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Recrystallization of biogenic carbonates in soils: consequences for palaeological studies

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The isotopic signatures of biogenic carbonate (BC) in fossils are commonly used to assess environmental conditions during the life time of organisms, their diets and extinction periods. As a proxy, BC represents in many cases the only alternative to organic matter. However, BC in fossils may dissolve in embedded matrix and recrystallize with CO_2 respired by roots and microorganisms. Consequently, isotopic composition of BC can be re-equilibrated and the original paleoenvironmental signal may be lost. The dynamics of these processes still remains poorly understood. Here the results of BC recrystallization under controlled conditions have been presented. We aimed 1) To determine the recrystallization amounts of BC as a function of time, 2) To investigate the effects of geogenic carbonates (GC) availability in embedded matrix on recrystallization rate of BC and 3) To evaluate the effects of organic matter (OM) presence in the BC structure on its recrystallization.

Loess and a loamy soil were selected as carbonate containing and carbonate free matrixes, respectively. Shells of "Pacific little-neck clams (*Protothaca staminea*)" were selected as BC. To evaluate the role of OM presence in the BC structure, heated ($550^{?}$C) and not heated shells were used. The shells were washed by means of ultrasonic and crashed to a size of 2-2.5 mm. The ^{14}C labeled CO_2 (pCO_2= 2%) was injected into the airtight bottles. The samples were incubated at room temperature and water content of 60% of water holding capacity of matrixes for 1, 3, 10, 21 and 56 days. At each time the ^{14}C activity was measured in bottle air, dissolved organic and inorganic carbon, matrixes and the shells.

The recrystallization of shells started even after one day of incubation. However, the amounts of recrystallization were increased by the time. The recrystallization of $CaCO_3$ was higher in shells without OM. Elimination of OM probably increases the porosity of shell structure and led to better water penetration into the shells. Recrystallization was higher in BC surrounded by loess compared to that in carbonate free loamy soil. GC in loess can undergo dissolution as well. This leads to release of Ca^{2+} ions which may partially be recrystallized on shells. Based on the recrystallization rate of shell carbonate, we extrapolated the time for their full recrystallization. Our results showed that a full recrystallization of shells needs ca. 90 years for shells without OM in loess to ca. 300 years for shells containing OM in carbonate free loamy soil. Consequently, the original isotopic signature will be vanished completely in the shell structure after this period. Our results suggest that the recrystallization of BC may proceed relatively rapidly: between decades and centuries. The study further shows the high potential of ^{14}C labelling for understanding the processes of diagenetic alteration of BC in soils and sediments.