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Thermal Influences on Shells: an Archaeological Experiment from the Tropical Indo-pacific

Annette Oertle[1,2,3] · **Katherine Szabó**[4]

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Abstract

Thermal influences on marine molluscs are poorly understood across all disciplines, including archaeology. This presents potential issues for further analysis including radiocarbon dating and stable isotope analysis, as well as hindering our understandings of processing and preparation methods for shell in the past. Different methods of burning or heating may not always leave visual signs on a shell; however, a variety of structural and chemical changes may take place. Here, we present an experimental study using modern-day shells of five tropical marine species designed to explore how various thermal interventions modified shells in terms of microstructure (scanning electron microscope) and mineralogy (X-ray diffraction). We found distinct differences between the taxa using varied temperatures and durations, with shell microstructure playing a key role in responses to thermal stresses. This study highlights the importance of acknowledging this variation, both when structuring research as well as seeking to interpret archaeological shell remains.

Keywords Thermal alteration · Microscopy · Experimental archaeology · Shell microstructure

Introduction

As a biocarbonate, archaeological shell is vulnerable to a wide range of taphonomic processes, from acid dissolution, to weathering, to structural alteration when subjected to high temperatures. Whilst some of these processes leave clear visual signatures (e.g. Claassen, 1998; Hammond, 2014; Stein, 1992; Weiner, 2010), some, such

✉ Annette Oertle
annette.oertle@univie.ac.at

[1] Department of Evolutionary Anthropology, University of Vienna, Vienna, Austria

[2] Max Planck Institute for the Science of Human History, Jena, Germany

[3] Human Evolution and Archaeological Sciences (HEAS), University of Vienna, Vienna, Austria

[4] Pre-Construct Archaeology, Cambridge, UK

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as internal crystalline changes, are more difficult to pinpoint without further analysis. Given the likely exposure of much archaeological shell to fire and heat via cooking processes, we can also assume that variables likely to induce structural changes are commonly present. Although the literature is still scant on the precise nature of such taphonomic transformations, the impact of thermal alteration on archaeological shell and the interaction with subsequent post-depositional processes has received greater attention in recent years (Milano *et al*., 2018; Muckle, 1980; Villagran, 2019). Experimental studies (discussed below) have been the principal approach to achieving a greater understanding of the impact of thermal processes on shell, with methodologies primarily drawing upon ethnographic observations of various cooking methods.

Archaeological shell material that has undergone thermal alteration can sometimes be identified through visible changes such as thermal fracture and discolouration; however, lower temperature methods (e.g. boiling) may not alter the shell surface to the same extent (or at all) that elevated temperature and/or direct contact methods (e.g. roasting) can (Aldeias *et al*., 2016). Microscopic or structural transformations (Balmain *et al*., 1999; Milano & Nehrke, 2018; Yoshioka & Kitano, 1985), on the other hand, may be more pronounced and provide a better understanding of thermal effects on shell. Whilst the methods and degree of heating applied to shells will influence the transformations seen, so too will the initial structure of the shell. The microstructures of shells vary between shell taxa (Bøggild, 1930) and, as such, individual examination is required to avoid oversimplifying patterns in the effects on thermally altered shell. This paper examines the effects of varying thermal influences on marine shell by observing the macroscopic, microscopic, and mineralogical changes on taxa with cross-lamellar, foliate, prismatic, and nacreous microstructures.

Heating Shellfish: Experimental and Ethnographic Studies

Experimental studies have attempted to understand and identify the traces that different cooking methods leave on archaeological shell material in addition to distinguishing between natural and cultural fires. There is a range of larger methodological considerations that need to be included in experimental studies that take ethnographically and ethnohistorically observed methods of cooking (e.g. boiling, roasting on fires/coals, heating in earth ovens, and steaming (see studies cited in Waselkov, 1987) into account. Roasting and heating molluscs over a fire are common methods of cooking and have been described in numerous ethnographies (e.g. Bird & Bliege-Bird, 1997; Kalm, 1966; McGee & Hewitt, 1898; Meehan, 1982; Oberg, 1973; Quinn, 1967) as taking a relatively short period of time, indeed only a few minutes (Meehan, 1982:87). Domestic fire temperatures can range between 317 and 950 °C (Wolf *et al*., 2013) depending on fuel type, whilst boiling cooks the mollusc at relatively low temperatures (100 °C); however, some form of water retaining vessel is necessary (Leach, 1981). Each of these cooking methods is variable in themselves and as such makes it difficult to identify not only whether molluscs have been cooked but also through which method. In addition, the complex issue

of distinguishing between cooking, incidental burning, or landscape fires (cultural vs natural) is largely absent but has primarily focused on micromorphological differences (Aldeias & Bicho, 2016; Berna *et al*., 2007; Duarte *et al*., 2019; Villagran, 2014, 2019). Experimental studies exploring cooking methods and natural vs cultural thermal processes need to be undertaken with a range of variables in mind (e.g. thermal method, duration, temperature, shell type, and scale of analyses).

Most experimental research to date has focussed upon differentiating the traces of different types of cooking upon shell, and it is generally assumed that any visible discolouration or physical alteration from cooking is dependent on the temperature, proximity, and duration of the shell's exposure to heat. Additionally, experimental analyses of burnt shells have primarily explored macroscopic changes (d'Errico *et al*., 2015; Spennemann, 2004); however, recent studies have focussed on microscopic effects on structure, as well as mineral and isotopic composition (Aldeias *et al*., 2016; Milano *et al*., 2016, 2018; Müller *et al*., 2017; Villagran, 2014). Although each of these studies provides valuable data on the effects of thermal alteration on shell, each overlooks a particular variable or component that can impact these results. There is little acknowledgement in the literature regarding how shells of different microstructural types will likely react to thermal processes in very different ways. Microstructural variation is an important variable to consider as different structures degrade in distinct ways (Szabó, 2017), which has impacts on the visible traces of thermal alteration. We take as our starting point that the way in which is shell is put together will influence the way in which it transforms and, eventually, disaggregates.

Additionally, there is little acknowledgement in the literature regarding how heating versus burning may result in substantially different modifications. We expect that the heating and burning of shell would have different outcomes as they are two different processes. Burning (a form of combustion) is a chemical reaction between a fuel and oxygen in which heat is produced (Turns, 1996) and flames are emitted within the primary combustion zone. Various gases, smoke, and vapour are also emitted during the burning process. On the other hand, heating is a more stable process with an even temperature of hot air surrounding the material being cooked (Urone and Hinrichs, 2012). It is not the purpose of this paper to attempt to match traces of burning or heating to particular cooking or heating methods but rather to highlight the variable nature of shell cooking and how that can manifest in terms of macro, micro, and mineralogical traces between varying taxa. Further experimental studies are needed to help distinguish traces of burning, heating, and unintentional heat exposure to be able to attempt identification of cooking methods on archaeological shell.

Formation of a Shell

The shells of different molluscan taxa are constructed in a great variety of ways that result in diverse structural properties. Molluscs create their shells by periodically depositing calcium carbonate ($CaCO_3$) layers, which result in the formation of growth lines (Vermeij, 1993). There is an episodic nature to shell growth,

where the punctuated 'growth' lines are in fact periods of stagnation. The ocean is supersaturated with calcium and dissolved carbon dioxide (Chave & Suess, 1970; Vermeij, 1993) which are the building blocks for shell. The fabric of a shell is made up of biogenic calcium carbonate crystals (calcite or aragonite) along with an organic matrix (Lowenstam & Weiner, 1989; Vermeij, 1993).

Calcite is the more stable form of $CaCO_3$, and aragonite crystals will eventually morph into calcite, either as a part of the fossilisation process or at high temperatures (Solem, 1974). This is referred to as recrystallisation. Biogenic aragonite tends to recrystallise at around 280–400 °C (Yoshioka & Kitano, 1985); however, experimental studies on shell (Aldeias *et al*., 2016; Balmain *et al*., 1999; Milano *et al*., 2016; Müller *et al*., 2017; Staudigel & Swart, 2016) show that the point of conversion of primary biogenic aragonite to secondary calcite is variable between species and occurs at temperatures around 250–500 °C (Fig. 1). A second conversion occurs around 600–900 °C where biogenic calcite is stated to convert to calcium oxide (Herbert, 2008). Despite an array of studies on the effects of heating on various mollusc species in the areas of biology and chemistry (e.g. Balmain *et al*., 1999; Bourrat *et al*., 2007), few studies explore these effects in terms of use to archaeology. The experimental studies presented here thus attempt to more closely incorporate the range of variables, and likely transformations, seen in complex, multivariable non-laboratory contexts.

