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Assessing elemental ratios as a paleotemperature proxy in the calcite shells of patelloid limpets

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A B S T R A C T

Archaeological shell and fish middens are rich sources of paleoenvironmental proxy data. Patelloid limpet shells are common constituents in archaeological middens found along European, African, and South American coastlines. Paleotemperature reconstructions using oxygen isotope ratios of limpet shells depend on the ability to constrain the oxygen isotope ratio of seawater; therefore, alternative proxies are necessary for coastal localities where this is not possible. The study evaluates whether Mg/Ca, Sr/Ca, Li/Ca, Li/Mg, and Sr/Li ratios are reliable proxies of sea surface temperature (SST) in the calcite layer of shells of the patelloid limpets, *Patella vulgata* and *Nacella deaurata*. We compare Mg/Ca, Sr/Ca, Li/Ca, Li/Mg, and Sr/Li ratios to the seasonal variations in contemporaneous $\delta^{18}O_{shell}$ values, which primarily record seasonal changes in SST. Elemental ratios (Mg/Ca, Sr/Ca, Li/Ca, Li/Mg, and Sr/Li) show no significant correlations with reconstructed SST in *P. vulgata* and *N. deaurata* shells, nor do they show sinusoidal cycles expected from a SST proxy. In addition, shell $\delta^{13}C$ values show no significant ontogenetic trends, suggesting that these limpets exhibit little change in metabolic carbon incorporation into the shell with increasing ontogenetic age. Although shell growth rate exhibits a logarithmic decrease with age based on calculated linear extension rates, growth rate does not correlate with elemental profiles in these limpets. Overall, elemental ratios are not reliable recorders of paleotemperature in patelloid limpets.

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1. Introduction

Archaeological shell middens potentially contain archives of high-resolution seasonal variations in coastal sea surface temperature (SST). Limpet shells are common constituents in archaeological middens along European, African, and South American coastlines (Álvarez et al., 2011; Balbo et al., 2011). Oxygen isotope ratios ($^{18}O/^{16}O$) of modern and archaeological limpet shells from the genera *Patella*, have been used to reconstruct seasonal-scale SST and ocean circulation patterns during the Late Quaternary (Shackleton, 1973; Cohen and Tyson, 1995; Fenger et al., 2007; Ferguson et al., 2011; Colonese et al., 2012; Surge and Barrett, 2012; Wang et al., 2012). Oxygen isotope paleothermometry is based on the temperature dependence of the fractionation of biogenic carbonate and ambient waters (reviewed in Grossman, 2012). There is an inverse relationship between carbonate $\delta^{18}O$ values and temperature,

where increases in temperature result in a decrease in carbonate $\delta^{18}O$ values. Such studies depend on the ability to constrain the $\delta^{18}O$ value of seawater ($\delta^{18}O_{water}$) for accurate paleotemperature calculations. Freshwater inputs to coastal environments influence $\delta^{18}O_{water}$ values making it difficult to constrain $\delta^{18}O_{water}$ when freshwater inputs cannot be quantified. This is especially important in estuarine environments which are subject to seasonal variations in freshwater inputs. Alternative proxies, such as elemental ratios, are potentially useful for such coastal localities where traditional paleotemperature reconstruction methods, such as $\delta^{18}O$ values, are unreliable.

Elemental ratios have been used as paleotemperature proxies in corals (Smith et al., 1979; de Villers et al., 1995; Quinn et al., 2006) and foraminifera (reviewed in Baker et al., 2005) with varying degrees of success, and appear problematic in bivalves (e.g., Klein et al., 1996; Vander Putten et al., 2000; Gillikin et al., 2005; Freitas et al., 2006; Surge and Walker, 2006; Surge and Lohmann, 2008; Wisshak et al., 2008; Poulain et al., 2015). In general, factors that control elemental ratios in molluscs appear to vary among studies (e.g., Carré et al., 2006; Klein et al., 1996; Takesue and van Geen, 2004; Freitas et al., 2006; Sosidan et al., 2006; Poulain et al., 2015). For instance, some studies suggest elemental ratios such as Sr/Ca and Mg/Ca ratios reflect changes in

growth rate (e.g., Gillikin et al., 2005; Sosidan et al., 2006; Surge and Walker, 2006; Surge and Lohmann, 2008), while others suggest a biological control (e.g., Wanamaker et al., 2008). These kinetic and metabolic controls appear to be unpredictable among different genera or even within the same species from the same locale (e.g., Lorrain et al., 2005). Therefore, further investigations on the incorporation of minor and trace element ratios in mollusk shells are warranted.

Few studies have investigated elemental ratios as an independent paleothermometer in limpet shells (Schifano and Censi, 1986; Foster and Chacko, 1995; Ferguson et al., 2011) and none to our knowledge have considered *Nacella* in their investigations. In addition, this is the first study to examine a suite of elemental ratios as paleotemperature proxies in patelloid limpets. Previous studies that investigate the δ^{18}O-Mg/Ca relationship in *Patella* shells produce conflicting results. Schifano and Censi (1986) found that *Patella* from the Gulf of Bonagia, Sicily, exhibited different Mg and Sr relationships to temperature depending on the season. In this case, winter growth showed no correlation to temperature, in contrast with high correlation during summer ($R^2 = 0.99$; Schifano and Censi, 1986). On the other hand, Ferguson et al. (2011) concluded that Mg/Ca ratios and δ^{18}O values record the full range of SST in the Mediterranean, although shells without a clear δ^{18}O-Mg/Ca relationship were omitted from the paleotemperature reconstruction. These seasonal breakdowns in the Mg/Ca-SST relationship have also been noted in bivalves (Vander Putten et al., 2000; Mouchi et al., 2013). Such enigmatic breakdowns in the δ^{18}O-Mg/Ca relationship are not well understood, but may be species specific.

