

IDENTIFICATION AND BE, LI CONTENT ASSESSMENT OF MINERALS IN GRANITOID ROCK SAMPLES BY LIBS

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1. INTRODUCTION

LIBS is a versatile, laser ablation-based atomic emission spectroscopy technique, which allows the fast and direct analysis of solid and liquid (even gaseous) samples with minimum sample preparation, in a non-contact, marginally destructive way [Galbács 2015, Fortes 2013, Hahn 2012]. Its routine configuration already makes trace (ppm level) elemental analysis possible for all elements of the periodic table. One of the most appealing characteristics of LIBS is the possibility of direct solid sample analysis, which makes it of interest also to geologists and mineralogists. LIBS geochemical analysis is generally directed towards one or the other of two primary and related goals: quantitative analysis of the elemental contents of rocks/minerals (e.g. ore prospecting) and identification of the minerals (e.g. mapping of geochemical and mineralogical footprints, provenance analysis). LIBS is being increasingly explored by geologists and the mining and mineral processing industry in the last 10–15 years and is now more and more used for the analysis of geological material (GEOLIBS) [Harmon 2019, Harmon 2013].

2. EXPERIMENTAL

2.1. Instrumentation

LIBS experiments were performed on a J-200 tandem LA/LIBS instrument (Applied Spectra, USA), in the LIBS mode. This instrument is equipped with a 266 nm, 6 ns Nd:YAG laser source and a six-channel CCD spectrometer with a resolution of 0.07 nm. For every laser shot, the full LIBS spectra over the wavelength range of 190 to 1040 nm

were recorded in the Axiom data acquisition software, using a 0.5 μs gate delay and 1 ms gate width. During the experiments, a 40 μm laser spot size was maintained. The pulse energy was generally set at 17.5 mJ and the laser repetition frequency was 10 Hz. The number of repeated measurements in one sampling location (without translation) was ten. The first shots were clean-up shots, so the spectra originating from them were discarded. Measurements were performed at 4-5 sampling points in each mineral grain (sampling was done in a total of 128 locations for biotite, 155 for feldspar, 83 for quartz and 4 for amphibole). LIBS experiments were carried out under argon, continuously rinsing the ablation cell with a gas flow rate of 1 L/min. Argon gas increases the signal intensities and the continuous flow decreases the fallout of ablation debris around at the crater. Contact profilometry measurements were performed on a Veeco Dektak 8 Advanced Development Profiler. The tip had a radius of curvature of 2.5 μm and the force applied to the surface during scanning was 30 μN . The horizontal resolution was set to 0.267 μm and 3.175 μm in the x and y scan directions, respectively. The vertical resolution was 40 \AA . Optical images of the rock samples were taken with an Olympus BX-43 microscope equipped with an Olympus DP-73 camera, under polarized and transmitted light.

2.2. Samples

Three samples (M1, M2, M3) were prepared from the Mórággy Granite rock for the study. The main mass of the Mórággy Hills belongs to the Eastern Mecsek Mountains of Hungary and consists of monzogranite, with monzonite inclusions crosscut by leucocratic dykes. The rock types of the Mórággy Granite Formation can be divided into four main groups: monzogranite (typical granitoid rocks); hybrid rocks; monzonite (dark in colour and rich in magnesium and iron-bearing minerals) and leucocratic (light) dykes of different compositions. Our studied samples are of the monzogranite type, i.e. a granite variant with 35–65% feldspar. Mórággy Granite contains common rock-forming minerals, quartz, biotite and, to a lesser extent, amphibole.

Two kinds of sample preparation were performed on the studied rock samples: bulk (polished surface) samples were prepared for LIBS measurements, whereas 30 μm thin sections were cut for mineral identification by transmission optical microscopy (in polarized and transmitted light).

