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DATING THACH LAC: CRYPTIC CaCO_3 DIAGENESIS IN ARCHAEOLOGICAL FOOD SHELLS AND IMPLICATIONS FOR ^{14}C

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ABSTRACT. In many locations around the world, shell radiocarbon dates underpin archaeological research. The dating of shell brings the chronological relationship between the sample and target event (e.g., hunting and food preparation) into congruence, while shells are valuable geochemical proxies for understanding past climate dynamics and environments. However, this information can be lost as the shell, composites of biopolymers and carbonate minerals (mostly calcite and or aragonite), undergo diagenetic alteration. While studies into Pleistocene-age carbonates are common in the radiocarbon literature, there has been little research into the impact of alteration on Holocene-age shells used to interpret recent societal developments. The limits of our understanding of these diagenetic changes became evident when dating *Placuna placenta* (naturally calcitic) and *Tegillarca granosa* (naturally aragonitic) shells from the site of Thach Lac in Vietnam. These shells returned ages significantly younger than associated charcoal and terrestrial bone at the site, but standard tests for secondary recrystallization (XRD and staining techniques) did not indicate any alteration. Further investigation revealed that cryptic recrystallization (i.e., of the same crystal structure) had occurred in both the calcite and aragonite shells. This finding suggests recrystallization may have an undetected impact on some shell radiocarbon dates.

KEYWORDS: aragonite, calcite, cryptic recrystallization, shell, Vietnam.

INTRODUCTION

The archaeological site of Thach Lac is located at coordinates 105°57'42.68E/18°21'59.09N in Thach Lac Commune, Ha Tinh Province, north-central Vietnam (Figure 1). It is approximately 4 km from the modern coastline in a low-lying landscape consisting of a relict dune field formed as the sea receded between the mid-and later Holocene (Boyd and Lam 2004). Thach Lac was situated on or close to the coast throughout its history (Grono et al. forthcoming). The deposits at Thach Lac were approximately 2 m deep and included 11 well-stratified cultural layers with two hiatuses. The *in situ* midden consisted almost entirely of *Placuna placenta* (windowpane oyster) and *Tegillarca granosa* (blood cockle) shells. Radiocarbon (^{14}C) dates (18 charcoal and 8 Cervidae [deer] tooth dentine), ceramics (and other material culture remains), and stratigraphy indicate three distinct phases separated by sterile layers; the Quynh Van phase starting ca. 3090 BC and ending by ca. 2850 BC, the Thach Lac phase dating to between ca. 2940 BC and ca. 2370 BC, and the Bau Tro phase starting ca. 2470 and ending ca. 2160 BC. Dates on *P. placenta* shells from the site returned ages up to 2000 years younger than associated bone and charcoal ages; much too young for ^{14}C reservoir or dietary offsets that may be caused by the introduction of contemporary terrestrial carbon sources into the nearshore estuarine environment (cf.,

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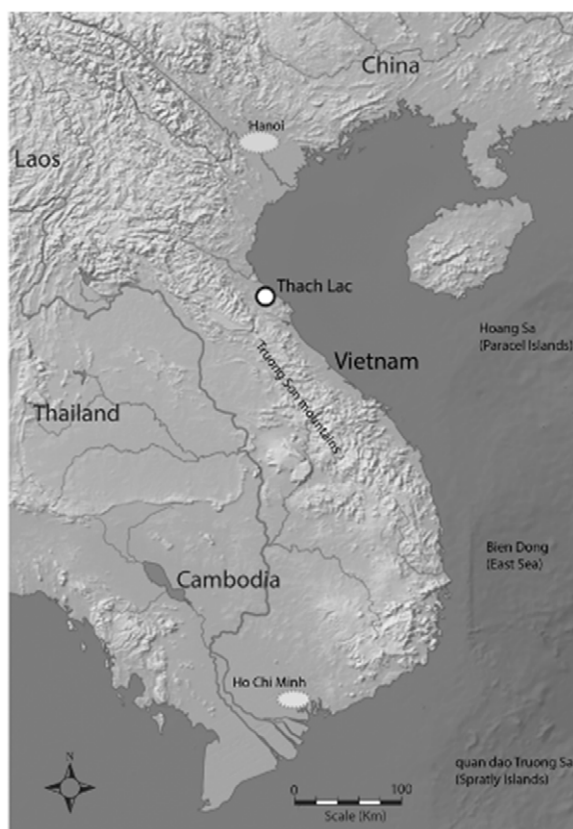


Figure 1 Location of Thach Lac, Vietnam.

Petchey et al. [2012, 2018] who discuss the impact of contemporary and ancient sources of terrestrial carbon in estuarine shellfish). Moreover, significant differences in duplicate ^{14}C analysis of the same shell negated the possibility of disturbance between layers, meaning that contamination was the most likely cause of the offsets (Figure 2).

Because *Placuna* sp. shells are naturally calcite, the processing laboratory was unable to use standard inhouse tests to check for recrystallization; instead, having to rely on visible inspection to assess the quality of the samples (i.e., cracking across growth rings indicative of the formation of large calcite crystals, natural staining patterns, and a translucent, pearly appearance) (see Supplemental Appendix 1). Therefore, assuming the ages of the *Placuna* shells were in error because of secondary calcite contamination, naturally aragonitic *Tegillarca* sp. shells from the same contexts were sampled for x-ray diffraction (XRD) analysis with the assumption that any contamination would be more obvious (calcite and aragonite are polymorphs of calcium carbonate and have the same chemical formula but a different crystal structure which can be quantified by XRD). The *Tegillarca* shells had a soft chalky appearance that undermined the ribs but a dense, apparently unaffected core (Figure 3). These visible characteristics are typical of shell alteration (cf., McGregor and Gagan 2003), but there was no evidence of recrystallization in the XRD spectra (Supplemental Appendix 1). The *Tegillarca* sp. radiocarbon results were also variable but not as young as the *Placuna* results (Figure 2). However, dates on burnt *Tegillarca* shells,

