WHEN CRYSTALS BECOME DUST: SPELEOTHEM DEGRADATION PROCESSES IN PRAILEAITZ I CAVE (NORTHERN SPAIN)

IÑAKI VADILLO[1*], ARANTZA ARANBURU[2], ENEKO IRIARTE[3], MARTÍN ARRIOLABENGOA[2], ANA BERRETEAGA[4,5], L. DAMAS[2], P. GARCÍA[2]

[1] Dept. of Geology. Group of Hydrogeology. Faculty of Science, Universidad de Málaga. 29071 Málaga
[2] Dept. of Mineralogy and Petrology. Faculty of Science and Technology, UPV/EHU. Ap 644-48080 Bilbao
[3] Laboratory of Human Evolution, Dept. of Historical Science and Geography, University of Burgos, Edificio I+D+I, Plaza de Misael Buñuelos s/n, 09001 Burgos
[4] Dept of Stratigraphy and Paleontology. Faculty of Science and Technology, UPV/EHU. Ap 644-48080 Bilbao
[5] School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Williamson Building, Manchester M13 9PL

* Iñaki Vadillo, Vadillo@uma.es

Introduction

Praileaitz I Cave is located in Gipuzkoa (Basque Country, Spain). An important network of caves has been identified in this area with archaeological materials from the Upper Palaeolithic. In addition to archaeological materials, in August 2006 a series of red painted signs was discovered inside the cave.

Purpose and methodology of study

Within the cavity there are evident signs of deterioration of different types and generations, affecting both the host rock and the speleothems. The supports of many of the paintings, specifically the drapes, are in a clear state of deterioration due to disintegration of the texture of the speleothem, resulting from selective dissolution of the crystals and the creation of intercrystalline porosity. To analyse and study the different types of degradation and their causes, we gathered a total of 14 samples of speleothems and rock throughout the cave. The speleothems sampled are of different types and come from different growth phases. In order to monitor the parameters that may be causing the pathologies of degradation, a protocol was drawn up for measuring the environmental parameters and the condensation water and drip water in the cave. To analyse the water from the cave, samples were taken at four representative drip points in the cave and from condensation water.

The protocol established for addressing the problem of the different pathologies in the speleothems includes a combination of various techniques: (1) Conventional optical microscopy, (2) Scanning electron microscope, (3) X-ray diffraction analysis, (4) isotopic analyses of $\delta^{13}C$ and $\delta^{18}O$ from micrite, speleothem and host rock and (5) water chemistry and isotopic analysis.

Pathologies in the speleothems of Praileaitz I

The pathologies fundamentally develop on speleothems that are now inactive or sporadically active with weak dripping, regardless of their morphology and formation phase. In Praileaitz I cave we distinguish three types of “pathologies” with clearly distinguishable zoning throughout the cave: (1) through organic activity, (2) generation of micrite or “moonmilk” and (3) sheeting/dissolution.

Degradation resulting from organic activity (root colonisation and bioturbation) has only been detected at the entrance to the cave, which receives direct sunlight.

Micritization and formation of “Moonmilk” cover different types of support including the host rock and the different types of speleothems and are white and porous in

texture. It is normally millimetric, formed by a network of matt white calcite crystals of less than 4 μm.
Dissolution/sheeting alteration affects inactive speleothems, mainly of drape type and stalactites, and the host rock, creating intercrystalline porosity or hemispheric dissolution. This pathology involves an alteration in the textural features of the speleothems through sheeting or loss of material from the surface layers ("onion-skin") along the growth lines.

Causes of the Pathologies

The two main internal pathologies described in Praileaitz I cave are simply a differential reflection of a single process: condensation of the humidity in the interior of the cave. The greatest proliferation of the alteration of a micritization/ "moonmilk" formation type takes place in the near entrance chambers, where there are very sharp fluctuations in temperature and humidity between spring-summer and autumn-winter, leading to humidification-dehumidification (evaporation) cycles that determine the greater and lesser creation of condensation water on the walls and speleothems of the cave. This variability in the ambient conditions in the most external area of the cave results in neoformation of acicular micritic calcite during the months of greatest temperature and a fall in humidity in the cave, from the dissolved carbonate (speleothem) in a period of greater condensation. In contrast, in the inner chambers of the cave, both the temperature and the humidity (close to 100%) remain constant throughout the period with sharp increases in CO_2 concentrations in the months of May-November, increasing the dissolution effects from the condensation water.
A narrow passage at different elevations between external and internal chambers serves as a climatological barrier to energy/mass fronts from the exterior. This particular physiography is important because it prevents the energy fronts (heat-cold) from entering the internal sector and allows constant climatic conditions in this interior sector of the cave. At the same time, however, these conditions are aggressive for the speleothems, due to the high concentration of CO_2 and the constant availability of condensation water, which means that the alteration processes described occur with greater intensity and duration.

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