UNIVERSIDAD DE MÁLAGA

LIBS ANALYSIS OF GEOLOGICAL SAMPLES

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A speleothem is a secondary mineral deposit formed in caves. These deposits have recently emerged as prime archives for paleoclimate studies. A close relationship between the hydro- logical conditions during speleothem formation and its growth rates and composition has been demonstrated. Stalagmites (mostly comprised of $CaCO_3$ either as calcite or aragonite) are particularly useful for palaeoclimate applications, thanks to their relatively simple geometry. Elemental chemical indicators include the substitution rate of divalent cations (Sr, Mg, Ba) for Ca in its structure. In addition, elements associated with the detrital layer (aluminosilicate minerals; Al and Si) may be also trapped in stalagmites. All of these parameters may be influenced by climatic processes. In this sense, Mg/Ca, Ba/Ca, and Sr/Ca concentration ratios are often monitored with the objective to correlate the speleothem composition with the climatic processes. In some cases, seasonal differences in climate or cave environments result in subannual scale geochemical variation in stalagmites. At typical stalagmite growth rates, annual layers may range from tens of microns to millimetres depending on the drip rate. Thus, the analysis of trace elements in speleothems at high spatial resolution is therefore desirable

LASER TECHNIQUE

Laser technology could be considered as an alternative method in the analysis of geological samples. LIBS is based on the laser-matter interaction when a laser pulse of high power impacts the sample surface to generate a microplasma of high temperature and electron density.

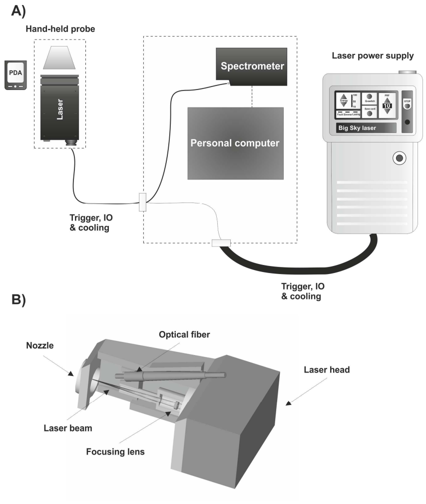

Figure 1. Schematic diagram of a portable LIBS instrument used for the in-situ analysis of speleothems.

Pulses from a laser source are focused on the sample using an appropriate optical configuration. Then, the plasma light (containing the analytical information concerning the sample) is collected and guided to the detector. The characteristic atomic emission peaks in the LIB spectrum enable identification of the elements contained in the material. In the case of the instrument employed. Figure 1 shows a Schematic diagram of a portable LIBS instrument used for the analysis of geological samples.

LIBS ADVANTAGES

Advantages of laser-induced breakdown spectroscopy (LIBS) for geological exploration:

- No sample preparation
- Analysis at atmospheric pressure and room temperature
- No sample restriction in size and shape
- In-situ analysis in real environments
- Good lateral and in-depth resolution
- Fast analytical response
- Qualitative and quantitative analysis
- Spot size in the order of a few micrometers in diameter
- No destructive analysis
- Capability for remote and stand-off analysis

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Figure 2. Photo of the man-portable laser system during the field campaign carried out in the Nerja Cave.

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The Laser Laboratory has pioneered the design, building and development of sensors, which integrate analytical technologies into mobile platforms that may be moved to any real-world environment, therefore allowing the in-situ analysis of the sample of interest. Figure 2 shows a snapshot of the man-portable laser system during the field campaign carried out in the Nerja Cave. LIB spectra corresponding to the matrix of the speleothem is characterized by the emission lines of C, Mg and Ca, according to the typical marble composition of the Cave of Nerja (Figure 3). In addition, the alteration layer usually presents significant amounts of iron, silicon and aluminum, that may help in estimating its thickness (Figure 4). Concerning trace elements such as Sr, Mg, P and Ba,
En cuanto a los componentes minoritarios como Sr, Mg, P y Ba, are often used as paleoclimatic indicators. Thus, the ratios of these elements to calcium offers a valuable climate information about wet and dry periods from the speleothem formation (Figure 5).

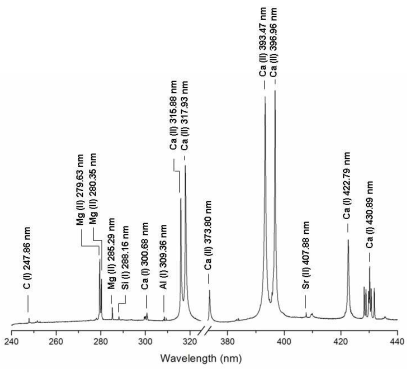

Figure 3. Chemical characterization of a speleothem by LIBS.

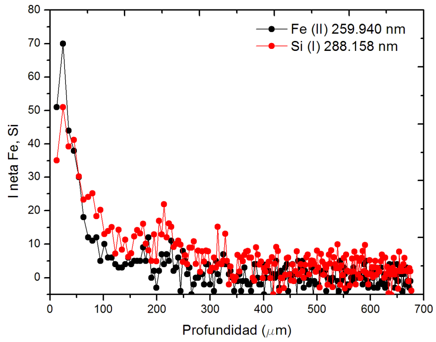

Figure 4. LIBS depth profile of Fe and Si intensity in a speleothem

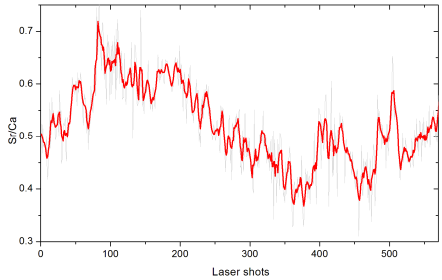

Figure 5. Variation of the Sr/Ca signal along the growing axis of the speleothem.

CONCLUSIONS

The minimum damage of the sample surface and its easy portability makes laser-induced breakdown spectroscopy an ideal method for the analysis of geological materials.