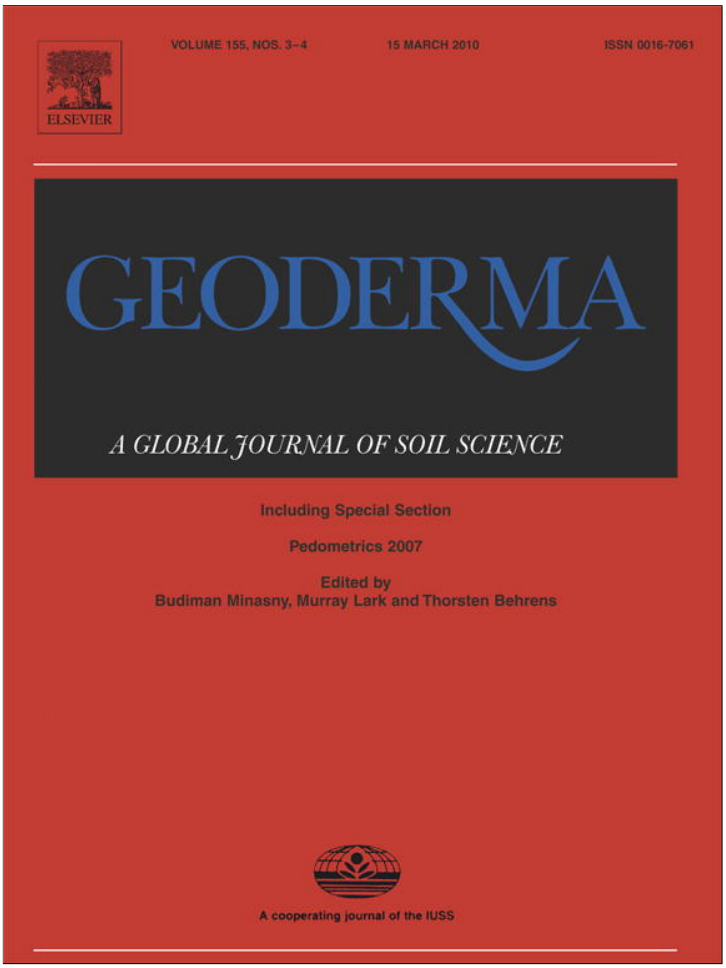

Geoderma 155 (2010) 351–358

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Effect of CO_2 concentration on the initial recrystallization rate of pedogenic carbonate — Revealed by ^{14}C and ^{13}C labeling

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ARTICLE INFO

Article history:
Received 23 December 2008
Received in revised form 31 July 2009
Accepted 20 December 2009
Available online 18 January 2010

Keywords:
Pedogenic carbonate genesis
$CaCO_3$ recrystallization
CO_2
^{14}C
Loess
Inorganic carbon

ABSTRACT

In calcareous parent material, pedogenic carbonate formation mostly involves dissolution and recrystallization of lithogenic carbonates with CO_2 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 ($\delta^{13}C$ and $\delta^{18}O$) and past atmospheric CO_2 concentrations as well as for radiocarbon dating of soils. For such investigations, the recrystallization rate of primary $CaCO_3$ 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 $CaCO_3$ of loess at three CO_2 concentrations was estimated by isotopic exchange between primary $CaCO_3$ and the ^{14}C of artificially labeled CO_2. Loess was used for the study as a parent substrate for soil formation to simulate initial rates of $CaCO_3$ recrystallization. CO_2 concentrations of 380 ppm, 5000 ppm and 50,000 ppm lead to recrystallization rates of $4.1 \cdot 10^{-7}$ day^{-1}, $8.1 \cdot 10^{-7}$ day^{-1} and $16.9 \cdot 10^{-7}$ day^{-1}, respectively. The relation between CO_2 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 $\cdot 10^3$ years, strongly depending on CO_2 concentration. We expect faster recrystallization rates under field conditions because of permanent CO_2 supply by root and rhizomicrobial respiration. This impedes the equilibrium between the inorganic C pools in solid, liquid and gaseous phases.

