Topsoil alterations influence the genesis and composition of unusual organic-rich speleothems in volcanic caves from the Canary Islands

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Abstract. This multidisciplinary study combines the use of mineralogy, chromatography, light stable isotopes and nuclear magnetic resonance spectroscopy to reveal the origin of black sludge-like speleothems found in a volcanic cave from La Palma Island (Spain). The combination of these analytical tools permitted the identification of specific biomarkers for tracing the potential sources of the organic compounds identified in these speleothems. Analytical pyrolysis revealed the presence of polysaccharides, plant lipids and specific terpenoids derived from the surface vegetation. In addition, 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 surface area in 2012. The $\delta^{13}C$ data of the cave speleothems, topsoil and overlying vegetation confirmed that the organic fraction of the speleothem samples is a combination of partially charred vegetation and organic compounds from the andic soil over the cave.

Introduction

Speleothems, or secondary mineral deposits found in caves, are usually formed due to the dissolution of primary minerals from the host rock and subsequent precipitation of secondary minerals. Both limestone caves and lava tubes may contain a variety of speleothems, such as stalactites and stalagmites. Their formation is greatly prompted by water-rock interactions and climate conditions, which determine how much water drip into the cave [1]. In humid climates or during heavy precipitation a rapid speleothem growth may occur, whereas in arid climates or during drought the growth is moderated or ceased. Changes occurred on the soils over caves may also influence speleothem composition and formation. Hence, the composition, abundance and growth pattern of speleothems may be indicative of land use and climate changes, as reported by several authors [2, 3].

Soils in volcanic regions (including the Canary Islands, Spain) are mainly allophanic Andosols, which generaly composed of poorly crystalline clay minerals, such as allophanes and imogolite, and Fe and Al oxyhydroxides. These minerals are prone to form organo-mineral structures, which contribute to a stronger resistance of the soil to water erosion, an efficient protection of organic carbon against microbial decomposition and to the stability of the subterranean environment. However, these high amount of organic matter (OM) is easily combusted during wildfires [4]. Therefore, wildfire events over Andosols constitutes an additional risk to destroy the protecting topsoil and subsequently promotes erosion, leaching and transport of OM to the underlying cave environments.

Cave sedimentation typically results from the allogenic deposition of surface soils into caves. These sediments can provide information on local climate and other variables, such as possible changes in vegetation type, hydrology and geomorphology [5]. Similarly to sedimentary organic matter, cave speleothems are also key sites for organic matter (OM) deposition, offering the opportunity to study global climate changes and local environmental events [6]. Thus and taking into account that the soils overlying volcanic caves are a major source of carbon, the $\delta^{13}C$ of the organic fraction of speleothems can provide useful information on the origin of the OM of speleothems. Moreover, stable isotopes ($\delta^{13}C$, $\delta^{15}N$) and C/N ratios can be valuable indicators of OM origin and decay [6]. In an attempt to achieve an accurate characterization of the organic fraction of the ooze-like deposits found in MZ04 Cave in La Palma (Canary Islands) and unveil their nature and origin, analytical pyrolysis (Py-GC/MS), ^{13}C cross-polarisation magic-angle spinning nuclear magnetic resonance spectroscopy (^{13}C CPMAS NMR) and stable isotope analyses were performed.

Materials and methods

Site description and sampling. In a lava tube (MZ04 Cave) from La Palma Island, in Canary Islands (Spain), black deposits with a gelatinous texture were observed and collected from the wall and ceiling of the cave. In addition, the topsoil (0-5 cm) and charred vegetation over the cave were collected for comparison purposes.

Analytical Pyrolysis (Py-GC/MS) was performed using a double-shot pyrolyzer attached to a gas chromatograph. One mg of sample (speleothems, topsoil and surface vegetation) was pyrolysed at 500°C for 1 min and the evolved gases directly injected into the GC/MS. Chromatographic conditions were similat to those reported by Miller et al. [1]. The relative abundance of each pyrolysis product was expressed as a percentage (%) of the total chromatogram area, after the integration of peak areas.

