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Evaluation of Laser Induced Breakdown Spectroscopy (LIBS) for detection of trace element variation through stalagmites: potential for paleoclimate series reconstruction

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ABSTRACT

Laser Induced Breakdown Spectroscopy (LIBS) is applied to evaluate the potential of this technique for characterizing trace element ratios (particularly Mg/Ca and Sr/Ca) in the speleothems (cave deposits of calcium carbonate such as stalagmites) that are commonly used to reconstruct time series of past climate change. These geological materials are characterized by a relatively simple internal stratigraphy that reflects their growth history and geochemical changes through that history can reflect variability in environmental parameters such as temperature and rainfall. In this paper, the characterization of methodological and experimental parameters such as sample preparation, microsample size and representativity, sensitivity, linearity, and replicability reveals the high potential of the technique and show clear advantages versus other commonly-used techniques.

1. INTRODUCTION

Inherent advantages to the LIBS technique (which include high speed analysis, little or no sample preparation, and high sensitivity) are making it a very versatile tool in many research areas [1]. Earth Sciences are not an exception, and emergent disciplines such as paleoclimatology require methods capable to yield high-resolution geochemical data through heterogeneous materials to obtain paleoclimate information. Speleothems (cave deposits such as stalagmites and stalactites) are an excellent example [2]. They are widely used in paleoclimate reconstruction because they grow during hundreds or thousands of years by the addition of successive layers of calcium carbonate [3], and simultaneously they are capable of recording past environmental conditions in their chemical composition. The calcium carbonate contains varying amounts of trace elements such as Mg, Sr, Ba, and others, which can be interpreted as climate proxies because their relative abundance can be controlled by environmental factors like surface temperature or rainfall [4-10]. If the growing age is known, speleothems allow the construction of high-resolution series of climate variability [2-9,11-19].

Several analytical techniques allow the detection of trace elements in speleothems. However, in most cases it is necessary to find a balance between the volume of sample and the accuracy and precision required, and take into account the speed and cost of the analytical procedure. Laser Induced Breakdown Spectroscopy (LIBS) has great potential as an analytical technique since it provides sufficient analytical sensitivity to detect the most abundant trace elements in $CaCO_3$ micro-samples. It is also much faster since can analyze various trace elements simultaneously [20]. Therefore, it has become a very useful tool to analyze geological samples [21-24]. However, none of these papers has evaluated the potential of the technique in a systematic way, e.g. validating the results by means of tests focused in homogeneity and reproducibility of the analysis, which is one of the main objectives of this paper.

LIBS technique involves the generation of plasma in air at atmospheric pressure by focusing a high-

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energy laser beam on the surface of a sample of interest. An optical fibre is used to capture the emission light from the plasma and a spectrometer is used to identify the elemental composition of the target; it can detect point-to-point differences of the elements that form the atomic composition of the sample.

In this paper, an analytical approach to the study of speleothems by LIBS is presented. Several control tests were conducted to check the reliability and accuracy of the technique as well as the representativeness of the data. For this purpose, a stalagmite retrieved from Kaite cave (Ojo Guareña Karst Complex, Spain) was selected, and the Mg/Ca and Sr/Ca intensity ratios were chosen for analyses because of their potential to reconstruct past environmental changes. Variations in these ratios through the growth history of a stalagmite can be used as paleoenvironmental or paleoclimatic indicators because the rate of incorporation of trace elements to the speleothem calcite can be indirectly controlled by environmental factors such as surface temperature or rainfall. Establishing cause/effect relationships between climate and trace element concentration is however not, a straightforward task, and requires complex, long-term monitoring programs capable of characterizing the hydrochemistry of the cave system. If we accept that the distribution coefficients of Mg and Sr are not significantly affected by the small temperature changes of cave air [25], partitioning of Sr^{2+} and Mg^{2+} in calcite under karst analogue experimental conditions or by the minor variations occurring in stalagmite growth rates [11], the research must be focused on the cave drip-waters from which the stalagmite grows. Because the composition of drip-waters depends on water-soil and water-rock interactions occurring before the water reaches the cave, any change in the soil or in climate parameters such as rainfall and temperature can modify the hydrochemistry of drip-water, and thus the trace-elements concentration of the stalagmite. The complex processes involving climate, soil evolution, and water-rock interaction with the host carbonate rock should be clearly understood in order to generate reliable transfer functions between stalagmite geochemistry and paleoclimate in each cave.

