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Effect of temperature and rhizosphere processes on pedogenic carbonate recrystallization: Relevance for paleoenvironmental applications

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ABSTRACT

In soils of arid and semiarid climates, dissolution of primary (lithogenic) carbonate and recrystallization with CO_2 from soil air leads to precipitation of pedogenic carbonates and formation of calcic horizons. Thus, their carbon isotope composition represents the conditions prevailing during their formation. However, the widespread use of the isotopic signature ($\delta^{13}C$, $\delta^{18}O$, $\Delta^{14}C$) of pedogenic carbonates for reconstruction of local paleovegetation, paleoprecipitation and other environmental conditions lacks knowledge of the time frame of pedogenic carbonate formation, which depends on climatic factors. We hypothesized that temperature-dependent biotic processes like plant growth and root and rhizomicrobial respiration have stronger influence on soil $CaCO_3$ recrystallization than abiotic temperature-dependent solubility of CO_2 and $CaCO_3$.

To assess the effect of temperature on initial $CaCO_3$ recrystallization rates, loess with primary $CaCO_3$ was exposed to $^{14}CO_2$ from root and rhizomicrobial respiration of plants labeled in $^{14}CO_2$ atmosphere at 10, 20 or 30 °C. ^{14}C recovered in recrystallized $CaCO_3$ was quantified to calculate amounts of secondary $CaCO_3$ and corresponding recrystallization rates, which were in the range of 10^{-6}–10^{-4} day^{-1}, meaning that 10^{-4}–10^{-2}% of total loess $CaCO_3$ were recrystallized per day. Increasing rates with increasing temperature showed the major role of biological activities like enhanced water uptake by roots and respiration. The abiotic effect of lower solubility of CO_2 in water by increasing temperature was completely overcompensated by biotic processes. Based on initial recrystallization rates, periods necessary for complete recrystallization were estimated for different temperatures, presuming that $CaCO_3$ recrystallization in soil takes place mainly during the growing season. Taking into account the shortening effect of increasing temperature on the length of growing season, the contrast between low and high temperature was diminished, yielding recrystallization periods of 5740 years, 4330 years and 1060 years at 10, 20 and 30 °C, respectively. In summary, increasing $CaCO_3$ recrystallization rates with increasing temperature demonstrated the important role of vegetation for pedogenic $CaCO_3$ formation and the predominantly biotic effects of growing season temperature.

Considering the long periods of pedogenic carbonate formation lasting to some millennia, we conclude that methodological resolution of paleoenvironmental studies based on isotope composition of pedogenic carbonates is limited not by instrumental precision but by the time frame of pedogenic carbonate formation and hence cannot be better than thousands of years.

1. Introduction

Pedogenic (secondary) carbonate is a common constituent of continental sediments and soils as well as paleosols of arid to subhumid climates (Eswaran et al., 2000), mostly with mean annual precipitation of less than 500 mm (Birkeland, 1999). Pedogenic $CaCO_3$ forms by precipitation of Ca^{2+} from soil minerals (e.g. primary $CaCO_3$) or external sources with dissolved CO_3^{2-} (Borchardt and Lienkaemper, 1999). This precipitation is caused by a decrease of CO_2 partial pressure, increase of Ca^{2+} and HCO_3^- concentrations, or a combination of both (Birkeland, 1999; Krauskopf and Bird, 1995).

The usually good preservation of pedogenic carbonates in arid and semiarid climates makes them an important tool for the assessment of paleoclimatic conditions and paleovegetation. The link between the photosynthetic pathway of vegetation (C_3 or C_4 plants) and the $^{13}C/^{12}C$ ratio in pedogenic carbonates was established when Cerling (1984) showed that carbon (C) in pedogenic carbonates does not derive from lithogenic $CaCO_3$ of soil parent material, but from soil CO_2. With the latter being released mainly by respiration of roots and associated microorganisms (Amundson et al., 1998), $\delta^{13}C$ analyses of pedogenic carbonates has become a widespread method to determine the assemblage of the predominant local paleovegetation (e.g. Buck and Monger, 1999; Ding and Yang, 2000; Kovda et al., 2006; Pustovoytov et

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al., 2007a; Quade and Cerling, 1995). Additionally, $\delta^{18}O$ of pedogenic carbonates records paleotemperatures and precipitation (Dworkin et al., 2005) because the former is related to the isotopic composition of meteoric water (Cerling, 1984). Recent studies have demonstrated the suitability of pedogenic carbonates for the clumped isotope approach (Ghosh et al., 2006), thereby enabling their use as paleothermometer. Furthermore, pedogenic carbonates are used to estimate the age of pedogenesis or of sediments by radiocarbon dating (e.g. Amundson et al., 1994; Pustovoytov et al., 2007b).

One important aspect of these paleoenvironmental and chronological studies is their temporal resolution, which is limited by the time frame of pedogenic carbonate formation (Royer et al., 2001). Further, recrystallization by postsegregational alteration may cause loss of the paleoenvironmental and chronological information within pedogenic carbonates (Gocke et al., 2010, 2011a; Kuzyakov et al., 2006). So far, the time frame of pedogenic carbonate formation as well as that of their postsegregational alteration remains unknown. Based on carbon isotope composition of soil carbonates ($\delta^{13}C$, Nordt et al., 1998; $\Delta^{14}C$, Pendall et al., 1994) within chronosequences of known age, formation periods of pedogenic carbonates were suggested to be in the range of thousands of years. However, these approaches face the problems of (1) too low sensitivity of ^{13}C natural abundance for differentiation of small amounts of C involved in isotopic exchange between carbonate and soil CO_2, and (2) often too low chronological resolution of chronosequences. In addition, due to very low rates of pedogenic carbonate formation and recrystallization, values obtained from field conditions usually represent average rates over large time periods during which unstable climatic conditions presumably led to considerably varying $CaCO_3$ formation and accumulation rates (Gile et al., 1981; McFadden and Tinsley, 1985). Therefore, initial rates of pedogenic $CaCO_3$ formation and their dependence on environmental factors (e.g. primary $CaCO_3$ content of parent material, precipitation and temperature) remain unknown.

