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Cation exchange retards shell carbonate recrystallization: consequences for dating and paleoenvironmental reconstructions

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ABSTRACT

The radiocarbon method has been frequently used to date mollusk shell carbonate. The accuracy of estimated ages, however, depends on the degree and completeness of shell carbonate recrystallization. Although the effect of contamination of the shell $CaCO_3$ with environmental carbon (C) is well known, the role of Ca^{2+} in diagenetic processes remains unclear. Addition of young C to shells during diagenesis occurs in soil solution, where the Ca^{2+} concentration is in equilibrium with exchangeable Ca^{2+} and/or weathering of Ca-bearing minerals. While the exchange process takes place within seconds, the dissolution equilibrium requires longer timescales (on the order of months). It has therefore been hypothesized that the dissolution and recrystallization of shell carbonate in soils with higher cation exchange capacity (CEC) should proceed slower compared to those with low CEC. The objective was to determine the effects of soil CEC and exchangeable cations on shell carbonate recrystallization using the ^{14}C labeling approach. Shell particles of the bivalve *Protothaca staminea* were mixed with carbonate-free sand ($CEC = 0.37\ cmol^{+}\ kg^{-1}$) (Sand), a loamy soil ($CEC = 16\ cmol^{+}\ kg^{-1}$) (Loam) or the same loamy soil saturated with KCl, where exchangeable cations were replaced with K^{+} (Exchanged). The high-sensitivity ^{14}C labeling/tracing approach was used to determine carbonate recrystallization rates. Shell carbonate recrystallization after 120 days in Loam and Exchanged (0.016 and 0.024 mg $CaCO_3$, respectively) showed one order of magnitude lower recrystallization than in Sand (0.13 mg $CaCO_3$). A high level of soil exchangeable Ca^{2+} decreased the solubility of shell carbonate and consequently its recrystallization because the exchange is faster than dissolution. Therefore, soil CEC and cation composition are determinant factors of shell carbonate recrystallization. Shells in soils with low CEC may undergo more intensive recrystallization; hence they may need further pretreatments before the dating procedure.

1. Introduction

The radiocarbon (Δ^{14}C) age of shell carbonate has a long history of application for dating purposes (Arrhenius et al., 1951; Kulp et al., 1951; Scholl, 1964; Douka et al., 2010; Pigati et al., 2010). To achieve reliable dating, however, shell carbonate should behave as a closed system in respect to C after deposition in soils (Pigati et al., 2010). An addition of merely 10–15% modern C from the embedding soil matrix, for example, may lead to an 11 ka age difference in ca. 30 ka year-old shells (Webb et al., 2007). Modern C addition to shell carbonate occurs by precipitation of secondary carbonate minerals on shells, when the solubility constants are achieved in soil solution. Therefore, the ions' concentration in soil solution will be the key determinant of secondary carbonate formation rates (Pate et al., 1989). The Δ^{14}C of these newly formed secondary carbonates, however, will differ from the Δ^{14}C of shell carbonate and reflect the time of precipitation rather than shell carbonate age. Thus, a complete understanding of the processes by which secondary carbonate can become incorporated into shell material is critical for evaluating the veracity of shell ^{14}C ages.

Several approaches have been proposed to solve the problem of ^{14}C contamination in radiometric dating of biogenic carbonates in soils and sediments. The non-modified carbonate can be mechanically separated from the newly-formed fraction and be dated thereafter (Douka et al., 2010). Usually, however, the risk of encountering diagenetically altered carbonate is assessed by comparing the measured ^{14}C ages of carbonate with the known ages of other, independent sources (Pigati et al., 2004, 2013; Pustovoytov and Riehl, 2006; Magee et al., 2009). Furthermore, the rate of carbonate recrystallization in soil can be estimated experimentally by ^{14}C-labeling of CO_2 under controlled conditions (Kuzyakov et al., 2006; Gocke et al., 2012). The latter method offers a possibility of studying the effects of recrystallization on ^{14}C contamination of carbonates within a relatively short time (weeks to months). At the same time,

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precise knowledge of the effects of specific soil properties on carbonate recrystallization is needed to extrapolate experimental results to natural soils and sediments.