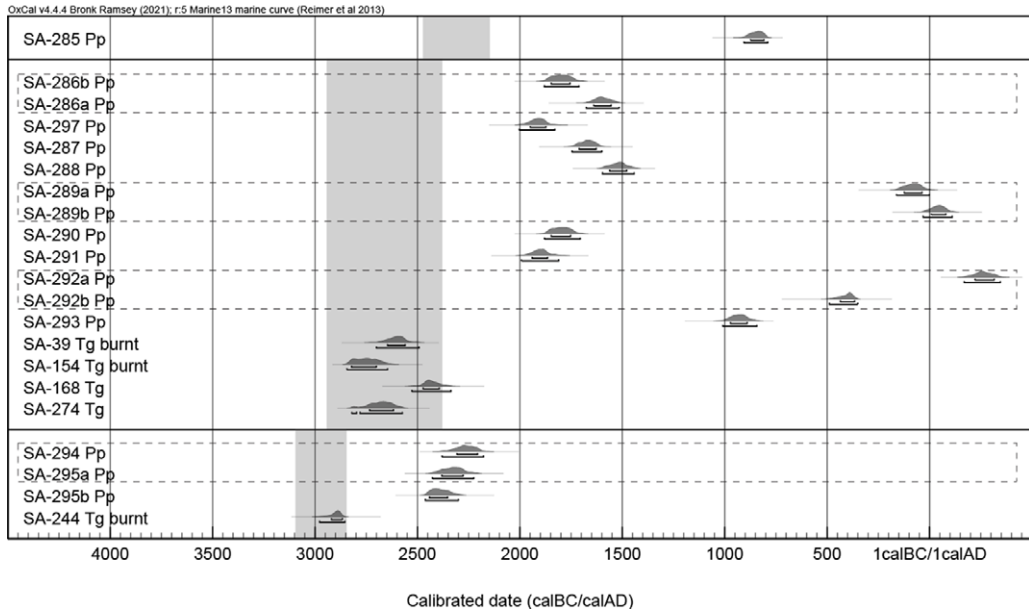


Figure 2 Shell radiocarbon ages (shell dates calibrated with OxCal v4.4 [Bronk Ramsey 2021] using the Marine13 [Reimer et al. 2013]). Tg = *Tegillarca granosa*. Pp = *Placuna placenta*. The gray vertical bars indicate expected boundary age ranges (95% probability) based on bone and charcoal dates. Boxes with dashed outlines group repeat analyses.

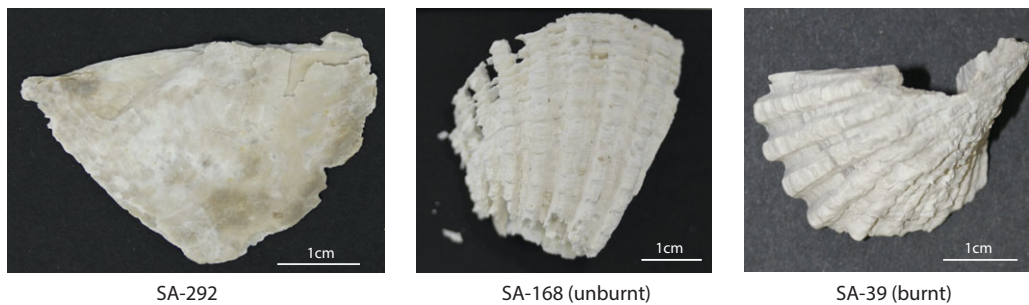


Figure 3 Photos of representative *Placuna placenta* (SA-292) and *Tegillarca granosa* (SA-168 and SA-39) shells after sandblasting to remove altered material.

altered to calcite by high-temperature cooking fires at the time of deposition (easily identified by gray/perpendicular cracks [c.f., Milano et al. (2016)] and confirmed by XRD), were consistent with the bone and charcoal chronology for the site. In contrast to the unburnt *Tegillarca* shells, the burnt material was robust, with minor dissolution pits on the surface but no evidence of chalky alteration (Figure 3).

These results raised several questions that needed further investigation:

1. Why could we not detect secondary contamination in the XRD spectra of the aragonitic *Tegillarca granosa* shells?

2. Was it possible that secondary CaCO_3 contamination was concentrated using standard shell pretreatment techniques?
3. Why did temperature-induced alteration of aragonite to calcite appear to preserve the ^{14}C signature in the *Tegillarca* shells?
4. Could we develop techniques to detect secondary contamination in naturally calcitic *Placuna placenta* shells? This was especially important because *Placuna placenta* dominate many shell mounds associated with the Quỳnh Văn culture (Piper et al. 2021).

BACKGROUND

Marine molluscan shells are predominantly comprised of high-magnesium bio-calcite (HMC; $>4\%$ MgCO_3) and/or bio-aragonite. These two alloforms have almost identical compositions but different thermal stability and solubility to abiogenic (non-biological) carbonates that can form during secondary recrystallization following burial. Once buried, bio-HMC and bio-aragonite eventually recrystallize to low magnesium abiogenic calcite (LMC; $0\text{--}4\%$ MgCO_3) (i.e., bio-HMC has a similar solubility to bio-aragonite, but both are much more soluble than abiogenic LMC) (Morse et al. 2006). However, it is difficult to make generalizations about the alteration of bio-skeletons because of the wide range of possible influences post-deposition (e.g., microbial attack, soil pH, temperature, age, presence of other carbonates, and water circulation), as well as factors such as the specific carbonate form, the original microstructure of the shell, the amount and distribution of the organic matter, porosity and if relevant, the temperature and method of cooking (Casella et al. 2018; Forjanés et al. 2021).

Alteration of the crystalline structure can change the isotopic signal of the shells and may result in older or younger ^{14}C ages depending on the depositional environment (Fairbanks et al. 2005; Webb et al. 2007; Douka et al. 2010). Considered to be rare, syntaxial overgrowths (Webb et al. 2007) or cement infill (Enmar et al. 2000) of the same crystalline structure (i.e., cryptic recrystallization) are of specific concern when dating carbonates. Therefore, the ability to obtain a reliable shell ^{14}C date relies on identifying and removing secondary recrystallization. A range of techniques have been utilized to evaluate recrystallization, including visible inspection either by optical and electron microscopes (e.g., Vita-Finzi and Roberts 1984; Yates 1986; Bezerra et al. 2000; Webb et al. 2007), x-ray crystallography (e.g., Chappell and Polach 1972; Vita-Finzi and Roberts 1984; Bezerra et al. 2000; Douka et al. 2010), isotope analysis (e.g., Bezerra et al. 2000; Yates et al. 2002), Raman micro-spectroscopy (e.g., Webb et al. 2007; Lindauer et al. 2018), Fourier transform infrared spectroscopy (e.g., Loftus et al. 2015) and qualitative staining techniques (e.g., Brock et al. 2010).

