CaCO$_3$ recrystallization in saline and alkaline soils

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A B S T R A C T

Are desert ecosystems a stable sink for atmospheric CO$_2$? Although the uptake of atmospheric CO$_2$ by soil during the nighttime is detected in deserts and some semi-deserts, the underlying mechanisms remain elusive. In order to determine the factors affecting the CO$_2$ fluxes into soil and to reveal the relationship between CO$_2$ fluxes and carbonate formation and recrystallization in saline and alkaline soils, four soils with contrasting salinity from two sites, Aksu and Yingbazar, along the Tarim River were analysed. Soils were incubated in ^{14}CO$_2$ labelled atmosphere for 90 days at three CO$_2$ concentrations: 0.04%, 0.4% and 4%. The ^{14}C activity was measured in soil water and air, as well as in carbonates after 2, 14 and 90 days. The ^{14}C incorporation in CaCO$_3$ increased with corresponding ^{14}C decrease remaining in the CO$_2$. The highest ^{14}C incorporation into CaCO$_3$ (54%) was observed in the Yingbazar saline soil. The carbonate recrystallization rates increased logarithmically (r^2 > 0.97) with the CO$_2$ concentration. The average carbonate recrystallization rate from three sampling times was highest in the Yingbazar saline soil under 4% CO$_2$ (8.45×10^{-6} day^{-1}) and lowest in the Aksu alkaline soil under 0.04% CO$_2$ (0.03×10^{-6} day^{-1}). The average carbonate recrystallization rate increased with electric conductivity (corresponding to soil salinity) but decreased with pH ($R^2 = 0.99$ for 4% CO$_2$). The alkaline soils incorporated less ^{14}C into CaCO$_3$ than the saline soils. At the highest CO$_2$ concentration of 4%, the full recrystallization period of the remaining primary carbonates was 10- to 100-fold shorter than at the lower CO$_2$ concentrations. Therefore, besides soil chemical parameters (e.g. pH, CaCO$_3$ content), CO$_2$ concentration (respiration of microorganisms and roots) is an important factor for CaCO$_3$ recrystallization and formation of pedogenic carbonates in desert soils. It is the most important factor for CaCO$_3$ recrystallization and so, for the formation of pedogenic carbonates.

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1. Introduction

Soils play an important role as carbon (C) sources (Ge et al., 2008; Wu et al., 2009) for changes in land use or as C sinks (Prentice and Fung, 1990) because of human activities. Desert and semidesert ecosystems are considered to be CO$_2$ sinks (Stone, 2008) because of the wide distribution of alkaline and CaCO$_3$ containing soils, which can be turned into carbonates. In west China, the average annual net ecosystem CO$_2$ exchange (NEE) was -25.0 ± 12.7 g C m^{-2} yr^{-1} from 2002 to 2012 in saline desert soil (Ma et al., 2014). The CO$_2$ uptake in alkaline and saline soils is estimated to be 0.3–3.0 μmol m^{-2} s^{-1} (Xie et al., 2009). The Mojave desert soil in southwestern USA took up 102 ± 67 and 110 ± 70 g C m^{-2} in 2005 and 2006, respectively (Wohlfahrt et al., 2008). The C uptake of desert soils is therefore significant but may vary depending on soil properties.

The main mechanisms for the CO$_2$ flux into soil measured during the night in deserts and oasis cotton fields in Xinjiang, in the northwest of China, remains elusive (Stone, 2008). The CO$_2$ uptake at night cannot be attributed to photosynthesis, emphasizing the existence of abiotic processes for high CO$_2$ absorption (Ma et al., 2013; Xie et al., 2009). Using the δ^{13}C abundance in CO$_2$ (Walvoord et al., 2005) showed that CO$_2$ release from desert soil was derived from autotrophic and heterotrophic respiration components in the root zone and from calcite dissolution in deep water table settings. Via ^{13}CO$_2$ dissolution in air-free water (Ma et al., 2014), desert soil are a sink for bicarbonate in shallow groundwater. Pedogenic carbonates are described as earthworm biospheroliths, rhizoliths and calcified roots, hypocoatings, nodules, clast coating, calcretes and laminar caps (Zamanian et al., 2016b). Pedogenic carbonate-rhizolithes can form near the root zone as a function of water content, increased CO$_2$ concentration and dissolved CaCO$_3$ movement (Cramer and Hawkins, 2009; Gocke et al., 2010a; Gocke et al., 2014; Gocke et al., 2011a). The neoformation of pedogenic carbonates was discovered in saline–alkaline soil for 13 years irrigation (water contain Ca^{2+} and Mg^{2+}) and fertilization (Bughio et al., 2016). The secondary CaCO$_3$ precipitated in the soil with changing soil

respiration and CO_2 content (Cerling, 1984). Dissolution of primary carbonates and re-precipitation of secondary carbonates in soils can be observed according to the following equation (Kuzyakov et al., 2006):

$$CaC^0O_3 + C^nO_2 + H_2O \leftrightarrow CaC^nO_3 + C^0O_2 + H_2O.$$
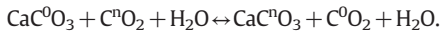
Based on the equation $CaCO_3(calcite) + 2H^+ \leftrightarrow Ca^{2+} + CO_2(g) + H_2O$ H_2O (Lindsay, 1979), pH affects the carbon balance in soil (Ma et al., 2010; Saaltink et al., 2013; Varadharajan et al., 2013). Moreover, pH and soil salinity affect the CO_2 efflux and carbonate recrystallization by biochemical and physicochemical processes. Most studies however, pay little (or no) attention to the effects of salinity and alkalinity, alone or in combination, on carbonatization, which shows the genetic relationship between carbonate and soil CO_2 concentration.

