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μ-XRF Analysis of Trace Elements in Lapis Lazuli-Forming Minerals for a Provenance Study

Debora Angelici,[1,2] Alessandro Borghi,[1] Fabrizia Chiarelli,[2] Roberto Cossio,[1] Gianluca Gariani,[2] Alessandro Lo Giudice,[2,3] Alessandro Re,[2,3] Giovanni Pratesi,[4] and Gloria Vaggelli[5]

[1]*Dipartimento di Scienze della Terra, Università di Torino, Via Valperga Caluso 35, 10125 Torino, Italy*
[2]*Dipartimento di Fisica, Università di Torino, Via Pietro Giuria 1, 10125 Torino, Italy*
[3]*INFN Sezione di Torino, Via Pietro Giuria 1, 10125 Torino, Italy*
[4]*Museo di Storia Naturale, Università di Firenze, Via G. La Pira 4, 50121 Firenze, Italy*
[5]*CNR—Isitituto di Geoscienze e Georisorse, Via Valperga Caluso 35, 10125 Torino, Italy*

Abstract: This paper presents new developments on the provenance study of lapis lazuli started by our group in 2008: during the years a multi-technique approach has been exploited to obtain minero-petrographic characterization and creation of a database considering only rock samples of known provenance. Since the final aim of the study is to develop a method to analyze archeological findings and artworks made with lapis lazuli in a completely non-invasive way, ion beam analysis techniques were employed to trace the provenance of the raw material used for the production of artifacts. Continuing this goal and focusing the analysis on determination of more significant minero-chemical markers for the provenance study of trace elements in different minerals, the method was extended with the use of micro X-ray fluorescence (μ-XRF), to test the potential of the technique for this application. The analyzes were focused on diopside and pyrite in lapis lazuli samples of known provenance (Afghanistan, Tajikistan, and Siberia). In addition, μ-XRF data were compared with micro proton-induced X-ray emission (μ-PIXE) results to verify the agreement between the two databases and to compare the analytical performance of both techniques for this application.

Key words: lapis lazuli, μ-XRF, μ-PIXE, trace elements, archeometry

Introduction

Lapis lazuli is a blue semi-precious stone widely used since ancient times. The first traces of its use date 7,000 years ago for different purposes: beads, gems, seals, and small decorative artworks were widely distributed in the Ancient East. With the passage of millennia this blue rock continued to be appreciated and used by ancient civilizations, despite its rare occurrence, the limited number of the quarries, and the difficulty in reaching them in inaccessible places (Da Cunha, 1989). The only source of lapis lazuli known in ancient times were located in Afghanistan (Wyart et al., 1981), although other quarries might have been exploited since antiquity (Herrmann, 1968; Nibbi, 1981; Casanova, 2013); few of them have been considered in recent studies (Ballirano & Maras, 2006; Zöldföldi et al., 2006). For this reason, a provenance study of lapis lazuli could provide answers to some important issues, for example the use and dissemination of this rock through ancient trade routes, since written testimonies from ancient times are scanty or absent (Tosi, 1974).

Lapis lazuli may be either metamorphic or magmatic rock whose mineral content is characterized by widespread or localized occurrence of a blue feldspathoid, mostly lazurite, a sulphur-bearing member of the sodalite group (Hogarth & Griffin, 1976; Hassan et al., 1985). Paragenesis of lapis lazuli is further composed by a wide variety of mineral phases, the most common being diopside, wollastonite, calcite, pyrite, k-feldspar, and phlogopite (Hogarth & Griffin, 1978).

Our study in this field began in 2008 through a multi-technique approach (Lo Giudice et al., 2009) with the aim of obtaining petrographic and minero-chemical information in order to identify some peculiar markers that reflect different quarry districts for lapis lazuli. Owing to the complexity and heterogeneity of the rock and the need for collecting secure results linked to the provenance, the study was started on rock samples of known provenance, coming from four different quarry districts located in Afghanistan (Badakhshan), Tajikistan (Pamir Mountains), Siberia (Lake Baikal area), and Chile (Ovalle).

For the first step of the study, we prepared petrographic sections from the rock samples and their preliminary characterization by means of an optical microscope, cold-cathodoluminescence, μ-Raman spectroscopy, and SEM [scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM-EDX) and scanning electron microscopy-cathodoluminescence (SEM-CL)] to identify the occurrence and distribution of the main mineral phases in the rocks, their chemical composition, and their characteristic luminescence spectra. In this way we obtained an appreciable characterization of these rocks, but since the ultimate goal is analysis of archeological findings and artworks made with

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*Corresponding author. debora.angelici@unito.it