

# **Micro-XRF and micro-XANES study of the distribution and oxidation state of uranium in stalagmite**

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Speleothems are well known paleoclimate archives but their potential for monitoring environmental pollution has not been fully explored [1, 2]. Our objective was to determinate the possible effect of the four-decade-long uranium (U) ore mining activity on the environment, as recorded by a cave deposit. For this propose, the Trio Cave had been selected. It is located in the western part of the Mecsek Mountains (S. Hungary) at the base of the Szudo Valley, approx. 1.5 km east of the nearest entrance and air shaft of the Mecsek uranium mine (mine-pit no. IV). A stalagmite located about 150 m into the cave was drilled and the 42 cm-long core was investigated for stable isotope and trace element composition using continuous-flow mass spectrometry and laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), respectively. The uppermost ca. 3 cm of the core was selected for this study, which represents the last few hundred years (based on an estimated growth rate of 0.05 mm/year by  $^{230}\text{Th}$  age dating of older parts of the core). Uranium concentration in stalagmite sample increased radically (especially in the topmost 1.3 mm), starting from a background value of 0.2-0.3  $\mu\text{g/g}$ , increasing gradually to about 2  $\mu\text{g/g}$ , followed by constant values for about 0.5 mm, and then declining to about 1.5  $\mu\text{g/g}$  [3, 4]. LA-ICP-MS revealed the higher uranium concentration in the surface than in the older part of the samples. However, it did not provide information on the microscopic heterogeneity and the chemical form of uranium present in the sample. Therefore additional methods were selected which can show the valence state of uranium and can look deeper into the sample. Synchrotron based X-ray analytical methods (micro-XRF and XANES) are known to be suitable for recording globally increasing anthropogenic emission of sulphur into the atmosphere [1] and for determining valence state of uranium in stalagmites [5].

The micro-distribution and the oxidation state of uranium in the stalagmite sample were investigated using micro-XRF and micro-XANES at the micro-fluorescence Beamline L of HASYLAB (Hamburg, Germany). The white beam of a bending magnet was monochromatized by a Si(111) double monochromator. A polycapillary half-lens (X-ray Optical Systems) was employed for focusing a beam of  $1\times 1 \text{ mm}^2$  down to a spot size of 15  $\mu\text{m}$  diameter. The absorption spectra were recorded in fluorescent mode, tuning the excitation energy near the L3 absorption edge of U by stepping the Si(111) monochromator, while recording the U-L $\alpha$  fluorescent yield using an energy-dispersive Radiant silicon drift detector. The used energy step size varied between 0.5 (edge region) to 2 eV (more than 50 eV above edge).  $\text{UO}_2$ ,  $\text{UO}_3$  and  $\text{U}_3\text{O}_8$  particles were used as standards. The collection of the elemental maps was performed at an excitation energy of 17500 eV.

Close (ca. 200  $\mu\text{m}$ ) to the upper brink of the polished site of stalagmite sample, vertical scan was performed with 100  $\mu\text{m}$  stepping. An enhanced U (and Pb) bearing microscopic grain was detected ca. 1 mm from the brink. Following the rough scan, a detailed mapping was carried out on a larger area of  $2\times 1 \text{ mm}^2$  using 30  $\mu\text{m}$  horizontal and 20  $\mu\text{m}$  vertical stepping. The mapping revealed a belt, wherein plenty of U-, Th-, REE-, Pb-containing minerals are present (Figure 1a). The belt is approximately 1040  $\mu\text{m}$  to the upper margin of the sample and ca. 400  $\mu\text{m}$  thick. Micro-XANES measurements were performed on grains containing U at the highest concentrations and on the matrix as well. The interpreted results with spectra of standards are presented on Figure 1b, showing that uranium is in tetravalent state (same absorption edge as  $\text{UO}_2$ ) within the grains and mostly in hexavalent (similar absorption edge as  $\text{UO}_3$ ) in the matrix. The relatively low uranium

concentration, the significant amount of rubidium and strontium in the sample studied made the XANES measurements problematic in the case of the uranium in matrix (see Figure 1b).

The synchrotron based X-ray analytical methods (micro-XRF and XANES) we used clearly revealed that uranium measured by LA-ICP-MS is present not only in hexavalent state as a substitution of Ca in the matrix of stalagmite but also in tetravalent state in accessory minerals. Moreover, the present investigations pointed out that these minerals are present in a distinct rim, which represent a rainy event, when these minerals were washed out by rainwater from the overburden formations.

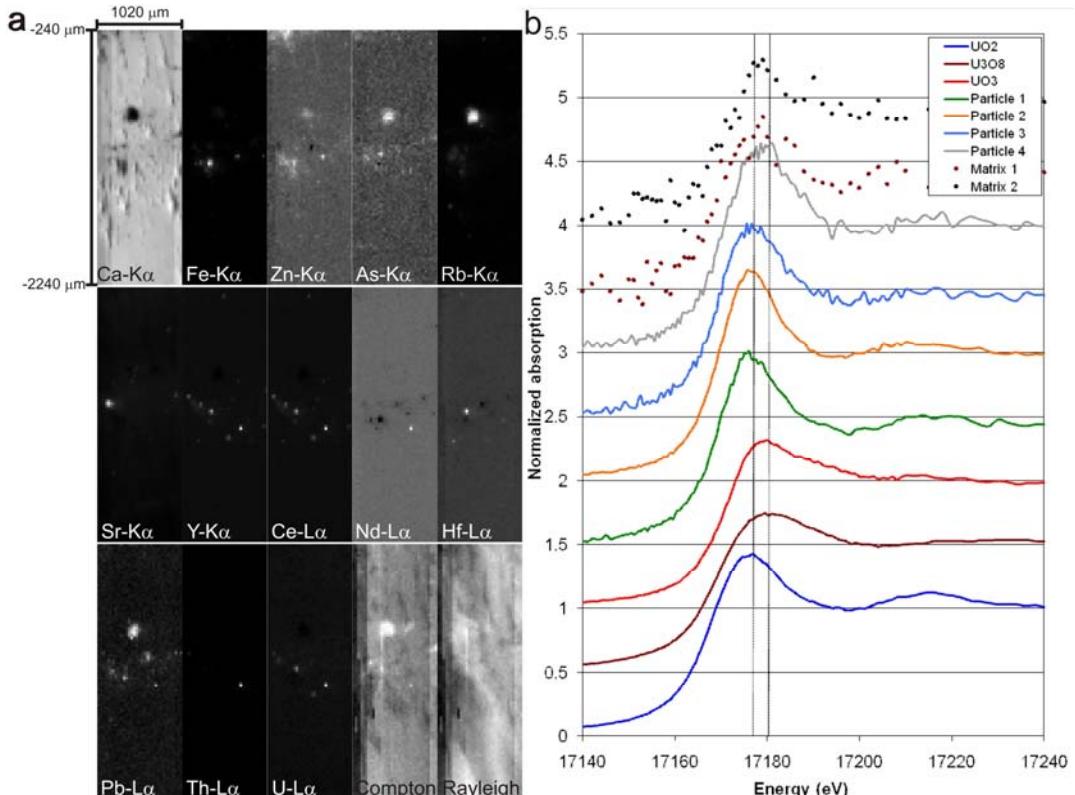


Figure 1: X-ray intensity maps recorded on a ca. 2  $\text{mm}^2$  area of the stalagmite sample (a). Micro-XANES spectra collected on the stalagmite sample (matrix and U-rich grains), compared to those of standards (b).

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## References

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