

## **Fungal implication in secondary calcium carbonate accumulation in soils and caves**

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Fungi are often associated with secondary CaCO<sub>3</sub> in soils and caves, mainly with two features, Needle Fibre Calcite (NFC) and calcitic nanofibers. The origin of these two features remains controversial. Both biological and physicochemical processes have been proposed to explain their formation. NFC has been observed inside organic sleeves, interpreted as fungal hyphae. Furthermore, field observations, as well as size and structure homology between NFC bundles and fungal strands have confirmed involvement of fungi. Investigations of calcitic nanofibers, often observed together with NFC, may provide new insights regarding the relationship between these two features and fungi.

Electron microscope observations show that nanofibers could originate from the partial decay of the fungal cell wall. During organic matter decay cell wall nanofibrils (e.g. chitin and  $\beta$ -glucans) are released into the soil where they are exposed to mineralizing pore fluids, leading to their calcitic pseudomorphosis. To test this hypothesis of a biological origin of calcitic nanofibers an experimental approach was chosen: first, fungal hyphae were partially digested with enzymes selectively hydrolysing non-fibrous material from the fungal cell wall. In a second step the remaining fibrillar components were exposed to conditions similar to those in natural environments in order to induce CaCO<sub>3</sub> nucleation. Fungal remains and CaCO<sub>3</sub> precipitates were analyzed by TEM and SEM.

Calcium plays a crucial role in fungal metabolism. It is translocated in the hyphae and can accumulate in the cell wall and vacuole. We propose that when exposed to carbonate saturated solutions CaCO<sub>3</sub> can precipitate on fungal organic template.

As a result, when associated with NFC bundles, nanofibers could indicate relicts of organic sheaths, supporting the hypothesis of a genetic link between fungi, nanofibers, and consequently NFC. On a global scale, this emphasizes the important roles of both organic matter and fungi in the coupled carbonate-carbon cycle.