Available online at www.sciencedirect.com

SCIENCE DIRECT®

Geoderma 131 (2006) 45–58

GEODERMA

www.elsevier.com/locate/geoderma

Carbonate re-crystallization in soil revealed by ^{14}C labeling: Experiment, model and significance for paleo-environmental reconstructions

Y. Kuzyakov*, E. Shevtzova, K. Pustovoytov

Institute of Soil Science and Land Evaluation, Hohenheim University, Germany

Received 21 June 2004; received in revised form 6 March 2005; accepted 9 March 2005
Available online 21 April 2005

Abstract

A high CO_2 concentration in soil resulting from microbial and root respiration is the main factor controlling the dissolution of primary (lithogenic, geogenic) carbonates and the formation of secondary (pedogenic) carbonates. Although several estimations of soil age and many paleo-environmental reconstructions are based on the radiocarbon age and/or $\delta^{13}C$ of secondary carbonates, many assumptions are difficult to check experimentally because of long-term $CaCO_3$ re-crystallization processes. In the present study we used the isotopic exchange between primary carbonates of loess and ^{14}C respired from the rhizosphere of wheat that was artificially labeled in a $^{14}CO_2$ atmosphere under controlled conditions. An ascending number of $^{14}CO_2$ pulses (1 . . . 4) showed a linear increase of rhizosphere ^{14}C recovered in the $CaCO_3$ of loess. Based on this connection, the initial re-crystallization rates of loess carbonate were calculated by linear regression: for loess containing 27% $CaCO_3$, the initial rate of carbonate re-crystallization was 0.000029 day^{-1}. Subsequently, using linear and exponential approaches with different lengths of growing season, we extrapolate the observed $CaCO_3$ re-crystallization on longer time periods. The calculations show that at least 100 years, but probably between 400 and 2000 years, are necessary for full (99%) re-crystallization of the $CaCO_3$ of loess. We suggest a general equation for calculating the remaining not re-crystallized $CaCO_3$ depending on time of soil formation (t): $\%CaCO_3\ (t) = 100 \cdot \exp(-t \cdot 0.00078 \cdot \text{Growing-Season-Length}/365/\text{initial-}CaCO_3\text{-percentage})$. Different approaches for calculating the period of secondary carbonate re-crystallization are discussed and compared with literature data. We conclude that despite the high analytical precision of radiocarbon dating and $\delta^{13}C$ mass spectrometry of secondary carbonates (used, e.g. for paleo-environmental reconstructions), the methodological resolution cannot be better than the periods necessary for $CaCO_3$ re-crystallization.

Keywords: Rhizosphere and root respiration; Pedogenic carbonate genesis; Secondary carbonates; $CaCO_3$ re-crystallization; CO_2; ^{14}C; Paleo-environmental reconstructions; Loess

* Corresponding author.
E-mail address: kuzyakov@uni-hohenheim.de (Y. Kuzyakov).

0016-7061/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.geoderma.2005.03.002

1. Introduction

Secondary carbonates (frequently termed pedogenic carbonates) represent one of the most characteristic morphological features of soils of arid and semiarid regions. This allows a distinction of different soil types according to the World Reference Base and to many national soil classifications (US Soil Taxonomy; Russian Soil Classification, etc.). The depth and intensity of carbonate accumulation and the morphological shape of the secondary carbonates allow inferences to be drawn about the genesis of soil horizons and sometimes about the stages of soil development under different past climatic conditions (Birkeland, 1999 and references therein; Khokhlova et al., 2001).

Over the last two decades, several Earth Science disciplines have shown a substantially increased interest in pedogenic carbonates. According to the model of Cerling (1984) based on $\delta^{13}C$ data, inorganic carbon in secondary carbonates originates not from the parent material, but from the isotopic exchange with dissolved CO_2 coming from root and microbial respiration. The dissolution of primary carbonates and the re-precipitation of secondary carbonates in a soil can therefore be presented as follows

$$CaC^{o}O_3 + C^{n}O_2 + H_2O = CaC^{n}O_3 + C^{o}O_2 + H_2O \quad (1)$$

where $CaC^{o}O_3$ contains old C (C^{o}) originated from parent material and $C^{n}O_2$ is the CO_2 from root and microbial respiration containing new C (C^{n}). This model assuming full isotopic exchange between old and new C enabled subsequent studies based on $\delta^{13}C$ investigating the climatic and atmospheric conditions prevailing when secondary carbonates were formed. Paleo-environmental reconstructions based on secondary carbonates became possible (Cerling et al., 1993; Quade and Cerling, 1995; Quade et al., 1994, 1995; Wang et al., 1996; Monger et al., 1998; Deutz et al., 2001; Royer et al., 2001). Pedogenic carbonates were also accepted as a promising tool to determine the absolute age of soils and sediments based on ^{14}C (Chen and Polach, 1986; Amundson et al., 1994; Wang et al., 1996), U/Th dating (Sharp et al., 2003), as well on growth rate of carbonate cutans on stones (Vincent et al., 1994; Pustovoytov, 2003). The radiocarbon age of secondary carbonates in soil showed that most $CaCO_3$ contains essentially "new" C presumably originated from root and microbial respiration (Amundson et al., 1994; Wang et al., 1996; Pustovoytov, 2002).

Under favorable conditions–mainly in buried soils and/or in arid environments–secondary carbonates can represent a closed system in terms of carbon isotopes for thousands and even millions of years (Cerling, 1991; Wang et al., 1993; Amundson et al., 1994; Quade et al., 1994; Lee and Hisada, 1999; Royer et al., 2001). In some cases, however, secondary carbonates can undergo re-crystallization processes (and hence isotopic re-equilibration, as shown in Eq. (1)) in a soil or sediment (Bowler and Polach, 1971; Pendall et al., 1994; Nordt et al., 1998; Budd et al., 2002). Understanding this process and estimating its rates is crucial in paleo-environmental and geochronological studies that interpret the isotopic composition of secondary carbonates.

Little is known about the rates of carbonate formation and re-crystallization in soils. There are several reasons for this. Secondary carbonate can be quantified based on the difference in the stable carbon isotope signatures of secondary and primary carbonate (Nordt et al., 1998). This approach, however, depends on model values, which might not represent the facts. Furthermore, the re-crystallized portion of secondary carbonate cannot be estimated with stable carbon isotopes as long as the photosynthetic pathway of the local vegetation does not change. Finally, the ^{13}C natural abundance method is not sensitive enough to differentiate small amounts of C involved in isotopic exchange. Radiocarbon dating seems to be more promising in this respect. Based on the radiocarbon ages of different carbonate fractions in desert soils in alluvial deposits of known age in the southwest USA, Pendall et al. (1994) concluded that the carbon isotopic composition in carbonate in the uppermost 40 cm below the soil surface requires between 1000 and 3200 years to be entirely re-equilibrated. However, similar calculations are problematic for the most soil chronosequences because of their relatively low chronological resolution (for example 10^3–10^5 years in the most river terraces) and because the initial ^{14}C content in the carbonate prior to re-crystallization is mostly unknown. Therefore, the carbonate re-crystallization rate cannot be calculated. At present, it is also difficult to investigate carbonate re-crystallization

processes experimentally under natural conditions in the field. Although very informative, the radiocarbon age of secondary carbonates is a cumulative parameter allowing conclusions about the long-term processes, which mostly take place over thousands of years (Amundson et al., 1994; Pendall et al., 1994; Wang et al., 1996). This parameter is not suitable to draw conclusions about the actual rates of the isotopic exchange or to calculate the initial rate of secondary carbonate formation.

