Effect of CO₂ concentration on the initial recrystallization rate of pedogenic carbonate — Revealed by ¹⁴C and ¹³C labeling

M. Gocke a,⁎, K. Pustovoytov b, Y. Kuzyakov a

a Department of Agroecosystem Research, University of Bayreuth, 95447 Bayreuth, Germany
b Institute of Soil Science and Land Evaluation (310), University of Hohenheim, 70593 Stuttgart, Germany

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A B S T R A C T

In calcareous parent material, pedogenic carbonate formation mostly involves dissolution and recrystallization of lithogenic carbonates with CO₂ of soil air, leading to a complete exchange of lithogenic carbon with soil-derived carbon. Interest in pedogenic carbonates has increased in recent decades because they are a useful tool for reconstructing paleoclimatic conditions (δ¹³C and δ¹⁸O) and past atmospheric CO₂ concentrations as well as for radiocarbon dating of soils. For such investigations, the recrystallization rate of primary CaCO₃ by pedogenic carbonate formation and the dependence of the recrystallization rate on environmental factors are essential, but still unquantified factors. The recrystallization rate of primary CaCO₃ of loess at three CO₂ concentrations was estimated by isotopic exchange between primary CaCO₃ and the ¹⁴C of artificially labeled CO₂. Loess was used for the study as a parent substrate for soil formation to simulate initial rates of CaCO₃ recrystallization. CO₂ concentrations of 380 ppm, 5000 ppm and 50,000 ppm lead to recrystallization rates of 4.1·10⁻⁷ day⁻¹, 8.1·10⁻⁷ day⁻¹ and 16.9·10⁻⁷ day⁻¹, respectively. The relation between CO₂ concentrations and recrystallization rates was described by a saturation curve. Under the tested experimental conditions, complete (95%) recrystallization of loess carbonate and formation of pedogenic carbonate would take 4.9–20.0·10³ years, strongly depending on CO₂ concentration. We expect faster recrystallization rates under field conditions because of permanent CO₂ supply by root and rhizomicrobial respiration. This impedes the equilibrium between the inorganic C pools in solid, liquid and gaseous phases.

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1. Introduction

Globally, soils contain a total of 659–748·10¹⁵ g carbon (C) as CaCO₃ in the upper 1 m (Batjes, 1996). Sahrawat (2003) summarizes all carbonates in soils as the soil inorganic carbon (SIC) pool. In arid and semiarid regions, the SIC pool is the main C pool in terrestrial ecosystems, but under certain conditions (e.g. soil acidification) the pool might release CO₂ from soil and thus contribute to the greenhouse effect (Lal and Kimble, 2000).

Pedogenic carbonate is a typical product of soil formation under arid to semi-arid climatic conditions. Over the last two decades, an increasing number of studies demonstrated the potential of pedogenic carbonate as a (paleo)environmental proxy, an indicator of past CO₂ concentrations and a chronological tool. The pedogenic carbonate is formed at carbon isotopic equilibrium between itself and soil CO₂ (Cerling, 1984; Nordt et al., 1996). Therefore, δ¹³C reflects the photosynthetic pathway of the predominant local vegetation (Cerling et al., 1989; Amundson et al., 1989; Cerling and Quade, 1993). This fact served as the basis for reconstructions of paleoenvironmental conditions and dating based on pedogenic carbonates is their complete recrystallization and preservation through time. Note, however, that pedogenic carbonate and other carbonate materials in soils can pass through diagenetic alteration, recrystallize and thus lose a substantial part of their initial stable isotopic and/or radiometric information (Cerling, 1991; Pendall et al., 1994; Nordt et al., 1998; Pustovoytov and Leisten, 2002; Budd et al., 2002). Accurate paleoenvironmental reconstructions and chronological studies based on pedogenic carbonates require knowledge about the time scale of secondary carbonate formation. Up to now, however, the
recrystallization rates of such carbonate, as well as the dependence of this rate on environmental factors (e.g. temperature and CO2 concentration in soil air), remain unknown.