Unfortunately, if secondary mineralization is detected, methods of removal are limited. Acid-etching of shells is routinely used to remove surface contamination, but the higher solubility of bio-aragonite relative to abiogenic calcite and aragonite, and that of bio-calcite to abiogenic calcite, means these treatments may concentrate the more resistant replacement mineral (Chappell and Polach 1972; Vita-Finzi and Roberts 1984; Chiu et al. 2005; Morse et al. 2006). Measurement of sequential CO_2 fractions removed by stepped hydrolysis, following the methods of Burr et al. (1992) and Yokoyama et al. (2000), can be used to investigate the nature and age of secondary recrystallization and help assess the reliability of the final result (see also Lindroos et al. [2014] who used similar techniques to date burnt shell in

mortar). Treatments that take advantage of differences in density between aragonite and calcite are promising but untested on a wide range of shellfish (Douka et al. 2010; Russo et al. 2010) and are unlikely to be useful where cryptic recrystallization has occurred.

Cooking will also affect the structure and biochemistry of archaeological shells. The effect of heating is often obvious in aragonitic shells, which recrystallize to calcite by 500°C (Li et al. 2015; Milano et al. 2016), but detection is more difficult in naturally calcitic shells. High temperatures can introduce exogenous carbon to bone carbonate (Hüls et al. 2010; van Strydonck et al. 2010), but there has been very little research on ^{14}C anomalies in burnt shells. In tests on 7000 and 3000-year-old archaeological shells from sites located in mangroves and salt flats in the Gulf of Oman, Lindauer et al. (2018) identified a larger scatter in the ^{14}C data for unheated aragonitic shells than shells with evidence of burning. They, therefore, concluded that burnt material is useful for dating archaeological contexts. However, much more work is required to confirm this for a wide range of shell taxa and depositional environments.

METHOD

Initially, shell processing followed the standard methodology employed at the Waikato University radiocarbon laboratory. First, the shell was visibly inspected for contamination (cracking perpendicular to growth rings, indicative of the formation of large calcite crystals associated with burning or softening/powdering of the shell surface associated with dissolution and precipitation). Next, a chemical stain (Feigl staining; Friedman [1959]) was used to identify the presence of calcite, a method that can identify specific areas where secondary recrystallization has occurred. Detection of secondary contamination in naturally calcitic shells (e.g., oysters) relies on visible inspection and the presence of a pearly luster. The shell was then cleaned by air abrasion with 20–50 μm aluminum oxide powder and crushed into <3 mm diameter fragments. The sample (35–45 mg) was then etched in 1M HCl to remove ~40% of the surface. CO_2 was collected from ~20 mg of shell fragments by reaction with 85% H_3PO_4 , and cryogenically separated CO_2 was reduced to graphite with H_2 at 550°C using an iron catalyst. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were measured at the University of Waikato using an isotope analyzer (Los Gatos Research model CCIA-46) following the method outlined in (Petchey et al. 2018). Pressed graphite was sent to the Keck Radiocarbon Dating Laboratory, the University of California, for ^{14}C measurement (Southon et al. 2004). After receiving the initial anomalous ^{14}C results, we evaluated the shells further using X-ray diffraction (XRD) analysis, scanning electron microscope (SEM) imaging, and stepped hydrolysis.

XRD Analysis

XRD spectral analysis was undertaken to test for low levels of secondary mineralization using a Panalytical Empyrean diffractometer operating at 45 kV and 40 mA, using $\text{Cu K}\alpha$ radiation with a scan speed of 0.134670 degrees/sec from 20–40° 2 θ . In addition, standard carbonate mixtures were developed using (a) bio-calcite from modern *P. placenta* shell (from Thailand) and (b) bio-aragonite from modern *T. granosa* shell (from Tongatapu). The samples and standards were hand-ground to avoid mineralogical changes caused by heat. Using the standard mixtures, we established that the lower detection level of calcite in an aragonite powder was ~0.4%. XRD spectra of the archaeological shells are given in Supplemental Appendix 1.

SEM Imaging

High magnification SEM imaging of the shells was used to assess the possibility of cryptic recrystallization. Fragments of unprocessed *T. granosa* and *P. placenta* shells were snapped to create fresh breaks. The specimens were mounted with carbon paste and coated with platinum using the Quorum Q150V ES Plus Sputter Coater. Images were taken using a Hitachi Regulus 8230 FEG-SEM at the University of Waikato. The fractured surfaces were compared to modern and literature examples (Larsen [2015] for *Tegillarca* and Ling and Ortiz [2013] for *Placuna*), while burnt shells were compared to examples given in Milano et al. (2016). SEM images of the modern and archaeological shells are shown in Figures 4, 5, and 8.

Stepped Hydrolysis

To investigate the reproducibility of the ages, we used a process of stepped acidification removing successive aliquots of CaCO_3 . Initially, 90% of the surface of two *Tegillarca* shells (Wk-42442; SA-55 and Wk-42436; SA-168) was removed, dated, and the results compared to dates of unpretreated subsamples of the same shells. Then, a more extensive experiment was undertaken using a *Placuna* shell (Wk-41911; SA-292), whereby 45 mg was loaded as a single intact fragment into a side-arm vessel and reacted with ~ 10 mL of 100% H_3PO_4 . The evolved CO_2 was periodically withdrawn from the reaction vessel at $\sim 10\%$ intervals, quantified monometrically, and graphitized. The results are presented in Figure 6.