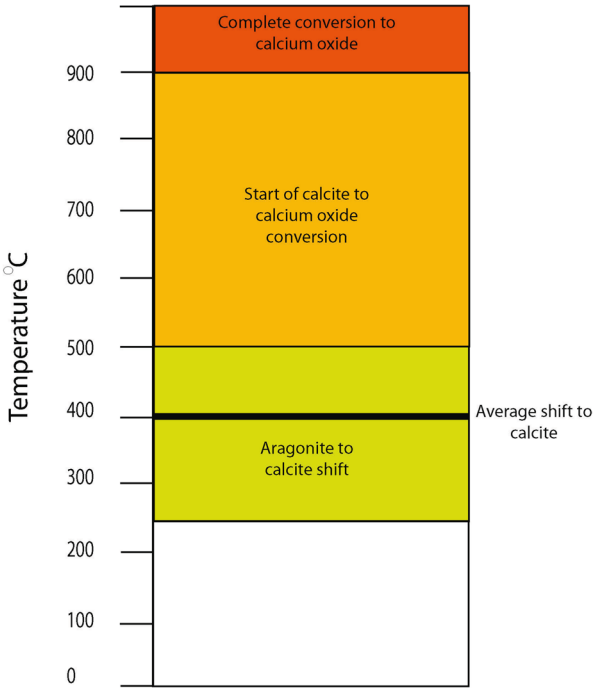

Fig. 1 Chemical changes in the constituents of mollusc shells after being exposed to different temperatures (adapted from Herbert, 2008:274). Temperature ranges taken from numerous studies (e.g. Aldeias *et al*., 2016; Balmain *et al*., 1999; Bourrat *et al*., 2007; Li *et al*., 2015; Müller *et al*., 2017; Parker *et al*., 2010; Staudigel & Swart, 2016)

Shell Microstructure

Numerous microstructural types are produced by molluscs (see Bøggild, 1930; Carter & Clark II, 1985) but the most common types are cross-lamellar, prismatic, foliate, nacreous, and amorphous (Fig. 2). Each of these microstructures reacts differently to external processes such as force or temperature (Clark II, 1999) and as such should be considered separately in terms of both morphology and mineralogy, to compare the effects of thermal alteration. The species selected for the experimental work here were carefully chosen not only to represent not just an array of these

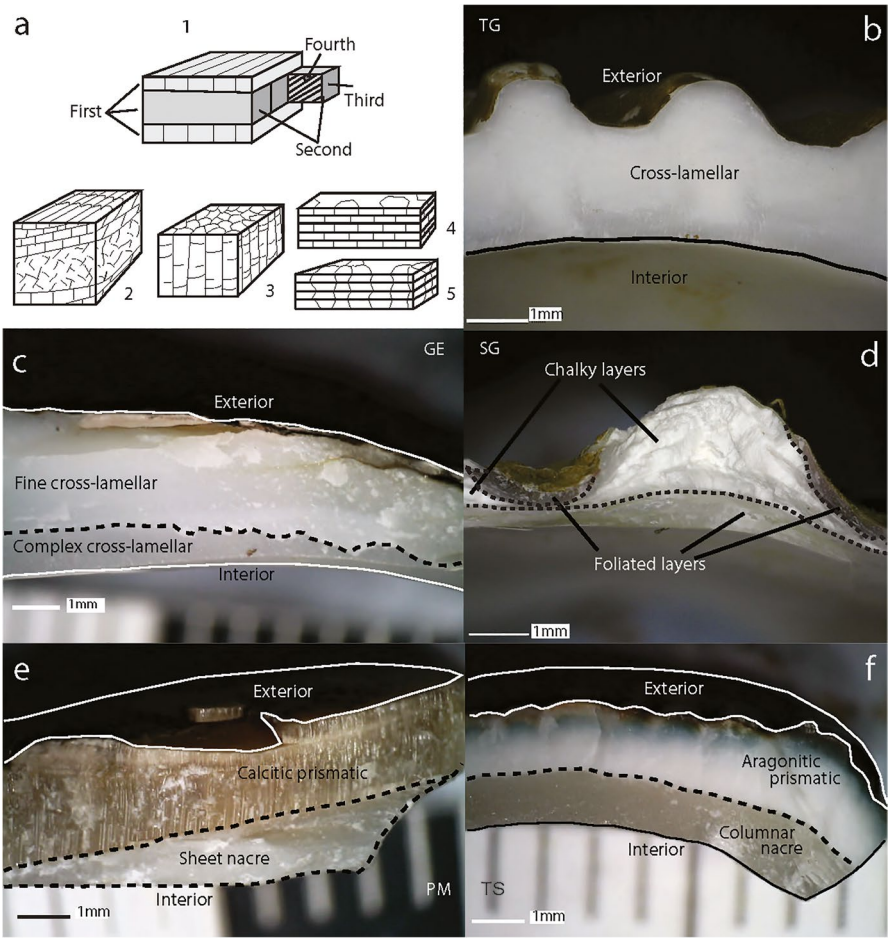

Fig. 2 Microstructure of different shell species. **a** 5 types of microstructures: (1) cross-lamellar showing four orders of lamellar construction (2) foliate (with chalky layer at centre) (3) prismatic (4) sheet nacre and (5) columnar nacre; **b** *Telligarca granosa* showing cross-lamellar structure; **c** *Geloina expansa* showing fine and complex cross-lamellar layers; **d** *Saccostrea glomerate* showing interchanging chalky and foliate layers; **e** *Pinctada maxima* showing prismatic and sheet nacre layers; **f** *Turbo setosus* showing prismatic and columnar nacre layers

major microstructural types, but also to reflect species frequently encountered in high numbers in tropical (and sometimes sub-tropical) archaeological sites. These include *Tegillarca granosa*, *Geloina expansa*, *Saccostrea glomerata*, *Pinctada maxima*, and *Turbo setosus* (see Table 1).

Cross-lamellar microstructures (Fig. 2a.1) are hierarchical and are made up of aragonitic crystallites with an organic matrix (chitins, proteins, and glycoproteins) surrounding the third-order lamellae (Levi-Kalisman *et al*., 2001; Uozumi *et al*., 1972). Tablets are stacked to create mutually parallel, rod-, blade-, or lath-like basic structural units (third-order lamellae) which are aggregated into block-like first-order lamellae (Carter *et al*., 2012; Dauphin & Denis, 2000). These lamellae are angled in alternating directions, meaning that there is no clean path of fracture (Currey & Kohn, 1976) and any force is re-routed between each angled layer (Szabó, 2017). How different structures affect the fracture mechanics of each species is important to understand in terms of the process of particulars of fragmentation in archaeological contexts. This microstructure is the most common form found in evolved gastropods and bivalves (Almagro *et al*., 2016). *Tegillarca granosa* (Arcidae) and *Geloina expansa* (Corbiculidae) are built of cross-lamellar microstructures (Fig. 2b, c) as seen in SEM images (Fig. 3a and b). *G. expansa* also has cross-lamellar sub-layers, with the upper exterior made of fine cross-lamellar and the lower interior made of complex cross-lamellar (Isaji, 1993). This sub-layering can be seen using low-power microscopy (Fig. 2c).

Foliate microstructures (Fig. 2a.2) are composed of long calcitic blade-like laths (Kent, 1992) set parallel to one another, with sharply angular, pointed terminations on the depositional surface (Carter *et al*., 2012). These laminae/folia are rather weak and tend to flake and splinter instead of fracturing cleanly (Zuschin *et al*., 2003). The oyster, *Saccostrea glomerata*, is constructed of a foliate and chalky structure (Fig. 2d). Chalky microstructures occur within calcitic foliated shell layers of many taxa within the superfamily Ostreoidea. This chalky microstructure has mutually parallel and irregularly aggregated blades or leaflets (Fig. 3c middle). Both the

Table 1 Methods and species of shells used in the experiment and corresponding microstructural types

Method	Duration	Species	Species microstructure
Coals (burning)	5	*Tegillarca granosa* (blood cockle)	Cross-lamellar
Flame (burning)	5	*Geloina expansa* (mud clam)	Cross-lamellar
400 °C (heating)	5	*Saccostrea glomerata* (Sydney rock oyster)	Foliate
600 °C (heating)	5	*Pinctada maxima* (gold-lipped pearl oyster)	Calcitic prismatic exterior, sheet nacre interior
Coals (burning)	10	*Turbo setosus* (common turban)	Aragonite prismatic exterior and columnar nacre interior
Flame (burning)	10		
400 °C (heating)	10		
600 °C (heating)	10		

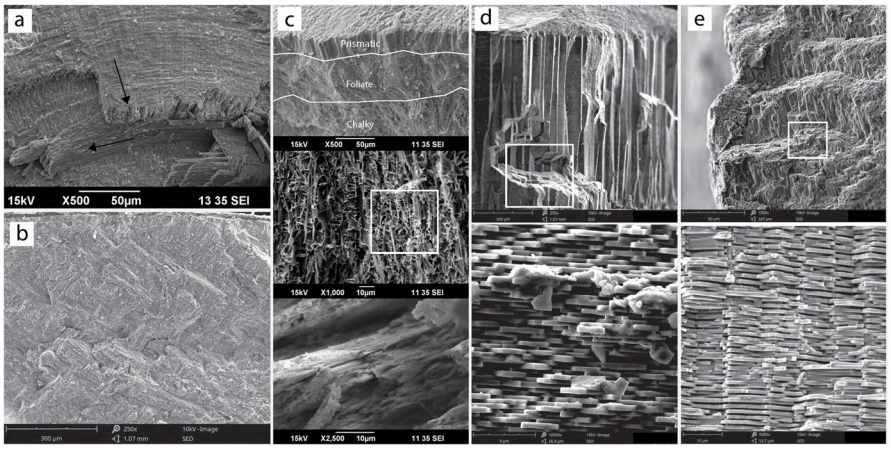

Fig. 3 SEM images of modern shell microstructures. a *Telligarca granosa* with various orders of crossing lamellar (arrows showing different directions of lamellar structure), **b** *Geloina expansa* also showing crossed-lamellar structure, **c** *Saccostrea glomerata* showing mix of layers at top, focus on chalky layer with blades and leaflets in centre, and folia in bottom image, **d** *Pinctada maxima* with prismatic layer (focus on prisms) in top image and sheet nacre in bottom, **e** *Turbo setosus* showing prismatic layer (focus on same prism structure) in top image and columnar nacre in bottom image

foliate and chalky layers are structurally similar, with differences in orientation and aspect of the result of variations in growth conditions (Checa *et al*., 2018).

