



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 CaCO₃ with environmental carbon (C) is well known, the role of Ca²⁺ in diagenetic processes remains unclear. Addition of young C to shells during diagenesis occurs in soil solution, where the Ca²⁺ concentration is in equilibrium with exchangeable Ca²⁺ 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 ¹⁴C 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 ¹⁴C 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 CaCO₃, respectively) showed one order of magnitude lower recrystallization than in Sand (0.13 mg CaCO₃). A high level of soil exchangeable Ca²⁺ 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.

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1. Introduction

The radiocarbon ($\Delta^{14}\text{C}$) 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 $\Delta^{14}\text{C}$ of these newly formed secondary

carbonates, however, will differ from the $\Delta^{14}\text{C}$ 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 ¹⁴C ages.

Several approaches have been proposed to solve the problem of ¹⁴C 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 ¹⁴C 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 ¹⁴C-labeling of CO₂ under controlled conditions (Kuzyakov et al., 2006; Gocke et al., 2012). The latter method offers a possibility of studying the effects of recrystallization on ¹⁴C 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.

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 $\text{Na}_2^{14}\text{CO}_3$ was added to one of the plastic vials. The concentration of $\text{Na}_2^{14}\text{CO}_3$, considering the air volume in bottles after subtraction of soil and water, was 2% CO_2 partial pressure after neutralizing the $\text{Na}_2^{14}\text{CO}_3$ by acid. 2% $p\text{CO}_2$ is the common soil $p\text{CO}_2$ 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 $\text{Na}_2^{14}\text{CO}_3$ 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 $\text{pH} = 8.1$ 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

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	

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