Many studies over the last 10–20 years that have investigated C input by plants into the soil based on artificially applied ^{14}C and/or ^{13}C isotopes (labeling in $^{14}CO_2$ or $^{13}CO_2$ atmosphere) have clearly distinguished between root-derived C and soil organic matter C (reviewed by Whipps, 1990; Kuzyakov and Domanski, 2000; Kuzyakov, 2001). These studies have also shown that most of the root-derived C–especially that released as root exudates, secretes, sloughed cells, etc.–is decomposed by rhizosphere microorganisms to CO_2 within a few hours or days (Verburg et al., 1998; Jones and Hodge, 1999). The released CO_2 typically remains in the soil for a few days or weeks and, according to the model of Cerling (1984), can contribute to dissolution and the isotopic exchange with CO_3^{2-} of the $CaCO_3$ of parent material (see above). We hypothesized that artificial labeling of plants in a $^{14}CO_2$ atmosphere and the subsequent release of $^{14}CO_2$ in the rhizosphere would allow the distinction not only (1) between root-derived C and soil organic matter-derived C as shown in many previous studies (the references above), but also (2) between root-derived C and loess C in carbonates. If the hypothesis holds true and ^{14}C labeling enables the incorporation of root-derived C into the $CaCO_3$ of loess (isotopic exchange) to be measured, then the initial rate of formation of secondary carbonates can be estimated. Therefore, we used ^{14}C labeling of plants to assess the rate of re-crystallization of disseminated carbonate in loess samples under laboratory conditions. The loess samples were exposed to CO_2 respired by rhizosphere microorganisms and by roots of plants that photosynthetically assimilated a ^{14}C labeled carbon dioxide. Although this highly sensitive method has been frequently used in experiments on rhizosphere respiration (reviewed by Whipps, 1990; Kuzyakov and Domanski, 2000; Kuzyakov, 2001), to our knowledge it has never been applied in inorganic soil carbon research.

2. Material and methods

To test the hypothesis and to estimate the initial rates of secondary carbonate formation, wheat was grown on loess under controlled conditions. Loess was used instead of soil for three reasons. Firstly, CO_2 evolved by decomposition of soil organic matter may interfere with root-derived CO_2, complicating the picture of isotopic exchange. Secondly, the carbonates in the most soils are pedogenic, i.e., they have been dissolved and precipitated many times. The $CaCO_3$ crystals are therefore larger than those of loess $CaCO_3$ and their dissolution rates are much slower. Thirdly, the soils developed from loess parent material contained initially a very low level of organic C that was very similar to the conditions in our experiment.

2.1. Loess

Loess samples for the experiment were taken from an open-cast mine at Nussloch, SW Germany (49.19°N, 8.43°E, 217 m asl.) (Bente and Löscher, 1987). A set of thermoluminescence and two radiocarbon dates suggest that most of the loess–palaeosol sequence formed during the last glacial–interglacial cycle (Zöller et al., 1988; Hatté et al., 1998). The loess sample for the experiment was taken from 15 m depth, presumably from a middle to lower pleniglacial section of the loess–palaeosol sequence. The sample represented a loose, sandy–loamy material, light yellowish-gray in color; it contained 27% $CaCO_3$. Three hundred seventy grams of loess (air-dried and sieved on a 2-mm screen) was filled in each container. Ten milliliters of water extract from a loamy Haplic Luvisol (originated from loess) was added to the loess to introduce microorganisms.

2.2. Wheat growing and experimental layout

Four seeds of spring wheat (*Triticum aestivum* L.) that were pre-germinated for 2 days were put in each container and grown under 27/22 °C day/night temperature, a 14-h photoperiod and 800 μmol m^{-2} s^{-1} light intensity. The loess moisture was maintained

at 60% of water holding capacity (WHC = 28% of soil weight) and was adjusted gravimetrically. The absence of leaching from the experimental pots allowed $CaCO_3$ mass balance calculation.

The plant pots were a polycarbonate filtration device "CombiSart" (volume = 250 ml, Merck®-Laborkatalog, 2000). However, the real volume of the device including the space under the lid is about 340 ml (7 cm height and 8 cm i-∅). The soil was separated from the outlet in the bottom of the CombiSart device by a perforated filter support, delivered together with the filtration device, overlain by two layers of perforated (holes = 0.5 mm) polyethylene (Kuzyakov and Siniakina, 2001).

One day before each labeling, the plants were fertilized four times with 100 mL standard full nutrient solution (Erenoglu et al., 2002) containing 56, 82, and 7.75 μg mL^{-1} of N, P, and K, respectively.

The experimental layout included 6 treatments:

1) Control: loess without plants and without labeling.
2) Wheat grown on loess, sealed before the labeling, and labeled only once.
3) Wheat grown on loess, sealed before the labeling, and labeled twice.
4) Wheat grown on loess, sealed before the labeling, and labeled three times.
5) Wheat grown on loess, sealed before the labeling, and labeled four times.
6) Wheat grown on loess, not sealed before the labeling, and labeled four times.

Thus, the plants of different variants were labeled one to four times. The loess-root compartment of the last variant with 4 labelings was not sealed.

The first labeling took place on day 21 after germination. The subsequent labelings occurred in 4-day intervals, i.e., the last labeling was conducted on day 33.

2.3. ^{14}C labeling and sampling

A day before labeling, every hole with plants was sealed with a two-component silicone paste (NG 3170 from Thauer & Co. Dresden) that overlaid a 2-mm layer of low-melting-point Paraffin (MP = 43 °C). The seal was tested for air leaks. The sealing allows an airtight separation of root-loess air from the atmospheric air. The plant pots of one treatment (No. 6, see above) were not sealed to allow an undisturbed exchange of air inside and outside of the pots. Before first labeling, all pots were flushed with atmospheric air to remove all CO_2 originated from root and rhizomicrobial respiration and accumulated in the pots during the previous growth of wheat.

All pots were labeled simultaneously in a labeling chamber ($0.5 \times 0.5 \times 0.6$ m^3) having an air fan for intensive internal air circulation. A label consisting of 210 kBq of ^{14}C as $Na_2{}^{14}CO_3$ solution was put in a 20-ml vial connected with tubings to the labeling chamber. The addition of 3 ml of 5 M H_2SO_4 to the $Na_2{}^{14}CO_3$ solution in the vial through a Teflon tube allowed complete evolution of $^{14}CO_2$ into the chamber. Assimilation took place within 2 h after the $^{14}CO_2$ pulse had been applied. Thereafter, any unassimilated $^{14}CO_2$ was removed by pumping the air from the chamber through 50 mL of a 1.0 M NaOH solution during 1 h. The top part of the chamber was then removed and the plants were grown under normal atmospheric conditions.

In contrast to all previous studies of our research group, the trapping of CO_2 evolved from the root-loess compartment was not continuous and was not started directly after labeling. This allowed the $^{14}CO_2$ evolved during 4 days to accumulate between two subsequent labelings; it also allowed an isotopic exchange of respired $^{14}CO_2$ with the $CaCO_3$ of the loess. All the CO_2 released in the root-loess compartment over the 4 days was trapped during a ca. 2-h period shortly before the next labeling or cutting (for the variant that had already received the final labeling). After the CO_2 trapping and before the next labeling, the air in the root-loess compartment was flushed with CO_2-free atmospheric air to supply the roots and the microorganisms with oxygen.