1. Introduction

Globally, soils contain a total of 659–748 $\cdot 10^{15}$ g carbon (C) as $CaCO_3$ 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 CO_2 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 semiarid 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 CO_2 concentrations and a chronological tool. The pedogenic carbonate is formed at carbon isotopic equilibrium between itself and soil CO_2 (Cerling, 1984; Nordt et al., 1996). Therefore, $\delta^{13}C$ 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 paleovegetation (Quade and Cerling, 1995; Wang et al., 1996, 1997; Monger et al., 1998; Buck and Monger, 1999; Deutz et al., 2001; Pustovoytov et al., 2007). Moreover, diffusion models allow an estimation of former CO_2 concentrations in the Earth's atmosphere (Cerling, 1991, 1992; Tanner et al., 2001). The $\delta^{18}O$ values of pedogenic carbonates are governed by the oxygen isotopic composition of meteoric water (Cerling, 1984), which in turn can reflect multiple factors (Cerling and Quade, 1993; Hsieh et al., 1998; Monger et al., 1998; Deutz et al., 2001). Finally, pedogenic carbonates are used as a tool for chronological studies (e.g. Vincent et al., 1994; Amundson et al., 1994; Wang et al., 1996; Pustovoytov, 2002; Pustovoytov et al., 2007).

One of the most important prerequisites for all these paleoenvironmental reconstructions 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

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doi:10.1016/j.geoderma.2009.12.018

recrystallization rates of such carbonate, as well as the dependence of this rate on environmental factors (e.g. temperature and CO_2 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 $^{14}CO_2$ 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 ^{14}C recovered in loess $CaCO_3$, Kuzyakov et al. (2006) calculated an initial recrystallization rate of $2.9 \cdot 10^{-5}$ day^{-1}. The authors concluded further that the time needed for complete recrystallization of $CaCO_3$ 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 $\delta^{13}C$ 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 CO_2 accumulation within the plant pots, leading to a faster reaction between dissolved CO_2 and solid $CaCO_3$ than under field conditions.

$CaCO_3$ recrystallization is clearly affected by soil CO_2 concentration. Under field conditions, this concentration depends on vegetation and various soil properties, and varies between 0.035% and about 3.5% in volume (Davidson, 1995). The main aim of the present work was to determine the effects of CO_2 concentration as an isolated parameter, and the effects of the recrystallization period on the recrystallization rate of pedogenic carbonate without plants. The method we apply is similar to that of Kuzyakov et al. (2006) and consists of quantifying the recrystallization rate of pedogenic carbonates by isotopic exchange with ^{14}C of artificially labeled soil CO_2.

^{14}C pulse labeling is a very sensitive approach, and thus suitable to estimate rates of very slow processes like $CaCO_3$ recrystallization. Using ^{14}C has the advantage of a very low detection limit (10^{-13} mol, by scintillation counting) compared to ^{13}C measurement (10^{-7} mol, by common mass spectrometry analyses). Nevertheless, in treatments with CO_2 concentrations higher than the atmospheric level, ^{13}C was applied simultaneously with ^{14}C to allow a comparison of the calculated recrystallization rates based on both ^{14}C and ^{13}C 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 $CaCO_3$ is even and diffuse — no visual recrystallization took place — and the $CaCO_3$ 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 CO_2 concentration in soil air. Secondly, contrary to most soils, loess has a high $CaCO_3$ content, which facilitates the recovery of applied ^{14}C. In summary, by using loess we simulated the initial steps of soil formation on typical loose silt loamy parent material containing $CaCO_3$. The used loess was taken from an open cast mine at Nussloch (SW Germany, see Bente and Löscher, 1987) and contained 29% $CaCO_3$. For sedimentological and stratigraphic information on the loess from Nussloch, see Kuzyakov et al. (2006) and references therein.

