Confirmation of Mg/Ca ratios as palaeothermometers in Atlantic limpet shells

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Abstract

This study provides a reassessment of the use of Magnesium to Calcium (Mg/Ca) ratios in Atlantic limpet shells to determine past sea surface temperatures (SST). While *Patella depressa* along the Spanish shoreline has repeatedly produced reliable correlations between SST and Mg/Ca ratios, this is not the case for other patelloid species. *Patella vulgata*, *Nacella deaureata*, and *Nacella magellanica* 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 that confirm a good relationship with SST. Our dataset also reassesses a specimen which was previously unsuccessful in providing significant correlations between 18O and Mg/Ca ratios. By reassessing these species and including modern and archaeological samples (n=12) 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. As a result, these species can in the future 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 18O or clumped oxygen isotope analysis.

# 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 (Robson, Hausmann, and Milner 2024). They have successfully been studied in the past in the context of coastal subsistence economies, site occupation on seasonal (Shackleton 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, Surge, and Mithen 2012; André Carlo Colonese et al. 2012; Ferguson et al. 2011). Determining past sea surface temperature (SST) change largely relies on the measurement of 18O-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) (Graniero et al. 2017; Ferguson et al. 2011), to have an alternative measure, that potentially provides a more accurate SST estimate than 18O-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; Niklas Hausmann et al. 2023).

Problematically, links between Mg/Ca ratios and SST changes in many marine mollusc shells, including limpets, have shown to be unreliable (Surge and Lohmann 2008; Wanamaker et al. 2008; Schöne et al. 2010; Freitas et al. 2012; Graniero et al. 2017; Poulain et al. 2015; Vihtakari et al. 2017). This is particularly the case where there is little available additional information on metabolic processes, organic components of the shell matrix, intra-increment and intra-shell variability, and growth rates, which can independently and unpredictably affect Mg/Ca ratios and confound their interpretation as temperature proxy. Confusingly, in some cases multiple different temperature equations have been found for the same species (see Freitas *et al*. (2012) and Vihtakari *et al*. (2017) and references therein). Coeval specimens sharing one locality can also show differences in their relation to SST (N. Hausmann et al. 2019). Where the use of Mg/Ca as a palaeotemperature proxy was successful, anomalous patterns in some specimens had still to be filtered out by hand, 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 (N. Hausmann et al. 2019; A. Garcı́a-Escárzaga et al. 2015; Asier Garcı́a-Escárzaga et al. 2018). There remains a lack of clarity for Atlantic limpet species, particularly since it was last shown here, that they are not reliable recorders of palaeotemperature (Graniero et al. 2017).

In this study we will repeat and expand the analysis of Atlantic limpets to determine the reliability of Mg/Ca ratios as palaeotemperature proxies. To do this, we sampled a set of previously published and unpublished limpet specimens dating to modern and archaeological contexts using LIBS. LIBS allows us to carry out 2D imaging of entire shell sections, which helps us to navigate the complex elemental structure of the shell and better separate the external, temperature-related changes from the internal and less understood factors that influence the Mg/Ca ratio. By working with already published datasets, we were able to simultaneously avoid costs for new high-resolution 18O-data, to use real-world examples, and to also provide pilot-data for areas of existing research interest. Generally establishing the usefulness and reliability of Mg/Ca as SST proxy in limpets should help to provide a platform for such future research and an important stepping stone to a better understanding of elemental ratios in other marine mollusc shells.

# Materials and Methods

## Limpet specimens

The analysed specimens, their origin and respective studies with research background information can be found in Table [1](#Table_1). Here we will briefly summarise their contextual information, which can be accessed in more detail at the respective studies (Nicastro et al. 2020; Surge and Barrett 2012; Graniero et al. 2017). While those studies also included other specimens, their accessibility or state of preservation did not allow them to be re-analysed.

