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Recrystallization of shell carbonate in soil: ^{14}C labeling, modeling and relevance for dating and paleo-reconstructions

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ABSTRACT

Mollusk shells are commonly present in a broad array of geological and archaeological contexts. The shell carbonate can serve for numerical age determination ($\Delta^{14}C$) and as a paleoenvironmental indicator ($\delta^{18}O$, $\delta^{13}C$). Shell carbonate recrystallization in soils, however, may re-equilibrate the carbon (C) isotopic signature with soil CO_2. The equilibration dynamics remain poorly understood because of the absence of suitable experimental approaches. Here we used the artificial ^{14}C-labeling technique to study the process of shell carbonate recrystallization as a function of time.

Organic-free and organic-containing shell particles of *Protothaca staminea* were mixed with loess or a carbonate-free loamy soil. The mixtures were placed in air-tight bottles, where the bottle air containing $^{14}CO_2$ ($pCO_2 = 2\%$). The ^{14}C activity of shells was measured over time and related to the recrystallization of shell carbonate.

Recrystallization of shell carbonate already began after one day. The recrystallization rates were 10^{-3}% day^{-1} in organic-containing shell embedded in soil and $1.6 \cdot 10^{-2}$% day^{-1} in organic-free shells in loess. Removal of organic compounds increased shell porosity, and so, increased the contact surface for exchange with soil solution. Organic-free shells recrystallized much faster in loess (0.56% in 56 days) than in other treatments. Recrystallization was 2 to 7 times higher in loess (in the presence and absence of organic compounds, respectively) than in carbonate-free soil. Loess carbonate itself can recrystallize and accumulate on shells, leading to overestimation of shell carbonate recrystallization. A model for shell carbonate recrystallization as a function of time was developed. The model considers the presence or absence of organic compounds in shell structure and geogenic carbonates in the embedding matrix. The model enabled all results to be fitted with $R^2 = 0.98$.

The modelled time necessary for nearly full recrystallization (95% of shell carbonate) was 88 years for organic-free shells in loess and up to 770 years for organic-containing shells in carbonate-free soil. After this period, the original isotopic signature will vanish completely and will be replaced by a new $\delta^{13}C$ and $\Delta^{14}C$ signature in the shell structure. Thus, shell carbonate recrystallization may proceed relatively rapidly in terms of geologic time. This is necessary to consider in the interpretation of dating results and paleoenvironmental reconstructions.

1. Introduction

Mollusk shells are among the most common findings at archaeological sites (Thomas, 2015, and references therein). Their carbonate fraction represents a useful paleoenvironmental and chronological proxy (Pigati et al., 2004; Pigati et al., 2010; Xu et al., 2010; Pigati, 2013; Yanes et al., 2013). The $CaCO_3$ fraction of shells can be especially useful for such investigations if the preservation of organic compounds is poor, such as in arid environments or coastal regions (Russo et al., 2010; Zazzo and Saliège, 2011). Under such circumstances, shell carbonate can be the only alternative to paleoenvironmental and chronological studies (Chappell and Pollach, 1972; Újvári et al., 2014).

Mollusk shells are usually well preserved in sediment after burial (Pigati et al., 2004; Pigati et al., 2010), but their elemental and/or isotopic composition can be influenced by recrystallization processes (Webb et al., 2007; Collins, 2012). Recrystallization occurs following soil dryness, increased Ca^{2+} concentration and/or a drop in soil CO_2 partial pressure (Chappell and Pollach, 1972; Russo et al., 2010). Since the amount of soil CO_2 and its isotopic composition is in equilibrium with CO_2 respired by roots and rhizosphere organisms, the isotopic signature ($\delta^{13}C$, $\Delta^{14}C$) of recrystallized carbonate will equilibrate with soil CO_2 (Cerling et al., 1989). In this case, the $\delta^{13}C$ in recrystallized carbonate in soil will save fingerprints of dominant vegetation during the recrystallization phase and the $\Delta^{14}C$ will reflect the age of the recrystallization event. The presence of even a few percent of modern C can significantly affect the results of paleoenvironmental and chronological studies based on shell carbonate (Webb et al., 2007). For instance, the presence

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of 10–15% of modern C as carbonate in 30 ka-old shells leads to an 11 ka error in age (Webb et al., 2007).

Considering the significant effect of modern C on radiocarbon dating, various techniques have been proposed to assure the fidelity of geochemical signals. Evidence of recrystallization can be detected using optical and electron microscopes (Cochran et al., 2010), X-ray analysis (Chappell and Pollach, 1972; Piepenbrink, 1989; Cochran et al., 2010), trace element measurements (Shemesh, 1990; Oliver et al., 1996; Cochran et al., 2010) and density analysis (Russo et al., 2010). It is also advisable to verify the consistency of measured ages with other datable materials or stratigraphic positions (Bonadonna et al., 1999; Webb et al., 2007; Janz et al., 2009). The selected samples should also be subjected to physical and chemical pre-treatments such as soaking in acid or mechanical abrasion, to reduce the influence of suspected recrystallization (Krueger, 1991; Bezerra et al., 2008).

Despite the progress in laboratory methods, the dynamics of shell carbonate recrystallization in sedimentary environments and its affecting factors remain poorly understood. Furthermore, in some cases the proposed techniques for sample selection may have drawbacks. In certain environments the recrystallized carbonate could be aragonitic (Webb et al., 2007). Analysis with a scanning electron microscope is restricted to a small portion of the samples, which risks overlooking recrystallized carbonates when these are few (Douka et al., 2010), especially when the recrystallized carbonate is patchily distributed (Webb et al., 2007).

