Pedogenic carbonate formation: Recrystallization versus migration—Process rates and periods assessed by ^{14}C labeling

Martina Gocke,[1] Konstantin Pustovoytov,[2] and Yakov Kuzyakov[3]

[1] Under arid to semihumid climatic conditions, dissolution of primary carbonate and recrystallization with carbon (C) from soil CO_2 leads to accumulation of significant amounts of pedogenic (secondary) carbonate. Most soils of arid and semiarid regions contain a carbonate accumulation horizon, the depth of which is related to climatic conditions and properties of parent material. It remains unclear whether this carbonate migrates from the upper horizons before or after recrystallization with soil CO_2. The aim of this study was to determine recrystallization rates during initial pedogenesis and to estimate the accumulation depth of secondary carbonate based on C isotopic exchange during secondary carbonate formation in an experiment with alternating moisture conditions. Maize grown on 1 m high loess-filled columns was pulse labeled in $^{14}CO_2$ atmosphere every 3 weeks. After 6 months, portions of secondary (recrystallized) $CaCO_3$ were determined in 5 cm segments, based on ^{14}C respired in the rhizosphere and subsequently incorporated into newly formed secondary carbonate. More than 80% of recrystallized carbonate ($Ca^{14}CO_3$) was leached from the uppermost 15 cm of the loess column, and more than 70% of total secondary carbonate were accumulated in a depth between 15 and 50 cm. Based on the recrystallization rate calculated for the uppermost 15 cm of the loess column ($1.77 \pm 0.26 \cdot 10^{-5}$ day^{-1}), between 300 and more than 1,700 years are necessary for complete decalcification of the upper 15 cm. Our modeled data are consistent with formation of calcic horizons under relatively humid conditions.

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1. Introduction

[2] Pedogenic (secondary) carbonates are a characteristic feature of soils of arid to semihumid climatic conditions [*Jenny*, 1994; *Birkeland*, 1999; *Eswaran et al.*, 2000], and constitute as soil inorganic carbon (SIC) 30–40% to the global soil carbon inventory [*Batjes*, 1996; *Eswaran et al.*, 2000].

[3] In soils and paleosols not affected by groundwater, secondary carbonates constitute important archives of paleo-environmental conditions: stable carbon and oxygen isotopic composition (δ^{13}C, δ^{18}O), morphology, depth of carbonate accumulation can be used to assess paleovegetation, paleo-temperatures, paleorainfall, and paleo-pCO_2.

[4] As pedogenic carbonates are precipitated in isotopic equilibrium with soil CO_2 [*Cerling*, 1984; *Nordt et al.*,

1996] released mainly by root and rhizomicrobial respiration, their carbon stable isotopic composition ($\delta^{13}C_{carb}$) reflects the photosynthetic pathway of the vegetation present during their formation [*Cerling et al.*, 1989; *Amundson et al.*, 1989]. Therefore, pedogenic carbonates have served as a tool for reconstructing paleovegetation in a number of studies [*Wang et al.*, 1996; *Pustovoytov et al.*, 2007; *Monger et al.*, 2009]. As shown by several studies, regional environmental conditions prevailing during formation of pedogenic carbonates can be reflected in their morphological occurrence [*Gile et al.*, 1966; *Courty et al.*, 1994; *Khokhlova et al.*, 2001; *Pustovoytov*, 2002; *Khokhlova and Kouznetsova*, 2004]. In moderately to strongly developed soil profiles, pedogenic carbonates typically occur within one soil horizon [*Gile et al.*, 1966; *Birkeland*, 1999], which is called carbonate accumulation horizon or calcic horizon (Bkc), if it meets the criteria of WRB [*IUSS Working Group WRB*, 2006]: ≥15 cm thickness, ≥15 wt-% $CaCO_3$, ≥5 wt-% more $CaCO_3$ than underlying horizon or ≥5 wt-% secondary carbonate. The depth of the top of the calcic horizon can show a wide range between 0 cm (in some Calcisols) and more than 2 m below the surface (in some modern or relict steppe soils such as Phaeozems), descending deeper as

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rainfall increases [*Jenny*, 1994; *Birkeland*, 1999]. This depth is also important for the degree of isotopic re-equilibration of carbonate with soil CO_2 [*Pendall et al.*, 1994], the prerequisite for the suitability of pedogenic carbonates as a tool for paleoenvironmental reconstructions based on stable isotopic composition as described above.

[5] Besides precipitation, the depth of carbonate leaching and of secondary $CaCO_3$ accumulation within the soil profile depends on further climatic conditions like temperature and evapotranspiration [*Arkley*, 1963; *Lal and Kimble*, 2000; *Retallack*, 2005; *Rubio and Escudero*, 2005] and other factors, e.g., vegetation, relief, surficial run-off, amount of available Ca^{2+} and HCO_3^- ions (either inherited or incorporated from dust or rainfall), depth of water penetration and properties of the parent material [*Arkley*, 1963; *Klappa*, 1983; *McFadden and Tinsley*, 1985; *Jenny*, 1994; *Birkeland*, 1999; *Nordt et al.*, 2006]. Moreover, strongly alternating moisture conditions enhance carbonate accumulation by dissolution and downward transport during wet seasons and $CaCO_3$ precipitation in lower parts of the soil profile during dry seasons because of increasing saturation of the soil solution with respect to Ca^{2+} and CO_3^{2-}.

[6] In paleosols, depth of carbonate accumulation and morphology stages, describing the increasing level of carbonate impregnation (as established by *Gile et al.* [1966] and expanded by *Machette* [1985]; stages I–VI), have been used for reconstruction of paleoprecipitation [e.g., *Retallack*, 2005] (see review by *Sheldon and Tabor* [2009]) and determination of soil age [*Gile*, 1993]. Rates of carbonate accumulation, which reveal higher values in gravelly soils when compared to non-gravelly soils [*Gile and Grossman*, 1979; *Lal and Kimble*, 2000], are of great importance for chronosequence studies of soils and paleosols and for estimation of ages of Quaternary deposits [*Birkeland*, 1999].

[7] Most work concerning carbonate accumulation in non-gravelly soils was performed in New Mexico and the Southwestern USA, where soils developed mainly on non-calcareous parent materials and the rate of carbonate accumulation is presumed to depend mainly on rates of $CaCO_3$ influx from dust and/or rainfall [e.g., *Gile et al.*, 1966; *Machette*, 1985; *McFadden and Tinsley*, 1985]. In calcareous parent material like loess, in contrast, the rate of pedogenic carbonate buildup is a function of the rate at which originally present $CaCO_3$ can be dissolved and translocated by leaching waters in a soil profile [*Birkeland*, 1999]. Moreover, previous studies assessed the time frame for carbonate translocation and formation of calcic horizon only indirectly, based on soil age and carbonate content [*McFadden and Tinsley*, 1985] or on theoretical calculations of water movement [*Arkley*, 1963]. Very slow processes of carbonate alteration by pedogenic processes [*Kuzyakov et al.*, 2006; *Gocke et al.*, 2010, 2011] rule out determination of these rates in the field. Another uncertainty is that primary and secondary carbonate cannot always be distinguished [*Lal and Kimble*, 2000; *Eswaran et al.*, 2000], in particular in soils developed on calcareous sediments like loess, because secondary carbonates are not necessarily recognizable morphologically (e.g., concretions).

