	<b>Experiment title: High-resolution geochemical characterization of carbonates in annually laminated stalagmites for palaeoclimatic interpretations</b>	<b>Experiment number:</b> CH-1365
<b>Beamline:</b> ID 21 ID 22	<b>Date of experiment:</b> from: 30 August 2002 to: 7 September 2002	<b>Date of report:</b> 29 May 2003
<b>Shifts:</b> 9 (ID 21) 6 (ID 22)	<b>Local contact(s):</b> Dr. Jean Susini  Dr. Andrea Somogyi	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists):  Silvia Frisia e Andrea Borsato  Museo Tridentino di Scienze Naturali Via Calepina 14 38100 TRENTO- ITALY		

## Report:

Experiment CH-1365 was our first experiment on high-resolution geochemical characterization of Alpine cave deposit (stalagmites) specimens, which are good archives of palaeoclimatic data. In particular, aim of the experiment was to determine possible differences in trace element distribution in stalagmites characterized by different fabrics that develop under diverse hydrological conditions.

Preliminary results have been presented at the “Climate Change: the Karst Record” congress at Montpellier 11-14 May 2003, of which we include the abstract and figures from communication. The relative manuscript is currently in preparation.

### **Synchrotron X-ray fluorescence analysis of annually laminated (and non-laminated) Alpine stalagmites**

S. Frisia <sup>(1)</sup>, A. Borsato <sup>(1)</sup>, A. Somogyi <sup>(2)</sup> and J. Susini<sup>(2)</sup>

(1) Museo Tridentino di Scienze Naturali, via Calepina 14, 38100 Trento, Italy,

(2) European Synchrotron Radiation Facility, F-38043 Grenoble Cedex, France

Annual layering in stalagmites has been defined by textural changes, by alternation of thin brown, inclusion-rich, and clear, thicker carbonate layers associated in couplets, by changes in mineralogy, and by UV-luminescence intensity. All types of annual layering variations in the Holocene have been interpreted as primarily due to seasonal rainfall rate and temperature fluctuations through their control on cave drip-water supersaturation. Soil CO<sub>2</sub> production, which leads to greater amount of dissolved calcium being generated is

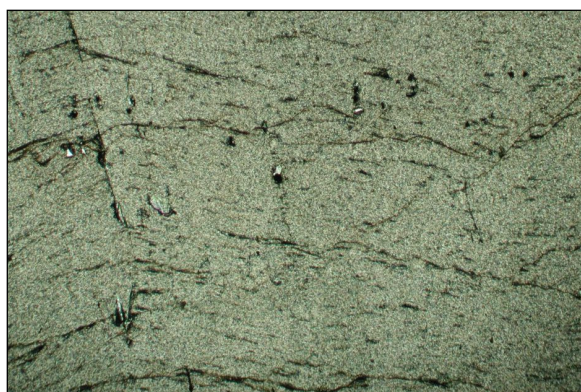
believed to be the primary control of annual layer thickness variability. In aqueous solution at low supersaturation with respect to calcite, however, foreign ions may also play a role in controlling calcite growth rates. In cave aqueous solutions metal uptake is dominated by sorption, and co-precipitation reactions can be quite significant. A wide range of soil-derived metals and organic molecules can potentially perturb growth mechanism and decrease growth rate. Calcite surface structure is known to control trace element incorporation, and, thus, high-resolution geochemical characterization of annual layering is needed to interpret both calcite growth rate and chemistry in terms of environmental factors.

We analyzed the chemical composition of two alpine stalagmites, which show optically visible annual laminae, by X-ray fluorescence spectrometry (XRF) by taking advantage of the high-brilliance X-ray beam available at the European Synchrotron Radiation Facility (ESRF) at Grenoble (France). We selected an area characterized by annual lamina thickness change from 20  $\mu\text{m}$  to 100  $\mu\text{m}$ , corresponding to the passage from Little Ice Age-type (LIA) to Recent-type climate conditions. Each annual lamina consists of translucent, non-UV-fluorescent calcite, capped by a thin layer of brown colored, UV-fluorescent calcite associated with organic matter in colloidal form. Scanning micro-XRF experiments performed at the ID21 and ID22 beam-lines of the ESRF aimed at correlating annual lamina structure and trace element distribution by measuring the 2D elemental distribution with  $\mu\text{m}$  spatial resolution.

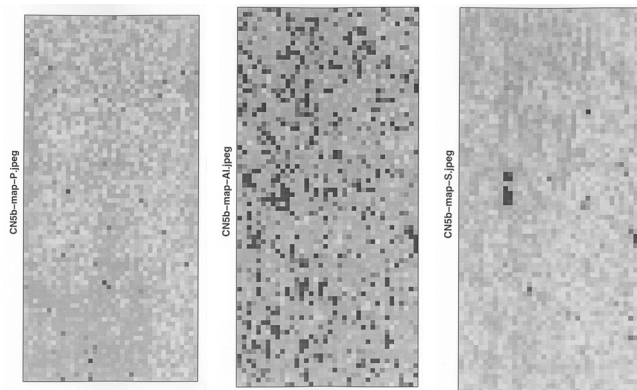
In particular, we sought for the lateral distribution of P, which was previously detected by Ion Probe measurements, throughout the dark layers capping each lamina. The results show that indeed P is present, and it is distributed along the whole dark top layer of each lamina, which rules out possible structural effects, and supports incorporation due to real changes in dripwater chemistry. The dark layers also contain Br, Fe and Zn, whereas Sr is present in the light, translucent part of each lamina.