Prismatic microstructures can be found as the outermost layer of shells (Fig. 2e, f) in taxa such as *Pinctada maxima* (Pteriidae) and *Turbo setosus* (Turbinidae). The crystal tablets (crystallites) are stacked to form long polygonal columns/prisms that are arranged side-by-side and aligned perpendicular to the shell surface (Fig. 2a.3). The prismatic microstructure lends itself to clean breaks that move downwards until the force dissipates laterally upon hitting the (typically) inner nacreous layer (Szabó, 2017). There are four categories of prismatic microstructures: simple, fibrous, spherulitic, and composite (Carter, 1990). Both *P. maxima* and *T. setosus* have simple prismatic exterior layers (Fig. 3d and e top); however, *P. maxima* is made of calcite whereas *T. setosus* is aragonite. The simple prismatic structure is composed of prisms which are made of calcite/aragonite crystallites, lateral lines, and insoluble organic sheaths (Kobayashi & Samata, 2006).

Nacre (columnar and sheet) is aragonitic and is generally the strongest form of microstructure (Fig. 2e, f). The nacre tablets are surrounded by an organic matrix in a 'brick-and-mortar'-like structure (Watabe, 1988). Sheet nacre (Fig. 2e) is where the tablets are laid down horizontally uniform in thickness across the surface of the shell interior (Fig. 2a.4) (Suzuki & Nagasawa, 2013) and is characteristic of bivalves. Columnar nacre (Fig. 2f), seen in gastropods (Suzuki & Nagasawa, 2013; Wilbur & Saleuddin, 1983), is made up of tablets or platelets of aragonite stacked in columns with each covered in an organic matrix (Fig. 2a.5). Nacre is high in organic material; however, once the mollusc dies, the organic material decays and the shell quickly loses its strength (Vermeij, 1993). Numerous studies on the mechanical properties of nacreous material have provided a greater understanding of the form and function

of this microstructure (Currey *et al*., 2001). Despite its structural strength, nacre is vulnerable to shearing if force is applied parallel to the nacre sheets (Szabó, 2017). Thermal processes on nacre can also affect the structural strength of the nacreous arrangement. *P. maxima* and *T. setosus* also contain an interior nacreous layer; however, *P. maxima* is constructed of sheets (Fig. 3d bottom) as opposed to the columns in *T. setosus* (Fig. 3e bottom).

Methodology

The aim of these experiments was to identify and map various markers of burning/heating on different mollusc species through visual, microscopic, and mineralogical signatures. The experiments were undertaken in the field on the island of Malaita in the Solomon Islands as well as in the Zooarchaeology Laboratory at the University of Wollongong, Australia. The field experiment was undertaken concurrently with ethnoarchaeological studies of gathering, processing, and discard practices in the Solomon Islands (see Oertle & Szabó, 2019), providing suitable shell samples and combustible materials. For each of these experiments, different processes of burning/heating on various mollusc species were undertaken for differing durations. The different processes were based on methods of cooking observed in the field from numerous ethnographic records (see Waselkov, 1987), which included direct flame, indirect flame on coals, and heating via an oven.

Four different microstructures (crossed-lamellar, foliate, nacre, and prismatic) were targeted for these thermal experiments. Each of these microstructures can be found in certain shell species (see Figs. 2 and 3) and thus five species (Table 1) were selected due to their availability and prominence in Indo-Pacific archaeological shell deposits. Bulk samples of each of these species, with known taphonomic histories, were sourced from known locations to be used for these experiments.

Saccostrea glomerata (SG) was sourced from an oyster farm in Nowra, NSW, Australia. Freshly shucked mollusc meat was removed and the shell was left to air-dry in the shade for 7 days then bagged and accessioned. *Pinctada maxima* (PM) samples were sourced from Cygnet Bay Pearl Farm and Clipper Pearls, WA, Australia, and accessioned. *Geloina expansa* (GE) and *Tegillarca granosa* (TG) were sourced live from the Honiara central markets in the Solomon Islands. Both species had to be boiled for 15–20 min for the valves to open and the meat was then removed. The valves were then left to air-dry for 2–3 days. The *Turbo setosus* (TG) samples were live-collected at Langa Langa Lagoon, Malaita, Solomon Islands, then boiled for 20–25 min to cook and open. The meat was removed and the shells were left to air-dry in the shade for 2–3 days.

Recent experimental studies by Milano *et al*. (2016) and Aldeias *et al*. (2016) showed that boiling at 100 °C created no visual changes and had no effect on the microstructure, mineralogy, or isotopic profile of the shell. The only change appeared in *P. turbinatus*, with a slight shift in the nacre platelet organisation when boiled for 60 min (Milano *et al*., 2016:17). Based on these studies, the preparation by boiling for some of the mollusc species during this experiment was determined to have no effect on microstructure due to the short duration and low temperatures

used. Although these studies show that boiling had no discernible effect on the selected species, this may not necessarily be the case for all taxa or microstructures. Nevertheless, the mollusc samples used in the following experiment were not cooked (50–100 °C) for more than 25 min (the total time it took for a large stock pot full of the shells and water to be brought to a boil). It was not possible to record the exact timing for the *GE* and *TG* values to open due to the large number of shells boiled at once; however, a duration of 5–15 min of boiling (85–100 °C) can be estimated; thus, we can be confident that these mollusc samples are comparable to the live-caught molluscs and in turn provide an adequate-base comparison for thermal and chemical experiments.

Every shell sample was given an accession number, weighed, length and width measured, and photographed. The burning/heating experiment included four different methods: direct flame (in campfire) and indirect flame (coals, campfire), oven heating at 400 °C and at 600 °C (muffle furnace). These two temperatures were chosen to cover expected aragonite to calcite recrystallisation at approximately 400 °C and a higher flame temperature at roughly 600 °C. Four samples of each species were kept unburnt as controls and the size/weight of each shell was kept as similar as possible for each species. The durations of 5 min and 10 min were selected due to the short duration of cooking needed for a mollusc to be cooked, particularly with bivalves (Meehan, 1982). The 5- and 10-min durations were applied to each of the methods, with two shell samples used within each experimental phase. This resulted in a total of eight different thermal experimental studies (Table 1).

Burning and Heating Methods

In the field, a small fire was made on a cement fireplace with coconut fibres, shell, and fronds, as well as a wood known locally as *Agua* (*Pometia pinnata*). Two thermocouple probes were positioned into the fire close to where the shells were placed (Fig. 4a). The probes were connected to a data logger (QuadTemp2000) and then through to the laptop software to record temperatures in real time.

Four shells of each species were placed on burning pieces of wood (Fig. 4a) with flames ranging between temperatures of 532–680 °C. After 5 min, two of the shells were removed and the other two at 10 min. Once the direct flame method was undertaken for each shell species, the fire was left to die down to burning coals with temperatures averaging around 400 °C (Fig. 4b, c). This temperature was chosen based on the stated temperature range that aragonite recrystallises to calcite (Aldeias *et al*., 2016; Balmain *et al*., 1999; Milano *et al*., 2016; Müller *et al*., 2017; Staudigel & Swart, 2016).

The flame temperatures of fires can have a wide range, between 300 and 1500 °C (David, 1987; Wolf *et al*., 2013; Wright & Bailey, 1982), and the temperatures reached on a shell surface are not uniform. Unlike the controlled muffle furnace heated samples, the burning with fire method was more actualistic as there was a variation in temperatures even with the same experimental method and duration (three instances of fires were made as all the shells could not fit at once). Thermocouple probes placed next to the shells had distinctly different

Fig. 4 Progress photos during burning and heating experiment. **a** Showing fire for flame method, **b** and **c** showing coal methods, **d** showing samples before inserting into muffle furnace for heating method

temperature ranges for each method (Fig. 5), and thus, the aim of having a variation between the different cooking methods was met.

