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Mollusk carbonate thermal behaviour and its implications in understanding prehistoric fire events in shell middens

Stefania Milano[a,b,*], Susanne Lindauer[c], Amy L. Prendergast[d], Evan A. Hill[e], Chris O. Hunt[f], Graeme Barker[g], Bernd R. Schöne[b]

[a] Department of Human Evolution, Max Planck Institute for Evolutionary Anthropology, Deutscher Platz 6, 04103 Leipzig, Germany
[b] Institute of Geosciences, University of Mainz, Joh.-J.-Becherweg 21, 55128 Mainz, Germany
[c] Curt-Engelhorn-Zentrum Archaeometry gGmbH, Klaus-Tschira-Archaeometry-Centre, C4, 8, 68159 Mannheim, Germany
[d] School of Geography, University of Melbourne, 221 Bouverie St, Carlton 3053, VIC, Australia
[e] School of Natural and Built Environment, Queens University Belfast, Elmwood Ave, Belfast BT9 6AY, United Kingdom
[f] School of Natural Sciences and Psychology, Liverpool John Moores University, Byrom Street, Liverpool, United Kingdom
[g] McDonald Institute for Archaeological Research, University of Cambridge, Downing St, Cambridge CB2 3ER, United Kingdom

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A B S T R A C T

Archaeological shell middens are particularly important for reconstructing prehistoric human subsistence strategies. However, very little is known about shellfish processing, especially when related to the use of fire for dietary and disposal purposes. To shed light on prehistoric food processing techniques, an experimental study was undertaken on modern gastropod shells (*Phorcus lineatus*). The shells were exposed to high temperatures (200–700 °C) to investigate subsequent mineralogy and macro- and microstructural changes. Afterwards, the three-pronged approach was applied to archaeological shells from Haua Fteah cave, Libya (*Phorcus turbinatus*) and from shell midden sites in the United Arab Emirates (*Anadara uropigimelana* and *Terebralia palustris*) to determine exposure temperatures. Results indicated that shells from the Haua Fteah were exposed to high temperatures (600–700 °C) during the Mesolithic period (ca. 12.7–9 ka), whereas specimens from the Neolithic period (ca. 8.5–5.4 ka) were mainly exposed to lower temperatures (300–500 °C). The thermally-induced changes in *A. uropigimelana* and *T. palustris* shells from the South East Arabian archaeological sites were similar to those seen in *Phorcus* spp. suggesting a broad applicability of the experimental results at an interspecific level. Although heat significantly altered the appearance and mineralogy of the shells, $^{14}C_{AMS}$ ages obtained on burnt shells fit within the expected age ranges for their associated archaeological contexts, indicating that robust radiocarbon ages may still be obtained from burnt shells. Our study indicates that the combination of microstructural and mineralogical observations can provide important information to infer shellfish processing strategies in prehistoric cultures and their change through time.

1. Introduction

Shells grow incrementally throughout the lifetime of mollusks and function as protection and support structures. Shells also serve as excellent palaeoenvironmental archives (i.e. Jones, 1983; Schöne et al., 2004; Butler et al., 2013), because they faithfully record the physical and chemical conditions of their ambient environment and temporal changes to these. Such information is stored in the form of geochemical and structural properties (Epstein et al., 1953; Goodwin et al., 2001; Schöne, 2008). Sclerochronology is the research field that studies the temporal context of shell chemical composition (i.e. stable isotopes and trace elements) and physical accretionary patterns to produce extremely highly resolved palaeoenvironmental reconstructions (Schöne et al., 2005; Miyaji et al., 2007; Milano et al., 2017; Oschmann, 2009). For example, shell oxygen isotope content ($\delta^{18}O_{shell}$) is routinely used as paleothermometer (Schöne et al., 2005; Ferguson et al., 2011; Prendergast et al., 2013; Prendergast and Schöne, 2017).

A rapidly growing interest in the research field of sclerochronology supports the spread of its methodologies and approaches to different disciplines such as archaeology and environmental biomonitoring (Mannino and Thomas, 2002; Andrus, 2011; Steinhardt et al., 2016; Schöne and Krause, 2016). The analysis of mollusk shell material is especially relevant within the framework of prehistoric archaeology. Shellfish have been an important dietary component since the

* Corresponding author at: Department of Human Evolution, Max Planck Institute for Evolutionary Anthropology, Deutscher Platz 6, 04103 Leipzig, Germany.
E-mail address: stefania_milano@eva.mpg.de (S. Milano).