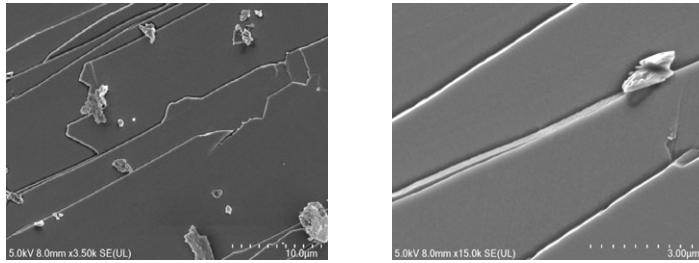
RESULTS

Unburnt Shell

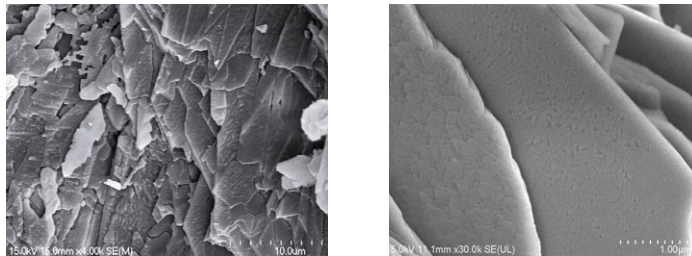
All archaeological specimens returned XRD spectra indicative of aragonite for *T. granosa* and calcite for *P. placenta* in keeping with expectations (Supplemental Appendix 1). SEM images of modern *P. placenta* shell show a lamellar microstructure (Figure 4a) forming elongated tile-like structures arranged in overlapping sheets. This structure is susceptible to recrystallization at plate boundaries, as demonstrated by the dissolution shown in archaeological specimens SA-291 and SA-292 (Figures 4b and d). At higher magnification, the development of calcite crystals on the surface of the laths is visible SA-291 and SA-289 [Figure 4c and d]). In contrast, fractured modern *T. granosa* surfaces have a crossed-lamellar microstructure (Figure 5a). Images of the archaeological specimens show considerable disruption to this structure (SA-168 and SA-55) in keeping with our initial observations that the surfaces were soft and powdery (Figures 5b, c, and d). Unfortunately, static charging prevented higher magnification images from being taken of these specimens, but low magnification images indicate the magnitude of alteration; images of SA-55 show extensive dissolution to the aragonite crystals (Figure 5d), while acicular fibrous secondary aragonite growths occur in the cracks on the surface of SA-168 (Figure 5c).

Stepped Hydrolysis

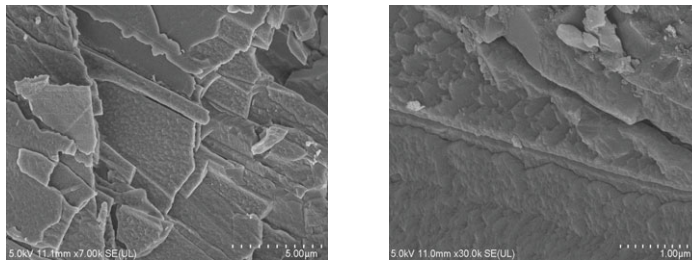
Dates on successive aliquots of CO_2 removed during stepped hydrolysis of the *Placuna* shell SA-292 (Wk-41911) initially got younger, then increased in age, with the oldest fraction removed when only 10% of the sample was left. However, the expected age for the site based on ^{14}C dates of bone and charcoal was never reached (Figure 6). This initial trend towards younger ages suggests preferential removal of the more soluble bio-HMC before the secondary abiogenic LMC. Yokoyama et al. (2000) recommend discarding the first



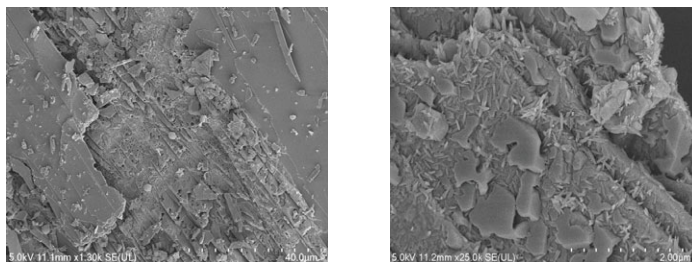
A. SEM images of modern *P. placenta*: Foliated, calcite laths arranged in parallel.



B. SA-292 (Wk-41911): Erosion and overgrowths on *P. placenta* calcite laths.



C. SA-289 (Wk-41904): Pitting and blocky calcite overgrowths on laths.



D. SA-291 (Wk-41909): Dissolution between laths and growth of blocky calcite and needles on lath surfaces.

Figure 4 SEM images of *Placuna placenta* shells.

50% of CO₂ collected in this manner but suggested that the results were reliable if the subsequent three aliquots produced identical ages. Based on this recommendation, the ages for the last few fractions of SA-292 (Wk-41911) indicate unreliable results. Radiocarbon dates of pretreated and unpretreated *Tegillarca* samples typically show an improvement in expected age with more extensive pretreatment (Figure 7). In general, we could not remove all secondary carbonate from the unburnt shells using acid digestion, a finding that, in hindsight, is not all that surprising because bio-aragonite is more soluble than inorganic aragonite, and bio-calcite is more soluble than inorganic calcite.

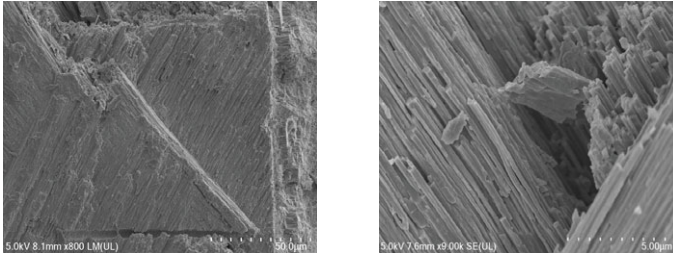
Burnt Shell

Several *Tegillarca* shells showed stress fracturing perpendicular to growth bands, were light gray, and dense with no evidence of powdery alteration (Supplemental Appendix 1). These changes were attributed to burning, where the aragonite crystals have altered to calcite. The XRD spectra confirmed that these shells were 100% calcite (Supplemental Appendix 1). SEM imaging of these burnt *Tegillarca* shells (Figure 8) show that the expected cross-lamellar structure had been replaced by a low porosity, heterogeneous matrix. Milano et al. (2016) noted that a blocky transformation to aragonite laths started around 300°C. However, the changes observed in the Thach Lac *Tegillarca* shell did not occur in the Milano et al. (2016) study until sustained temperatures of ~500°C were achieved for a prolonged period. The burnt *Tegillarca* shells appear to have a ¹⁴C signature comparable to the bone and charcoal dates from the site, even when unpretreated (Figure 9). This suggests that there has been little exchange of ¹⁴C when burnt and minimal secondary contamination during burial. For the *Placuna* shells, we could not find evidence of the platelets merging into blocky units, as would be expected if previously heated to high temperatures. Macroscopically the oyster shells display patchy iridescence and brown-white discoloration, both characteristics identified as early signs of heating to low temperatures (~300°C) by Milano et al. (2016:20).

