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Analytical Note

Effect of the wavelength on laser induced breakdown spectrometric analysis of archaeological bone☆

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ABSTRACT

The analytical exploitation of the laser induced plasma suffers from its transient behavior due to some nonlinear effects. These phenomena are matrix-dependent and limit the use of LIBS to mostly semi-quantitative precision. The plasma parameters have to be kept as constant as possible during LIBS measurements. Studying archaeological bone samples using LIBS technique could be more difficult since these samples are less tough in their texture than many other solid samples. Thus, the ablation process could change the sample morphological features rapidly resulting in poor reproducibility and statistics. Furthermore archaeological bones are subjected to diagenesis effects due to burial environment and postmortem effects. In the present work comparative analytical study of UV (266 nm) and IR (1064 nm) LIBS for archaeological bone samples belonging to four ancient Egyptian dynasties representing the middle kingdom (1980–1630 BC), 2nd intermediate period (1630–1539/23 BC), Roman–Greek period (30 BC–A.D. 395) and the late period (664–332 BC). Measurements have been performed under identical experimental conditions except the laser wavelength to examine its effects. Elemental fluctuations within the same dynasty were studied for reliable information about each dynasty. The analytical results demonstrated that UV-LIBS gives a more realistic picture for bone elemental composition within the same dynasty, and bone ash could be more suitable as a reference material for bone calibration in the case of UV-LIBS.

1. Introduction

Bone and teeth are calcified tissues where hydroxyapatite is a predominant constituent mineral. Trace elements are commonly found in the mineral phase of these calcified tissues, although some elements could be associated with the organic phase. The elemental composition in bones and teeth varies in concentrations (from several percents to ng per g) depending on the diet intake. In the case of human some elements are essential for bone development. Elements in minor and trace concentrations such as iron, magnesium, zinc, chromium, copper, and manganese are associated with bone development. The bone microstructure is often well-preserved down to the μm scale in fossil specimens recording growth marks and other histological features that are often used for life history reconstructions [1]. The chemical compositions of the mineral phase bioapatite and the protein phase, predominantly collagen, yield important information about palaeobiology and palaeoecology [1]. Elemental analysis of bone's major, minor and trace elements has been used to provide information about the relation between nutrition and diseases, health effect of trace element excess or deficiencies, to investigate exposure to toxic pollutants such as lead (Pb) in historical populations and to explore the source of specific nutritional deficiencies among ancient communities [2,3]. This can be attributed to the fact that once incorporated into the hydroxyapatite structure of the bone a number of elements are known to leach out very slowly [4]. Several factors could influence the concentration of trace elements in bone, especially in buried samples. Factors affecting bone trace element content (in addition to the diet intake) include: remodeling process [5], bone diseases [5–7], and direct exposure from contaminated materials [8,9]. Buried bones are exposed to different environmental conditions that can affect their natural elemental composition. Soil conditions such as temperature, pH, and water exposure can cause changes in the mineral composition of bones leading to exchange of ions with the environment [9]. Archaeological bones from different ancient Egyptian dynasties have been studied before. Discrimination between bones from different dynasties has been also demonstrated [3]. Different dynasties showed different levels of strontium which could be an indication of different dietary habits [3]. Elemental fluctuation within the same dynasty due to individual variations or different individual postmortem effects could lead to an unrealistic picture for the whole dynasty.

The aim of the present work is to study the laser wavelength effect on the elemental fluctuations in the LIBS spectra of archaeological bones within the same dynasty using conventional LIBS arrangement

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at two different excitation wavelengths, namely 1064 nm and 266 nm. Stratigraphic changes of the laser induced plasma will be also demonstrated to examine best conditions for LIBS measurements of archeological bones.

2. Methodology

2.1. Samples

The archeological bone samples used in the present study were from four different ancient Egyptian dynasties representing the middle kingdom (1980–1630 BC), 2nd intermediate period (1630–1539/23 BC), the late period (664–332 BC) and the Roman–Greek period (30 BC–AD 395). The archeological samples were authenticated and provided officially by the Egyptian Supreme Council of Antiquities from two different archaeological regions. The Roman–Greek, 2nd intermediate and Late period samples were from Sakkara nearby Cairo, while the middle kingdom and 2nd intermediate period samples were from Aswan in upper Egypt. Bone pellets from each dynasty were prepared by grinding the sample, mixing without binder for 10 min using an automatic mixer machine (Spex Sample Prep, Mixer/Mill 8000 M) and then pressing into a pellet using an automatic press (Spex Sample Prep, X-press 3630), to assure reproducibility, set at 25 tons of pressure for 1 min for each 5 g pellet. Bone ash standard was obtained from the National Institute of Standards and Technologies (NIST 1400). It consists of bone ash that was blended to a high degree of homogeneity. It has certified composition values (Ca 38.18%, P 17.9%, Mg 0.68%, Sr 249 μg/g, Fe 660 μg/g, Pb 9.07 μg/g, K 186 μg/g, Zn 181 μg/g.) and