[8] *Kuzyakov et al.* [2006] and *Gocke et al.* [2011] showed that it is possible to estimate very small portions of secondary (recrystallized) $CaCO_3$ in loess (<0.1% of total loess carbonate) even after time intervals as short as a few weeks

by ^{14}C labeling and isotopic exchange approach. The rate of loess carbonate recrystallization by formation of secondary carbonate was determined in newly formed $CaCO_3$ by quantifying ^{14}C assimilated by plants in an artificial $^{14}CO_2$ atmosphere and respired by root and rhizomicrobial respiration. Recrystallization rates in the range of 10^{-5} day^{-1} were obtained, i.e., per day 0.001% of the total loess carbonate were recrystallized, leading to complete recrystallization within few thousands of years. These studies, however, did not take into account carbonate translocation by percolating water.

[9] The main aim of the present study was (1) to show the depth-related distribution of secondary carbonate obtained by alternating drying and wetting, and (2) to visualize this relation in the initial stage of pedogenesis on a calcareous parent material. Further aims were to quantify leaching of carbonates from the upper layers and of accumulation in lower layers and to estimate the period necessary for complete decalcification of upper layers. As carbonate migration from upper layers is the prerequisite for formation of an accumulation horizon, this time period roughly indicates the maximum age of calcic horizons in loess.

2. Materials and Methods

2.1. Experimental Setup

[10] To test the effect of carbonate leaching on the depth of secondary $CaCO_3$ accumulation, maize (*Zea mays* [L.], cv. Tassilo) was grown on loess. This plant species was chosen because of its deep-rooting properties. The loess was sampled at the open cast mine of the HeidelbergCement AG, Nussloch (SW Germany, N 49°18′41.1,″ E 8°43′37.2,″ 211 m a.s.l.) from a depth of 15 m below present surface. C_{carb} content of the loess is 32.9 mg g^{-1}, corresponding to a $CaCO_3$ content of 274 mg g^{-1}. The loess-paleosol sequence of Nussloch was deposited mainly during the last glacial-interglacial cycle [*Antoine et al.*, 2001]. Loess was used as plant growing medium instead of soil, because it is not influenced by modern pedogenic processes like humification, leaching or calcification. The carbonate in loess is homogeneous and has a small uniform grain size (tens of μm). In addition, C_{org} content of the loess is low (0.3 mg g^{-1}; *Wiesenberg et al.* [2010]). Hence, CO_2 concentration and fluxes from root and rhizomicrobial respiration during the experiment were not altered considerably by CO_2 released from microbial decomposition of previously present organic matter, as would be in the case of natural soil. In summary, the experiment simulated conditions of initial soil formation in sedimentary calcareous parent material.

[11] Acryl glass tubes (Plexiglas® XT; Röhm, Germany) with an inner diameter of 46 mm and a height of 1 m were used to pot the plants. Each tube had one opening at the top for plant growth and three sidewise inlets, on at the bottom and two at the top (Figure 1). For ease of sampling (see below), the acryl glass tubes were lined with polyethylene terephthalate foil (Nalophan®; Kalle, Germany) with an inner diameter of 43 mm. Each lined tube was filled with 1,600 g of air-dried and sieved (2 mm) loess. The height of each loess column was 85 cm, resulting in a loess density of 1.3 g cm^{-3}.

[12] Ten maize plants were grown on loess under controlled laboratory conditions, one plant per acryl glass tube. The maize seedlings were first germinated on wet filter
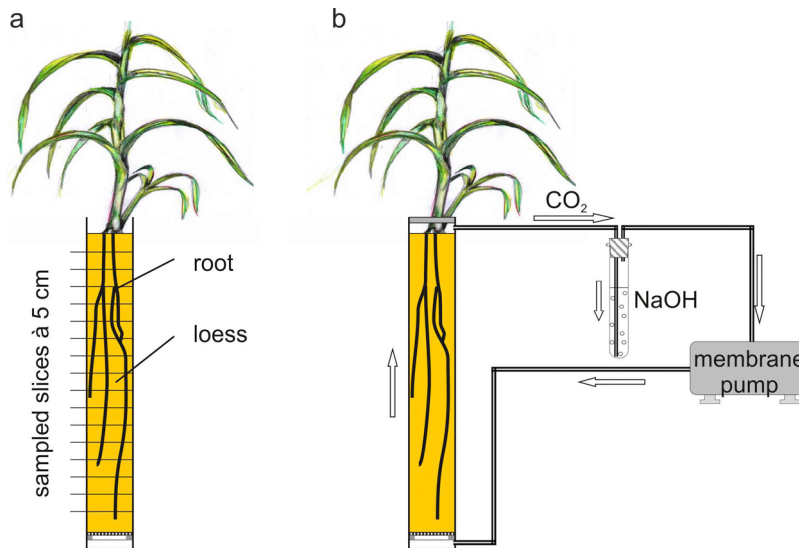
Figure 1. (a) Experimental layout with acryl glass tubes used as plant pots, and sampling design for the loess-root compartment, (b) trapping of respired CO_2 in NaOH solution, shown for sealed pots.

paper and transferred to the plant pots after 3 days. For the introduction of microorganisms, 10 ml of soil extract from a Haplic Luvisol (developed from loess) were added to each plant pot. The plants were grown at 14/10 h day/night periods and light intensity of 300 μmol m^{-2} s^{-1}. For nutrient supply, the plants were treated with Hoagland nutrient solution [*Hoagland and Arnon*, 1950] which was adapted to the high $CaCO_3$ content in loess [see *Gocke et al.*, 2011]. The applied nutrient solution contained 138, 62 and 469 μg ml^{-1} of N, P and K, respectively. ^{14}C contents of loess, soil extract and nutrient solution were below detection limit.

[13] Twenty-one days after planting, five of the plant pots were sealed with non-toxic two-component silicone rubber (Tacosil 145, Thauer and Co., Germany) between roots and shoots and the seal was tested for air leaks. The purpose of the sealing was to separate the air in the root-loess compartment from the atmospheric air and thus to avoid loss of ^{14}C labeled and total CO_2 released by root and rhizomicrobial respiration. The other five plant pots were not sealed to allow air exchange between atmosphere and the root-loess compartment, thus simulating natural conditions. Immediately before applying the first ^{14}C pulse label, every plant pot was flushed with fresh air to remove all previously accumulated CO_2 from root and rhizomicrobial respiration. For this purpose, the bottom inlet of each pot was connected to the output of a membrane pump (Type SMG4, Gardner Denver Thomas GmbH, Germany) for several hours. Afterwards, the inlets of the five sealed plant pots were plugged.

2.2. ^{14}C Pulse Labeling

[14] Twenty-one days after planting, the 10 maize plants were labeled for the first time in an airtight acryl glass chamber (0.5 · 0.5 · 1.6 m^3) equipped with an internal ventilation unit for equal distribution of the ^{14}C labeled CO_2. The labeling procedure was described in detail elsewhere [*Kuzyakov et al.*, 2006; *Gocke et al.*, 2011; *Fischer et al.*, 2010]. Briefly, the chamber was connected by tubing to a flask containing 10 ml of diluted $Na_2^{14}CO_3$ solution (ARC

Inc., USA) with 407 kBq per plant pot. $^{14}CO_2$ was released by adding 3 ml of 5 M H_2SO_4 to the label solution and was pumped through the acryl glass chamber in a closed cycle for 10 min by a membrane pump. The plants were labeled in $^{14}CO_2$ atmosphere during 4 h. C_4 plants reach the CO_2 compensation point, where CO_2 uptake equals CO_2 respiration, already after 30 min [*Kuzyakov and Cheng*, 2004], however we chose a longer time period to allow for complete assimilation of the ^{14}C labeled CO_2. After that time, the air of the acryl glass labeling chamber was pumped through 15 ml of 1 M NaOH to remove the remaining unassimilated CO_2. The chamber was opened and the plants continued growth under normal conditions.

