	Experiment title: Micro-XRF, micro-XANES and micro-FT-SRIR investigation of S and P compounds in speleothems: implication for environmental processes and human impact	**Experiment number**: EC88
Beamline: ID21	**Date of experiment**: from: 6-12-2006 to: 12-12-2006	**Date of report**: 3-05-2007
Shifts: 18	**Local contact(s)**: Dr Jean SUSINI (e-mail: susini@esrf.fr)	*Received at ESRF:*

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Report:

Micro XRF were here combined with FT-SRIR at ID21 on stalagmites. All the used specimens were extremely well dated. Two showed annual growth laminae recording atmospheric phenomena (Specimens: Gibraltar and BS). Two were selected because the time of change in land use above the passage and of major environmental changes were excellently constrained (specimens Bilbo and GS5). A specimen with good U/Th ages was analysed because of its fabric changes, incredibly high resolution isotopic record, but undetectable chemical cycles by other techniques. This specimen, from a deep cave, was also used as reference for "pure calcite" in the FT_SRIR analyses. With respect to the original proposal, we had an additional specimen from Turkey, which contained the Santorini Eruption, whereby its interest was in the opportunity to detect the event via trace elements and obtain a precise date for the explosion event (Sample Sofurar-1).

Experimental methods: All samples had good transparency, and their fabric changes allowed precise correlation with the visible features. Due to a change in the optical microscope setting, this time we found slightly more difficult keeping track of the features, as part of the specimen was not visible.

Setup: Samples (200μm thick double polished sections and one 1 cm-thick double polished penci)l, with excellent transparency, were excited with energy of 2.89 keV in order to stimulate Kα radiation from light elements (up to Cl) (same setting as for ME1103). Monochromator Si (111).

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. Our "routine" procedure, which demonstrated to be successful in previous experiments, was to perform "rapid" recognition micro XRF scans by using 1μm diameter analytical spot, with 1μm step advance. This allowed to select the best areas were to perform

maps. At first recognition maps were performed to gain better insight on the nature of the peaks detected through scans (30 x 30 pixels). Then, longer maps were carried out (ca 250 x 30 pixels).

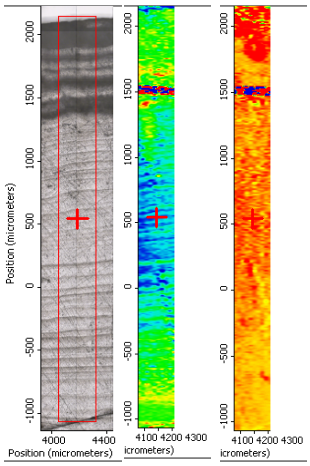
This was the first time we used the micro FT-SRIR microscopy technique at ID21 on speleothem calcite, in the range from 700 to 4000 cm^{-1}. We carried with us some reference standards of Humic and Fulvic acid so that their spectra could be stored in the ESRF spectra library and serve as compariconfor other users. The standards were: SUOW OM-IHSS Suwannee River Natural Organic Matter Batch 1N101; SUW HA- IHSS Suwanee River Humic Acid Standard Batch 1S 101H; SUW FA- IHSS Suwanee River Fulvic Acid Standard Batch 1S101F; ALD HA – Aldrich HA lot 53008, NA salt techmical grade directly derived from peat and no longer available; NORD HA – IHSS Nordic Aquatic Humic Acid Reference 1R 105 H; NORD FA – IHSS Nordic Aquatic Fulvic Acid Reference 1R 105 F. Plus, the Katerloch speleothem calcite was good reference of pure, OM-free calcite.

Results

1) we recognized different distribution of S, Cl, Mg and P in the specimens from diverse climate settings, ages and with different fabrics. In particular, changes in environmental conditions (land use or opening of the cave to the aerosol-laden boundary layer, were marked by S and Cl concentrated in micrometer-sized particles. Increase in atmospheric S loading (often associated with Cl) in the anthropogenic era is thus unequivocally demonstrated by micro XRF analyses. Current, parallel isotope analyses fingerprinted this S as definitely of industrial origin.

2) The specimen from Sofurar shows subtle geochemical cycles, and distinctive S and Cl peaks at around the expected time of the Santorini eruption. Further U/Th dating at high resolution is in progress to bracket the exact age of the peaks. Then, we will have an exact age for this archaeologically important explosive event.

3) The FT-SRIR indicate that most speleothem calcite from shallow caves, or caves where transmissivity is rapid, contains organic matter in the lattice. The presence of water has also been detected. We know that it is structural water from NMR analyses. The Katerloch specimen was actually pure calcite, as expected from the micro XRF analyses (“clean” sample) and by the long residence time of the feeding water in the aquifer. The results are still being processed by B. Fanget, as their group would like to compare our data with their newly developed UV-fluorescence instrument at Chambery.



FT-SRIR analyses of sample ER78 showing the thin section (left, Little Ice Age, that is pre-year 1840 AD, at the top), the distribution of H_20 (middle) and of CH_2 (right). Water is mostly concentrated in the dark portion of the laminae. The band at 1500 micrometers is an artefact.

Publications:
A chapter on Fluid inclusions, petrography, mineralogy is being prepared for a Blackwell Publishing book edited by S. Burns on Speleothems, palaeoclimate and environmental research by S. Frisia. This will contain some of the results obtained, and in particular the FT-SRIR images.