Environment-sensitive trace element concentration in speleothems as detected by synchrotron µ-XRF

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Synchrotron radiation (SR) µ-XRF allow detection of sub-annual variations of environment-sensitive tracer elements in speleothems. At the European Synchrotron Radiation Facility, elements with low atomic numbers were measured at the ID21 beamline, where the microprobe was set to 4.5 keV for elements lighter than Ca, and a specific study of S-species was performed by XANES.

At the ID22 beamline, excitation energy of 17.3 keV made possible the detection of the K-lines of all the elements up to Y and the L-lines of Pb. A coordinate system allowed precise relocation of the analyzed regions. Visible boundaries between annual laminae allowed for precise correlation with the thin section used for ion probe analyses.

At ID21 the fluorescence signal comes from quasi-surface depths, but it is much deeper at ID22. However, similarity in the shape and thickness of the Y peak, whose signal comes from ca. 140 µm depth, and the P peak (whose signals comes from ca. 4 µm), allowed to infer that the layered structure of the stalagmite is reproduced even for the elements detected at ID22. The elemental markers in the synchrotron maps were spaced apart precisely as the visible lamina, and the P peaks from the ID21 data can be exactly aligned with the Y peak and Sr through from the ID22 data. Concerns about registration related to different depths of X-ray excitation at the two beamlines were not a problem.

The SR µ-XRF measurements are quantitative in a relative sense. Intensities were thus standardized to absolute concentrations by comparison with ICP-MS and ion probe analyses. The Sr concentration was used to test the quantification of the synchrotron intensity data. The resulting standardization was accurate for Sr, Zn, and Pb, whereas Cu and Y were underestimated by a factor of 10 and 5 respectively. ICP-MS analyses, confirmed the rising sulphate concentration in the past 150 years althought with a lower enrichment factor.

The standardization methodology proposed here is, therefore, to be considered with caution, and more work must be carried out aimed at quantification of SR µ-XRF trace element data.