Flame temperatures fluctuated between 532 and 680 °C throughout the experiment (see Fig. 5). Shell species were added to the fire at staggered intervals due to space and timing and therefore have different temperature ranges. The burning of wood also caused shifting of the temperature probes on occasion. Figure 5 shows relatively small variability in the temperature of coals over 10 minutes, whilst there is greater variability during the flame method experiment. The temperature for coal *Turbo setosus*, however, is an outlier as the probe recorded temperatures between 520 and 640 °C. This may have been due to the probes shifting during the experiment or some other factor.

The heating experiments were undertaken with a muffle furnace at the University of Wollongong. The furnace was set to 400 °C and left for 30 min to preheat before the shells were added. Four shells of each species were placed in the furnace with two removed after 5 min and the remaining two after 10 min (Fig. 4d). The furnace temperature was then increased to 600 °C and four more shells of each species were placed in the furnace, again with two removed at 5 and 10 min intervals.

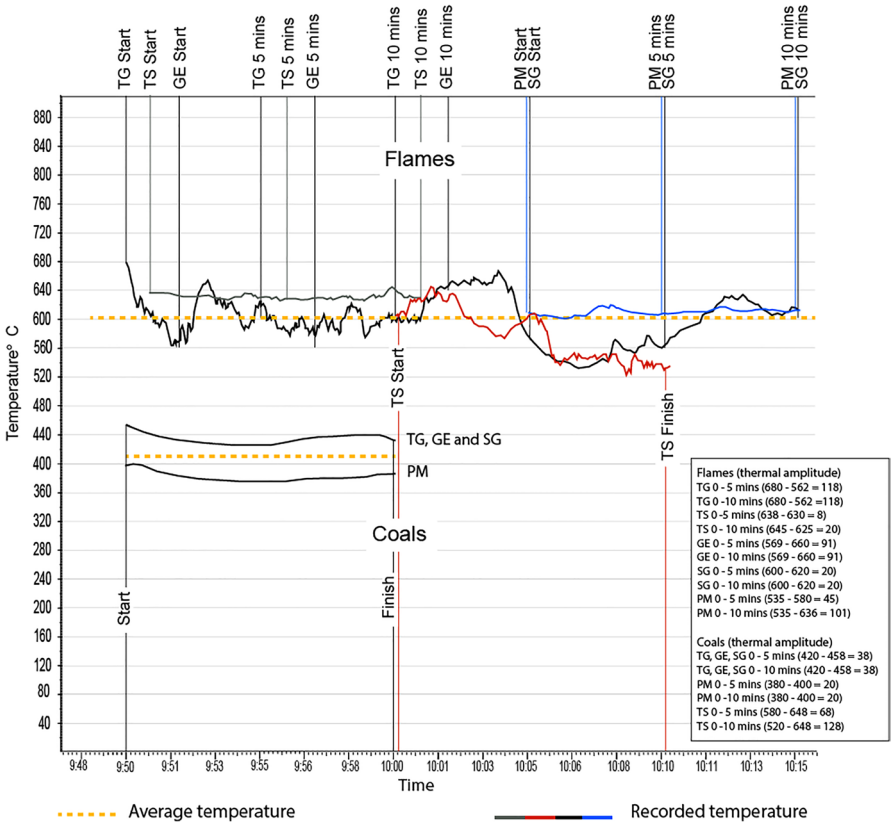

Fig. 5 Recorded temperatures during burning experiment for coal and flame methods. Lines showing start and end points for different species during the flame method (TG - Telligarca granosa; GE - Geloina expansa; SG - Saccostrea glomerata; PM – Pinctada maxima; TS – Turbo setosus). Three instances of fires (flame method) were made to fit all the different shells, shown in black, grey, and blue temperature lines. For the coal method, TG, GE, and SG were placed on the coals and removed at the same time. Separate fires were made for PM and TS (red line). Issues with the probe moving during the experiment resulted in higher than normal temperatures recorded for TS coals (in red). The minimum and maximum temperatures experienced by each shell are outlined as thermal amplitude

Analyses

The shells were left to cool after burning and heating then photographed, weighed, measured, and analysed using a low-power microscope. Subsamples were taken for SEM and mineralogical analyses (XRD). These subsamples were taken from predetermined locations on the shell (Fig. 6). For SEM analyses, section fractures (undertaken by hand and with pliers to snap the shell) were taken from the *x* (perpendicular) and *y* (parallel) axis of the margin and body, as well as the *x* axis from the umbo/apex. The XRD subsamples were taken from three points on the margin, central body, and the umbo/apex. For mollusc species with

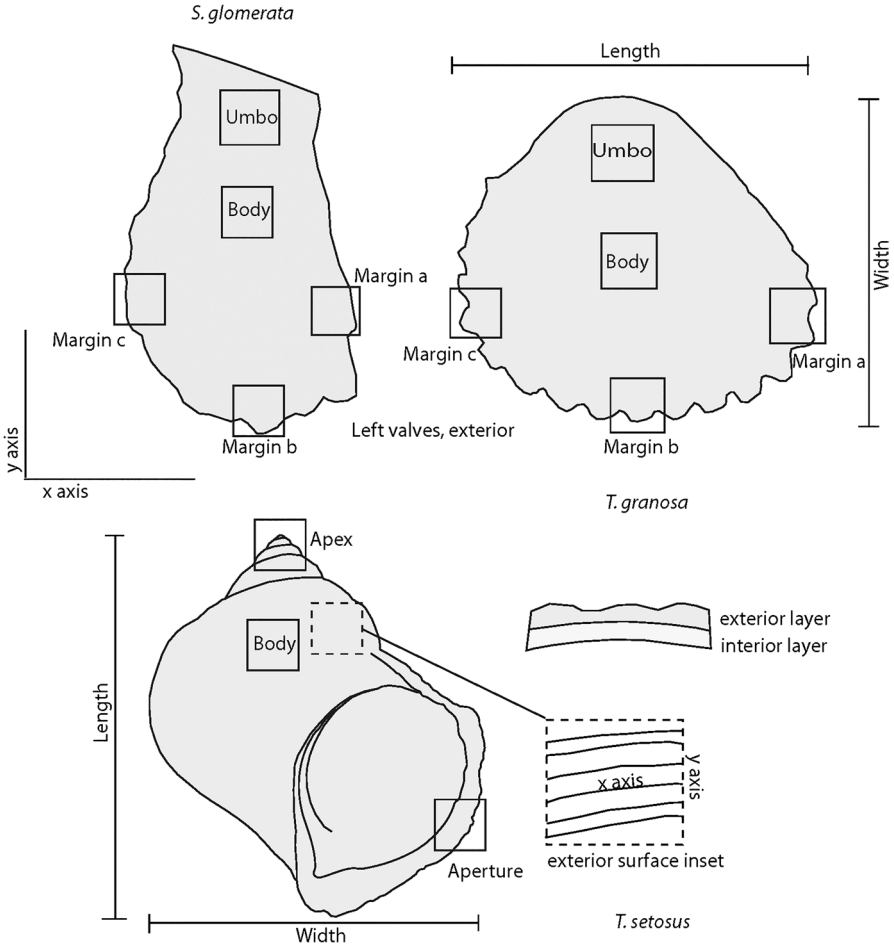

Fig. 6 SEM and XRD subsampling locations on different shell types (boxes). Length and width measurements are shown plus x and y axis for bivalves and gastropods, as well as subsampling of interior and exterior layers in multi-layered species

more than one microstructure (*P. maxima* and *T. setosus*), subsamples of both the interior nacre and the exterior prismatic surfaces were taken.

The fractured SEM subsamples were placed on stubs with non-conductive tape. Gold or carbon was sputter-coated on the stubs/shells before being inserted into the SEM. Two different models were used (JOEL 4870 EDS and PHENOM 2000), with comparative images taken from each individual subsample showing the same structure, and as such ensuring that the images were comparable for analytical purposes. Images were taken at 100, 250, 500, 1000, and 2500-micron magnification under secondary electron.

To determine any mineralogical transformation, subsamples were crushed into fine powder in an agate mortar and pestle with ethanol/acetone due to its fast

evaporation and to reduce production of heat during crushing. The powder samples were run through the X-ray diffraction machine (Spellmann X-ray generator attached to a copper X-ray tube with a Philips Goniometer). Normal machine settings were used — start: 4, finish: 70, step size: 0.02, scan speed: 2/min. Results were analysed on Traces and Siroquant to assess aragonite/calcite percentages. A comparison of percentages from each specimen was undertaken to examine the extent of any aragonite to calcite recrystallisation.

Control Comparisons

To distinguish any changes caused by thermal alteration, modern control mollusc samples of each species were examined under SEM for visual comparison and XRD for mineralogical comparison. For SEM analysis, all sub-samples were coated in 15 nm of gold (Au) and analysed on a JEOL JSM-6490LV. The ratio of aragonite and calcite was calculated using the programs Siroquant v.4 and GBC Traces v.6. SEM images of control sections were taken of both the *x* and *y* axes (Fig. 6) to show the different directions the lamellae have been laid down to create each of the structural layers.

