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Multi-regional calibration of *Patella caerulea* as a palaeothermometer using oxygen isotope values and Mg/Ca ratios

Danai Theodoraki,[1,2] Marcello A Mannino,[3] Amy L Prendergast,[4] Bernd R Schöne[5] and Niklas Hausmann[1]

Abstract

This study presents a comprehensive calibration of the *Patella caerulea* as a palaeotemperature archive across the Central and Eastern Mediterranean, focusing on Mg/Ca ratios and $\delta^{18}O$ values. We analysed 131 modern specimens collected from 22 localities, with a focus on the Aegean region. Our results demonstrate strong correlations between Mg/Ca ratios and the temperature proxy $\delta^{18}O_{shell}$, with a mean R^2 value of 0.89. These findings reinforce the utility of Mg/Ca as a reliable, though specimen-specific, proxy for relative SST variations, supporting its role in reconstructing seasonal temperature patterns and revealing areas of interest for subsequent methods. Additionally, oxygen isotope data from both shells and water samples at selected sites agreed well with element chemical data (Mg/Ca), confirming the usefulness of SST estimates based on $\delta^{18}O$ values as well as the season of death in ~80% of studied specimens. Findings of the present study enhance our understanding of the applicability of *P. caerulea* as a palaeotemperature archive and provide a robust baseline for future palaeoclimate studies in Mediterranean archaeological contexts.

Keywords

Laser-induced breakdown spectroscopy, Mediterranean, Mg/Ca ratios, *Patella* sp., sclerochronology, stable oxygen isotopes

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Introduction

Shells of the *Patella* genus have been shown to serve as reliable palaeothermometers using oxygen isotope analysis (Colonese et al., 2012; Fenger et al., 2007; Ferguson et al., 2011; Gutiérrez-Zugasti et al., 2017; Prendergast and Schöne, 2017; Shackleton, 1973) and more recently Mg/Ca ratios (Cobo et al., 2017; Hausmann et al., 2019a, 2023). The study of *Patella* spp. and other limpet shells as palaeothermometers or indicators for season of capture in archaeological sites has a long history (Colonese et al., 2011, 2012; Deith and Shackleton, 1988; Fenger et al., 2007; García-Escárzaga et al., 2020; Parker et al., 2020; Shackleton, 1973; Surge and Barrett, 2012; Wang et al., 2012). Among gastropods, limpet shells are the most commonly studied molluscs due to their simple anatomy and ubiquity along most of the world's rocky shorelines (Hausmann, 2024).

Limpets were collected by past human societies not only for consumption but also as tools, bait or adornments, among others. The study of shells from archaeological contexts can contribute to the reconstruction of human diet, environmental conditions, manufacture and use of artefacts, marine resources exploitation and management and seasonality of activities (Bar-Yosef Mayer, 2005; Çakirlar, 2014; Claassen, 1998; Firth, 2021). The relatively short life-span of limpets makes the shells advantageous for the study of short-term climatic events, and their sessility for the study of site-specific climatic events. Additionally, since they are commonly found in archaeological contexts their direct connection enables us to relate palaeoenvironmental and palaeoclimatic data to the broader archaeological context of the site, linking environmental change with past human activities (Leng and Lewis, 2016; West et al., 2018).

Before applying geochemical analyses to archaeological samples, it is essential to first validate the technique using modern samples from the same species and similar locations. This has been done on *Patella* spp. shells before in various parts of the world, including South Africa, Spain, Argentina, Scotland, the Gibraltar strait (North Africa and South Europe) and parts of the Mediterranean (Colonese et al., 2012; Fenger et al., 2007; Ferguson et al., 2011; Gutiérrez-Zugasti et al., 2017, 2025; Prendergast and Schöne, 2017; Shackleton, 1973). Researchers in these studies detected regional offsets in shell $\delta^{18}O$ values from equilibrium with surrounding water. This offset was attributed to so-called 'physiological' (Epstein et al., 1951) or 'vital' effects (Urey et al., 1951) that may disrupt isotopic equilibrium of the shells and is typically species-specific. These effects refer to metabolic processes that influence how environmental information is captured in the geochemical composition of biogenic hard structures (Schöne et al., 2011). The offset can be incorporated into

[1]Leibniz-Zentrum für Archäologie, Germany
[2]Vor- und Frühgeschichtliche Archäologie, University of Mainz, Germany
[3]Department of Archeology and Heritage Studies, Aarhus University, Denmark
[4]School of Geography, University of Melbourne, Australia
[5]Institute of Geosciences, University of Mainz, Germany

Corresponding author:
Danai Theodoraki, Leibniz-Zentrum für Archäologie, Mainz, Germany & Vor- und Frühgeschichtliche Archäologie, University of Mainz, Ludwig-Lindenschmit-Forum 1, Mainz 55116, Germany.
Email: danai.theodoraki@leiza.de