Climate Change: The Karst Record
7th International Conference
KR7 “Down Under”

Melbourne, Australia
29th September – 3rd October 2014
Scientific Programme and Abstracts
The western half of the Tropical Pacific is the hot spot of cyclogenesis on Earth, with an average of 10 cyclones impacting the SW Pacific region per year. During El Niño years, cyclone activity migrates eastwards and affects the islands and populations of the central Pacific. To evaluate the capacity of the sampled speleothems to register cyclones hitting the Pacific, the potential of Laser-Induced Breakdown Spectroscopy (LIBS) has been investigated. Despite its potential and advantages, (low cost, non-destructive, rapid analysis, essentially no sample preparation...) LIBS has been only sporadically used in speleothems (e.g., Vadillo et al. 1998, Ma et al. 2010, Galbacs et al., 2011, Forte et al., 2012) with promising but still very preliminary results. The technique provides semi-quantitative elemental measurements with micrometric spatial resolution. Main advantage is direct sampling by laser ablation under atmospheric pressure and in situ analysis of the plasma. The analytical technique is performed by laser beam focusing over a sample. The great amount of energy deposited in a small area (microns) is able to vaporize, atomize and ionize the sample 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.

This work presents an evaluation of the performance of LIBS as anayser to construct accurate trace element time-series based in speleothems. For this a series of tests performed on polished sections of a stalagmite were made. The chosen stalagmite, retrieved from Kaita Cave (Northern Spain), consists of calcite and shows a well-defined micrometric annual laminaton. The steps followed to perform the evaluation refer to two aspects: adaptation of the appropriate sample strategy for the analysis and characterization of precision of the technique in terms of repeatability under controlled and stable working conditions (fixed plasma temperature and laser pulse length). The selected elemental ratios for the study were Mg/Ca and Sr/Ca, which are among the most frequently used ones for paleohydrological/paleoclimate studies.

The reconstruction of paleoclimate series from speleothems commonly involves large amounts of geochmical analyses performed from tiny samples. So the task requires of analytical techniques capable of achieving a good balance between: 1) the volume of material analysed (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. Unfortunately, when working with speleothem trace elements, that balance is not always conveniently reached.

In the task of looking for new techniques for trace element analyses in speleothems, the potential of Laser-Induced Breakdown Spectroscopy (LIBS) has been investigated. Despite its potential and advantages, (low cost, non-destructive, rapid analysis, essentially no sample preparation...) LIBS has been only sporadically used in speleothems (e.g., Vadillo et al. 1998, Ma et al. 2010, Galbacs et al., 2011, Forte et al., 2012) with promising but still very preliminary results. The technique provides semi-quantitative elemental measurements with micrometric spatial resolution. Main advantage is direct sampling by laser ablation under atmospheric pressure and in situ analysis of the plasma. The analytical technique is performed by laser beam focusing over a sample. The great amount of energy deposited in a small area (microns) is able to vaporize, atomize and ionize the sample 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.

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To choose the adequate sampling method 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 was based in twelve analyses that revealed a remarkably lateral continuity in both Mg/Ca and Sr/Ca intensity ratios. After the measurements, the laser induced damage was determined by optical microscopy to assess both the spatial distribution of the spots along the growth layer and their morphology and diameter. The spot area shows an ellipsoidal shape crater around 300μm of average diameter, lower than the thickness of the growth layer (average 450μm wide).

The analytical repeatability was assessed by measuring Mg/Ca and Sr/Ca intensity ratios of 140 single points along two transects separated 3mm, parallel to the growth axis of the stalagmite, showing a good match between both transect. The average pulse length was 4ns and the stability of the signal was assessed from repetitive measurements on the same spot area (20 laser shots at each sample position). The plasma temperature was monitored by the ratio of emission intensities of two lines of calcium: Ca (I) at 430.77 nm and Ca (II) at 318.13 nm (ICa430.77/ICa318.13), showing that the plasma temperature is kept nearly constant throughout the experiment LIBS, minimizing the effect matrix and providing more accurate results.

Results support LIBS as a suitable system for trace elements analysis on speleothems. Main advantages of the technique are: relatively low operational costs and less maintenance and man-power compared to other techniques. The technique demonstrates good precision and is able of simultaneous detection of several species.

References