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Analysis of rock samples collected from rock hewn churches of Lalibela, Ethiopia using laser-induced breakdown spectroscopy

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ABSTRACT

With the aim to study alteration processes of the rock hewn churches from Lalibela (Ethiopia), we applied Laser Induced Breakdown Spectroscopy (LIBS) technique to measure the elemental composition both of the bulk rock materials and their external layers, exposed to the environmental factors. The analytical plasma was generated by nanosecond pulses of an Nd: YAG laser emitting at 1064 nm. Different major and minor sample constituents were detected, including Ca, Mg, Na, Fe, Ti, Al and K. The detected O emission originates both from air surrounding and the sample, while the intensity of N lines, coming exclusively from air, was used for the LIBS signal normalization. By depth profiling of the weathered basalt rock, we observed a lower presence of K in the external layers, corresponding to the first 5 laser shots. The emission from this element is anti-correlated with the line intensities from O, and this was attributed to the variations in relative abundances of clay minerals and K-feldspar. The analogue measurements were performed on the tuff rock, and compared to the spectra from powder samples containing only the external soft material, scratched from the rocks. These analyses show an abundance of H in the weathered, wetted layers and suggest that cations are lost from the constituent primary minerals and replaced by H^+; this process disrupts the lattice structure and causes a marked loss of strength. The studies presented here demonstrate that LIBS is a useful technique for studying the alteration processes in the rocks, caused by environmental factors.

1. Introduction

Ethiopia is one of the countries in the world known for its ancient rock-hewn churches. The largest groups of the rock hewn churches are situated in central and eastern Tigray (Asrat, 2002) and Lalibela. The latter location is famous for its extraordinary complex of monolithic churches, carved about 800 years ago during the Empire of King Lalibela. The main cluster of 11 churches is located in the middle of the village and they are: Bete Medhane Alem, Bete Michael Golgotha, Bete Maryam, Bete Meskel, Bete Danaghel, Bete Amanuel, Bete Merkorios, Bete Aba Libanos, Bete Gebriel Rufael, and Bete Giyorgis. Since 1978, these churches and their surrounding area have been included in UNESCO's World Heritage List (Asrat and Ayallew, 2011) (Fig. 1). The churches are still used daily for religious practices and ceremonies, while during major religious occasions large crowds of believers and pilgrims travel to the site. The churches have been exposed to different environmental factors, both physical (temperature and humidity) and biological (biodeteriogens), and also to human impact (pollutant releases) (Delmonaco et al., 2009). Water absorption represents the main factor contributing to a deterioration of the exposed rock materials and structures, in terms of direct rainfall, soil infiltration, capillarity and diffuse humidity, for the alteration of basalt (Delmonaco et al., 2009). Another study from Asrat and Ayallew (2011) reported material loss due to deep weathering activated by rain water penetration, while the leakage of groundwater affects most of the Lalibela churches too. This exposure has resulted in severe degradation of the churches, most of which are now considered to be in critical conditions. According to the state party report, presently the conservation and restoration of rock hewn churches of Lalibela is one of the main world concerns. The first restoration attempt of the Lalibela rock-hewn churches was carried out in 1920 (Delmonaco et al., 2009). Currently, most of the churches are protected by shelters in order to prevent the erosive effects of rainfall, especially on the roof rock cover, and by temporary scaffolding to prevent collapse of the most exposed structures.

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Fig. 1. a) Location of the Lalibela site (UNESCO); b) distribution of the 11 rock-hewn churches; powder samples collected from c) Bete Gebriel Rufael-internal; d) Bete Gebriel Rufael (BGR-E); e) Bete Giyorgis-Mahilet (BG-I); f) Bete Giyorgis-external; g) Bete Michael Golgotha.

During weathering of basaltic rocks induced by hydrothermal processes, different major and trace elements in the material are mobilized from the original rock (Ignacio et al., 2007; Aiuppa et al., 2000; Greenough et al., 1990; Lagat, 2007; Franzson et al., 2010). In another study (Gan-Lin et al., 2007), Fe and Al were relatively enriched while Ca, Mg, K and Na and Si were strongly diminished during the rock weathering and the corresponding soil formation.

In many cases the presence of biological colonization by lichens and macroscopic plants is quite evident. For the study of biological aspects of weathering of rocks and minerals, lichen-encrusted rocks provide an ideal environment due to a direct relationship between lichens and their substrates (Adamou and Violante, 2000). Lichens alter the mineral substrates both through physical and chemical processes. Lichens also have a significant impact in the chemical weathering of rocks by the secretion of various organic acids, particularly oxalic acid, which can effectively dissolve minerals and chelae metallic cations (Adamou and Violante, 2000; Chen et al., 2000). As a result of the weathering induced by lichens, many rock-forming minerals exhibit extensive surface corrosion.

LIBS is an analytical technique that enables the determination of the elemental composition of materials on the basis of the characteristic atomic emission from a micro-plasma produced by focusing a high-power laser on or inside a material. LIBS have been used in a wide variety of analytical applications for the qualitative, semi-quantitative or comparative analysis. Analysis can be carried out without physical contact with the examined sample, since only