	Experiment title: **Speleothem sulphur: validation of winter climatic proxy**	**Experiment number:** EC710
Beamline: ID 21	**Date of experiment:** from: 31st-Jan 2011 to: 03rd Feb 2011	**Date of report:** November 2011
Shifts: 6	**Local contact(s): Barbara Fayard**	*Received at ESRF:*

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Report:

The main objective of this experiment was to obtain records of annual sulphur variability within calcareous stalagmites in well-studied cave environments to investigate their suitability as a proxy for the occurrence of distinctive winter versus summer conditions. The relationship between sulphur concentration and seasonality arises indirectly because sulphate ions compete with carbonate ions to be incorporated into calcium carbonate (calcite). Sulphate concentrations in calcite are higher when the pH of dripwater is relatively low (when carbonate ions are much less abundant than bicarbonate). Dripwater pH in turn depends on the CO_2 content of cave air which varies seasonally in a characteristic way at a given cave site. Apart from sulphate, certain trace elements are enriched by enhanced transport in the wet season, or alternatively alkaline earths can be enriched where there is a distinct dry season; either way an entirely separate annual variability can exist for comparison with the sulphate.

Beam time was used to map sulphur concentrations in two annually laminated speleothems at sub-annual resolution, thereby testing the association between sulphur incorporation and cave air CO_2 content. The time period corresponding to peak sulphur incorporation was extablished through mapping of trace element markers which de-limited the annual cycle.

This tested the following hypothesis: In appropriately ventilated caves, the annual variation in sulphur abundance in speleothems can act as a proxy for the length (severity) of the winter season.

Obir Cave: Austria (Obi84)

Cave ventilation dynamics at this site dictate low partial pressures of CO_2 during the winter season. This drives enhanced de-gassing of drip waters, increased pH, a greater proportion of carbonate ions and hence rapid growth rates with low sulphate ion incorporation. The reverse situation in summer leads to distinct seasonality in the sulphate concentrations. Annual marker horizons of enhanced Zn concentrations (and Pb, not shown) are related to heavy autmunal rainfall events and flushing into the cave environment (Figure 1). A long scan of overy 100 years will be used to compare with monhly temperature records – temperature controls the switch between summer and winter PCO_2 levels and hence sulphate abundances.

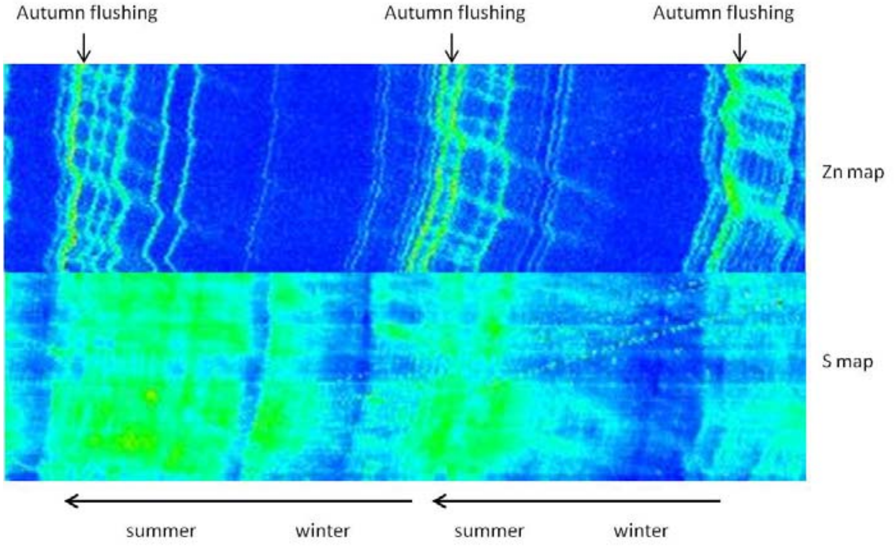

Figure 1: Obi 84 Sulphur and Zinc over 3 annual cycles

Ragged staff cave: Gibralter (Gib-10)

Seasonality in cave ventilation at this site produces a summer high in cave atmospheric CO_2 content and winter low. The expected pattern of seasonal sulphur variation based on the model of drip water degassing and pH outlined above would be for corresponding decreases in S content during the winter season. This generates antipathetic variations with trace elemts Mg, Sr and Ba, which rely on conditions of high supersaturation (hence low P_{CO_2}) for an enhanced concentration within the speleothem calcite. Figure 2 demonstrates this antipathetic variation over several annual cycles, using Sr to demarcate winter seasons and annual cyclicity.

Lower St. Michaels cave: Gibraltar (GIB-04)

As a part of the same system, but with contrasting seasonal ventilation, stalagmite Gib-04 displays an identical antipathetic variation with strontium, but where high P_{CO_2} depicts winter season conditions, corresponding to higher levels of sulphur incorporation.

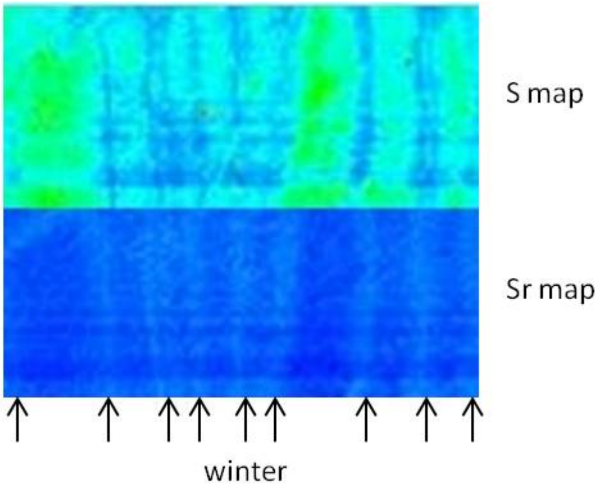

Figure 2: Sulphur and strontium over several annual cycles in Gib-10

Research outcomes:

High resolution imaging of sulphur in conjunction with selected trace elements has enabled demarcation of growth seasons and analysis of sulphur variation within a single annual cycle. This has clearly linked the role of pH and CO_2 degassing rates as a key control on the incorporation of sulphur into the carbonate crystal lattice. This supports laboratory experimentation addressing trace element partitioning under variable pH conditions and builds towards using variations in speleothem sulphur content as an indicator for the severity of winter seasons.