2. SAMPLE PREPARATION

The selected stalagmite is being studied in the framework of a broad paleoclimate research program. It was reconstructed from several broken pieces collected in the Buda hall in the innermost part of Kaite cave. The stalagmite is conical in shape and very elongated (112 cm long, 5-6 cm in diameter). It consists exclusively of calcite, and shows an internal stratigraphy defined by a pervasive micron-scale growth lamination. Unpublished U-series age-dating performed within the research project indicates that the stalagmite grew during the middle Holocene, and confirms the annual character of the lamination.

The pieces of the stalagmite were prepared for analyses according to the following steps: 1) each piece was cut vertically along the growth axis of the stalagmite; 2) 19 successive slabs of 5x8x0.5 cm were prepared to perform petrographic sections with a thickness of 500 microns; 3) the surface of each petrographic section was polished. All sections were studied under a petrographic microscope in order to characterize the internal microstratigraphy and to select the most favourable areas for the analysis. Figure 1 shows a petrographic section of the speleothem.

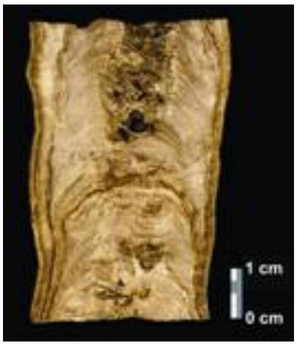

Figure 1: Stalagmite retrieved from Kaite cave (Ojo Guareña Karst Complex, Spain) showing stratigraphy and dimensions.

3. EXPERIMENTAL SET-UP

LIBS technique and the methodology used in the present work together with the most significant experimental conditions have been previously described [26, 27]. Briefly, LIBS measurements were obtained using a Q-switched Nd:YAG laser (Quantel, Brio model) operating at 1064 nm, with a pulse duration of 4 ns full width at half maximum (FWHM), 4 mm beam diameter and 0.6 mrad divergence. The laser fluence was fixed to 20 J/cm² and the repetition rate was 1 Hz. Samples were placed over an X–Y–Z manual micro-metric positionator with a 0.5 µm stage of travel at every coordinate to ensure that each laser pulse impinged precisely on selected area of the speleothem surface. The laser beam was focused with a 100 mm focal-distance lens. Emission from the plasma was collected with a 4 mm aperture, and 7 mm focus fused silica collimator placed at 3 cm from the sample, and then focused into an optical fiber (1000 µm core diameter, 0.22 numerical aperture), coupled to a spectrometer. The spectrometer system was a user-configured miniature single-fiber system EPP2000, StellarNet (Tampa, FL, U.S.A.) with a CCD detector with a spectral resolution of ±0.5 nm. A grating of 300 l/mm was selected; a spectral resolution of 0.5 nm

was achieved with a 7 µm entrance slit. The wavelength range used was from 200 to 1000 nm.
Each point analysed was exposed to 3 laser shots before performing the measurements to eliminate any impurity on the surface. The recorded spectra are the average of 20 laser pulses at each single position. The lateral resolution between spectra was 500 µm. The spectral data was processed using an interface created in Matlab software (Mathworks, 2010a).

4. RESULTS AND DISCUSSION

Mg/Ca and Sr/Ca which are among the most frequently used indicators in paleohydrological/paleoclimate studies were selected [11,28-31]. Figure 2 shows a typical LIBS spectrum of the speleothem sample measured at atmospheric pressure. The more important emission lines were assigned using NIST database [32].