In soils, shell carbonate may be found very well preserved (i.e. without recrystallization) or up to nearly completely recrystallized (Chappell and Pollach, 1972). Various biological and environmental parameters seem to control the rate of dissolution and subsequently recrystallization of shell carbonates (Yates et al., 2002). These include porosity (Nielsen-Marsh and Hedges, 1999; Collins, 2012) and organic compounds present in the shell structure (Hall and Kennedy, 1967; Nielsen-Marsh and Hedges, 2000), microbial attack (Nielsen-Marsh and Hedges, 1999; Janz et al., 2009), soil pH (Piepenbrink, 1989; Berna et al., 2004), presence of geogenic carbonates (GeoC) for example limestone (Yates et al., 2002; Berna et al., 2004), water availability (Douka et al., 2010; Cochran et al., 2010) and water circulation (Forman and Polyak, 1997), temperature (Douka et al., 2010) and age (Chappell and Pollach, 1972).

The dissolution of shell carbonate can begin immediately after burial (Fairbridge, 1967) and be associated with changes in elemental composition (Walls et al., 1977; Ragland et al., 1979) and exfoliation (Yates, 1986). Dissolution is related to surface area (Nielsen-Marsh and Hedges, 1999; Collins, 2012), which increases with pore space of the skeletal structure (Henrich and Wefer, 1986; Nielsen-Marsh and Hedges, 2000). Therefore, recrystallization may occur both at the surface and/or inner parts of a shell fragment (Yates, 1986). Exfoliation and oxidation of organic compounds causes gaps and pore spaces in the shell structure, making it more susceptible to recrystallization (Yates, 1986; Webb et al., 2007). In isotopic studies, heating of samples is usually used to eliminate organic compounds (Dauphin et al., 2006). Heating also causes some crystallographic changes in shell structure (Collins, 2012). The occluded water will be removed (Lécuyer and O'Neil, 1994) and trace elements become mobile (Lécuyer, 1996; Dauphin et al., 2006). Therefore, heating increases shell porosity (Collins, 2012) and thus promotes recrystallization. Recrystallization on the shell surface may not merely reflect shell carbonate dissolution. If other source(s) of carbonate (e.g. GeoC) are present in the embedding matrix or if soluble Ca is available, then carbonate may precipitate on the shell surface from external sources as well (Yates et al., 2002; Prendergast and Stevens, 2014). As a consequence, shells embedded in calcareous soils may be contaminated by secondary carbonate, which can exhibit a higher susceptibility to recrystallization (Forman and Polyak, 1997).

The low solubility of calcium carbonate ($K_{sp} = 10^{-9}$ at 25 °C) (Robbins, 1985) and its low recrystallization rate complicate experimental research on shell carbonate recrystallization under controlled laboratory conditions. Recently, the sensitive technique of ^{14}C labeling (Kuzyakov et al., 2006; Gocke et al., 2010; Gocke et al., 2011) has been shown to help understand the processes and dynamics of recrystallization and its effects on the C isotopic composition of shell carbonate. This technique is based on $^{14}CO_2$ labeling of the soil atmosphere and subsequent tracing of ^{14}C activity in a carbonate sample in the soil. The method enables the amount of recrystallized carbonate and rate of recrystallization to be calculated. In this study we 1) determine the recrystallization of shell carbonate as a function of time, 2) investigate the effect of geogenic carbonates in soil on shell carbonate recrystallization rates, and 3) evaluate the effect of organic compounds on recrystallization. Based on the experimentally measured recrystallization, we discuss the consequences for dating and paleoenvironmental reconstructions based on the C isotopic composition of shell carbonate.

2. Material and methods

2.1. Matrix materials and shells

Loess deposits and a loamy soil were chosen as matrix materials. Loess and soil were collected from a single profile in an open mine in Nussloch, SW Germany (49.19 N, 8.43 E, 217 m asl. (Kuzyakov et al., 2006)). The soil was collected from the A horizon at a depth of 0.1 m (Table 1) and the loess from 10 m depth. The loess comprised 29.8% $CaCO_3$ equivalent and 0.19% organic carbon content with silt loam as particle size distribution (for further information about loess see (Antoine et al., 2009). Loess and soil samples before beginning the experiment were air dried and sieved through a 2 mm pore size screen.

Pacific little-neck clams (*Protothaca staminea*) were selected as shell materials. The shells were collected from the North Sea coast in northwest Germany (53.68 N 6.99 E). The shells were washed carefully with distilled water ultrasonically to exclude the contaminants and dried at 60 °C overnight. The dried shells were broken to small particles with a hammer and sieved to a particle size ranging from 2 to 2.5 mm. To examine the effects of organic compounds on shell carbonate recrystallization rate, half of the shells were heated to 550 °C in a furnace for 3 h to eliminate the organic compounds (Table 2).

2.2. Experiment setup

300 mg (16–20 particles) of organic-containing and organic-free shells were mixed with 7.8 g of loess or soil and packed into 25 mL glass bottles with an inner surface area of 7.07 cm^2. The bulk density of loess and soil in bottles were 1.1 g cm^{-3}. The depth of loess and soil in bottles was 1 cm hence led to equal CO_2 diffusion in the whole

Table 1
Chemical and physical properties of the soil.

Texture	$pH_{1:1}$	$CaCO_3$ content	Organic matter	Cation exchange capacity	Exchangeable cations			
		%			Ca^{2+}	Mg^{2+}	K^+	Na^+
					$cmol^+ kg^{-1}$			
Silty clay loam	6.8	–	1.1	16.3	13.2	2.05	0.42	0.02

Table 2
Elemental composition of shell carbonates before and after organic compounds elimination by heating at 550 °C.