2.2. Experiment layout

As experimental conditions, three time periods (4, 16 and 65 days) after the labeling and three CO_2 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 29 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 ^{14}C as $Na_2^{14}CO_3$ (ARC Inc., USA) was diluted with de-ionized water in a 30 ml vial. Previously, the water was slightly alkalinized to prevent loss of ^{14}C activity by exchange with atmospheric CO_2. Increasing amounts of 99% ^{13}C-enriched $Na_2^{13}CO_3$ (Isotec™, Ohio/USA) were added to the label solution, leading to the respective CO_2 concentrations above the atmospheric value of 380 ppm. The amounts of $Na_2^{13}CO_3$ necessary to achieve CO_2 concentrations of 5000 ppm (0.42 mg of $Na_2^{13}CO_3$ 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, $^{14}CO_2$ and $^{13}CO_2$ were released by adding 3 ml of 5 M H_2SO_4 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 CO_2 stayed in the head space of the label vial and in the PVC tubings between that vial and the membrane pump. This unused $^{14}CO_2$ and $^{13}CO_2$ was trapped in 10 ml of 1 M NaOH and considered for calculations based on ^{14}C 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 $CaCO_3$ recrystallization is a rather slow process (rate $3 \cdot 10^{-5}$ 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 CO_2 from root and rhizomicrobial respiration is involved in $CaCO_3$ recrystallization. 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 CO_2 trapping washing flask filled with 15 ml of 1 M NaOH and the air was pumped for 20 min (Fig. 1b). Thus, gaseous CO_2 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 alkalinized 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 H_3PO_4, and the CO_2 evolving from $CaCO_3$ was trapped in 12 ml of 2 M NaOH during 4 h to ensure complete CO_2 absorption. An aliquot of this NaOH was titrated to assure that the total $CaCO_3$ content in loess had not changed during the experiment by formation of authigenic carbonate.

2.4. ^{14}C analysis

After the labeling, ^{14}C activities of the residue of the label solution and of the remaining CO_2 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 ^{14}C measurements were done by a 1450 LSC & Luminescence Counter (MicroBeta TriLux, Perkin Elmer Inc., USA). The ^{14}C counting efficiency was at least 70%; the measurement error did not exceed 3.5%. The absolute ^{14}C activity

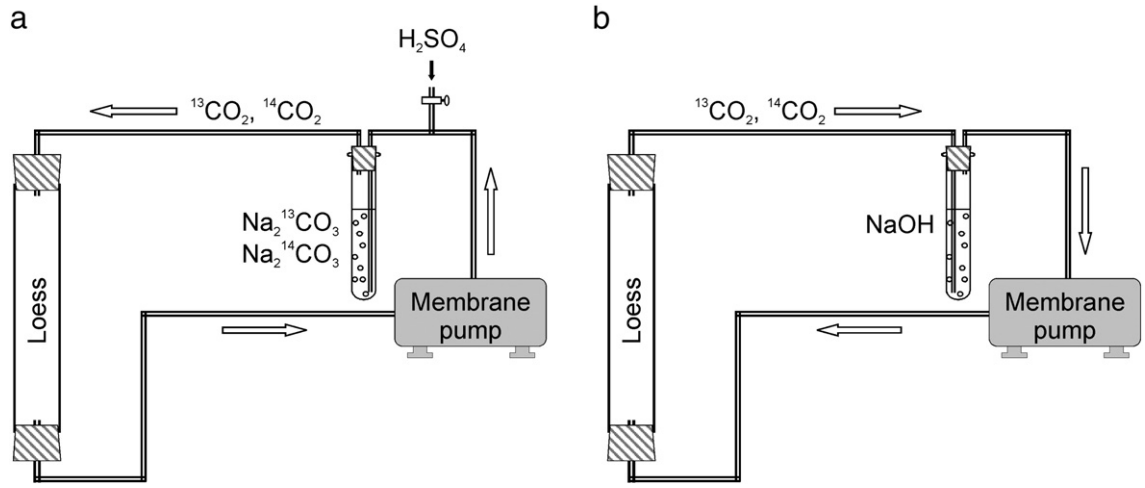

Fig. 1. Experimental setup. (a) Labeling procedure: ^{13}C and ^{14}C labeled CO_2 is released by addition of H_3PO_4 to the label solution and pumped through the loess sample. (b) Trapping of gaseous CO_2 in NaOH before sampling of the loess.

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_3PO_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 ($^{14}C_{av}$) was calculated according to the equation:

$$^{14}C_{av} = {}^{14}C_{input} - {}^{14}C_{res} - {}^{14}C_{NaOH} \quad (1)$$

With $^{14}C_{input}$: total input activity of the label; $^{14}C_{res}$: activity of undissolved residue of label solution (percentage of input <1%); $^{14}C_{NaOH}$: activity of unused $^{14}CO_2$ trapped in NaOH.