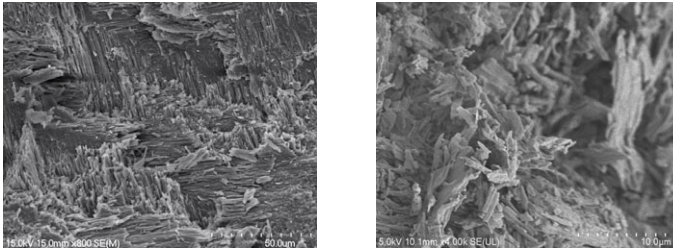
DISCUSSION

The SEM and XRD analyses presented in this paper confirmed the presence of structural and crystalline changes within the Thach Lac shells without any noticeable change in carbonate alloform. Previously, it has been assumed that meteoric diagenesis (influenced by water of atmospheric origin), as expected for the site of Thach Lac, should favor the precipitation of abiogenic calcite following burial because this is less soluble than aragonite and reaches supersaturation in diagenetic fluids first. Conversely, it is thought that shallow seawater diagenesis favors the precipitation of abiogenic aragonite because it has a higher Mg:Ca ratio, and Mg²⁺ interferes with calcite precipitation (Morse et al. 1997; Webb et al. 2007; Sun et al. 2015). In the rare cases where secondary aragonite overgrowths are present (e.g., Webb et al. 2007), soil chemistry and the ease of precipitation on original bio-aragonite crystals are thought to be responsible. However, these traditional explanations of carbonate chemistry do not adequately describe how both aragonite and calcite secondary crystals could form on archaeological shells recovered from the same site.

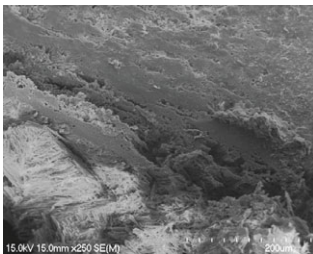
Recent research into carbonate precipitation by Forjanec et al. (2021), and Casella et al. (2018) may provide an explanation. They describe a multi-step process whereby alteration starts with bio- aragonite/calcite dissolution at the same time as abiogenic precipitation within the natural porosity of the crystal matrix and the voids left by organic decay. Structural differences



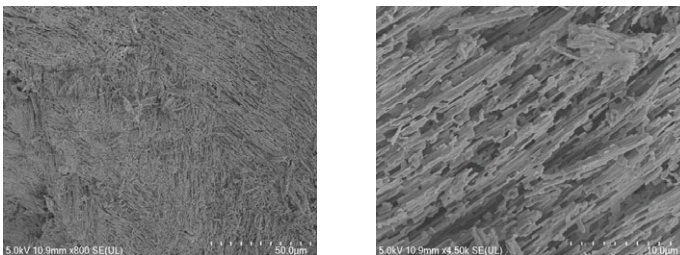
A. SEM images of modern *Tegillarca granosa*: Cross-lamellar structure.



B. i. SA-168 (Wk-42436): Cross-lamellar aragonite crystals.
ii. Disrupted crystals near edge of shell.



C. SA-168 (Wk-42436): Acicular, fibrous secondary aragonite formed within a crack.



D. SA-55 (Wk-42442): Disrupted cross-lamellar structure with eroded aragonite laths.

Figure 5 SEM images of *Tegillarca granosa* shells.

Lab no.	Radiocarbon Age (bp)	Percent Dissolved
Wk-41911c	2198±20	0-11%
Wk-41911d	2120±21	11-23%
Wk-41911e	2111±24	23-34%
Wk-41911f	2156±25	34-44%
Wk-41911g	2219±22	44-56%
Wk-41911h	2313±21	67-78%
Wk-41911i	2590±22	90-100%

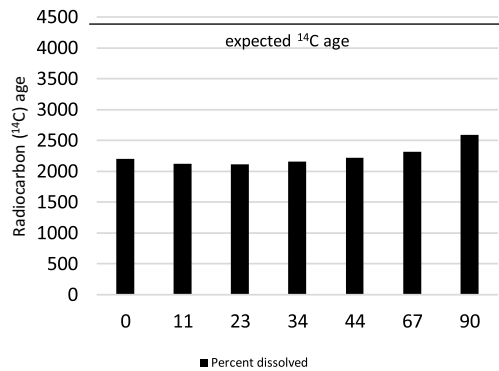


Figure 6 Stepped hydrolysis results for Wk-41911 (SA-292) *Placuna placenta*. Each fraction represents a portion of the sample that was selectively dissolved.

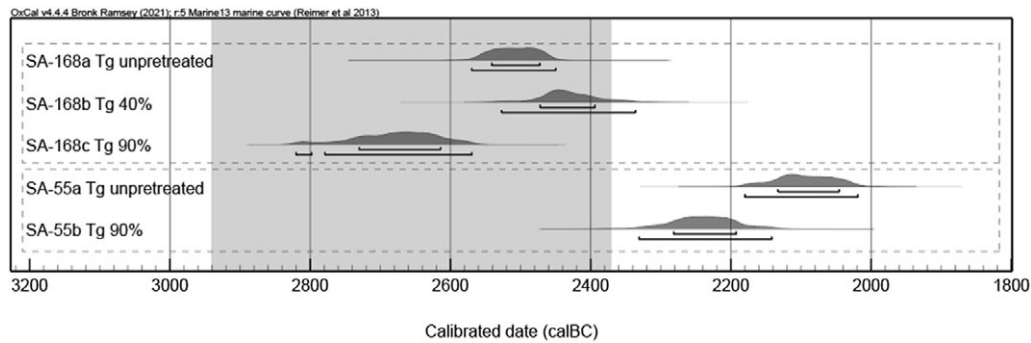


Figure 7 Unburnt *Tegillarca granosa* (Tg) radiocarbon ages following different pretreatment strategies (shell dates calibrated with OxCal v4.4 [Bronk Ramsey 2021] using the Marine13 [Reimer et al. 2013]). The gray bar indicates the expected age range for Thach Lac phase based on bone and charcoal 95% probability ranges given in the text. Dashed rectangles link dates on the same sample—the different percentages of surface removed are outlined at the left of the figure.

between the *Placuna* and *Tegillarca* shells suggest diagenesis will immediately take different routes. Specifically, the crossed-lamellar structure of *Tegillarca* shells is low in organics (e.g., only ~1% compared to ~5% in shells where platelets form [Lia et al. 2017]). The high organic component in foliated structures opens the *Placuna* shells to more extensive diagenetic effects, especially between the laths where standard ¹⁴C clean-up chemistry does not reach. Greater porosity and more organics in the outer layers of aragonitic cross-lamellar shells (Lia et al. 2017; Forjanes et al. 2021) may also explain observed alteration to the outer ridges of the Thach Lac *Tegillarca* shells even though the body remains intact. Once diagenesis starts, two main factors favor the formation of secondary abiogenic aragonite instead of calcite: (i) the presence of Mg²⁺ ions in the fluid and (ii) the fact that