Elemental composition	Al	Ca	Fe	K	Mg	Mn	Na	P	S
	mg g^{-1}								
Organic-containing shells	0.02	365	0.54	0.25	0.35	0.02	4.81	0.31	0.71
Organic-free shells	0.03	370	0.60	0.29	0.39	0.02	4.94	0.33	0.75

sample. Thereafter, 1.97 mL distilled water was added to each bottle. The water content corresponded to 60% of the saturated water content of loess and soil. Two plastic vials (0.5 mL) were also placed into each bottle (Fig. 1): one for the labeling and the second for removal of remaining CO_2 (see Section 2.4), and the bottles were sealed air tight. The experiment therefore included four treatments:

a) Organic-containing shells in Loess (Org + loess)
b) Organic-free shells in Loess (NoOrg + loess)
c) Organic-containing shells in soil (Org + soil)
d) Organic-free shells in soil (NoOrg + soil)

2.3. Labeling technique and sampling

^{14}C labeled Na_2CO_3 (0.2 mL, 0.9 kBq) was injected by syringe into one of the vials in each bottle (Fig. 1). Injecting H_3PO_4 (0.07 M) into the vial containing $Na_2^{14}CO_3$ released the $^{14}CO_2$. The concentration of ^{14}C in shells was negligible comparing to the added ^{14}C. Therefore, the initial ^{14}C of shells has no effect on the measured and calculated results. The partial pressure of CO_2 (pCO_2) in bottles was 2% which is the common CO_2 concentration at presence of roots and microbial respiration in soils (Pausch and Kuzyakov, 2012). The necessary amount of $Na_2^{14}CO_3$ to reach the mentioned pCO_2 was calculated considering the ideal gas law (1 mol = 22.4 L). The air volume was determined by subtracting the volume of matrix particles and the added water from the total volume of bottle. The labeled samples were incubated for time periods of 1, 3, 10, 21 and 56 days at room temperature. At the end of each period, 0.4 mL of 1 M NaOH solution was injected into the second vial to absorb CO_2 in the bottle's air. After one day of CO_2 absorption, the bottles were opened. Loess and soil along with shell particles were washed with 10 mL of slightly alkalinized distilled water to remove dissolved organic (DOC) and inorganic (DIC) carbon. Then the samples were let dry at 60 °C overnight. Afterward the shell particles were separated from the matrixes using tweezers. To ensure that no loess or soil materials remained on the shell surface, the shell particles were washed again ultrasonically and dried at 60 °C. Dried shell particles were then ground to fine homogenized powder.

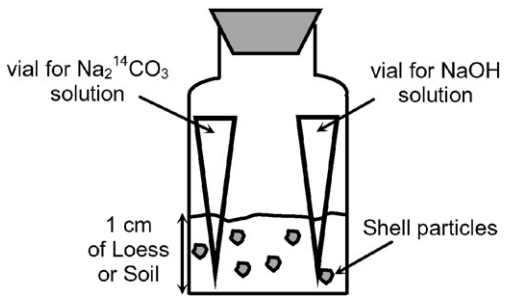

Fig. 1. The experiment layout and the labeling technique. $^{14}CO_2$ was released by injecting H_3PO_4 into the vial containing $Na_2^{14}CO_3$. The $^{14}CO_2$ remaining at the end of the recrystallization period (not participated in recrystallized carbonate) was trapped before each sampling by adding NaOH into the second vial. The H_3PO_4 was injected by syringe through the septa at the beginning of labeling, and NaOH injected at the end of labeling.

2.4. ^{14}C analyses

The ^{14}C activity was quantified in five carbon pools: shells, loess and soil, soluble phase (DIC and DOC), remaining CO_2 in the bottle's air, and the remaining labeling solution. This measurement enabled us to calculate the budget and distribution of added ^{14}C in the samples.

The carbonate in shell particles, loess and soil was released as CO_2 by adding H_3PO_4 to an aliquot of shell particles (0.1 g), loess (0.5 g) and soil (2.0 g). The released CO_2 was trapped in 1.5 mL of 1 M NaOH solution overnight. Adding phenolphthalein to an aliquot of this NaOH solution clarified if the NaOH solution was not completely neutralized by absorption.

An aliquot of the above-mentioned alkali solutions as well as solutions containing dissolved C and labeling remaining were mixed with scintillation cocktail (Rotiszint EcoPlus, Carl Roth, Germany). After the chemiluminescence decayed, the ^{14}C activity of solutions was measured using a multi radio isotope counter (Beckman LS6500, USA). The ^{14}C counting efficiency was at least 70% and the measurement error was 5% at the maximum.

2.5. Calculations and statistical analyses

Considering the total amount of C and total ^{14}C activity added to the bottles, the measured ^{14}C activity in NaOH solutions related to the shells, loess and soil will reveal the amount of C recrystallized as carbonate on shells, loess and soil, respectively. The ^{14}C activity was recalculated as a percentage of the measured ^{14}C activity in relation to the total ^{14}C added to the bottles and also as the amount of recrystallized carbonate (mg) on shell particles, loess and soil. The experiment was done with 4 replications for each sampling period. The mean values, standard errors and regression lines were calculated and drawn using SigmaPlot 12.0 (Systat Software Inc., California, USA). The significance of differences between recrystallization amount of various treatments was calculated by post-hoc Fisher LSD test at $\alpha = 0.05$ error probability level (STATISTICA 10, StatSoft Inc., Tulsa, USA).

3. Results

As expected, the highest ^{14}C activity was measured in air bottle CO_2 for all treatments except NoOrg + Loess (Fig. 2). The highest ^{14}C activity for NoOrg + Loess was instead in the loess. ^{14}C activity was generally higher in the loess than the shell particles (Fig. 2). ^{14}C activity in the shells, however, increased continuously with time.

The amount of recrystallized matrix carbonate was 0.51 mg in NoOrg + loess after two months, while the value for Org + loess was 0.05 mg (Fig. 3). Recrystallization in soil was calculated as 0.0038 to 0.0041 mg.

