# Rhizoliths in loess - determination of the origin using organic geochemical approaches 

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Pedogenic (secondary) carbonates have been generated mainly under arid and semiarid conditions by interaction with soil CO2. Usually, hundreds to thousands of years are necessary for a formation of secondary CaCO 3 . d13C of pedogenic carbonates reflects the photosynthetic pathway of the predominant local vegetation, because secondary CaCO 3 is formed in isotopic equilibrium with soil CO 2 released by root and rhizomicrobial respiration. Therefore, d13C of pedogenic carbonates is used for paleoenvironmental reconstructions.
Rhizoliths are a special form of pedogenic carbonate formed by encrustation of plant roots. While the organic part of the root is mainly degraded during decomposition, carbonatic, bone-like structures remain in the terrestrial sediments. They occur locally abundant in calcareous sediments like loess. In contrast to very long formation of other types of pedogenic carbonates, these calcified roots are built probably within a few decades or even years. In some previous studies, rhizoliths were attributed exceptionally to coniferous trees. The aim of our study was to elucidate the origin of rhizoliths on a molecular level in combination with stable C isotopic composition (d13C) of carbonatic and organic parts of the rhizoliths. The comparison of isotopic values and the carboxylic acid composition in rhizoliths and in the adjacent loess should provide information on the sources of both materials. While loess sedimentation commonly occurs under steppe-like conditions, roots entered the loess later probably under different climatic conditions and consequently might derive from a different vegetation.
Loess-derived rhizoliths as well as loess ( $30 \% \mathrm{CaCO}, 0.3 \%$ Corg) from Nussloch (SW Germany) were analysed for d 13 C of CaCO 3 and Corg, as well as carboxylic acid composition.
d 13 C values of rhizolith Corg, rhizolith carbonate and primary loess carbonate showed values of $-25.1 \% \mathrm{o}$, $-10.7 \% \mathrm{o}$ and $-1.2 \%$ [V-PDB], respectively. d13C of Corg indicates the C3 photosynthetic pathway of the vegetation present at rhizolith formation. The difference of $14.4 \%$ o between organic C and rhizolith carbonate C is related to an isotopic fractionation by molecular diffusion ( $4.5 \% \mathrm{o}$ ) and carbonate equilibrium reactions ( $10-$ $11 \%$ o).
Carboxylic acid composition of the rhizolith matter confirmed the C 3 photosynthetic pathway of former vegetation by its CAR (carboxylic acid ratio $=\mathrm{C} 24 /(\mathrm{C} 22+\mathrm{C} 26))$ value of 0.43 . Moreover, comparison of carboxylic acid distribution patterns in organic matter of loess and that of rhizoliths disproved the prevalent opinion about rhizolith formation taking place simultaneously with loess sedimentation: Loess organic matter yielded a combined signal from shoot and root biomass with high amounts of long chain carboxylic acids (C22-C32). This reflects former steppe conditions with grass vegetation, which is in accordance with loess sedimentation during glacial periods. In contrast, rhizolith organic matter contained lower amounts of very long chain carboxylic acids (C26-C30), thus reflecting more likely roots from bush or tree vegetation. Shape of rhizoliths and thin sections indicate the latter as well.
Rhizoliths in loess sequences are not formed during sedimentation. They entered the sediment later and originate from different vegetation than present at the time of sedimentation, which could be more like savannah type vegetation. More analyses on different rhizoliths are planned to determine if there are different sources of rhizoliths and if rhizoliths of different shapes might by attributed to specific vegetation.