Overview of the modern and archaeological limpet specimens analysed in this study.

| **Context** | **Study** | **Species** | **Location** | **Sample ID** | **Previous analyses** |
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| Modern | (Nicastro et al. 2020) | *N. deaureata* | Cambaceres Bay | ND-1016-3 | Stable oxygen |
|  |  |  | - Tierra del | ND-1016-4 | and carbon |
|  |  | *N. magellanica* | Fuego (AR) | NM-1016-1 | isotope analysis |
|  |  |  |  | NM-1016-3 |  |
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|  | (Graniero et al. 2017) | *P. vulgata* | Rack Wick Bay - | ORK-LT5 | Stable oxygen |
|  |  |  | Westray (UK) |  | and carbon |
|  |  |  |  |  | isotope analysis; |
|  |  |  |  |  | Mg, Li, Sr, Ca. |
|  |  |  |  |  |  |
| Archaeological | (Surge and Barrett 2012) | *P. vulgata* | Rack Wick Bay - | QG1-7188-1 | Stable oxygen |
|  |  |  | Westray (UK) | QG1-7189-2 | and carbon |
|  |  |  |  | QG2-1061-1 | isotope analysis |
|  |  |  |  | QG2-1064-1 |  |
|  |  |  |  | QG2-7180-1 |  |
|  |  |  |  | QG2-7180-2 |  |
|  |  |  |  | QG1-7246-1 |  |

There are two main locations that we sourced specimens from: the Beagle Channel in Tierra del Fuego (Argentina) and the island of West Ray in Orkney (UK). Four modern specimens were collected from the Beagle Channel in Cambaceres Bay in October 2016. The area receives around 570 mm precipitation but the channel waters are predominantly influenced by marine currents and in the period of October 2015 to October 2016 stayed around 30.7 ± 0.7 psu (Nicastro et al. 2020). SSTs range from 4.7ºC in August to 10ºC in February ([Figure 1](#fig-SSTs) - red).

On Westray one modern shell (ORK-LT5) was collected in Rack Wick Bay in August 2009 and has previously been analysed using stable carbon and oxygen isotopes, as well as LA-ICP-MS (Graniero et al. 2017). Westray lies about 70 km north of the Scottish mainland and experiences virtually no freshwater input with salinity values of 34.0 – 34.5 psu (Inall et al. 2009). The annual SST ranges from 6.3ºC in March to 13.8ºC in August ([Figure 1](#fig-SSTs) - blue).

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| Figure 1: Monthly Sea Surface Temperature values averaged from years. SST values were sourced from Good et al. (2020). |

We also studied 7 archaeological specimens of *P. vulgata* coming from Quoygrew on Westray dating to 900 – 1200 CE. These shells have previously been studied to characterise seasonal temperature change during the Medieval Climate Anomaly and the Little Ice Age (Surge and Barrett 2012). Together they show a range of lifespans, with some comparatively long for their size (QG1-7246-1, 12 years within 16 mm of growth) making them particularly susceptible to time-averaging. That said, the majority are under 5 years old.

## Methods

### Mg/Ca ratios

Mg/Ca elemental imaging was carried out using Laser Induced Breakdown Spectroscopy at the Leibniz Zentrum für Archäologie (Mainz-Germany) using previously published methods (Niklas Hausmann et al. 2023). These involve the ablation of the shell section using an infrared (1064 nm) laser (1–2 mJ, 100 Hz) onto a surface area of 20–30 µm to generate a plasma plume. This plume emits light, which is measured using a synchronised spectrometer (delay time = 0.5 µs, integration time = 1 µs). The resulting light spectrum quantifies the emission lines of Magnesium (MgII; 279.553 nm) and Calcium (CaII; 315.887 nm) to determine their intensity ratio. While these two peaks alone do not represent the molar concentrations of both elements (as opposed to calibration free LIBS; e.g. (Martı́nez-Minchero et al. 2022)), the intensity ratio is linearly correlated to the molar concentration (N. Hausmann et al. 2017) and can be used as a reliable indicator of Mg/Ca changes within the shell carbonate. All values reported here at in arbitrary units based on the ratio of intensities of the peaks above.

Using this system we carried out elemental imaging of the shell specimens at a resolution of 50–100 µm distance between sampling spots. Each spot was irradiated 10 times with the 3 first spectra discarded as a cleaning step and the remaining spectra summed to get an average Mg/Ca intensity ratio for each sample spot. Subsequently, we re-sampled the section using a line scan at 10 µm resolution. This leads to an overlap between sample spots, but also allows for a continuous record without gaps. Intensity ratios were filtered for cases with high relative standard deviation (i.e. more than 10%). These occurred in places where the previous sampling procedures for carbonate powder as part of the oxygen isotope analysis left an uneven sample surface introducing variability in the plasma generation and thus uncertainty in the data of these locations.