The carbon isotope signature ($\delta^{13}C$) in soil carbonates has been used to determine the C sources (Bughio et al., 2016; Canti, 2009; Manning et al., 2013; Xu and Liu, 2010), establish the paleo climate (Hough et al., 2014; Moore et al., 2013; Riera et al., 2013; Takeuchi et al., 2010) and reconstruct the geo-chronology (Gocke et al., 2010b; Kraimer and Monger, 2009; Kuzyakov et al., 2006) and vegetation (C3 and C4) (Agrawal et al., 2012; Liu et al., 2011). However, the rate of carbonate formation and $\delta^{13}C$ stabilization remains unclear. Isotopic exchange with $^{14}CO_2$ is likely to be the only feasible way to estimate the rate of the slow carbonate recrystallization process (Gocke et al., 2010b). Compared with other approaches, ^{14}C labelling has much higher sensitivity, is more efficient and precise, has a lower cost of purchase and analysis, and has more convenient sample preparation methods for assessing recrystallization rates (Gocke et al., 2011c; Kuzyakov and Domanski, 2000).

We assume that physicochemical processes (e.g. recrystallization as a pedogenic carbonate and dissolution of CO_2 in cold soil water) are responsible for the CO_2 flux from atmosphere into saline and alkaline soils. Using the example of soils from the Tarim River Basin and by labelling with a $^{14}CO_2$ atmosphere, we determined the temporal dynamics (2, 14, 90 days) and recovery in various C pools, depending on three initial CO_2 concentrations (0.04%, 0.4% and 4%). The objectives of this study were (i) to examine factors affecting CO_2 fluxes when only physicochemical processes are considered and (ii) to reveal the relationship between CO_2 and carbonate recrystallization in saline and alkaline soils.

2. Materials and methods

2.1. Soil sampling

The soil sampling area has a typical temperate continental arid climate, with mean minimum and maximum temperatures during the vegetation period (April–November) of 16.6 °C and 34.8 °C, respectively, and a mean annual precipitation of 72 mm (1982 to 2012) (Tutiempo, 2015; Zhao et al., 2015). Four soils were sampled at Aksu (40°37′N, 80°45′E, altitude 1028 m a.s.l.) and Yingbazar (41°18′N; 85°.22′E, altitude 978 m a.s.l), Xinjiang, which are located in the upstream portion and the middle of the Tarim River, respectively (Fig. 1). The accumulation of salt and gypsum in the Tertiary sediments in Xinjiang explains the large areas of saline and alkaline soils (72 Mio ha), which occupy 33% of all agricultural fields (Chen et al., 2007). Two areas of soil at each location were sampled in the Ap horizon of 0–30 cm depth in the cotton fields under plastic mulching and drip irrigation conditions (Table 1). Based on their pH and EC, soil samples were identified as Aksu alkaline (AAlk), Aksu saline (ASal), Yingbazar alkaline (YAlk), and Yingbazar saline (YSal) (Table 1). Soil samples were air-dried, sieved through a 2-mm mesh and stored at 4 °C before use.

2.2. Experimental design

The experiment included $^{14}CO_2$ labelling, incubation and sampling for the four saline and alkaline soils (AAlk, ASal, YAlk, YSal) (Fig. 2). The experiment was conducted at room temperature with three sampling times (2, 14, and 90 days). The ^{14}C-CO_2 (0.04%, 0.4% and 4% concentration) was emitted as a product of the reaction of H_2SO_4 with $Na_2^{14}CO_3$. In a small glass vessel (12 ml volume), 0.8 ml water was added to 6 g of air-dried soil to achieve 15% water content in the soil. After labelling, the vessels were kept in a dark cabinet to avoid effects from algae and autotrophic microorganisms.

2.3. Labelling and sampling

For the labelling, ^{14}C (140 kBq) in the form of Na_2CO_3 was added to 5 ml of a slightly alkalinized Na_2CO_3 solution (0.00015, 0.015, or 0.15 mol l^{-1}), which was used to reach a specific initial CO_2 concentration (0.04%, 0.4% and 4%, respectively). The solution was alkalinized
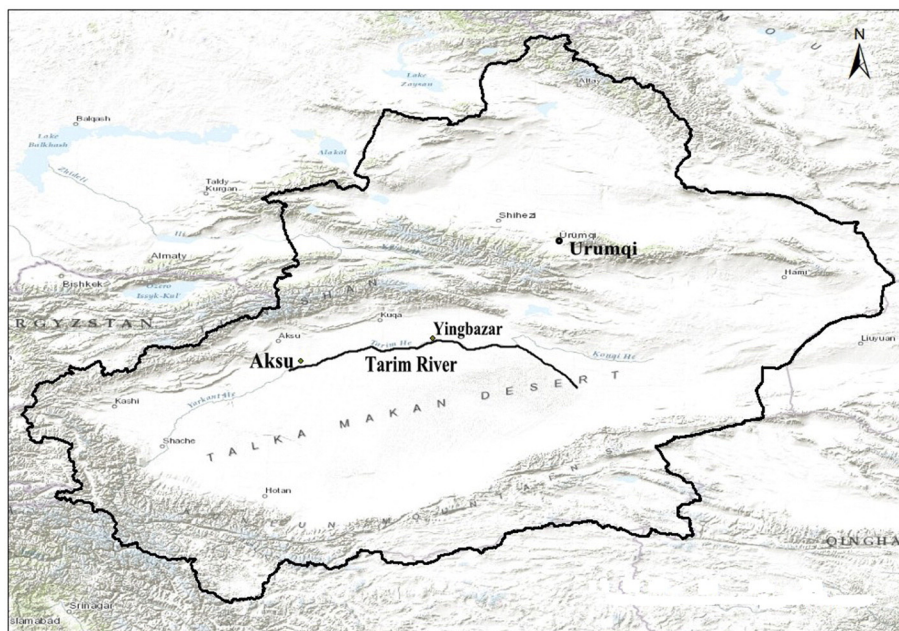

Fig. 1. Experimental locations of Aksu and Yingbazar soils in the Tarim River Basin, Xinjiang Province, China.