Although previous studies have investigated elemental ratios such as Sr/Ca, Li/Ca, Li/Mg, and Sr/Li in calcifying organisms, there appears to be considerable variation as to how these ratios are related, if at all, to environmental conditions. For instance, Sr/Ca profiles recorded in aragonitic shells of modern marine gastropods were found to covary with shell δ^{18}O profiles (Sosidan et al., 2006; Gentry et al., 2006). Sosidan et al. (2006) established that this seasonal variation in Sr/Ca ratios of *Conus* shells is due to seasonal changes in growth rate based on the covariance of Sr/Ca ratios with δ^{18}O values and linear extension rate. In inorganic calcium carbonate, we expect Sr/Ca ratios to show a temperature dependence in aragonite due to the co-precipitation of Sr with aragonite, but not in calcite (Kinsman and Holland, 1969; Tesoriero and Pankow, 1996). However, in bivalves the relationship between Sr/Ca ratios and temperature appears to be primarily related to growth rate irrespective of shell mineralogy (e.g., Purton et al., 1999; Takesue and van Geen, 2004; Gillikin et al., 2005; Lorrain et al., 2005; Poulain et al., 2015).

Li/Ca ratios in calcite foraminifera have been investigated as a proxy for temperature, calcification rate, and carbonate ion concentration (Delaney et al., 1985; Hall and Chan, 2004; Marriott et al., 2004; Hathorne and James, 2006). Although Li/Ca ratios increase in planktonic and benthic foraminiferal tests as temperature decreases, other factors appear to be the dominant drivers of Li/Ca ratios including microhabitat, growth rate, mineralogy, and genetic variation among species (Hall and Chan, 2004). Similarly, Li/Mg ratios have been used to reconstruct SST in aragonitic *Porites* corals from the Indo-Pacific, however there is likely a biological component to the relationship as well (Hathorne et al., 2013). In bivalves the Li/Ca-SST relationship is less clear; although Li/Ca ratios showed seasonal cycles in *Arctica islandica*, they only exhibit a weak correlation between Li/Ca ratios and temperature (Thébault et al., 2009). Correlations between growth increment width and river discharge suggest that fluctuations in bivalve Li/Ca ratios may be related to calcification rate and/or riverine inputs of Li (Thébault et al., 2009; Thébault and Chauvaud, 2013). Finally, Füllenbach et al. (2015) proposed Sr/Li ratios serve as a paleotemperature proxy in aragonitic bivalve shells from brackish environments; however, environments in their study are considered marine. Even so, this proxy will be investigated alongside the previously discussed elemental ratios to test whether Sr/Li ratios can be applied to coastal marine environments, which may be susceptible to freshwater influence.

In summary, the present study evaluates whether Mg/Ca, Sr/Ca, Li/Ca, Li/Mg, and Sr/Li ratios are reliable proxies of SST in calcite shells of the patelloid limpets, *Patella vulgata* and *Nacella deaurata*. To test this hypothesis, we compare these elemental ratios to seasonal variations in contemporaneous δ^{18}O$_{shell}$ values, which primarily record seasonal changes in SST.

2. Materials and methods

2.1. Shell and water samples

Patella vulgata were collected alive from the rocky intertidal zone in Whitley Bay, Northumberland, England in June 2001 (Fig. 1A; specimen NL-0601-3 from Fenger et al., 2007) and in Rack Wick Bay, Westray, Orkney, Scotland in August 2009 (specimen ORK-LT5)
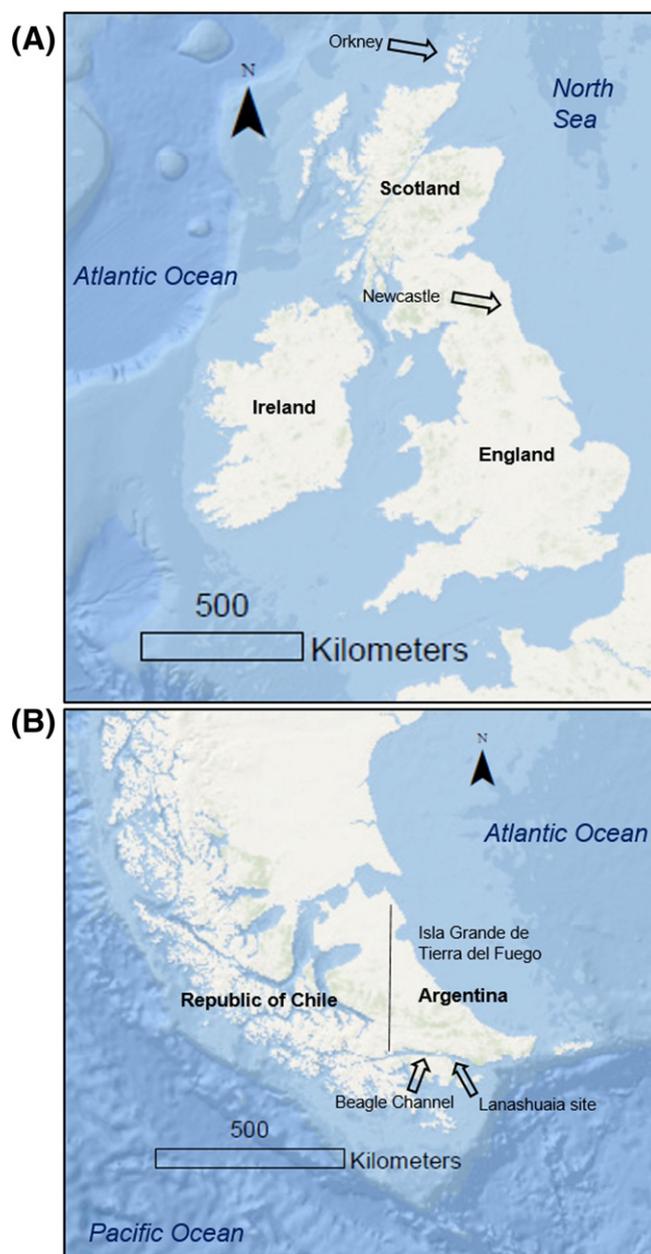
Fig. 1. Maps of study locations. (A), Map of study site in Newcastle and Orkney, United Kingdom. Shells were collected from Newcastle at St. Mary's Lighthouse and Rack Wick Bay, Westray, Orkney. (B), Map of study site in Tierra del Fuego, Argentina. Shells were collected from the archaeological shell midden Lanashuaia II in the Beagle Channel; modern shells were collected from a nearby site.