### Oxygen isotopes

High-quality oxygen isotope values (18O) were acquired from previous publications on *P. vulgata* (Surge and Barrett 2012; Graniero et al. 2017), *N. deaureata* and *N. magellanica* (Nicastro et al. 2020), in which detailed descriptions of the stable isotope analysis methodology can be found. In short, all shells were sectioned along the main growth axis to expose the internal growth structure. From the exposed section carbonate powder samples were acquired using a micromill with resolutions of 100–200 µm and by targeting the calcitic M+2 layer of the shells. Analytical precision of the isotope values was consistently at 0.05–0.10‰ and values are reported in per mil units (‰) relative to the VPDB (Vienna Pee Dee Belemnite) standard.

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| Figure 2: Isotope values of Nacella sp. limpet shells from Cambaceres Bay. |

[Figure 2](#fig-Nac_iso) and [Figure 3](#fig-Pat_iso) show the previously acquired sequential 18O-values of limpet shells by species (*Nacella* sp., and *Patella vulgata*, respectively. Due to the high sampling resolution, all shells show seasonally resolved and multi-year quasi-sinusoidal records of SST change, with *Nacella* sp. shells living 2–3 years and *P. vulgata* living regularly over 3 years. In those instances where longer lifetimes are encountered (i.e. specimen QG1-7246-1, [Figure 3](#fig-Pat_iso) b) the temporal-resolution is reduced from more than a dozen of samples per year, to only around 7.

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| Figure 3: Isotope values of Patella vulgata limpet shells from Quoygrew (QG, a-g) and Rack Wick Bay (ORK, h) on Westray, Orkney. |

## Dynamic Time Warping

Because it is not possible to directly associate the exact sample locations used in the analysis of stable oxygen isotopes with the LIBS data, we used dynamic time warping (DTW) to align the time series of 18O-values and Mg/Ca ratios. DTW is an algorithm that measures similarity between two proxy-sequences, which may vary in sampling resolution or interval. By stretching or compressing sections of the series, DTW finds the probable alignment between the two sequences. This allows us to compare the proxy data sets more effectively, ensuring that the temporal dynamics of each shell are accurately matched despite possible discrepancies in sampling intervals or rates. We applied the DTW algorithm using the dtw package in R (Giorgino 2009; R Core Team 2020), which provides a robust framework for aligning time series data. This involved selecting appropriate distance measures and constraints to ensure meaningful alignment. The process involved iterative adjustments to minimise the overall distance between corresponding points in the two data sets.

# Results

## *Patella vulgata*

The elemental imaging of *P. vulgata* shells consistently showed repeating patterns of Mg/Ca intensity ratio changes with high Mg/Ca intensity ratios indicating and low ratios indicating low temperature periods. As examples, [Figure 4](#fig-Pat_LIBS) shows the 2D-distribution of elemental ratios across the entire section of ORK-LT5 and the preserved anterior side of QG1-7188-1 (additional maps can be found in the supplementaries). The repeating patterns are found across the calcitic layers that are exterior to the myostracum (layers m+2 and m+3) as well as the layers that are interior (m-2) (Fenger et al. 2007). The layer m-1, which is also interior, consists of aragonite and is seen in [Figure 4](#fig-Pat_LIBS) in grey, as its Mg/Ca intensity ratio consistently falls below the range of interest (0.2 and above). Compared to other patelloid shells, some of whose interior is almost entirely made of aragonite, this layer is very thin.

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| Figure 4: Example LIBS maps and line scans of analysed specimens. (a+b) ORK-LT and (c+d) QG1-7188-1. Note that the ranges of Mg/Ca intensity ratios are not identical but are chosen arbitrarily to increase contrast. Areas in grey consist of low-Mg aragonite and fall outside the chosen colour-range. |

Both specimens in [Figure 4](#fig-Pat_LIBS) show increased Mg/Ca intensity ratios towards the outside of the shell and some degree of intra-increment variability. This is particularly visible in [Figure 4](#fig-Pat_LIBS) c, where Mg/Ca intensity ratios range from ~0.5–0.7 in the first year of growth (9–12 mm on the y-axis). A similar pattern is visible in the interior m-2 layer of ORK-LT5 ([Figure 4](#fig-Pat_LIBS) a), which increase towards the anterior of the shell (0–10 mm on the x-axis).