The recrystallization of shell carbonate already took place on the first day and increased exponentially with time (Fig. 4). The values in the loess were 2 to 7 times higher (for Org + loess and NoOrg + loess, respectively) than for shells in the carbonate-free soil. Removing organic compounds from the shell material increased recrystallization of shell carbonate. Therefore, the difference between the amounts of recrystallization in organic-containing and organic-free shells increased as a function of time. The highest measured recrystallization rate for 300 mg shell carbonate was $1.6 \cdot 10^{-4}$ day^{-1} in NoOrg + loess, while the lowest was $1.0 \cdot 10^{-5}$ day^{-1} in Org + soil. The presence of organic compounds in the shell decreased the recrystallization rates by a factor of 4 in loess and 2.6 in soil. Shell carbonate recrystallization after two months in loess was 0.56% in organic-free shells and 0.14% in organic-containing shells. In soil, recrystallization was 1.2 times higher for the organic-free shells (ca. 0.08%) than for organic-containing shells (0.06%).

Theoretically, the entire shell fragment can undergo dissolution and recrystallization. The higher the recrystallization rate, the less non-recrystallized or original shell carbonate will remain. Therefore, after two months, NoOrg + Loess showed the lowest (99.44%) and

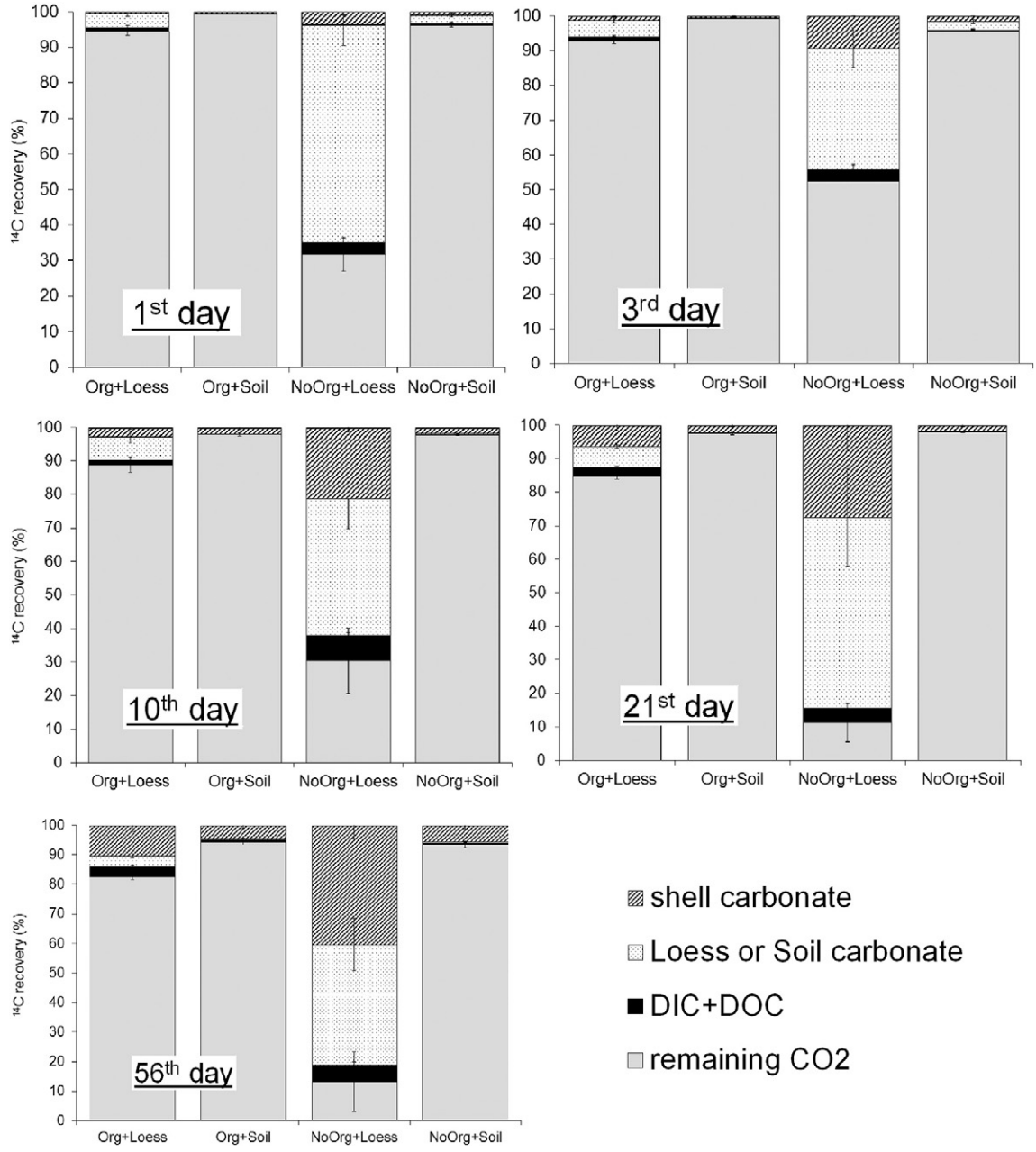

Fig. 2. The distribution of measured ^{14}C activity between phases depending on time after labeling. Bar lines show standard errors.

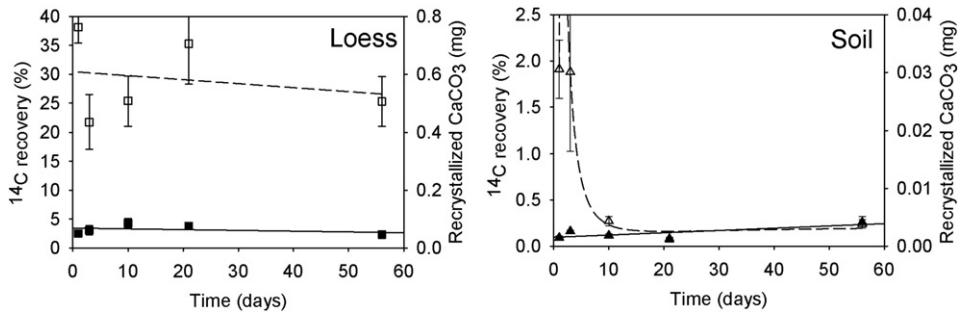

Fig. 3. ^{14}C activity and recrystallized amounts of $CaCO_3$ in loess and soil depending on recrystallization time. The filled and open symbols refer to the shells containing and free of organic compounds, respectively. Bar lines show standard errors. Note the different scales of Y axes.