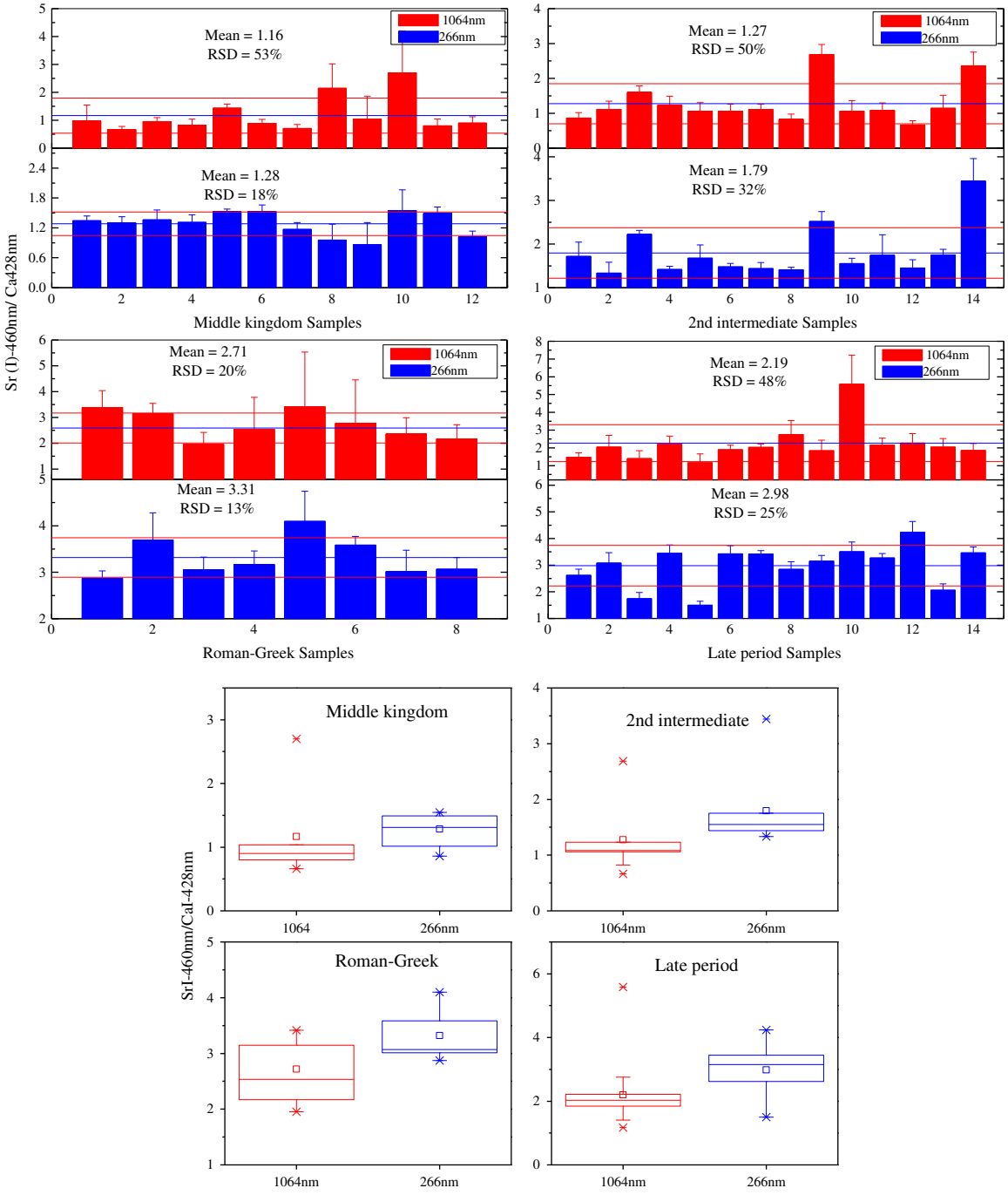

Fig. 1. Elemental fluctuation of (Sr) within the same dynasty.