So far, initial $CaCO_3$ recrystallization rates can be assessed only under controlled conditions, as introduced by Kuzyakov et al. (2006). Their approach uses the C isotopic exchange of primary (lithogenic) $CaCO_3$ with ^{14}C labeled CO_2 from soil air during recrystallization and formation of secondary $CaCO_3$. ^{14}C from rhizosphere respiration of plants pulse-labeled in $^{14}CO_2$ atmosphere was quantified in loess $CaCO_3$ to calculate amounts of secondary (recrystallized) $CaCO_3$. After application of 1–4 $^{14}CO_2$ pulses in 4 day intervals, leading to an approximately linear increase of amounts of recrystallized $CaCO_3$, the authors calculated an initial recrystallization rate of $2.9 \cdot 10^{-5}$ day^{-1}. This means that per day, 0.003% of total loess $CaCO_3$ was recrystallized. Extrapolation of this rate on longer time periods showed that at least 400 years, but probably thousands of years are necessary for complete recrystallization in loess containing 27% $CaCO_3$. This approach was further applied to reveal the dependence of initial recrystallization rates on CO_2 concentration in loess pore space (Gocke et al., 2010) as well as on root vicinity (Gocke et al., 2011a). These studies showed that $CaCO_3$ recrystallization rates strongly increase with increasing CO_2 concentration and therefore are higher in the rhizosphere than in loess distant from roots. Further environmental factors affect pedogenesis and might play an important role for the reactions between $CaCO_3$, CO_2 and H_2O.

Temperature is one of these factors. Pedogenic carbonates are abundant and were most often described in soils of warm climates, but were also observed in soils of colder climates, e.g. Alaska (Marion et al., 1991) and Spitzbergen (Courty et al., 1994). While the dependence of pedogenic carbonate accumulation rates and depth on amounts of rainfall has often been investigated (e.g. Arkley, 1963; Marion, 1989; McFadden and Tinsley, 1985; Nordt et al., 2006), the effect of temperature on initial $CaCO_3$ recrystallization rates was not quantified so far. Marion (1989) found no correlation between modern mean annual temperature and accumulation rates of Pleistocene calcic horizons. However, the role of temperature is reflected e.g. by its role in isotopic fractionation during secondary $CaCO_3$ formation (Romanek et al., 1992). Pustovoytov (2003) stated that increasing temperature can influence the intensity (i.e. thickness) of $CaCO_3$ accumulation on clasts in several ways which might partly counteract each other: via stimulation of evaporation, by controlling $CaCO_3$ solubility and by enhancing pCO_2 in soil.

Biotic processes like plant growth, root and rhizomicrobial respiration are promoted by increasing temperature which might lead to enhanced recrystallization at high temperature because of higher CO_2 concentration in soil. However, abiotic factors, mainly solubility of CO_2 and $CaCO_3$, decrease with increasing temperature. This controversy does not allow a simple prediction of the effects of temperature on formation of pedogenic carbonates and their recrystallization rates. Therefore, we evaluated these effects on initial $CaCO_3$ recrystallization rates and calculated periods experimentally by applying the ^{14}C isotopic exchange approach at different temperature levels. The aim of this work was to reveal, which temperature-controlled factor – abiotic effect of CO_2 and $CaCO_3$ solubility or intensity of biological activity – exerts more influence on secondary $CaCO_3$ formation and recrystallization in soils. Further aim was to confirm the assumption that faster recrystallization occurs in rhizosphere compared to loess distant from roots, as shown by Gocke et al. (2011a), and to reveal the influence of temperature on this effect.

2. Material and methods

2.1. Experimental layout and ^{14}C labeling

Maize (*Zea mays* [L.], cv. Tassilo) was chosen for the ^{14}C multiple pulse labeling experiment because of its fast growth and because this plant does not entail a strong decrease of pH in rhizosphere, which might lead to artificial promotion of $CaCO_3$ recrystallization. As shown before, in maize experiments a major part of soil CO_2 is derived directly from root biomass, compared to a small portion of microbial-derived CO_2 (Werth and Kuzyakov, 2008). Plants were grown on loess from Nussloch, SW Germany with high $CaCO_3$ content (274 mg g^{-1}, Gocke et al., 2011b) and low C_{org} content (0.3 mg g^{-1}, Wiesenberg et al., 2010). Loess was chosen to avoid interference of CO_2 fluxes by microbial decomposition of old organic matter, and to simulate initial pedogenesis on a calcareous sedimentary parent material which is globally abundant. Polycarbonate filtration devices (CombiSart, Sartorius AG, Germany) were used as plant pots, with three inlets in the lid and one main opening for growth of the plant shoots. In each plant pot with 420 g air-dry loess, one pre-germinated maize seedling was grown under controlled conditions of 14/10 h day/night periods, 20 °C and light intensity of 300 μmol m^{-2} s^{-1}, and loess moisture was adjusted to 70% of water holding capacity (WHC; 100% WHC = 28% of loess weight) once a day. Plants were kept in three plant growth chambers (Adaptis A1000, Conviron, Canada) during the entire experiment. For nutrient supply, plants were fertilized with Hoagland nutrient solution (Hoagland and Arnon, 1950) modified after Gocke et al. (2011a).

Two days before the first labeling, three treatments were separated by decreasing the temperature to 10 °C in one plant growth chamber and increasing it to 30 °C in another plant growth chamber. Thus, three levels of mean temperature during the growing season were simulated: 10, 20 and 30 °C. One day before the first ^{14}C labeling, plant pots were flushed with air to remove all previously respired CO_2, and three plants in each treatment were sealed around the shoots with silicone rubber (NG 3170, Thauer & Co., Germany) to prevent loss of respired CO_2 by air exchange between the loess-root compartment and the atmosphere.

Starting from an age of 14 days after planting, plants received 1 to 4 ^{14}C isotopic pulses á 407 kBq in intervals of 5 days. For this purpose, plants were exposed to artificially labeled $^{14}CO_2$ atmosphere in an airtight acrylic glass chamber for 3 h. $^{14}CO_2$ was released by dissolving $Na_2^{14}CO_3$ (ARC Inc., USA) in H_2SO_4. A detailed description of the

labeling procedure is given in Kuzyakov et al. (2006) and Gocke et al. (2011a). Because of very low recrystallization rates, $^{14}CO_2$ pulse labeling was applied up to 4 times to receive more reliable results than from one pulse labeling. The experiment was conducted with 3 replications per sampling date and per temperature treatment, resulting in a total of 15 plant pots per treatment:

1) Plants in open pots, labeled once
2) Plants in open pots, labeled twice
3) Plants in open pots, labeled three times
4) Plants in open pots, labeled four times
5) Plants in sealed pots, labeled four times

In between the labelings, plants continued growth under normal conditions. In contrast to most other ^{14}C labeling studies, rhizosphere CO_2 was not flushed out of the loess-root compartment between the labeling procedures. This allowed accumulation of root-respired $^{14}CO_2$ and isotopic exchange between the latter and loess $CaCO_3$.