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emergence of anatomically modern humans (~300 kyr ago; de Lumley, 1966), due to their easy accessibility, reliable availability throughout the year and source of proteins and micronutrients essential for physical development (Erlandson, 2001; Broadhurst et al., 2002; Marean et al., 2007; Fa, 2008).

The application of sclerochronology substantially broadens the potential use of mollusk shells in archaeology. Besides being suitable palaeoenvironmental archives, the shells become a key tool for understanding the response of human behaviour to climatic changes. For instance, $\delta^{18}O_{shell}$ is used to constrain the season of mollusk collection (Mannino et al., 2007; Burchell et al., 2013; Prendergast et al., 2016). In turn, seasonality provides information on the seasonal mobility of hunter-gatherer societies and helps to identify whether sites were permanently or ephemerally occupied (Shackleton, 1973; Mannino and Thomas, 2002; Eerkens et al., 2013). However, the processes related to mollusk preparation, consumption and disposal are still largely unknown (Milano et al., 2016). In some cases, it has been observed a modification of the shell structure by removal of the gastropod apex with stone tool, thorn or canine tip to allow the mollusk to be sucked out (Girod, 2011). As for bivalves, the shells were sometimes scarred or wholesale smashed (Hammond, 2014). Evidence of pyrotechnology associated with mollusk shell middens suggests that a certain degree of heat exposure may have been involved in some cases (Erlandson et al., 1999; Berna and Goldberg, 2008; Taylor et al., 2011). However, few studies have addressed the reconstruction of such processes in the framework of prehistoric marine resource exploitation (Andrus and Crowe, 2002; Aldeias et al., 2016; Milano et al., 2016) and this study will be the first instance where this has been carried out.

The present study builds upon previous work by Milano et al. (2016) who found that significant structural and chemical changes occurred in modern mollusk shells when they were heated at ≥300 °C for 20 min or more. Here, we investigate the effects of a shorter heat exposure (5 min), since shellfish are generally thought to be processed for short periods of time. To achieve this aim, modern *Phorcus lineatus* are used as a calibration tool to understand the response to thermal treatments at the macro-, microstructural and geochemical level. These findings are then applied to archaeological specimens from the Haua Fteah, eastern Libya (*Phorcus turbinatus*) to test whether high temperatures exposure can be detected in archaeological shells of the same genus using the three-pronged approach developed in the experimental phase. Archaeological specimens from the United Arab Emirates (*Anadara uropigimelana* and *Terebralia palustris*) are used to understand the efficacy of this three-pronged approach on a broader scale to other mollusk species. Furthermore, given the importance of shells for radiocarbon dating coastal sites and the abundance of burnt shells in middens (Douka et al., 2014; Lindauer et al., 2016), we present preliminary results on the influence of thermal alterations on shell radiocarbon dating results.

2. Materials and methods

A total of 41 shells were analysed (Table 1). Fifteen live-collected shells of *P. lineatus* were used for the experimental phase. The archaeological material consisted of eighteen specimens of *P. turbinatus* selected from key occupation contexts in the Mesolithic and Neolithic layers from the Haua Fteah cave in Libya, as well as six specimens of *A. uropigimelana* and two specimens of *T. palustris* from shell midden sites near Kalba in the United Arab Emirates (Fig. 1).

2.1. Shell material: P. lineatus and P. turbinatus

Phorcus spp. are rocky shore gastropods living in the intertidal zone along the Mediterranean (*P. turbinatus:* Menzies et al., 1992; Schembri et al., 2005; Mannino et al., 2008; Prendergast et al., 2013) and Eastern North Atlantic coasts (*P. lineatus:* Kendall, 1987; Donald et al., 2012; Gutiérrez-Zugasti et al., 2015). Both species are sensitive to seasonal environmental changes, specifically water temperature fluctuations. Furthermore, they are extremely abundant in prehistoric sites of this region (Mannino and Thomas, 2001; Colonese et al., 2011; Hunt et al., 2011; Bosch et al., 2015; Gutiérrez-Zugasti et al., 2015). Therefore, many previous studies have used their geochemical data for palaeoenvironmental reconstructions (Mannino et al., 2003; Colonese et al., 2009; Prendergast et al., 2016).

