	Experiment title: High-resolution geochemical characterization of carbonates in annually laminated stalagmites for palaeoclimatic interpretations	**Experiment number**: CH-1458
Beamline: ID 21	**Date of experiment**: from: 12 jun 03 to: 17 jun 03	**Date of report**: August 1, 2003
Shifts: 15	**Local contact**: Dr. Jean Susini	*Received at ESRF*

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Materials and methods:

Double polished thick sections from annually laminated stalagmites (ER 78, Savi, BS 21) were mounted on special plastic specimen holders for ID 21 and glued with Zaplack (no S-containing glue).

At ID 21, SXRF was used for both mapping of trace elements (we obtained 18 maps), and long line scans (15 scans, among which 4 at very high resolution, i.e. 1 micrometer-steps). The analyses were carried out under vacuum, with beam tuned to S edge - Excitation energy 2.45 to 2.55keV. Spot size: 1 micrometer.

Constant control of the analysed spot was possible through the beamline microscope and camera. We, thus, could follow simultaneously the scan and the microstratigraphy

(structure of the lamina), with the great advantage of observing at the same time the structure of the lamina and that of the spectrum for each element.

We realized that through polishing we might have induced some artifacts regarding the distribution of surface-sensitive elements. Fortunately, we could control this through the observation of the pattern in the oxygen maps. Oxygen is the most sensitive to roughness in sample surface. The map of oxygen intensity distribution mimicks the surface texture induced by polishing, and, therefore, acted as reference to determine exactly the position of specific features within the sample. No other light elements seem to follow the oxygen pattern. We, therefore, conclude that the concentration distribution observed in the Mg, P, Si, S maps were real, and not artifacts.

We could use all the allocated beamtime successfully.

Results:

The following results apply to all specimens:

S: is mostly present in sulfate. Sulphur seems to be concentrated in P-rich layers, along micro cracks and as particles, in association with Si, Mg and P. Sulphur appears to increase in concentration towards the last 100 years. In Savi we found a S-rich layer, which may be the record of volcanic emission (to be checked with the age model). Further synchrotron analyses would help to decipher the potential of stalagmites as archives of atmospheric aerosol concentration changes. In particular, if we will be able to demonstrate that sulphate layers record episodes of volcanic emissions, this will be a major breackthrough in palaeoclimate investigation.

Si: This element appears to be concentrated in grains and at crystal boundaries

P: This element appears to be concentrated in the dark layers within the laminae. It shows some co-variance with S. However, its trend differs from that of S, and of all the other elements. P is the light trace element which is clearly most related to the dark layers (where heavier elements such as and Br are concentrated, see report of experiment CH 1365).P seems to show a long wavelength (circa 3 mm) variability superimposed to the short-term variability. This is very important, because P was considered to be "flushed in" during flushing episodes. Experiment CH-1458 data indicate that P is NOT "flushed in". Further analyses are needed (coupled with drip-water analyses which are currently being carried out) to understand if we are confroted with a combination of water chemistry and kinetic effects.

Mg: Mg does not show long-term trends, its content is relatively constant. It is present both as trace element in calcite, and as component of allochtonous inclusions (silicates). For the identification of inclusions, maps proved fundamental. This information will be very useful when comparing synchrotron and SIMS data.