# Interspecies comparisons of Mg/Ca ratios in limpet shells

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#### Abstract

This study provides a short reassessment of the use of Magnesium to Calcium (Mg/Ca) ratios in Atlantic limpet shells to determine past sea surface temperatures. While Patella vulgata along the Spanish shoreline has since then repeatedly produced reliable correlations between sea surface temperature and Mg/Ca ratios, this is not the case for other patelloid species. Patella vulgata and Nacella deaureata have been studied using Mg/Ca with mixed or contrary results. In this study, we present elemental maps of various such species together with stable oxygen isotope values for some of the specimens. Our dataset also includes specimens that were previously unsuccessful in providing significant correlations between <sup>18</sup>O and Mg/Ca ratios. By reassessing these previous specimens and including a wider range of modern and archaeological samples from three patelloid species (P. vulgata, N. deaureata, and N. magellanica) we further add to the growing set of evidence for the reliable use of Mg/Ca ratios to detect palaeotemperature change and serve as a means to determine ontogenetic age and season of capture as well as to reveal locations of interest within the growth record (i.e. annual temperature minima and maxima) for the targeted analysis using <sup>18</sup>O or clumped oxygen isotope analysis.

Keywords: Sclerochronology, Limpets, Elemental Ratio, Mg/Ca

### 1. Introduction

Limpet shells are commonly found within archaeological sites and and past shorelines due to their robust carbonate structure and the long-term use of limpets as a marine food source. They have successfully been studied in the past in the context of coastal subsistence economies, site occupation on seasonal (SHACK-LETON, 1973; Parker et al., 2018; Bosch et al., 2018) or long-term scale (Ortiz et al., 2015), as well as palaeotemperature (Fenger et al., 2007; Surge and Barrett, 2012; Wang et al., 2012; Colonese et al., 2012; Ferguson et al., 2011). Determining past sea surface temperature (SST) change largely relies on the measurement of <sup>18</sup>O-values within the calcitic parts of the shell, but attempts have been made to also use elemental ratios, such as magnesium to calcium (Mg/Ca), to have an alternative measure, that potentially provides a more accurate SST estimate than <sup>18</sup>O-values, which are also affected by changes in salinity. In addition, the data acquisition of elemental ratios — either through laser-ablation-isotope-ratio-mass-spectrometry (LA-ICP-MS) or laser induced breakdown spectroscopy (LIBS), can be much faster and cost-effective, increasing the number of specimens that can be studied overall (Durham et al., 2017; Hausmann et al., 2023).

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Problematically, links between Mg/Ca ratios and SST changes in limpets have also been shown to be unreliable (Graniero et al., 2015) and even where they were successful, anomalous patterns in some specimens had to be filtered out, reducing the overall robustness of the results of those successful studies (Ferguson et al., 2011).

While recent research particularly of *Patella* sp. in the Mediterranean and Southwest Europe have provided promising results (Hausmann et al., 2019; García-Escárzaga et al., 2015, 2018). There remains unclarity for Atlantic limpet species, particularly since it was last shown here, that they are not reliable recorders of palaeotemperature (Graniero et al., 2015).

#### 2. Materials and Methods

#### 2.1. Limpet specimens

#### 2.1.1. Modern specimens

The analysed specimens, their origin and studies with background information can be found in Table 1.

Table 1: Table 1 Overview of the modern and archaeological limpet specimens analysed in this study {#tab:specimens}

Context	Study	Species	Location	Sample ID	Previous analyses
Modern	(Nicastro et al., 2020)	N. deaureata	Bahía Cambaceres Exterior - Tierra del Fuego (AR)	ND-1016-3	Stable oxygen and carbon isotope analysis
			1 4080 (1110)	ND-1016-4	
		N. magellanica		NM-1016-1 NM-1016-3	
	(Graniero et al., 2017)	P. vulgata	Rack Wick Bay - Westray (UK)	ORK-LT5	Stable oxygen and carbon isotope analysis; Mg, Li, Sr, Ca,.
Archaeological	(Surge and Barrett, 2012)	P. vulgata	Rack Wick Bay - Westray (UK)	QG1-7188-1	Stable oxygen and carbon isotope analysis
				QG1-7189-2 QG2-1061-1 QG2-1064-1	v
				QG2-7180-1 QG2-7180-2 QG1-7246-1	
	This study	N. magellanica N. deaureata N. deaureata N. magellanica N. magellanica N. magellanica	Heshkaia 35	Heshkaia_35-1 Heshkaia_35-2 Heshkaia_35-3 Heshkaia_35-4 Heshkaia_35-5 Heshkaia_35-6	none