Here, we address the effect of the cation exchange capacity (CEC), one of the main inherent soil characteristics, on the diagenetic alteration of shell carbonate using the ^{14}C labeling technique. The concentration of cations, i.e. Ca^{2+}, in soil solution is in equilibrium with the exchangeable Ca^{2+} on surfaces of clay minerals and organic matter and with the dissolution of Ca-bearing minerals such as calcite in shell structure. The concentration of exchangeable Ca^{2+} in soils depends on total clay content and total soil organic matter as well as the mineralogy of dominant clay minerals. $CaCO_3$ solubility in soil solution is controlled by CO_2 partial pressure in soil atmosphere (Karberg et al., 2005) which is usually between 0.15 and 2.5% and may reach even to 12% (in Stolwijk and Thimann, 1957). Therefore, in slightly acidified soil solution i.e. following CO_2 dissolution, the solubility of $CaCO_3$ increases (Aylward, 2007). However, the exchange process is completed within a few seconds to a few days and is faster than dissolution equilibria —months to years (Sears and Langmuir, 1982). Therefore, the exchange process is the main source of cations buffering changes in soil solution chemistry, for example following acidification (Sears and Langmuir, 1982; Norrström, 1995).

Considering that the exchange rate is faster than dissolution, we hypothesized that shell recrystallization will be the slowest in soils with high CEC. This is because cations released from exchange sites will buffer changes in soil solution chemistry before shell carbonate dissolution can reach the equilibrium. Accordingly, shell carbonate undergoes less dissolution and consequently less recrystallization. Here we examine the role of soil matrix CEC on shell carbonate recrystallization using ^{14}C labeling. The objectives were to: (1) determine how soil CEC affects the rate of carbonate recrystallization in shells, (2) clarify whether the elemental composition of cations modifies the recrystallization rates, and (3) underline the consequences for radiocarbon dating and paleoenvironmental reconstructions.

2. Materials and methods

2.1. Matrix materials

Carbonate-free sand particles and a carbonate-free loamy soil were used to examine the effect of CEC on shell carbonate recrystallization (Table 1). Sand particle diameters ranged from 0.5–1.5 mm. The particle size distribution of loamy soil (Loam) was 25.1% clay, 68.4% silt and 6.5% sand.

To examine the effect of cation types at the soil exchange sites and the concentration of exchangeable Ca^{2+} on shell carbonate recrystallization, a subsample of the Loam saturated with 1 N KCl to substitute exchangeable Ca^{2+} with potassium (K). 33 mL of KCl solution was added to 5 g of soil. The suspension was shaken for 5 min followed by 5 min centrifugation in 2500 rpm. After decanting the supernatant, the procedure of KCl addition and centrifugation was repeated two more times. Subsequently, the exchanged soil was washed out 3–4 times with distilled water to remove the remaining chlorine ions (Cl^-) from the soil solution. The presence of Cl^- in the supernatant was tested by adding a few drops of 1 M $AgNO_3$. The absence of white precipitate showed the complete removal of Cl^-. The treated soil (Exchanged) was dried afterward at 105 °C overnight.

Table 1
Exchangeable cations in sand and soil and cation contents in shells.

	Ca^{2+}	K^+	Mg^{2+}	Na^+	CEC
		$mmol^+ kg^{-1}$			
Sand	0.79	0.06	0.17	0.07	3.71
Loam	132	4.21	20.5	0.22	163
Exchanged	19.4	119	4.33	0.26	156
		$mg g^{-1}$			
Shell	370	0.29	0.35	4.80	

2.2. Experimental setup and analyses

300 mg of heated (550 °C) shell particles of Pacific little-neck clams (*Protothaca staminea*) (Table 1) in the size range of 2–2.5 mm were mixed with 7 g of Sand, Loam and Exchanged in 250 mL glass bottles. 1.68 mL of distilled water was added to the Sand as well as 2.37 mL to the Loam and Exchanged to bring the soil moisture to 80% of water holding capacity. Two 1.5 mL plastic vials were placed in the bottles for labeling (see below). The bottles were then sealed air-tight and kept at room temperature for 5, 20, 60 and 120 days.

