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Pedogenic carbonate in Quaternary paleosoils from Hungary

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Mezo- and micromorphology, mineralogy and chemical (including stable and Sr isotope) composition of secondary (pedogenic) carbonate was studied in several Quaternary paleosoils from Hungary. The parent rocks of the soils are both calcareous (travertine, loess) and non-calcareous ("red clay").

Macroscopically visible amounts of aggregates of calcite needles can be found in the paleosoil of Buda Castle travertine (Budapest). Its micromorphology (40 to 200 μm long monocrystals as smooth rods and serrated-edged crystals) and texture (randomly distributed crystals, bundles of subparallel crystals forming coatings and alveolar structure in vugs and pores) suggests that needles are calcified fungal sheaths and produced by fungal biomineralization. The stable isotope composition of calcite needles (δ^{18}O = -7.1 permil and δ^{13}C = -7.3 permil on average vs. V-PDB) indicates significant incorporation of organically-derived CO_2 and probably biological influence on needle genesis.

In loess and its intercalated soils the distribution of discrete small scale carbonate precipitations (less than a few millimetres in size) related directly or indirectly to biological activity of plants and animals can indicate the environmental and climatic conditions during deposition (Becze-Deák et al., 1997). The Basaharc Double pedocomplex, a reference soil horizon in the Young Loess Series in Hungary, was investigated at its type locality (Basaharc, north of Budapest). Calcified root cells, hypocoatings, calcite needles from fungal biomineralization and earthworm calcite spheroids were identified in the soil horizons. Their distribution and amount (except calcite needles) was similar in both horizons, however, the stable isotope compositions of the bulk soil samples were different. In the lower (BD2) soil $\delta^{13}C_{bulk}$ values as low as -18.7

permil were measured, while in the upper (BD1) soil the lowest $\delta^{13}C_{bulk}$ value was -12.5 permil. The stable isotope composition of carbonate nodules in both soil and the host loess was fairly constant ($\delta^{13}C_{nodules}$ = -9.6 to -10.7 permil, $\delta^{18}O_{nodules}$ = -7.8 to -8.9 permil vs. V-PDB) indicating similar environmental conditions during pedogenesis of the two soil horizons. The calcified root cells from the lower soil can exhibit similar or lower $\delta^{13}C$ values ($^{13}C_{rootcells}$ = -20.9 to -28.0 permil, $\delta^{18}O_{rootcells}$ = -15.6 to -17.0 permil vs. V-PDB) than that of the bulk soil. It is, however, unlikely that the shift of $\delta^{13}C_{bulksoil}$ values is caused by calcified root cells as proposed by Boguckyj et al. (2006), because of their relatively low amount in the soil.

Calcrete concretions with septarian voids and fractures filled with some mm sized, euhedral calcite crystals are not widespread in soils. A Vertisol-type “red clay” soil sedimentary complex on the pediment of the Mátra Mountains (Northern Hungary), however, contains huge amount of calcrete nodules and their evolved forms, septarian concretions of several ten cm in size. Although the extreme amount of carbonate might suggest that its redistribution could also have been induced by evolved groundwater within the phreatic zone, the stable isotope composition of nodules and concretions indicates pedogenic-shallow groundwater origin ($\delta^{13}C$ = -8.9 to -12.3 permil, $\delta^{18}O$ = -5.9 to -10.4 permil vs. V-PDB). Calcrete formation probably occurred in the temporarily waterlogged parts of the “red clay”. Late-stage Mn-rich euhedral calcite in the concretions exhibits the lowest $\delta^{13}C$ values, possibly due to larger incorporation of isotopically light organic CO_2 in an early diagenetic environment during shallow burial of the paleosoil. Sr isotope composition of nodules and concretions is between 0.7116 and 0.7125 indicating a mixed source for Ca (in situ weathering, local inputs and atmospheric dust). The Sr signatures decrease upwards in the “red clay” profile, which suggests an increasing contribution of Ca from the overlying loess (atmospheric dust).

The characteristic of pedogenic carbonates with different forms and origin in the above mentioned Quaternary paleosoils is their $\delta^{13}C$ values lower than -7 permil implying a significant contribution of C3-dominated organic carbon during carbonate precipitation.

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