There are two basic approaches to assess the recrystallization rate of carbonate in soil. The first is to analyze the distribution of stable isotopic composition and/or radiocarbon age of carbonate over a soil profile of known age (Pendall et al., 1994; Pustovoytov and Leisten, 2002; Pustovoytov, 2003). The second approach is based on the rates of isotopic exchange under controlled conditions (Kuzyakov et al., 2006). It involves measuring the 14CO2 that is photosynthetically assimilated by plants, respired by their root systems and associated microorganisms, and finally included by recrystallization into newly formed carbonate. The present study addresses certain unresolved questions in that latter work. Based on a linear increase of rhizosphere 14C recovered in loess CaCO3, Kuzyakov et al. (2006) calculated an initial recrystallization rate of 2.9 · 10−3 day−1. The authors concluded further that the time needed for complete recrystallization of CaCO3 is at least 100, but probably 400–2000 years, depending on the assumptions when extrapolating the observed initial recrystallization rate. These estimations demonstrated the constraints for the chronological resolution of paleoenvironmental reconstructions based on δ13C of pedogenic carbonate: evidently, the carbon isotopic signature of an earlier stage in the environmental history of a site can be replaced by a new isotopic signal relatively rapidly compared with the actual age of the proxy. The above study probably overestimated the recrystallization rate due to CO2 accumulation within the plant pots, leading to a faster reaction between dissolved CO2 and solid CaCO3 than under field conditions.

CaCO3 recrystallization is clearly affected by soil CO2 concentration. Under field conditions, this concentration depends on vegetation and various soil properties, and varies between 0.035% and about 3.5% (by scintillation counting) compared to 13C measurement (10−7 mol, by mass common spectrometry analyses). Nevertheless, in treatments with CO2 concentrations higher than the atmospheric level, 13C was applied simultaneously with 14C to allow a comparison of the calculated recrystallization rates based on both 14C and 13C labeling.

2. Material and methods

2.1. Loess

Instead of soil, loess from a depth of 15 m below present surface was used for the experiment for the following reasons. Firstly, loess from this depth is not influenced by recent pedogenic processes. Therefore, the distribution of CaCO3 is even and diffuse — no visual recrystallization took place — and the CaCO3 crystals are as small as after initial loess formation. The loess contains little organic C; therefore, no significant microbial decomposition from organic sources can alter the CO2 concentration in soil air. Secondly, contrary to most soils, loess has a high CaCO3 content, by scintillation counting) compared to 13C measurement (10−7 mol, by mass common spectrometry analyses). Nevertheless, in treatments with CO2 concentrations higher than the atmospheric level, 13C was applied simultaneously with 14C to allow a comparison of the calculated recrystallization rates based on both 14C and 13C labeling.

As experimental conditions, three time periods (4, 16 and 65 days) after the labeling and three CO2 concentrations (380, 5000 and 50,000 ppm) were chosen.

For each replication, one metal pipe (length 10.2 cm, inner diameter 1.6 cm) was filled with 28 g of air-dried and sieved loess. After moistening the loess to 70% of water holding capacity (WHC = 28% of loess weight), each metal pipe was closed by connecting its ends with PVC tubings and a joint.

2.3. Labeling and sampling

For the labeling, 92.5 kBq of 14C as Na213CO3 (ARC Inc., USA) was diluted with de-ionized water in a 30 ml vial. Previously, the water was slightly alkalized to prevent loss of 14C activity by exchange with atmospheric CO2. Increasing amounts of 99% 13C-enriched Na213CO3 (Isotec™, Ohio, USA) were added to the label solution, leading to the respective CO2 concentrations above the atmospheric value of 380 ppm. The amounts of Na213CO3 necessary to achieve CO2 concentrations of 5000 ppm (0.42 mg of Na213CO3 per sample) or 50,000 ppm (4.52 mg) were calculated by the air volume available within pore space of loess (0.32 ml per 1 g of loess minus the volume of added water) as well as within tubings, the membrane pump and the vial containing the label solution. After connecting the metal pipe to the label vial by PVC tubings, 14CO2 and 13CO2 were released by adding 3 ml of 5 M H2SO4 to the label solution and pumped through the loess sample for 10 min in a closed cycle by a membrane pump (Type SMG4, Gardner Denver Thomas GmbH, Germany) (Fig. 1a). After the labeling, the PVC tubings of the metal pipes were closed by a joint. A small part of the labeled CO2 stayed in the head space of the label vial and in the PVC tubings between that vial and the membrane pump. This unused 14CO2 and 13CO2 was trapped in 10 ml of 1 M NaOH and considered for calculations based on 14C activity.