Following sealing, 0.2 mL of $Na_2^{14}CO_3$ was added to one of the plastic vials. The concentration of $Na_2^{14}CO_3$, considering the air volume in bottles after subtraction of soil and water, was 2% CO_2 partial pressure after neutralizing the $Na_2^{14}CO_3$ by acid. 2% pCO_2 is the common soil pCO_2 in the presence of living roots (Pausch and Kuzyakov, 2012). Afterwards by injecting 0.2 mL of 1 M H_3PO_4 solution into the vial containing $Na_2^{14}CO_3$ solution, the ^{14}C-labeled CO_2 was released into the bottle's air as the first labeling ($t = 0$). The second labeling was done in the same way at day 55 ($t = 55$). The ^{14}C activity at both labeling times was 9.35 kBq in Sand and 6.92 kBq in Loam and Exchanged.

One day before opening the bottles at each sampling date (i.e. 5, 20, 60 and 120 days), 0.4 mL of 1 N NaOH was injected into the second plastic vial to trap the remaining CO_2, i.e. not incorporated in carbonate recrystallization. The amount of recrystallized carbonates on shells and in matrices was calculated, considering the known C amounts added to the bottles, the total added ^{14}C and the measured ^{14}C activity in shells and matrices (Kuzyakov et al., 2006).

After opening of bottles, the matrices were washed with 10 mL of distilled water. The shell particles were removed from the matrices with tweezers and washed ultrasonically to remove any adhering matrix particles. Shell particles as well as the matrix materials were ground into a fine powder. 0.1 g of shell powder and 2 g of matrix materials were acidified to release carbonates as CO_2, which was trapped in 1 M NaOH solution. Then, scintillation cocktail (Rotiszint EcoPlus, Carl Roth, Germany) was added to an aliquot of alkali solutions (i.e. NaOH in plastic vials and NaOH used to trap released CO_2 by acidification of shells and matrices) and washing water. After few hours waiting for chemiluminescence decay, ^{14}C activity was measured by a multi radio-isotope counter (Beckman LS6500, USA). The ^{14}C counting efficiency was at least 70% and the measurement error was 5% at maximum.

Besides the treatments containing shell particles, solely matrix materials with the same water content and labeling procedures were prepared to determine whether carbonate precipitation takes place because of Ca^{2+} release from exchange sites. Recrystallization in these samples, however, was measured just at the end of experiment i.e. after 120 days.

CEC of the matrix materials and the composition of exchangeable cations were measured at each sampling period. CEC and exchangeable cations were determined by percolating soil samples with 100 mL of 1 M NH_4Cl adjusted to $pH = 8.1$ for 4 h (König and Fortmann, 1996) and measuring cations in percolates using an inductively coupled plasma-atomic emission spectrometer (iCAP 6300 Duo VIEW ICP Spectrometer, Thermo Fischer Scientific GmbH, Dreieich, Germany).

The concentration of cations in shell particles (Table 1) as well as the concentration of dissolved ions in matrix solutions at the beginning of the experiment and in the matrix solutions at each sampling date were also determined using an ICP spectrometer.

2.3. Statistics

The statistical analyses were done using STATISTICA 10 (StatSoft Inc., Tulsa, USA). The mean values and standard errors were calculated for 4 replications of each treatment at each sampling period. The significance of differences between the amounts of recrystallized carbonates between treatments at various dates was analyzed using the post-hoc Fisher LSD test at α = 0.05 probability level.

3. Results

The highest shell carbonate recrystallization (Fig. 1, top) during the first labeling was in Sand with an average of 0.043 mg for days 5 and 20, followed by Loam and Exchanged, with 0.010 and 0.003 mg, respectively. During the second labeling, shell carbonate recrystallization in Sand and Exchanged increased, while shell carbonate recrystallization was fairly constant in Loam. The average shell carbonate recrystallization between dates 60 and 120 was 0.131, 0.016 and 0.024 mg in Sand, Loam and Exchanged, respectively.