For trapping CO_2, PVC tubes conducted air through one of the three inlets into the CombiSart device lid to a washing flask with NaOH and to a membrane pump. Air with $^{14}CO_2$ originating from root and microbial respiration was adsorbed in NaOH in the washing flask. The outlet of the membrane pump was connected with the bottom part of the CombiSart device, ensuring air circulation in the whole closed system without any $^{14}CO_2$ losses. This standard system was used very frequently in the past to estimate the transfer of root-derived C (as ^{14}C) into

the soil (Kuzyakov et al., 2001; Kuzyakov and Siniakina, 2001).

Four days after the final labeling, the plants of the respective treatment were cut at the base, the loess-root column was removed from the CombiSart device, and the roots were carefully picked from the loess with tweezers. The very poor structure of loess simplifies root extraction.

2.4. Sample analysis

^{14}C in CO_2 collected in 30 mL of 1 M NaOH solution was measured on 5-mL aliquots added to 15 mL scintillation cocktail EcoPlus (Roth Company, Germany) after the decay of chemiluminescence. The ^{14}C counting efficiency was about 89% and the ^{14}C-activity measurement error did not exceed 2%. The absolute ^{14}C-activity was standardized by SQP(E) method of external standard using standard LKB-Wallac library.

The total content of C-CO_2 collected in the NaOH solution was measured by titration of 1 mL aliquot with 0.1 M HCl against phenolphthalein after addition of 0.25 M $BaCl_2$ solution (Black, 1965).

After the root extraction, the loess was mixed and washed with 700 mL deionised water to remove the dissolved carbonates and organic substances released by roots and microorganisms. The amount of organic C (C_{org}), inorganic C (C_{in}), and ^{14}C activity in this washing water was measured before and after addition of HCl excess. C_{org} and C_{in} were measured using the automatic analyzer DIMATEC 100 (Fa. Dimatoc). The addition of HCl allowed the dissolved carbonates to be driven out and their $^{14}C/C$ ratio to be estimated; it also enabled the $^{14}C/C$ ratio of the remaining organic substances to be estimated.

To estimate the incorporation of root-derived C (^{14}C) into the loess carbonates, 10 g of loess (after removing roots, soluble carbonates and organic substances) was carefully treated with 1 L of 0.1 M H_3PO_4 (Boutton and Yamasaki, 1996). The CO_2 evolved by H_3PO_4 neutralization of $CaCO_3$ was trapped with 100 mL of 1 M NaOH. The amount of CO_2 trapped in NaOH as well as its ^{14}C activity were estimated by titration and scintillation counting as described above.

Shoots, roots and loess were dried at 60 °C, mixed and pulverized in a ball mill (Retsch) prior to analysis for radioactivity and for total C and N. Radioactivity of shoots, roots and soil samples was measured after combustion of 1 g of sample within an oxidizer unit (Canberra Packard Co. Ltd, Model 307) with the scintillation cocktail Permafluor E^+ by a Liquid Scintillation Counter (Rackbeta 1411, Wallac).

2.5. Calculation and statistical analyses

All the ^{14}C data are presented as percentages of total assimilated ^{14}C. The total assimilated C was calculated according to the equation:

$$^{14}C_{ass} = {}^{14}C_{input} - {}^{14}C_n - {}^{14}C_r, \quad (2)$$

with $^{14}C_{ass}$: activity of total assimilated ^{14}C; $^{14}C_{input}$: total input activity introduced as $Na_2{}^{14}CO_2$; $^{14}C_n$: activity of the NaOH solution after flushing the upper chamber; $^{14}C_r$: ^{14}C residue not volatilized after H_2SO_4 addition ($\ll 1\%$). The CO_2 amount in the pots was corrected for atmospheric CO_2.

The following approach was used to calculate the incorporation of root-derived C into the loess carbonates and the initial rate of secondary carbonate formation. Firstly, the ^{14}C specific activity ($^{14}C_{SA}^{CO_2}$) of CO_2 evolved by roots and microorganisms was calculated as the ratio between ^{14}C activity ($^{14}C^{CO_2}$) and total C ($^{14}C_t^{CO_2}$) in CO_2 trapped after 4 days of CO_2 accumulation in the root-loess compartment:

$$^{14}C_{SA}^{CO_2} = \frac{^{14}C^{CO_2}}{C_t^{CO_2}} \quad (3)$$

Secondly, we assume that the C incorporated into the loess in the scope of CO_3^{2-} isotopic exchange has the same ^{14}C specific activity as the C of CO_2 evolved by roots and microorganisms during 4 days after each labeling. Therefore, to calculate the amount (mg) of root-derived C incorporated into the loess by re-crystallization ($C_t^{Re\ cryst}$), the ^{14}C activity of CO_2 evolved by H_3PO_4 neutralization of $CaCO_3$ ($^{14}C^{CaCO_3}$) was divided by ^{14}C specific activity of CO_2 evolved by roots and microorganisms:

$$C_t^{Re\ cryst} = \frac{^{14}C^{CaCO_3}}{^{14}C_{SA}^{CO_2}} \quad (4)$$

Thirdly, to calculate the rate of $CaCO_3$ re-crystallization, the amount of re-crystallized CO_3^{2-} was

divided by the total amount of $CaCO_3$ in the loess of the pot ($C_t^{CaCO_3}$) and divided by the time (t) between the begin of the first and the end of the last labeling (maximum 16 days):

$$\text{Rate} = \frac{C_t^{\text{Re cryst}}}{C_t^{CaCO_3} \cdot t} \quad (5)$$

The experiment was conducted with four replicates. Standard errors of means are presented on figures. The significance of differences between the treatments was calculated by t-test at the 0.05 error probability level.

3. Results

3.1. Balance of assimilated $^{14}CO_2$

Before calculating the contribution of rhizosphere respiration to the formation of secondary carbonates, it is necessary to evaluate the ^{14}C balance in order to estimate the amount of C that was translocated below ground as well as the amount of assimilated ^{14}C respired as rhizosphere CO_2 by roots and microorganisms.

Based on the distribution of ^{14}C 4 days after the respective labeling, most of the assimilated C remained in the shoots (Fig. 1a). Between 21 and 29