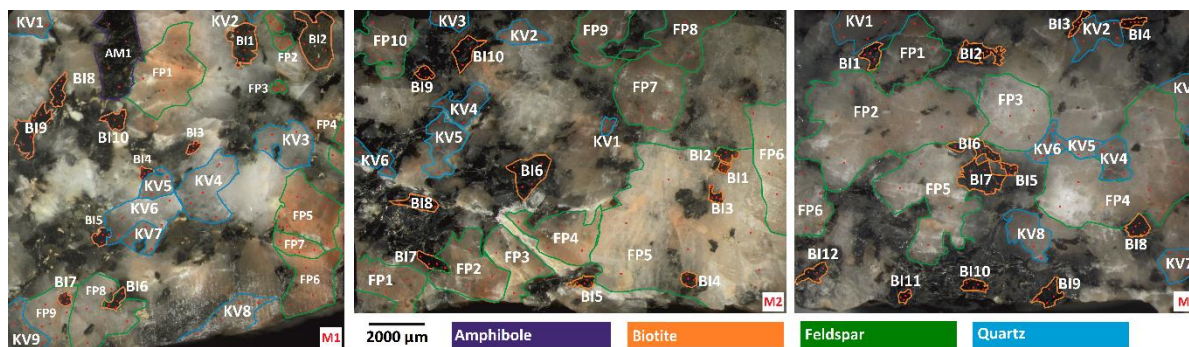


Figure 1. Microscope images of the rock samples M1, M2 and M3 (Mórágý). The four studied mineral types are indicated in the images with abbreviations and borderline colours: AM= amphibole (purple), BI= biotite (orange), FP= feldspar (green), KV= quartz (blue). Individual laser sampling locations are indicated by red dots.

3. RESULTS AND DISCUSSION

3.1. Compositional heterogeneity study of the mineral grains

Most mineral grains in igneous rocks grow during a longer time under various physical (first of all pressure and temperature) circumstances and changing chemical conditions resulting in internal chemical zoning patterns. These changes in chemical composition usually can be detected by different optical methods. Minerals of magmatic rocks, such as the granitoid rocks studied here, are usually zoned.

The extent of heterogeneity of the mineral grains in the samples was first investigated by repeated measurements. Individual LIBS spectra were collected from 10 shots delivered at 4–5 locations within each mineral grain. Spectra within each mineral across locations or depths (intra-mineral variations) were then compared to each other using the linear correlation function. It was generally found that there is a reasonable similarity of spectra, indicated by correlation factors of at least 0.85 in most cases.

3.2. Laser ablation characteristics of the mineral grains

To assess this, we investigated the laser ablation craters in the mineral grains by using contact profilometry. The results indicate that quantitative analysis (or certain discriminative analysis) can only be attempted with reasonable accuracy if matrix-matched calibration or at least crater volume normalization (with a general silicate standard, such as the NIST 6XX glass series) is performed.

3.3. Qualitative discrimination of mineral grains

3.3.1. Classification by using random forests

Random forests (RF) is a multivariate method of classification, which can be considered to be the advanced version of the classification (or decision) tree approach. In the present application, we trained the RF with datasets on M1 and optimized the number of trees as well as the number of nodes. It was found that the out-of-bag error initially steeply decreases with the increase in the number of trees and asymptotically reaches its minimum at around 50. Simultaneously, the increase of the number of nodes clearly deteriorated the out-of-bag error. RF gave good, well-balanced results.

3.3.2. Classification by using linear discriminant analysis

Linear discriminant analysis (LDA) is a widely employed classification technique. It constructs a linear regression model of the dataset and generates a linear surface in the multi-dimensional variable space that separates the classes. We tested canonical LDA on our uncompressed LIBS data. The overall classification accuracy was good correlated to the result of RF. False classifications can be mostly associated with quartz and feldspar.

3.4. Quantitative assessment of the distribution of selected trace elements

Beryllium is widely used, e.g. in telecommunications infrastructure, advanced medical diagnostics instrumentation, automobile components and aeroplane equipment. Lithium is also a greatly sought-after metal, as it is used in large amounts in batteries, ceramics and glass, lubricating greases and polymer production. Recent years have seen a particularly steep leap in the need for lithium batteries. For these reasons, governments and companies are actively searching for new Li and Be sources, as well as new technologies for economically extracting them. LIBS is a technique which has great potential in this quantitative application, because it is ideal to measure light elements.