[15] The plants were labeled 3 times in 3 week intervals. One week after the third labeling, plants were harvested and new maize seedlings were planted on the loess. Similar to the first plants, these were grown for 3 weeks, then labeled 3 times in time intervals of 3 weeks. In total, 3 maize plants grew in each acryl glass tube consecutively. The experiment thus consisted of three cycles of plant growth (named A, B and C), with each of them lasting 10 weeks and comprising 3 labelings.

2.3. Moisture Conditions

[16] Nutrient solution and water were always added from the top of the plant pots to simulate natural rainfall. In the following, all indications for the water level in loess-root compartments refer to the uppermost 60 cm of the loess column. The first 2 weeks after planting, loess moisture was held at 70% of water holding capacity (WHC = 28% of loess weight), i.e., 220 ml. All of the 10 plants always received the same volume of nutrient solution at one time. The individual difference to the total water loss was added as de-ionized water.

[17] Seven days before the first labeling, loess moisture was decreased until it reached a minimum level of 30–35% of WHC, corresponding to 94–110 ml. To obtain a maximum effect of carbonate migration on the depth of secondary

$CaCO_3$ accumulation, the water level was raised to 70% of WHC again 21–22 h after the beginning of each labeling. This time period was chosen because most of the CO_2 recently assimilated by maize plants is released into rhizosphere during the first hours after uptake [*Kuzyakov and Cheng*, 2004].

[18] Between the labelings, the water level of the plant pots was adjusted gravimetrically to 70% of WHC only when it reached the minimum level of 30% of WHC, corresponding to a water content of 94 ml. The intervals between two waterings decreased with increasing age and size of the maize plants. The time lags were between 2 and 8 days, depending on the plants' water loss by evapotranspiration. Due to differing plant growth, one cycle of plant growth comprised 12, 9 and 19 wettings for cycle A, B and C, respectively.

[19] In total, moisture conditions corresponded to daily precipitation of 18.5 ± 2.3 mm.

2.4. Sampling and Analyses

[20] After the labeling, ^{14}C activities in the residue of the label $Na_2^{14}CO_3$ solution and in unassimilated CO_2 trapped in NaOH were measured on 1 ml aliquots mixed with 2 ml of scintillation cocktail (Rotiszint EcoPlus; Carl Roth, Germany). The ^{14}C measurements were done using a liquid scintillation counter (LSC; 1450 LSC and Luminescence Counter, MicroBeta TriLux; Perkin Elmer Inc., USA) standardized by SQP(E) with ^{14}C counting efficiency $\geq 70\%$ and measurement error $\leq 3.5\%$.

[21] In contrast to previous studies [*Kuzyakov et al.*, 2006; *Gocke et al.*, 2011], root-respired CO_2 was removed not just prior to the subsequent labeling. Instead, CO_2 accumulated in the loess-root compartment was pumped out in one week intervals and analyzed for ^{14}C and total C (C_t) analyses. This time frame was chosen because the time intervals between the individual ^{14}C pulses of 3 weeks were too long for roots in sealed plant pots to grow without fresh air supply. Most of the recently (thus ^{14}C labeled) assimilated CO_2 is respired into the rhizosphere within the first 3 days [*Kuzyakov and Cheng*, 2004], and the C isotopic exchange between available CO_2 and $CaCO_3$ is completed within less than 4 days [*Gocke et al.*, 2010]. Hence, 7 days after the labeling, most of the ^{14}C tracer available in loess air CO_2 was already incorporated into loess carbonate by recrystallization.

[22] One, two and three weeks after each labeling, CO_2 from root and rhizomicrobial respiration of every plant pot was pumped through 15 ml of 1 M NaOH for 90 min by a membrane pump. For the sealed plant pots, CO_2 trapping was done in a closed system (Figure 1b). ^{14}C activity of respired CO_2 was measured on 1 ml aliquots of NaOH as described above. Total carbon content of respired CO_2 was determined by precipitating trapped CO_2 with 1 M $BaCl_2$ solution. NaOH was then titrated with 0.01 M HCl against phenolphthalein [*Zibilske*, 1994]. CO_2 concentration in the plant pots was calculated from the amount of CO_2-C trapped in NaOH. After removing the rhizosphere CO_2, each plant pot was flushed with atmospheric air for 20 min. Afterward, inlets of the sealed pots were plugged again, and the plants either continued growth under normal conditions or were labeled.

[23] At the end of the experiment, the lined acryl glass tubes containing loess and roots were frozen. Afterwards, foil liners with loess and roots were pulled out and cut into

5 cm slices from the top to the bottom (17 slices per plant pot; Figure 1a). After thawing of the samples, roots were removed from loess in each slice by tweezers and washed with 50 ml of de-ionized water. Immediately afterwards, loess from each slice was carefully mixed and water content was determined gravimetrically: The wet samples were weighed, dried until weight constancy, and weighed again. Loess moisture is expressed as mass-%. Three grams of loess were washed with 10 ml of de-ionized water to remove dissolved inorganic and organic carbon (DIC and DOC). Loess and root samples (each of them 85 in total) as well as shoot biomass from the harvested plants (30 in total) were dried at 60°C and grinded in a ball mill (MM200, Retsch, Germany).

[24] To analyze ^{14}C incorporated into plant biomass, total carbon of the plant material was converted into CO_2 by combustion at 800°C ('Feststoffmodul 1300', AnalytikJena, Germany). The evolved CO_2 was trapped in 8 ml of 1 M NaOH and subsequently analyzed for ^{14}C activity by LSC (see above). The amount of ^{14}C incorporated into solid organic substances (loess C_{org}) was determined in the same way at 550°C and measured in 5 ml aliquots.

[25] The solution from loess washing, containing dissolved inorganic and organic carbon (DIC, DOC), was measured on 4 ml aliquots for ^{14}C activity in total dissolved carbon and, after release of CO_2 from DIC by adding 0.2 ml of 1 M HCl, in DOC. ^{14}C activity of DIC was calculated by subtracting the ^{14}C in washing water before and after DIC release.

[26] To measure ^{14}C incorporated into loess carbonate, two grams of every dried loess sample were treated with 15 ml of 3 M H_3PO_4. CO_2 evolving from $CaCO_3$ was trapped in 12 ml of 2 M NaOH and analyzed for ^{14}C activity on 6 ml aliquots of NaOH added to 12 ml of scintillation cocktail. This method, tested before with a ^{14}C enriched plant sample, was used instead of combustion (the usual method for soil samples), because combustion would lead to CO_2 release not only from carbonate but also from organic matter accumulated in loess during plant growth. An aliquot of the NaOH containing CO_2 evolved from $CaCO_3$ was titrated (see above) to test whether total $CaCO_3$ content of loess had changed in the individual slices after plant growth as a result of carbonate redistribution.

[27] ^{14}C measurements of larger aliquots for loess $CaCO_3$, loess C_{org}, DIC and DOC were performed on a LS 6500 Multipurpose Scintillation Counter (Beckman, USA) with ^{14}C counting efficiency $\geq 90\%$ and measurement error $\leq 4\%$. The absolute ^{14}C activity was standardized by the H number method, using a ^{137}Cs external standard.

2.5. Calculations and Statistical Analyses

[28] After each labeling, the portion of ^{14}C assimilated by maize plants ($^{14}C_{ass}$) was calculated as follows:

$$^{14}C_{ass} = {}^{14}C_{input} - {}^{14}C_{res} - {}^{14}C_{NaOH} \qquad (1)$$

with $^{14}C_{input}$ as input ^{14}C activity, $^{14}C_{res}$ as ^{14}C activity of the residue of the label $Na_2^{14}CO_3$ solution and $^{14}C_{NaOH}$ as ^{14}C activity of unassimilated CO_2 trapped in NaOH after 4 h.