The metal pipes then stayed closed for different time periods. As minimal experimental duration, we chose 4 days, because a previous study by Kuzyakov et al. (2006) had shown that CaCO3 recrystallization is a rather slow process (rate 3 · 10−5 day−1) and we expected even lower values in our experiment without plants. A maximum time period of 65 days was chosen because this interval reflects the vegetative period in arid regions, i.e. the time in which CO2 from root and rhizomicrobial respiration is involved in CaCO3 crystallization. The interval of 16 days was chosen as an intermediate period between those two. After 4, 16 or 65 days, the respective metal pipes were connected to a CO2 trapping washing flask filled with 15 ml of 1 M NaOH and the air was pumped for 20 min (Fig. 1b). Thus, gaseous CO2 remaining after recrystallization was removed from the loess sample and trapped in NaOH. Afterwards, the loess was pulled out from each metal pipe and carefully mixed. Five grams of loess were washed with 50 ml of slightly alkalized de-ionized water to elute dissolved inorganic carbon (DIC), and dried at 90 °C for 24 h. Two grams of the dried loess were treated with 15 ml of 3 M H3PO4, and the CO2 evolving from CaCO3 was trapped in 12 ml of 2 M NaOH during 4 h to ensure complete CO2 absorption. An aliquot of this NaOH was titrated to assure that the total CaCO3 content in loess had not changed during the experiment by formation of authigenic carbonate.

2.4. 14C analysis

After the labeling, 14C activities of the residue of the label solution and of the remaining CO2 in NaOH were measured on 1 ml mixed with 2 ml of scintillation cocktail (Rotiszint EcoPlus, Carl Roth, Germany) after decay of chemiluminescence (for NaOH). The 14C measurements were done by a 1450 LSC & Luminescence Counter (MicroBeta Trilux, Perkin Elmer Inc., USA). The 14C counting efficiency was at least 70%; the measurement error did not exceed 3.5%. The absolute 14C activity...
was standardized by SQP(I) by adding increasing amounts of NaOH as a quencher.

After opening the metal pipes, $^{14}$C activity of CO$_2$ in NaOH and of DIC in water was measured on 1 ml aliquots as described above. The $^{14}$C activity of loess carbonate, released as $^{14}$CO$_2$ by H$_3$PO$_4$ addition and trapped in NaOH, was measured on 6 ml aliquots added to 12 ml of scintillation cocktail. Larger aliquots were chosen for the $^{14}$C analysis of samples with expected low $^{14}$C activities (i.e. in loess carbonate). The $^{14}$C counting efficiency of the used device (LS 6500 Multi-Purpose Scintillation Counter, Beckman, USA) was at least 90% and the measurement error did not exceed 4%. The absolute $^{14}$C activity was standardized by the H number method, using a $^{137}$Cs external standard.

2.5. $\delta ^{13}$C sample analysis

$\delta ^{13}$C analysis was conducted in loess samples in two analytical replications from each time period. $\delta ^{13}$C of loess carbonate was determined in amounts between 450 and 880 µg of loess on a Delta Plus XL isotope ratio mass spectrometer (Thermo Finnigan MAT, Bremen, Germany) connected to an elemental analyzer EA 3000 (Hekatech, Wegberg, Germany). $\delta ^{13}$C in carbonate of the initial loess as well as loess from the 380 ppm CO$_2$ treatment (no $^{13}$C applied) were also measured. Results are given in ‰ relative to the V-PDB reference standard.

2.6. $^{14}$C and $^{13}$C calculation and statistical analysis

The $^{14}$C results are presented as percentage of recovered $^{14}$C activity. The total $^{14}$C activity added to each replication ($^{14}$C$_{\text{av}}$) was calculated according to the equation:

$$^{14} \text{C}_{\text{av}} = ^{14} \text{C}_{\text{input}} - ^{14} \text{C}_{\text{res}} - ^{14} \text{C}_{\text{NaOH}}$$ (1)

With $^{14}$C$_{\text{input}}$: total input activity of the label; $^{14}$C$_{\text{res}}$: activity of undissolved residue of label solution (percentage of input <1%); $^{14}$C$_{\text{NaOH}}$: activity of unused $^{14}$CO$_2$ trapped in NaOH.

The $^{14}$C specific activity ($^{14}$C$_{\text{in situ}}$) of the label applied for each CO$_2$ concentration was calculated as the ratio of total input $^{14}$C activity ($^{14}$C$_{\text{input}}$) and total C content in applied CO$_2$ ($^{12}$C$_{\text{total}}$):

$$^{14} \text{C}_{\text{in situ}} = \frac{^{14} \text{C}_{\text{input}}}{^{12} \text{C}_{\text{total}}}$$ (2)