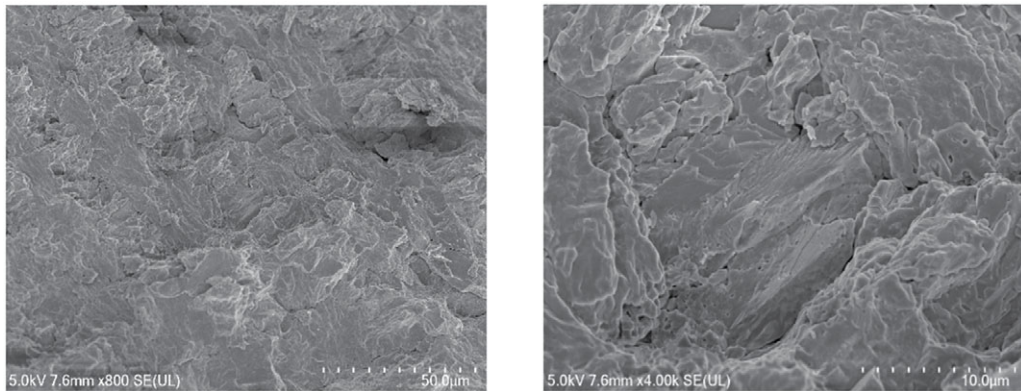


Figure 8 SEM images of burnt *Tegillarca granosa* shell SA-39.

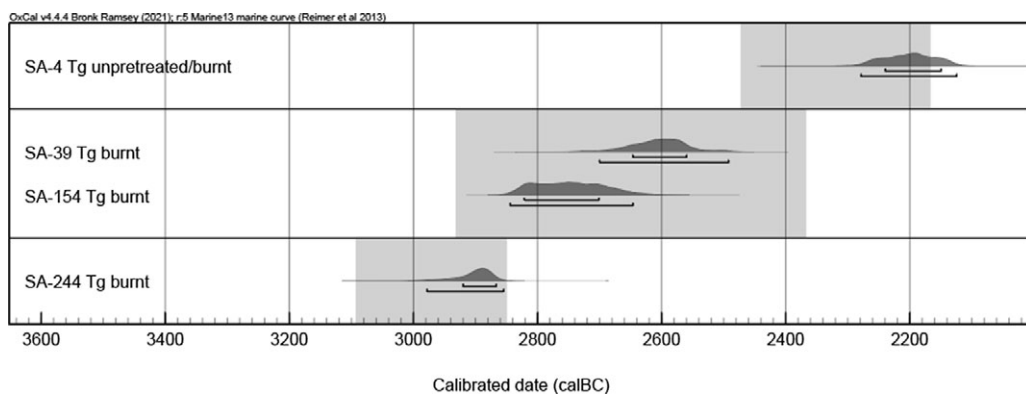


Figure 9 Burnt shell radiocarbon ages (shell dates calibrated with OxCal v4.4 [Bronk Ramsey 2021] using the Marine13 [Reimer et al. 2013]). Tg = *Tegillarca granosa*. The gray bars indicate the expected age range for each phase/layer based on bone and charcoal 95% probability ranges given in the text.

heterogeneous nucleation and crystal growth take place at lower energies (Sun et al. 2015; Forjanés et al. 2021). Because of these lower energy requirements, Casella et al. (2018) found that during the early stages of alteration, crystallites may retain the phase of the host crystal. Moreover, in environments undersaturated with aragonite, secondary aragonite and calcite nucleation may co-occur (Forjanés et al. 2021). It is also possible that in a solution supersaturated with abiogenic (secondary) calcite, the calcite will precipitate out of solution while the shell bio-calcite dissolves (Morse et al. 2006). This difference in solubility has implications for our ability to remove this contaminant using standard wet chemistry techniques. More work using different acid etching techniques is needed to see if improvements in age can be made to these Thach Lac shells.

Our ^{14}C data suggest that *Placuna* shells from Thach Lac have been more greatly affected by secondary alteration. In a series of boiling and roasting experiments on modern shells, Milano et al. (2016) noted that the nature of change is dependent on the original crystalline structure, with nacre (aragonite) platelets affected at lower temperatures. Therefore, the platelet structure of *Placuna* may have been structurally compromised at lower temperatures and be more

suspectable to diagenesis, even when there are few obvious signs of temperature-induced alteration. On the other hand, burnt *Tegillarca* shells thermally altered to calcite had a dense heterogeneous matrix resistant to diagenetic changes (Figure 8). A difference between unburnt and burnt shell ^{14}C results was not immediately apparent to Lindauer et al. (2018) when comparing dates from sites in the Gulf of Oman. However, they did notice a larger statistical scatter in the ^{14}C data for the unheated shells, which may reflect subtle diagenetic changes in an environment where secondary alteration was minimal. With some caveats because of uncertainties around the uptake of ^{14}C during burning, we agree with Lindauer et al. (2018) that archaeological contexts can be dated reliably using burnt material.

Our results have implications for constructing a reliable chronological framework for the mid-Holocene archaeological record along the coasts of north and north-central Vietnam. For example, numerous Quynh Van shell mounds in Nghe An Province are constructed almost entirely of *Placuna* valves with concentrated lenses of *Tegillarca* shell with little in the way of other datable materials. Consequently, several sites have been dated using either *Placuna* or unidentified marine shells and have produced erroneous dates between ca. 3000 BC and ca. AD 400 (Nguyen 1998; Pham and Nguyen 2001), but a comparison of dates of other materials from the same contexts is absent. Together with Thach Lac, our recent comprehensive dating of Ru Diep, another shell mound in Ha Tinh Province, suggests a tightly constrained chronology for the Quynh Van commencing shortly before 3000 cal. BC and ending no later than 2800 cal. BC (Lam et al. 2020; Piper et al. 2021). Therefore, we recommend a cautious approach to the future dating of Quynh Van sites and other shell mounds within the region that combines shell dating with results on other datable materials and considers the possibility of cryptic recrystallization in mollusk samples. Given the inability of current techniques to detect cryptic recrystallization in shell, we recommend SEM imaging if anomalies in ^{14}C are suspected. Whether SEM imaging should be part of routine quality assurance protocols is yet to be determined, but unpublished data (FP) for several locations across the tropical Pacific indicate cryptic recrystallization is not a regular occurrence in archaeological materials and may be limited to specific hydrological and geological environments.