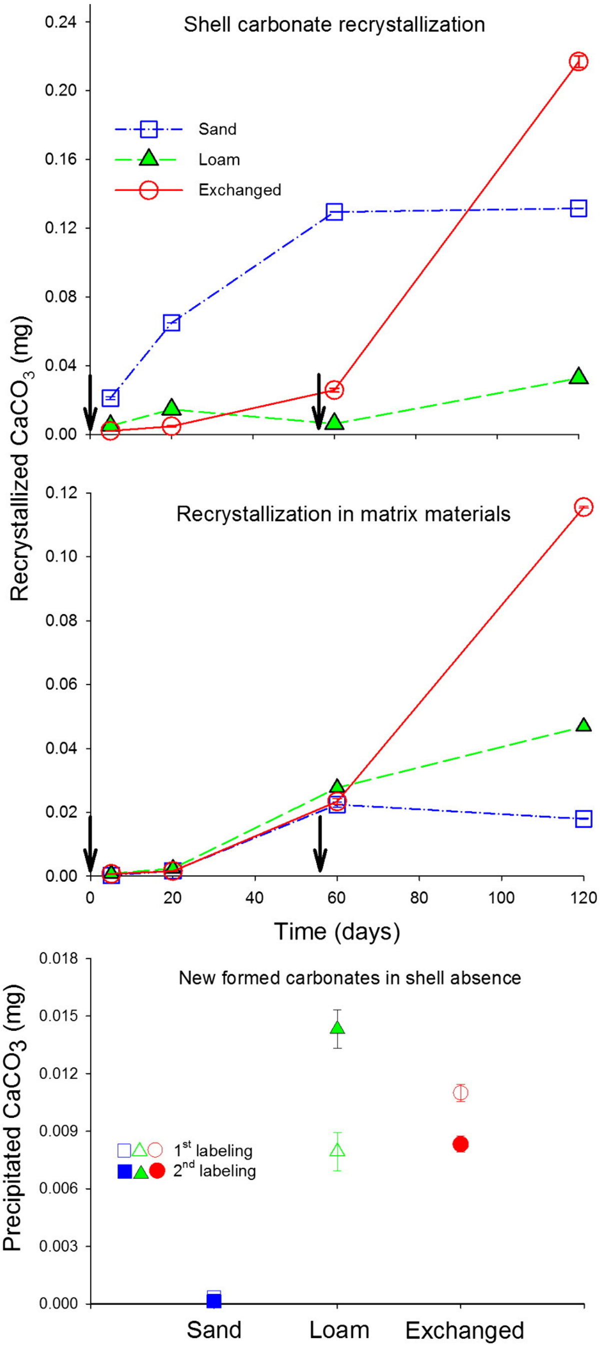

Fig. 1. (top) Carbonate recrystallization of shells in various matrixes. (middle) Carbonate recrystallization inside the matrix materials in the presence of shell particles. (bottom) Carbonate recrystallization inside the matrix materials in the absence of shell particles after 120 days. Black arrows show the time of labeling at the beginning of the experiment and at day 55.

The amounts of precipitated carbonates during first labeling in the presence of shell particles were similar in Sand, Loam and Exchanged (Fig. 1, middle). After the second labeling the precipitated carbonate increased by up to two orders of magnitude in Sand and Exchanged and one order of magnitude in Loam, compared to the first labeling.

Carbonate precipitation was also detected in matrices without the presence of any shell particles (Fig. 1, bottom). The precipitated carbonates in these matrices after 120 days and with one labeling pulse were 0.0004, 0.0079 and 0.0110 mg in Sand, Loam and Exchanged, respectively. After second labeling, the amounts of formerly precipitated carbonates decreased to 0.0001 mg in Sand and 0.0083 mg in Exchanged, whereas in Loam the value increased to 0.0143 mg (Fig. 1, bottom).