2.2. Sampling and ^{14}C analysis

Five days after each labeling, rhizosphere CO_2 accumulated in the loess-root compartments was flushed out and trapped in NaOH solution to form Na_2CO_3. An aliquot of this solution was titrated with HCl against Phenolphthalein (Zibilske, 1994) to determine the amount of C in root-respired CO_2. Another aliquot was mixed with scintillation cocktail (Rotiszint, Roth, Germany) and analyzed for ^{14}C activity by a liquid scintillation counter (LS 6500 Multi-Purpose Scintillation Counter, Beckman, USA).

Afterwards, three plant pots were harvested for analyses (see below), while the remaining plants received the next ^{14}C isotopic pulse. From the plant pots selected for analyses, shoots were cut and roots were separated from loess with tweezers. This loess, in the following called non-rhizosphere loess, was washed with deionized water to remove dissolved organic and inorganic carbon (DOC, DIC). Rhizosphere loess, the material sticking to the roots, was obtained by washing roots with deionized water and filtration of this washing solution. All samples were dried at 90 °C and ground in a ball mill (MM200, Retsch, Germany).

To determine ^{14}C activity in loess $CaCO_3$, samples were treated with H_3PO_4 (Gocke et al., 2011a) to release CO_2 only from loess $CaCO_3$ but not from organic compounds in loess (root fragments, exudates). CO_2 was trapped in NaOH and an aliquot of the solution was measured as described above.

Total organic and inorganic carbon contents in washing solution were measured using a N/C analyzer (Multi N/C 2100, AnalytikJena, Germany).

2.3. Calculation and statistics

CO_2 concentrations in the loess-root compartment were determined at each sampling date, based on the amount of CO_2–C obtained from titration of the NaOH solution, as well as volume of the Sartorius device, loess density, volume of added nutrient solution and water, and thus free (air filled) volume.

Calculation of amounts of recrystallized $CaCO_3$ was based on ^{14}C incorporated in $CaCO_3$ by isotopic exchange with rhizosphere CO_2. We assume equal ratios of ^{14}C/total C for rhizosphere CO_2 and for C that was incorporated into the loess carbonate by recrystallization. Because ^{14}C was highly enriched compared to the level of natural abundance, the isotopic fractionation during the experiment was negligible. The ^{14}C/total C ratio (^{14}C specific activity, $^{14}C^{sp}_{CO_2}$) was calculated from accumulated CO_2 in sealed plant pots, where the original ratio was not altered by exchange with atmospheric air. Afterwards, amounts of recrystallized $CaCO_3$ ($CaCO_{3recryst}$) were calculated based on carbonate ^{14}C activities in unsealed plant pots ($^{14}C_{CaCO_3}$), where CO_2 concentrations more likely reflected natural conditions Eq. (1).

$$CaCO_{3_{recryst}} = \frac{^{14}C_{CaCO_3}}{^{14}C^{sp}_{CO_2}} \quad (1)$$

with $^{14}C^{sp}_{CO_2}$ as $^{14}C/C_t$ ratio of respired CO_2 in sealed plant pots and $^{14}C_{CaCO_3}$ as ^{14}C activity of loess $CaCO_3$ in unsealed plant pots.

The $CaCO_3$ recrystallization rate was determined according to Eq. (2):

$$CaCO_3 \text{ recrystallization rate} = \frac{CaCO_{3_{recryst}}}{CaCO_{3_t} \bullet t} \quad (2)$$

with $CaCO_{3_t}$ as amount of total $CaCO_3$ and t as the time between first labeling and respective sampling. As shown before (Gocke et al., 2011a; Kuzyakov et al., 2006), amounts of recrystallized $CaCO_3$ increase in an approximately linear way during growth of young plants. Therefore, only recrystallization rates averaged from all 4 sampling dates are presented in the figures.

Based on calculated rates, periods necessary for complete recrystallization of loess $CaCO_3$ were estimated in Eq. (3). Most likely, repeated recrystallization of primary and secondary $CaCO_3$ prior to definite precipitation of secondary $CaCO_3$ causes an exponential increase of secondary $CaCO_3$ (Kuzyakov et al., 2006). We considered the situation that 95% of total loess $CaCO_3$ was recrystallized, because under field conditions, a remaining portion of $\leq$5% of primary $CaCO_3$ is too small to be detected by isotope ratio mass spectrometry (IRMS) analysis on the level of ^{13}C natural abundance. Further, notable $CaCO_3$ recrystallization takes place predominantly during the growing season (Kuzyakov et al., 2006), when high soil CO_2 concentration and permanent CO_2 supply by root and rhizomicrobial respiration impede equilibrium of the $CaCO_3$–CO_2–HCO_3^- system (Gocke et al., 2010, 2011a). Therefore, length of the growing season (GS) was taken into account in Eq. (3):

$$t = \frac{-\ln(0.05)}{GS \bullet RR} \quad (3)$$

with t as $CaCO_3$ recrystallization period, GS as growing season in days $year^{-1}$ and RR as recrystallization rate in $days^{-1}$.

Mean values and standard errors of the mean are presented in figures. The sample set was tested for significance of differences between temperature levels using two-way ANOVA with a significance level of $\alpha = 0.05$, followed by post hoc Fisher LSD test. Statistical analysis was carried out using STATISTICA for Windows (version 7.0, StatSoft Inc., Tulsa, USA).

3. Results

3.1. Amounts of recrystallized $CaCO_3$ and recrystallization rates

From the first to the last sampling date, amounts of recrystallized $CaCO_3$ increased approximately in a linear way (not shown here). After four labeling procedures, i.e. 20 days after the first labeling, portions of recrystallized $CaCO_3$ were at minimum $6.2 \cdot 10^{-3}$% and at maximum 1.9% of total loess $CaCO_3$ (Table 1).