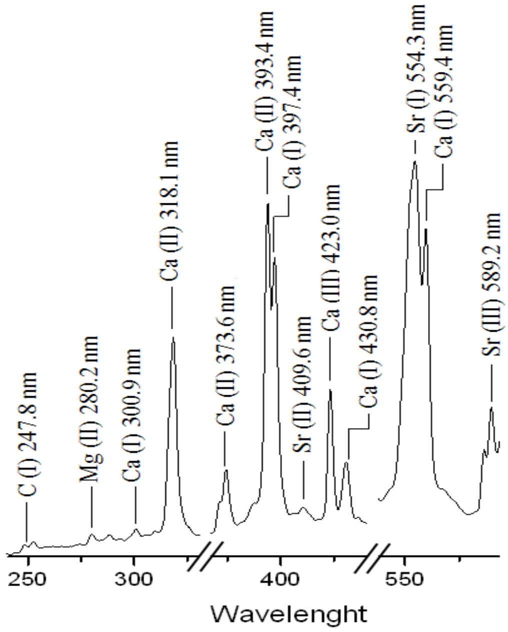

Figure 2: Typical LIBS spectrum of speleothem sample.

The plasma temperature can be checked by monitoring the ratio of two atomic spectral lines in the LIBS experiment (Boltzmann plot) [20,24]. If there is no significant variation in the temperature of the plasma during the experimental measurements, a more accurate comparison between the emission intensity of the spectral lines and the corresponding analytical response is obtained. In this work, the plasma temperature was monitored by the ratio of emission intensities of two lines of calcium: Ca (I) at 430.8 nm and Ca (I) at 445.4 nm ($I_{Ca430.8}/I_{Ca445.4}$). Figure 3 shows that the plasma temperature is kept nearly constant throughout the LIBS measurements, minimizing the matrix effect and providing more accurate results. Therefore, emission intensity variations of the elements in the speleothem sample can only be attributed to elemental concentration changes, enabling paleoclimatic studies.

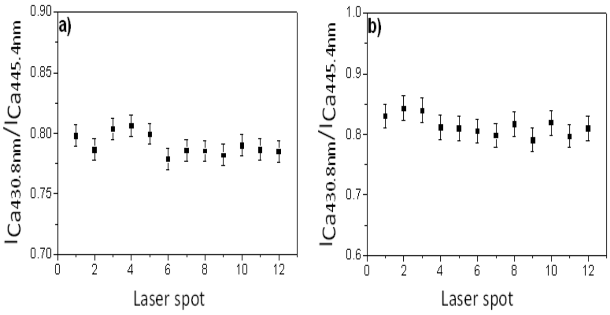

Figure 3: Graph of the ratio of intensities between the two lines of calcium: a) in the same layer, b) in two parallel lines along the growing axes.

4.1 Homogeneity test

A series of measurements were made on the polished section of the stalagmite in order to check the homogeneity of the sample in terms of uniformity of results along a single (annual) growth layer. The test included twelve analyses that revealed a remarkably lateral continuity in both Mg/Ca and Sr/Ca intensity ratios. Figures 4a and c show the results obtained to check the lateral continuity of the growth layer. Figure 4b shows a picture of the thin layer where the uniformity tests were performed, showing the craters left by the LIBS shots.
Even with the micrometric positioning system, the stratigraphy of the thin layer does not allow tracing in the same layer for the first four values in the continuity test as shown in Figure 4a, which are clearly out of line and whose intensity values are also outside the "normal" trend observed in the other measured points. However, a high correlation between Mg/Ca and Sr/Ca ratios with great stability within the layer is observed, showing annual layer uniformity and repeatability.