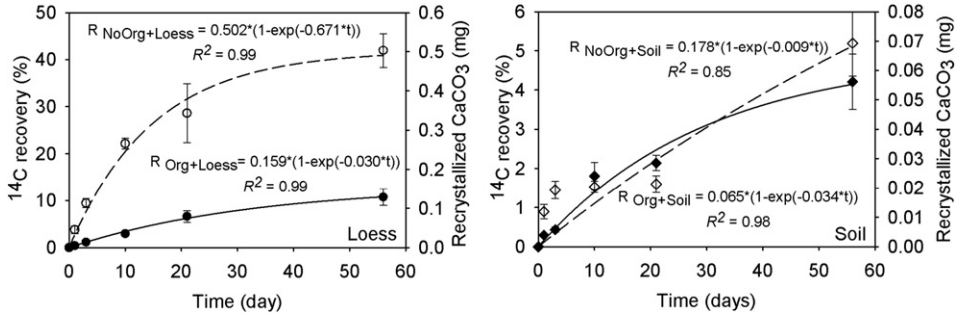

Fig. 4. ^{14}C activity and recrystallized amounts of $CaCO_3$ on shells in loess and soil as a function of time (R_i). The filled and open symbols refer to the shells containing and free of organic compounds, respectively. Bar lines show standard errors. Note the different scales on Y-axes.

Org + Soil the highest (99.94%) amounts of remaining, non-recrystallized shell carbonate (Fig. 5). Carbonate recrystallization is exponential with time (Kuzyakov et al., 2006) and, according to the equation, never reaches 100%. We therefore calculated the time necessary for recrystallization of 95% of the shell carbonate, and considered this as the time for full recrystallization. It is important to stress that for this assessment, the recrystallization is considered as an uninterrupted and uniform process. The exponential equations calculated from our experimental results leveled off at values far from complete recrystallization at least in NoOrg + Loess. However, to have an estimation of full recrystallization, fitted exponential equations were extrapolated to 5% remaining shell carbonate. This showed the time necessary for full recrystallization of shell carbonate in NoOrg + loess was around 90 years (Fig. 5, b). The corresponding values for shell carbonate in Org + Loess, NoOrg + soil and Org + soil were respectively around 320, 700 and 770 years (Fig. 5, c and d).

4. Discussion

4.1. Matrix carbonate recrystallization in loess and carbonate-free soil

Recrystallization of matrix carbonate was higher in the loess than in the carbonate-free soil. Recrystallization in loess was expected because it contained ca. 30% $CaCO_3$ (i.e. GeoC). The dissolution of GeoC and isotopic re-equilibration with labeled $^{14}CO_2$ during recrystallization introduced ^{14}C into the loess carbonate (Gocke et al., 2010). Unexpectedly, we also measured ^{14}C in the matrix of carbonate-free soil following shell carbonate dissolution and recrystallization.

Recrystallization in NoOrg + soil was higher in the first 10 days (Fig. 3, Soil). This confirms the results of Lécuyer (1996), who showed that heating (>400 °C) increases the release of Ca^{2+} from shell structure into to the leachate (i.e. deionized water). The released Ca^{2+} into the soil solution and consequently recrystallization inside the soil, however,