The ^{14}C specific activity ($^{14}C_{SA}^{CO_2}$) of the label applied for each CO_2 concentration was calculated as the ratio of total input ^{14}C activity ($^{14}C_{input}$) and total C content in applied CO_2 (C_{total}^{input}):

$$^{14}C_{SA}^{CO_2} = \frac{^{14}C_{input}}{C_{total}^{input}} \quad (2)$$

The ^{14}C activity of the total amount of loess in each metal pipe ($^{14}C_{CaCO_3}$) was calculated from the ^{14}C activity of the 2 g of loess dissolved with H_3PO_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 $CaCO_3$ ($C_{total}^{recryst}$) was calculated as:

$$C_{total}^{recryst} = \frac{^{14}C_{CaCO_3}}{^{14}C_{SA}^{CO_2}} \quad (3)$$

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 ($C_{total}^{CaCO_3}$) and divided by the labeling period (4, 16, or 65 days) of the loess samples:

$$Rate = \frac{C_{total}^{recryst}}{C_{total}^{CaCO_3} \cdot t} \quad (4)$$

Recrystallization rates of the loess carbonate were also calculated by ^{13}C of CO_2 label accumulated within loess carbonate. For this purpose, $\delta^{13}C$ 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 ^{14}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

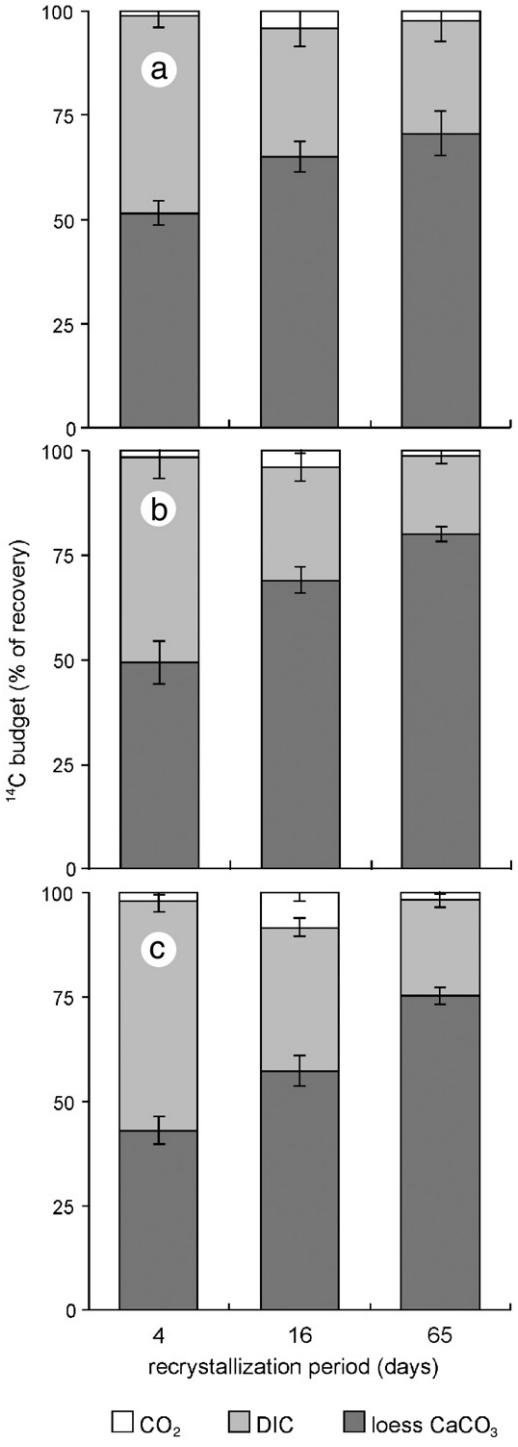

Fig. 2. ^{14}C distribution between calcium carbonate of loess, dissolved inorganic carbon, and gaseous CO_2 depending on the recrystallization period at three initial CO_2 concentrations of (a) 380, (b) 5000 and (c) 50,000 ppm.

from 49% to 80% at 5000 ppm and from 43% to 75% at 50,000 ppm CO_2 concentration. That means the ratio of $^{14}C_{CaCO_3}/^{14}C_{DIC}$ showed a stronger increase at enhanced CO_2 concentrations (5000 ppm, 50,000 ppm) compared to atmospheric CO_2 concentration (380 ppm).

