

# Sub-monthly to daily trace element distribution in annually laminated stalagmite mapped by synchrotron micro X-ray fluorescence

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The high spatial resolution (1-2  $\mu\text{m}$ ) and low detection limits of synchrotron radiation micro X-ray fluorescence (SR  $\mu$ -XRF) allowed detection of sub-monthly to daily trace elements variations in an annually laminated stalagmite from Grotta di Ernesto cave (NE Italy) with a mean resolution of  $7.8 \pm 5$  days for the last 150 years.

The concentration distribution of Y, Zn, Cu, Pb, P and Br follows clear annual cycles, which are characterized by symmetrical peaks, with a mean width of 4 hydrological months, centered around the visible thin, dark layer that marks the annual lamina in the reference thin sections. By contrast, the Mg and S peaks are offset and do not show clear annual variability. Fe appears to be randomly distributed.

The peak intensities of Y, Zn, Cu, Pb, P and Br reflect the selectivity of transport of these elements by organic colloids flushed from the soil zone during the autumnal infiltration. Sr displays a trough around the dark and thin autumn layer. The reduction in Sr coinciding with the increase in Y, Zn, Cu, Pb, Br, and in particular P, might indicate that Sr is being out-competed for incorporation at defect sites. Sr incorporation in calcite may, thus, reflect crystallographic properties rather than environmental factors.

The trace element concentration variability for the past 150 years seems to be more environmental- than climate-controlled. Peak abundance of colloid-transported elements in the early 20th century, in fact, reflects a period of deforestation above the cave, rather than a climate anomaly. Anthropogenic activity is further detected by the broad peaks in Zn, Cu, Fe and Sr concentration at the top of the sample, starting from 1984, when the cave was discovered, opened and excavated for archaeological investigations.

Coupling of SR  $\mu$ -XRF parallel scans and maps allowed clear distinction of the layered structure from tracers concentration associated with isolated particles, or irregular inhomogeneities.