The $^{14}$C activity of the total amount of loess in each metal pipe ($^{14}$C$_{\text{CaCO}_3}$) was calculated from the $^{14}$C activity of the 2 g of loess dissolved with H$_3$PO$_4$ (see previous chapter). The $^{14}$C specific activity of the added CO$_2$ is equal to the $^{14}$C specific activity of the recrystallized portion of CaCO$_3$. Therefore, the amount of recrystallized CaCO$_3$ ($^{14}$C$_{\text{recryst}}$) was calculated as:

$$^{14} \text{C}_{\text{recryst}} = \left( \frac{^{14} \text{C}_{\text{CaCO}_3}}{^{14} \text{C}_{\text{CO}_2}} \right)_{\text{SA}}$$ (3)

To calculate the recrystallization rate of the loess carbonate, the amount of incorporated C was divided by the amount of total C content of the loess carbonate ($^{12}$C$_{\text{total}}$) and divided by the labeling period (4, 16, or 65 days) of the loess samples:

$$\text{Rate} = \frac{^{14} \text{C}_{\text{recryst}}}{^{12} \text{C}_{\text{total}}} \cdot t$$ (4)

Recrystallization rates of the loess carbonate were also calculated by $^{13}$C of CO$_2$ label accumulated within loess carbonate. For this purpose, $^{13}$C values from mass spectrometric analysis (%) were converted into atomic % and the calculation was done based on $^{13}$C mass balance.

The experiment was done with 4 replicates. Standard errors of means are presented in figures. Significance of differences between the treatments was analyzed by one-way ANOVA with $\alpha = 5\%$ significance level.

3. Results

3.1. $^{14}$C distribution between the C pools

After addition of $^{14}$CO$_2$ to the loess and recrystallization, the maximal $^{14}$C activity was recovered in loess CaCO$_3$ (except for the first sampling date at 50,000 ppm CO$_2$ concentration), followed by $^{14}$C in DIC; the minimal $^{13}$C activity was found in remaining CO$_2$ (Fig. 2). The part of $^{14}$C recovered in DIC decreased from values between 47% and 55% after 4 days to values between 19% and 27% after 65 days. In contrast, an increasing amount of $^{14}$C was recovered in loess carbonate. At the lowest CO$_2$ concentration (380 ppm), the part of $^{14}$C recovered in loess carbonate increased from 52% after 4 days to 71% after 65 days. Values between the 4th and 65th day ascended.
from 49% to 80% at 5000 ppm and from 43% to 75% at 50,000 ppm CO2 concentration. That means the ratio of $^{14}\text{CaCO}_3/^{14}\text{DIC}$ showed a stronger increase at enhanced CO2 concentrations (5000 ppm, 50,000 ppm) compared to atmospheric CO2 concentration (380 ppm).

### 3.2. CaCO$_3$ recrystallization rates and periods calculated based on $^{14}$C incorporation

Within every single CO2 concentration, the amount of recrystallized carbonate (as percent of total loess carbonate) did not change significantly over the 65-day experiment period. On the other hand, the applied CO2 concentrations led to significantly different amounts of recrystallized carbonate. After 4 days, the amount of recrystallized C of loess carbonate was $1.6 \times 10^{-4}$, $3.3 \times 10^{-4}$ and $6.8 \times 10^{-4}$% of initial CaCO$_3$–C for 380, 5000 and 50,000 ppm, respectively (Table 1). These values correspond to recrystallization rates of $4.1 \times 10^{-7}$ day$^{-1}$, $8.1 \times 10^{-7}$ day$^{-1}$ and $16.9 \times 10^{-7}$ day$^{-1}$ (Table 2).

As the amount of recrystallized carbonate did not change significantly over time within each CO2 treatment, the average amount in every single CO2 treatment over the whole recrystallization period is presented in Fig. 3 against CO2 concentration. The values increased with increasing CO2 concentrations; the curve showed a rather steep rise under low CO2 concentrations (up to a few thousand ppm), but was less steep at very high concentrations. We used a simple equation to calculate the dependence of the amount of recrystallized CaCO$_3$ on the CO2 concentrations and fitted the parameters by non-linear regression (Eq. (5)). As a recrystallization period >4 days was unimportant for the amount of CaCO$_3$ recrystallized, we did not include time in the equation.

Based on this equation with fitted parameters we roughly estimated the recrystallized CaCO$_3$ amounts ($C_{\text{recryst}}$) depending on CO2 concentration ($C_{\text{CO2}}$) in soil air as:

$$C_{\text{recryst}} = 0.000544 \times (1 - e^{-0.000117 C_{\text{CO2}}}) + 0.00011$$  \hspace{1cm} (5)

From these initial rates, the time necessary for complete CaCO$_3$ recrystallization can be estimated in two ways. The first assumes that the once-formed secondary carbonate is not affected by recrystallization again, leading to a linearly increasing amount of recrystallized carbonate. With this approach, the CaCO$_3$ of loess with 29% carbonate content will be completely recrystallized after approximately 6300, 3200 or 1500 years at a CO2 concentration of 380, 5000 or 50,000 ppm, respectively (Table 3).