[29] The ^{14}C specific activity of CO_2 respired by roots and rhizosphere microorganisms was calculated as the ratio

Table 1. Dry Biomass of Plants[a] (g)

	Shoots 1. Sampling	Shoots 2. Sampling	Shoots 3. Sampling	Roots (Total) 3. Sampling
Open	6.9 ± 0.2	4.7 ± 0.2	9.8 ± 0.5	11.6 ± 0.7
Sealed	7.0 ± 0.4	5.0 ± 0.5	11.7 ± 0.7	n.d.

[a]Mean values $\pm$ SEM, n = 5.

of ^{14}C activity ($^{14}C_{CO_2}$) and total C content in respired CO_2 (C_{CO_2}):

$$^{14}C_{CO_2}^{sp} = \frac{^{14}C_{CO_2}}{C_{CO_2}} \quad (2)$$

The main prerequisite of our study was that the ^{14}C specific activities of respired CO_2 ($^{14}C_{CO_2}^{sp}$) and of C incorporated into the loess carbonate by recrystallization are equal. This can be assumed because the study was done with strongly enriched ^{14}C some orders of magnitude higher than natural ^{14}C abundance, making isotopic fractionation negligibly low. Portions of recrystallized $CaCO_3$ ($CaCO_{3_{recryst}}$) were calculated according to equation (3), based on ^{14}C activity of loess $CaCO_3$ ($^{14}C_{CaCO_3}$) and ^{14}C specific activity of respired CO_2.

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

We used $^{14}C_{CO_2}^{sp}$ from sealed pots, where loss of total and ^{14}C labeled CO_2 was prevented, and $^{14}C_{CaCO_3}$ from open pots, where undisturbed exchange of air inside and outside the pots reflected more likely natural conditions in terms of CO_2 concentration in loess, when compared to sealed pots.

[30] The initial $CaCO_3$ recrystallization rate was calculated as the amount of recrystallized $CaCO_3$ ($CaCO_{3_{recryst}}$, in mg) divided by the total amount of carbonate in loess ($CaCO_{3_t}$, in mg) and by the time (t) between the first labeling and the final harvesting (182 days). The recrystallization rate with dimension day^{-1} shows which percentage of the total carbonate was recrystallized per day if the value is multiplied with 100.

$$CaCO_3 \text{ recrystallization rate} = \frac{CaCO_{3_{recryst}}}{CaCO_{3_t} \cdot t} \quad (4)$$

Based on the initial recrystallization rate, the time period necessary for complete (95%) recrystallization of the loess carbonate was calculated. Most likely, an exponential decrease of the remaining primary $CaCO_3$ can be assumed [Kuzyakov et al., 2006; Gocke et al., 2011] because of repeated recrystallization of both primary and secondary carbonate. Carbonate recrystallization requires a high CO_2 concentration in soil [Gocke et al., 2010] which occurs mainly during the growing season [Fierer et al., 2005]. Therefore, the length of growing season (GS; in days per year) was included in equation (5) to estimate the portion of $CaCO_3$ recrystallized under field conditions ($CaCO_{3_{recryst}}(t)$):

$$CaCO_{3\,recryst}(t) = 100 \cdot \left(1 - e^{t \cdot rate \frac{GS}{365}}\right) \quad (5)$$

Mean values and standard errors of the mean are presented in figures. The sample set was tested for significance of differences using one-way ANOVA with a significance level of $\alpha = 5\%$, followed by post hoc LSD test. Statistical analysis was carried out using STATISTICA for Windows (version 7.0, StatSoft Inc., Tulsa, USA).

3. Results

3.1. Plant Biomass and Loess Moisture

[31] Total amounts of dry shoot biomass were significantly different between the three cycles of plant growth, with smallest amounts in the second and largest amounts in the last cycle (Table 1), but did not differ significantly between open and sealed plant pots, except for the last sampling.

[32] At the end of plant growth (30 weeks), the loess was completely rooted from top to bottom. Most of dry root biomass (2.7 ± 0.4 g) occurred in the uppermost 5 cm of the loess column, and decreased to <1 g below 5 cm, reaching <0.4 g at a depth of 50–85 cm (Figure 2a).

[33] Loess moisture, measured after the final harvesting of plants, was highest between 40 and 45 cm ($6.6 \pm 0.9\%$), and reached the lowest values (mostly <3%) below 55 cm (Figure 2a). Although these values of the final water contents are not representative for the whole time of plant growth, the depth-related pattern was in agreement with the calculated depth (60 cm) of maximal moisture penetration at water level of 70% of WHC.

3.2. ^{14}C Budget

[34] The total ^{14}C activity applied for all 9 labelings was 36.63 MBq, from which $99.7 \pm 0.3\%$ were assimilated by the maize plants. The remaining 0.3% (0.11 MBq) was found after labeling in the residue of the label $Na_2^{14}CO_3$ solution and in unassimilated CO_2 from the labeling chamber, trapped in NaOH.

[35] In open plant pots, recovery of ^{14}C activity in loess, DIC and DOC, plant biomass and CO_2 from root and rhizomicrobial respiration in total was 38% (32–43%) of the added ^{14}C label (Table 2), meaning that more than 60% of assimilated ^{14}C were lost by shoot respiration during plant growth under normal conditions.

[36] Based on the recovered ^{14}C label, most ^{14}C was found in maize biomass, with $74.4 \pm 1.0\%$ in aboveground biomass and $18.2 \pm 0.8\%$ in roots. In general, only small parts of the ^{14}C label were incorporated into below ground C pools by exudation and respiration of roots: $1.0 \pm 0.1\%$ in loess $CaCO_3$, $1.1 \pm 0.1\%$ in CO_2 respired by roots and associated microorganisms, 4.0 ± 0.2 in organic matter (loess C_{org}), mainly representing not extractable root debris, and $1.3 \pm 0.1\%$ in DIC and DOC (Table 2).

3.3. Rhizosphere CO_2

[37] From the open plant pots, all above- and belowground C pools (see Table 2) were analyzed for ^{14}C, whereas sealed pots were used only to obtain ^{14}C specific activities of
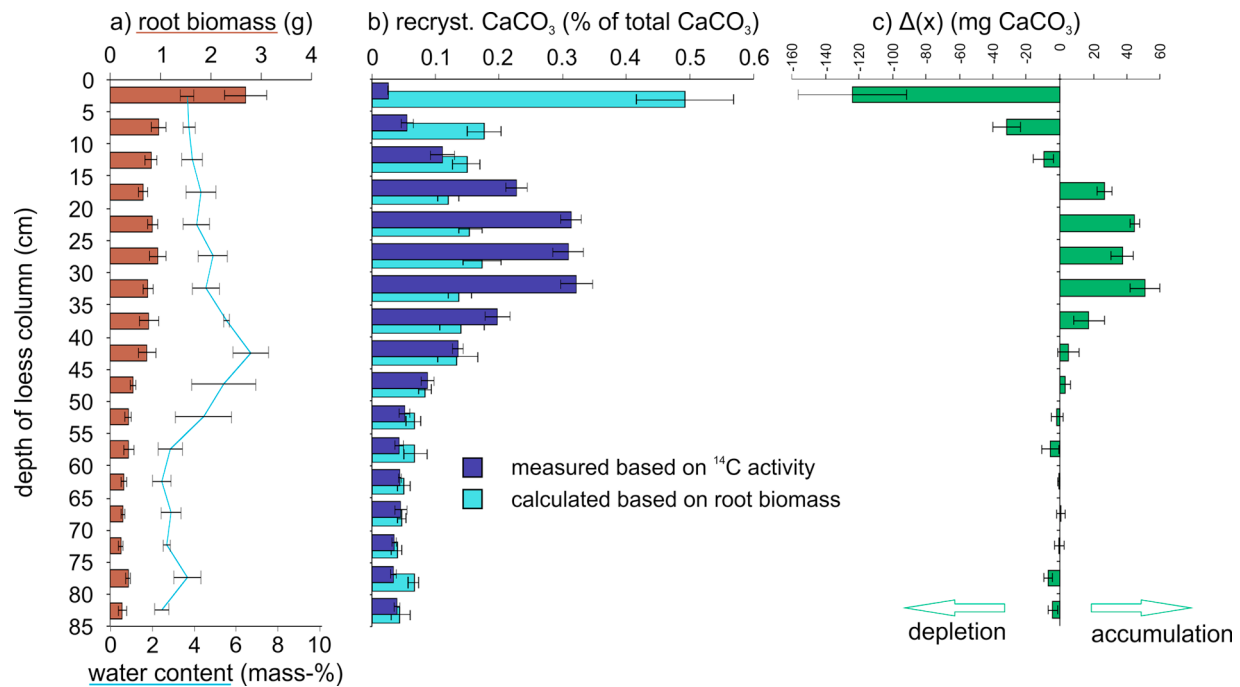
Figure 2. Depth-dependant distribution of (a) amounts of root biomass and loess moisture measured at the end of the experiment, (b) portions of secondary $CaCO_3$ measured based on ^{14}C tracer, and theoretically recrystallized $CaCO_3$, assuming no downward translocation (see equation (7)), (c) (left) loss and (right) accumulation of secondary $CaCO_3$ (see equation (8)). Mean values ± SEM, n = 5.