3.2. $CaCO_3$ recrystallization rates and periods calculated based on ^{14}C incorporation

Within every single CO_2 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 CO_2 concentrations led to significantly different amounts of recrystallized carbonate. After 4 days, the amount of recrystallized C of loess carbonate was $1.6 \cdot 10^{-4}$%, $3.3 \cdot 10^{-4}$% and $6.8 \cdot 10^{-4}$% of initial $CaCO_3$–C for 380, 5000 and 50,000 ppm, respectively (Table 1). These values correspond to recrystallization rates of $4.1 \cdot 10^{-7}$ day^{-1}, $8.1 \cdot 10^{-7}$ day^{-1} and $16.9 \cdot 10^{-7}$ day^{-1} (Table 2).

As the amount of recrystallized carbonate did not change significantly over time within each CO_2 treatment, the average amount in every single CO_2 treatment over the whole recrystallization period is presented in Fig. 3 against CO_2 concentration. The values increased with increasing CO_2 concentrations; the curve showed a rather steep rise under low CO_2 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 CO_2 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 ($C_{total}^{recryst}$) depending on CO_2 concentration (CO_2) in soil air as:

$$C_{total}^{recryst} = 0.000544 \cdot (1 - e^{-0.000117 \cdot CO_2}) + 0.00011 \quad (5)$$

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 CO_2 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 CO_2. Thus, the amount of remaining, not recrystallized carbonate ($CaCO_3(t)$) exponentially decreases, depending on time and recrystallization rate (Eq. (6)). In this case, CO_2 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).

$$CaCO_3(t) = 100 \cdot e^{-t \cdot rate} \quad (6)$$

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 ± 0.40‰. At both lowest CO_2 concentrations, no significant change of $\delta^{13}C$ values of $CaCO_3$ occurred over time: samples of the 380 ppm CO_2 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 CO_2 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 (-2.09‰). These $\delta^{13}C$ changes over time were not significant. At the highest applied CO_2 concentration (50,000 ppm), $\delta^{13}C$ increased after

Table 1
Amounts of recrystallized $CaCO_3$ (% of initial $CaCO_3$) after 4, 16 and 65 days under initial CO_2 concentrations of 380, 5000 and 50,000 ppm, calculated based on ^{14}C incorporation. SEM in brackets.

CO_2 (ppm)	380	5000	50,000
4th day	$1.6\ [\pm 0.1] \cdot 10^{-4}$	$3.3\ [\pm 0.7] \cdot 10^{-4}$	$6.8\ [\pm 0.5] \cdot 10^{-4}$
16th day	$1.3\ [\pm 0.5] \cdot 10^{-4}$	$4.9\ [\pm 0.7] \cdot 10^{-4}$	$5.5\ [\pm 0.7] \cdot 10^{-4}$
65th day	$1.0\ [\pm 0.1] \cdot 10^{-4}$	$2.4\ [\pm 0.1] \cdot 10^{-4}$	$7.2\ [\pm 0.2] \cdot 10^{-4}$

Table 2
Recrystallization rates (day^{-1}) calculated based on ^{13}C and ^{14}C incorporation. SEM in brackets. For ^{13}C, the recrystallization rate could not be calculated at 380 ppm CO_2 concentration (or at 5000 ppm CO_2 concentration after a recrystallization period of more than 4 days) because the $\delta^{13}C$ values of the respective replications were lower than the value of unlabeled loess.

	1st sampling date (4th day)		2nd sampling date (16th day)	
CO_2 (ppm)	^{13}C	^{14}C	^{13}C	^{14}C
380	nd	$4.1\ [\pm 0.1]\cdot 10^{-7}$	nd	$0.8\ [\pm 0.3]\cdot 10^{-7}$
5000	$3.6\ [\pm 1.1]\cdot 10^{-6}$	$8.1\ [\pm 1.7]\cdot 10^{-7}$	nd	$3.1\ [\pm 0.4]\cdot 10^{-7}$
50,000	$14.2\ [\pm 6.2]\cdot 10^{-6}$	$16.9\ [\pm 1.2]\cdot 10^{-7}$	$6.4\ [\pm 4.1]\cdot 10^{-6}$	$3.4\ [\pm 0.4]\cdot 10^{-7}$

4 days up to +3.44‰ and at 16th day up to +7.41‰, then decreased again to +0.12‰.

