RAMAN SPECTROSCOPIC CHARACTERISATION OF GREEN-BLUE STALACTITES IN LANTZ CAVE (NAVARRA, NORTH OF SPAIN). S. Fdez-Ortiz de Vallejuelo*, K. Castro, I. Martínez-Arkarazo and J.M. Madariaga,

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Speleothems, including stalactites, stalagmites and columns, are typically associated with mineral precipitation in the dark, enclosed environments of caves, and theirs growth is related to climatic controls as temperature, precipitation and vegetation cover [1,2].

Cave of Lantz is located between a large number of relatively small Roman mines caves, 2.5 Km far away from the Lantz village (Navarra, north of Spain). It is considered one of the most perfect manifestations of green speleothems in the world.. The cave's speleothems (stalactites, stalagmites, etc.) vary widely in their morphology and mineralogy causing different shades. In our case, this study was focused on green surface coloration of stalactites.

For the characterization of speleothem samples from Lantz cave, directly on the surface, different analytical techniques were used: X-ray Micro-Fluorescence (μ-EDXRF) using portable ArtTax μ- EDXRF equipment by Rontec (nowadays Brucker AXS; Berlin, Germany) to determine the elemental composition and Raman spectroscopy using InnoRam ultramobile spectrometer (B&WTEK$_{INC}$, Newark, USA) provided with a 785 nm excitation laser with a nominal laser power of 225 mW and a CCD detector, for the characterization of the molecular composition. Treatment and interpretation of the results was carried out with Omnic Nicolet software (Madison, Wisconsin, USA).

In addition to the predominantaragonite (small and large crystals), calcite (columnar, fiber, and grain coating mats) and dolomite [3,4], other minerals were identified. These minerals were cuprite (copper(I) oxide, Cu_2O), hollandite (barium manganese oxide, $BaMn_8O_{16}$) and azurite (basic copper carbonate, $2CuCO_3{\cdot}Cu(OH)_2$). In these samples, quartz and carbon particles were also found.

The Raman spectra of the aragonite and dolomite minerals are shown in Figure 1.

Apart from the elements involved in the mentioned minerals, As, Co and Fe were identified by X-ray microfluorescence as trace elements. The results were correlated with mineral compositions found by Raman measurements.

Water samples were measured by Inductively coupled plasma mass spectrometry (ICP-MS) for interpreting trace elements (Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Sn, Sb, Ba and Pb) ratios of speleothems and freshwater deposits.

According to the results, trace element concentrations vary between drip waters of these green stalactictes and waters from other parts of the cave.

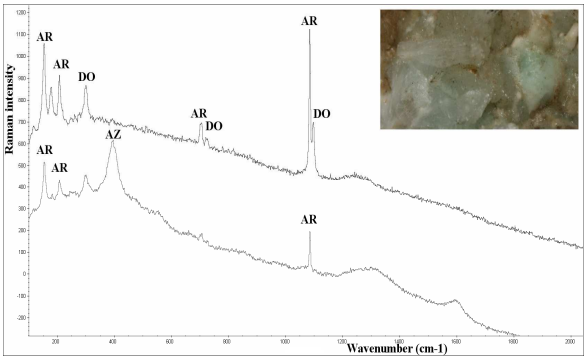

Figure 1. Raman spectra of samples of green-blue stalactite from cave of Lantz; AR: aragonite, $CaCO_3$; DO: dolomite, $CaMgCO_3$ and AZ: azurite, $2CuCO_3{\cdot}Cu(OH)_2$.

References

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