The significant increase in soil exchangeable Ca^{2+} was evident in Sand (Fig. 2, top). The values in Loam showed a decreasing trend, while in Exchanged it remained constant (Fig. 2, top). Unlike the exchangeable Ca^{2+}, the exchangeable sodium (Na^+) showed an exponential increase over time in all matrices (Fig. 2, bottom). Considering the negligible amounts of exchangeable Na^+ in the matrices, the source of Na^+ should be solely shells (Table 1). Therefore, soil exchangeable Na^+ was a good indicator showing shell dissolution as well as exchange process.

The concentration of dissolved Ca^{2+} in matrix solutions increased over 120 days in Sand but decreased in Loam and Exchanged (Fig. 3 top). Nonetheless, only the concentrations of dissolved Ca^{2+} in Sand during first labeling were significantly different with Loam and Exchanged. The Na^+ concentration increased exponentially in all solutions, without a difference between matrices at each sampling time (except day 120 for Sand).

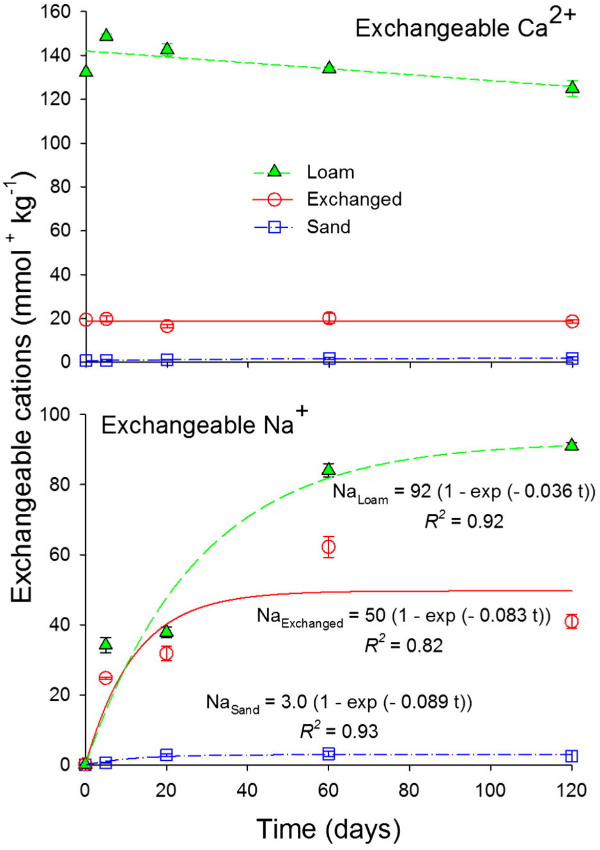

Fig. 2. Changes in concentrations of exchangeable Ca^{2+} (top) and exchangeable Na^+ (bottom) during the 120-day experiment period. Trend lines are shown in different styles.