Results

The effects of different thermal methods and durations can be seen with thermal fracture and discolouration in macroscopic images (Figs. 7 and 8) as well as morphing of different microstructural types (Fig. 9). Mineralogical results (Fig. 10) from different locations on each shell also highlight the variability of recrystallisation occurring between species, thermal methods, and duration. Each of the five species used in this study presents unique results in how varying thermal processes affected the macroscopic, microscopic, and mineralogical state of the shell (see Supp. 1 for more detail). Measurements of weight, length, and width of each shell before and after thermal alterations also show a large range in weight loss between species, as well as the length and width (primarily) gained (Fig. 11, Supp. 2 Table 1).

Thermal Fracture, Colouration, and Metrics

Changes in colouration on both the exterior and interior surfaces for each of the mollusc species are similar between matching temperatures regardless of whether the mollusc was burnt or heated (Figs. 7 and 8). The exterior surface provides a more structured gradation of colour compared to the interior surface. Higher temperatures leave grey/black or white colouration on the exterior surface, whereas lower temperatures can leave an array of yellow, olive, brown, or light grey colouration depending on the species (see Supp. 2 Table 2). This shows that no single colour can be used to identify specific temperatures on archaeological mollusc material due to the range of microstructures and thermal methods.

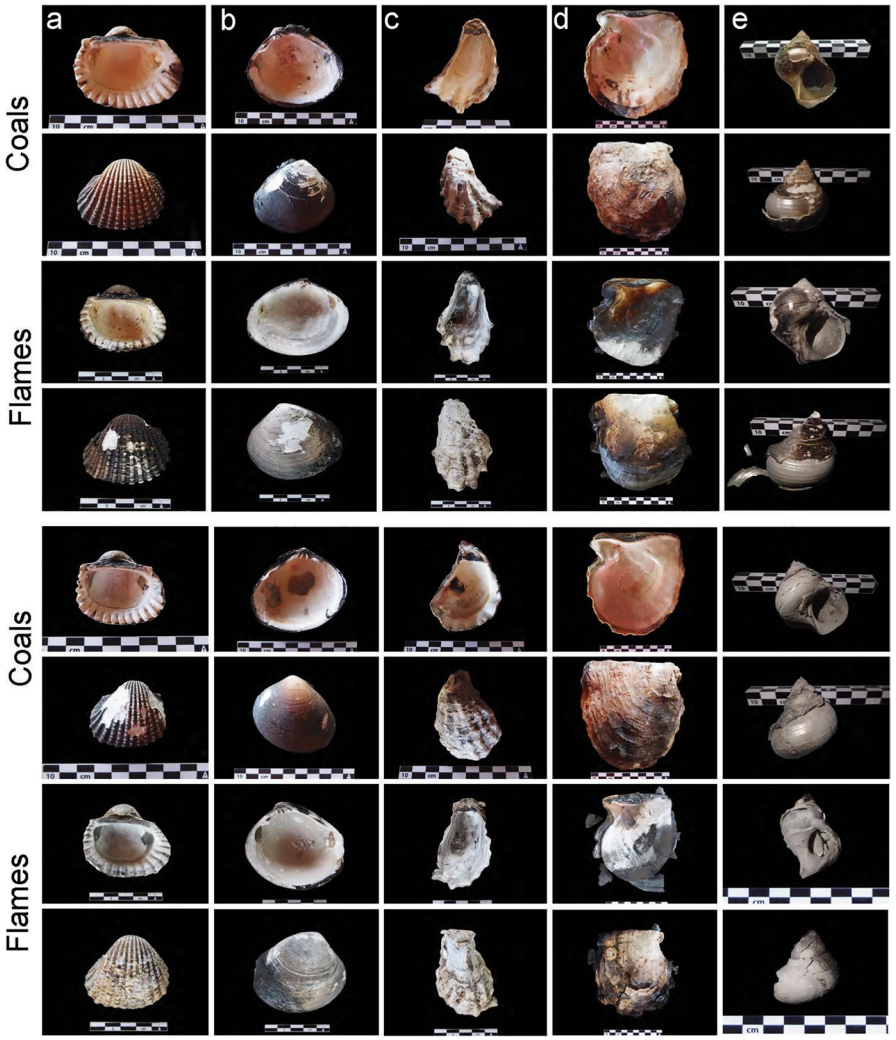

Fig. 7 Macro photos of *Telligarca granosa* (**a**), *Geloina expansa* (**b**), *Saccostrea glomerata* (**c**), *Pinctada maxima* (**d**), and *Turbo setosus* (**e**) interior and exterior after burning methods. Upper half– 5 minute duration, lower half – 10 minute duration. See Supp. 2 Table 2 for the recorded Munsell colours

The initial and final measurements of length and width show differences between species for the varying burning and heating methods (see Supp. 2 Table 1). The differences in length and width were calculated into the percentage of change (loss/gain) for each of the 16 experimental samples. An average percentage of loss/gain was calculated from the two samples for each method (Fig. 12). Negative values were due to thermal fracture where margins were lost from the main body. There is variation in percentage of change (Fig. 12) with each of the five species, with *P. maxima* showing the greatest loss of length (−14.5 to 0%) and *T. granosa* with the

Fig. 8 Macro photos of *Telligarca granosa* (**a**), *Gelonia expansa* (**b**), *Saccostrea glomerata* (**c**), *Pinctada maxima* (**d**), and *Turbo setosus* (**e**) interior and exterior after heating methods (400 °C and 600 °C). Upper– 5 minute duration; lower – 10 minute duration. See Supp. 2 Table 2 for the recorded Munsell colours

lowest gains (0 to 3%). The width percentage of loss/gain is greater than the length percentages for nearly all methods and species. This suggests that the expansion of the microstructure has a greater effect along the *y* axis for bivalves, which can be explained by the direction of growth lines and their subsequent separation from one another. This separation can be seen macroscopically, with cracking focused along the *x* axis growth lines. For *T. setosus*, the greater expansion of width in some samples is more likely associated with the separation of the prismatic and nacreous layers from one another due to the orientation and direction of growth for these structures. The negative percentages for *P. maxima* are due to thermal fracturing causing shell to be lost. Assuming that the lower temperature shells cannot be identified as

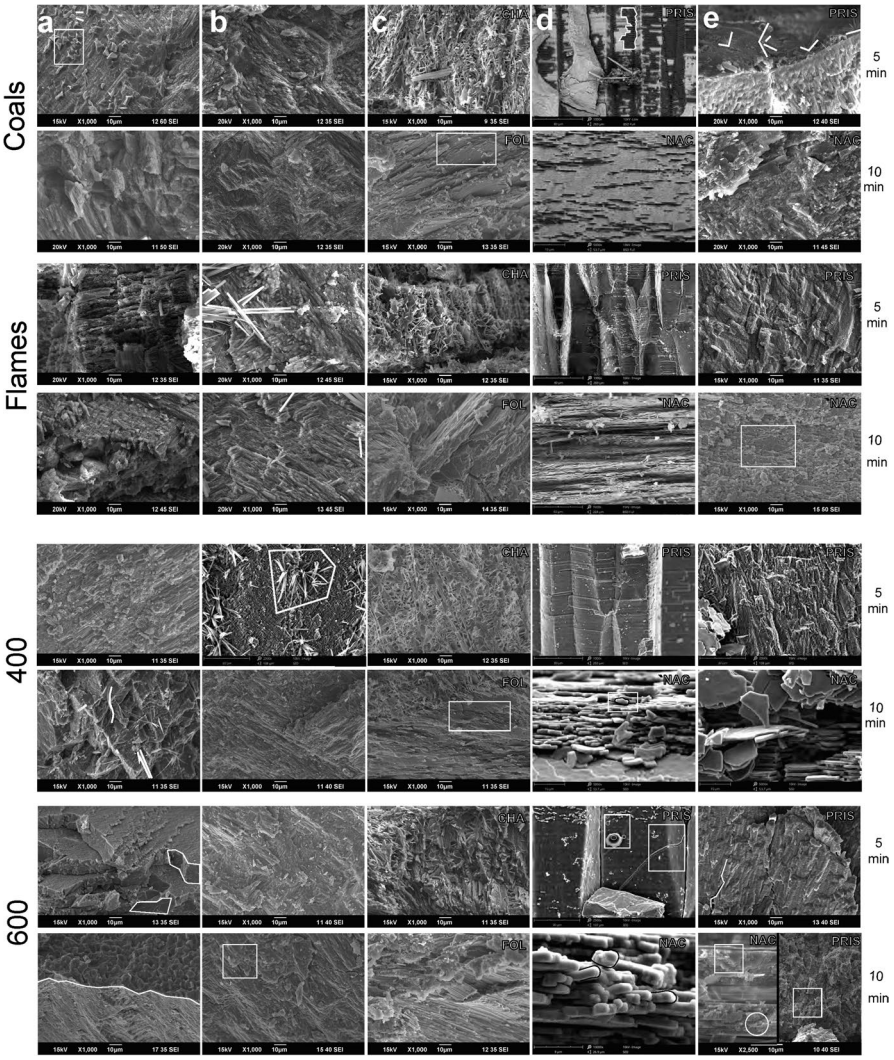

Fig. 9 SEM micrographs for each species and thermal method. *Telligarca granosa* (**a**), *Geloina expansa* (**b**), *Saccostrea glomerata* (**c**), *Pinctada maxima* (**d**), and *Turbo setosus* (**e**). CHA, chalky structure; FOL, foliate structure; PRIS, prismatic structure; NAC nacreous structure. Aragonite (acicular) needles showing in **a** coals 5 min, 400 10 min; **b** flames 5 and 10 min, 400 5 min; **e** prismatic coals 5 min. Cross-lamellar structure morphed in amorphous structure in **a** and **b** 600 5 and 10 min. Foliate structure becoming more amalgamated **c** coals 10 min and 400 10 min. Remaining organic matrix on prisms in **d** coals 5 min. Thermal cracks in **d** and **e** 600 5 min and rounded patches of remaining organic layer in **d** 600 5 min. Loss of prism structure by "eating" away **e** in 600 10 min right. Rounding of nacre tables in **d** and **e** 400 and 600 10 min (left) with nanoscale holes in **e** 600 10 min and amalgamated/amorphous structure in **e** flames 10 min