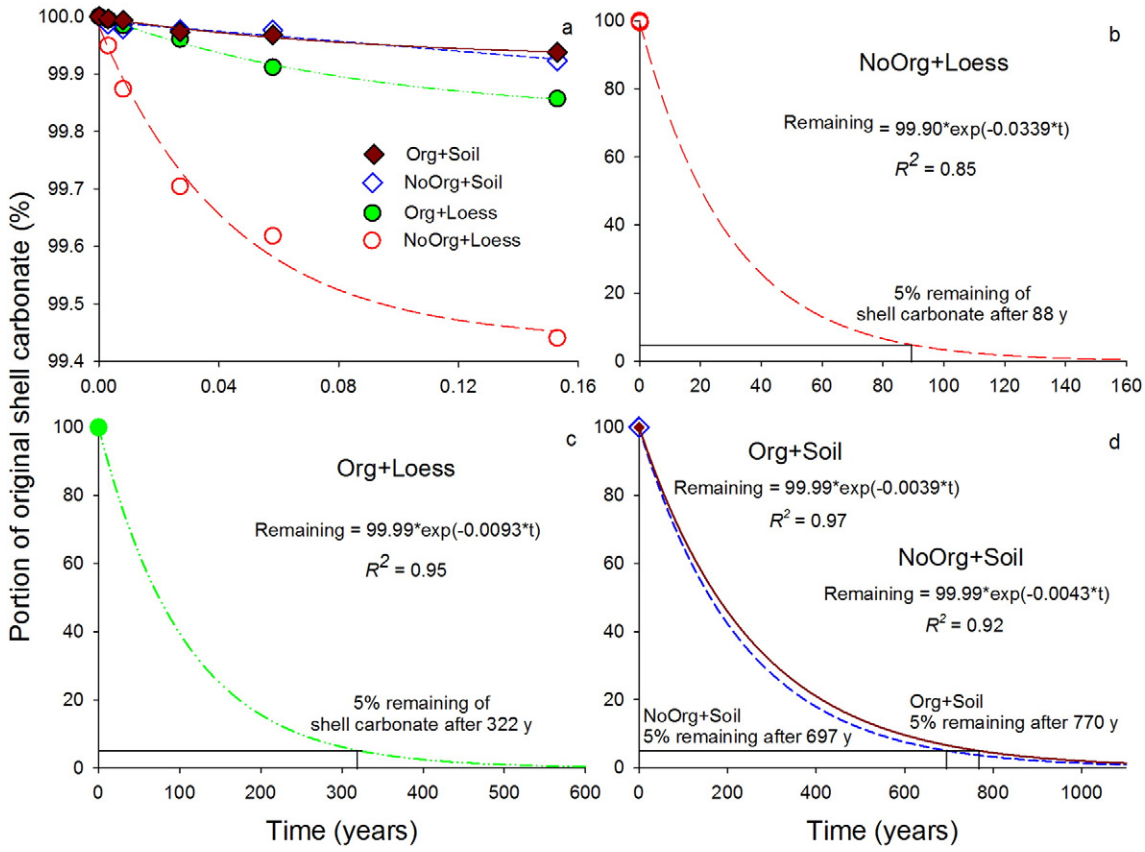

Fig. 5. (a) Percentage of shell carbonate remaining not-recrystallized after 56 days, (b, c and d) the calculated time for full recrystallization of shell carbonate containing or free of organic compounds in loess or soil (95% recrystallization assumed as full recrystallization). Circles and diamonds refer to shells in loess and loamy soil, respectively. Filled and open symbols show shells containing and free of organic compounds, respectively. The model line for each treatment is shown in different line styles.

rapidly decreased with time (Fig. 3, Soil). This can be explained by the following. (1) The recrystallized carbonate had been dissolved in the solution and later recrystallized on shells instead of the soil. A higher rate of dissolution for recrystallized carbonate than shell carbonate is expected because of the very fine particle size, and hence large surface area, of recrystallized carbonate (Nordt et al., 1998). (2) The Ca^{2+} ions of recrystallized carbonate had been exchanged with other ions (e.g. K^+ or Na^+) on exchange sites of clay minerals or SOM. Therefore, other forms of carbonate such as Na_2CO_3 or K_2CO_3 were generated and leached out by soil washing. A similar exchange occurs in aquifers because of calcite dissolution in geologic time spans. The higher affinity of Ca^{2+} to clay minerals can displace Na^+, K^+ and even Mg^{2+} (Appelo, 1994).

4.2. Recrystallization of shell carbonate

The measured shell carbonate recrystallization after one day confirms that carbonate dissolution and recrystallization can start immediately after the exposure of carbonate to CO_2 (Fairbridge, 1967). Furthermore, recrystallization increases with elimination of organic compounds from the shell structure and in the presence of GeoC in the embedding matrix when compared to the organic-containing shells in a carbonate-free matrix (Fig. 4). To discuss about the effect of organic compounds elimination and presence of GeoC on shell carbonate recrystallization, the recrystallization amounts in NoOrg + soil, Org + loess and NoOrg + loess were compared to Org + soil.

4.2.1. Effects of organic compound elimination on shell carbonate recrystallization

According to Fig. 4 (Loess), shell carbonate recrystallization in Org + soil ($R_{Org\ +\ soil}$) as a function of time (t) can be modelled with Eq. (1).

$$R_{Org+soil}(mg) = 0.065 \times (1 - \exp.(-0.034 \times t)) \quad (1)$$

Heating up to 550 °C eliminated nearly all shell organic compounds (Dauphin et al., 2006) and their protective effect (Hall and Kennedy, 1967; Nielsen-Marsh and Hedges, 2000). Organic compound elimination also increases shell porosity, increasing the contact surface between shell carbonate and solution and thus promoting carbonate dissolution (Collins, 2012) and recrystallization. Therefore, the recrystallization difference between NoOrg + soil and Org + soil (i.e. organic-free and organic-containing shells in soil, respectively) shows the effect of organic compounds on shell carbonate recrystallization. We suggest introducing a term characterizing the effect of organic compounds elimination on shell carbonate, K_{org} (Eq. (2)).

$$K_{org}(mg) = R_{NoOrg+soil} - R_{Org+soil} \quad (2)$$

where $R_{NoOrg\ +\ soil}$ and $R_{Org\ +\ soil}$ are the amounts of recrystallized carbonate on organic-free and organic-containing shells in soil, respectively.

The difference in recrystallization between $R_{NoOrg\ +\ soil}$ and $R_{Org\ +\ soil}$ for all measured dates was similar. Therefore, the average of all dates (0.0048 ± 0.008 mg $CaCO_3$) was used as the constant amount (K_{org}) to show the effect of organic compounds elimination. Accordingly, adding 0.0048 mg to Eq. (1) yields the amount of recrystallization for NoOrg + soil (R^2 between observed and predicted data: 0.75).

4.2.2. The effect of geogenic carbonate on shell recrystallization

The higher recrystallization rates of shell carbonate in loess versus soil (Fig. 4) demonstrated the effect of GeoC on shell carbonate recrystallization (Forman and Polyak, 1997). Therefore, higher recrystallization of organic-containing shells in loess (Org + loess) versus Org + soil shows the effect of GeoC (K_{GeoC}) on recrystallization (Eq. (3)).

$$K_{GeoC}(mg) = R_{Org+loess} - R_{Org+soil} \quad (3)$$

where $R_{Org\ +\ loess}$ and $R_{Org\ +\ soil}$ are the amounts of recrystallized carbonate for organic-containing shells in loess and soil, respectively, for each measuring date.

The amount of carbonate recrystallization due to the presence of GeoC increased exponentially with time. Therefore, instead of merely calculating the mean (as a constant amount), Eq. (4) was used to show this trend.

$$K_{GeoC}(mg) = 0.0667 \times (1 - \exp.(-0.107 \times t)) \quad (4)$$

To test the accuracy of Eq. (4), the calculated amounts of recrystallized $CaCO_3$ using this equation were added to the results of Eq. (1) to estimate the extent of recrystallization in Org + loess. The R^2 between measured amounts of recrystallization and the predicted data for Org + loess was 0.88. We assumed, however, that the dissolution rates of GeoC (i.e. loess carbonate) and shell carbonate were similar. Considering the disseminated structure of loess carbonate and fine particle size distribution compared to the shell carbonate, higher dissolution and recrystallization of loess carbonate is expected.