Table 1

Sample list with shell name, age, growth rate, and isotope values.

ShellName	Age (years)	Length sampled (mm)	Mean extension rate (mm/year)	Min $\delta^{ls}O$	Max $\delta^{ls}O$	$\Delta^{18}O$ (Max-Min)	Average $\delta^{18}O$	SD $\delta^{18}O$	Min $\delta^{13}C$	Max $\delta^{13}C$	$\Delta^{13}C$ (Max-Min)	Average $\delta^{13}C$	SD $\delta^{13}C$
Newcastle, UK													
Patella (NL 0601-3)	6	10.7	l.8	0.6	3.4	2.8	2.0	0.7	−1.5	0.5	2	−0.2	0.4
Orkney, UK													
Patella (ORK LT5)	5	11.7	2.3	0.2	3.4	3.2	2.5	0.6	−0.6	0.8	1.4	0.1	0.3
Tierra del Fuego, AR													
Nacella (ND-ARCH-1)	0.5	5.5	11.0	0.2	2	1.8	1.4	0.5	2.1	2.6	0.5	2.4	0.1
Nacella (ND-ARCH-3)	1.5	8.3	5.5	0.2	2.5	2.3	1.2	0.7	1.1	2.4	1.3	1.8	0.4
Nacella (ND-MOD-1)	4	15	3.8	0.7	3.8	3.1	1.9	0.6	1.2	2.3	1.1	1.7	0.3
Nacella (ND-MOD-6)	2.5	7.5	3.0	0.7	2.8	2.1	1.8	0.6	0.7	1.9	1.2	1.5	0.4

(Table 1; Fig. 1A). Periodic measurements made in previous studies indicate that these locations have normal marine salinity, ranging from 34.0 to 34.8 in Whitley Bay (Fenger et al., 2007; Surge and Barrett, 2012).

Modern *N. deaurata* were collected from the lower intertidal zone of the Beagle Channel (the Outer Cambaceres Bay identified as CE in Fig. 1 of Colonese et al., 2012), Tierra del Fuego, Argentina in August 2009 (specimens ND-MOD-1 and ND-MOD-6; Table 1, Fig. 1B). The Beagle Channel is semi-enclosed and has restricted exchange with Pacific waters (Antezana, 1999). It is influenced by river discharge and summer meltwater (Gordillo et al., 2008; Colonese et al., 2012). The monthly average temperature and salinity from 2009 to 2010 are 7.0 ± 1.6 °C and 34.4 ± 1.8 psu, respectively, in Outer Cambares Bay (Colonese et al., 2012), similar to ongoing monthly monitoring in the Beagle Channel (beginning in October 2015) that indicates that the range in temperature is 10.1 ± 2.4 °C and the range in salinity is 30.6 ± 0.8 psu. Two archaeological *N. deaurata* shells (between 1155 ± 40BP (CNA 1056) and 1385 ± 25BP (CNA 590) Evans et al., 2016) were selected from the previously excavated Lanashuaia II site (Colonese et al., 2012) (specimens ND-ARCH-1 and ND-ARCH-3). We refer the reader to Fenger et al. (2007) and Colonese et al. (2012) for more information about the ecology of these two species.

Waters samples from the shore of Outer Cambacares Bay (Beagle Channel, 54°52′49.62″S 67°16′26.49″W) were collected once a month to characterize the seasonal variation in oxygen isotope ratios. Monthly sample collection began in October 2015 and will continue for an entire year. We report our water analyses to date (October 2015 to March 2016) together with previously published $\delta^{18}O_{water}$ values from Colonese et al. (2012). Water was collected and tightly sealed in 30 ml glass vials. Water $\delta^{18}O$ were measured on a gas-source isotope ratio mass spectrometer (Finnigan Delta S) at the University of Arizona. Samples were equilibrated with CO_2 gas at approximately 15 °C in an automated equilibration device coupled to the mass spectrometer. Standardization is based on international reference materials VSMOW and SLAP. Precision is 0.08‰ or better for $\delta^{18}O$ based on replicates of internal standards.