Considering the amounts of recrystallized $CaCO_3$ from all 4 sampling dates, these portions corresponded to $CaCO_3$ recrystallization rates in the range of 10^{-6}–10^{-4} day^{-1}. Both root vicinity and temperature had a significant effect on recrystallization rates: In each temperature treatment, the rates were significantly (20 to 70 times) lower in non-rhizosphere loess compared to rhizosphere loess, and values were smallest for plants grown at 10 °C and highest for those grown at 30 °C (Table 1, Fig. 1). Further, rates at 30 °C were significantly higher

Table 1
Portions of $CaCO_3$ recrystallized in non-rhizosphere (NRL) and rhizosphere loess (RL) 20 days after the first labeling, and initial $CaCO_3$ recrystallization rates averaged from 4 sampling dates.

	10 °C	20 °C	30 °C
Amounts of recrystallized $CaCO_3$ [% of total $CaCO_3$]			
NRL	0.006 ± 0.001	0.011 ± 0.003	0.091 ± 0.005
RL	0.358 ± 0.029	0.488 ± 0.068	1.898 ± 0.105
Initial $CaCO_3$ recrystallization rates			
NRL [10^{-6} day^{-1}]	2.9 ± 0.3	5.7 ± 0.7	31.0 ± 4.0
RL [10^{-5} day^{-1}]	20.6 ± 2.0	27.8 ± 5.7	74.6 ± 8.7

compared to those at 10 and 20 °C in both rhizosphere and non-rhizosphere loess.

Within the range of applied temperatures (10 °C–30 °C), the dependence of $CaCO_3$ recrystallization rates on temperature was described by an exponential increase in non-rhizosphere (Eq. (4)) and rhizosphere loess (Eq. (5)).

$$CaCO_3 \text{ recrystallization rate} = 1.3 \cdot 10^{-8} \cdot exp(0.25 \cdot T) + 4.8 \cdot 10^{-6} \quad (4)$$

$$CaCO_3 \text{ recrystallization rate} = 9.3 \cdot 10^{-7} \cdot exp(0.21 \cdot T) + 2.6 \cdot 10^{-4}. \quad (5)$$

3.2. Plant respiration and water uptake, and dissolved inorganic and organic carbon

CO_2 concentration in the loess-root compartment after five days of accumulation did not change significantly between the four sampling dates within each treatment. Average CO_2 concentration in the unsealed pots was 2.2 ± 0.3 vol.%, 5.8 ± 0.6 vol.% and 6.0 ± 0.5 vol.% at 10, 20 and 30 °C, respectively (Fig. 2).

Water consumption by plants was lowest at 10 °C (0.1–1.3 ml day^{-1}), leading to decrease from the adjusted moisture conditions of 70% of WHC of 5% at maximum (Fig. 3). In contrast, higher water consumption occurred at 20 °C (0.2–5.3 ml day^{-1}), causing the moisture conditions to decrease to 58% WHC. At 30 °C, moisture conditions fell below 25% WHC, as water uptake by plants ranged between 7.2 and 48.2 ml day^{-1}. Further, the water uptake rate strongly increased with time at 30 °C, while it remained approximately constant at lower temperatures. Similar to CO_2 concentrations, amounts of dissolved inorganic carbon (DIC), which were not precipitated as secondary $CaCO_3$, did not change significantly with time for each treatment. After 5 weeks of plant growth in total, DIC contents of non-rhizosphere loess were only slightly increased compared to unplanted loess, and dissolved organic carbon (DOC) contents in unplanted and non-rhizosphere loess were within the same range (Fig. 4). While DIC contents were significantly higher in rhizosphere loess (0.03–0.16 mg g^{-1} loess) compared to non-rhizosphere loess (0.02–0.06 mg g^{-1} loess), temperature had no effect on DIC contents (Fig. 4).

DOC contents did not change significantly with time for each treatment and were not significantly different between temperatures in non-rhizosphere loess (0.01–0.08 mg g^{-1} loess), but decreased significantly in rhizosphere loess with increasing temperatures (1.06 ± 0.14 vs. 0.59 ± 0.09 vs. 0.42 ± 0.06 mg g^{-1} loess; Fig. 4).

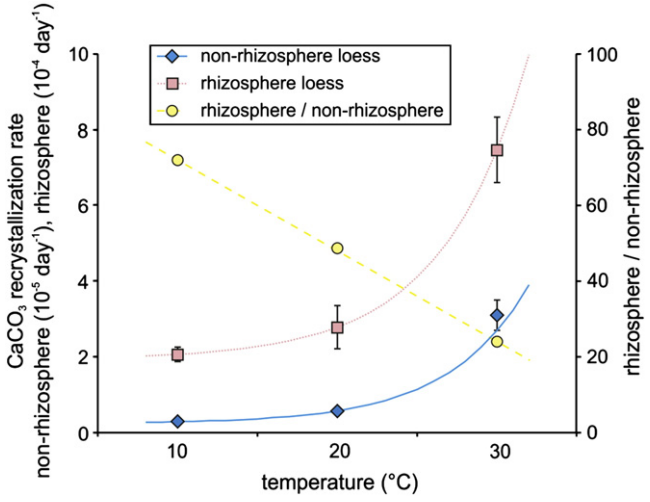

Fig. 1. Dependence of $CaCO_3$ recrystallization rates (averaged from 4 sampling dates) in non-rhizosphere and rhizosphere loess on temperature (note one order of magnitude different Y axes scales for rhizosphere and non-rhizosphere loess) and ratio of these rates in rhizosphere vs. non-rhizosphere loess.

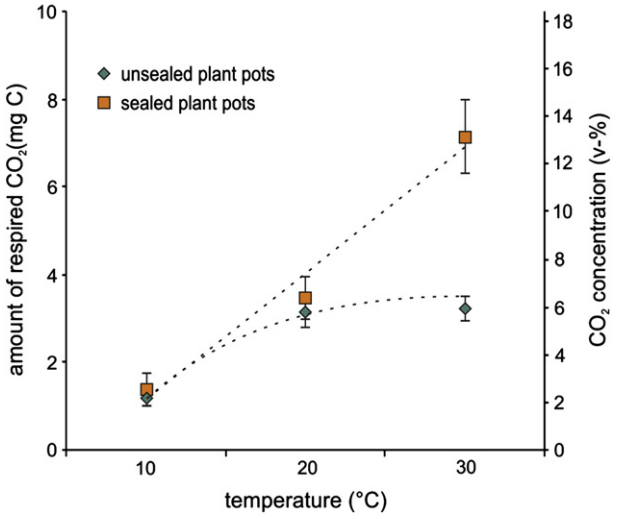

Fig. 2. Comparison of CO_2 concentrations at three temperatures in open and sealed plant pots. CO_2 concentrations represent the amount of CO_2 accumulated during 5 days.