4.2 Repeatability test

The analytical repeatability was assessed by measuring Mg/Ca and Sr/Ca intensity ratios of 140 single points along two parallel lines separated by 3 mm, collinear to the growth axis of the stalagmite in the same thin section. The results (Figures 5a and c) show a good match between the two transects analyzed. Figure 5b shows the laser shots realized on the surface of speleothem. This test allowed comparing the relationship of Mg/Ca and Sr/Ca to evaluate the stability and irregularities/mergers within the annual layers, which could have a major influence on the analysis.

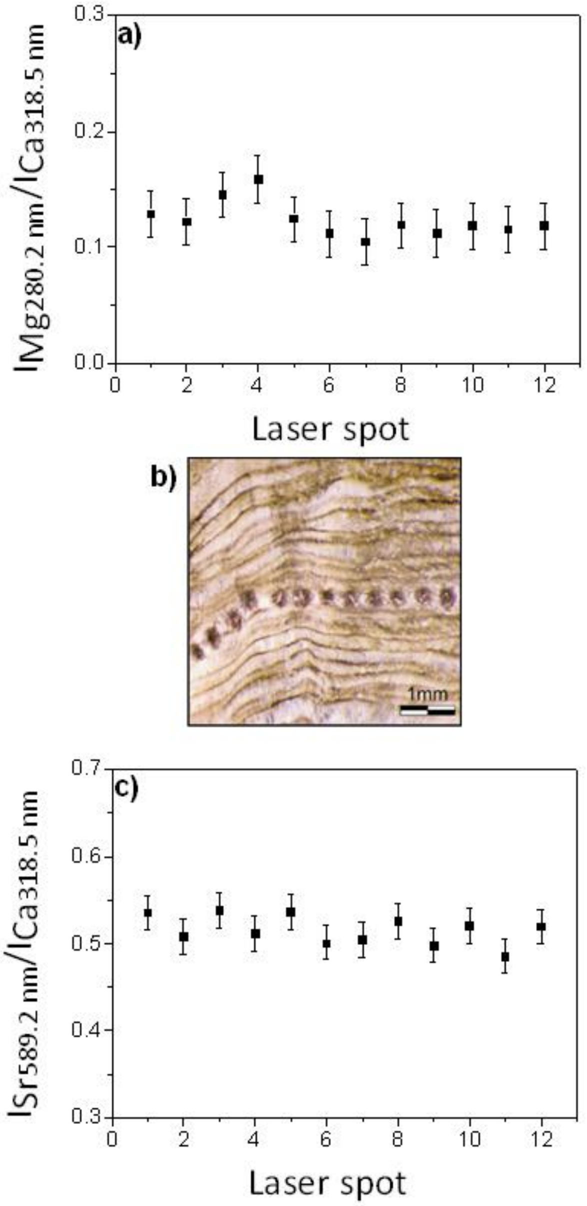

Figure 4: a) lateral homogeneity of the Mg / Ca ratio, b) picture of the layer growth, and c) lateral homogeneity of the Sr / Ca ratio.

As seen in these figures, the tendency of the intensity ratios Mg/Ca and Sr/Ca in the parallel lines along the axis of growth is very similar and the maximum and minimum trends are maintained in both lines. Small differences can be explained by the concentration of Ca which also varies along the growth axis. On the other hand, the stratigraphy of the stalagmite (displacement along growth axes) must be taken into account when explaining the differences in the relationships of emission lines, since there are irregularities and mergers between annual growth layers.