3.4.1. Mapping of Be and Li

Step scanning with non-overlapping laser spots (resolution: 40 μm , laser pulse energy: 5 mJ) was employed in this investigation. Spectral intensity-based elemental maps for Be II 313.0 nm and Li I 670.7 nm lines can be seen in **Figure 2**. Here we demonstrate that it is possible to identify the type of mineral that contains most of the targeted trace elements. As Li^+ has a cation radius rather close to that of Mg^{2+} , in most crystal lattices Li incorporates to the position occupied by Mg. Among the studied phases, biotite and amphibole are the minerals where the $\text{Mg}\leftrightarrow\text{Li}$ exchange is possible. As there is no exchangeable cation in its structure, not surprisingly, quartz has the least traces of these metals. The distribution of Be and Li among the grains seem to be qualitatively correlated.

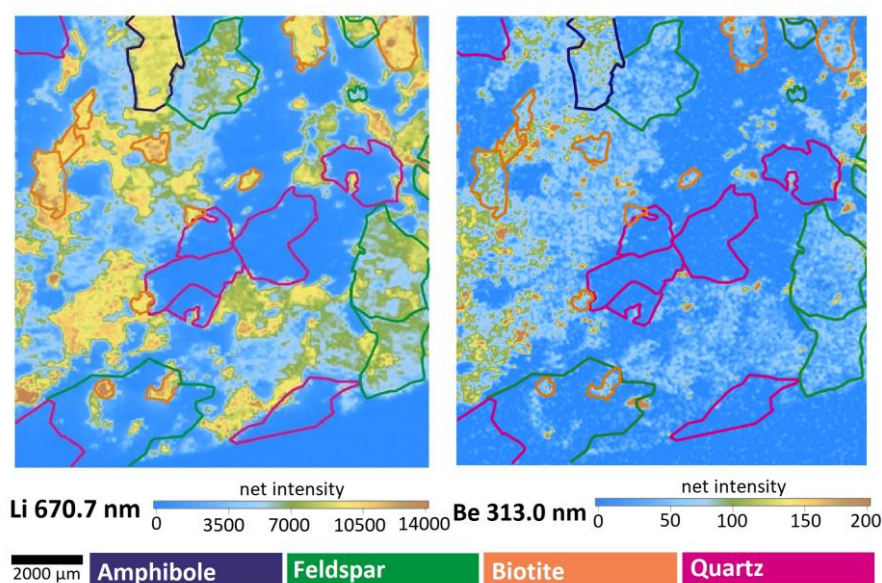


Figure 2. Intensity-based step-scan LIBS elemental maps of the M1 sample. Colors of the contours are indicating the mineral types, as seen in **Figure 1**.

3.4.2. Quantitative estimation of the Be and Li content

We also performed calculations to quantitatively assess the Be and Li content in the mineral grains of samples M1 to M3. Net Intensity data for the Li I 670.7 nm and Be II 313.0 nm spectral lines were converted to concentrations by calibration using matrix-matched standards. The NIST 612 standard was used for quartz calibration based on their similar laser ablation behaviour (similar crater volumes). The results justify the assumption suggested by the intensity-based elemental maps namely that the Li and Be content varies concertedly in all three minerals. The mass of the metals present in the grains naturally changes with the size of the grain. Not surprisingly, quartz contains the smallest amounts of both metals. It is also apparent that feldspar is the best source of Be, whereas biotite is for Li.

4. CONCLUSIONS

We have shown that LIBS mapping and spatially resolved local analysis is an efficient and practical approach for the classification of mineral grains (quartz, feldspar, biotite, amphibole) and for prospecting of technologically relevant elements in granitoid rock samples. We have tested three statistical approaches for the classification and it was demonstrated that better than 92% classification accuracy is achievable by using random forests and linear discriminant analysis. Direct classification by assessing the presence of the characteristic elements (decision tree based on indicative spectral lines)

is a powerful method but can lead to large failure rates in case of relatively impure minerals, such as quartz.

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