the lattice structure of the mineral. In some cases substitutional trace elements in the crystal can activate the process so that this technique is able to reach a sensitivity of some parts per million (ppm). Unfortunately it is not usually possible to quantify the elemental contents by analysing the intensity of the CL signal due to competition between luminescence centres and chemical elements that work as quenchers. However, by means of SEM-EDX and SEM-CL it is possible to obtain both the elemental composition of a small area (a few μm^2) and its luminescence properties in the ultraviolet (UV) visible spectral range.

Due to the heterogeneous nature of lapis lazuli (which may include lazurite, diopside, pyrite, calcite, wollastonite and K-feldspar, amongst other minerals), it is very difficult to