The recrystallization rate of carbonate was calculated based on the accumulation of ^{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 ^{13}C accumulation were one order of magnitude higher than the results of the ^{14}C calculation (Table 2). Recrystallization rates based on ^{13}C and ^{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, ^{13}C as well as ^{14}C, showed that labeled C was incorporated into the loess carbonate by recrystallization. However, calculation with either ^{14}C activity or ^{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 ^{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 ^{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 ^{13}C approach equals or even exceeds the differences between treatments estimated by the ^{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 ^{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 ^{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 ^{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 ^{14}C is probably the only possibility to estimate such slow processes rates. The further discussion therefore focuses only on ^{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.

Table 3
Calculated periods (rounded up to ten years) necessary for the recrystallization of 95% of initial loess carbonate (for loess containing 29% $CaCO_3$). 95% Confidence intervals of the recrystallization periods are given in brackets.

	380 ppm	5000 ppm	50,000 ppm
Linear[a]	6340 years [5940–6790]	3200 years [2270–5420]	1540 years [1360–1780]
Exponential[a]	20,000 years [18,730–21,410]	10,080 years [7140–17,100]	4860 years [4280–5620]

[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.

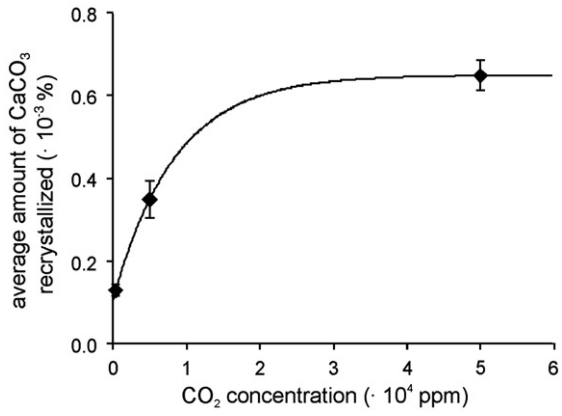

Fig. 3. Amount of recrystallized calcium carbonate as percentage of total loess carbonate (averaged from all three sampling dates) depending on CO_2 concentration.

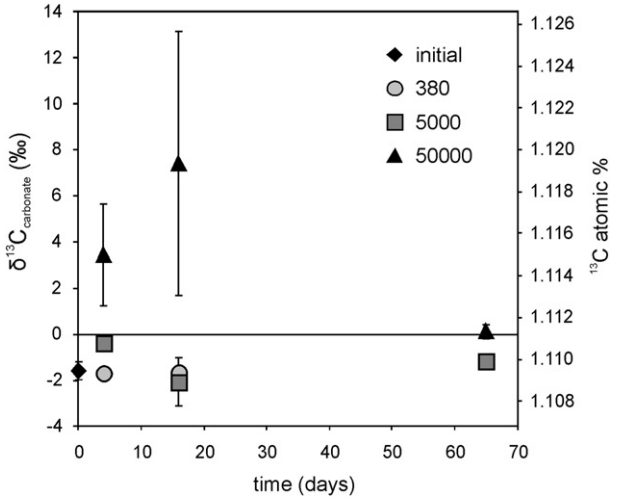

Fig. 4. Change of $\delta^{13}C$ values depending on time and CO_2 concentration. The secondary axis represents the ^{13}C atomic % calculated from $\delta^{13}C$ values.