2.2. Preparation of shell cross sections

Shells were sectioned from anterior to posterior using a Gryphon diamond band saw (Fig. 2A). Each half of the sectioned shells were mounted on separate microscope slides and cut into thick sections using a Buehler Isomet low-speed saw. Both thick sections were ground and polished with 1 μm diamond suspension grit (Buehler). One polished thick section was used for isotopic and elemental analyses (3 mm thick) and the other was used to make acetate peels (0.5 mm thick). Acetate peels were prepared by etching the shell surface with 5% HCl solution for 30 s. After etching the surface, shells were drenched in acetone, then carefully covered with a 76.2 μm (0.003 in.) thick acetate sheet for 45 min. Acetate peels were used to enhance the visibility
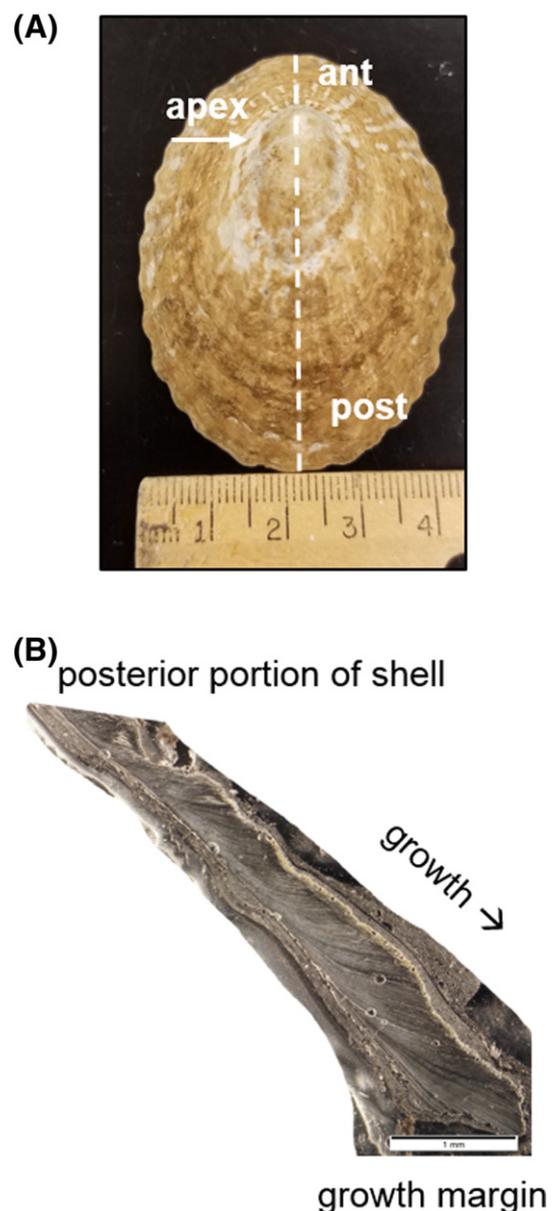
Fig. 2. Shell images. (A) Shells were cut through the apex along the axis of maximum growth shown by the dashed red line from anterior (ant) to posterior (post). (B) Photomicrograph of an acetate peel of *N. deaurata* shell cross section (ND MOD-1), showing enhanced visibility of growth lines.

of growth lines (Fig. 2B). Growth increments were used to guide isotopic sampling.

2.3. Stable isotopic analysis ($\delta^{18}O$ and $\delta^{13}C$)

Samples for isotopic analysis were micromilled at submonthly resolution guided by prominent growth increments using a computerized Merchantek micromill. *P. vulgata* shells are comprised of seven shell layers of both calcitic and aragonitic mineralogy (see Fenger et al., 2007 for details). Carbonate microsamples were collected from the inner calcitic layer of *Patella* and *Nacella* specimens (i.e., layer m + 2; Fenger et al., 2007; Ferguson et al., 2011; Colonese et al., 2012). Shell NL 0601-3 was previously analyzed by Fenger et al. (2007). All other isotope samples were analyzed using a Kiel III coupled to a Finnigan MAT 252 gas-ratio mass spectrometer at the University of Arizona. Analytical precision is 0.08‰ for $\delta^{13}C$ and 0.10‰ for $\delta^{18}O$. Isotopic ratios are reported relative to the Vienna-Pee Dee Belemnite (VPDB) standard.

Sea surface temperature reconstructions were calculated using the following paleotemperature equation for calcite (Friedman and O'Neil, 1977 modified from Tarutani et al., 1969):

$$1000 \ln\alpha = \left(2.78 \times 10^6\right)/T^2 - 2.89 \quad (1)$$

$$\alpha_{shell-water} = \left(\delta^{18}O_{shell} + 1000\right)/\left(\delta^{18}O_{water} + 1000\right) \quad (2)$$

where α is the fractionation factor between shell carbonate and water, T is temperature (°C),

$\delta^{18}O_{water}$ is the oxygen isotope ratio of ambient water versus Vienna-Standard Mean Ocean Water (VSMOW). The annual average $\delta^{18}O_{water}$ values for Newcastle and Orkney, UK are 0.10 ± 0.04‰ for the North Sea (Hickson et al., 1999) and 0.31 ± 0.17‰ for Rack Wick Bay (Surge and Barrett, 2012), respectively. Both locations are fully marine and are not significantly influenced by freshwater runoff (Fenger et al., 2007; Surge and Barrett, 2012 and references therein). The $\delta^{18}O_{water}$ value for the Beagle Channel (Outer Cambaceres Bay identified as CE in Fig. 1 of Colonese et al., 2012), Tierra del Fuego, Argentina is -1.3 ± 0.2‰ based on an average of monthly measurements taken from December 2009 to October 2010 by Colonese et al. (2012) and October 2015 to March 2016 from this study (Table 2). Gordillo et al. (2015) also suggest $\delta^{18}O_{water}$ values at this site are relatively constant and that is appropriate to assume a constant $\delta^{18}O_{water}$ value for paleotemperature reconstruction. It is unlikely that the archaeological *Nacella* shells came from Inner Cambaceres Bay, given that modern day *Nacella* of this size are not present in the Inner

Table 2
Compilation of $\delta^{18}O_{water}$ values for Tierra del Fuego, AR from Colonese et al. (2012) and this study relative to VSMOW.

Date	$\delta^{18}O_{water}$ (‰)	Reference
Dec-09	−1.3	Colonese et al. (2012)
Jan-10	−1.6	Colonese et al. (2012)
Feb-10	−1.4	Colonese et al. (2012)
Apr-10	−1.2	Colonese et al. (2012)
Jim-10	−1.3	Colonese et al. (2012)
Aug-10	−0.8	Colonese et al. (2012)
Oct-10	−1.2	Colonese et al. (2012)
Oct-15	−1.3	This study
Nov-15	−1.5	This study
Dec-15	−1.4	This study
Jan-16	−1.2	This study
Feb-16	−1.4	This study
Mar-16	−1.2	This study
Average	**−1.3**	All data
Standard deviation	**0.2**	All data

Cambaceres Bay and are harvested primarily from the Outer Bay for human consumption (Briz i Godino, pers. comm.). *Nacella* prefer to inhabit environments with a high level of wave movement, which does not describe conditions in the Inner Cambaceres Bay (Briz i Godino, pers. comm.). *Patella* shell $\delta^{18}O$ values were corrected for the +1.01‰ predictable offset observed by Fenger et al. (2007). Colonese et al. (2012) found that *Nacella* precipitate their shells in isotopic equilibrium requiring no correction factor to be applied.