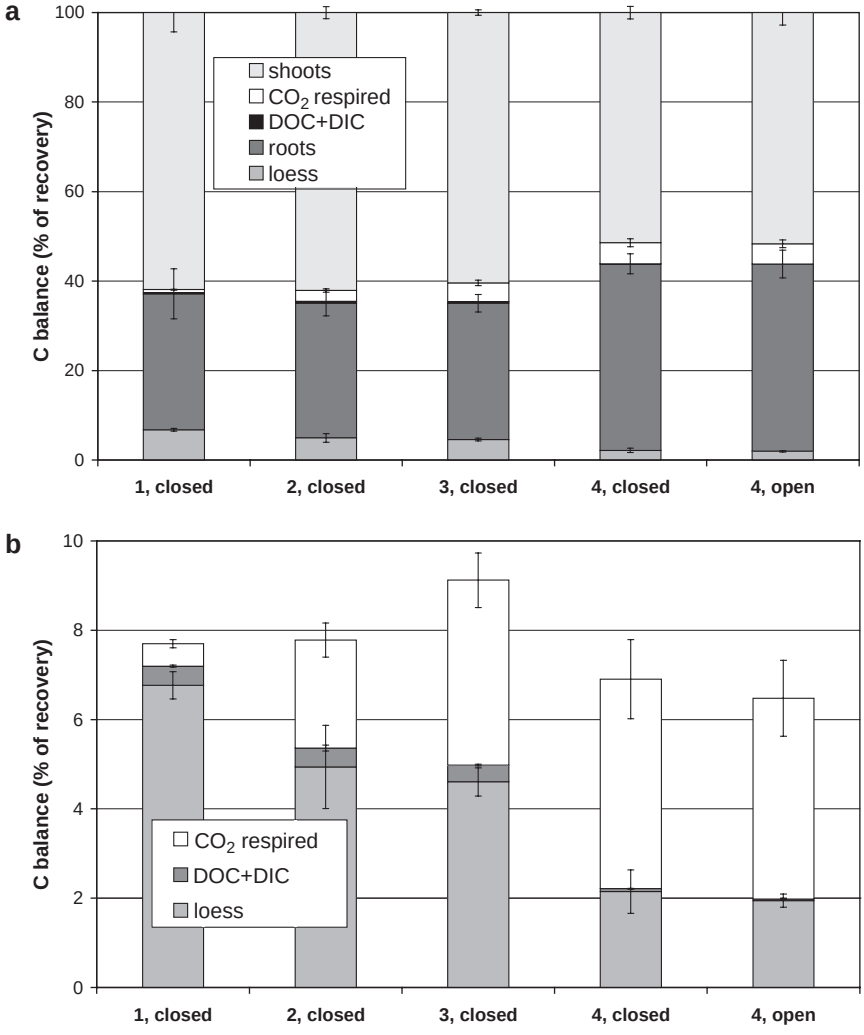

Fig. 1. Balance and distribution of ^{14}C assimilated by wheat after one to four labelings in closed and open pots. Percentage of ^{14}C recovery ± SE.

days after planting, about 60% of the net assimilated C was incorporated in the shoots. About 50% of net assimilated C was incorporated in the shoots on day 33. Roots were the second sink of assimilated C, amounting to between 30% of ^{14}C for the first three labeling dates and 42% for the last labeling. The incorporation of ^{14}C in shoots, roots and loess in the variant with open pots (pots not sealed before labeling, labeled 4 times) was practically the same (no significant differences by *t*-test) as that in the plants labeled 4 times and harvested at day 36. This clearly shows that sealing with silicone had no effect on the distribution of assimilated C in the plants. We can therefore conclude that the total amount of $^{14}CO_2$ respired from the soil of the variant with open pots (not measured because open to the atmosphere) was the same as in the variant with plants labeled 4 times and harvested at day 36.

Two other minor parts of below-ground translocated assimilated C were ^{14}C in loess and in evolved CO_2 (Fig. 1b). The percentage of ^{14}C incorporated in loess decreased nearly linearly during the study period from 6.8% to 2.1% of net assimilated $^{14}CO_2$. At the same time, the percentage of ^{14}C found in evolved CO_2 increased from 0.5% to 4.7%.

A very small (<0.43% of recovered ^{14}C activity) amount of ^{14}C was found in the water after washing the loess. This washing water contains organic C (root exudates and their microbial metabolites) and inorganic C (HCO_3^- from dissolved CO_2 of root and rhizomicrobial respiration). Acidification of the DOC+DIC solution allowed us to estimate the ^{14}C in organic and inorganic forms (Fig. 2). In small plants, the amount of ^{14}C recovered in DIC was higher than that in exudates. During the plant growth, the amount of ^{14}C in DIC decreased and that in DOC increased. This corresponds well with the increasing total amount of exudates during the root growth. As in the ^{14}C balance in Fig. 1, the distribution of ^{14}C between DOC and DIC in the closed pots with 4 labelings is nearly the same (no significant differences) as in open pots.

3.2. $^{14}CO_2$ in the rhizosphere and CO_2 concentration in soil air

Between 0.5% and 4.7% of recovered ^{14}C were found as CO_2 in the rhizosphere of wheat. Usually, the labeled CO_2 evolved in the rhizosphere (frequently termed root-derived CO_2 or rhizosphere respiration) reflects two main processes: root respiration and respiration of microorganisms decomposing root exudates, secretes, sloughed root cells, root hairs, dead root cells, etc. However, during the short period between each labeling and sampling in our experiment (4 days), only root exudates and secretes can be

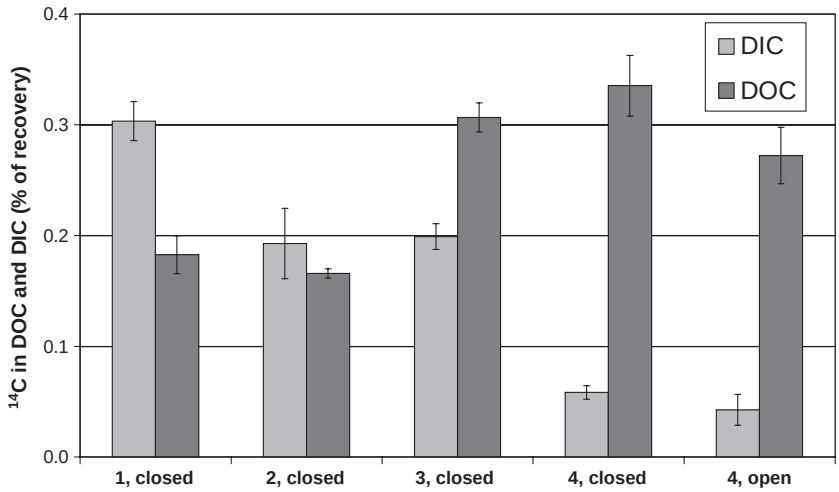

Fig. 2. Dissolved organic (DOC) and inorganic (DIC) carbon in water extract from the loess-root compartment after cutting the plants. Percentage of ^{14}C recovery ± SE.

decomposed. A longer period between labeling and end of CO_2 trapping will no doubt lead to an increase of ^{14}C in CO_2 along with a simultaneous decrease in the ^{14}C recovered in the roots and DOC.

To calculate the CO_2 concentration in soil air, we estimated the pore space of loess based on loess density in the pot and standard tables for soils of different particle size fractions (Finnern, 1995). The amount of water added (60% of WHC = 16.8% of soil mass) was subtracted from the total pore space to obtain the air volume. Finally, the amount of CO_2 trapped in NaOH four days after closing the pots was recalculated to the CO_2 volume according to the universal gas law and expressed as a percentage of the total air volume. For sealed pots, the CO_2 percentage was between 11.7% and 16.5%, showing an increased rhizosphere respiration (Fig. 3). These values are higher than the CO_2 concentrations frequently measured under natural conditions. Note, however, that these values present the CO_2 concentration at the end of day 4 in sealed pots having no exchange with atmospheric air. If we accept a linear increase of CO_2 concentration during 4 days due to constant root and microbial respiration activity, then an average concentration of about 6–8% would be more reliable for field conditions as well. Thus, as in the open pots, the CO_2 concentration at the end of the 4-day period amounts to about 5.9% (Fig. 3). The CO_2 concentration in pots without plants was much lower than that in planted loess, continuously increasing from 0.03% on day 24 to 0.25% on day 36 (Fig. 3).