Table 1
Chemical and physical properties of soils from two experimental stations in the Tarim River Basin.

Location	Sample nr.	pH_{H2O} (1:5)	EC (1:20) (mS cm^{-1})	$CaCO_3$ (%)	C_{org}[a] (%)	N_{tot}[b] (%)	CO_3^{2-} g kg^{-1}	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+
Aksu	AAlk[c]	8.50	0.32	19	0.5	0.05	0.01	0.4	0.3	1.6	0.5	0.3	0.30	0.10
	ASal[d]	8.24	1.35	14	0.4	0.08	0.00	0.1	0.5	8.2	2.5	0.3	0.80	0.10
Yingbazar	YAlk[e]	8.90	1.72	17	0.3	0.07	0.00	0.2	0.6	0.6	0.1	0.1	0.49	0.04
	YSal[f]	7.87	3.67	18	0.5	0.07	0.00	0.2	0.8	0.9	0.2	0.1	0.54	0.05

[a] Organic carbon.
[b] Total nitrogen.
[c] Aksu alkaline soil.
[d] Aksu saline soil.
[e] Yingbazar alkaline soil.
[f] Yingbazar saline soil.

slightly to prevent loss of ^{14}C activity by exchange with atmospheric CO_2. The CO_2 concentrations were calculated as the vessel volume minus the soil and water volume (0.8 ml) and tubes (Fig. 2). After 100 μl $Na_2^{14}CO_3$ (corresponding to the concentrations of 0.04%, 0.4%, and 4% CO_2) was added to the left micro test tubes in the glass vessels, the glass vessels were closed and made gastight. Then, 100 μl 1.84 mol l^{-1} H_2SO_4 was added to the left micro test tube, using syringes to release $^{14}CO_2$ (Fig. 2). The soil vessels were stored in a dark chamber.

For sampling, 0.2 ml 1 M NaOH was added to the right micro test tubes using syringes after 2, 14, 90 days, respectively. Afterwards, the vessels were left overnight in a dark chamber. Then, the glass vessels were opened, and 50 μl liquid was withdrawn from the micro test tubes to measure ^{14}C residue activity (left tube) and $^{14}CO_2$ activity (right tube). Three grams of fresh soil was taken from each glass vessel and washed with 20 ml of slightly alkalinized de-ionized water to elute dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC). One milliliter of liquid was taken from the above mixtures to measure ^{14}C (DOC + DIC) and ^{14}C (DOC) activity, respectively. DOC was determined by adding 4–5 drops of 1 M HCl to DIC and measuring after the release of CO_2. The water content in the soil was measured by oven-drying at 105 °C. Washed soils were put in the oven to dry overnight at 80 °C. Two grams of the dried soils was transferred to closed bottles and treated with 10 ml 5 M H_3PO_4. The CO_2 evolved from $CaCO_3$ was trapped in 10 ml of 2 M NaOH overnight to ensure complete CO_2 absorption. One milliliter of NaOH with entrapped CO_2 was used to measure ^{14}C ($Ca^{14}CO_3$) activity (Fig. 2).

2.4. ^{14}C analysis

The ^{14}C activities in solutions (^{14}C-CO_2 in NaOH, ^{14}C-$CaCO_3$, ^{14}C-DOC, ^{14}C-DOC + DIC and ^{14}C-residue after labelling) and during sampling times (2, 14 and 90 days) were measured by sample solutions with ^{14}C, along with 2 ml of scintillation cocktail (Rotszint EcoPlus, Carl Roth, Germany). The ^{14}C measurements were performed with a Beckman LS 6500 Liquid Scintillation Counter (Beckmann Counter Inc., USA) after the decay of the chemiluminescence.

