

Assessing the origin of unusual organic formations in lava caves from Canary Islands (Spain)

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Lava tubes, like other caves, contain a variety of speleothems formed in the initial stage of a lava tube formation or due to leaching and subsequent precipitation of secondary minerals. Primary and secondary mineral formations in lava caves are mainly composed of silicate minerals, although secondary minerals common in limestone caves have been also reported in this type of caves. In addition, unusual colored deposits have been found on the walls and ceilings of lava tubes, some of them of unknown origin and composition.

A brown to black-colored mud-like deposits was observed in “Llano de los Caños” Cave, La Palma Island, Canary Islands, Spain. These black deposits coat the wall and ceiling of the lava tube where sub-horizontal fractures occur. FESEM-EDS, X-ray micro-computed tomography and mineralogical analyses were conducted for morphological, 3D microstructural and compositional characterization of these unusual speleothem samples. These techniques revealed that they are mainly composed of amorphous materials, suggesting an organic carbon composition. Hence, analytical pyrolysis (Py-GC/MS), solid-state ^{13}C Nuclear Magnetic Resonance (NMR) and stable isotope analysis were applied to assess the nature and origin of the black deposits. The combination of these analytical tools permits the identification of specific biomarkers (di- and triterpenoids) for tracing the potential sources of the organic compounds in the speleothems. For comparison purposes, samples from the topsoil and overlying vegetation were also analyzed.

Chromatograms resulting from the Py-GC/MS showed an abundance of polysaccharides, lipids and terpenoids typically derived from the vegetation of the area (*Erica arborea*). In addition, levoglucosan, polycyclic aromatic hydrocarbons and N-containing heterocyclic compounds were detected. They probably derived from the leaching of charred vegetation resulting from a wildfire occurred in the area in 2012. The lack of the typical pattern of odd-over-even in the series of n-alkanes observed for the topsoil and black deposits has been recognized as an indication of fire. The ^{13}C NMR spectrum of the black deposits showed a mixture of alkyl and O-alkyl compounds, carboxylic compounds and polysaccharides. Stable isotope analysis of $\delta^{13}\text{C}$ performed on the cave black deposits, topsoil and vegetation confirmed that the source of the organic fraction of the sample is a combination of partially charred vegetation (mainly *Erica*) and organic compounds from the andic soil over the cave. Therefore, these black deposits are the result of an input of plant organic matter and charred vegetation into the cave from rock fractures, which may constitute an important source of energy for cave organisms.

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