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Stable calcium isotope composition of a pedogenic carbonate in forested ecosystem: the case of the needle fibre calcite (NFC).

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Calcium (Ca), carbon (C) and oxygen (O) are important elements in terrestrial environment, as their biogeochemical cycles are directly related to the storage of atmospheric carbon. Nevertheless, contrarily to C and O, Ca isotope composition has been only poorly studied in the terrestrial carbonates. Needle Fibre Calcite (NFC) is one of the most common pedogenic carbonates, unless its origin is still under debate. Recent studies explain its formation by precipitation inside fungal hyphae. Due to this possible biogenic origin, NFC can be considered as a potential bridge between the biochemistry (precipitation inside organic structure) and geochemistry (pedogenic carbonate related to soil conditions) of the Ca. Thus, the study of the Ca isotope composition of NFC seem to be of first interest in order to shed light on the behaviour of Ca in terrestrial environment, especially when precipitation of secondary carbonates is involved. The sampling site is situated in the Swiss Jura Mountains and has been chosen due to a previous complete study of the C and O isotope composition of NFC in relation to the ecosystem, which represent a good precondition for the understanding of the NFC Ca isotope signatures in this context.

In this study, the implication of the fungi in the origin of NFC is investigated, by comparing the Ca isotope composition of NFC and a purely physicochemical calcite cement (LCC), both precipitated in the same environment. The δ^{44}Ca signature of NFC and LCC crystals were used to determine possible differences of the precipitation rate during their formation. NFC and LCC have similar δ^{18}O composition and are supposed to precipitate at the same temperature (Milliere et al., 2011a). Thus the study of Ca isotope composition of NFC seems to demonstrate that the elongated shape of the calcite needle can be explained by different precipitation processes than the rhombohedric calcite crystals precipitated in the same environment; and more precisely, the specific shape of NFC could be ascribed to a growth related to fungal organic molecules or potentially inside fungal hyphae.

Three microscopic morphologies of NFC, previously defined (Milliere et al., 2011a), have been also examined in order to trace the evolution of the NFC inside the soil porosity. The Ca isotope composition of the simple needles, which are supposed to be the original form of NFC are the less fractionated compared to the soil solution, whereas the Ca isotope composition of the two other microscopic morphologies, namely the simple needle with nanofibres and the simple needle with overgrowths, are more fractionated, like the LCC, indicating potentially the influence of biogenic processes in the formation of the simple needles.

Milliere L, Hasinger O, Bindschedler S, Cailleau G, Spangenberg JE, Verrecchia EP. 2011a. Stable carbon and oxygen isotopic signatures of pedogenic needle fibre calcite. Geoderma 161, 74-87.