CONCLUSION

Radiocarbon dates of shells from the site of Thach Lac reflect the effects of a continuum of secondary recrystallization over time, with calcite *Placuna placenta* shells being more affected than aragonite *Tegillarca granosa* shells. For both taxa, it was impossible to detect this secondary recrystallization using established methods such as XRD analysis or staining techniques because of cryptic recrystallization (recrystallization of the same crystal alloform). This presence of both aragonite and calcite secondary recrystallization in the same site suggests heterogeneous nucleation in an environment undersaturated in aragonite. Moreover, differences in crystal structure appear to have significantly affected the susceptibility of *Placuna* to secondary contamination, resulting in much younger ages for these shells, indicative of a continuum of ^{14}C exchange over time. Unfortunately, we could not remove this secondary CaCO_3 with standard wet chemistry AMS processing techniques. Our results also indicate that burning and the associated crystal changes protected shells from diagenesis and the ^{14}C dates of burnt *Tegillarca* shell from Thach Lac are reliable. However, we could not identify any burnt *Placuna* shells to confirm this observation for shells naturally composed of calcite.

Our findings do not appear widespread in Holocene shell archives, but because high magnification SEM imaging of dated shells is uncommon, the impact of cryptic recrystallization may be under-represented in the literature. Ultimately, the presence of secondary recrystallization depends on a range of factors, including the hydrology and soil chemistry of the site. Therefore, further tests on other sites from different environments and temporal contexts are needed to confirm if cryptic recrystallization is more widespread and what effect this may have on the ^{14}C ages of mollusk shells.

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SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit <https://doi.org/10.1017/RDC.2022.63>

REFERENCES

- Bezerra F, Vita-Finzi C, Filho FP. 2000. The use of marine shells for radiocarbon dating of coastal deposits. *Brazilian Journal of Geology* 30(1): 211–213.
- Boyd WE, Lam DD. 2004. Holocene elevated sea levels on the north coast of Vietnam. *Australian Geographical Studies* 42:77–88.
- Brock F, Higham T, Ditchfield P, Brock Ramsey C. 2010. Current pretreatment methods for AMS radiocarbon dating at the Oxford Radiocarbon Accelerator Unit (ORAU). *Radiocarbon* 52(1): 103–112.
- Bronk Ramsey C. 2021. OxCal Program v4.4, Radiocarbon Accelerator Unit. University of Oxford.
- Burr GS, Edwards RL, Donahue DJ, Druffel ERM, Taylor FW. 1992. Mass spectrometric ^{14}C and U-Th measurements in coral. *Radiocarbon* 34(3): 611–618.
- Casella LA, He S, Griesshaber E, Fernández-Díaz L, Greiner M, Harper EM, Jackson DJ, Ziegler A, Mavromatis V, Dietzel M, Eisenhauer A. 2018. Hydrothermal alteration of aragonitic biocarbonates: Assessment of micro- and nano-structural dissolution–reprecipitation and constraints of diagenetic overprint from quantitative statistical grain-area analysis. *Biogeosciences* 15:7451–7484.
- Chappell J, Polach HA. 1972. Some effects of partial recrystallisation on ^{14}C dating late Pleistocene corals and molluscs. *Quaternary Research* 2: 244–252.
- Chiu T-C, Fairbanks RG, Mortlock RA, Bloom AL. 2005. Extending the radiocarbon calibration beyond 26,000 years before present using fossil corals. *Quaternary Science Reviews* 24(16–17): 1797–808.
- Douka K, Hedges REM, Higham TFG. 2010. Improved AMS ^{14}C dating of shell carbonates using high-precision X-ray diffraction and a novel density separation protocol (CARDS). *Radiocarbon* 52(2–3):735–751.
- Enmar R, Stein M, Bar-Matthews M, Sass E, Katz A, Lazar B. 2000. Diagenesis in live corals from the Gulf of Aqaba. I. The effect on paleo-oceanography tracers. *Geochimica et Cosmochimica Acta* 64(18):3123–3132.
- Grono E, Friesem DE, Lam TMD, Nguyen TT, Hamilton R, Bellwood P, Piper PJ, Denham T. Forthcoming. Microstratigraphy reveals cycles of occupation and abandonment at the mid-Holocene coastal site of Thach Lac, northern-central Vietnam. *Archaeological Research in Asia*.
- Friedman GM. 1959. Identification of carbonate minerals by staining methods. *Journal of Sedimentary Research* 29:87–97.
- Fairbanks RG, Mortlock RA, Chiu T-C, Cao L, Kaplan A, Guilderson TP, Fairbanks TW, Bloom AL, Grootes PM, Nadeau M-J. 2005. Radiocarbon calibration curve spanning 0 to 50,000 years BP based on paired $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and ^{14}C dates on pristine corals. *Quaternary Science Reviews* 24:1781–1796.