2.5. Calculations and statistical analysis

The calculations for carbonate recrystallization rate followed those reported in previous publications (Gocke et al., 2010b; Kuzyakov et al., 2006). The ^{14}C results are presented as a percentage of ^{14}C activity recovered. The increase in total ^{14}C activity of each replicate ($^{14}C_{av}$) was calculated with the following equation:
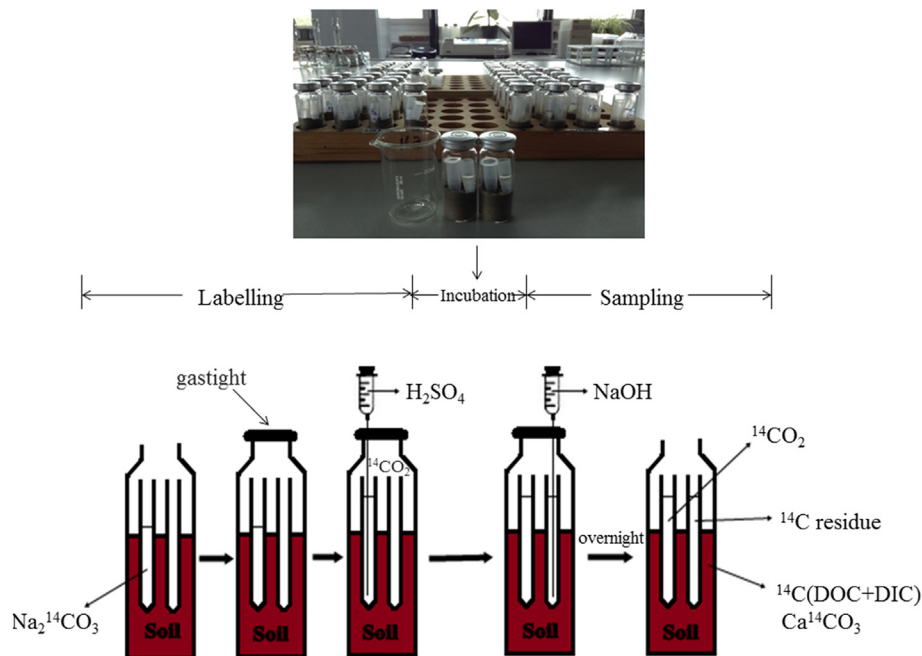
$$^{14}C_{av} = {}^{14}C_{input} - {}^{14}C_{res} \qquad (1)$$

Fig. 2. Schematic diagram of the experimental design and procedure.

where $^{14}C_{input}$ is the total input activity of the label and $^{14}C_{res}$ is the activity of undissolved residue from the labelling solution (<0.1%).

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

$$^{14}C_{SA}^{CO_2} = \frac{^{14}C^{CO_2}}{C_t^{CO_2}} \quad (2)$$

The ^{14}C activity ($^{14}C_{CaCO_3}$) was calculated from the ^{14}C activity in 1 ml NaOH with entrapped CO_2 by adding H_3PO_4 to 2 g soil. The ^{14}C specific activity of the added CO_2 is equal to the ^{14}C specific activity of the recrystallized portion of $CaCO_3$. Therefore, the amount of recrystallized $CaCO_3$ ($C_{total}^{recryst}$) was calculated as:

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

The recrystallization rate of the soil carbonate was calculated as the amount of incorporated C divided by the amount of total C content ($C_{total}^{CaCO_3}$) of the soil carbonate and divided by the labelling incubation period (2, 14 or 90 days).

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

Four replicates were measured in this experiment. One-way analysis of variance (ANOVA) was used to determine the effects of CO_2 concentrations, incubation time and soil type on carbonate recrystallization rates. STATISTICA v.10.0 (StatSoft Inc., USA) and Sigmaplot v.12.0 (Systat Software Inc., San Jose, CA, USA) software were used for data analysis and figure production, respectively.

3. Results

3.1. ^{14}C activity in CO_2 and $CaCO_3$

^{14}C in the remaining CO_2 generally decreased with time by 5–29% of the total ^{14}C input from 2 to 90 days; correspondingly, the ^{14}C content in $CaCO_3$ increased by 6–53% of the total ^{14}C input during that time. The sum of ^{14}C in CO_2 and $CaCO_3$ always sum to 90% (Fig. 3). This means that only a small proportion of less than 5% of ^{14}C exists in each of DIC and DOC. When considering soil properties, the Aksu alkaline soil (AAlk) had the highest amount of ^{14}C in CO_2 and the lowest amount of ^{14}C in $CaCO_3$, whereas the Yingbazar saline soil (YSal) had the lowest amount of ^{14}C in CO_2 and the highest amount in $CaCO_3$ (Fig. 3). In general, the alkaline soils incorporated less ^{14}C into $CaCO_3$ than the saline soils.

3.2. $CaCO_3$ recrystallization rate

The carbonate recrystallization rates increased logarithmically (y = ln (a + bx), $r^2 > 0.97$) with the CO_2 concentration (Fig. 4). The $CaCO_3$ recrystallization rate increased with the CO_2 concentration (0.04%, 0.4%, and 4%) (Fig. 4, p < 0.001). The recrystallization rate under 0.04% CO_2 was 10 to 100 times smaller than that under 0.4% and 4% CO_2, respectively (Fig. 4). The carbonate recrystallization rate in the alkaline soils was slower than that in the saline soils. The recrystallization rate mainly depended on the partial pressure of the labelled CO_2.

3.3. Relationship between $CaCO_3$ recrystallization rates and soil pH and EC

The $CaCO_3$ recrystallization rate, averaged over 3 sampling times, showed a strong relationship with EC and pH ($R^2 > 0.90$) (Fig. 5). The average $CaCO_3$ recrystallization rate for 3 sampling times increased with
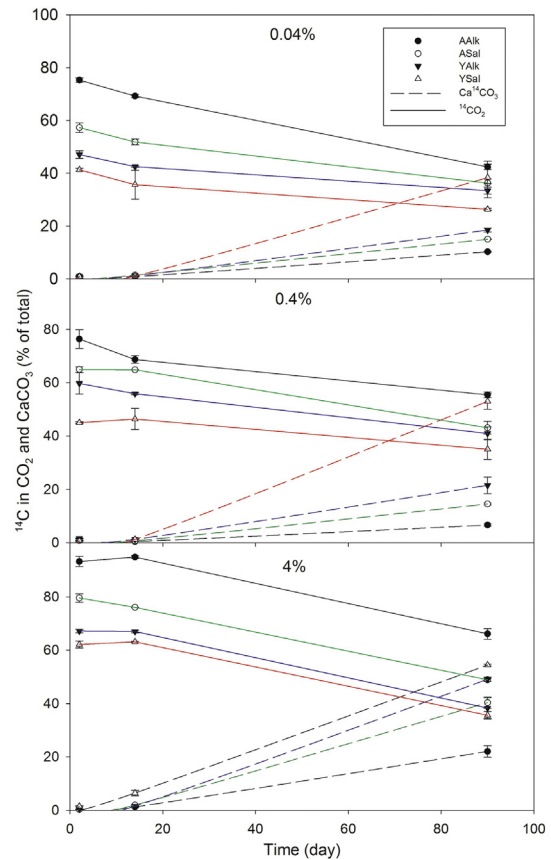