Context	Study	Species	Location	Sample ID	Previous analyses	
		N. deaureata	N. magellanica N. deaureata N. magellanica		Heshkaia_35-7 Heshkaia_35-8 Heshkaia_35-9	

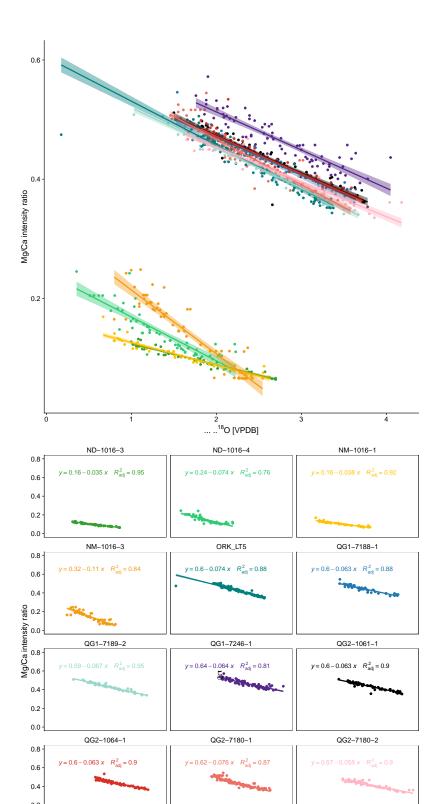


- $\it 2.1.2.\ Archaeological\ specimens$
- 2.2. Oxygen isotopes
- 2.3. Mg/Ca ratios

## 3. Results

- 3.1. Patella vulgata
- 3.2. Nacella deaureata
- 3.3. Nacella magellanica

4.



# 5. Discussion

# 5.1. Other correlations

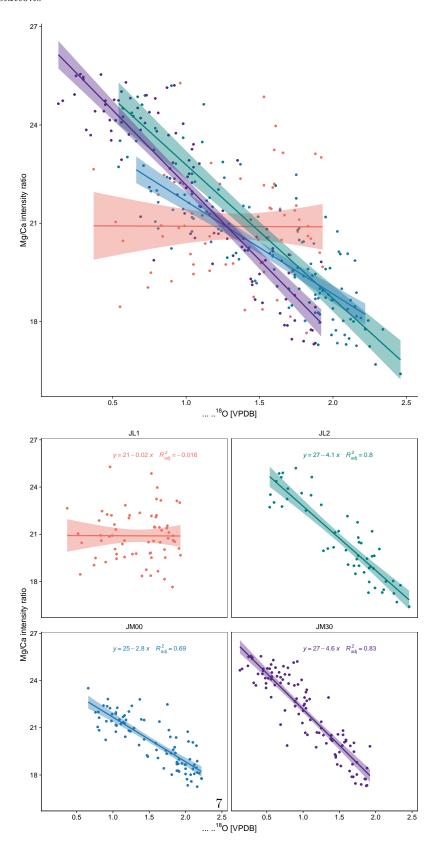
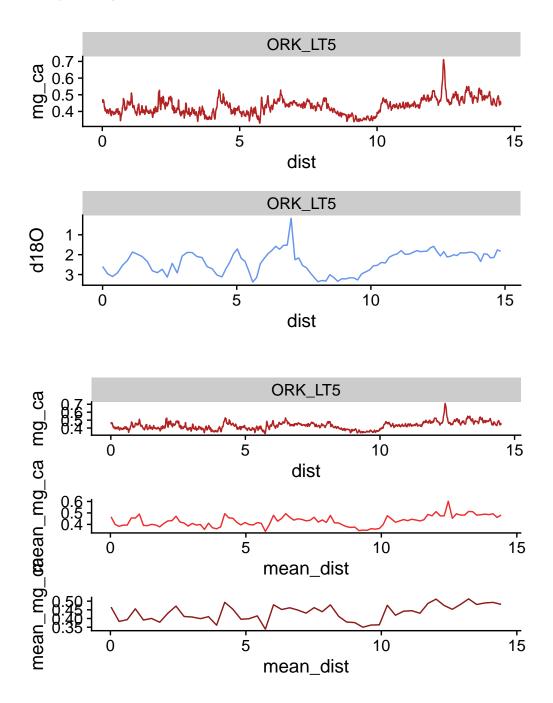