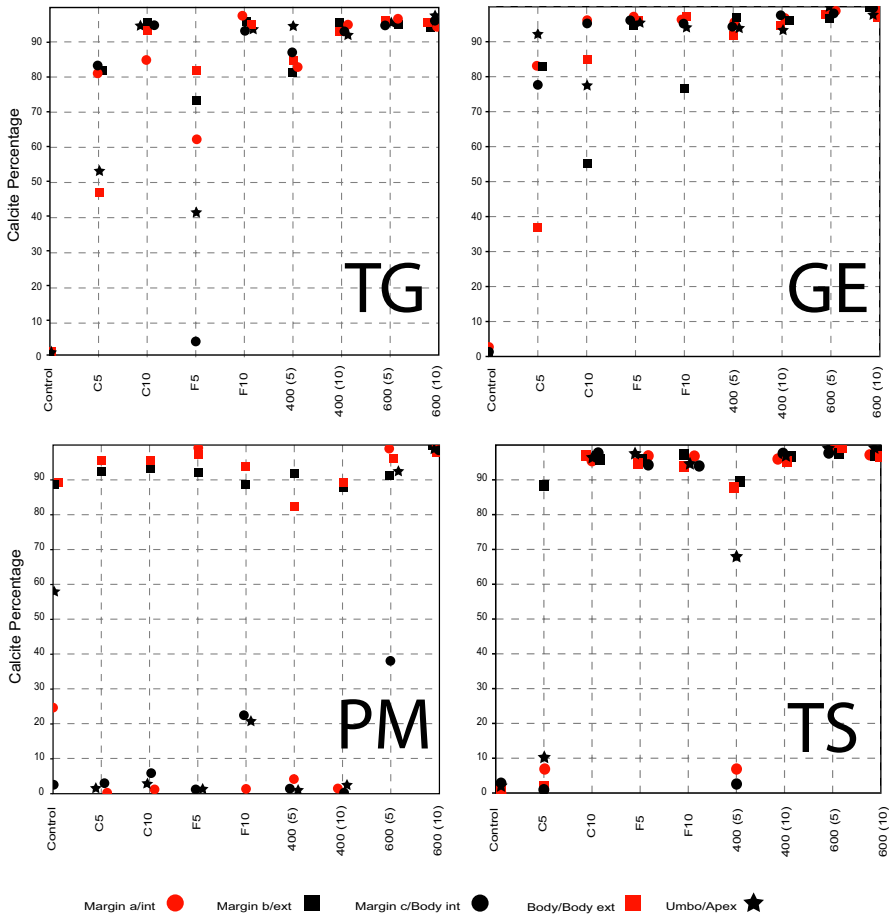

Fig. 10 Percentage of calcite at different shell locations before and after thermal experiments. C5 = coals 5 minutes; C10 = coals 10 minutes; F5 = flame 5 minutes; F10 = flame 10 minutes; 400 (5) = 400 °C 5 minutes; 400 (10) = 400 °C 10 minutes; 600 (5) = 600 °C 5 minutes; and 600 (10) = 600 °C 10 minutes. TG = *Telligarca granosa* ; GE = *Geloina expansa*; PM = *Pinctada maxima*; and TS = *Turbo setosus*. TG and GE with margin a, b, c, Body and Umbo. PM with Margin int/ext, Body int/ext, and Umbo. TS with Margin int/ext, Body int/ext, and Apex

burnt through colouration and thermal fracture, the difference in metric results can potentially impact biometric analyses and interpretations of exploitation.

Microstructural Changes and Patterns

The transformation of cross-lamellar structures begins with rounding of the third and fourth lamellae; the degree of which increases with temperature and duration (Fig. 9). This is followed by the loss of a clear first- and second-order lamellae due to a melding of individual lamellae. The surfaces become uneven and rounded with nanoscale holes appearing on the *y* axis. Aragonite (acicular) needles

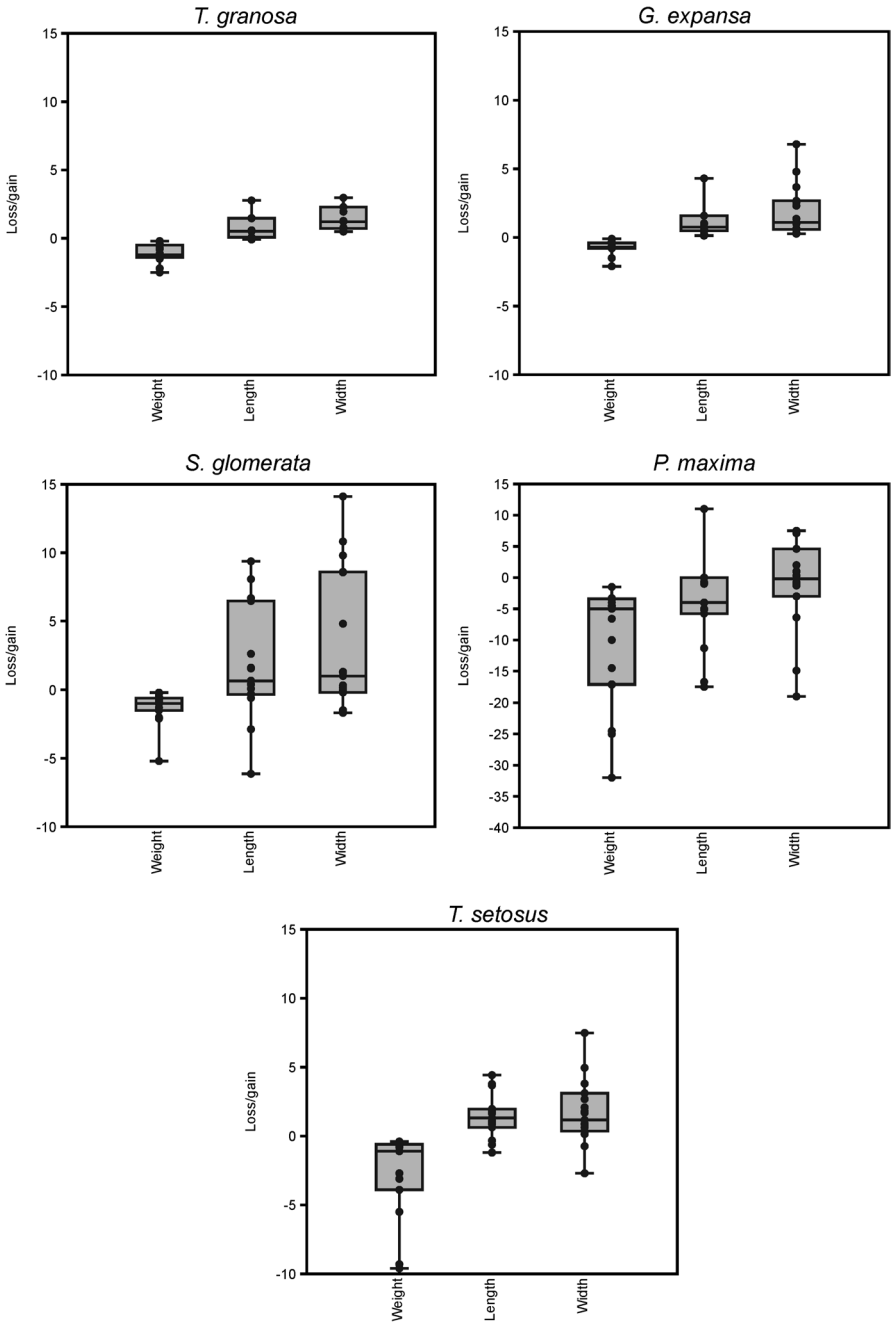

Fig. 11 Boxplots showing the range of weight (g), length (cm) and width (cm) lost/gained after thermal burning and heating. Variances between the mean, quartile and interquartile ranges highlight the irregularity of measurements between species and microstructures