Fig. 3. ^{14}C in $CaCO_3$ and CO_2 (means ± 3%) depending on three initial CO_2 concentrations (0.04%, 0.4%, and 4%) after three incubation periods (2, 14, and 90 days) in four soils (AAlk, ASal, YAlk, and YSal). AAlk: Aksu alkaline soil; ASal: Aksu saline soil; YAlk: Yingbazar alkaline soil; YSal: Yingbazar saline soil.

increasing EC and decreased with pH, complimentary at the 4% initial $^{14}CO_2$ concentration (Fig. 5). The Yingbazar soils always had a higher average carbonate recrystallization rate than the Aksu soil because of their higher salinity (Fig. 5).

The average $CaCO_3$ recrystallization rate was highest at 4% initial CO_2 concentration and was 10 times bigger than that with 0.4% and 100 times larger than that with 0.04% CO_2 concentration (Fig. 5). The average $CaCO_3$ recrystallization rate was highest (8.45×10^{-6} day^{-1}) with 4% CO_2 concentration for Yingbazar saline soil (YSal) and lowest (0.03×10^{-6} day^{-1}) with 0.04% CO_2 concentration for Aksu alkaline soil (AAlk) (Fig. 5). The saline soils had higher $CaCO_3$ recrystallization rates than the alkaline soils.

4. Discussion

4.1. Factors affecting ^{14}C in carbon pools

The majority of ^{14}C added to the system as CO_2 became incorporated into $CaCO_3$. Together with the added CO_2, the $CaCO_3$ represents 88% of the total ^{14}C recovered after 90 days under 4% CO_2. The ^{14}C in $CaCO_3$ increased significantly with decreasing ^{14}C in CO_2 (Fig. 3). The amount of CO_2 dissolved in the soil solution during the first hour of incubation increased linearly with increasing initial CO_2 concentration in the headspace (Oren and Steinberger, 2008). The equilibrium included carbonate dissolution. Using the $\delta^{13}C$ signatures, Bertrand et al. (2007) found that the CO_2 produced in soils with pH > 7 originated from both organic and mineral sources. The decrease in ^{14}C in the CO_2 fraction used for carbonate recrystallization via the exchange of ^{14}C with ^{12}C followed the equation (Kuzyakov et al., 2006):
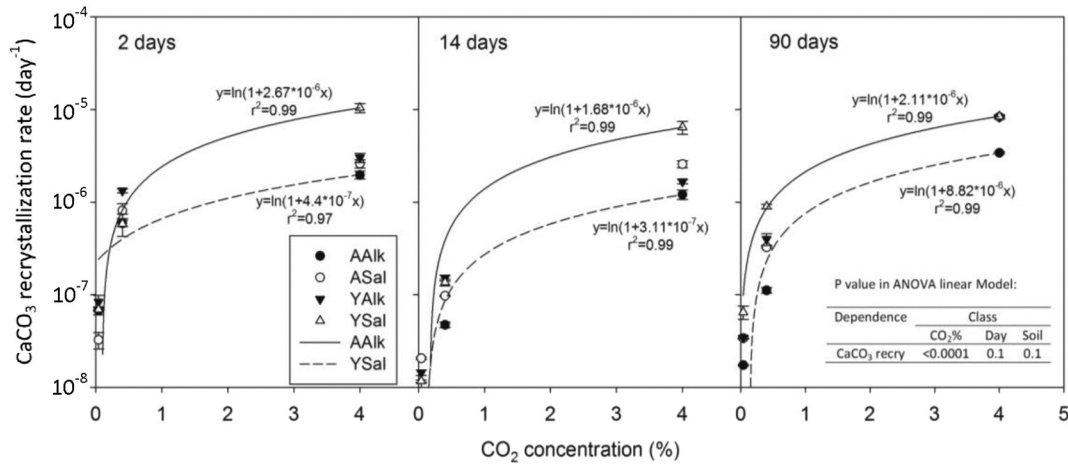
Fig. 4. Carbon recrystallization (means ± 3%) depending on three initial CO_2 concentrations (0.04%, 0.4%, and 4%) at three incubation periods (2, 14, and 90 days) in four soils (AAlk, ASal, YAlk, and YSal). The upper line (AAlk) and lower line (YSal) showed the data range. AAlk: Aksu alkaline soil; ASal: Aksu saline soil; YAlk: Yingbazar alkaline soil; YSal: Yingbazar saline soil.

$$CaC^0O_3 + C^nO_2 + H_2O \leftrightarrow CaC^nO_3 + C^0O_2 + H_2O.$$
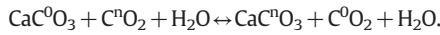
^{14}C in DIC was of minor importance, averaging less than 3% of the total ^{14}C. The ^{14}C content in DIC vibrated over 90 days but did not reach an equilibrium. DOC comprised only microbial decomposition products because the experiment was conducted without plants. ^{14}C in DOC was found in small amounts (<6% of total). Bacteria may incorporate ^{14}C from DIC, but the levels at which they do so are of minor importance under the conditions of this experiment. Miltner et al. (2004) also found that the labelled $^{14}CO_2$ was transferred to soil organic compounds (1.3 μmol C g^{-1} soil after 61 days) without plants.