4.2.3. The combined effect of organic compounds and geogenic carbonate on shell carbonate recrystallization

Differences between the measured amounts of recrystallization in NoOrg + loess and NoOrg + soil should also show the effect of GeoC on shell carbonate recrystallization. However, these differences did not agree with the results of Eq. (3). Furthermore, adding K_{org} (calculated as 0.0048 mg) to K_{GeoC} (Eq. (5)) did not yield the measured recrystallization of shells in NoOrg + loess. Eliminating the protective effect of shell organic compounds (Hall and Kennedy, 1967; Nielsen-Marsh and Hedges, 2000) as well as increasing the shell porosity (Collins, 2012) made shell carbonate more vulnerable to dissolution. Accordingly, recrystallization took place not only on the shell surface but also in the interior of the shell structure (Yates, 1986). Organic compound elimination therefore intensified the effect of GeoC (K_{GeoC} in the equations below) on shell carbonate recrystallization. To show this intensification we used the difference between measured amounts of recrystallization in NoOrg + loess and Org + soil (Eq. (6)). Adding the term intensification (int.) to Eq. (5) equating it to Eq. (6) allows the amount of intensification to be calculated (Eq. (7)).

$$\begin{aligned} K_{(GeoC+NoOrg)} &= (R_{Org+loess} - R_{Org+soil}) + (R_{NoOrg+soil} - R_{Org+soil}) \\ &= R_{Org+loess} + R_{NoOrg+soil} - 2R_{Org+soil} \end{aligned} \quad (5)$$

$$K_{(GeoC+NoOrg)} = R_{NoOrg+loess} - R_{Org+soil} \quad (6)$$

$$\begin{aligned} &K_{(GeoC+NoOrg+int.)} = E_{(GeoC+NoOrg)} = \\ &R_{Org+loess} + R_{NoOrg+soil} - 2R_{Org+soil} + int. = R_{NoOrg+loess} - R_{Org+soil} \rightarrow \\ &int. = (R_{NoOrg+loess} - R_{Org+soil}) - (R_{Org+loess} + R_{NoOrg+soil} - 2R_{Org+soil}) = \\ &(R_{NoOrg+loess} + R_{Org+soil}) - (R_{Org+loess} + R_{NoOrg+soil}) \end{aligned} \quad (7)$$

We used Eq. (8) to determine the ratio between the calculated recrystallization due to intensification (Eq. (7)) and the effect of GeoC and organic compound elimination (Eq. (5)). Since Eq. (8) predicts similar values for all dates, the mean of all dates was used as the constant rate, showing intensification of $K_{int.} = 4.80 \pm 1.1$. Using this calculated constant rate (K_{int}), we estimated the amount of recrystallized shell carbonate in NoOrg + loess as a function of time (Eq. (9)). The formulated equation (Eq. (9)) was then used to predict shell carbonate recrystallization ($R_{shell\ carbonate}$) of all treatments on all dates. The R^2 of the linear regression between measured and predicted data of all treatments and dates using Eq. (9) was 0.98 (Fig. 6).

$$K_{int.} = int./K_{(GeoC+NoOrg)} = 4.8029 \quad (8)$$

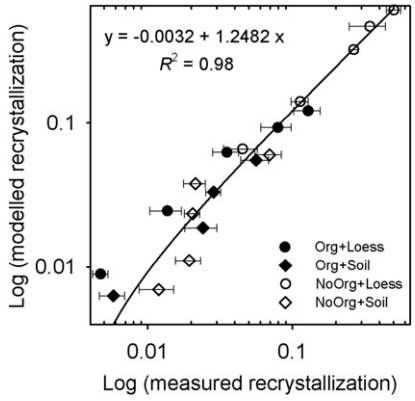

Fig. 6. The relation between modelled amounts of shell-carbonate recrystallization using Eq. (9) for all treatments and times with measured recrystallization. Bar lines show standard errors of measured recrystallization of each of four treatments at various dates.

$$R_{\text{shell carbonate}} = R_{\text{Org+soil}} + K_{\text{GeoC}} + K_{\text{NoOrg}} + \text{int.} = \left(R_{\text{Org+soil}} + K_{\text{GeoC}} + K_{\text{org}}\right) \times K_{\text{int.}} \quad (9)$$

4.3. Time required for full recrystallization of shell carbonate

Full recrystallization time calculated in this study was at least 10 times shorter than earlier estimations of 90% recrystallization after 7000 y (Chappell and Pollach, 1972). Different properties of the deposition areas (Yates et al., 2002) are one reason for the various estimates. In the littoral zone (Chappell and Pollach, 1972) water circulation (Forman and Polyak, 1997) washed out the dissolved Ca^{2+} ions, prolonging the time necessary for full recrystallization of shell carbonate. Moreover, solubility of $CaCO_3$ in seawater with alkaline pH (Jacobson, 2005) is lower than in soil solution ($pCO_2 = 2\%$) (Pausch and Kuzyakov, 2012). Also noteworthy is that our time estimation is based on the assumption that shell carbonate recrystallization is a continuous process.

The recrystallization process is exponential in time (Kuzyakov et al., 2006). Since the recrystallized carbonate is thought to first fill all the gaps in the outer shell layers and cover the shell surface (Webb et al., 2007), it protects the rest of the shell carbonate from further dissolution. Therefore, pre-treatments (e.g. washing with acids) before ^{14}C dating of shell carbonate provide more reliable dates (Yates, 1986). In calcareous soils or sediments (e.g. loess), where the recrystallization involves not only shell carbonate but also GeoC (Yates et al., 2002; Prendergast and Stevens, 2014), the time necessary for full recrystallization will be longer than estimated. In turn, recrystallized carbonate on the shell surface will undergo repeated recrystallization. This can buffer CO_2 reactions and protect the shell carbonate from further recrystallization. Analysis of this time delay requires a specific experimental layout.