respired CO_2, which are crucial for calculation of portions of recrystallized $CaCO_3$. For most of the samplings, ^{14}C specific activities were higher in the sealed pots when compared to the open pots. In sealed pots, ^{14}C specific activities were highest at the first CO_2 trapping, i.e., one week after each labeling, and decreased considerably toward the two following CO_2 trappings. This trend can be explained by constant CO_2 release from root and rhizomicrobial respiration on the one hand, and decreasing portions of mobile ^{14}C within the plant (i.e., not incorporated in plant tissue) on the other hand. Moreover, ^{14}C specific activities measured one week after each labeling were highest after the first and lowest after the third labeling within the life span of each plant (Figure 3a), as plant growth led to increased storage of assimilated C and thus of ^{14}C in the plant. In open pots,
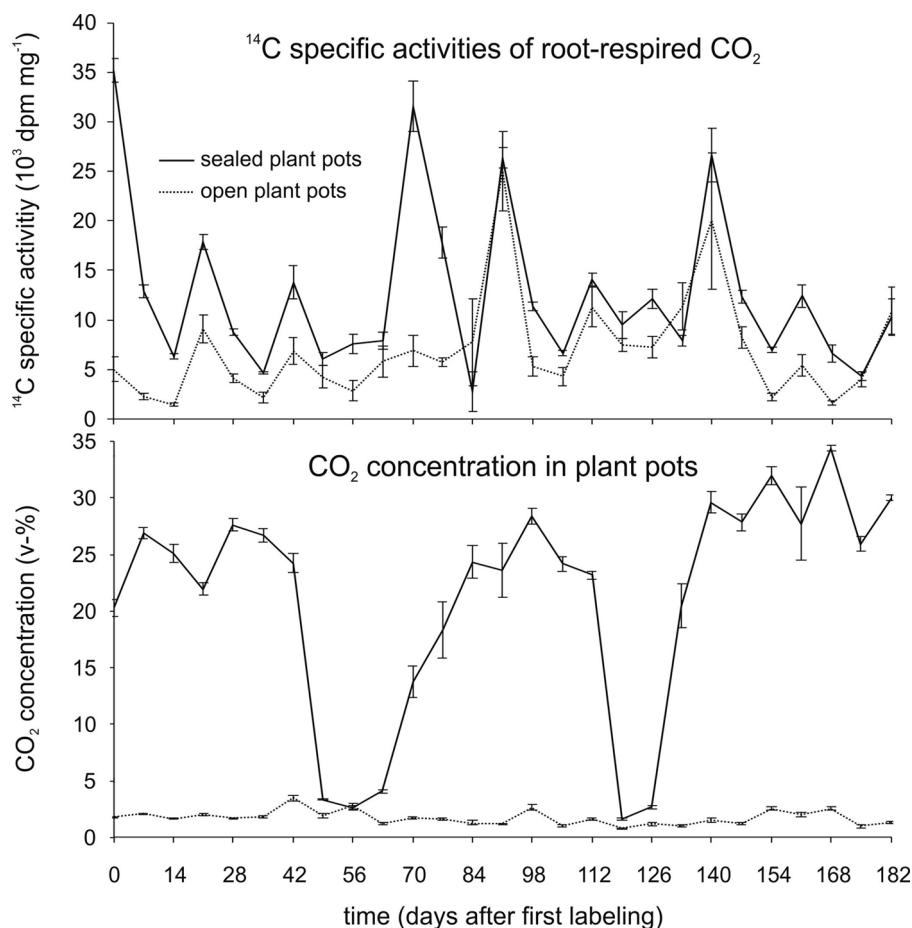
temporal variations of ^{14}C specific activities showed a similar pattern, but with a lower range between lowest and highest values when compared to sealed pots.

[38] CO_2 concentrations in open plant pots, calculated from amounts of CO_2-C trapped in NaOH, were $1.7 \pm 0.1\%$ (for water content 70% of WHC: $1.9 \pm 0.1\%$; 30% of WHC: $1.5 \pm 0.1\%$; absolute range 0.6–4.0%; Figure 3b). Variations were low when compared to CO_2 concentrations in sealed plant pots (for water content 70% of WHC: $24.0 \pm 2.2\%$; 30% of WHC: $18.5 \pm 1.7\%$; absolute range 1.4–39.4%). In contrast to sealed pots, where CO_2 could not disappear between the CO_2 trappings, it is reasonable that in open pots, rather constant CO_2 concentrations entailed a constant rate of $CaCO_3$ recrystallization. Therefore the complete time interval from the first labeling of A plants to the harvesting of C plants (182 days) was used for the calculation of recrystallization rates (equation (4)).

[39] The depth-dependent distribution of CO_2 concentrations in the columns was not determined in our experiment. However, we assume that depth-related variation of CO_2 concentrations in the plant pots was considerably lower than temporal variations shown in Figure 3b. It was shown previously that carbonate recrystallization rates increase with increasing CO_2 concentration, and that the relation is described by a saturation curve within the range of naturally occurring soil CO_2 concentrations (0.038 to 5%) [*Gocke et al.*, 2010]. In the present study, the mean value of 1.7% CO_2 was already near to saturation. Therefore, it was assumed that even in lower parts of the loess column, where amounts of root biomass were low, CO_2 concentrations were high enough, and did not limit $CaCO_3$ recrystallization.

Table 2. Total [14]C Recovery After Subsequent Growth of 3 Maize Plants, Each of Them for 10 Weeks, in Different Below- and Aboveground Pools as Percentage of Recovered ^{14}C and Percentage of Input [14]C

	Open Plant Pots
[14]C [% of ^{14}C recovery]	
Shoots	74.4 ± 1.0
>Roots	18.2 ± 0.8
>DIC + DOC	1.3 ± 0.1
>respired CO_2	1.1 ± 0.1
>loess C_{org}	4.0 ± 0.2
>loess $CaCO_3$	1.0 ± 0.1
[14]C [% of ^{14}C input]	
sum of all compartments	37.8 ± 2.0

Figure 3. Temporal course of (top) ^{14}C specific activities of root-respired CO_2 during the experiment, (bottom) CO_2 concentrations in plant pots, accumulated during 7 days. Mean values $\pm$ SEM, n = 5.