Line scans also indicate well the quasi-sinusoidal change of Mg/Ca intensity ratios expected based on the stable isotope data and elemental-imaging. That said, some of the variability of Mg/Ca intensity ratios within one season such as the summer period of QG1-7188-1 between 0.5 and 2.0 mm distance to the shell edge ([Figure 4](#fig-Pat_LIBS) d), is visible in a more dramatic manner than it appears in the 2D-image, showing the downside of line-scanning as opposed to the broader milling approach used for the analysis of carbonate powder (Ferguson et al. 2011).

[Figure 5](#fig-Pat_Comp) shows the line scan of ORK-LT5 in comparison to its 18O-values (similar graphs for other specimen can be found in the supplementaries). The measurements of the distance to the shell edge are not entirely identical, most likely because one growth increment can have a range of distances to the edge, depending on where one measures, and a line scan along the interior would be shorter than a line scan along the exterior. That said, increases and decreases of both proxies seem to mirror each other and to be well aligned.

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| Figure 5: Comparison of LIBS line-scan and sequential 18O-values of specimen ORK-LT5 |

Aligning the records programmatically using dynamic time warping, allowed us to compare them directly to determine specimen-specific equations and quantify the correlation of both proxies ([Figure 6](#fig-Pat_Corr)). The equations for all specimens are different but the majority (barring one: QG1-7246-1) do seem to cluster around shared parameters (18Ο = 0.6 – 0.065 \* Mg/Ca). The various coefficients of determination (R2) range between 0.81 (QG1-7246-1) and 0.95 (QG1-7189-2). These specimens are also the oldest and youngest specimens, respectively, suggesting that lower growth rates and time averaging had a negative effect on the correlation of both proxies. The mean R2 value of the individual *P. vulgata* specimens is 0.89, suggesting a generally good fit between the two proxies.

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| Figure 6: Correlation graphs for Patella vulgata specimens. |

## *Nacella* sp.

The LIBS data for *Nacella* sp. specimens is less straightforward with shells being much thinner and thus patterns being more difficult to make out. Both specimens (ND-1016-3 and NM-1016-3) shown as example in [Figure 7](#fig-Nac_LIBS) (see additional graphs in supplementaries) also experience increases of Mg/Ca intensity ratio towards the exterior of the shell, similar to the *P. vulgata* specimens from Orkney. This intra-increment heterogeneity combined with the thinness of the shell, further complicates their analysis compared to *P. vulgata* or other *Patella* species (N. Hausmann et al. 2019). Nevertheless, repeating patterns were visible in the anterior section of the shell, which were also mirrored in the inner layers (m-2) of specimens NM-1016-3 ([Figure 7](#fig-Nac_LIBS) b).

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| Figure 7: Example LIBS maps and line scans of analysed Nacella sp. specimens. (a+c) ND-1016-3 and (b+d) NM-1016-3. Note that the ranges of Mg/Ca intensity ratios are not identical but are chosen arbitrarily to increase contrast. Areas in grey consist of low-Mg aragonite and fall outside the chosen colour-range. Note the inset in (c) where the shell edge has been resampled using a higher resolution (50 µm instead of 100 µm) to better understand the Mg/Ca ratios at the shell edge. |

Interestingly, the Mg/Ca intensity ratios in the *Nacella* sp. shells were much lower (0.05–0.30) than those seen in other patelloid species (e.g. 0.3–0.7 in *Patella vulgata* above, or 0.5–1.5 in Hausmann *et al*. (2023)) using the same emission lines. While the intensity ratio depends chiefly on the chosen emission lines to calculate the proportion of the chosen Magnesium to the chosen Calcium peak, the low ratios still indicate lower concentrations than seen elsewhere, or seen only in aragonitic parts of e.g. *Patella* shells. Similar observations have been made before (Graniero et al. 2017). Strong intra-increment heterogeneities are visible along the exterior of the shells (m+3 layer), where Mg/Ca intensity ratios are higher, particularly in specimen ND-1016-3 ([Figure 7](#fig-Nac_LIBS)). The step from lower to higher along the increment is not gradual, as is the case in NM-1016-3 (see inset of [Figure 7](#fig-Nac_LIBS) b), but rather step-wise. Sampling across this boundary in a linear scan would most likely lead to erroneous results. Also sampling across gradual changes as in NM-1016-3 can influence the overall correlation graph for a specimen.