After full recrystallization of shell carbonate, however, the isotopic composition of C is no longer related to the environmental conditions during the life time of the mollusk or its diet regime. The C isotopes will contain information about the properties of the environment in which it is embedded and the recrystallization conditions (Prendergast and Stevens, 2014).

4.4. Significance of the results for archaeology and paleoenvironmental research

The findings of this study have implications in archaeology and related disciplines. Since shell carbonate can serve both as a dating material and a paleoenvironmental proxy, a profound understanding of its geochemical behavior in cultural layers, soils and sediments over long periods of time is essential. Moreover, it frequently represents the only proxy record available, especially in arid regions. It should be also noted that some archaeological sites, such as shell middens, consist almost entirely of shell carbonate (Álvarez et al., 2011). The findings are, further, equally relevant to research on other finds of carbonate materials in cultural layers, for example egg shells (Magee et al., 2009).

Notwithstanding the existence of analytical tools for testing the integrity of mollusk shell carbonate for dating purposes or paleoenvironmental reconstructions, surprisingly little is known about the dynamics of diagenetic shell recrystallization in different sedimentological environments. The relatively low rate of carbonate dissolution limits the feasibility of reproducing the process with conventional methods. Currently, the outcome of shell carbonate exposure to CO_2 in different sedimentological settings appears difficult to predict without experiment or modeling. To sum up, three issues of our study deserve particular attention.

(1) The ^{14}C-labeling approach enables detecting of very low concentrations of newly-formed $CaCO_3$. Our data showed that the ^{14}C label is present in both shell and matrix carbonate very soon after the exposure to $^{14}CO_2$. The method thus offers a new experimental perspective for research on the recrystallization of biogenic carbonates under fine-tuned, controlled, laboratory conditions. The proposed model also suggests an approach to estimate and predict the extent of recrystallization in a given sample when investigating paleoenvironment reconstructions, or for dating purposes.

(2) Most chronological and paleoecological studies neglect both the character of original organic matter in a mollusk shell and the carbonate content of its ambient matrix. Our experiments demonstrate that these parameters are essential when assessing the probability of carbonate recrystallization and interpreting radiometric and isotopic shell characteristics (Fig. 7). This is especially important if archaeological contexts involve burned material with mollusk shells (Rodrigues et al., 2009).

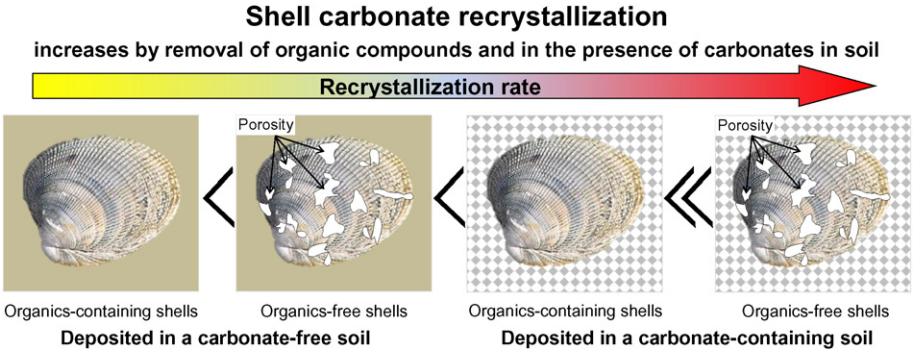

Fig. 7. Shell carbonate recrystallization depending on presence of organic compounds in shell structure and geogenic carbonates in soil. Organic compounds elimination increases shell porosity and make it vulnerable to recrystallization. Geogenic carbonates may also undergo dissolution and may recrystallize on shell surface or fill shell´s structural porosities.

(3) When extrapolating the results of this study to real archaeological settings, it must be borne in mind that the conditions of our experiment comply with a relatively limited spectrum of geochemical systems. Experimental conditions corresponded to the CO_2 concentrations occurring commonly in the uppermost horizons of exposed (non-buried) soils with developed root systems of vegetation and a certain degree of microbial activity. In terrestrial environments, such conditions are rare at depths greater than ca. 1 m below the land surface and in extremely cool, hot or dry climates. Also, except in wet tropical environments, the annual soil CO_2 production is usually not uninterrupted, but restricted in time to the vegetative period. Its duration and combination with other climate parameters should be taken into account when the recrystallization period is the focus of interest.

A key goal for future research will be to increase the practical value of ^{14}C-labeling research on mollusk shells by conducting experiments that approximate natural carbonate recrystallization processes. The experiments should be appropriately modified by adding living root systems and varying factors such as depth, temperature and moisture regimes. Furthermore, future investigations should focus on comparisons between experimentally deduced recrystallization values and native samples of shell carbonate of known age that have been exposed to CO_2 under known or predictable conditions.

5. Conclusions

Shell carbonate recrystallization begins very soon after embedding in soils and increases exponentially with time. Within two months, 0.06 to 0.56 mg per 100 mg shell carbonate was recrystallized, depending on the presence of organic compounds in the shell structure and geogenic carbonates in the soil.

Shell and environmental properties affect the rates of shell carbonate recrystallization. Removing structural organic compounds and thus enhancing shell porosity increased the rate by 0.0048 mg (2–2.5 mm shell size). In the presence of geogenic carbonate, shell recrystallization increased because part of the recrystallized carbonate originated from re-precipitation of dissolved geogenic carbonate. The effect of geogenic carbonates was time-dependent and was intensified after elimination of structural organic compounds with associated increases in shell porosity. This intensification increased the measured recrystallized carbonate up to 4.8 times compared with pristine shells in carbonate-free soil. Recrystallization should be considered when interpreting of dating results and paleoenvironmental reconstructions.

The ^{14}C labeling approach was sensitive in assessing recrystallization rates of biogenic carbonate such as shell carbonate, within reasonably short times. ^{14}C labeling provides a useful tool to examine the effects of individual factors on shell carbonate recrystallization.

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