4. Discussion

4.1. Influence of temperature on $CaCO_3$ recrystallization rates

At each of the three temperatures, amounts of recrystallized $CaCO_3$ increased approximately in a linear way from the first to the last sampling. This confirmed the assumption that during the initial stage (weeks–months) of plant growth, constant CO_2 release by roots and rhizomicroorganisms entails constant $CaCO_3$ recrystallization (Gocke et al., 2011a; Kuzyakov et al., 2006). With the graph of the trend curves intersecting the time axis approximately at the date of the first labeling, their slopes corresponded to initial recrystallization rates in loess, which were in the range of 10^{-6}–10^{-4} day^{-1} and strongly increased with temperature (Fig. 1).

Generally, increasing temperature accelerates the adjustment of a reaction equilibrium between reactants (Krauskopf and Bird, 1995), an effect which was not assessed here. However, it was shown that initial $CaCO_3$ recrystallization rates themselves are strongly influenced by temperature: in non-rhizosphere loess, rates were one order of magnitude higher at 30 °C compared with 10 °C (Fig. 1). This is about 2.5 times stronger than it could be expected by the common Q_{10} of about 2 (Davidson et al., 2006). This can partly be explained by the character of the $CaCO_3$–CO_2–HCO_3^- system: at higher temperature, low solubility of CO_2 entails decreasing $CaCO_3$ solubility, thus promoting $CaCO_3$ precipitation (Arkley, 1963), if dissolved Ca^{2+} and CO_3^{2-} are present.

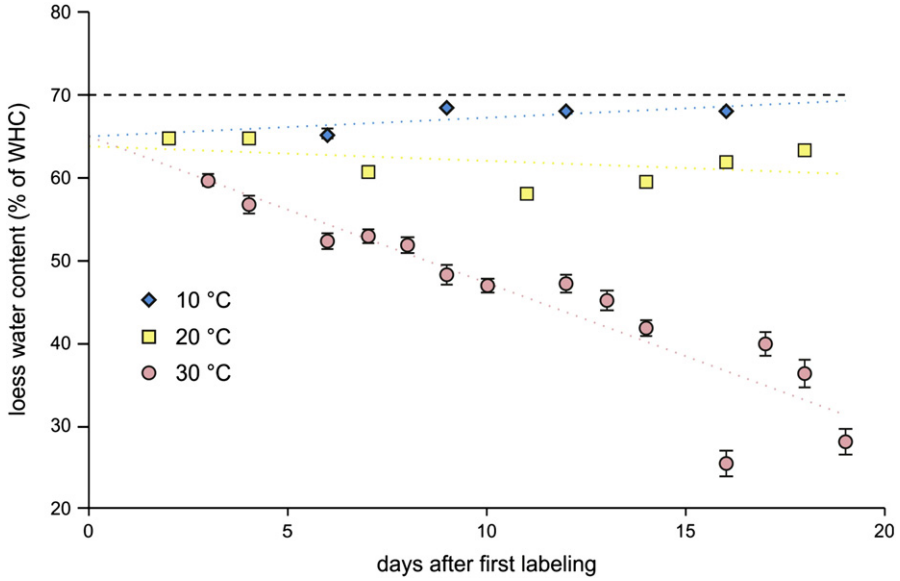

Fig. 3. Minimum loess moisture levels, resulting from different plant transpiration rates at 10, 20 and 30 °C. Difference between 70% of water holding capacity (WHC; dashed line) and dotted lines reflects daily variation of water content before gravimetric adjustment to 70% of WHC.

On the other hand, a considerable amount of $CaCO_3$ has to be dissolved before precipitation, which is promoted by increasing amounts of dissolved CO_2. Decreasing solubility of CO_2 and to lesser extent of $CaCO_3$ with increasing temperature (Krauskopf and Bird, 1995) predicts lower recrystallization rates at high temperatures and vice versa, which disagrees with our findings.

Quite the contrary, CO_2 concentrations in the planted microcosms were higher at 20 and 30 °C compared to 10 °C (Fig. 2). Our results suggest considerable influence of biological activity on recrystallization rates, as plant growth, root respiration and exudation and microbial respiration are promoted by increasing temperature (Orlov et al., 1997).

It was shown before that recrystallization rates strongly depend on CO_2 concentrations, with higher values at high CO_2 concentration and vice versa. The recrystallization rates in loess without plants increased strongly in the range between atmospheric CO_2 concentration (0.04 vol.%) and ~2 vol.%, whereas saturation was reached in the range between 2 and 3 vol.% (Gocke et al., 2010). In the present study, however, CO_2 concentration in each treatment was within or above this

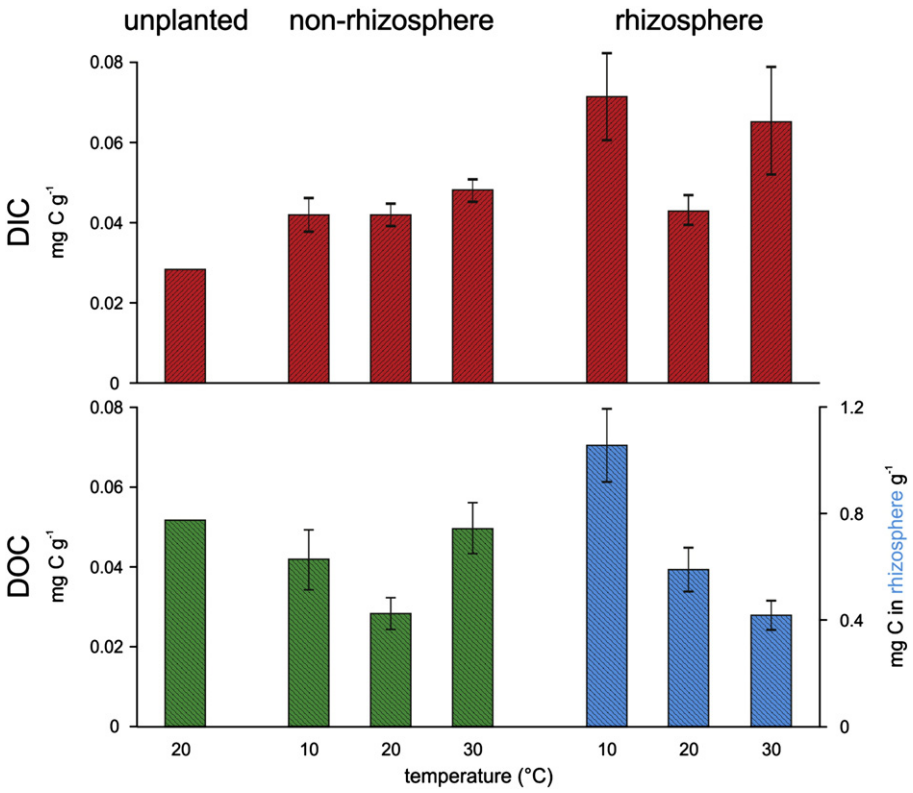

Fig. 4. Comparison of DIC and DOC contents in unplanted, non-rhizosphere and rhizosphere loess, normalized to 1 g loess. Only values for unsealed plant pots are shown.