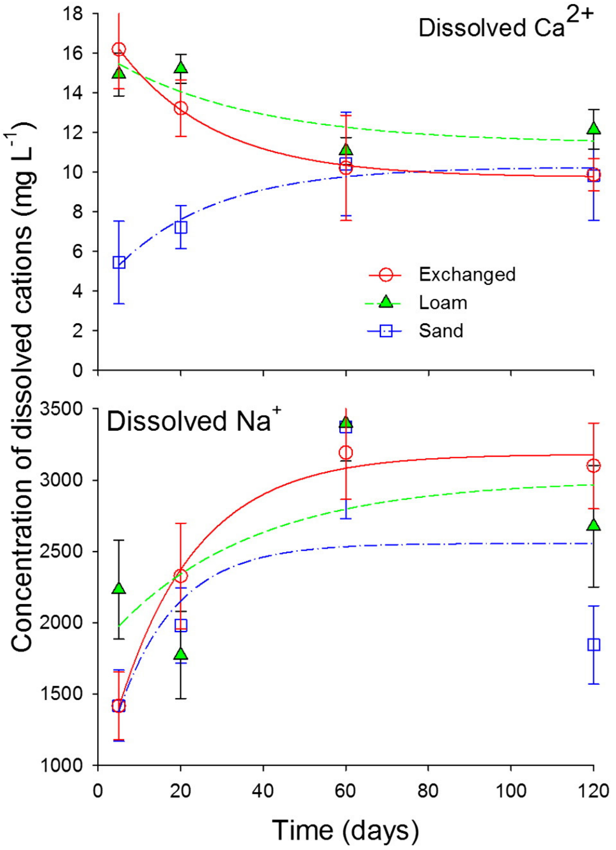

Fig. 3. Changes in concentrations of dissolved Ca^{2+} (top) and dissolved Na^+ (bottom) during the 120-day experiment period.

4. Discussion

Shell carbonate dissolution and release of Ca^{2+} from exchange sites occurred concurrently with changes in soil solution chemistry (Levy, 1980) — in the present case CO_2 release into solution due to an increase in pCO_2 by labeling (Pate et al., 1989). Soil exchangeable Ca^{2+} was released to buffer excess H^+ ions (Norrström, 1995) following CO_2 dissolution. The released exchangeable Ca^{2+} was bound to bicarbonate ions, leading to precipitation of new-formed $CaCO_3$. Hence, more carbonate was precipitated in Loam and Exchanged with higher exchangeable Ca^{2+} compared to Sand (Fig. 1, bottom). Consequently, more carbonate precipitation is expected following further CO_2 dissolution i.e. after the second labeling. Carbonate precipitation, however, increased only in Loam (Fig. 1, bottom). The decline in the content of formerly precipitated carbonates in Exchanged and Sand should solely reflect partial dissolution of these carbonates. Due to lower exchangeable Ca^{2+} in Exchanged and Sand, carbonate dissolution took part in buffering excess H^+ (Levy, 1980; Kelly et al., 1998; Chadwick et al., 2003). As long as Ca^{2+} ions remain in soil solution, more CO_2 in the form of HCO_3^- will be neutralized, i.e. $Ca(HCO_3^-)_2$ in solution vs. solid $CaCO_3$. The effective contribution of carbonates to H^+ buffering is also recognizable by comparing the carbonate amounts precipitated in matrices with and without shells. Precipitation in Exchanged and Sand matrices containing shells was higher than in matrices without shells (Fig. 1, middle and bottom).

Shell carbonate dissolution is confirmed by tracing changes in soil exchangeable Na^+ concentration (Fig. 2, bottom). The exchangeable Na^+ increased in all matrices over 120 days, despite negligible initial concentrations both as exchangeable or dissolved Na^+ (Figs. 2 and 3 bottom, at $t = 0$). Accordingly, the exponential increase of exchangeable Na^+ should be due solely to shell carbonate dissolution and release of dissolved Na^+ into soil solutions. Na is present in mollusk shell structure (Table 1), and concentrations exceeding 2000 ppm are generally indicative of shells from marine environments (Hahn et al., 2012; Findlater et al., 2014; O'Neil and Gillikin, 2014). An increasing Na^+ concentration (Fig. 3, bottom) therefore had to exchange Na^+ with other cations on soil exchange sites (Ferrell and Brooks, 1971; Levy, 1980). Although the concentrations of other elements on soil exchange sites, especially of exchangeable Ca^{2+}, remained nearly constant (Fig. 2, top), Loam and Exchanged with higher CEC showed more exchangeable Na^+ than Sand (Fig. 2, bottom). The lower value in Exchanged vs. Loam, however, reflects the inability to exchange K^+ ions that were fixed in soil clay minerals.

Shell carbonate dissolution and recrystallization were the highest in Sand because it has the lowest CEC. Therefore, more shell carbonate was dissolved to buffer excess H^+ (Porder et al., 2015). An increase in soil CEC and exchangeable Ca^{2+} decreases the solubility of shell carbonate and consequently the recrystallization. This is because exchange processes have faster rates than dissolution (Fig. 4). Following changes in soil solution chemistry, e.g. increasing soil pCO_2, shell carbonate recrystallization increases comparatively slowly in soils with high CEC (Fig. 4). This calls for examining the properties of the environment embedding the shells, especially the total clay content and mineralogy as well as the composition of exchangeable and dissolved cations during sampling for radiocarbon dating. Furthermore, more precise models describing shell carbonate diagenesis are required including soil CEC and exchangeable cation parameters.