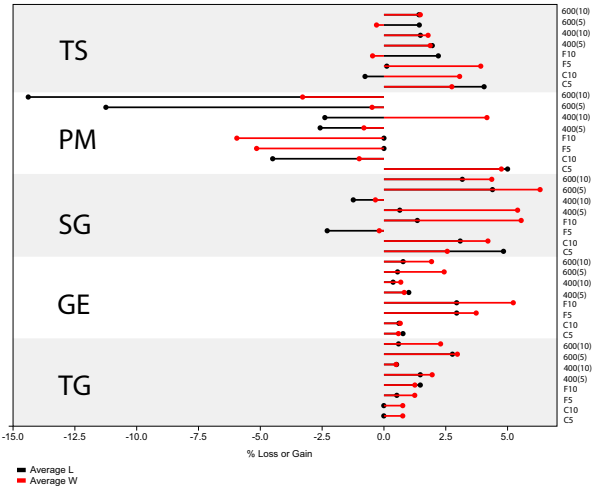

Fig. 12 Average percentage of change for length and width for each species of shell after thermal methods. For the most part, higher temperatures appear to cause greater changes in the average length and width of the shell. The loss of length or width attributed to thermal fracturing causing margins to be detached and lost during burning and heating

primarily appear on shorter duration samples in *T. granosa* and *G. expansa*, and also more frequently compared to other microstructural types. The cross-lamellar structure is then lost at higher temperatures and durations with the microstructure morphing to a solid amorphous structure with random fragmentation.

In comparison to *G. expansa*, *T. granosa* has greater cross-lamellar strength and can withstand greater thermal influences, evidenced by calcite percentages (Fig. 10) and the structural changes seen in SEM micrographs (Fig. 9). This may be due to the additional thickness (relative to size) of *T. granosa* that creates a denser and more robust shell compared to *G. expansa*. Also, the different sub-layers of the cross-lamellar microstructure in *G. expansa* separate from one another with thermal influences, which ultimately weakens the shell overall. Cross-lamellar fragmentation occurs along the *x* axis growth lines (see Fig. 4), with the margin separated from the body. In an archaeological context, we would expect cross-lamellar bivalve mollusc species to fragment along the *x* axis if exposed to high temperatures. This fragmentation pattern may be seen archaeologically with shell fragments separated into margins, body and umbo/hinge; however, other taphonomic processes (see Harris *et al*., 2017) would most likely exacerbate fragmentation rates due to the weakened structural integrity of the shell. Other processes may also cause similar fragmentation patterns; thus, further experimental studies would need to be undertaken to assess equifinality.

The foliate microstructure shows rounding and melding into amorphized structures for both the folia and chalky layers in *S. glomerata* after burning and heating. Temperature and duration in oven-heating caused quicker structural changes than the burning methods. *S. glomerata* fragmentation is random and the shell tends to splinter rather than break along edges. Archaeologically, this fragmentation pattern would be difficult to distinguish from non-thermally altered shell, especially after edges have worn down, and the internal organic 'glues' have decayed, from weathering or dissolution.

The organic-rich prismatic layer in *P. maxima* slowly 'crumbles' away with increasing temperature and shifts from a lath structure to one which is more jigsaw-like (Fig. 9d, 400 °C 5 min). From there, it then shifts to a structure of honey-comb tendrils then into scattered spots (Fig. 9d, 600 °C 5 min). The prism structures also crack with higher temperature (Fid. 9d, 600 °C 5 min). On the other hand, the thermal progression of the prismatic layer of *T. setosus* begins with aragonite needle formation (Fig. 9e, coals 5 min), followed by increasing cracks, melding of prisms, and less distinction of spherical granules into aggregations until prism structure is lost and morphed into an amorphous structure (Fig. 9e, 600 °C 5 min). Finally, depressions in the structure occur that 'eat' away the surface (Fig. 9e, 600 °C 10 min right). The difference in thermal progression between sheet and columnar nacre also confirms the greater strength (Currey, 1977) in the sheet nacre found in *P. maxima* (Fig. 9d). Despite the changes in individual nacre tablet morphology in *P. maxima*, the overall sheet structure remains, whereas in *T. setosus*, the individual tablets morph together (Fig. 9e, 600 °C 10 min), thus becoming homogenous and losing the overall structure.

P. maxima and *T. setosus* fragmentation is also variable between the prismatic and nacreous layers. The exterior prismatic layer is easily displaced from the interior nacreous layer, with breakage along the *x* axis growth lines (Figs. 7 and 8). At higher temperatures, both layers lose structural integrity and can disintegrate. Fragmented pieces of the prismatic layer are expected to be seen archaeologically, with the interior nacreous layer remaining largely intact. Molluscs that have undergone lower temperature burning or heating would most likely preserve archaeologically, with the hinge/umbo remaining intact. The nacreous layer remains the strongest microstructure even after thermal influences, which may be one of the reasons this material commonly worked (e.g. Trochidae spp. and *Nautilus* spp.) in the Pacific (Szabó, 2010, 2017). From this, we can assume certain fragmentation and breakage patterns of particular mollusc species that are related to thermal influences. The preservation of fragmented thermally influenced shell will likely deteriorate with corresponding taphonomic processes such as acid dissolution, weathering, and trampling.

Mineralogy

The overall results for *T. granosa* (*TG*) showed variability between both duration and temperature. Oven-heated samples showed that recrystallisation occurred more readily, with calcite percentages higher than the open fire methods for both duration and temperature (Fig. 10). A near complete recrystallisation occurred after 10 min regardless of the temperature or method type. Like *T. granosa*, duration was the key variable over all other factors for *G. expansa* (*GE*), with a consistent increase of calcite at 10 min durations. Open fire methods of burning showed that increased temperature affected recrystallisation to a greater degree (Fig. 10), whilst the oven-heated samples reached near-complete recrystallisation. The different results between the two cross-lamellar species show that oven-heating has a greater effect on *G. expansa* than it does on *T. granosa*. In terms of recrystallisation at different

shell locations, no clear pattern could be discerned apart from the umbo showing lower percentages for lower durations during burning (Fig. 10).

The different prismatic layers of *P. maxima* (PM) and *T. setosus* (TS) show how variable this structure can be due to the crystal morphology (Fig. 10). The large calcite prismatic structure in PM has greater thermal resistance in comparison with the numerous smaller aragonite prismatic structures in TS. The organic sheaths covering the prisms in PM may play a role in protecting the structure from thermal alteration; however, more study needs to be undertaken. Although the prismatic exterior layer of PM is primarily calcitic (Fig. 10), the aragonitic prismatic layer of TS recrystallises to calcite more than PM for the majority of the methods (Fig. 10). The nacreous interior of PM also changes very little in comparison to the TS nacre layer, where the calcite percentages remain low for the respective coal (5) and 400 °C (5) methods (Fig. 10). Recrystallisation of PM nacre only begins to occur during the flame and 600 °C methods.

Discussion

Examination of the combined results from each of the mollusc species reveals an array of interesting patterns that can be used in conjunction with previous studies (Aldeias, 2017; Aldeias *et al*., 2016; d'Errico *et al*., 2015; Milano *et al*., 2016, 2018; Müller *et al*., 2017; Spennemann, 2004; Villagran, 2014) to help identify and better understand thermally influenced shell material. One of the first aspects noted with each of the experimental shells in this study was variability in the degree of thermal fracture and the effect on structural integrity at a macroscopic level. High-power microscope images further highlighted changes in the microstructure of each species, with high variability in how each structure fractures and changes morphologically. This variability was not only between different microstructural types but also within the same microstructure type (cross-lamellar and prismatic). In addition, the recrystallisation of aragonite to calcite varied greatly between species and shell location. The degradation of the microstructure weakens the overall shell strength, which in turn increases shell fracture.

The microstructural pattern of thermal progression is similar in both open fire-burning and oven-heating methods. Some samples showed greater thermal degradation in the oven-heated samples than the open-fire burnt samples. It is possible that this could be attributed to the stable heating conditions that the oven/furnace provided in contrast to the volatile burning methods. These results highlight the importance of these variables in experimental studies on shell cooking or heating methods. To identify particular thermal methods on archaeological material, it is necessary to have a greater understanding of how different shell structures/species react to different variables. Studies by Aldeias *et al*. (2016), Milano *et al*. (2016), and Villagran (2014) for example have made important first steps towards understanding the various effects that different cooking methods, temperatures, and durations have on particular shell species; however, microstructural alterations also need to be explored. Studies also show that at normal earth surface pressure, together with carbonation at temperatures above 600 °C, pyrogenic aragonite in the shape of acicular crystals can

form (Toffolo, 2021; Toffolo *et al*., 2017; Toffolo & Boaretto, 2014). These acicular crystals were present on some of the experimental samples that underwent flames and 600 °C temperatures but also on a couple of the coals and 400 °C samples. As the process of formation of pyrogenic aragonite is still ambiguous, it is possible that other factors besides temperature are at play, such as microstructure, relative humidity, and CO_2 pressure (Toffolo, 2021).

