The origin of fibrous microcrystalline calcite: abiotic, biotic or polymer induced?

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Fibrous microcrystalline calcite (FMC), incorporating needle fibre calcite (NFC) and calcite nanofibres, is a typical carbonate form in vadose terrestrial settings, often associated with diverse microbial features and exopolymeric substances (EPS). Although a purely physicochemical origin has been postulated in many occasions, prevailing concepts imply biologically induced mineralisation, either by mediation of fungi [1] or filamentous bacteria [2]. These hypotheses are mostly based on the intrinsic association of FMC with microorganisms, the fact that many of these microbes are culturable and able to precipitate carbonate in the lab, geochemical and crystallographical evidence, and morphological arguments, i.e., resemblance in dimensions and morphology between calcite fibres and fungal hyphae and filamentous bacteria.

To explore their abiogenic vs. biogenic origin we have studied FMC material from moonmilk speleothems in four Slovenian caves and from Mediterranean calcareous soils. Micro-morphological features of FMC observed under SEM are strikingly similar to those of calcite crystals formed *in vitro* by non-classical pathways of crystallization. The smooth character of the NFC rods, their spatial crystallographic orientation, and the presence of droplets or bobbles at the tip of the crystals are typical features of calcite fibres precipitated by polymer-induced liquid precursor mechanisms (PILP) [3]. Single-crystal, high aspect ratio, flexible like nanofibres of similar sizes of those found in FMC in nature have been precipitated in the lab in the presence of Poly(Allylamine Hydrochloride) [4] by aggregation of amorphous particles, which are incorporated into the fibres uniquely at their tips, before crystallizing.

In cave moonmilk and related settings in soils, microbial EPS can influence crystal morphology and growth of distinctive nonequilibrium forms of calcite without living organisms and metabolic processes directly involved in mineralisation.

[1] Bindschedler *et al*. (2012) *Geomicrobiolog J*, **29**, 301-313. [2] Cañaveras *et al*. (2006) *Naturwissenschaften*, **93**, 27-32. [3] Olszta *et al*. (2004) *Chem Mater*, **16**, 2355-2362. [4] Cantaert *et al*. (2013) *Chem Mater*, **25**, 4994-500.