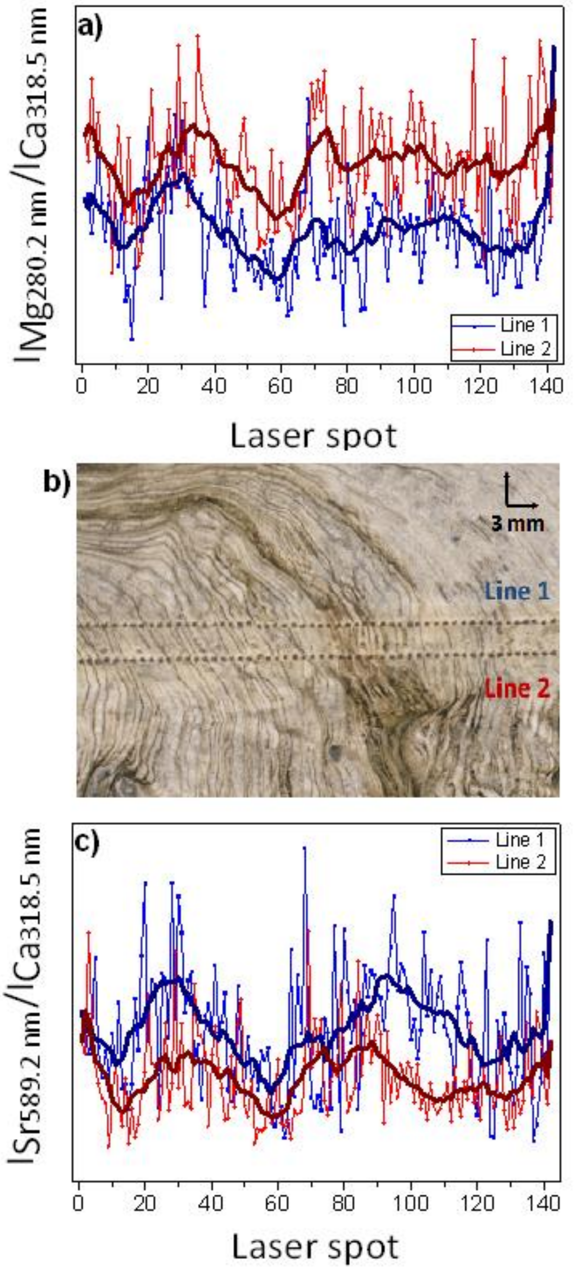

Figure 5: a) Results of replicability test for Mg/Ca ratio, b) picture of laser shots, c) results for the Sr/Ca ratio. Line 1 and 2 has been shifted for better observation. (The displacement along growth axes has not been taken into account)

Results show that speleothem sections can be adequately analyzed by LIBS, despite of the sample inhomogeneity. On the other hand, homogeneity and reproducibility tests demonstrate two aspects: 1) LIBS has enough sensibility from analytical point of view, which can be observed by uniform lateral continuity and 2) enough resolution from geological point of view, as shown by microstratigraphical succession analysis. In addition the test demonstrates that the speleothem samples had not suffered dissolution and/or recrystallization process that could alter the composition otherwise the homogeneity and replicability were not be observed.

Another advantage of LIBS is its capacity to analyze speleothem proxies at several points performing a simultaneous multielemental scanning even providing a map of elemental distribution at a cost much less as compared to other techniques. Thus, the tests demonstrate that LIBS is a suitable technique to obtain compositional evolution series through dated speleothem with paleoclimatic interest.

CONCLUSIONS

LIBS has been employed for detection of variations in trace elements along stalagmites. Tests performed by LIBS show its potential for the reconstruction of paleoclimate series and have been reported for the first time. The tests lead to improve and develop a methodology to analyze a speleothem sample and decipher paleoclimatic information stored on it.

In spite of difference in the homogeneity between successive layers of the speleothem, the LIBS technique performed efficiently, providing accurate results as demonstrated by the repeatability and replicability tests.

The reconstruction of paleoclimate series from speleothems commonly involves large amounts of geochemical analyses performed from tiny samples, so LIBS has demonstrated being an analytical techniques capable of achieving a good balance between: 1) the volume of material analyzed (and hence the spatial scale of analysis), 2) the precision and accuracy of the results, and 3) the speed and cost of the analytical process. Mainly, because although the LIBS technique only vaporizes a minuscule fraction of the sample in each laser shot, it provides good analytical sensitivity to the trace elements present in the speleothem.

LIBS allow replicability of high-speed analysis, even for long series, revealing the high potential of the technique and clear advantages over other commonly-used techniques, with reasonable spatial *resolution and excellent reproducibility.*

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