3.4. Secondary $CaCO_3$

[40] The total $CaCO_3$ content in each 5 cm-slice was identical before and after the experiment. Based on ^{14}C labeling we calculated that 533.7 ± 28.2 mg of loess $CaCO_3$ ($0.12 \pm 0.01\%$) were recrystallized in the complete column (0–85 cm) after 182 days. This corresponds to an amount of secondary $CaCO_3$ of 368 g m^{-2}. The corresponding recrystallization rate amounts for $6.8 \cdot 10^{-6} \pm 0.4 \cdot 10^{-6}$ day^{-1}. Extrapolating this rate to longer periods, the time necessary for complete (95%) recrystallization of the loess carbonate was calculated. It is likely that the carbonate (primary and secondary) is recrystallized several times before being incorporated in concretions. Therefore, an exponential approach was chosen for estimation of recrystallization periods (see section 2.4, equation (5)). Depending on length of the growing season (GS), periods between 14,400 years (GS one month) and 2,400 years (GS six months) were calculated for 95% recrystallization of total loess carbonate (Figure 4a).

[41] Portions of recrystallized $CaCO_3$ showed a depth-dependant distribution. However, largest portions of recrystallized $CaCO_3$ (>0.3% of total loess $CaCO_3$) did not occur in the depth of largest root biomass, but between 20 and 35 cm depth. Lowest portions of recrystallized $CaCO_3$ (<0.1%) were found in the uppermost 10 cm as well as in a depth of 45–85 cm (Figure 2b). This distribution results from $CaCO_3$ migration and should be considered when estimating recrystallization periods of loess carbonate.

4. Discussion

4.1. ^{14}C Distribution Among C Pools and Methodological Approach

[42] The ^{14}C analyzed compartments (Table 1) accounted for $37.8 \pm 2.0\%$ of assimilated ^{14}C, indicating that the maize plants respired >60% of the assimilated ^{14}C via the shoots. While in short-term ^{14}C labeling experiments (<1 day) usually ^{14}C recovery rates of 60–70% are obtained [e.g., *Fischer et al.*, 2010], shoot respiration causes larger loss of input ^{14}C in experiments of 1 month and longer [*Werth and Kuzyakov*, 2006] (this study).

[43] The largest portion of assimilated ^{14}C was found in shoots, followed by roots (74.4 and 18.2%, respectively). Values for shoots were in a similar range to previous studies with maize, whereas root values were higher than literature data [*Werth and Kuzyakov*, 2006; *Nguyen et al.*, 1999]. This is related to the considerably longer duration of the present study when compared to other ^{14}C labeling experiments, thus allowing a larger portion of assimilated ^{14}C to be incorporated into root tissue. In contrast, during short-
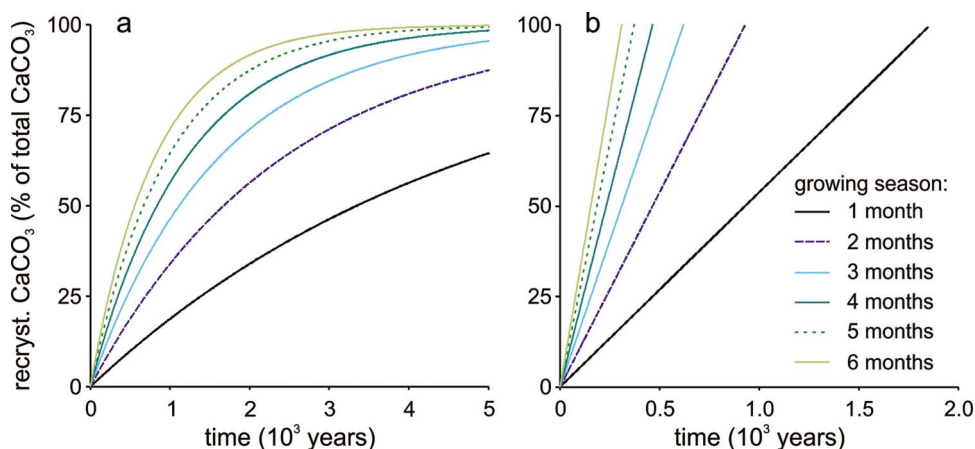
Figure 4. (a) Recrystallization periods, based on recrystallization rate from the complete loess column: $6.8 \pm 0.4 \cdot 10^{-6}$ day^{-1}, (b) periods necessary for complete decalcification of the uppermost 15 cm of the loess column, based on theoretical rate calculated for this depth interval: $1.77 \pm 0.26 \cdot 10^{-5}$ day^{-1}. Mean values $\pm$ SEM, n = 5.

term experiments, a larger part of assimilates allocated belowground is used by grasses for root exudation and respiration [Hill et al., 2007]. Except for root-respired CO_2, which did not represent true values in open pots because of CO_2 exchange with atmospheric air, loess $CaCO_3$ yielded the smallest portion of recovered ^{14}C activity. The reason for this is the faster accumulation of assimilates mainly in organic C pools (fresh biomass, rhizodeposits). Nevertheless, the calculation of very small portions of recrystallized $CaCO_3$ was possible based on isotopic exchange between root-respired CO_2 and loess $CaCO_3$ after the ^{14}C labeling.

4.2. Depth-Related Distribution and Accumulation Rate of Secondary CaCO₃

[44] Based on the method applied (trapping of C of dissolved $CaCO_3$ in NaOH and titration of NaOH solution, see section 2.4), the total $CaCO_3$ content in each 5 cm-layer was similar before and after plant growth. In contrast to the total $CaCO_3$, the portions of recrystallized $CaCO_3$ calculated based on incorporated ^{14}C showed a depth-related distribution pattern: Largest values were found in 20–35 cm, and very small portions of recrystallized $CaCO_3$ were found in the uppermost 5–10 cm and in the lower part of the loess column (45–85 cm; Figure 2b). This pattern did not reflect the distribution of root biomass, but more resembled the graph of the final loess moisture with a defined peak in a certain depth (Figure 2a), indicating an effect of water percolation and alternating wetting and drying on the depth of carbonate accumulation. This suggests that in the uppermost part of the loess column (at least up to 15 cm depth) the $CaCO_3$ was dissolved and removed, whereas immediately below that depth (particularly 15–40 cm) the dissolved Ca^{2+} and $H^{14}CO_3^-$ were reprecipitated as $Ca^{14}CO_3$. These redistributed portions of carbonate, however, were far below the detection limit by mass changes and could be revealed only by ^{14}C labeling.

[45] Under field conditions, main factors leading to this reprecipitation by driving the reaction of equation (6) to the left, are decrease of CO_2 partial pressure, increase of the

concentration of Ca^{2+} and HCO_3^-, or a combination of these [Krauskopf and Bird, 1995; Birkeland, 1999].

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad (6)$$
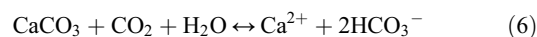
[46] Two explanations for the depth-related distribution of secondary carbonate obtained from the loess columns come into question. First, it might be deduced from the distribution of root biomass with highest amounts in the uppermost 5 cm, that the CO_2 concentration is very high at the top and strongly decreases beneath, causing the above mentioned change from prevailing dissolution into mainly $CaCO_3$ reprecipitation. This might be expected because CO_2 concentration strongly influences rates of carbonate recrystallization [Gocke et al., 2010]. In vicinity of roots, higher rates are obtained when compared to soil distant from roots [Gocke et al., 2011] because of steep decrease of CO_2 concentration from the root surface toward root-free soil [Gollany et al., 1993; Hinsinger et al., 2003]. However, the high amounts of root biomass in 0–5 cm are mainly the result of three cycles of plant growth, with crown and brace roots of maize providing high amounts of plant biomass but only little fine root hairs producing CO_2. Ignoring the uppermost 5 cm, particularly high portions of recrystallized $CaCO_3$ (20–35 cm) occurred within the zone of relatively high amounts of root biomass of 0.7–1 g (5–45 cm; Figure 2a) and not below. Moreover, only small portions of recrystallized $CaCO_3$ were found in greater depth although the loess column was completely rooted and probably high CO_2 respiration rates, related to youngest roots [Larionova et al., 2006] prevailed also in the deeper parts of the loess column. This makes the CO_2 concentration as the only reason for the distribution pattern of secondary carbonate rather unlikely.