Studies of thermal alteration on shell reveal that results differ even between the same microstructural type (Li *et al*., 2015, 2017; Liang *et al*., 2008). Li *et al*. (2015) found that the cross-lamellar structure in conch shells (*Busycon carica*) remained despite the phase transformation from aragonite to calcite at 500 °C; however, this architecture was lost at 900 °C, with the microstructure turning to a granular amorphous structure. Thermal treatment at 310 °C removed the biopolymer revealing nanoparticles in the third-order lamellae (Li *et al*., 2015). The progression of microstructural and mineralogical changes in *B. carica* is different to both *G. expansa* and *T. granosa*, which reiterates the variable nature of microstructure in different molluscs. This was also the case for the nacreous layers of *P. maxima* and *T. setosus* in this study. Balmain *et al*. (1999) found *P. maxima* aragonite morphed to calcite at 300–400 °C, with the calcite beginning to change into calcium oxide around 500–600 °C to full transformation to calcium oxide at 900 °C. A similar result was found during burning and heating methods in this study with the interior nacreous layer of *P. maxima* converting to a higher percentage of calcite during the flame and 600 °C methods. The recrystallisation of *T. setosus* nacre occurred at 400 °C only after prolonged (10 min) exposure to heat. This suggests columnar nacre reacts more quickly to thermal alteration than sheet nacre. Studies on the effect of heat treating on nacre have shown that at 500 °C, the nacreous structure keeps the brick-mortar architecture, with individual platelets converted to calcite and nanoscale holes on the surfaces and boundaries of platelets (Huang & Li, 2009). As the organic matrix is considered an adhesive (Chen & Pugno, 2013) that helps to glue the nacre platelets together, it is expected that the organics lost during heating will impact the structural integrity of the shell. Therefore, distinctions in nacreous sheet or columnar structure will mean variation in degradation; however, more study needs to be undertaken to understand the differences between these microstructures.

On a mineralogical level, each species of mollusc reacted differently to the variables of duration and temperature. The calcite percentages (Fig. 10) showed a wide range of variation between the different methods for each species. By determining the presence of aragonite in shells through XRD and FTIR at an archaeological site, it can be assumed that preservation is good (Stein, 1992; Toffolo, 2021; Weiner, 2010). Conversely, shells containing some or entirely made of calcite indicate recrystallisation and a poor state of preservation (Weiner, 2010:160); however, whether recrystallisation was due to taphonomic processes after site formation or due to thermal processes is difficult to distinguish. Variability in calcite percentages between different taxa/microstructural types present in the site may be more indicative of short and low temperature burning or heating processes (as seen in Fig. 10) if shells were originally aragonitic. However, further experimental studies on other taphonomic processes, such as dissolution, would help determine what processes are degrading archaeological shell and to what extent.

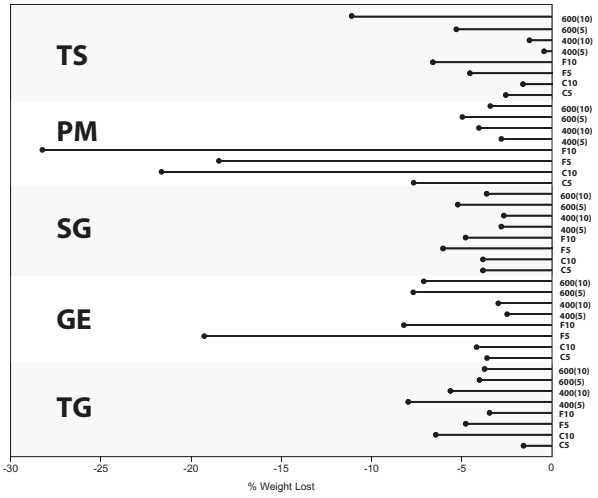

Fig. 13 Average percentage of change for weight for each species after thermal methods. High variability between species and methods, however, greater temperature appears to cause the greatest shifts in weight

In addition, the mineralogical preservation of aragonitic shells does not necessarily imply that the microstructure is unaltered (Toffolo, 2021), which is again evidenced in the SEM images (Fig. 9).

The percentage of change for weight loss is once again variable between species (Fig. 13). Samples with 5% or more change can be attributed to the loss of original shell material from thermal fracture. This has implications for archaeological shell analysis in terms of using weight as a measure of abundance. Others have cautioned the use of weight in shell quantification as it cannot be assumed that individual shells have all undergone the same taphonomic processes throughout the site (Mason, 1998; Thomas & Mannino, 2017). Thus, weight is not a consistent representation of shell quantity and cannot be used reliably to create arguments pertaining to site formation or human behaviours associated with the shell material. This is evidenced by the variability of weight lost through varying thermal methods on a range of mollusc species (Figs. 11 and 13) in this study.

The analysis of microstructural changes reveals that the temperature and duration zones for aragonite needle creation are highly variable between microstructural types as well as mollusc species. Higher temperatures and durations (particularly in heating) can result in a complete loss of aragonite, with recrystallisation to calcite and in some cases a further loss of calcite to calcium oxide (Herbert, 2008; Yoshioka & Kitano, 1985). The progression of thermal alteration weakens the shell overall, which means that this loss of structural integrity has implications for shell preservation as well as fragmentation. Although not measured in this study, it is known (Epstein *et al*., 1953; Milano *et al*., 2016; Müller *et al*., 2017; Staudigel & Swart, 2016) that temperature affects isotopic composition with carbon and oxygen decreasing with increased temperature. This has implications for palaeoclimatic reconstruction and other stable isotope–based interpretations if thermally altered shells are mistakenly analysed. Although Lindauer *et al*. (2018) found that heated shell specimens from Kalba, UAE, had similar radiocarbon ages as the unheated specimens, other taphonomic processes like hard-water (Douka *et al*., 2010) may

still affect radiocarbon ages. Therefore, taphonomic analysis (including identifying thermal alteration) is an important first step in archaeological shell analyses.

The issue of identifying whether evidence of burning/heating was from human activities or natural events is an ongoing area of study (Bellomo, 1993; Goldberg *et al*., 2017; Sorensen & Scherjon, 2018) and has implications for questions regarding early fire-use and cooking behaviours (Bentsen, 2014; Gowlett & Wrangham, 2013). The process of cooking our food is an integral part of human evolution (Parker *et al*., 2016) that has enabled us to digest a wider range of flora and fauna. Benefits included higher calories, sterilisation of bad bacteria, and increasing dietary breadth (Wollstonecroft, 2011). The consumption of molluscs by anatomically modern humans in South Africa is argued by some to have been the beginning of complex cognition in modern human brain development due to the increase of omega fatty acids (Kyriacou *et al*., 2014; Kyriacou *et al*., 2016; Marean, 2010). Cooked shellfish can have higher caloric values and reduce consumption risks associated with raw seafood (Aldeias *et al*., 2016). Therefore, identifying thermal influences on shell (whether through cooking or natural events) is a key question in archaeomalacology. Approaches to identify burning at a site primarily focus on mineralogy and changes in sediments (Goldberg *et al*., 2017; Miller *et al*., 2010; Zamanian *et al*., 2016) with few studies exploring shell remains (Duarte *et al*., 2019; Villagran, 2014). Although accurate visual identification of burning on different species of shell is possible when exposure to high temperatures (~600 °C) occurs, lower temperature exposure might not be visible for all shell species, particularly with boiling compared to roasting methods (Milano *et al*., 2016). Other methods of thermal alteration (not related to cooking) should also be considered, such as natural fires, artefact production (Szabó, 2010; 2017), or waste discard. Further experimental studies looking at different thermal methods on shell will provide a much-needed understanding on this highly variable area of archaeomalacology.

Conclusion

Thermal processes impact the morphology and integrity of shells and can be one of the most obvious taphonomic processes when examining archaeological shell material. However, lower temperatures and durations of thermal influences may not be visually identifiable on a macroscopic level, especially if other taphonomic processes are affecting the appearance of the shell. The impact of burning and heating on molluscs is shown to alter an array of macroscopic, microscopic, and mineralogical aspects, which are important to consider when analysing archaeological shell material. Variability in method-type, temperature and duration each alters a shell's macro and micro-morphology, as well as its mineralogical composition. This experimental study showed that each of the five species of shell and their corresponding microstructural types reacted to thermal influences differently. Thus, we can expect to see variations in the archaeological record due to the range of differing species that can be deposited at a site. Examining archaeological signatures of burning and heating on shell (from cooking, natural fires, or artefact production) is difficult due to our lack of understanding of the specific effects that certain methods have on

individual species. These studies provide a valuable basis from which to examine thermal alteration on different species and explore how varying methods affect mineralogy as well as macro and microscopic changes.

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Data Availability Supplementary data included.

Code Availability Past3 used for basic statistics.

Declarations

Conflicts of Iinterest The authors declare no competing interests.

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