Journal of Archaeological Science: Reports 7 (2016) 14–26

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: www.elsevier.com/locate/jasrep

Effects of cooking on mollusk shell structure and chemistry: Implications for archeology and paleoenvironmental reconstruction

Stefania Milano, Amy L. Prendergast, Bernd R. Schöne *

Institute of Geosciences, University of Mainz, Joh.-J.-Becherweg 21, 55128 Mainz, Germany

ARTICLE INFO

Article history:
Received 1 January 2016
Received in revised form 24 March 2016
Accepted 24 March 2016
Available online xxxx

Keywords:
Shell microstructure
Raman spectroscopy
Stable oxygen isotopes
Paleotemperature reconstruction
Food treatment
Heating
Phorcus (*Osilinus*) *turbinatus*
Mediterranean
Shell midden archeology

ABSTRACT

Mollusk shells excavated from archeological sites have been used to reconstruct paleoenvironment, human foraging, and migratory patterns. To retrieve information on past environment or human behavior, chemical signatures such as oxygen stable isotopes ($\delta^{18}O_{shell}$) are analyzed. Shell archeological remains usually represent food waste. Thermal treatments such as boiling and roasting may influence shell structure and biochemical composition. However, little is known about the relationship between changes at macro-, microstructural and chemical levels. This work is a calibration study on modern *Phorcus* (*Osilinus*) *turbinatus* shells. A simulation of two different cooking methods (boiling and roasting) was carried out at four temperatures (100 °C, 300 °C, 500 °C and 700 °C) for two durations (20 min and 60 min). The structure and biochemistry of shells boiled at 100 °C did not significantly change. However, treatments at higher temperatures strongly affected both the structure and the biochemistry of the shells. At 300 °C the external coloration, as well as nacre iridescence, were altered. Raman spectroscopy revealed that, at this temperature, the aragonite-calcite polymorphic transformation starts. Scanning electron microscope (SEM) analysis showed drastic changes in the microstructural organization also beginning at 300 °C. Furthermore, the isotopic $\delta^{18}O_{shell}$ values were significantly affected. Increasing cooking temperatures resulted in an enhancement of the above-mentioned alterations. These results provide a set of temperature-related morphological, structural and biochemical characteristics for investigating the thermal behavior of biocarbonates and for estimating different cooking treatments in archeological record.

1. Introduction

The contribution of shellfish to prehistoric Mediterranean subsistence has been demonstrated by the recovery of marine mollusk shells from numerous archeological sites along the coasts of the Mediterranean Sea (Erlandson, 2001; Aura et al., 2009; Colonese et al., 2011, 2014; Hunt et al., 2011; Barker et al., 2012; Bosch et al., 2015). Evidence of visibly burnt shells in archeological middens supports the hypothesis that shellfish diets could include a certain level of cooking (Stringer et al., 2008; Taylor et al., 2011; Douka et al., 2014). In fact, despite the evidence of a terrestrial-centered diet (Garcia Guixe et al., 2006; Craig et al., 2010), these prehistoric populations integrated marine resources as a protein supplement to their diets (Lubell et al., 1994; Richards and Hedges, 1999). In particular, shells of the gastropod *Phorcus* (*Osilinus*) *turbinatus* are commonly found in Mediterranean archeological deposits (Mannino et al., 2007, 2008; Colonese et al., 2011; Prendergast et al., 2013, in press-a; Bosch et al., 2015).

These remains offer a valuable source of information on the ancient environment and human–environment interactions. Shell carbonate is deposited periodically (resulting in the formation of growth increments and lines, e.g., Clark, 1975; Jones, 1980; Schöne et al., 2007) and generally in oxygen isotopic equilibrium with ambient water (Epstein et al., 1951; Wefer and Berger, 1991; Lécuyer et al., 2004). This allows the preservation of environmental signatures (Shackleton, 1974; Schöne et al., 2004). The shell $\delta^{18}O_{shell}$ value is commonly used as paleothermometer to reconstruct sea surface temperature at the time of shell deposition (Epstein et al., 1953; Schöne et al., 2003; Ferguson et al., 2011; Surge and Barrett, 2012). Furthermore, the $\delta^{18}O_{shell}$ composition of the last deposited shell material can be used to determine the season of shellfish foraging (Shackleton, 1973; Andrus and Crowe, 2000; Mannino et al., 2003; Burchell et al., 2013a; Prendergast et al., in press-a). Another method used by Milner (2001) in order to evaluate season of death of *Ostrea edulis* is based on shell growth patterns. By measuring the growth between the last annual line and the ventral margin it is possible to determine the moment of death with an error of ± 1 month (Milner, 2001). Ancient subsistence practices and site occupation can be interfered from the seasonality of shellfish foraging, leading to information about prehistoric feeding habits, settlement patterns and human movements (Mannino and Thomas, 2002; Mannino et al., 2011; Burchell et al., 2013b; Bosch et al., 2015; Prendergast et al., in press-a). Furthermore, the stable carbon isotopic signature of mollusk shells ($\delta^{13}C_{shell}$) contains valuable information on the environment during lifetime of the organism and its physiology. The origin of the carbon of the $CaCO_3$ and the proper

* Corresponding author.
E-mail address: schoeneb@uni-mainz.de (B.R. Schöne).

http://dx.doi.org/10.1016/j.jasrep.2016.03.045
2352-409X/