Carbonate dissolution rates depend on the $CaCO_3$ saturation state in solution. Any changes in the chemical composition of soil solution are initially buffered by releasing the exchangeable cations (Levy, 1980). Accordingly, soil CEC is the key determinant of carbonate recrystallization rates. The effect of CEC on shell carbonate recrystallization is important for any studies related to paleoenvironment reconstructions based on carbonate $\delta^{13}C$ signatures and radiocarbon dating. This is especially the case in areas where the shell carbonate fraction is the only available proxy, for example in arid regions due to decomposition of organic materials (Zazzo and Saliège, 2011). Furthermore, various types of biogenic carbonates such as bones (Zazzo et al., 2009), eggshells (Janz et al., 2009), teeth (Feakins et al., 2013) and calcified seeds (Pustovoytov et al., 2004) are also frequently used for paleoenvironment reconstructions and dating. These biogenic carbonates may undergo diagenesis as well. Biogenic carbonate diagenesis, however, proceeds at relatively slow rates, making it difficult to study diagenesis rates in short periods

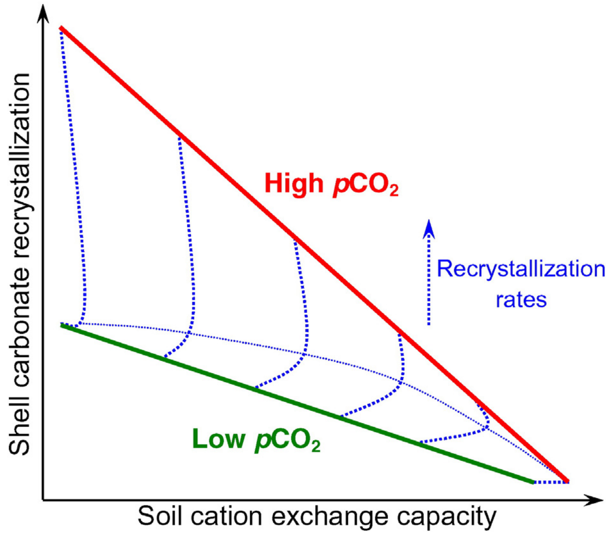

Fig. 4. Shell carbonate recrystallization depending on soil cation exchange capacity and Ca^{2+} concentration: Shell carbonate recrystallization decreases as soil CEC increases (green and red lines). Shell carbonate recrystallization rates in similar time spans increase faster in soils with less CEC with increasing soil pCO_2 (Blue dotted lines).

(Kuzyakov et al., 2006). ^{14}C labeling showed a high potential to trace very small changes in shell $CaCO_3$–C isotopic composition following dissolution and recrystallization. Therefore, ^{14}C labeling may overcome the above limitation, which makes it suited to study the diagenesis dynamics of biogenic carbonates under various environmental conditions. Moreover, ^{14}C labeling can be recommended in investigations related to weathering of Ca-bearing minerals. Tracing ^{14}C activity added as a label to systems similar to the ones in this study, but containing individual minerals instead of shells, may help reveal the weathering rates of such minerals.

5. Conclusion

Shell carbonate dissolution and recrystallization decrease with increasing soil CEC. This is because the equilibrium between exchangeable and dissolved cations will be reached much faster than mineral dissolution, e.g. of $CaCO_3$ in shells. Therefore, the isotopic composition of shells may show less variation than the initial amounts in soils with relatively high CEC. This effect of CEC calls for including parameters such as total CEC and the equilibria between exchangeable and dissolved cations in models predicting shell diagenesis. ^{14}C labeling showed a high potential to trace minor changes in the isotopic composition of shells following diagenesis and thus to better understand diagenesis dynamics. The ^{14}C labeling approach can also be used to determine the weathering rates of other Ca-bearing minerals.

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