The second approach assumes that both the primary loess carbonate and the secondary carbonate will react repeatedly with soil air CO2. Thus, the amount of remaining, not recrystallized carbonate ($CaCO_3(t)$) exponentially decreases, depending on time and recrystallization rate (Eq. (6)). In this case, CO2 concentrations of 380, 5000 or 50,000 ppm will lead to complete CaCO$_3$ recrystallization periods of 20,000, 10,000 or 4900 years, respectively (Table 3).

$$CaCO_3(t) = 100 \times e^{-\text{rate}}$$  \hspace{1cm} (6)

### 3.3. $\delta^{13}$C values of loess carbonate and resulting recrystallization rates

Calcium carbonate of the original, unlabeled loess from Nussloch showed a $^{13}$C natural abundance of $-1.59 \pm 0.40$‰. At both lowest CO2 concentrations, no significant change of $\delta^{13}$C values of CaCO$_3$ occurred over time: samples of the 380 ppm CO2 treatment (no $^{13}$C applied) plotted very near to the initial value, with $-1.71%$ after 4 days and $-1.67%$ after 16 days. At a CO2 concentration of 5000 ppm, $\delta^{13}$C values plotted only slightly above the value of unlabeled loess, with $-0.41%$ after 4 days and $-1.16%$ after 65 days (Fig. 4). After 16 days the value was lower ($-2.99%$). These $\delta^{13}$C changes over time were not significant. At the highest applied CO2 concentration (50,000 ppm), $\delta^{13}$C increased after

<table>
<thead>
<tr>
<th>CO2 (ppm)</th>
<th>380</th>
<th>5000</th>
<th>50,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>4th day</td>
<td>$1.6 \pm 0.1 \times 10^{-4}$</td>
<td>$3.3 \pm 0.7 \times 10^{-4}$</td>
<td>$6.8 \pm 0.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>16th day</td>
<td>$1.3 \pm 0.5 \times 10^{-4}$</td>
<td>$4.5 \pm 0.7 \times 10^{-4}$</td>
<td>$5.5 \pm 0.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>65th day</td>
<td>$1.0 \pm 0.1 \times 10^{-4}$</td>
<td>$2.4 \pm 0.1 \times 10^{-4}$</td>
<td>$7.2 \pm 0.2 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
The recrystallization rate of carbonate was calculated based on the accumulation of $\delta^{13}C$ for samples of the 5000 ppm treatment (first sampling date) and 50,000 ppm treatment (first and second sampling date) because only these samples showed $\delta^{13}C$ values considerably above the value of unlabeled loess. The last sampling date (65th day) was not included because of the strong decrease of $\delta^{13}C$ values between day 16 and the end of the experiment.

In general, the recrystallization rates calculated based on $\delta^{13}C$ accumulation were one order of magnitude higher than the results of the $\delta^{14}C$ calculation (Table 2). Recrystallization rates based on $\delta^{13}C$ and $\delta^{14}C$ from the 5000 ppm treatment could be compared only for the first sampling date, because the $\delta^{13}C$ value after 16 days plotted below that of unlabeled loess (Fig. 4).

### 4. Discussion

#### 4.1. Isotopic exchange approach

The isotopic exchange between C of loess carbonate and artificial CO$_2$ label was used to estimate the recrystallization rate of loess CaCO$_3$. Both applied C isotopes, $\delta^{13}C$ as well as $\delta^{14}C$, showed that labeled C was incorporated into the loess carbonate by recrystallization. However, calculation with either $\delta^{14}C$ activity or $\delta^{13}C$ enrichment within recrystallized loess carbonate yielded different results. As the calculated amounts of recrystallized carbonate were very small (0.00008–0.00076% of total loess CaCO$_3$), a very sensitive method is necessary for short recrystallization periods such as in our experiment. The measurement accuracy of a mass spectrometric analysis is between 0.2% and 0.5‰. A variation of a few % between replications of the same treatment can occur due to inhomogeneous distribution of $\delta^{13}C$ incorporated into CaCO$_3$. Such a variation of a few % leads to differences in the estimated recrystallization rate of up to one order of magnitude. Results calculated based on $\delta^{14}C$ activity showed that the applied CO$_2$ concentrations led to differences of recrystallization rates between the CO$_2$ treatments of one order of magnitude or less. Thus, the variation of the $\delta^{13}C$ approach equals or even exceeds the differences between treatments estimated by the $\delta^{14}C$ approach: the latter is therefore more accurate. The two lower CO$_2$ concentrations (380 and 5000 ppm) did not lead to significant changes in $\delta^{13}C$, although artificial $\delta^{13}C$ (99%) was applied only to the latter one (Table 2). We assume that C of added $^{13}CO_2$ was incorporated into loess carbonate by recrystallization, similarly to the $\delta^{14}C$ approach, also in the 380 ppm treatment. However, these changes in $\delta^{13}C$ are presumably too small to be detected by mass spectrometry. We therefore conclude that the sensitivity of $\delta^{13}C$ measurements was neither high enough to estimate such slow recrystallization rates, nor to reveal small differences between the treatments. Accordingly, the isotopic exchange based on $\delta^{14}C$ is probably the only possibility to estimate such slow processes rates. The further discussion therefore focuses only on $\delta^{14}C$ labeling results.