2.4. Analysis of elemental ratios by LA-ICP-MS

High-resolution elemental analyses were conducted using a laser-ablation inductively-coupled mass spectrometer (LA-ICP-MS; CETAC LSX-213 frequency quintupled Nd:YAG laser ($\lambda = 213$ nm) coupled to a Perkin Elmer Elan 6100 DRC ICP-MS) in the Geology Department at Union College, NY (Table 3). Instrumental parameters and data reduction are discussed in Gillikin and Dehairs (2013) and O'Neil and Gillikin (2014). Spot analyses were completed (50 μm diameter) at constant spacing (150 or 300 μm). ThO/Th ratios were monitored daily to check for oxide formation and were always <0.6% (monitored using the NIST 612 glass standard). ^{43}Ca was used as an internal standard and ^{7}Li, ^{26}Mg, and ^{86}Sr were monitored. Data were calibrated using the silicate standard NIST612 with values from Pearce et al. (1992). Analysis of the U.S. Geological Survey pressed carbonate pellet MACS3 suggested a robust calibration and small error (percent relative standard deviations on 26 analyses over three analytical days are: Li = 5.6%, Mg = 4.6%, and Sr = 3.2%). The laser was shot in the inner calcitic layer of *Patella* specimens (i.e., m + 2; Fenger et al., 2007) and in the inner calcitic layer of *Nacella* specimens.

3. Results

3.1. Shell $\delta^{18}O$ and $\delta^{13}C$ values

Live-collected *Patella* and *Nacella* shells exhibit a quasi-sinusoidal trend in the temporal variation of $\delta^{18}O$ values (Fig. 3A, C, E and F). Their number of cycles (peak to peak or trough to trough) range from about 2.5 (ND-MOD-6, between 0 and 7.5 mm) to 6.5 (NL-0601-3, between 0 and 10.7 mm). In contrast, the oxygen isotope time series recorded in archaeological shell ND-ARCH-1 shows an incomplete cycle (between 0 and 5.5 mm), and specimen ND-ARCH-3 contains only one complete cycle (between 0 and 8.25 mm). Since temperature fluctuates seasonally, these shell $\delta^{18}O$ minima and maxima are used as measures of annual cycles. Assuming one cycle is equivalent to one year of growth as found in other limpet shells (Fenger et al., 2007; Surge et al., 2013), the ontogenetic age for modern specimens range from ~2.5–6.5 years, whereas the two archaeological shells are half a year to a year old. Table 1 summarizes the estimated age and descriptive statistics of the $\delta^{18}O$ and $\delta^{13}C$ time series for each individual. Values of $\delta^{18}O$ and $\delta^{13}C$ do not covary except in the last ~3 years of life of specimen NL-0601-3. There is no consistent ontogenetic trend in $\delta^{13}C$ values among specimens analyzed in this study (Fig. 4).

3.2. Linear extension rates

Mean annual linear extension rates (LER) were calculated based on $\delta^{18}O_{shell}$ minima and maxima, which represent summer and winter temperatures, respectively. Mean annual LER were calculated by estimating the number of years represented by the $\delta^{18}O_{shell}$ profile and measuring the distance along the shell. Mean LER over the lifetime of the limpets were lower in the UK (1.8 and 2.6 mm/year), than in Argentina (3.0 to 11.0 mm/year; Table 1). Furthermore, archaeological specimens have growth LER that are roughly 2–4 times higher than live-collected specimens of the same species at the same location. In shells where several years were sampled, mean annual LER show a

Table 3
Compilation of elemental ratio means, minima, and maxima for all shells in units of mmol/mol for Mg/Ca, Sr/Ca, and Li/Ca. Li/Mg and Sr/Li are unitless.

ShellName	Mean Mg/Ca	Min Mg/Ca	Max Mg/Ca	Mean Sr/Ca	Min Sr/Ca	Max Sr/Ca	Mean Li/Ca	Min Li/Ca	Max Li/Ca	Mean Li/Mg	Min Li/Mg	Max Li/Mg	Mean Sr/Li	Min Sr/Li	Max Sr/Li
Newcastle, UK															
Patella (NL 0601-3)	19.4 ± 4.1	12.4	35.1	1.6 ± 02	1.3	2.2	0.023 ± 0.007	0.000	0.037	0.001 ± 0.000	0.000	0.003	73 ± 20	43	136
Orkney, UK															
Patella (ORKLT5)	18.4 ± 3.0	12.0	25.4	1.5 ± 0.1	1.4	1.7	0.024 ± 0.010	0.008	0.046	0.001 ± 0.001	0.000	0.002	78 ± 40	33	199
Tierra del Fuego, AR															
Nacella (ND-ARCH-1)	2.1 ± 0.7	1.3	4.0	l.6 ± 0.l	1.3	1.9	0.048 ± 0.005	0.037	0.055	0.024 ± 0.007	0.012	0.039	34 ± 5	27	46
Nacella (ND-ARCH-3)	2.5 ± 1.7	1.3	12.7	l.6 ± 0.l	1.2	1.9	0.042 ± 0.006	0.020	0.055	0.020 ± 0.007	0.002	0.040	39 ± 6	30	69
Nacella (ND-MOD-1)	4.5 ± 4.0	1.7	32.6	1.5 ± 0.2	1.2	2.2	0.042 ± 0.011	0.022	0.060	0.013 ± 0.007	0.001	0.030	41 ± 24	22	175
Nacella (ND-MOD-6)	3.6 ± 1.5	2.2	8.6	1.7 ± 0.1	1.5	2.0	0.047 ± 0.007	0.029	0.059	0.015 ± 0.005	0.003	0.024	37 ± 7	30	60

logarithmic trend that decreases with ontogenetic age, although only one *Patella* (NL 0601-3) shows a statistically significant trend ($P \leq 0.05$) (Fig. 5).