3.3. Re-crystallized $CaCO_3$ and initial rates of secondary carbonate formation

Based on the ^{14}C activity incorporated in loess carbonates and released as CO_2 after H_3PO_4 treatment, we calculated the amount of CO_3^{2-} carbon derived from root and rhizomicrobial respiration and re-crystallized during the experiment (Fig. 4). The amount of C re-crystallized as $CaCO_3$ increased between the 1st and the last labeling, ranging from 0.033% to 0.116% of the $CaCO_3$ in the loess. Note that this increase was nearly linear, demonstrating constant re-crystallization rates. We therefore fit a linear regression model ($R^2 = 0.92$) to calculate the dependence between experiment duration (=re-crystallization period) and the percentage of re-crystallized $CaCO_3$. Interestingly, the observed line does not pass through point with 0;0 co-ordinates, but cut the X-axis at 17.5 days (Fig. 4). Our explanation for this phenomenon is that prior to 17.5 days the plants were small. Their root respiration and exudation were therefore small and the contribution of their rhizosphere respiration marginal. After 17.5 days, the amount of re-crystallized $CaCO_3$ increased in accordance with plant and root growth.

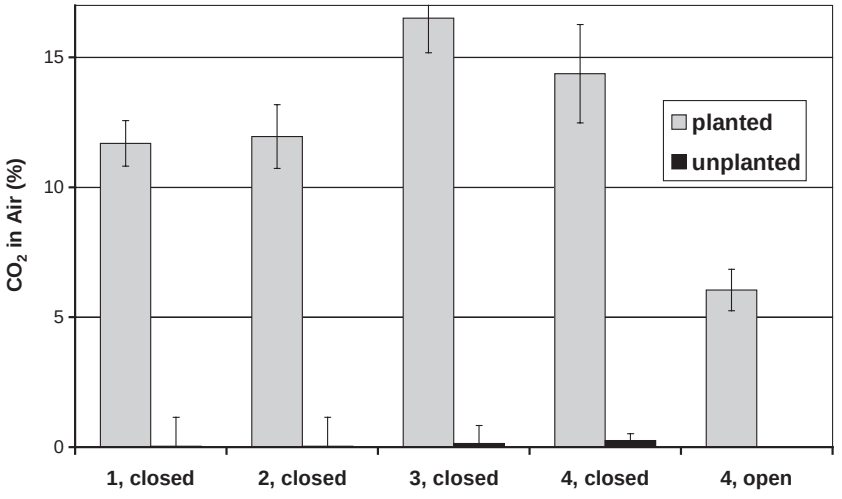

Fig. 3. CO_2 concentration (± SE) in soil air of planted and unplanted pots at different times.

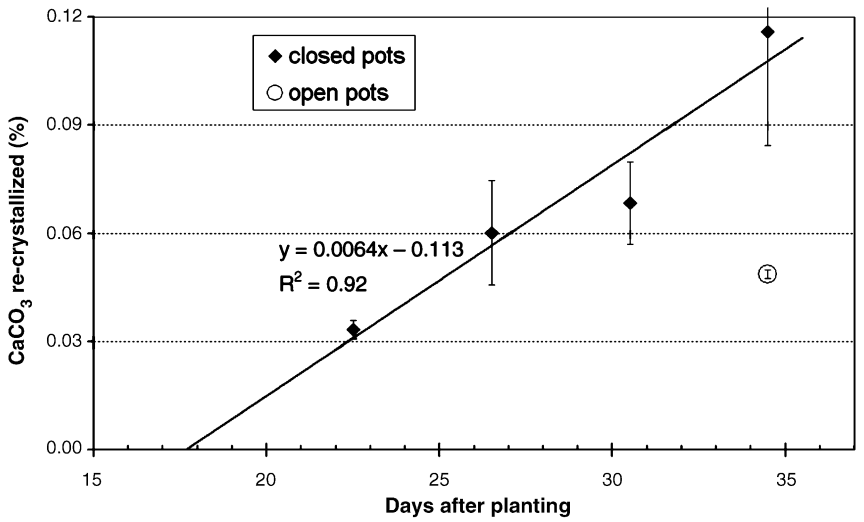

Fig. 4. Percentage (± SE) of re-crystallized $CaCO_3$ of loess in closed and open pots after different time periods and equation for calculating initial re-crystallization rates.

Despite the same distribution of ^{14}C between the plant organs (see above)–and therefore the same respiration in the rhizosphere of plants labeled 4 times in closed and open pots–the amount of re-crystallized $CaCO_3$ in open pots was 2.5 times less than that in closed pots. This directly reflects the lower CO_2 concentration in the rhizosphere of open pots (Fig. 3) because of CO_2 exchange with the atmospheric air. Thus, in the open pots 0.049% of the $CaCO_3$ was re-crystallized between the first labeling and the end of the last CO_2 trapping period. We therefore calculated the re-crystallization rate of $CaCO_3$ in the open pots according to the linear regression obtained for closed pots and the amount of $CaCO_3$ re-crystallized in the open pots (Fig. 4). This rate for open pots is about 0.0029% day^{-1}. This value represents the initial rate of secondary carbonate formation in the plant rhizosphere of a soil (loess) containing 27% $CaCO_3$.

3.4. Calculations of full re-crystallization period of $CaCO_3$

Using this value of the initial $CaCO_3$ re-crystallization rate, we can calculate the overall re-crystallization of loess carbonates using different approaches.

Firstly, we can accept the linear approach assuming that the re-crystallized amount of primary $CaCO_3$ remains constant during long periods. This also presupposes that $CaCO_3$ re-crystallized once will not be re-crystallized again. Although this assumption is not very realistic, such a calculation can suggest the shortest period necessary for full $CaCO_3$ re-crystallization. This linear approach showed that for loess having 27% $CaCO_3$, about 98 years are necessary for full re-crystallization (Fig. 5, straight line).

In the second approach, we accepted that not only the primary $CaCO_3$ (from loess), but also secondary $CaCO_3$ can be re-crystallized with the CO_2 of rhizosphere respiration. Accordingly, the amount of primary $CaCO_3$ that undergoes exchange with CO_2 continuously decreases. This interpretation is more realistic than the first one and corresponds to an exponential exchange (Fig. 5). Here, about 95% of the primary $CaCO_3$ will be exchanged after 300 years and 99% after 450 years. This age of secondary carbonates is much older than that obtained by the linear approach.

