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ORIGINAL PAPER

Provenance study of volcanic glass using 266–1064 nm orthogonal double pulse laser induced breakdown spectroscopy

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Double pulse laser induced breakdown spectroscopy in orthogonal configuration was used for the analysis of twelve samples of volcanic glass. Raw material and artifact samples originated from Czech, Slovak, German, Hungarian, Greek, Turkish, and Ukrainian sites. The primary 266 nm laser beam was focused onto a sample area of about 0.1 mm in diameter at the optimised energy of 10 mJ resulting in only very slight sample damage, almost unrecognizable even by a microscope. The secondary 1064 nm laser beam, positioned parallel to the sample surface and focused onto the intersection with the primary beam, induced a spark with enhanced radiation at the optimised energy of 100 mJ. Measurement of emission lines selected on basis of chemical composition, signal intensity, signal-to-background ratio, and minimum interference from the surrounding spectra: Si(I) 288.16 nm, Mg(II) 279.55 nm, 280.27 nm, Mg(I) 285.21 nm, Ca(II) 317.93 nm, Na(I) 589.59 nm, Al(I) 308.22 nm, Fe(II) 259.94 nm, Ti(II) 334.94 nm, Sr(II) 407.77 nm, Ba(II) 455.40 nm, K(I) 769.90 nm, provided experimental data sufficiently sensitive to differentiate the properties of the studied samples. Rare earth elements were not detected even though the double pulse technique is more sensitive than the single pulse variant. Visualisation methods of multidimensional statistical analyses such as radar chart, Chernoff faces, scatterplots, and the Spearman correlation matrix provided successful differentiation of the sample groups and/or particular samples by their origin.

Keywords: double pulse, laser induced breakdown spectroscopy, volcanic glass, obsidian, multidimensional statistics, provenance study

Introduction

Natural glasses have been exploited and studied in the past. Obsidian, which belongs to the group of glassy volcanic rocks such as tachylite (Taddeucci et al., 2004), palagonite, hyaloclastite, pitchstone (Heide & Heide, 2011), etc., is scattered throughout the world and represents one of the important natural raw materials used in the past for the manufacturing of tools and weapons due to its ability to provide an extremely sharp cutting edge (Přichystal, 2009). Typically, the goal of the studies using obsidian raw materials and artifacts is to find a relationship between the raw material deposits and the archaeological findings, and consequently, to trace ancient trade routes. The majority of these studies deal with obsidian sources from North America and Mesoamerica (Argote-Espino et al., 2012; Shackley, 2005). The current Web of Science database shows about 1100 references. From the analytical point of view, there are numerous techniques employed for the determination of obsidian elemental composition involving: Neutron Activation Analysis (NAA) (Frahm, 2012a; Tykot, 2002), X-Ray Fluorescence (XRF) (Grave et al., 2012; Shackley, 2010; Tykot, 2002) or portable XRF (pXRF) (Grave et al., 2012), Electron Probe

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