Figure 2: Correlation graphs for Ferguson et al. specimens

Table 2: Table 2: Overview of comparative correlations  $\{\# {\it tab} : {\it correlations}\}$ 

Species	Locality	Specimen	Correlation $\mathbb{R}^2$	Study
P. depressa	Northern Spain	LAN541	0.87	(García-Escárzaga et al., 2021)
		LAN545	0.86	
		LAN554	0.78	
		LAN559	0.82	
P. caerulea	Croatia	ISTPC1	0.9	(Hausmann et al., 2019)
		ISTPC2	0.84	,
	Crete	AF1911A	$0.91^{1}$	
		AF3003A	$0.92^{2}$	
	Israel	AKKPC2	0.96	
		AKKPC3	0.89	
		FRMPC1	0.84	
		FRMPC2	0.96	
	Libya	MO31A	0.83	
	v	MP64A	0.33	
		MP67A	0.96	
		MP68A	0.81	
	Malta	MA10	0.82	
	Tunisia	TUNPC1	0.81	
		TUNPC2	0.78	
	Turkey	ANTPC1	0.95	
		ANTPC2	0.93	
		KIZPC1	0.94	
		KIZPC2	0.86	
P. rustica	Gibraltar	m JL1	0.02	(Ferguson et al., 2011)
		JL2	0.8(0.79)	,
P. caerulea	Gibraltar	JM00	0.69(0.79)	
		JM30	0.83(0.79)	
P. vulgata	Orkney	ORK-LT5	not reported, here 0.88	(Graniero et al., 2017) and this study

 $<sup>^1\</sup>mathrm{SST}$  only, no other geochemical data available  $^2\mathrm{SST}$  only, no geochemical data available



### References

Bosch, M.D., Mannino, M.A., Prendergast, A.L., Wesselingh, F.P., O'Connell, T.C., Hublin, J.J., 2018. Year-round shellfish exploitation in the levant and implications for upper palaeolithic hunter-gatherer subsistence. Journal of Archaeological Science: Reports 21, 1198–1214. doi:10.1016/j.jasrep.2017.08.014.