3.3. Elemental ratios

Unlike oxygen isotope ratios, there does not appear to be regular annual cycles in any studied profiles of elemental ratios (Figs. 6–10). Similar to carbon isotope ratios, no ontogenetic trends are evident in any of the profiles of elemental ratios. In general, observe some cyclicity in *Patella* Mg/Ca profiles (Fig. 6E, F) and more flat lying trends in *Nacella* Mg/Ca profiles (Fig. 6A, B, D). Mg/Ca ratios in *P. vulgata* exhibit an apparent cyclicity, although these cycles do not correspond to a coeval $\delta^{18}O$ cycle and vary more than two-fold in the Northumberland shell (Fig. 6E). The Sr/Ca ratios exhibit cyclicity in some shells (Fig. 7C, F) and not others (Fig. 7A, E). When cyclicity is evident in Sr/Ca there is no associated relationship with co-occurring shell $\delta^{18}O$ values. The Li/Ca ratios were similar for all specimens ranging from ~0.02 to 0.06 mmol/mol, with the values fluctuating more rapidly than the $\delta^{18}O$ values (Fig. 8). Sr/Li ratios do not correspond with $\delta^{18}O$ curves and tend to be more flat laying than $\delta^{18}O$ profiles (Fig. 9). Li/Mg ratios appear to exhibit distinct cycles in ND MOD-6, ND MOD-1, and ND-ARCH-3, although these cycles do not correspond to a coeval $\delta^{18}O$ cycle (Fig. 10A, C, D).

3.4. Elemental ratio-SST relationship

To evaluate elemental ratio-SST correlations, reconstructed SST values were calculated using an established paleotemperature equation (Eqs. (1) and (2) above). Elemental ratios (Mg/Ca, Sr/Ca, Li/Ca, Sr/Li, Li/Mg) show no apparent relationship with reconstructed SST in *P. vulgata* (Fig. 11) and *N. deaurata* (Fig. 12) shells. Rather, the cross plots exhibit either a shotgun pattern or relatively flat trend. *Nacella deaurata* shells have lower Mg/Ca ratios (<10 mmol/mol) than *P. vulgata* (>10 mmol/mol). Sr/Ca ratios are relatively flat lying, and the range for all specimens is approximately 1 to 2 mmol/mol (Figs. 11, 12). Li/Ca and Li/Mg ratios have large scatter in the data for both species (Figs. 11B, E, 12B, E).
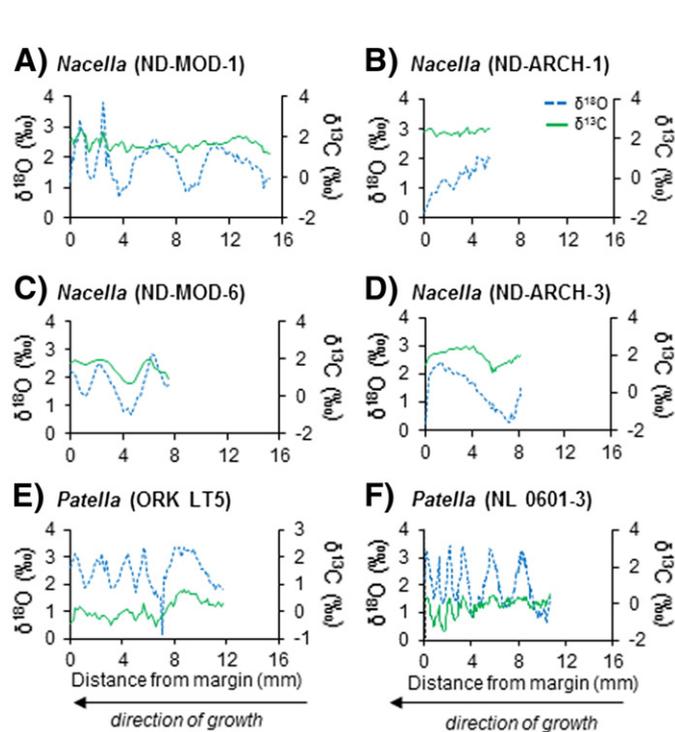
Fig. 3. *Nacella* and *Patella* shell $\delta^{18}O$ and $\delta^{13}C$ profiles (‰ VPDB). A-D, *Nacella deaurata* shells collected from Tierra del Fuego, Argentina. MOD = shells collected alive. ARCH = archaeological shells. E-F, *Patella vulgata* shells collected alive from Orkney (ORK) and Newcastle (NL), UK. The blue dashed lines represent $\delta^{18}O$ values and the green solid lines represent $\delta^{13}C$ values. Note that time and growth is from right to left.
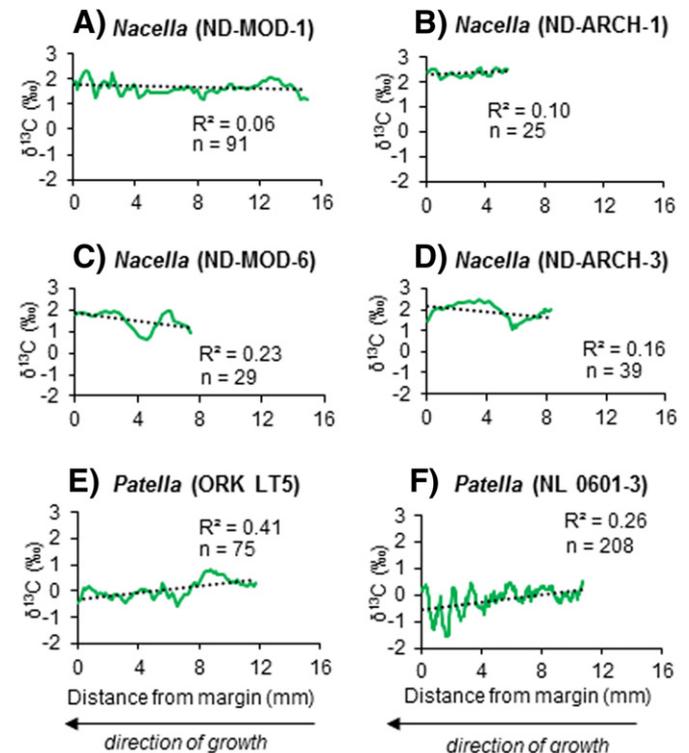
Fig. 4. $\delta^{13}C$ variation with distance from growth margin (mm) in *N. deaurata* (A–D) and *P. vulgata* (E, F) shells. Linear regression lines are shown with black dotted lines. *P*-values are <0.05 for (A) ND-MOD-1, (C) ND-MOD-6, (D) ND-ARCH-3, (E) ORK LT5, and (F) NL 0601-3. The *P*-value for (B) ND-ARCH-1 is 0.12.
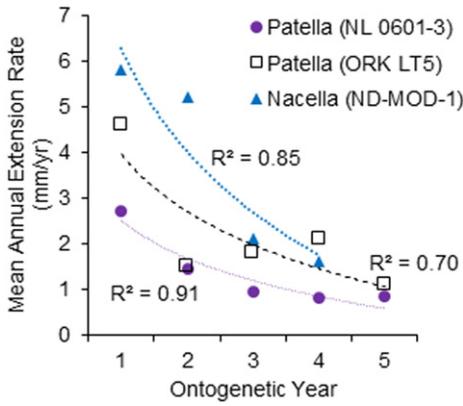
Fig. 5. Mean annual extension rate with ontogenetic year. Growth rates for *Patella* and *Nacella* specimens older than 2 years exhibit a negative logarithmic trend in mean annual extension rate over time. Only NL 0601-3 exhibits a statistically significant trend.