In the first and second approaches we accepted that the CO_2 concentration in the soil remains high during 365 days of the year, thus leading to a similar permanent exchange with primary carbonates as in the experiment. This assumption holds true for only a few places in the world. In the final approach we therefore accepted not only an exponential decrease of re-crystallization (as in approach 2), but also assumed that the growing season ranges between 2 and 10

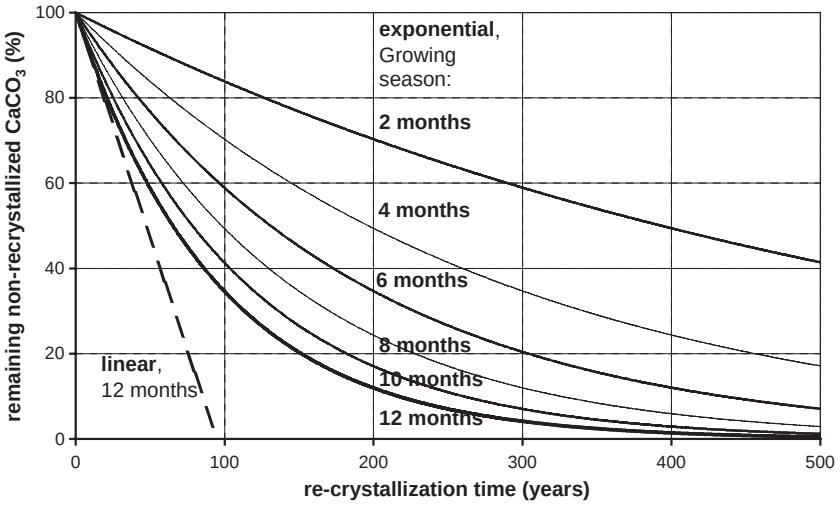

Fig. 5. Remaining amount (percentage) of non-re-crystallized $CaCO_3$ of loess calculated using various model approaches and considering different lengths of growing season.

months. This yielded a series of lines predicting the re-crystallization of $CaCO_3$ in loess with 27% $CaCO_3$ (Fig. 5). A short growing season strongly increases the re-crystallization time, which can extend to more than 1000 years.

Our study was conducted with a loess containing 27% $CaCO_3$. At lower percentages, full $CaCO_3$ re-crystallization would take less time. Assuming a linear dependence of re-crystallization rate on $CaCO_3$ percentage, we can suggest general equation for calculating the amount of remaining, non-re-crystallized $CaCO_3$ ($CaCO_3(t)$, in percent) depending on time (t, in years), growing season (GS, in days per year) and $CaCO_3$ percentage (%Lime):

$$\mathrm{CaCO_3}(t) = 100 \cdot \exp\left(-t \cdot 0.00078 \cdot \frac{\mathrm{GS}}{365 \cdot \%\mathrm{Lime}} \right) \quad (6)$$

where 0.00078 is the rate (day^{-1}) of $CaCO_3$ re-crystallization per 1% of $CaCO_3$ in loess.

4. Discussion

4.1. Isotopic exchange method

We used the exchange of ^{12}C by ^{14}C from rhizosphere respiration by plants artificially labeled in $^{14}CO_2$ atmosphere to estimate the re-crystallization of $CaCO_3$ from loess. Although similar approaches were frequently used in various rhizosphere and CO_2 flux studies (reviewed by Whipps, 1990; Kuzyakov and Domanski, 2000; Kuzyakov, 2001), to our knowledge this is the first time that such an approach has been used for carbonates. This isotopic exchange method showed that a very small amount (0.03–0.12%) of $CaCO_3$ was re-crystallized during the experiment. The estimation of such small amounts of re-crystallized $CaCO_3$ requires very sensitive ^{14}C labeling techniques or much longer re-crystallization periods. This study would not have been possible without the application of C isotopes because it requires distinguishing between primary $CaCO_3$ derived from loess and re-crystallized $CaCO_3$ derived from rhizosphere respiration.

Compared to earlier studies focusing on the turnover of organic C in the rhizosphere, the important difference of the present approach was the accumulation of respired CO_2 inside the soil–root pot. This corresponds more to natural conditions, in which the accumulation of respired CO_2 in soil horizons is in a steady state with the air diffusion and mass flow between soil and atmosphere. This allowed higher CO_2 concentrations in the pot and increased the re-crystallization of $CaCO_3$ from loess because the $CaCO_3$ dissolution strongly depends on CO_2 partial pressure.

4.2. Re-crystallization period of $CaCO_3$

The estimated initial rates of $CaCO_3$ re-crystallization correspond to the initial rate of formation of secondary carbonates; this allowed us to calculate the period necessary for full re-crystallization. Using different calculation approaches, we estimated the fastest and "real" times for full $CaCO_3$ re-crystallization. The fastest approach assumed a linear re-crystallization process and a 365-day growing season (high CO_2 concentration in the rhizosphere). A linear re-crystallization process implies that the $CaCO_3$ re-crystallized once does not participate in further re-crystallization. This circumstance partly corresponds to the formation of secondary carbonates as growing crystals, such as soft powdery lime accumulations, loess kindles or incrustation of stones in the form of carbonate cutans (Vincent et al., 1994; Pustovoytov, 2003).

The second approach assumes an exponential decrease of the remaining non-crystallized $CaCO_3$ and considers different lengths of the growing season. Here, once re-crystallized $CaCO_3$ can be re-crystallized again and again. This approach implies the absence of growing $CaCO_3$ crystals. It showed that at least 300 years are necessary for 95% $CaCO_3$ re-crystallization in a 365-day growing season. For growing seasons of 2, 4 and 6 months, 50%, 75% and 87% of the initial $CaCO_3$ will be re-crystallized in 400 years, respectively. These values are more relevant those calculated above using the linear approach or exponential approach based on a 365-day growing season.

4.3. Consequences for radiocarbon dating of soil carbonates and paleo-environmental research

The carbon isotopic composition of secondary carbonates has been successfully used in many studies on paleo-environments. A routine use of secondary carbonates in such studies faces the problem of re-crystallization (Pendall et al., 1994; Deutz et al., 2001). Knowledge about the alteration rates of carbonates in soils is relevant to a broad spectrum of theoretical geoscience issues, especially for paleo-climatic reconstructions and dating of late Quaternary soils and sediments. Our results are important for isotopic studies of secondary and lithogenic carbonates in soils. We can easily extrapolate our results at least to the uppermost 7 cm of natural soils (the reaction vessels' height). The model calculations suggest that the time required for full (99%) re-crystallization of calcium carbonate in the uppermost soil layer can range from about 400 to 3000 years depending on the growing season at the site and the initial $CaCO_3$ content of the soil. In the model, we calculated periods necessary for 99% re-crystallization. Values below 99% can lead to strong biases of the results. A simple calculation based on specific ^{14}C activity shows that an admixture of only 1% of initial $CaCO_3$ with a radiocarbon age above 70,000 years to the modern $CaCO_3$ (50 years) will yield an apparent age of about 133 years. Five percent admixture of old $CaCO_3$ will lead to an apparent age of about 480 years, which is about 10 times (!) higher than the real age.

Certain factors affecting re-crystallization rates are not considered in this study. For example, compared to diffuse loess carbonates, much lower re-crystallization rates should be expected for compact parent material such as limestone or carbonates as concretions, coatings on stone bottoms, etc. Other important factors presumably include the mean annual precipitation and temperature at the site, vegetation type, CO_2 concentration in soil air, etc. Our experimental laboratory conditions: (1) young and fine wheat roots having high specific respiration rates, (2) penetration and occupation of the whole loess volume by the roots, and (3) hampered CO_2 exchange with the atmospheric air (also in the open pots) led to CO_2 concentration in the loess-root compartment higher than it is usually observed under field conditions. Therefore, we expect that under field conditions the re-crystallization rates of $CaCO_3$ from the same substrate will be smaller and the calculated re-crystallization period will be longer than observed in the laboratory study.

