



Growth conditions and Ca sources of pedogenic needle fibre calcite (NFC)

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Needle fibre calcite (NFC) and nanofibres are microscopic features of secondary calcium carbonate accumulation commonly observed in soils and caves. Both NFC and nanofibre morphologies correspond to a needle-shaped monocystal. NFC has an average diameter of 1-2 μm and a length reaching 10^2 times its width, while nanofibres have an average width of 50-150 nm and lengths from 10 to 100 times their width. Three main groups previously identified by Millière et al. (2011) and corresponding to specific microscopic arrangements, have been identified in the Swiss Jura Mountains: simple needles (SN) corresponding to the original form of NFC, which can evolve into simple needles with calcitic overgrowths (SNO), and simple needles with nanofibres (SNN). It is suggested that both NFC and nanofibres are related to the presence of fungi, but despite intense work, its origin and the processes involved in its formation are still under debate. To better constrain their formation processes, different NFC morphotypes (SN, SNO, SNN) and a late calcitic cement (LCC) from the same soil depth, have been sampled in the Swiss Jura Mountains.

Strontium and calcium isotopic compositions and Sr/Ca ratios in the different reservoirs of NFC, soil water, throughfall, inorganic cements as well as host rock have been analysed to determine Ca sources and to investigate the formation mechanisms.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the various NFC types and LCC suggest that the contribution of Ca from the main Ca sources differs between NFC and LCC, implying different precipitation processes. In addition, the three microscopic morphological groups of NFC (SN, SNO, SNN) displayed Sr isotopic compositions different from each other, emphasizing a direct relationship between the NFC morphotypes and the origin of the Ca. Sr/Ca ratios and $\delta^{44}/^{40}\text{Ca}$ values of NFC and LCC crystal are used to determine possible differences in their growth rate and/or micro-environment during their formation. Crystals described as simple needles (SN) are enriched in ^{44}Ca and depleted in Sr compared to LCC, suggesting that the elongated shape of the SN crystal cannot be related to a rapid precipitation rate, but rather to a slow precipitation under semi-enclosed conditions. In contrast, LCC has a stronger enrichment in light Ca isotopes and is less depleted in Sr relative to the soil solution, suggesting more rapid precipitation. SNN and SNO overlap with the SN but are on average lighter in Ca isotopes and have higher Sr contents. Overall, NFC and LCC are explainable by calcite precipitation according to the Sr and Ca systematics of inorganic calcite of Tang et al. (2008b), with different precipitation rates and degrees of Ca and Sr consumption. Specifically, SN correspond to values of a calcite formed in a restricted environment, supporting the fungal hypothesis for the origin of NFC.

References:

Millière L et al. (2011a) Stable carbon and oxygen isotope signature of pedogenic needle fibre calcite: further insight into its origin and relationship with soil conditions. *Geoderma* 161: 74-87

Tang J et al. (2008b) $\text{Sr}^{2+}/\text{Ca}^{2+}$ and $^{44}\text{Ca}/^{40}\text{Ca}$ fractionation during inorganic calcite formation: II. Ca isotopes. *Geochimica et Cosmochimica Acta* 72: 3733-3745