The observed trace element distribution indicate that annual laminae in the studied alpine stalagmites result from real seasonal fluctuations in dripwater chemistry composition, which reflects seasonal flushing of soil-derived trace metals and organic molecules. At present the dripwater saturation state with respect to calcite is low ( $\text{SI}_{\text{calcite}} = 0.14 - 0.19$ ), the role of inhibitors such as P and Zn could thus be important. Under the recent relatively warm climate conditions, however, these elements do not seem to perturb stalagmite growth rate significantly. In the cooler LIA, however, dripwater barely at saturation can be expected, and the effects of growth inhibitors might have been stronger and thus possibly amplified lamina thickness reduction.

#### Columnar calcite from a deep cave (900 m below the surface)



Sample CN-5 Columnar Calcite



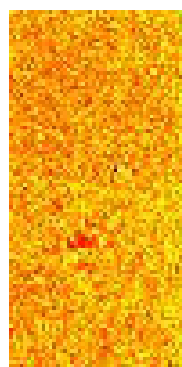
*Figure 2 No preferential trace element distribution (ID 21). Following this discovery, we did not pursue further characterization at ID 22.*

*Area of scans: 90  $\mu\text{m}$  x 200  $\mu\text{m}$*

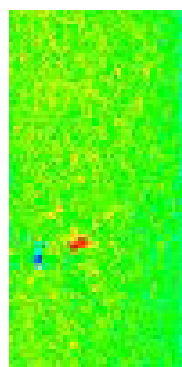
**Syncrotron analyses indicate that:** Trace elements and organic matter are adsorbed by the host rock during the long residence time of the water in the aquifer ( $> 1$  year). This results in the absence of detectable seasonal and annual climate-related trace-element signals in this stalagmite.



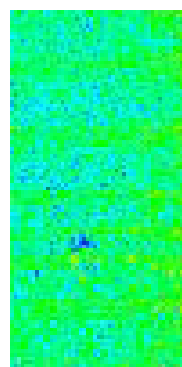
ER 78. Laminated columnar texture.  
Width of photo: 3 mm



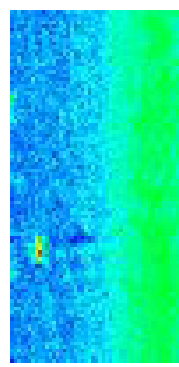
Mg



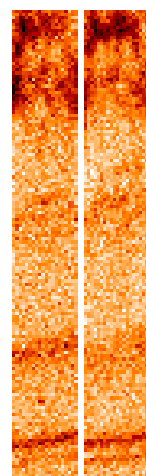
Na



P



S

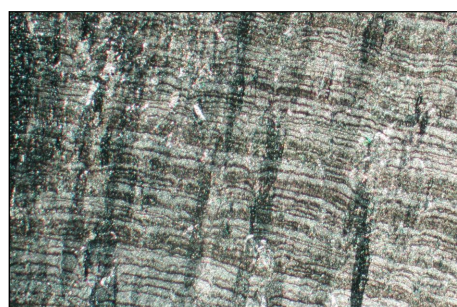


Y

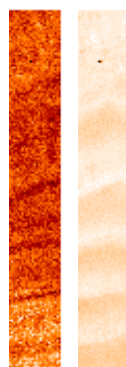
Zn

Map of element distribution in the specimen. Mg, Na, P, S detected at ID 21. Scan: 90 x 200  $\mu\text{m}$ . Y and Zn detected at ID 22. Scan: 90 x 700  $\mu\text{m}$ . P, Y and Zn are concentrated exclusively in the dark layer of each lamina. On the contrary, incorporation of S seems to be structurally controlled, rather than related to changes in water chemistry.

**Synchrotron analyses indicate that:** the concentration of trace elements in the dark layers of each lamina is not enough to determine a change in fabric, which is still columnar as in specimen CN-5, even though stalagmite ER 78 developed at only 20 m below ground and records interannual drip-water chemistry variations.



BS 21. Microcrystalline fabric.  
Base of photo: 7 mm.



Br

Sr



Zn

Sample BS 21 consists of microcrystalline fabric. Crystallite stacking is irregular. So, at crossed polars one sees extinction domains, rather than uniform extinction. Trace elements such as Fe, Br, Zn are preferentially concentrated in the dark layers. On the contrary, Sr is concentrated in the translucent layers. This distribution supports the inference that Fe, Br, Zn, Y, P are flushed from the soil during the rainy season, whereas Sr comes from the dissolution of the host rock. Maps obtained at ID 22. Scan: 90 x 700  $\mu\text{m}$

Experiment CH-1365 revealed that annual lamina structure (proportion of dark and light layers) depend on seasonal input of soil-derived elements in addition to organic molecules. The presence of growth inhibitors may determine changes in speleothem fabrics depending on their concentration in the fluid. The experiment shows that P is concentrated along the whole dark top layer of each lamina, which rules out possible structural effects, and supports incorporation due to real changes in dripwater chemistry. Finally, CH-1365 results indicate that stalagmites developed in deep caves may not show interannual geochemical variability. Lack of any particular pattern in trace element distribution hints to a possible similar behaviour for stable isotopes.

CH-1635 results prompted the need to get better insight on the chemical state of S and P, which we will investigate through a new experiment (CH-1458).