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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<sub>3</sub> with environmental carbon (C) is well known, the role of Ca<sup>2+</sup> in diagenetic processes remains unclear. Addition of young C to shells during diagenesis occurs in soil solution, where the Ca<sup>2+</sup> concentration is in equilibrium with exchangeable Ca<sup>2+</sup> 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 <sup>14</sup>C labeling approach. Shell particles of the bivalve *Protothaca staminea* were mixed with carbonate-free sand (CEC = 0.37 cmol<sup>+</sup> kg<sup>-1</sup>) (Sand), a loamy soil (CEC = 16 cmol<sup>+</sup> kg<sup>-1</sup>) (Loam) or the same loamy soil saturated with KCl, where exchangeable cations were replaced with K<sup>+</sup> (Exchanged). The high-sensitivity <sup>14</sup>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<sub>3</sub>, respectively) showed one order of magnitude lower recrystallization than in Sand (0.13 mg CaCO<sub>3</sub>). A high level of soil exchangeable Ca<sup>2+</sup> 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 <sup>14</sup>C ages.

Several approaches have been proposed to solve the problem of <sup>14</sup>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 <sup>14</sup>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 <sup>14</sup>C-labeling of CO<sub>2</sub> under controlled conditions (Kuzyakov et al., 2006; Gocke et al., 2012). The latter method offers a possibility of studying the effects of recrystallization on <sup>14</sup>C contamination of carbonates within a relatively short time (weeks to months). At the same time,

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