In the light of our results, the radiocarbon age of carbonates in the uppermost 7 cm of soils developed from loess or a similar parent material cannot exceed the order of 1000 years (for regions with semiarid conditions and a 6-month growing season) or 2.5–3 thousands years (for arid conditions and 2-month growing season). The literature, unfortunately, provides only few radiocarbon dates for carbonates of the uppermost 7 cm. This is because researchers are mainly interested in secondary carbonates located

below 7 cm (e.g. Pendall et al., 1994; Wang et al., 1997). To test our model calculations, we used the radiocarbon ages of $CaCO_3$ measured in 2-cm steps down to 8 cm depth in soils from different climatic conditions reported by Becker-Heidmann et al. (1996) (Table 1). These radiocarbon data principally support our extrapolations. The radiocarbon ages of total carbonate are $n \times 10^2$ years (Philippines, Luzon) under humid conditions, but are markedly higher in semiarid climates, ranging from about 3×10^3 years at 600–700 mm (India, Hyderabad and Israel, Akko) to about 7×10^3 years in the most arid area, with less than 500 mm precipitation per year (Israel, Qedma). So, dry climates may well lead to lower re-crystallization rates because of the shorter growing season. Despite some deviations, these radiocarbon ages are in the same order of magnitude as the values calculated by us. According to these data and our calculations, we conclude that the radiocarbon age of carbonates in the upper soil horizon shows not the formation time, but the period necessary for re-crystallization (~turnover time).

The radiocarbon ages of $CaCO_3$ in the two Rendzic Leptosols (Table 1) are much higher than calculated by us. We explain these deviations by the effect of the extremely high carbonate content and the high density of soil parent material. Less detailed ^{14}C data of other authors have demonstrated that numerous combinations of natural factors affect the carbonate dissolution/re-precipitation rates in different ways. Pendall et al. (1994) concluded that 1000 to 3800 years can be sufficient to completely re-crystallize carbonate in the first 40 cm of soil with 0.01–2.5% $CaCO_3$ under semiarid climatic conditions; this suggests higher re-crystallization rates than could be expected based on our model for 0–7 cm depth. On the other hand,

Table 1
Measured radiocarbon ages of carbonates in 0–7 cm depth from Becker-Heidmann et al. (1996) and period necessary for 95–99% $CaCO_3$ re-crystallization calculated by the model for the specific conditions

Soil (WRB), country	Parent material and $CaCO_3$ content	Mean annual precipitation (mm)/ mean annual temperature (°C)/ number of days with precipitation[a]	Soil depth (cm)	^{14}C age of $CaCO_3$ (uncal. years BP)	Calculated period, years; 95/99%
Haplic Gleysol, Philippines (Luzon)	volcanic ash alluvium, >3%	2150/26/150–160	0–2	180 ± 60	130/200
			2–4	40 ± 60	
			4–6	680 ± 70	
			6–8	765 ± 50	
Pellic Vertisol, India (Hyderabad)	basaltic alluvium, 0.5%	760/25.8/50–60	0–2	3110 ± 80	36/55
			2–4	2810 ± 80	
			4–6	3040 ± 80	
			6–8	3160 ± 80	
Calcic Vertisol, Israel (Akko)	No data	626/19/70–80	0–2	970 ± 60	–
			2–4	–	
			4–6	2900 ± 100	
			6–8	3410 ± 80	
Calcic Vertisol, Israel (Qedma)	Aeolian clay, 2.5%	465/19/70–80	0–2	12,050 ± 100	130/200
			2–4	7160 ± 110	
			4–6	7850 ± 70	
			6–8	8400 ± 70	
Rendzic Leptosol 1, France (Niort)	Limestone, >90%	790/15/150–160	0–2	7370 ± 80	2500/3800
			2–4	10,080 ± 110	
			4–6	11,730 ± 130	
			6–8	8220 ± 90	
Rendzic Leptosol 2, France (Niort)	Limestone, >90%	790/15/150–160	0–2	14,310 ± 170	2500/3800
			2–4	14,670 ± 170	
			4–6	12,880 ± 150	
			6–8	12,350 ± 140	

[a] Number of days with precipitation was taken as the vegetation period (because precipitation is usually limiting plant development under arid conditions).

carbonate ^{14}C ages over 20×10^3 years BP for the uppermost cm of arid soils in Texas reflect much lower carbonate re-crystallization rates (Valastro et al., 1968 cited in Amundson et al., 1994).

5. Conclusions

The isotopic exchange between lithogenic carbonates of loess and ^{14}C respired from the rhizosphere of wheat artificially labeled in $^{14}CO_2$ atmosphere showed very low $CaCO_3$ re-crystallization rates. For a loess containing 27% $CaCO_3$, the initial rate of carbonate re-crystallization was about 0.000029 day^{-1}. Extrapolating this observed rate on longer time periods showed that at least 100 years–but probably between 400 and 2000 years–are necessary to fully re-crystallize the $CaCO_3$ in the uppermost 7 cm layer of a soil formed in a loess sediment with that carbonate content. Therefore, despite the greater analytical precision of ^{14}C dating (e.g. Table 1), the methodological resolution of soil dating and paleo-environmental reconstruction methods based on secondary carbonates cannot be less than hundreds of years. In real soils, a number of factors govern the carbonate re-crystallization rates (climate, vegetation, depth under the soil surface, density of carbonate material, CO_2 concentration, etc.); these probably operate in a complex interaction with one another and are thus difficult to quantify and insert into the model calculations. Nonetheless, a comparison with radiocarbon ages of carbonate in the uppermost 7 cm layer of several soil profiles shows that our model agrees with the empirical data in terms of the order of magnitude. Our experiments and calculations demonstrate the potential of the ^{14}C labeling approach for investigating carbonates in soils (pedogenic and lithogenic) and show their relevance for geochronological and paleo-environment studies. More research is needed to elucidate the role of various other factors in the carbonate re-crystallization rates in soils.

Acknowledgements

This research was supported by The German Research Foundation (DFG) in the scope of fellowships for Y. Kuzyakov and K. Pustovoytov and The Lions-Club and The German Academic Exchange Service (DAAD) in the scope of a fellowship for K. Shevtzova. We thank D. Eckstein, V. Chercasov, and J. Kreer for use of the equipment for ^{14}C analyses.

References

Amundson, R., Wang, Y., Chadwick, O., Trumbore, S., McFadden, L., McDonald, E., Wells, S., DeNiro, M., 1994. Factors and processes governing the ^{14}C content of carbonate in desert soils. Earth and Planetary Science Letters 125, 385–405.

Becker-Heidmann, P., Scharpenseel, H.-W., Weichmann, H., 1996. Hamburg radiocarbon thin layer soils database. Radiocarbon 38, 295–345.

Bente, B., Löscher, M., 1987. Sedimentologische, pedologische und stratigraphische Untersuchungen an Lössen südlich Heidelberg. Göttinger Geographische Abhandlungen 84, 9–17.

Birkeland, P., 1999. Soils and Geomorphology. Oxford, New York. 430 pp.

Black, C.A., 1965. Methods of Soil Analysis: Part 2. American Society of Agronomy, Inc. Publisher, Madison, Wisconsin, pp. 1562–1565.

Boutton, T.W., Yamasaki, S.I. (Eds.), 1996. Mass Spectrometry of Soils. Marcel Dekker, New York.

Bowler, J., Polach, H., 1971. Radiocarbon analyses of soil carbonates: an evaluation from paleosoils in southeastern Australia. In: Paleopedology. Yaalon, D. (Ed.) Int. Soc. Soil. Sci. and Israel Univ. Press. pp. 97–108.