range (Fig. 2), suggesting that it cannot be the sole reason for the exponential increase of $CaCO_3$ recrystallization rates with temperature. DIC contents did not show contrasting values for different temperatures. This indicates that the maximal possible amount of CO_3^{2-} was dissolved in pore space solution. At the same time amounts of root exudates – as far as reflected by DOC – which could promote $CaCO_3$ dissolution by pH alteration, were not different between the temperatures (Fig. 4).

The influence of a further factor on $CaCO_3$ precipitation was discussed in Gocke et al. (2011a): water uptake by roots, leading to an increase of Ca^{2+} and HCO_3^- concentrations in soil solution to oversaturation close to the root surface, which finally causes precipitation of secondary $CaCO_3$ in a special form of pedogenic carbonates—rhizoliths (calcified roots). Comparing two times higher $CaCO_3$ recrystallization rates in rhizosphere compared to non-rhizosphere loess, it was concluded that this difference is partly caused by the roots' transpirational pull. In the present study, daily watering of plants to keep equal moisture in all treatments caused different variations of water content, depending on water consumptions and thus on temperature. Lowest variation occurred at 10 °C (65–70% WHC) and highest at 30 °C (25–70% WHC; Fig. 3). The reason for this is that transpiration of plants strongly increases by rising temperature, partly because of the increase of water pressure deficit. In contrast to CO_2 concentrations which increased only from 10 °C to 20 °C, but not from 20 °C to 30 °C, the water uptake presumably exerted main influence on $CaCO_3$ recrystallization rates, because strongly alternating wet and dry conditions promote dissolution and precipitation of $CaCO_3$ and consequently formation of secondary carbonates (Becze-Deák et al., 1997; Borchardt and Lienkaemper, 1999).

Generally, higher temperature leads to enhanced evapotranspiration (Lal and Kimble, 2000). However, the influence of vegetation on secondary $CaCO_3$ precipitation in general, as well as on formation of calcretes (indurated accumulation horizons of pedogenic carbonate) was often underestimated until the late 1970s (Goudie, 1996). Since then, dissolution of soil $CaCO_3$ was attributed to biogenic CO_2, but reprecipitation was still thought to be controlled by abiotic processes like pCO_2 decrease or evaporation of the soil solution (Salomons and Mook, 1976). In subsequent studies, for calcrete formation the biotic process of plant transpiration was considered to have stronger effects on suction pressure in soil compared to abiotic evaporation (Klappa, 1983). Schlesinger et al. (1987) showed for desert soils of New Mexico that roots can be responsible for a removal of up to 72% of incident precipitation by plant transpiration and concluded a significant influence of vegetation on $CaCO_3$ accumulation in soil. Similarly, Jones and Ng (1988) clearly showed the considerable influence of plants on secondary $CaCO_3$ precipitation in the vadose zone: While roots control the rhizosphere moisture level by evapotranspiration, associated microorganisms can enforce cementation, both processes leading to formation of rhizoliths. Following studies recognized the importance of mass flow to the roots, induced by transpiration, for pedogenic carbonate precipitation in general (e.g. Cramer and Hawkins, 2009).

In the present study, the influence of the water effect on $CaCO_3$ recrystallization rates was obvious not only present in the rhizosphere, where direct influence of living roots was expected to create temperature-dependent results, but even in loess distant to roots. There, the difference between different temperatures had an even stronger effect (factor ~11 between rates at 10 and 30 °C) compared to rhizosphere loess (factor ~4).

Comparison of recrystallization rates in rhizosphere and non-rhizosphere loess revealed ratios in the range between 20 and 100, with highest values at 10 °C (72), lower values at 20 °C (49) and lowest ratio at 30 °C (24; Fig. 1). We suggest that increased CO_2 concentration, higher gas viscosity and thus stronger CO_2 diffusion at higher temperature (White and Oostrom, 1996) led to enlarged volume of influence of rhizosphere respiration. This might have somewhat diminished the contrast between non-rhizosphere and rhizosphere loess with increasing temperature.

In contrast to the present findings, Gocke et al. (2011a) reported for wheat and ryegrass that $CaCO_3$ recrystallization rates were merely twice as high in rhizosphere loess when compared to non-rhizosphere loess. One possible cause for stronger differences between rhizosphere and non-rhizosphere recrystallization rates in the present study might be the impact of rhizosphere sampling: In consequence of irregular distinction between rhizosphere and non-rhizosphere material and different moisture levels at the sampling dates, varying portions of non-rhizosphere loess may be included in rhizosphere samples. Smallest absolute amounts of rhizosphere loess (8 ± 1 g) were obtained at 10 °C and highest amounts (23 ± 2 g) at 30 °C, meaning that potentially lowest amounts of non-rhizosphere loess were sampled as rhizosphere material at 10 °C and highest portion at 30 °C. A possible 'contamination' of rhizosphere loess with non-rhizosphere loess during sampling might also explain decreasing DOC contents in rhizosphere loess with increasing temperature (Fig. 4). In spite of these uncertainties, our findings clearly demonstrate the strong influence of living roots on $CaCO_3$ recrystallization rates in soil.

4.2. Effect of temperature on $CaCO_3$ recrystallization periods

Based on $CaCO_3$ recrystallization rates in non-rhizosphere and rhizosphere loess, we calculated the periods necessary for complete (95%) recrystallization of loess $CaCO_3$ by formation of secondary $CaCO_3$. Assuming repeated dissolution and reprecipitation of both primary and secondary $CaCO_3$ prior to formation of concretions, the amount of secondary $CaCO_3$ is expected to increase in an exponential way (Gocke et al., 2010, 2011a; Kuzyakov et al., 2006).

