GEOCHEMICAL EXPRESSION OF SPELEOTHEME GROWTH FROM XRFAND LA-ICP-MS: PALEOCLIMATIC IMPLICATIONS

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Carbonate cave deposits have a widespread use in deciphering climatic signals from the past using several proxies (e.g. stable isotope compositions). In the western central part of Portugal, the Mesozoic sediments of the Lusitanian basin are particularly susceptible to dissolve by interaction with meteoric waters and to develop karstic caves, especially in the Lower and Middle Jurassic limestone and dolomitic limestone formations. A set of the existing caves from Sicó and Estremadura Carbonate Massifs (e.g. Soprador do Carvalho, Buraca Grande and Ourão Caves, as well as Vale do Pena and Algar do Pena Caves) were detailed study and several speleothem samples (stalagmites and flowstones) were collected aiming to contribute to the deciphering of the climatic evolution of this region.
The selected cave stalagmite was collected in the main epiphreatic conduct of the Soprador do Carvalho Cave (an underground system located on the eastern border of the Sicó Massif) and was studied by handheld X-ray fluorescence to determine the major elements trends and by LA-ICP-MS for the analysis of the minor and trace-elements. The cave floor is covered by siliciclastic fine (clayey/sandy) and clast-supported conglomerate sediments carried into the cave from the adjacent areas by floodwater.
As expected, the chemical composition of the speleothem is dominated by the presence of calcium with all samples presenting counts of the same magnitude for this element, although the older portion of the stalagmite has slightly lower counts than the rest of it. Iron is another remarkable element that present a subtle tendency to be more concentrated in the outer (younger) layers. With LA-ICP-MS several transects were made on the thin sections covering layers of distinct optical characteristics. The older layers, which exhibit a more hyaline aspect, have higher counts of elements such as sodium, uranium and lead and lower counts on rare-earth elements and yttrium. More, the analysed elements oscillate between high counts and low counts from layer to layer along the entire sample. The oscillatory character of the trace-element distribution in the stalagmite can be interpreted as the result of the seasonal variations of meteoric water input, and time of residence on the hanging-wall formations, with periods of more efficient dissolution of the percolating water alternating with periods of less efficiency. The more general evolution observed in the composition of older and younger sectors of the speleothem can be interpreted as being the evidence for a probable change in the paleoclimate conditions of the area and perhaps can be used to detect underground flood events during the Quaternary.

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