In the present study, *P. lineatus* (previously known as *Osilinus lineatus* and *Monodonta lineata*) was selected as a modern reference and *P. turbinatus* (previously known as *Osilinus turbinatus*, *Monodonta turbinata* and *Trochocochlea turbinata*) for the archaeological case study. Despite being two distinct species, they share similar shell shape, size and the same microstructural organization and mineralogy and they live within the same microenvironments on the Mediterranean and Atlantic coasts. Their shell consists of two aragonitic layers with specific organizations. The outer shell layer (oSL) is arranged in spherulitic prismatic microstructures whereas the inner shell layer (iSL) consists of nacre (Mannino et al., 2008; Milano et al., 2016). The minor phenotypic and taxonomically relevant differences between the two species in shell colouration and aperture size likely do not influence the structural behaviour of the shell in reaction to thermal stress.

Table 1
List of studied specimens and details on their provenance.

ID	Species	Provenance	Period
A001	*P. lineatus*	Portugal	Modern
A001_M	*P. lineatus*	Portugal	Modern
A001_MR	*P. lineatus*	Portugal	Modern
A200	*P. lineatus*	Portugal	Modern
A200_M	*P. lineatus*	Portugal	Modern
A300	*P. lineatus*	Portugal	Modern
A300_M	*P. lineatus*	Portugal	Modern
A400	*P. lineatus*	Portugal	Modern
A400_M	*P. lineatus*	Portugal	Modern
A500	*P. lineatus*	Portugal	Modern
A500_M	*P. lineatus*	Portugal	Modern
A600	*P. lineatus*	Portugal	Modern
A600_M	*P. lineatus*	Portugal	Modern
A700	*P. lineatus*	Portugal	Modern
A700_M	*P. lineatus*	Portugal	Modern
M006_1	*P. turbinatus*	Haua Fteah, Libya	Capsian
M006_2	*P. turbinatus*	Haua Fteah, Libya	Capsian
M005_1	*P. turbinatus*	Haua Fteah, Libya	Capsian
M005_2	*P. turbinatus*	Haua Fteah, Libya	Capsian
M002_1	*P. turbinatus*	Haua Fteah, Libya	Capsian
M002_2	*P. turbinatus*	Haua Fteah, Libya	Capsian
M002_3	*P. turbinatus*	Haua Fteah, Libya	Capsian
U747_1	*P. turbinatus*	Haua Fteah, Libya	Neolithic
U747_2	*P. turbinatus*	Haua Fteah, Libya	Neolithic
U747_3	*P. turbinatus*	Haua Fteah, Libya	Neolithic
U743_1	*P. turbinatus*	Haua Fteah, Libya	Neolithic
U743_2	*P. turbinatus*	Haua Fteah, Libya	Neolithic
U743_3	*P. turbinatus*	Haua Fteah, Libya	Neolithic
U743_4	*P. turbinatus*	Haua Fteah, Libya	Neolithic
U742_1	*P. turbinatus*	Haua Fteah, Libya	Neolithic
U742_2	*P. turbinatus*	Haua Fteah, Libya	Neolithic
U742_3	*P. turbinatus*	Haua Fteah, Libya	Neolithic
U742_4	*P. turbinatus*	Haua Fteah, Libya	Neolithic
K4 SL Ana3	*A. uropigimelana*	Oman Sea	Bronze Age
K4 SL GA1	*A. uropigimelana*	Oman Sea	Bronze Age
K4 BZ GT1	*T. palustris*	Oman Sea	Bronze Age
K4 BZ UGT1	*T. palustris*	Oman Sea	Bronze Age
KSM UBL Ana2	*A. uropigimelana*	Oman Sea	Neolithic
KS Ana 1	*A. uropigimelana*	Oman Sea	Neolithic
KK1 Ana3	*A. uropigimelana*	Oman Sea	Neolithic
KK1 Ana4	*A. uropigimelana*	Oman Sea	Neolithic

2.2. Shell material: A. uropigimelana and T. palustris

A. uropigimelana and *T. palustris* inhabit tropical mudflats. *A. uropigimelana* is a bivalve of the Arcidae family (ark clams), which is