Budd, D.A., Pack, S.M., Fogel, M.L., 2002. The destruction of paleoclimatic isotropic signals in Pleistocene carbonate soil nodules of Western Australia. Palaeogeography, Palaeoclimatology, Palaeoecology 188, 249–273.

Cerling, T., 1984. The stable isotopic composition of modern soil carbonate and its relation to climate. Earth and Planetary Letters 71, 229–240.

Cerling, T., 1991. Carbon dioxide in the atmosphere: evidence from cenozoic and mesozoic paleosols. American Journal of Science 291, 377–400.

Cerling, T.E., Wang, Y., Quade, J., 1993. Expansion of C4 ecosystems as indicator of global ecological change in the Late Miocene. Nature 361, 344–345.

Chen, Y., Polach, H., 1986. Validity of ^{14}C ages of carbonate in sediments. Radiocarbon 28, 464–472.

Deutz, P., Montanez, I.P., Monger, H.C., Morrison, J., 2001. Morphology and isotope heterogeneity of late quaternary pedogenic carbonates: implications for paleosol carbonates as paleoenvironmental proxies. Palaeogeography, Palaeoclimatology, Palaeoecology 166, 293–317.

Erenoglu, B., Nikolic, M., Römheld, V., Cakmak, I., 2002. Uptake and transport of foliar applied zinc (^{65}Zn) in bread and durum wheat cultivars differing in zinc efficiency. Plant and Soil 241, 251–257.

Finnern, H. 1995. Bodenkundliche Kartieranleitung. Bundesanstalt für Geowissenschaften und Rohstoffe und Geologische Landesämter. 4. Auflage.

Hatté, C., Fontugne, M., Rousseau, D., Antoine, P., Zöller, L., Tisnerat-Laborde, N., Bentaleb, I., 1998. $\delta^{13}C$ variations of loess organic matter as a record of the vegetation response to climatic changes during the Weichselian. Geology 26, 583–586.

Jones, D.L., Hodge, A., 1999. Biodegradation kinetics and sorption reactions of three differently charged amino acids in soil and their effects on plant organic nitrogen availability. Soil Biology and Biochemistry 31, 1331–1342.

Khokhlova, O.S., Sedov, S.N., Golyeva, A.A., Khokhlov, A.A., 2001. Evolution of Chernozems in the Northern Caucasus, Russia during the second half of the Holocene: carbonate status of paleosols as a tool for paleoenvironmental reconstruction. Geoderma 104, 115–133.

Kuzyakov, Y.V., 2001. Tracer studies of carbon translocation by plants from the atmosphere into the soil (a review). Eurasian Soil Science 34, 28–42.

Kuzyakov, Y., Domanski, G., 2000. Carbon input by plants into the soil. Review. Journal of Plant Nutrition and Soil Science 163, 421–431.

Kuzyakov, Y., Siniakina, S.V., 2001. Siphon method of separating root-derived organic compounds from root respiration in non-sterile soil. Journal of Plant Nutrition and Soil Science 164, 511–517.

Kuzyakov, Y., Ehrensberger, H., Stahr, K., 2001. Carbon partitioning and below-ground translocation by *Lolium perenne*. Soil Biology and Biochemistry 33, 61–74.

Lee, Y., Hisada, K., 1999. Stable isotopic composition of pedogenic carbonates of the early Cretaceous Shimonoseki subgroup, western Honsu, Japan. Palaeogeography, Palaeoclimatology, Palaeoecology 153, 127–138.

Merck®-Laborkatalog, 2000. Verbrauchsmaterialien und Geräte. Merck Eurolab GmbH, Darmstadt. 516.18 pp.

Monger, H.C., Cole, D.R., Gish, J.W., Giordano, T.H., 1998. Stable carbon and oxygen isotopes in Quaternary soil carbonates as indicators of ecogeomorphic changes in the northern Chihuahuan Desert, USA. Geoderma 82, 137–172.

Nordt, L., Hallmark, C., Wilding, L., Boutton, T., 1998. Quantifying pedogenic carbonate accumulations using stable carbon isotopes. Geoderma 82, 115–136.

Pendall, E., Harden, J., Trumbore, S., Chadwick, O., 1994. Isotopic approach to soil carbonate dynamics and implications for paleoclimatic interpretations. Quaternary Research 42, 60–71.

Pustovoytov, K., 2002. ^{14}C dating of pedogenic carbonate coatings on wall stones at Göbekli Tepe (Southeastern Turkey). Neo-Lithics 2/02, 3–4.

Pustovoytov, K., 2003. Growth rates of pedogenic carbonate coatings on clasts. Quaternary International 106–107, 131–140.

Quade, J., Cerling, T.E., 1995. Expansion of C4 grasses in the late Miocene of North Pakistan: evidence from stable isotopes in paleosols. Palaeogeography, Palaeoclimatology, Palaeoecology 115, 91–116.

Quade, J., Solounias, N., Cerling, T.E., 1994. Stable isotopic evidence from paleosol carbonates and fossil teeth in Greece for forest or woodland over the past 11 Ma. Palaeogeography, Palaeoclimatology, Palaeoecology 108, 41–53.

Quade, J., Cater, J.M.L., Ojha, T.P., Adam, J., Harrison, T.M., 1995. Late Miocene environmental change in Nepal and the northern Indian subcontinent: stable isotopic evidence from paleosols. Geological Society of America Bulletin 107, 1381–1397.

Royer, D.L., Berner, R.A., Beerling, D.J., 2001. Phanerozoic atmospheric CO_2 change: evaluating geochemical and paleobiological approaches. Earth-Sciences Reviews 54, 349–392.

Sharp, W.D., Ludwig, K.R., Chadwick, O.A., Amundson, R., Glaser, L.L., 2003. Dating fluvial terraces by 230Th/U on pedogenic carbonate, Wind River Basin, Wyoming. Quaternary Research 59, 139–150.

Verburg, P.S.J., Gorissen, A., Arp, W.J., 1998. Carbon allocation and decomposition of root-derived organic matter in a plant–soil system of *Calluna vulgaris* as affected by elevated CO_2. Soil Biology and Biochemistry 30, 1251–1258.

Vincent, K., Bull, W., Chadwick, O., 1994. Construction of a soil chronosequence using the thickness of pedogenic carbonate coatings. Journal of Geological Education 42, 316–324.

Wang, Y., Cerling, T., Quade, J., Bowman, A., Smith, G., Lindsay, E., 1993. Stable isotopes of paleosols and fossil teeth as paleoecology and paleoclimate indicators: an example from the St. David formation, Arizona. Climate change in continental isotopic records. Geophysical Monograph 78.

Wang, Y., McDonald, E., Amundson, R., McFadden, L., Chadwick, O., 1996. An isotopic study of soils in chronological sequences of alluvial deposits, Providence Mountains, California. Geological Society of America Bulletin 108, 379–391.

Wang, H., Ambrose, S.H., Liu, C.-L.J., Follmer, L.R., 1997. Paleosol stable isotope evidence for early hominid occupation of East Asian temperate environments. Quaternary Research 48, 228–238.

Whipps, J.M., 1990. Carbon economy. In: Lynch, J.M. (Ed.), The Rhizosphere. Wiley, Chichester, pp. 59–97.

Zöller, L., Stremme, H., Wagner, G.A., 1988. Thermolumineszenz-Datierung an Löss-Pläboden-Sequenzen von Nieder-, Mittel- und Oberrhein. Chemical Geology (Isotope Geoscience Section) 73, 39–62.