Using a typical growing season of 4 months for maize, the plant used in the experiment, recrystallization periods of 8610 years, 4330 years and 800 years were calculated in non-rhizosphere loess for treatments with 10, 20 and 30 °C, respectively. Thus, the strong influence of increasing temperature on $CaCO_3$ recrystallization was reflected not only by increasing rates but also by corresponding one order of magnitude decreasing length of recrystallization periods. However, at equal amounts of precipitation, increasing temperature leads to decreasing length of the growing season, as less water is available to the roots. Recalculation of recrystallization periods with growing seasons of 6 months at 10 °C, 4 months at 20 °C and 3 months at 30 °C showed that for 95% recrystallization of loess $CaCO_3$, 5740 years, 4330 years and 1060 years would be necessary, respectively (Fig. 5a). In rhizosphere loess, significantly higher $CaCO_3$ recrystallization rates yielded considerably shorter time periods of 80, 90 or 45 years, if temperature-dependent growing seasons are assumed as above. These periods are even shorter if secondary $CaCO_3$ concretions form around the roots (rhizoliths; Klappa, 1980; Pustovoytov and Terhorst, 2004; Gocke et al., 2011a, b), preventing further dissolution and reprecipitation of $CaCO_3$. Consequently, linearly increasing amounts of recrystallized $CaCO_3$ would lead to complete recrystallization within 25, 30 or 15 years at 10, 20 and 30 °C (Fig. 5b). In both cases, similar rates at 10 and 20 °C (Table 1) entailed similar recrystallization periods in contrast to considerably shorter periods at 30 °C. In this case, the shortening effect of increasing temperature on growing season totally compensated the enhancing effect of increasing temperature on recrystallization rates. Therefore, under the modeled conditions, recrystallization periods were slightly shorter at 10 °C compared to those at 20 °C. These short recrystallization periods in rhizosphere agree with the assumption that rhizolith formation takes place during the life span of shrubs or trees (Gocke et al., 2011b). However, the majority of paleoenvironmental studies using stable isotope composition of pedogenic carbonates were performed on those concretion types which formed distant from roots, e.g. coatings (Pustovoytov et al., 2007a; Wang and Anderson, 1998) and nodules (Deutz et al., 2001; Dworkin et al., 2005; Pendall et al., 1994; Quade et al., 2007). The time frame of their formation or recrystallization is best reflected by extrapolation of

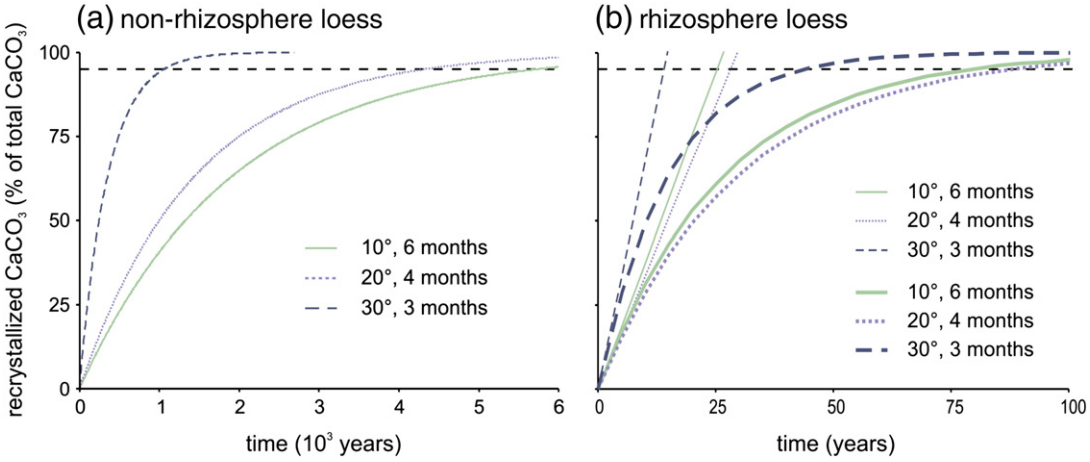

Fig. 5. Comparison of $CaCO_3$ recrystallization periods extrapolated from recrystallization rates at 10, 20 and 30 °C (note different scale on X axes). (a) Periods necessary for complete recrystallization of total $CaCO_3$ in non-rhizosphere loess, assuming temperature-dependent length of growing season, i.e. as an example 6 months at 10 °C, 4 months at 20 °C and 3 months at 30 °C. (b) Periods necessary for complete recrystallization of total loess $CaCO_3$ in rhizosphere loess, depending on formation of rhizoliths (straight lines) or repeated recrystallization (exponential lines). Black dashed lines represent the level of 95% recrystallization.

$CaCO_3$ recrystallization rates from non-rhizosphere loess. This means that (1) $CaCO_3$ in grassland soils is completely recrystallized within 10^2–10^3 years and that (2) formation and recrystallization of secondary $CaCO_3$ requires shorter periods under high temperatures compared to lower temperature.

The majority of studies on pedogenic carbonates was done in regions of arid and semiarid climatic conditions, e.g. in the deserts of Southwestern USA (e.g. Machette, 1985; Marion, 1989) and Western Asia (e.g. Pustovoytov et al., 2007a). Comparing the soil moisture contents at planted and at harvested plots, Schlesinger et al. (1987) already hypothesized the substantial role that roots might play for rate and depth of carbonate precipitation in arid soils by controlling the amount and movement of soil water and its Ca^{2+} and HCO_3^- concentration. Our findings show the significant indirect effect of ambient temperature on $CaCO_3$ recrystallization periods by controlling plant growth and associated biological processes like respiration and water uptake.

Under natural conditions, mixed effects of temperature combined with rainfall on $CaCO_3$ recrystallization rates and periods occur. As an example, under highly arid conditions, even shorter growing seasons should reinforce the shortening effect of increasing temperature on recrystallization periods, and therefore further diminish the contrast between slow $CaCO_3$ recrystallization at low temperature and vice versa. Additionally, cold arid climate decreases biological activity in soil (Orlov et al., 1997), and low CO_2 concentration from reduced rhizosphere respiration will entail lower $CaCO_3$ recrystallization rates corresponding to longer recrystallization periods (Gocke et al., 2010).

