## GROWTH MECHANISMS OF NEEDLE FIBRE CALCITE: IS MICROBIAL METABOLISM INVOLVED?

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Deposits of needle fibre calcite (NFC) have been considered as a representative example of microbial (fungal) biomineralisation in vadose terrestrial settings. Basic elements of NFC are strongly elongate, rod-shaped low-Mg calcite crystals with an average width of 1  $\mu$ m and length typically reaching 10<sup>2</sup> to 10<sup>3</sup> times their width. NFC occurs in pores, mm to dm in size, forming patchy, cotton-like aggregates, typically accumulating within the rooting zone of terrestrial plants in semiarid/sub-humid climatic regions, generally characterised by seasonal moisture deficit. In caves, NFC and nanofibrous calcite forms are the main component of calcite moonmilk – a porous, soft, microcrystalline speleothem that can contain up to 95% of interstitial water, showing a distinctive pasty and plastic texture.

The basic NFC rod shapes have been explained by calcite nucleation and growth inside 'organic sleeves' (fungal hyphae), which act as moulds, inducing atypical needle crystal shape. Although the hypothesis of fungal biomineralisation (as opposed to growth of NFC by rapid evaporation) has been supported by presumptive geochemical and mineralogical/crystallo-graphical evidence, the main argument has been founded on the similarity in dimensions and morphology of calcite fibres and fungal hyphae, their co-occurrence, and the fabric of NFC deposits.

Our study is based on material from actively precipitating moonmilk deposits in caves and secondary soil carbonates precipitating within extensive root systems of plants in calcareous substrates in Mediterranean and Alpine climates (Spain and Slovenia). Distinctive crystal shapes and growth patterns of NFC occurring in different underground ecosystems and geochemical settings strongly suggest a common mechanism of crystal growth, which is not necessarily related to fungi as in the generally accepted model. Morphological evidence against the NFC formation within a tubular (fungal) organic template is based on abundant complex branching NFC structures, composed of simple rods protruding as parallel outgrowths from a common NFC rod substrate. These ordered dendritic structures apparently exhibit a crystallographic control in NFC growth, following patterns similar to a crystal lattice. Furthermore, NFC rods observed in these structures, typically terminate with a droplet (bobble) at the tip of the crystal, a characteristic feature of calcite fibres precipitated in-vitro by polymer-induced liquid precursor mechanisms (PILP). Our study suggests that NFC crystal morphologies can be explained by concepts of non-classical crystallisation systems where polymeric substances probably provide a template for CaCO<sub>3</sub> nucleation and oriented growth. In cave moonmilk and related settings in soils, microbial EPS can influence crystal morphology and growth of these distinctive nonequilibrium forms of calcite without living organisms and metabolic processes directly involved in mineralisation

## Acknowledgements

This research was performed within the programme no. P1-0008 and the postdoc project no. Z1-7247 (AMP), both supported by the Slovenian Research Agency (ARRS).