[47] Fine sandy and silty soil parent material, like e.g., loess, provides suitable conditions for downward transport of dissolvable substances by water percolation [Jenny, 1994]. Therefore, a second explanation, attributing the distribution of recrystallized $CaCO_3$ to downward transport of

dissolved Ca^{2+} and HCO_3^-, is more likely. We hypothesize that downward transport of dissolved Ca^{2+} and $H^{14}CO_3^-$ did not take place directly by percolating water after watering of the maize plants, because this movement is too fast (usually between 10 and 100 cm day^{-1} in loessic soils) to dissolve and transport primary loess $CaCO_3$. Rather, the present solution (30% of WHC), saturated with respect to Ca^{2+} and CO_3^-, was displaced downward by the next portion of water when the moisture level was again increased to 70% of WHC. However, reprecipitation of these ions as $CaCO_3$ due to increasing saturation of the soil solution results from a mixed effect of water regime (decreasing amounts of percolating water with increasing depth [*Arkley*, 1963]) and roots (increasing water uptake [*Schlesinger*, 1985]). This agrees with the observation that maximum portions of recrystallized $CaCO_3$ occurred above the depth of maximum water content at 40–45 cm (this study; Figures 2a and 2b). The occurrence of minor portions of secondary $CaCO_3$ also in depths below the zone of maximum loess moisture result from a small effect of roots which grew down to the bottom.

[48] Based on previous findings [*Gocke et al.*, 2010, 2011], we assume that the amount of dissolved primary $CaCO_3$ in a certain depth depends mainly on soil CO_2 concentration and thus on the amount of living root biomass. This is because in C_{org}-poor loess, CO_2 respired in the rhizosphere was the main source for C isotopic exchange with primary $CaCO_3$ by formation of secondary carbonate. Consequently, we calculated the portions of $CaCO_3$ which should have been recrystallized theoretically in each 5 cm-slice (theoretically recryst. $CaCO_3$ (x)) in the case that no downward migration had occurred, i.e., assuming that each $CaCO_3$ molecule was dissolved and reprecipitated in the same depth.

$$\text{theoretically recryst. } CaCO_3(x) = \frac{\text{total measured recryst. } CaCO_3}{\text{total root biomass}} \cdot \text{root biomass}_x \qquad (7)$$

With total measured recryst. $CaCO_3$ as the portion of recrystallized carbonate within the complete loess column, calculated based on total ^{14}C activity in loess $CaCO_3$, total root biomass as the total amount of biomass within the loess column and root biomass$_x$ as the amount of root biomass in the according 5 cm-layer.

[49] By subtracting the theoretically calculated portion from the portion measured based on ^{14}C activity in individual layers, the amount of allocated $CaCO_3$ ($\Delta(x)$) was determined for each depth segment:

$$\Delta(x) = \text{measured recryst. } CaCO_3 - \text{theoretically recryst. } CaCO_3 \qquad (8)$$

Negative values, suggesting leaching and thus reduction of the portion of secondary $CaCO_3$, were obtained for the uppermost 15 cm (Figure 2c). In this part of the loess column $81.5 \pm 3.2\%$ of the $CaCO_3$ which underwent dissolution and isotopic exchange with respired $^{14}CO_2$ was lost by downward migration. Probably this amount was overestimated because of very high amounts of root biomass but at the same time few fine root hairs in the uppermost 5 cm

(as discussed above) and therefore, provides only a rough approximation. In contrast, positive values were calculated in a depth of 15–50 cm (Figure 2c). This zone comprised $72.6 \pm 4.5\%$ of the secondary $CaCO_3$ found in the loess column in total. In addition to $CaCO_3$ recrystallized in situ in this depth, another $97.2 \pm 8.5\%$ of secondary $CaCO_3$ were previously eluted from upper layer and accumulated in this depth by reprecipitation. Referred to area, the secondary carbonate content in this accumulation zone (15–50 cm) was 284 g m^{-2}. As mentioned above, these portions of redistributed secondary $CaCO_3$ were calculated based on ^{14}C tracer and are too low to be detected by mass changes.

[50] Permanent CO_2 supply by root and rhizomicrobial respiration impedes equilibrium of the system [*Gocke et al.*, 2011]. Since high soil CO_2 concentrations are maintained mainly during the growing season [*Fierer et al.*, 2005], notable $CaCO_3$ recrystallization takes place predominantly during that time [*Kuzyakov et al.*, 2006]. The length of the growing season depends on climatic conditions and can be as short as 2 months in arid regions. As pedogenic carbonates are formed mainly in those regions, our experiment simulated 3 years, each of them with 2 months of growing season. In this case, the amount of accumulated $CaCO_3$ corresponds to a storage rate of 94 g m^{-2} yr^{-1}.

[51] For natural soil profiles secondary carbonate contents were calculated based on parameters like densities, weights per unit area and thickness of the sampled interval [*Machette*, 1985]. The author obtained accumulation rates indirectly by dividing the carbonate content by the age of the soil, which was determined by other methods (e.g., based on archeological data or by numerical dating). Depending on climate, texture of soil parent material and carbonate buildup stage (as established by *Gile et al.* [1966]), different contents of pedogenic carbonate in calcic soils and paleosols were estimated, e.g., 22 kg m^{-2} [*Gile*, 1995], ~100 kg m^{-2} [*Gile*, 1995; *Landi et al.*, 2003] up to several 100 kg m^{-2} [*Sobecki and Wilding*, 1983; *Nordt et al.*, 2000]. Even under the arid climatic conditions of Lanzarote, values for the carbonate storage can vary between 1 and 1,000 kg m^{-2} [*Scheffer and Schachtschabel*, 2002]. Carbonate storage rates in literature range mainly between 1 and 5 g $CaCO_3$ m^{-2} yr^{-1} for desert soils [*Schlesinger*, 1985; *Marion*, 1989], whereas somewhat higher rates of up to 14 g m^{-2} yr^{-1} were obtained in grassland and forest soils of semiarid regions in Canada [*Landi et al.*, 2003]. The main reason for the considerably higher rate obtained in the present study (94 g m^{-2} yr^{-1}) is that most of the cited literature data were obtained from soils developed on non-calcareous parent material or parent material containing carbonate solely as dolomite. Hence, rates of carbonate accumulation in these soils are limited by the rate of Ca^{2+} influx by dust and/or rainfall, the weathering rates of Ca^{2+} bearing silicates, as well as the amount of Ca^{2+} entering the soil instead of being washed out. In contrast, for calcareous parent materials like loess, not Ca^{2+} availability, but rates of $CaCO_3$ dissolution and translocation by leaching waters are limiting factors for secondary carbonate accumulation [*Arkley*, 1963; *Birkeland*, 1999]. Further factors leading to the high accumulation rate of 94 g $CaCO_3$ m^{-2} yr^{-1} are 1) CO_2 concentration in the plant pots (1.7%) near to the upper limit of naturally occurring values [*Brook et al.*, 1983], 2) humid conditions during the experiment, both of these promoting dissolution of primary loess $CaCO_3$, 3)

strongly contrasting moisture conditions with faster alternation between 'humid' and 'arid' conditions than under natural conditions.

