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ESRF

ESRF	**Experiment title: High-resolution elemental variability in stalagmites and a new archive of sulphate aerosol and atmospheric chemistry changes**	**Experiment number**: ME-1103
Beamline: ID 21	**Date of experiment**: from: 23/06/05 08:00 to: 28/06/05 08:00	**Date of report**: 14/10/2005
Shifts: 15	**Local contact(s)**: Dr. Jean Susini	*Received at ESRF:*

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Report:

Aim of the experiment was to detect at high resolution the variability of sulphate in recent stalagmites, to test the reproducibility of the results from CH 1458, published by Frisia et al., 2005 (results from Exp. CH 1458) in a variety of geographic settings and under different soil cover thickness. A second objective was to detect lateral (time-equivalent) variability of trace elements which can be related to growth rate mechanisms.

We obtained beamtime only for ID 21, which hindered the possibility to determine the lateral variability of many heavy elements which was found to mark the autumnal laminae in specimen ER 76 and ER 78 (experiments CH 1365 and CH 1458) at ID 22. This issue should be tackled in the near future because it is extremely important to test the growth-rate vs. water chemistry influence on sub-annual elemental distribution in the speleothem archive of environmental changes, climate variability and anthropogenic impact on atmosphere and soil.

Samples (200μm to <1 mm thick double polished sections) were excited with energy of 2.9 keV in order to stimulate Kα radiation from light elements (up to Cl). Ca was not analysed, but the consistent beam conditions permit the assumption that excitation conditions were consistent; minor reductions in beam intensity of up to 10% were corrected for.

The experiment was successful. The only problems in summer are power shutdowns during thunderstorms, which prevented the full use of the allocated beamtime.

Five modern speleothem samples were examined from the present-day growth surface towards older layers along the vertical growth axis. An stalagmite from another northern Italian cave, Grotta Savi (Trieste) shows S-sulphate increase in the last 150 years as observed in ER 78 sample, confirming reproducibility of the data in similar thin-soil, high transmissivity settings. Both ER 78 and SV1 are located along atmospheric trajectories from the Mediterranean. Specimens from the Atlantic seaboard (Spain and Scotland) and from a ventilated cave in Austria, which cross-cuts a Pb-Zn mine did not show this pattern of S variation. However, experiment ME1103 yielded interesting discoveries.

Sample VAL-1 (Valporquero cave, N. Spain) is the first aragonite speleothem to be analyzed at ID21. Significant S was detected through scans, and mapping demonstrated that it was heterogeneously distributed between the aragonite fibers, matching the distribution of Si, whereas the concentrations within the crystals were low. The high Si concentrations obscured the Sr Lα signal that otherwise might have been detected.

Sample SU96-7 (Tartair cave, NW Scotland) displays over 1000 years of annual lamination, and growth rate variations have been related to climate (Proctor et al., 2000). Some previous analyses had been carried out by ion microprobe on the top ~70 years, but the more rapid synchrotron analyses allowed us to extend Sr, Mg, S and Cl distribution to approximately 300 years before Present. Mapping ensured that the scans were located away from intercrystalline impurities. S did not show the 20th century rise observed in ER 78 (CH 1458) and SV1 (this experiment) which may be a consequence of its remote position, or S-sequestration by overlying peat, or both factors. The high Mg and Sr contents allow long-term trends to be precisely determined, superimposed on the clear annual variations in Sr.

Sample Ob84 (Obir Cave, SE Austria, Spötl et al., 2005) is an annually-laminated speleothem the annual lamination of which appears to be related to ventilation. Solution-based ICP-MS work had established a chemical stratigraphy with increase in S and decrease in Pb and Zn during the 20th century. The XANES spectrum showed, in addition to small peaks for P, Cl and Mg, a large peak at 2.345 keV and a smaller one at 1.83 keV which could be identified confidently as Pb M peaks, based on previous work by Dr. Susini. The large Pb peak completely obscured the S signal. A small peak at 1.02-1.04 keV was identified as Zn Lα, rather than Na Kα, based on a knowledge of the Zn content of the sample and on its highly discrete spatial pattern, which in our experience is never shown by Na. Pb variability in Obir 84 shows a strong annual peak, as also noted for various heavy elements in the ID-22 researches on a stalagmite from ER 76 (Borsato et al, in preparation; results from Exp. CH 1365 and CH 1458). The Pb study on Obir 84 offers an interesting extra perspective since the fluorescence is generated almost at specimen surface in ID21, whereas at ID 22 the penetration depth is generated at several hundred of micrometers and, therefore, may come from non time-equivalent layers (Exp. CH 1365 and CH 1458). In addition to carrying out scans and mapping at 5 μm resolution, we also mapped a small area at 1 μm resolution, which makes this the highest-resolution study of its type so far. The resolutions clearly demonstrate that the Pb shows a ~20 μm-wide band representing a seasonal high, within which are one or two peaks, contained within the 1 μm-pixel size, and which must represent at most a few days growth – hence each one represents a discrete rainfall infiltration event. Mapping also shows that there are crystallographic factors controlling the distribution of elements, which become progressively more important from Pb to Zn to P to Mg.

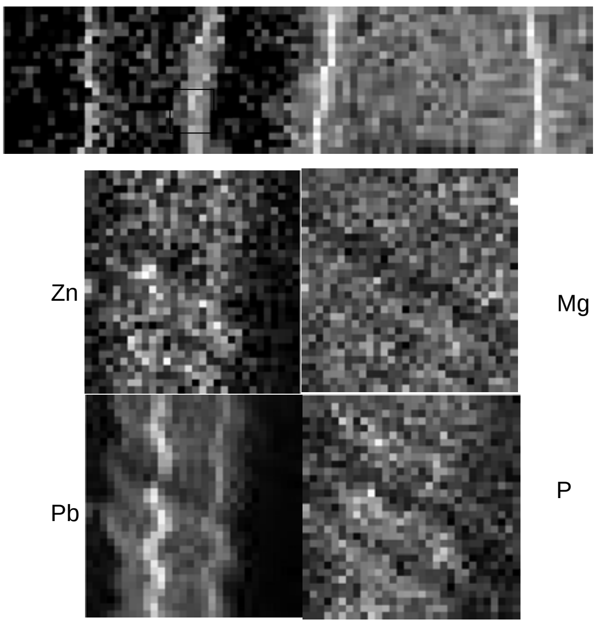

Figure caption: Sample Ob84. Upper diagram is a Pb map (5 μm pixels) showing four annual peaks (growth left to right). Box shows location of area shown enlarged in lower diagram. Lower diagram (1 μm pixels) showing distributions of Pb, Zn, P and Mg illustrating the detail of the annual peak in Pb (and Zn) versus the cross-cutting crystallographic controls on elemental distribution.

References

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Proctor, C. J., Baker, A., Barnes, W. L., Gilmour, M. A., 2000. A thousand year speleothem proxy record of North Atlantic climate from Scotland. Climate Dynamics 16, 815–820.

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