The direct or indirect influence of further factors on carbonate recrystallization in soil, e.g. soil moisture or primary $CaCO_3$ content, should be investigated. Together with the data presented, these results might be useful to develop a model for prediction of time spans of pedogenic carbonate formation and recrystallization under various climatic conditions.

4.3. Consequences for paleoenvironmental studies

Since recovery of the C isotopic relation between pedogenic carbonates and soil CO_2 (Cerling, 1984), carbon isotope composition of pedogenic carbonates has been used in numerous studies to assess paleoenvironmental conditions and age of pedogenesis. This requires long-term preservation of the isotopic signal, i.e. the soil has to act as a closed system, which is not true for all soils. Recrystallization and isotopic re-equilibration of existing pedogenic $CaCO_3$ with younger soil CO_2 may entail overprinting of the original isotope composition (Amundson et al., 1994; Pendall et al., 1994). For soils that lack postsegregational contamination of pedogenic carbonates, methodological resolution of paleoenvironmental and chronological studies is nevertheless restricted by the time frame of pedogenic carbonate formation (Royer et al., 2001). This time frame – 10^3 to 10^4 years according to Cerling (1984, 1999) – exceeds instrumental precision (IRMS for $d^{13}C$, AMS for radiocarbon dating). The exact time scale of pedogenic carbonate formation could not be assessed under field conditions so far (see chapter 1).

In the present study, we extrapolated $CaCO_3$ recrystallization rates obtained from ^{14}C labeling of plants under controlled conditions to estimate the periods necessary for complete (95%) $CaCO_3$ recrystallization by formation of secondary $CaCO_3$. Certain factors influencing the time scale of pedogenic $CaCO_3$ formation and recrystallization in soil could not be considered: Using plant pots that hamper CO_2 exchange with atmospheric air (also in unsealed pots), initial recrystallization rates were slightly raised by high CO_2 concentration in the loess-root compartment as well as by rather humid conditions. Consequently, ^{14}C labeling of plants under controlled conditions overestimated $CaCO_3$ recrystallization rates and underestimated recrystallization periods. Under natural conditions, somewhat lower soil CO_2 concentration should tend to slow down the process of secondary carbonate formation and recrystallization. Moreover, in arid regions where pedogenic carbonates typically form, reduced rooting density and rooting depth have to be considered, potentially leading to lower $CaCO_3$ recrystallization rates. Further, our results are valid only for soils developed on calcareous sedimentary parent material. In soils developed on more compact primary $CaCO_3$ or non-calcareous parent material, recrystallization rates are limited by lower $CaCO_3$ dissolution rates, rates of Ca^{2+} influx from external sources or weathering rates of Ca-bearing minerals (Birkeland, 1999).

Despite these restrictions, the estimated periods indicate the temporal order of magnitude of pedogenic carbonate recrystallization: Using plant pots of 7 cm height, we simulated the conditions in the uppermost 7 cm of a soil profile. In natural soil profiles, radiocarbon ages of pedogenic carbonate in this depth represent the time of recrystallization of secondary $CaCO_3$ rather than the time of its formation (Kuzyakov et al., 2006). Our findings are comparable to recrystallization periods calculated by Kuzyakov et al. (2006) on the basis of radiocarbon data from several soil profiles (Becker-Heidmann et al., 1996). These periods, ranging between some decades and thousands of years, were shorter at high temperatures (26 °C:

130 years) compared to lower temperatures (15 °C: 2500 years). As such detailed radiocarbon data are scarce for upper soil horizons, it was not possible to compare our estimated recrystallization periods to field data obtained from chronosequence studies with different temperature but constant rainfall. However, studies on pedogenic carbonate coatings grown on the lower side of clasts point at a similar direction: Pustovoytov (2003) compared $CaCO_3$ coating growth rates from soil profiles at Middle and Southeastern Europe, Western Asia, Russia and North America. These growth rates seemed to be slightly promoted by increasing temperature. Carbonate coatings form in gravelly parent material, while results from the present study were obtained from secondary carbonates formed in loess. Despite unequal formation and accumulation mechanisms in both types of parent material (Gile et al., 1966), this finding from Pustovoytov (2003) agrees with our results from controlled conditions.

Simple mass balance calculation (Kuzyakov et al., 2006) demonstrated that contamination of secondary $CaCO_3$ of Holocene age even with a small portion of primary $CaCO_3$ can entail strong overestimation of the true radiocarbon age. Therefore, the time necessary for recrystallization represents the upper limit of the resolution of paleoenvironmental studies based on isotope composition of pedogenic carbonates. For pedogenic carbonates which were not formed by encrustation of roots (i.e. rhizoliths), the precision of such paleoenvironmental reconstructions cannot be better than thousands of years, depending on length of the growing season, which in turn is affected by temperature.

5. Conclusions

For maize grown on loess, initial $CaCO_3$ recrystallization rates were in the range of 10^{-4} day^{-1}–10^{-6} day^{-1}. Rates were lowest at 10 °C, intermediate at 20 °C and highest at 30 °C, with values one order of magnitude higher compared to those at 10 °C. This strong increase was attributed to the boosting effect of temperature on shoot and root growth and associated rhizosphere processes, especially root and rhizomicrobial respiration. Additionally, enhanced moisture contrast resulting from the plants transpirational pull and, to a smaller extent, increased root and rhizomicrobial respiration under high temperature led to reinforced dissolution and reprecipitation of $CaCO_3$, as a result of enhanced moisture contrast and increased CO_2 concentrations. This showed the enormous significance of vegetation for pedogenic carbonate formation and recrystallization and demonstrated that the temperature as a climatic factor controls the recrystallization indirectly — by biotic processes.

The shortening effect of temperature on length of the growing season diminishes to some extent the contrast between low and high temperatures when regarding the periods necessary for complete recrystallization. In loess distant to living roots, the time frame of recrystallization was 5740 years at 10 °C, 4330 years at 20 °C and 1060 years at 30 °C if assuming growing seasons of 6, 4 and 3 months, respectively. These estimated periods reflect the minimum times for pedogenic carbonate formation or postsegregational alteration, as the experimental layout leads to overestimated recrystallization rates. These findings indicate that in grassland soils at least 10^3 years are necessary for complete (95%) recrystallization of loess $CaCO_3$ and formation of secondary $CaCO_3$. This time frame represents the upper limit of the temporal resolution of paleoenvironmental studies based on isotope composition of pedogenic carbonates.

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