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CO_2 concentration in soil air affects recrystallisation rate of primary $CaCO_3$

M. Gocke (1), K. Pustovoytov (2), **Y. Kuzyakov** (1)

(1) Dep. of Agroecosystem Research, University of Bayreuth, 95440 Bayreuth, Germany, (2) Institute of Soil Science and Land Evaluation (310), University of Hohenheim, 70593 Stuttgart, Germany (martina.gocke@uni-bayreuth.de / Phone: +49-921-552336)

Pedogenic (secondary) carbonates originate from dissolution and recrystallisation of lithogenic (primary) carbonates with CO_2 from soil air, leading to a complete exchange of the lithogenic with the athmospheric carbon (C) during time. Therefore, isotopic signature of pedogenic carbonates (δ^{13}C and δ^{18}O) will be used as important information for reconstruction of paleoclimatic conditions. Therefore, the interest in pedogenic carbonates increased over the last years. However, the recrystallisation rate of primary $CaCO_3$ by pedogenic carbonate formation and the dependence of the rate on environmental factors (i.e. CO_2 concentration in soil air) are not known. To ascertain this correlation was the main intention of this study.

Loess from Nussloch (SW-Germany) was chosen instead of soil because it contains solely primary $CaCO_3$, has high carbonate content (30%) and nearly no organic carbon. Within metallic tubes, air containing increasing CO_2 concentrations (400, 5000 and 50000 ppm) labeled with $^{14}CO_2$ was applied to the loess. After increasing time periods (3 days, 2 weeks, 2 months), the ^{14}C activity in loess carbonate, dissolved inorganic carbon (DIC), and CO_2 were measured by liquid scintillation counting.

The maximal ^{14}C activity was recovered in loess $CaCO_3$, followed by ^{14}C activity in DIC, and the minimal ^{14}C activity was in CO_2. ^{14}C activity in loess $CaCO_3$ and ^{14}C specific activity of input CO_2-C were used to calculate the amount of recrystallised loess carbonate. The amount of recrystallised $CaCO_3$ increased with increasing CO_2 concentration. After 3 days, the amount of recrystallised carbonate was 0.0002%,

0.0003% and 0.0006% of original $CaCO_3$ for 400, 5000 and 50000 ppm, respectively. Under 5000 and 50000 ppm CO_2 concentrations, an equilibrium between ^{14}C in DIC and $CaCO_3$ was not reached even after 2 months, and the increase of the ^{14}C activity in the loess carbonate was stronger at 50000 than at 5000 ppm.

CO_2 concentration in soil air, ranging from atmospheric values in the upper horizons up to 70000 ppm in deeper horizons, plays an important role for the soil $CaCO_3$ re-crystallisation.