	Experiment title: **Microcrystalline grains and coprecipitates in speleothem calcite: a micro-XRD and -XRF investigation**	**Experiment number**: EC104
Beamline: ID22	**Date of experiment**: from: 13-12-2006 to: 18-12-2006	**Date of report**: 03-05-2007
Shifts: 15	**Local contact(s)**: Dr Jean CAUZID (e-mail: jean.cauzid@esrf.fr)	*Received at ESRF:*

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Report:

Micro XRF coupled with micro XRD were carried out on selected speleothems to detect possible presence of Sr-rich phases and their distribution as indicative of co-precipitation or replacement phenomena. We also aimed at finding P-rich phases, such as monetite, which had been detected by NMR, but whose distribution in the specimens was unknown. Finally, we aimed at recognizing geochemical cycles in the heavy elements to compare them with the cycles detected through the light elements, and reproduce findings published in Borsato et al. (2007) as a result of previous ESRF experiments.

Experimental method

The same specimens used for EC88 were used, including the unexpected Sofurar stalagmite from Turkey. In particular, after the experiment at ID21, we aimed at detailing heavy element distribution across the "Santorini eruption" S and Cl peaks, as it is known that soil metals are mobilized under the more acidic conditions caused by volcanic aerosol fall-out.

Specimens were free-standing double-polished wafers, and one think pencil (1 cm thickness). μ-fluorescence mapping was carried out at the proposed 2 x 4μm and 2.5 x 2.5μm resolution. The excitation energy was 22 KeV. The same strategy as for ID21 (recognition scans & maps followed by selected high-resolution long scans and maps) was followed. Spectra were processed through batch fitting. The list of elements detected ranges from Ca to Pb, with the highest variety of trace metals in the Gibraltar specimen, possibly indicative of contamination by human activities. The micro XRD was

carried out on the opposite side of the specimen with respect to fluorescence, which was OK as the samples were we performed diffraction were very thin and transparent. The diffractograms were recorded by the CCD camera which was mounted when needed and removed when we just carried out micro XRF to avoid too much handling. We had been advised by the beamline scientist that X-ray absorption spectroscopy to study Sr speciation was not going to give good results, whereby we renounced.

Results

The most interesting specimen with respect to micro-XRF analyses was Sofurar, for which we performed excellent correlation between ID21 and ID22 scans. A sudden S rise at 11.1 corresponds to a negative Sr peak, and to a positive Br peak. A second sudden rise in S at 9.4 mm corresponds to a negative Sr peak, and to Ni, Nb, Mo positive peaks. We interpreted this as index for the Santorini explosion (see fig. below).
In addition, Sr shows high-frequency cicles that we interpreted as annual, in an otherwise non-visibly laminated sample. This would help to increase the resolution of the age model.
A very interesting feature observed was that the annual Sr cycles tend to disappear after the 9.4 mm event suggesting a change in hydrology. The Zn rise after the 9.4 mm event followed by a strong Cu rise triggered by an event (peak in Cu and Pb) at 7.1 mm can be related to the progressive mobilization of the heavy metals.
With respect to micro XRD, the data are srill being processed, but phases other than calcite (for example aragonite) were detected. This was our first attempt at micro XRD, and we are satisfied with the preliminary information obtained.