

José M. Vadillo · I. Vadillo · F. Carrasco · J. J. Laserna

Spatial distribution profiles of magnesium and strontium in speleothems using laser-induced breakdown spectrometry

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Abstract Laser-induced breakdown spectrometry (LIBS) has been applied to spatially locate several atomic species in speleothems taken from the Nerja's Cave (Málaga, Spain). Spatial distribution profiles of Mg at 285.21 nm and Sr at 407.77 nm were obtained while the laser was rastered through different paths along the sample. These elements were selected due to their importance as palaeoclimatic indicators. The 532 nm output of a Nd:YAG laser was used to irradiate the samples and generate the plasma that was spectrally analyzed and detected by using an intensified CCD detector. The signals were normalized to the Ca line to minimize pulse-to-pulse fluctuations in the laser source. Several studies were carried out to check for the point-to-point heterogeneity of the natural speleothem.

Introduction

The potential use of lasers as excitation sources for spectrometric analysis of geological samples was recognized soon after the development of the first laser devices. The capabilities of laser microanalysis in several fields, in particular in geochemistry have been well-studied by different authors [1]. The role of lasers in microanalysis of geological materials has been important in particular when coupled to ICP-OES or ICP-MS systems [2–4]. For trace analysis it seems clear that this choice offers great analytical advantages as the atomization and ionization take place in different steps. However, in many applications requiring a fast “atomic-screening”, when major elements are studied, or when semiquantitative analysis may be ad-

equated, the use of direct laser systems followed by optical emission spectrometry of the produced plasma is the best choice, in particular if multichannel optical detection systems are used. This technique is commonly called laser-induced breakdown spectrometry (LIBS). Several papers and reviews detailing the theoretical background and diverse applications of LIBS are available [5–8].

Briefly explained, LIBS is performed by precisely focusing a laser beam over a sample (typically a solid). The great amount of energy deposited in a small area is able to vaporize, atomize and ionize the sample in a single step, producing a high-temperature plasma. The spectral analysis of such plasma gives complete information about the atomic composition of the sample in the spot area. Monitoring the signal for a given atom while the beam is rastered along a path permits compositional profiles of the atom of interest in the sample to be obtained [9, 10]. If required, the acquisition of consecutive laser shots over the same position provides information on the variation of composition with depth [11–13]. As sample preparation and chamber evacuation are not necessary, and the spectral record is instantly digitized and stored, very rapid determinations can be performed at a fraction of the cost of most other microprobes [14].

In the present paper, LIBS is used to study the atomic composition in speleothems, a typical non-homogeneous geological material. Speleothem deposition is typically caused by the degassing of groundwaters which contain elevated carbon dioxide concentrations. Speleothems are formed in cave systems and exhibit several forms such as stalagmites, stalactites and flowstones, and widely consist of different calcium carbonate-based minerals (aragonite, calcite, dolomite and others) in different proportions. As a consequence, different amounts of Mn, Mg, Fe and Sr can be found depending on the relative abundance of the cited minerals, although the number and quantity of the components can greatly vary even within the same geological formation [15, 16]. This mineralogical diversity, combined with diverse crystal habits and elemental and isotopic variability, allows for great variation in speleothems in response to environmental conditions. As most

J. M. Vadillo · J. J. Laserna (✉)
Department of Analytical Chemistry, Faculty of Sciences,
University of Málaga, Campus of Teatinos,
E-29071-Málaga, Spain
e-mail: laserna@uma.es

I. Vadillo · F. Carrasco
Department of Geology and Ecology, Faculty of Sciences,
University of Málaga, Campus of Teatinos,
E-29071-Málaga, Spain