Line scans reflect well the changes previously indicated by 18O values and also indicate about two years of recorded growth. That said, the 2D imaging suggests that in both specimens a third summer can be added to the total record, which is not captured by the line scans.

[Figure 8](#fig-Nac_Comp) shows the line scans of ND-1016-3 and NM-1016-3 in comparison to their 18O-values (similar graphs for the other *Nacella* sp. specimen can be found in the supplementaries). Compared to the *P. vulgata* records, these mirror each other much more clearly, due to the brief period recorded in the shells and its simple make-up.

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| Figure 8: Comparison of LIBS line-scan and sequential 18O-values of Nacella sp. specimens. |

The *Nacella* sp. specimens showed similarly clustered correlations, which interestingly were not grouped by species. In fact, specimens ND-1016-3 (*Nacella deaureata)* and NM-1016-3 (*Nacella magellanica*) are almost identical in their fitted equations ([Figure 9](#fig-Nac_Corr)). Both also share a high coefficient of determination (R2) of 0.95 and 0.92 respectively, with the remaining specimens being somewhat lower (R2 = 0.76 for ND-1016-4 and R2=0.84 for NM-1016-3). The mean R2 value for each *Nacella* species is 0.86 for *Nacella deaureata* and 0.88 for *Nacella magellanica*. Why two specimens of different species are so well aligned is not entirely certain and randomness cannot for now be ruled out. That said, since they both have a high R2 value, it might just be that they were both minimally affected by factors other than SST, including the sampling location of our line scans.

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| Figure 9: Correlation graphs for Nacella sp. specimens |

# Discussion

The Mg/Ca ratios from the 2D elemental imaging present positive results on SST being the main factor behind Mg/Ca concentration in three Atlantic limpet species. Annually repeating patterns of increasing (spring/summer) and decreasing (autum/winter) SST were also visible in the line scans, albeit less straightforward than in the 2D-data. Nevertheless, the resulting R2-values for each species were high (*P. vulgata mean R2*=0.89, *N. deaureata mean R2*=0.86*, N. magellanica mean R2*=0.88). These results are similar to previously published data on *Patella* sp. shells (Table [2](#Table_2)): R2 values of *P. depressa* lie between 0.78 and 0.87 (Asier Garcı́a-Escárzaga et al. 2021), for *P. caerulea* from the Mediterranean between 0.78 and 0.96 — barring one outlier of 0.33 (specimen MP64A), which had increased Mg/Ca ratios in increments with rich organic contents (N. Hausmann et al. 2019).

Correlations of Mg/Ca with 18O and SST found in other studies. Bold R2 values are interpreted as outliers. \* indicates that only SST data and no other geochemical data was used. \*\* these samples were used to determine a shared R2-value of 0.79.

| **Species** | **Locality** | **Specimen** | **R2** | **Study** |
| --- | --- | --- | --- | --- |
| *P. depressa* | Northern Spain | LAN541 | 0.87 | (Asier Garcı́a-Escárzaga et al. 2021) |
|  |  | LAN545 | 0.86 |  |
|  |  | LAN554 | 0.78 |  |
|  |  | LAN559 | 0.82 |  |
| *P. caerulea* | Croatia | ISTPC1 | 0.9 | (N. Hausmann et al. 2019) |
|  |  | ISTPC2 | 0.84 |  |
|  | Crete | AF1911A | 0.91 |  |
|  |  | AF3003A | 0.92 |  |
|  | Israel | AKKPC2 | 0.96 |  |
|  |  | AKKPC3 | 0.89 |  |
|  |  | FRMPC1 | 0.84 |  |
|  |  | FRMPC2 | 0.96 |  |
|  | Libya | MO31A | 0.83 |  |
|  |  | **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 | **JL1** | **0.02** | (Ferguson et al. 2011) |
|  |  | JL2 | 0.8\*\* |  |
| *P. caerulea* | Gibraltar | JM00 | 0.69\*\* |  |
|  |  | JM30 | 0.83\*\* |  |
| *P. vulgata* | Orkney | ORK-LT5 | not reported, here 0.88 | (Graniero et al. 2017) and this study |