- Forjanés Pablo, Roda MS, Greiner M, Griesshaber E, Lagos NA, Veintemillas-Verdaguer S, Astilleros JM, Fernández-Díaz L, Schmahl WW. 2021. Long-term experimental diagenesis of aragonitic biocarbonates: from organic matter loss to abiogenic calcite formation. *Biogeosciences Discussions*. doi: [10.5194/bg-2021-222](https://doi.org/10.5194/bg-2021-222).
- Hüls CM, Erlenkeuser H, Nadeau MJ, Grootes PM, Anderson N. 2010. Experimental study on the origin of cremated bone apatite carbon. *Radiocarbon* 52(2):587–599.
- Lam TMD, Nguyen TT, Tran TKQ, Bellwood P, Higham C, Petchey F, Grono E, Nguyen C, Piper PJ. 2020. Ru Diep and the Quynh Van Culture of Central Vietnam. *Archaeological Research in Asia* 22. doi: [10.1016/j.ara.2020.100190](https://doi.org/10.1016/j.ara.2020.100190).
- Larsen SC. 2015. recrystallization of biogenic aragonite shells from archaeological contexts and implications for paleoenvironmental reconstruction. Master of Arts. The Faculty of Western Washington University.
- Li H, Jin D, Li R, Li X. 2015. Structural and mechanical characterization of thermally treated conch shells. *Journal of the Minerals Metals and Materials Society* 67:720–725. doi: [10.1007/s11837-015-1330-y](https://doi.org/10.1007/s11837-015-1330-y).
- Lia XW, Jia HM, Yanga W, Zhang GP, Chen DL. 2017. Mechanical properties of crossed-lamellar structures in biological shells: a review. *Journal of the Mechanical Behavior of Biomedical Materials* 74:54–71.
- Lindauer S, Milano S, Steinhof A, Hinderer M. 2018. Heating mollusc shells. A radiocarbon and microstructure perspective from archaeological shells recovered from Kalba, Sharjah Emirate, UAE. *Journal of Archaeological Science: Reports* 21:528–537.
- Lindroos A, Orsel E, Heinemeier J, Lill J-O, Gunnelius K. 2014. Radiocarbon dating of Dutch mortars made from burned shells. *Radiocarbon* 56(3):959–968.
- Ling Li, Christine Ortiz. 2013. Biological design for simultaneous optical transparency and mechanical robustness in the shell of *Placuna placenta*. *Advanced Materials* 25:2344–2350. doi: [10.1002/adma.201204589](https://doi.org/10.1002/adma.201204589).
- Lofthus E, Rogers K, Lee-Thorp J. 2015. A simple method to establish calcite: aragonite ratios in archaeological mollusc shells. *Journal of Quaternary Science* 30(8):731–735.
- McGregor HV, Gagan MK. 2003. Diagenesis and geochemistry of Porites corals from Papua New Guinea: implications for paleoclimate reconstruction. *Geochimica et Cosmochimica Acta* 67(12):2147–2156.
- Milano S, Prendergast AL, Schöne BR. 2016. Effects of cooking on mollusk shell structure and chemistry: Implications for archeology and paleoenvironmental reconstruction. *Journal of Archaeological Science: Reports* 7:14–26.
- Morse W, Wang Q, Tsio MY. 1997. Influences of temperature and Mg:Ca ratio on CaCO₃ precipitates from seawater. *Geology* 25(1):85–87.
- Morse JW, Andersson AJ, Mackenzie FT. 2006. Initial responses of carbonate-rich shelf sediments to rising atmospheric pCO₂ and “ocean acidification”: role of high Mg-calcites. *Geochimica et Cosmochimica Acta* 70:5814–5830.
- Nguyen TC. 1998. Van hoa Quynh Van. Nxb KHXH. Ha Noi. [Quynh Van Culture. Hanoi: Social Sciences Publishers].
- Petchey F, Ulm S, David B, McNiven IJ, Asmussen B, Tomkins H, Richards T, Rowe C, Leavesley M, Mandui H, Stanisic J. 2012. Radiocarbon marine reservoir variability in herbivores and deposit-feeding gastropods from an open coastline, Papua New Guinea. *Radiocarbon* 54(3–4):967–978.
- Petchey F, Clark G, Lindeman I, O’Day P, Southon J, Dabell K, Winter O. 2018. Shellfish isotopic insight into changing sea-level and associated impact on the first settlers of the Mariana Archipelago. *Quaternary Geochronology* 48: 180–194. doi: [10.1016/j.quageo.2018.10.002](https://doi.org/10.1016/j.quageo.2018.10.002).
- Pham LH, Nguyen QM. 2001. Cac Ket Qua Xac Dinh Nien Dai Bang Phuong Phap Radiocarbon O Viet Nam Va Mot So Nhan Xet, [The results of the radiocarbon dating in Vietnam and some reviews of new archaeological finds and discoveries in 2001], *Khao Co Hoc* 2001(3):80–101.
- Piper PJ, Lâm TMD, Nguyen KTK, Nguyen TT, Higham C, Petchey F, Grono E, Bellwood P. The Neolithic of Vietnam. 2021. In: Nam K, Higham C, editors. *The Neolithic of Vietnam*. Oxford Handbook to Southeast Asian Archaeology. Oxford: Oxford University Press. p. 194–214.
- Reimer PJ, Bard E, Bayliss A, Beck JW, Blackwell PG, Bronk Ramsey C, Buck C, Cheng H, Edwards RL, Friedrich M, Grootes PM, Guilderson TP, Hafflidason H, Hajdas I, Hatté C, Heaton TJ, Hoffmann DL, Hogg AG, Hughen KA, Kaiser KF, Kromer B, Manning SW, Niu M, Reimer RW, Richards DA, Scott EM, Southon JR, Staff RA, Turney CSM, van der Plicht J. 2013. IntCal13 and Marine13 radiocarbon age calibration curves 0–50,000 years cal BP. *Radiocarbon* 55(4):1869–1887. doi: [10.2458/azu_js_rc.55.16947](https://doi.org/10.2458/azu_js_rc.55.16947).
- Russo CM, Tripp JA, Douka K, Higham TF. 2010. A new radiocarbon pretreatment method for molluscan shell using density fractionation of carbonates in bromoform. *Radiocarbon* 52(3): 1301–1311.
- Southon J, Santos G, Druffel-Rodriguez K, Druffel E, Trumbore S, Xu X, Griffin S, Ali S, Mazon M. 2004. The Keck Carbon Cycle AMS Laboratory, University of California, Irvine: Initial operation and a background surprise. *Radiocarbon* 46(1):41–49.

- van Strydonck M, Boudin M, De Mulder G. 2010. The carbon origin of structural carbonate in bone apatite of cremated bones. *Radiocarbon* 52(2–3):578–586.
- Sun W, Jayaraman S, Chen W, Persson KA, Ceder G. 2015. Nucleation of metastable aragonite CaCO_3 in seawater. *PNAS* 112(11):3199–3204. doi: [10.1073/pnas.1423898112](https://doi.org/10.1073/pnas.1423898112).
- Vita-Finzi C, Roberts N. 1984. Selective leaching of shells for ^{14}C dating. *Radiocarbon* 26(1): 54–58.
- Webb GE, Price GJ, Nothdurft LD, Deer L, Rintoul L. 2007. Cryptic meteoric diagenesis in freshwater bivalves: Implications for radiocarbon dating. *Geology* 35(9):803–806.
- Yates T. 1986. Studies of non-marine mollusks for the selection of shell samples for radiocarbon dating. *Radiocarbon* 28:457–463.
- Yates TJS, Spiro BF, Vita-Finzi C. 2002. Stable isotope variability and the selection of terrestrial mollusc shell samples for ^{14}C dating. *Quaternary International* 87:87–100.
- Yokoyama Y, Esat TM, Lambeck K, Fifield LK. 2000. Last ice age millennial-scale climate changes recorded in Huon Peninsula corals. *Radiocarbon* 42(3):383–401.



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Dating Thach Lac: cryptic CaCO₃ diagenesis in archaeological food shells and implications for 14c

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