The reason for the $\delta^{13}C$ decrease towards the last sampling date remains unknown. We cannot rule out that microbial processes in the loess influenced the $\delta^{13}C$ value after 65 days.

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**Table 2**

<table>
<thead>
<tr>
<th>CO$_2$ (ppm)</th>
<th>1st sampling date (4th day)</th>
<th>2nd sampling date (16th day)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta^{13}C$</td>
<td>$\delta^{14}C$</td>
</tr>
<tr>
<td>380</td>
<td>nd</td>
<td>4.1 [$\pm$ 0.1] · 10$^{-7}$</td>
</tr>
<tr>
<td>5000</td>
<td>3.6 [$\pm$ 1.1] · 10$^{-6}$</td>
<td>8.1 [$\pm$ 1.7] · 10$^{-7}$</td>
</tr>
<tr>
<td>50,000</td>
<td>14.2 [$\pm$ 0.2] · 10$^{-6}$</td>
<td>16.9 [$\pm$ 1.2] · 10$^{-7}$</td>
</tr>
</tbody>
</table>

---

**Table 3**

<table>
<thead>
<tr>
<th>CO$_2$ concentration (ppm)</th>
<th>Calculated periods (rounded up to ten years) for the recrystallization of 95% initial loess carbonate (for loess containing 29% CaCO$_3$). 95% Confidence intervals of the recrystallization periods are given in brackets.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Linear$^a$</td>
</tr>
<tr>
<td></td>
<td>[5940–6790] years</td>
</tr>
<tr>
<td>380 ppm</td>
<td>6340 years</td>
</tr>
<tr>
<td>5000 ppm</td>
<td>3200 years</td>
</tr>
<tr>
<td>50,000 ppm</td>
<td>1540 years</td>
</tr>
<tr>
<td></td>
<td>[5940–6790] years</td>
</tr>
<tr>
<td></td>
<td>[2270–5420] years</td>
</tr>
<tr>
<td></td>
<td>[5420–5620] years</td>
</tr>
</tbody>
</table>

$^a$ Linear or exponential decrease in the amount of remaining primary CaCO$_3$. These two approaches are represented by straight and curved lines in Fig. 5.

---

**Fig. 3.** Amount of recrystallized calcium carbonate as percentage of total loess carbonate (averaged from all three sampling dates) depending on CO$_2$ concentration.

**Fig. 4.** Change of $\delta^{13}C$ values depending on time and CO$_2$ concentration. The secondary axis represents the $\delta^{14}C$ atomic % calculated from $\delta^{13}C$ values.
4.2. \( ^{14}C \) distribution and equilibria between C pools

According to the Henry Law, the solubility of \( CO_2 \) in water increases directly proportional to the \( CO_2 \) partial pressure in soil air. As dissolution of soil CaCO\(_3\) depends on the pH of the soil solution and thus on \( CO_2 \) partial pressure, increasing \( CO_2 \) concentrations should result in rising amounts of recrystallized CaCO\(_3\). Depending on the depth in the soil profile and biological activities by plants and microorganisms, the \( CO_2 \) concentration in soil air ranges between atmospheric values (approximately 0.038% in volume) and values one or two orders of magnitude larger than in the atmosphere (typically up to 3.5% in volume, Davidson, 1995). To test the effect of \( CO_2 \) concentration on the recrystallization rate of pedogenic carbonates, we applied three treatments covering approximately the natural range of \( CO_2 \) concentrations in soil air.