- Colonese, A.C., Verdún-Castelló, E., Álvarez, M., Briz i Godino, I., Zurro, D., Salvatelli, L., 2012. Oxygen isotopic composition of limpet shells from the beagle channel: implications for seasonal studies in shell middens of tierra del fuego. J. Archaeol. Sci. 39, 1738–1748. doi:10.1016/j.jas.2012.01.012.
- Durham, S.R., Gillikin, D.P., Goodwin, D.H., Dietl, G.P., 2017. Rapid determination of oyster lifespans and growth rates using LA-ICP-MS line scans of shell Mg/Ca ratios. Palaeogeogr. Palaeoclimatol. Palaeoecol. 485, 201–209. doi:10.1016/j.palaeo.2017.06.013.
- Fenger, T., Surge, D., Schöne, B., Milner, N., 2007. Sclerochronology and geochemical variation in limpet shells (patella vulgata): A new archive to reconstruct coastal sea surface temperature. Geochem. Geophys. Geosyst. 8.
- Ferguson, J.E., Henderson, G.M., Fa, D.A., Finlayson, J.C., Charnley, N.R., 2011. Increased seasonality in the western mediterranean during the last glacial from limpet shell geochemistry. Earth Planet. Sci. Lett. 308, 325–333. doi:10.1016/j.epsl.2011.05.054.
- García-Escárzaga, A., Clarke, L.J., Gutiérrez-Zugasti, I., González-Morales, M.R., Martinez, M., López-Higuera, J.M., Cobo, A., 2018. Mg/Ca profiles within archaeological mollusc (patella vulgata) shells: Laser-Induced breakdown spectroscopy compared to inductively coupled Plasma-Optical emission spectrometry. Spectrochim. Acta Part B At. Spectrosc. 148, 8–15. doi:10.1016/j.sab.2018.05.026.
- García-Escárzaga, A., Moncayo, S., Gutiérrez-Zugasti, I., González-Morales, M.R., Martín-Chivelet, J., Cáceres, J.O., 2015. Mg/Ca ratios measured by laser induced breakdown spectroscopy (LIBS): a new approach to decipher environmental conditions. J. Anal. At. Spectrom. 30, 1913–1919. doi:10.1039/C5JA00168D.
- García-Escárzaga, A., Martínez-Minchero, M., Cobo, A., Gutiérrez-Zugasti, I., Arrizabalaga, A., Roberts, P., 2021. Using mg/ca ratios from the limpet patella depressa pennant, 1777 measured by laser-induced breakdown spectroscopy (libs) to reconstruct paleoclimate. Applied Sciences 11, 2959. URL: http://dx.doi.org/10.3390/app11072959, doi:10.3390/app11072959.
- Graniero, L., Surge, D., Gillikin, D., 2015. Assessing the utility of elemental ratios as a paleotemperature proxy in shells of patelloid limpets, in: EGU General Assembly Conference Abstracts, adsabs.harvard.edu.
- Graniero, L.E., Surge, D., Gillikin, D.P., Briz i Godino, I., Álvarez, M., 2017. Assessing elemental ratios as a paleotemperature proxy in the calcite shells of patelloid limpets. Palaeogeogr. Palaeoclimatol. Palaeoecol. 465, Part B, 376–385. doi:10.1016/j.palaeo.2016.10.021.
- Hausmann, N., Prendergast, A.L., Lemonis, A., Zech, J., Roberts, P., Siozos, P., Anglos, D., 2019. Extensive elemental mapping unlocks Mg/Ca ratios as climate proxy in seasonal records of mediterranean limpets. Scientific Reports 9, 3698. doi:10.1038/s41598-019-39959-9.
- Hausmann, N., Theodoraki, D., Piñon, V., Siozos, P., Lemonis, A., Anglos, D., 2023. Applying laser induced breakdown spectroscopy (LIBS) and elemental imaging on marine shells for archaeological and environmental research. Sci. Rep. 13, 19812. doi:10.1038/s41598-023-46453-w.
- Nicastro, A., Surge, D., Briz i Godino, I., Álvarez, M., Schöne, B.R., Bas, M., 2020. High-resolution records of growth temperature and life history of two nacella limpet species, tierra del fuego, argentina. Palaeogeogr. Palaeoclimatol. Palaeoecol. 540, 109526. doi:10.1016/j.palaeo.2019.109526.
- Ortiz, J.E., Gutiérrez-Zugasti, I., Torres, T., González-Morales, M., Sánchez-Palencia, Y., 2015. Protein diagenesis in patella shells: Implications for amino acid racemisation dating. Quat. Geochronol. 27, 105–118. doi:10.1016/j.quageo.2015.02.008.
- Parker, W., Yanes, Y., Mesa Hernández, E., Hernández Marrero, J.C., Pais, J., Soto Contreras, N., Surge, D., 2018. Shellfish exploitation in the western canary islands over the last two millennia. Environ. Archaeol., 1–23doi:10.1080/14614103.2018. 1497821
- SHACKLETON, N.J., 1973. Oxygen isotope analysis as a means of determining season of occupation of prehistoric midden sites. Archaeometry 15, 133–141. URL: http://dx.doi.org/10.1111/j.1475-4754.1973.tb00082.x, doi:10.1111/j.1475-4754.1973.tb00082.x.
- Surge, D., Barrett, J.H., 2012. Marine climatic seasonality during medieval times (10th to 12th centuries) based on isotopic records in viking age shells from orkney, scotland. Palaeogeogr. Palaeoclimatol. Palaeoecol. 350-352, 236-246. doi:10.1016/j.palaeo.2012.07.003.
- Wang, T., Surge, D., Mithen, S., 2012. Seasonal temperature variability of the neoglacial (3300–2500 BP) and roman warm period (2500–1600 BP) reconstructed from oxygen isotope ratios of limpet shells (patella vulgata), northwest scotland. Palaeogeogr. Palaeoclimatol. Palaeoecol. 317, 104–113.