*P. rustica* has two studied specimens (JL1 and JL2) with R2-values of 0.02 and 0.8, respectively (Ferguson et al. 2011) ([Figure 10](#fig-Ferg)). Together with the data from two *P. caerulea* shells (JM00 and JM30 with R2-values of 0.69 and 0.83), the data from JL2 was used determine a general Mg/Ca-SST relationship with an R2-value of 0.79. JL1 was disregarded in that calculation, as well as the second year of growth in JM00, which produced anomalous data. While no additional information about those specimens is available, it seems likely that discarded the Mg/Ca ratios from JM00, which were interpreted as an ontogenetic trend, were potentially influenced by the same intra-increment heterogeneity we see in some of our shell specimens as well. Since these shells were analysed by homogenising the carbonate powder of the m+2 layer and the more exterior m+3 layer, these heterogeneities could potentially increased the Mg/Ca ratio unpredictably, leading to what might look like an ontogenetic trend in a linear dataset. Whether these anomalies affected JL1 in the same way, albeit stronger, is not clear but it might well be possible.

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| Figure 10: Correlation graphs for Ferguson et al., (2011) specimens. |

Another shell whose results we aim to explain further is ORK-LT5, which has previously been shown to have no substantial correlation with 18O or SST in implication (Graniero et al. 2017). Different to other specimens of this study, we were able to resample this specimen and to acquire Mg/Ca data on a slightly higher resolution (20–30 µm spots in a 100 µm raster compared to 50 µm spots spaced at 150–300 µm) and using 2 dimensions, as well as using a continuous high-resolution line-scan at (20–30 µm spots spaced at 10 µm) ([Figure 11](#fig-ORK_sub)). These additional data revealed previously missed summer peaks at around 2–3 mm distance to the shell edge (grey box in [Figure 11](#fig-ORK_sub)) and revealed additional growth at the very edge (dashed box in [Figure 11](#fig-ORK_sub)) mirroring the change towards warmer temperatures at the time of collection (August). Including these missing parts lead to a better alignment of both records and a resulting R2-value of 0.88 ([Figure 11](#fig-ORK_sub)).

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| Figure 11: Comparison of previous and new Mg/Ca data for ORK-LT5 explaining the previously unsuccessful correlation of Mg/Ca and 18O-values |

We were not able to resample the *Nacella* sp. specimens in Graniero *et al.* (2017), which had similarly unrelated records of 18O and Mg/Ca and pointed to no relationship between elemental ratios and SST at all. However, we were able to source other modern specimens of the same species from Tierra del Fuego, which shall serve here as an indicator. Similar to other patelloid shells, the results of the *Nacella* specimens in our study were successful with high R2-values (0.76–0.95) and suggest Mg/Ca as a reliable proxy for SST ([Figure 8](#fig-Nac_Comp) and supplementaries). Why these results are different from the studied *Nacella* sp. specimens in Graniero *et al*. (2017) is not obvious, but the occasional alignment of the Mg/Ca and 18O records of their shells (Figure 6 in Graniero *et al*. (2017)) indicate that there is some relationship that — potentially due to the low sampling resolution or intra-increment heterogeneity — is not perfectly visible, leading to an overall result of an uncorrelated relationship between Mg/Ca and SST.

# Conclusion

This study presents high-resolution and 2D information on Mg/Ca concentrations in modern and archaeological patelloid shells and their relationship to sea surface temperature. The results for *Patella vulgata*, *Nacella deaureata*, and *Nacella magellanica* were consistently promising with mean R2-values of 0.89, 0.86, and 0.88 respectively.

LIBS elemental imaging provided some insight into elemental anomalies found particulary in the external parts (m+3 layer) of the shell, which introduce intra-incremental heterogeneity and which cannot be reconciled with modern SST changes or SST changes recorded in the 18O of the same shells. Our 2D approach allowed us to avoid these areas of intra-increment heterogeneity and focus on areas that are predominantly controlled by changes in SST.

These results are particularly promising for future analyses of patelloid shells for the study of season of collection in archaeological sites as well as the reconstruction of sub-annual climatic conditions in the past. Shells of the species studied here are widely available along the European Atlantic façade and the Argentinian coastline and make up a significant part of marine mollusc remains in archaeological sites of those regions (Andre Carlo Colonese et al. 2011; Villagran et al. 2011; Zangrando et al. 2016). Improving their analysis in terms of cost and time efficiency through the benefits of LIBS, which can be used in this context as a screening tool for targeted 18O analysis focusing on annual minima and maxima revealed in the Mg/Ca record, will allow researchers to increase sample numbers and produce larger and more in-depth climatic studies than previously possible.

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