The \( CO_2 \) concentration strongly influenced the carbonate recrystallization rate (Eq. (5), Fig. 3). The three \( CO_2 \) concentrations in pore space led to three distinct distribution patterns of \( ^{14}C \) from the input \( CO_2 \) between solid CaCO\(_3\), dissolved inorganic carbon (DIC) and gaseous \( CO_2 \) within the loess samples. Given a constant \( CO_2 \) concentration, the reaction between gaseous and liquid phase (Eq. (7)) rapidly reaches an equilibrium (seconds to minutes). For this reason and due to the immediate contact between labeled \( CO_2 \) and loess pore water, the least recovered \( ^{14}C \) was found in the gaseous \( CO_2 \) compartment, and it stayed in the same percentage range of total recovered \( ^{14}C \) during all labeling periods. In contrast, more time is required to establish an equilibrium for the reaction between liquid and solid phase (Eq. (8)), leading to \( C \) exchange in dissolved form. This time span could not be assessed in our study, but it should be less than 4 days (probably several hours to a few days) because the amount of recrystallized CaCO\(_3\) did not change significantly after 4, 16 or 65 days. Therefore, the calculated rates have to be seen as minimum values, which however point out the order of magnitude of carbonate recrystallization rates under the conditions given in our experiment.

\[
\begin{align*}
CO_2 + H_2O &\rightleftharpoons H_2CO_3 \quad \text{(7)} \\
H_2CO_3 + CaCO_3 &\rightarrow Ca^{2+} + 2HCO_3^- \quad \text{(8)}
\end{align*}
\]

4.3. Recrystallization periods of loess carbonate

A linear and an exponential approach were used to calculate the decrease in the amount of remaining primary carbonate. The linear approach led to modeled recrystallization periods of 1500–6300 years for the \( CO_2 \) concentrations applied in this study (Fig. 5, straight lines). Such a linear recrystallization process is possible only in the presence of progressively growing CaCO\(_3\) crystals. Without an irreversible CaCO\(_3\) crystal growth, the fine-spread carbonate will be repeatedly recrystallized with pore-space \( CO_2 \), causing the decrease in the amount of not recrystallized carbonate to exponentially decelerate over time (Fig. 5, exponential lines). This is the most likely mode of carbonate recrystallization in real soil systems. In the case of the exponential approach, full (95%) carbonate recrystallization of the exposed loess carbonate takes approximately 20,000, 10,000 and 4900 years at 380, 5000 and 50,000 ppm \( CO_2 \) concentration, respectively (Table 3).

4.4. Relevance of the estimated recrystallization rates

The \( ^{14}C \) labeling method was first applied to estimate pedogenic carbonate recrystallization rates by Kuzyakov et al. (2006). The authors exposed wheat to an artificially labeled \( ^{14}C \) atmosphere to estimate the amount of root-derived \( C \) incorporated into loess carbonate. The initial recrystallization rate of \( 2.9 \times 10^{-5} \text{ day}^{-1} \) they calculated is 1–2 magnitudes of order higher than the results of the present study (calculated based on \( ^{14}C \) isotopic exchange), although we applied the relevant \( CO_2 \) concentrations. In the experiment with plants by Kuzyakov et al. (2006), various factors may have contributed to the faster recrystallization. Permanent \( CO_2 \) production by root and rhizomicrobial respiration hindered a steady state between \( CO_2 \) and \( CO_3^- \) in the liquid and solid phase (Eqs. (7) and (8)). The continuous flux of \( CO_2 \) into soil thus promotes carbonate recrystallization. Additionally, plants change the chemical environment in the soil: a decreased \( pH \), resulting from root exudates, led to a faster \( C \) isotope exchange compared to the present study without plants and with one-time \( CO_2 \) supply.

Furthermore, soil \( CO_2 \) profiles and \( CO_2 \) fluxes are in a complex relationship with environmental factors like \( CO_2 \) production, soil water content, soil temperature and gas diffusivity (Hashimoto and Komatsu, 2006). In upper soil horizons, \( CO_2 \) production is controlled mainly by vegetation. Spatial \( CO_2 \) distribution in a soil depends on morphological features of subsurface plant biomass, such as root thickness and root distribution within the soil profile (Hamada and Tanaka, 2001). As the \( CO_2 \) concentration decreases with increasing distance to the root surfaces, our results suggest highest carbonate recrystallization rates in the rhizosphere (the soil volume directly affected by processes of living plants; definition by Darrah, 1993). Temporal differences in \( CO_2 \) concentration, on the other hand, occur due to specific growing seasons.
per year, dependent on plant species and environmental factors like light intensity, temperature and moisture (e.g. Russo and Knapp, 1976). Carbonate recrystallization in soils is expected to be higher during the plant growing season than in winter months. Moreover, CO₂ concentration in soil is controlled by the plants’ growth rate, which differs considerably between grassland vegetation, agricultural crops and trees, and by the portion of assimilates used by the plant for rhizosphere processes (reviewed by Whipp, 1990; Kuzyakov and Domanski, 2000). As an example, ryegrass (Lolium perenne), a typical representative of grasslands under humid and semiarid climate, grows very slowly and puts a major part of the assimilates into rhizosphere respiration (Meharg grasslands under humid and semiarid climate, grows very slowly and puts a major part of the assimilates into rhizosphere respiration (Meharg 1992)).