4.2. The $CaCO_3$ recrystallization rate in saline and alkaline soils

The maximum amount of recrystallized $CaCO_3$ was always observed with high CO_2 concentration (Table 2, Figs. 4, 5, 7). In a previous study, CO_2 concentrations of 0.04%, 0.5% and 5% led to carbonate recrystallization rates of 0.8 to 4.1×10^{-7} day^{-1}, 3.1 to 8.1×10^{-7} day^{-1} and 3.4 to

16.9×10^{-7} day^{-1}, respectively, in a loess soil without plants (Gocke et al., 2010b) (Table 2). The average carbonate recrystallization rate was also lower at a CO_2 concentration of 0.04% but increased 10- to 100-fold with increasing CO_2 concentration from 0.04% to 0.4% and 4% in saline and alkaline soils. Considering that the CO_2 concentration is higher under field conditions, this may compensate substantially for the lower rate observed with 0.04% CO_2 concentration (Table 2, Fig. 5). Higher CO_2 concentrations induced higher carbonate recrystallization (Table 2, Figs. 4, 5 and 7), which is consistent with a previous finding by Gocke et al. (2010b). The carbonate recrystallization rates were one to two orders of magnitude lower without plants compared to rates found in experiments with plants (Gocke and Kuzyakov, 2011; Gocke et al., 2011b, 2011c, 2012; Kuzyakov and Larionova, 2005; Kuzyakov et al., 2006) (Table 2). Carbonate recrystallization rates can reach up to 600×10^{-6} day^{-1} in the field, depending on the observed CO_2 concentrations in cotton fields [3100–9200 μl l^{-1} (0.3%–1%) (Li et al., 2011) and 5000–25,000 μl l^{-1} (0.5%–2.5%) in the Aksu sampling station (Yu et al., 2015)].
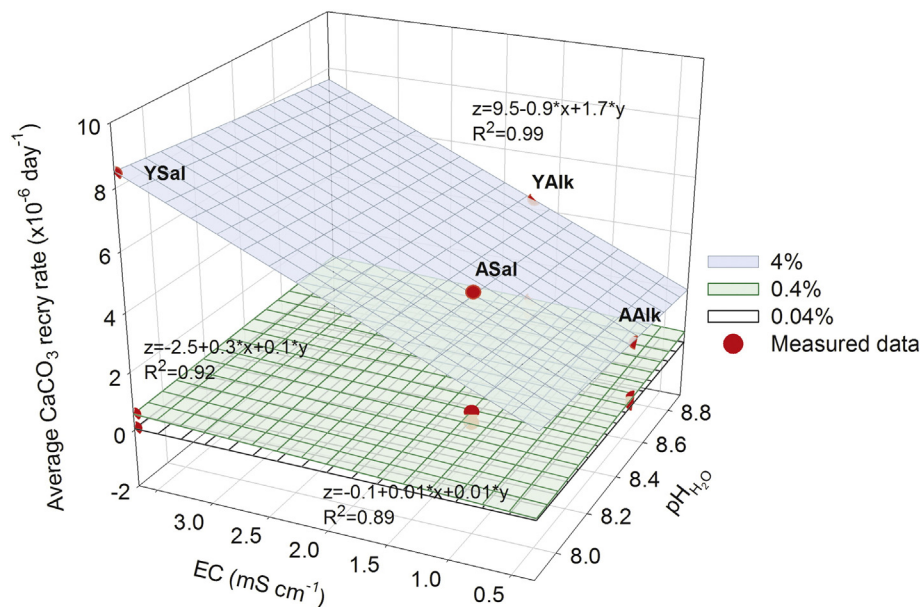

Fig. 5. Relationship between the $CaCO_3$ recrystallization rate ($\times 10^{-6}$ day^{-1}) (z) at three sampling times and the EC (y) and pH (x) depending on three initial CO_2 concentrations (0.04%, 0.4%, and 4%) in four soils (AAlk, ASal, YAlk, and YSal). AAlk: Aksu alkaline soil; ASal: Aksu saline soil; YAlk: Yingbazar alkaline soil; YSal: Yingbazar saline soil.

Table 2
Literature overview of studies investigating $CaCO_3$ recrystallization rates using the ^{14}C technique.

Reference	Plant	Soil	CO_2 (%)	Days	$RCaCO_3$[a] (day^{-1})
Kuzyakov et al. (2006)	Wheat	Loess	0.04	35	2.9×10^{-5}
Gocke et al. (2010b)	No	Loess	0.04	4	4.1×10^{-7}
			0.04	16	0.8×10^{-7}
			0.5	4	8.1×10^{-7}
			0.5	16	3.1×10^{-7}
			5	4	16.9×10^{-7}
			5	16	3.4×10^{-7}
Gocke et al. (2012)	Maize	Loess	0.04	182	6.8×10^{-6} (0–85 cm)
			0.04	182	1.77×10^{-5} (0–15 cm)
Gocke et al. (2011b)	Wheat	Loess	0.04	10, 25	3.2×10^{-5}
	Wheat	Rhizosphere	0.04	10, 25	6.8×10^{-5}
	Ryegrass	Loess	0.04	10, 25	2.8×10^{-5}
	Ryegrass	Rhizosphere	0.04	10, 25	4.7×10^{-5}
Gocke et al. (2011c)	Wheat	Loess	0.04	5	2.9×10^{-4}
	Ryegrass	Loess	0.04	5	1.1×10^{-4}
Gocke and Kuzyakov (2011)	Maize	Loess	0.04	20	2.9–3.1×10^{-6}
		Rhizosphere	0.04	20	20.6–74.6×10^{-5}
This study	No	Saline and alkaline	0.04	2	0.3–0.8×10^{-7}
			0.04	14	0.1–0.2×10^{-7}
			0.04	90	0.2–0.6×10^{-7}
			0.4	2	6.0–13.3×10^{-7}
			0.4	14	0.4–1.5×10^{-7}
			0.4	90	1.1–9.0×10^{-7}
			4	2	19.7–104.5×10^{-7}
			4	14	12.1–64.4×10^{-7}
			4	90	34.1–83.5×10^{-7}