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.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \tag{7}$$

$$H_2CO_3 + CaCO_3 \leftrightarrow Ca^{2+} + 2HCO_3^- \tag{8}$$

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 $2.9 \cdot 10^{-5}\,day^{-1}$ 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^{2-} 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

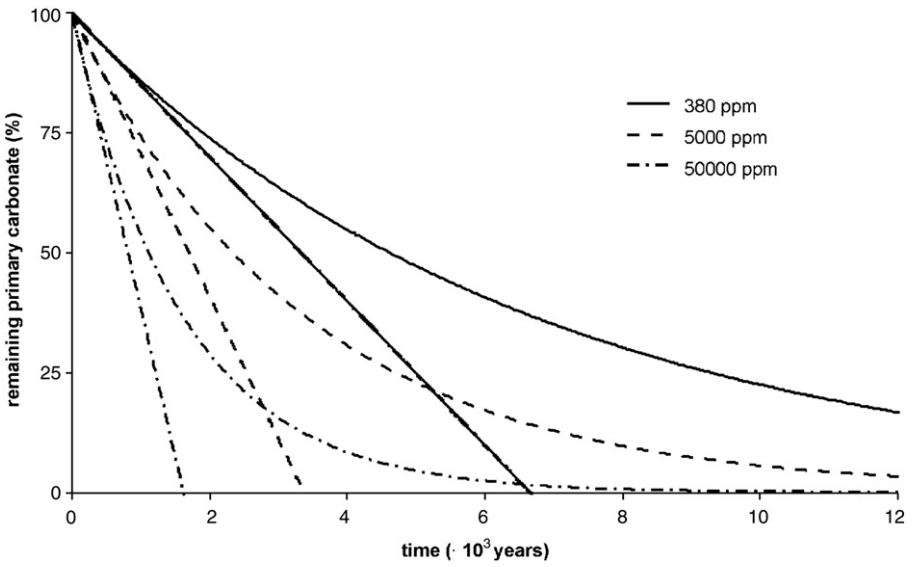

Fig. 5. Decrease in the amount of remaining primary carbonate over time, calculated separately for the three CO_2 concentrations. The straight lines were calculated by presuming that loess carbonate was recrystallized once. In contrast, the exponential lines represent the condition that $CaCO_3$ is affected several times by the recrystallization process (see text).

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, CO_2 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 Whipps, 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 and Killham, 1990, 1991). Maize (*Zea maize*), on the other hand, invests most of the photoassimilates for above-ground production (Todorovic et al., 2001; Kuzyakov and Cheng, 2004). The higher growth rate of maize might result in a higher recrystallization rate compared to grassland, but in the long-term, such differences could be compensated by stronger rhizosphere respiration and longer vegetation periods of pasture plants.

Temperature is another important factor governing the $CaCO_3$ equilibrium. On one hand, higher temperature leads to decreasing CO_2 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 CO_2, HCO_3^- and $CaCO_3$. Root respiration, exudation and microbial respiration are promoted by increasing temperature, boosting CO_2 production and $CaCO_3$ recrystallization. Moreover, higher temperature enhances plant and soil evapotranspiration and leaching (Lal 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 Ca^{2+} by clay minerals (Scharpenseel et al., 2000), thus removing the reactant necessary for re-precipitation of pedogenic $CaCO_3$. 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 CO_2 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 CO_2 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 CO_2 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, extraterrestrial soils etc.

We showed that the rate increases with increasing CO_2 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 CO_2 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, ^{14}C 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 $CaCO_3$.

Rising CO_2 concentration increases the CO_2 partial pressure, enhancing the dissolution and recrystallization of calcium carbonate from loess. Therefore, under field conditions the CO_2 concentration in soil air, ranging from atmospheric values up to approximately 100 times the atmospheric level, affects $CaCO_3$ recrystallization rates remarkably. The relation between the amount of recrystallized $CaCO_3$ and the CO_2 concentration is described by a saturation curve. In our study, CO_2 concentrations of 380, 5000 and 50,000 ppm led to initial recrystallization rates of $4.1 \cdot 10^{-7}$ day^{-1}, $8.1 \cdot 10^{-7}$ day^{-1} and $16.9 \cdot 10^{-7}$ day^{-1}. Assuming an exponential decrease of the remaining primary loess carbonate due to repeated reaction of the secondary carbonates with CO_2, 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 CO_2 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.

Acknowledgements

This study was funded by the German Research Foundation (DFG). We thank Prof. Gebauer (University of Bayreuth) and Dr. Armbruster (University of Hohenheim) for mass spectrometric analysis.

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