Temperature is another important factor governing the CaCO₃ equilibrium. On one hand, higher temperature leads to decreasing CO₂ solubility, thus diminished carbonate recrystallization should be expected. However, the role of temperature for several biological processes is much higher than its influence on the chemical equilibrium between CO₂, HCO₃⁻ and CaCO₃. Root respiration, exudation and microbial respiration are promoted by increasing temperature, boosting CO₂ production and CaCO₃ recrystallization. Moreover, higher temperature enhances plant and soil evapotranspiration and leaching (Tal and Kimble, 2000). The resulting variations in soil moisture might also contribute to faster carbonate recrystallization.

Soil texture (particle size distribution, clay content), aggregates and pore space geometry play an important role for gas diffusivity. According to Kawamoto et al. (2006), soil permeability generally increases from finer (sandy clay loam) to coarser (sand) textured soil but in many cases tends to be lowest in sandy loam soils. Another aspect of soil texture is the adsorption of Ca²⁺ by clay minerals (Scharpenseel et al., 2000), thus removing the reactant necessary for re-precipitation of pedogenic CaCO₃. Accordingly, soil with high clay content could restrict carbonate recrystallization directly and indirectly. This study gives a first insight into the direct effect of soil CO₂ concentration on carbonate recrystallization rates in potential soil environment without influence of rhizosphere. To provide permanent control on the state of isotopic composition of carbonate, we operated with loess samples in closed tubes, which is not a direct analogue to a soil milieu. However, our experiments involved components available in real soil systems: loess particles as solid phase, carbon dioxide as gas phase and water as fluid phase. Two aspects of the study are important to be seen. First, the interaction between CO₂ and soil is not complicated by specific effects of root systems. It helps to better understand the abiotic component of carbonate recrystallization in soils. Second, the influence of CO₂ on carbonate in the absence of plant roots theoretically can take place in some rare soil environments such as soils of extreme deserts, toxically affected soils, extraradial soils etc.

We showed that the rate increases with increasing CO₂ concentration. This supports the assumption that firstly, the rate should be higher in planted than in unplanted soil, and secondly, higher in root vicinity than in soil distinct to roots due to CO₂ release by root and rhizomicrobial respiration. In future studies we will expose plants to an artificially labeled atmosphere (as previously demonstrated by Kuzyakov et al. 2006) to show the incorporation of root-derived C into newly formed secondary carbonate under different environmental conditions.

5. Conclusions

As a very sensitive method, ¹³C labeling is a useful tool to assess slow rates of steady state processes in soils; it is probably the only approach for estimating the recrystallization rate of pedogenic CaCO₃. Rising CO₂ concentration increases the CO₂ partial pressure, enhancing the dissolution and recrystallization of calcium carbonate from loess. Therefore, under field conditions the CO₂ concentration in soil air, ranging from atmospheric values up to approximately 100 times the atmospheric level, affects CaCO₃ recrystallization rates remarkably. The relation between the amount of recrystallized CaCO₃ and the CO₂ concentration is described by a saturation curve. In our study, CO₂ concentrations of 380, 5000 and 50,000 ppm led to initial recrystallization rates of 4.1 · 10⁻⁷ day⁻¹, 8.1 · 10⁻⁷ day⁻¹ and 16.9 · 10⁻⁷ day⁻¹. Assuming an exponential decrease of the remaining primary loess carbonate due to repeated reaction of the secondary carbonates with CO₂ full (95%) recrystallization of the loess carbonate would take 4900–20,000 years. In soil under growing plants, however, much higher recrystallization rates (at least 1–2 orders of magnitude) and thus shorter recrystallization periods occur due to permanent CO₂ production by root and rhizomicrobial respiration.

Further research is necessary to elucidate the effect of biotic and abiotic factors like depth below the soil surface, properties of carbonate material, plant species, moisture, temperature or carbonate content of soil on the recrystallization rate of pedogenic carbonates.

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