[a] Recrystallization rate.

4.3. Relationships between $CaCO_3$ recrystallization rates and pH and EC

There was a close relationship between the carbonate recrystallization rate and the pH and EC of the soil at different CO_2 concentrations ($R^2 > 0.99$) (Figs. 5, 7). In particular, the daily mean CO_2 efflux shows a significant negative correlation with EC for the saline soil from the Tarim River Basin (Ma et al., 2013; Xie et al., 2009). The soil EC affects the amount of exchangeable Ca^{2+}, Na^+, Mg^{2+}, and K^+ (Table 1). The high level of soil exchangeable Ca^{2+} and high soil CEC decreased shell carbonates recrystallization because the cation exchange is faster than dissolution (Zamanian et al., 2016a). The same trend was found between the two location soils, but the combination of soil alkalinity and gypsum affect the results. The soils from Aksu have 2–8 g kg^{-1} SO_4^{2-} content in the topsoil (Zhao et al., 2015), which was much higher than soil from Yingbazar (<1 g kg^{-1}) (Table 1). The carbonate dissolution rate increases with the initial ESP level (Li and Keren, 2008). As soil in Aksu has higher sodium, sulphate content, higher Ca^{2+} and lower EC, the soil had a lower carbonate recrystallization compared to the soil in Yingbazar. By watering with Ca^{2+} and Mg^{2+} containing water, the SIC sequestration rate is 0.38, 0.27, 0.23, and 0.12 Mg C ha^{-1} yr^{-1} in saline and alkaline soil for the OFH (organic fertilization at high level), OFL (organic fertilization at low level), MF (mineral fertilization), and CK (no fertilization) treatments, respectively, in the North China Plain, China (Bughio et al., 2016). As a higher content of Ca^{2+} and Mg^{2+} in soil was discovered in two stations (Table 1), it is greatly hypothesised that the watering and fertilization treatment have effect on the new formation of soil inorganic carbon.

By contrast, the soil alkalinity significantly affects $CaCO_3$ dissolution (Li and Keren, 2008) and positively affects the CO_2 fluxes (Ma et al., 2013; Xie et al., 2009). The carbonate recrystallization increased with the decreased pH mainly through increased carbonate solubility ($\log[Ca^{2+}] = 9.74 - 2 \times pH - \log CO_2$ at a temperature of 25 °C) (Lindsay, 1979). Overall, the carbonate recrystallization rate was highest for the Yingbazar saline soil (YSal), which had the lowest pH and the highest EC (Fig. 5). However, although the Yingbazar alkaline soil (YAlk) had the highest pH (8.9) it did not show the lowest $CaCO_3$ recrystallization rate. The Yingbazar soils generally had higher EC than the Aksu soils.

4.4. Extrapolation of $CaCO_3$ recrystallization rates and estimation of periods of pedogenic carbonate formation

We accepted that the CO_2 concentration in the soil remains high, leading to a similar permanent exchange with primary carbonates as in a previous experiment (Kuzyakov et al., 2006). We made assumptions of both (1) an exponential decrease in the remaining primary carbonate (Gocke and Kuzyakov, 2011; Gocke et al., 2010b, 2011b, 2011c, 2012; Kuzyakov et al., 2006) and (2) a linear change in the remaining primary carbonate (Gocke et al., 2013) (Fig. 6). With an exponential decrease as the model, the $CaCO_3$ can be recrystallized repeatedly (Eq. (5)), which shows that not only the primary $CaCO_3$ but also the secondary $CaCO_3$ can recrystallize with the CO_2 produced by rhizosphere respiration. With a linear decrease, the recrystallized $CaCO_3$ will not be recrystallized again (Eq. (6)), which is not very realistic but can suggest the shortest period necessary for full $CaCO_3$ formation.

$$CaCO_3(t) = 100 \times e^{-t \times \text{Rate}} \tag{5}$$

$$CaCO_3(t) = 100 - 100 \times \text{Rate} \times t \tag{6}$$

where Rate is the carbonate recrystallization rate (per year) and t is the time (years).

In the case of the exponential approach (Eq. (5)), 95% of full carbonate recrystallization takes approximately 200, 15, and 1000 years in Yingbazar saline soil (YSal) at CO_2 concentrations of 0.04%, 0.4% and 4%. In Aksu alkaline soil, recrystallization takes approximately 300, 30, and 4000 years, respectively (Fig. 6). These extrapolations clearly show that very long periods are necessary for the formation of pedogenic carbonates.