Nacella deaurata shells have Li/Mg ratios an order of magnitude higher than *P. vulgata* shells (Fig. 10).

4. Discussion

There are no apparent elemental ratio-SST trends in shells of *P. vulgata* and *N. deaurata*, therefore Mg/Ca, Sr/Ca, Li/Ca, Sr/Li, and Li/Mg are not reliable recorders of SST in paleoenvironmental studies (Figs. 11 and 12, respectively). At Blythe, UK, approximately 20 km from Newcastle, average annual SST trends exhibit a clear sinusoidal trend ranging from about 5 °C in February to 14 °C in August (Fig. 13A). In the Beagle Channel, compiled SST from 1963 through 2011 show a distinct, consistent sinusoidal trend ranging from about 5 °C in July/August to 10 °C in January (Fig. 13B). At both sites, shell $\delta^{18}O$ values reflect this distinct sinusoidal trend (e.g., Fig. 3), especially in specimens older than 1.5 years. Based on the paleotemperature
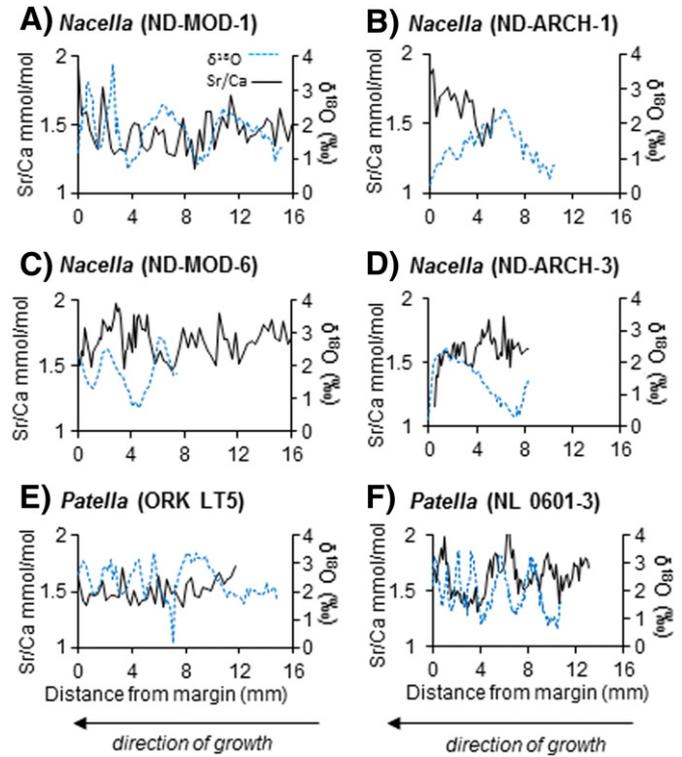
Fig. 7. Shell Sr/Ca ratios and $\delta^{18}O$ values for *N. deaurata* (A–D) and *P. vulgata* (E, F). The blue dashed line indicates $\delta^{18}O$ values and the black solid line indicates Sr/Ca values. Note that time and growth is from right to left.