Solid-state ^{13}C Nuclear Magnetic Resonance Spectroscopy (NMR) was performed using a Bruker Avance III HD 400 MHz and zirconium rotors of 4 mm OD with magic-angle spinning of the rotor at 14 kHz and a contact time of 1ms. Over 60 000 scans were accumulated for each sample. The ^{13}C chemical shifts were calibrated relative to tetramethylsilane (0 ppm) with glycine (COOH at 176.08 ppm). Spectra were quantified by integration of the following chemical shift regions: alkyl C (0-45 ppm), N-alkyl/methoxyl C (45-60 ppm), O-alkyl C (60-110 ppm), aromatic C (110-140 ppm),O-substituted aromatic C (140-160 ppm) and carboxyl/amide C and carbonyl C (160-220 ppm). The relative abundance of each typical C resonance region was expressed as relative percentage of the total C resonance area (assumed to be 100%) [7].

Stable isotope analyses ($\delta^{15}N$, $\delta^{13}C$). Bulk isotopic signature of light elements ($\delta^{13}C$ and $\delta^{15}N$) was determined in triplicate by coupling the elemental micro-analyzer to a continuous flow Delta V Advantage isotope ratio mass spectrometer (IRMS) (Thermo Scientific, Bremen, Germany) (C/TC-IRMS) via a ConFlo IV interface unit.

Results and Discussion

Py-GC/MS

Analytical pyrolysis reported the presence of specific biomarkers (di- and triterpenoids) as well as abundant polysaccharides and plant lipids typical of the local vegetation (*E. arborea* and *P. canariensis*). Polycyclic aromatic hydrocarbons and N-containing heterocyclic compounds detected were related to 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 black deposits from this lava tube suggested the alteration of the OM of the andosol over the cave probably due to the wildfire event.

Solid-state ^{13}C NMR spectroscopy

The ^{13}C NMR spectra confirmed the abundance of polysaccharides in the OM fraction of the speleothem. They are typically derived from fresh soil OM and microorganisms. The peak corresponding to the aromatic-C region found in the speleothem is probably owed to the incorporation of charred residues which were leached from the topsoil.

Stable isotope analyses

The $\delta^{13}C$ value of the cave black deposits was similar to those measured for the topsoil and surface vegetation. The value of $\delta^{15}N$ obtained for the black deposit was caracteristic of N fixation (from 0 to 7 ‰), being 4‰ generally considered the average of land plants (Maksymowska et al., 2000).

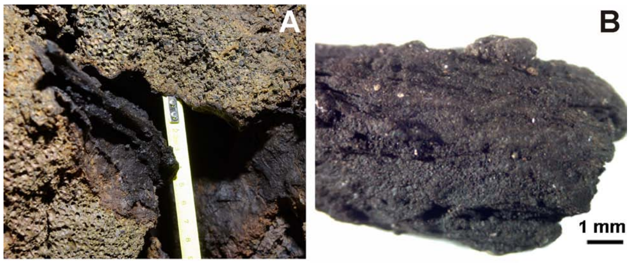

Figure 1. Black ooze-like deposits from MZ04 Cave, La Palma Island, Spain. A) Photography of the black deposits in the lava tube. B) Stereomicroscopy image showing their texture.

Stable isotope analysis confirmed that the organic fraction of the ooze deposits are a combination of partially charred vegetation and organic compounds from the andic soil located over the cave. Therefore, these cave deposits are the result of an input of plant OM and charred vegetation into the cave through rock fractures, which may constitute an important source of energy for cave organisms. Wildfire probably contributed to increase the alteration of the soil properties, such as porosity and water retention capacity, which promoted the leaching of OM and its input into the cave. Moreover, different depositional conditions occurred after the wildfire, which influenced the formation of the organic rich deposit.

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