



## **Pyrolytical evidence of the abiotic origin of moonmilk formations from Castañar cave (Cáceres, Spain)**

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Castañar cave (Cáceres, Spain) characteristically contains a series of Mg-Si phases forming fibres and films associated to aragonite, magnesite, huntite and spheroidal dolomite in moonmilk, which form coatings and crust speleothems. These Mg-Si phases consist of kerolite, sepiolite and its admixtures. Under scanning electron microscope kerolite appears as colloform, smooth masses or films. Sepiolite mostly occurs as isolated fibres 50 to 200 nm thick and up to 50  $\mu\text{m}$  long and mats of interwoven fibres of several shapes, which often look like jelly, flexible-like films. Both minerals are highly hydrated and with low crystallinity.

In order to evaluate a possible role of organic matter in the biogeochemical formation of these minerals, two samples of moonmilk and 4 controls were analyzed by analytical pyrolysis (Py-GC/MS). The pyrolyzate of the samples consisted mainly of a) methoxyl-lacking benzenes, b) unsaturated and saturated hydrocarbons, c) polycyclic aromatic and d) hydroaromatic hydrocarbons. This chemical assemblage is not compatible with a recent biogenic origin of the organic matter in the moonmilk. This is suggested by the small proportions of fatty acids in addition to the lack of nitrogen- and carbohydrate-derived compounds. In fact, most of the aromatic compounds (e.g., phenols and catechols) which would be expected from plant or microbial biomass were in negligible proportions whereas methoxyphenols (typical lignin-derived compounds) were completely absent, suggesting no contribution from biomass of vascular plants. Conversely, the signature of alkyl compounds found in these samples (homologous series) is compatible with that in coals, kerogens or other forms of fossil organic matter. In particular, the whole pyrograms resembled the control shale from the host rock, which suggests that the organic matter was in fact inherited from the host rocks.

Concerning the mineral phase, the low crystallinity and textures of kerolite and sepiolite indicate formation by direct precipitation in the cave waters via recrystallization of a gel precursor, under specific local conditions of high alkalinity and activity of Mg and Si.

In conclusion, the low amount of organic matter content and its molecular composition, in addition to the lack of clear organic features and the general context indicates that kerolite and sepiolite precipitation in Castañar cave was most probably abiotic.