4.3. Time Needed for Complete Leaching of CaCO₃ From Upper Horizons

[52] Because secondary carbonate accumulation did not occur in the uppermost part of the loess column, we suggest that the rate of carbonate migration, resulting from downward transport of dissolved Ca^{2+} and HCO_3^- by percolating water, is higher than the rate of in situ recrystallization of loess $CaCO_3$ by C exchange between carbonate and root-respired CO_2. It was calculated for very old soils of Pleistocene age that strong leaching resulted in loss of both pedogenic and lithogenic carbonate [*Nordt et al.*, 2000]. However, we assume that in our experiment only secondary carbonate was transported downward, i.e., isotopic exchange of primary $CaCO_3$-C and ^{14}C from root and rhizomicrobial respiration occurred prior to or simultaneously with carbonate migration. This can be expected because only dissolved Ca^{2+} and HCO_3^- can be transported by percolating water and isotopic equilibrium between dissolved carbonate and respired CO_2 is reached within few days [*Gocke et al.*, 2010]. This indicates that, given the permanent presence of moisture, the rate at which a carbonate accumulation horizon forms in loess is limited by the $CaCO_3$ recrystallization rate rather than the rate of its downward transport. This possibility was mentioned before by *Arkley* [1963]. Hence, recrystallization rates based on the theoretical portions of secondary carbonate (equation (7)) were calculated for the uppermost 15 cm where secondary $CaCO_3$ was lost due to downward migration. The rate was $1.77 \cdot 10^{-5} \pm 0.26 \cdot 10^{-5}$ day^{-1}. As the uppermost 15 cm of the loess column were dominated by $CaCO_3$ depletion (Figure 2c), only the first part of the recrystallization process, i.e., $CaCO_3$ dissolution, is relevant here. Each $CaCO_3$ molecule is dissolved once before being transported to deeper layers. Therefore, to calculate time periods necessary for decalcification of the uppermost 15 cm we did not use the exponential approach shown in sections 2.4 and 3.4, but assumed a linear removal of primary $CaCO_3$. Thus, dissolution of 95% of total loess carbonate in the uppermost 15 cm takes between 300 years (GS six months) and 1,760 years (GS one month; Figure 4b). This implies that for loess containing 27.4% primary $CaCO_3$, at least hundreds of years are necessary for leaching of upper loess layers and carbonate accumulation in deeper horizons by pedogenic processes at precipitation of 18.5 mm day^{-1}.

4.4. Comparison With Field Conditions

[53] Under controlled conditions of our study, the calculated time intervals of 300–1,760 years have to be regarded as maximum ages for carbonate accumulation horizons in loess. Under field conditions, however, periods in which significant amounts of pedogenic carbonate are accumulated are longer. This study underestimated the time intervals because of (1) high CO_2 concentrations in plant tubes (1.7%) favoring dissolution of primary loess $CaCO_3$, (2) high precipitation (18.5 mm day^{-1}) enforcing dissolution of $CaCO_3$ and fast downward transport of dissolved Ca^{2+} and HCO_3^- and (3) overestimated theoretical portions of recrystallized carbonate and corresponding recrystallization rates in the

uppermost 15 cm of the loess column because of high amounts of root biomass in the uppermost 5 cm.

[54] Furthermore, it has to be considered that (1) within the accumulation horizon, $CaCO_3$ is dissolved and reprecipitated several times before forming concretions or an impregnated horizon, (2) during pedogenesis, the carbonate accumulation zone might migrate downward, usually below the depth of maximal soil moisture [*Birkeland*, 1999] which was not yet the case after six months (Figure 2); (3) in regions of arid climate, grass vegetation with less root and aboveground biomass compared to maize might lead to lower recrystallization rates because of lower root respiration and transpirational pull, resulting in longer recrystallization periods, and (4) $CaCO_3$ recrystallization rates were estimated for loess, i.e., loose material with high $CaCO_3$ content and small silt-sized calcite crystals. For soil parent material with coarser carbonatic fragments or with higher density, rates are presumably lower, leading to longer recrystallization periods.

[55] Various time intervals for leaching and carbonate accumulation between 300 years and more than 10,000 years were obtained or suggested from natural soil and paleosol profiles by different methodological approaches: Under humid climates of Northwestern Europe, 300 years were sufficient for complete leaching of calcareous parent materials with less than 10% initial $CaCO_3$ content [*Jenny*, 1994]. In contrast, *Arkley* [1963], on a theoretical basis of depth-dependent water movement, calculated typical ages of carbonate accumulation horizons in loess soils of 8,500–11,600 years for the semiarid Great Plains. For soil development on non-calcareous parent material, *Lal and Kimble* [2000] assumed that probably tens of thousands of years are necessary for the accumulation of carbonate amounts sufficient to form calcic horizons which can be attributed to the final stage VI of carbonate accumulation according to *Machette* [1985]. This suggests that the accumulation of significant amounts of secondary carbonate in Holocene soils is possible and that carbonate content of the parent material effects its rate. Another important factor for the duration of carbonate accumulation is rainfall. Considering the fact that pedogenic carbonates accumulate mainly under arid to semiarid climatic conditions, our study probably underestimated the time necessary for formation of calcic horizons, because dry conditions lead to lower carbonate recrystallization rates. However, under more humid climatic conditions, shorter periods than the above mentioned are required for formation of calcic horizons. *Alexandrovskiy* [2000] showed for the Northern Caucasus region that a carbonate accumulation horizon had developed below an anthropogenic limestone pavement on a loessic funeral mound during the second half of the Holocene, within only 3.5–5 kyrs. In terms of magnitude, these data fit with our modeled accumulation periods based on the ^{14}C approach, when keeping in mind that semihumid climate of the Northern Caucasus entails lower $CaCO_3$ recrystallization and translocation, thus longer time intervals for calcic horizon formation compared to the extremely wet conditions in this study, which resulted in a formation period of almost 1,000 years with 2 months growing season (Figure 4).

5. Conclusions

[56] The ^{14}C labeling and isotopic exchange approach was applied to estimate portions of secondary $CaCO_3$ by quantifying ^{14}C, assimilated by plants and respired in

rhizosphere. Carbonate recrystallization rates in the range of 10^{-5} to 10^{-6} day^{-1} were obtained. The secondary carbonate showed a distinct depth-related distribution with highest portions in the zone between 20 and 35 cm, i.e., within a zone of high amounts of root biomass, but above the zone of maximal loess moisture measured at the end of the experiment. Presumably, the depth interval of maximal accumulation of secondary CaCO$_3$ was determined by decreasing amounts of percolating water with increasing depth, as well as by water uptake by roots, both leading to increasing saturation of the soil solution with respect to Ca^{2+} and HCO$_3^-$, and finally reprecipitation of CaCO$_3$. Assuming migration of secondary carbonate and the dependence of in situ dissolved carbonate amounts on amounts of root biomass, we showed that more than 80% of recrystallized CaCO$_3$ were removed from the uppermost 15 cm of the loess column within six months of plant growth. Based on calculated recrystallization rates and depending on the length of growing season, periods of at least 300, but probably more than thousand years are necessary for complete decalcification of the uppermost 15 cm. Because of the extremely wet (18.5 mm day^{-1}) experimental conditions, these estimates represent the maximum time of decalcification of upper soil horizons and formation of carbonate accumulation horizons.

[57] Based on redistribution of ^{14}C in carbonate we clearly showed that a calcic horizon is formed by migration of recrystallized CaCO$_3$ and so, its isotopic signature can be used for paleoenvironmental reconstruction. However, the precision of such reconstructions cannot be better than the periods necessary for calcic horizon formation.

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