The highest CO_2 concentration of 4% can shorten the $CaCO_3$ formation time by a factor of 10 and 100 compared to the lower CO_2 concentrations of 0.4% and 0.04%, respectively. In the case of the linear approach (Eq. (6)), 95% of full carbonate recrystallization of the remaining primary carbonates takes approximately 50, 5, and 0.3 thousand years in Yingbazar saline soil (YSal) at CO_2 concentrations of 0.04%, 0.4% and 4%; by contrast, this process takes 100, 10, and 1000 years in Aksu alkaline soil (AAlk), respectively (Fig. 6).
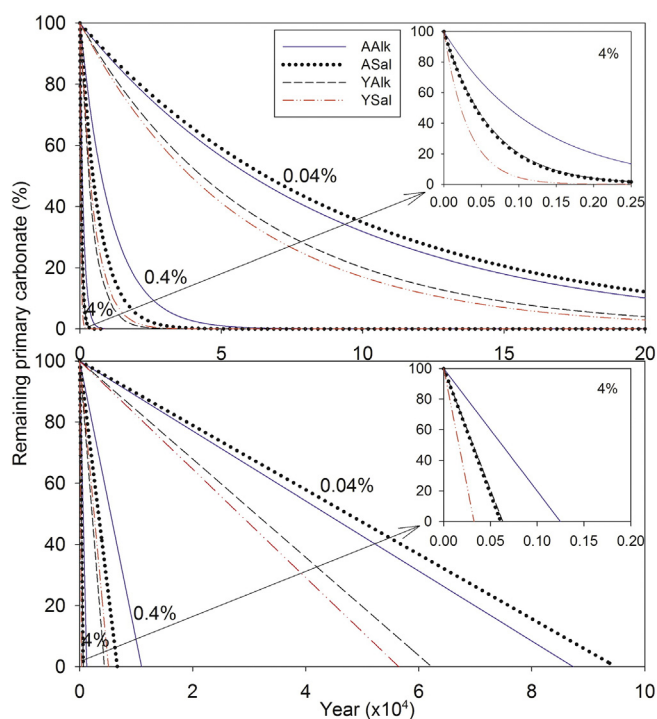
Fig. 6. Decrease in the amount of remaining primary carbonate, depending on three initial CO_2 concentrations (0.04%, 0.4%, and 4%) in four soils (AAlk, ASal, YAlk, and YSal). AAlk: Aksu alkaline soil; ASal: Aksu saline soil; YAlk: Yingbazar alkaline soil; YSal: Yingbazar saline soil.

In a warm climate, temperature substantially increases the annual CO_2 release (Atkin et al., 2000), and respiration by roots, as well as mineralization of C released in the rhizosphere, is more temperature-sensitive than the mineralization of organic matter in the soil (Boone et al., 1998). Soil carbonate cannot be recrystallized with atmospheric CO_2 because the CO_2 flow is from soil to atmosphere. Instead, a mixture of soil C sources from roots and microorganisms causes recrystallization. Higher soil CO_2 concentrations were discovered during the growing season (Fischer et al., 2010) and near roots (Gocke and Kuzyakov, 2011; Gocke et al., 2011b; Zhao and Zhao, 2012). This is because of lower biological activity during the winter period. The carbonate recrystallization rates were different for plant species: 2.9×10^{-5} day^{-1} (Kuzyakov et al., 2006) and 3.2×10^{-5} day^{-1} for wheat (Gocke et al., 2011b), 2.9–3.1×10^{-6} day^{-1} for maize (Gocke and Kuzyakov, 2011), and 2.8×10^{-5} for *Lolium perenne* (ryegrass) (Gocke et al., 2011b) in the
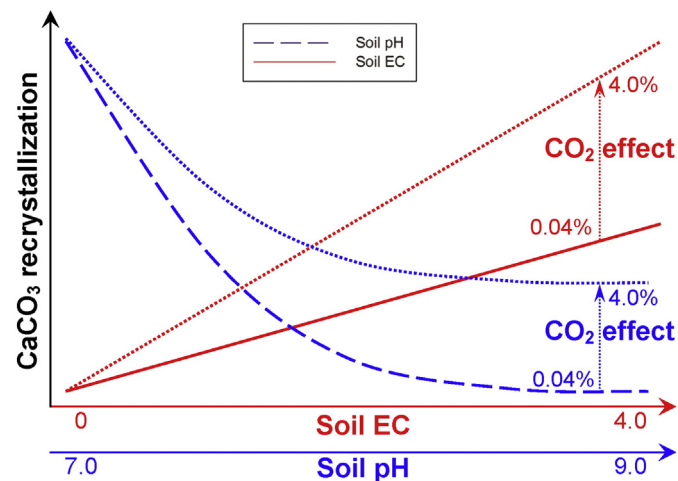
same loess soil (Table 2). Higher CO_2 concentrations allow quicker recrystallization. Respiratory activities of roots and microorganisms can force CO_2 exchange. Contrary to our hypothesis, recrystallization is favored in saline over the alkaline soils.

5. Conclusions

There is a strong exchange between CO_2 and $CaCO_3$ in soil, especially at high CO_2 concentrations. Consequently, all biological activities in soil, increasing CO_2 concentration due to respiration, strongly stimulate $CaCO_3$ recrystallization and thus, accelerate the periods of pedogenic carbonate formation. The highest CO_2 concentration of 4% shortened the complete (95%) recrystallization period of carbonates by a factor of 10 to 100 compared to lower CO_2 concentrations. The average carbonate recrystallization increased with salinity (i.e., higher EC) but decreased with pH. This at least partly explains the CO_2 influx from the atmosphere into the saline and alkaline soils of deserts and semi-deserts.

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