

CONTENT OF RARE EARTH ELEMENTS IN A SPELEOTHEM ANALYZED BY ICP-MS AND CL-SPECTROSCOPY. Fernandez-Cortes, A.¹, Cuezva, S.¹, Cañaveras, J.C.², García-Guinea, J.¹, Sanchez-Moral, S.¹.
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In the framework of a pilot study to search radiation sources and uranyl groups associated to the host rock and sediments, in a cavity with very high radon levels (Castañar cave, Spain) some Rare Earth Element (REE) mineralization's have been detected in a carbonate stalactite. REE contents of the analyzed host-rock slates [1] by ICP-MS displayed spatially-heterogeneous concentrations, ranging from 20-44 ppm, 9-22 ppm, 8-23 ppm for Ce, La and Y, respectively. The REE signal is smoothed in the speleothem sample; ≤ 1 ppm, 0.2-0.9 ppm, 0.1-4.2 ppm for Ce, La and Y, respectively, values much higher than in other studied speleothems [2]. Cathodoluminescence (CL) analyses have allowed to obtain the whole spatially resolved spectra of the REE pattern along a concentric sequence of mineral precipitation of calcium-carbonate phases (Fig. 1). CL-spectra shows a wider range of spectral luminescence emissions corresponding to others REEs for B layer (calcite 90%, aragonite 10% by XRD), compared with the more external layer A (calcite \pm phyllosilicates) where the intensity of the maximum CL-emissions are smoothed and Ce^{3+} prevails and hide others REE's emissions. Fig. 2 shows a detailed CL spectrum for the growth layer B with a high density of REE: Sm^{3+} , Sm^{4+} , Dy^{3+} , Ce^{3+} , Eu^{3+} or Tb^{3+} . The periodic enrichment of some REE (La, Ce) within the laminations of a speleothem reflect times of more intense weathering that usually correspond to relatively warm and humid climatic phases [2–3]. According with these authors, the higher concentration of Ce, La and Y in the external calcite layer (A) could indicate its growth during a phase with stronger weathering and more dynamic hydrology. REE mobilizations from the host-rock to this growth band corresponded to these major REEs. Simultaneously, the CaCO_3 solubility could increase linked to a lower ratio of mineral precipitation due to REE-inhibition. An opposite pattern could be inferred for the inner layer B where the hydrodynamic conditions probably favored long times residence of seepage water and a higher interaction with the siliceous host-rock. This predominant REE-source entailed the incorporation and concentration of other REEs (Dy, Sm, Eu) and SiO_4^{4-} , Si-O groups into the CaCO_3 lattices producing CL emission. The relative decrease of La, Ce and Y seems to be coeval to a more pronounced CL-anomalies of these minors REEs, as well as a uranium accumulation in this growth layer (19.3 ppm, 5 times higher than layer A).

An additional CL-spectrum of the growth layer nearest to fed conduit (Fig. 1,C) shows an intermediate pattern of REE's emissions with respect to A and B layer. Thus, the CL-anomalies of the minors REEs are smoothed, except for Sm^{3+} and Dy^{3+} . Originally, the REE's contribution in this growth layer could be associated to similar hydrodynamic conditions of B layer but corresponding to an early stage.

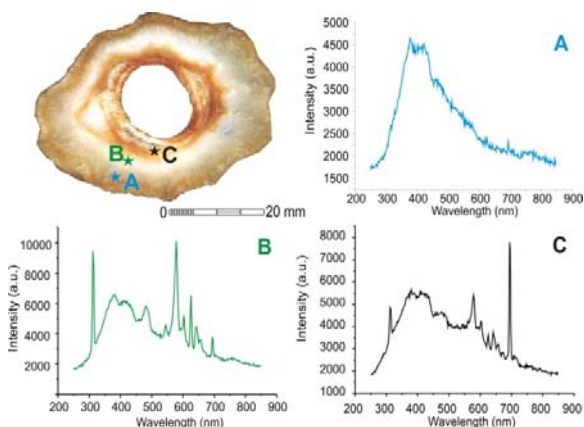


Fig 1. REE and U concentrations and CL spectra for each concentric layer of calcium-carbonated phases.

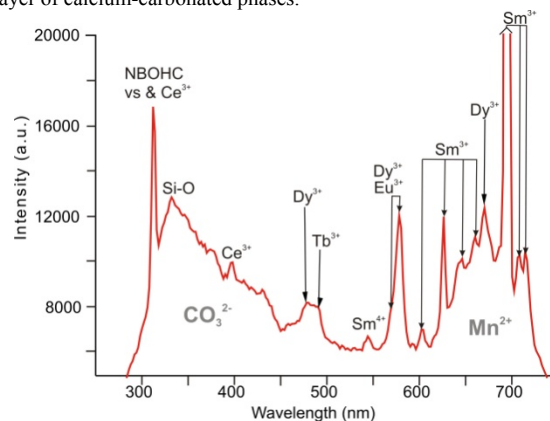


Fig 2. Detailed CL spectrum with high REEs' density corresponding to layer B.

References

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