equation (Eqs. (1), (2)), these temperature ranges account for a roughly 2‰ range in shell $\delta^{18}O$ values at Newcastle and a 1‰ range in the Beagle Channel. A compilation of monthly $\delta^{18}O_{water}$ data from Tierra del Fuego
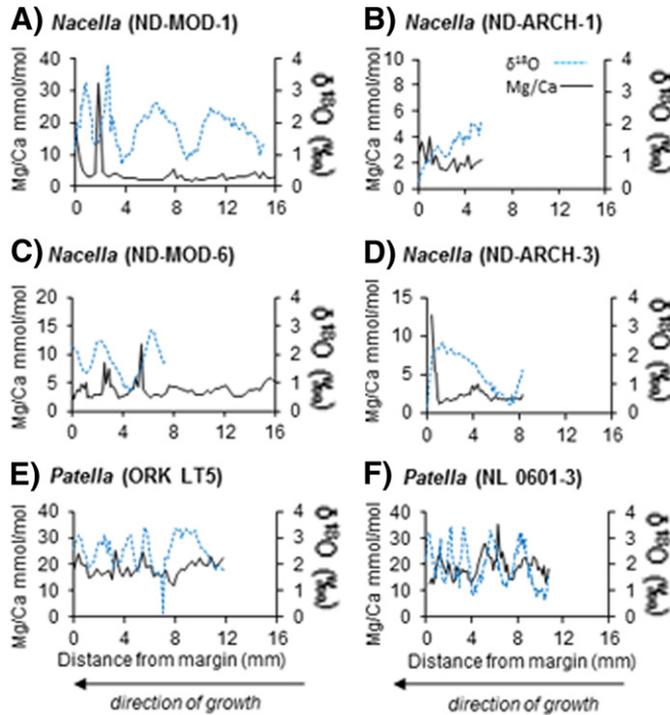
Fig. 6. Shell Mg/Ca ratios and $\delta^{18}O$ values for *N. deaurata* (A–D) and *P. vulgata* (E, F). The blue dashed line indicates $\delta^{18}O$ values and the black solid line indicates Mg/Ca values. Note that time and growth is from right to left.
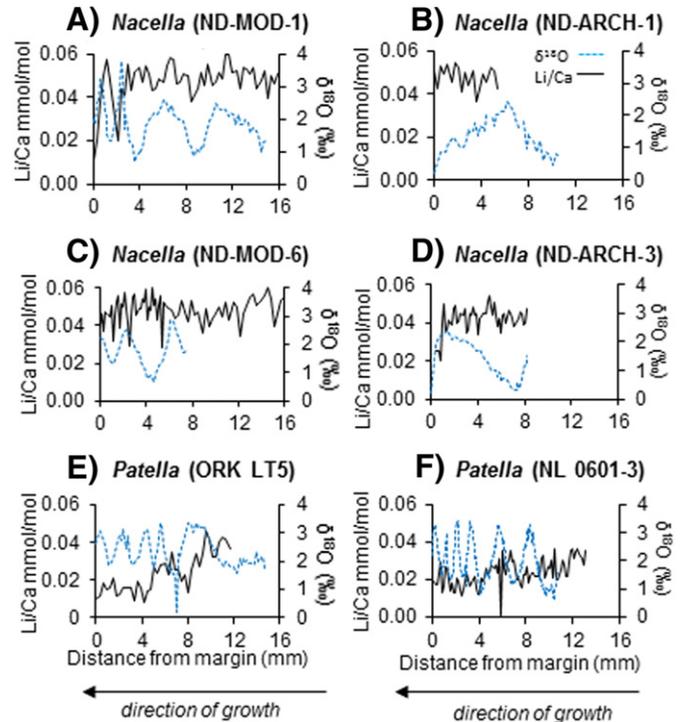
Fig. 8. Shell Li/Ca ratios and $\delta^{18}O$ values for *N. deaurata* (A–D) and *P. vulgata* (E, F). The blue dashed line indicates $\delta^{18}O$ values and the black solid line indicates Li/Ca values. Note that time and growth is from right to left.
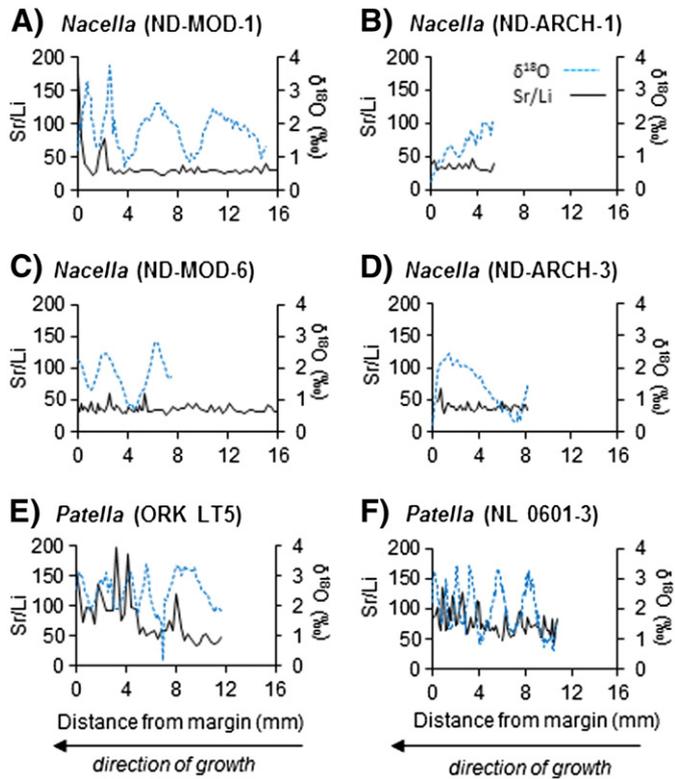
Fig. 9. Shell Sr/Li ratios and δ18O values for *N. deaurata* (A-D) and *P. vulgata* (E, F). The blue dashed line indicates δ18O values and the black solid line indicates Sr/Li values. Note that time and growth is from right to left.

indicates that variability in δ18O$_{water}$ values is minimal (0.2‰; Table 2). Therefore, shell δ18O values are most strongly driven by variations in SST. The annual cyclicity in shell δ18O values is mainly driven by
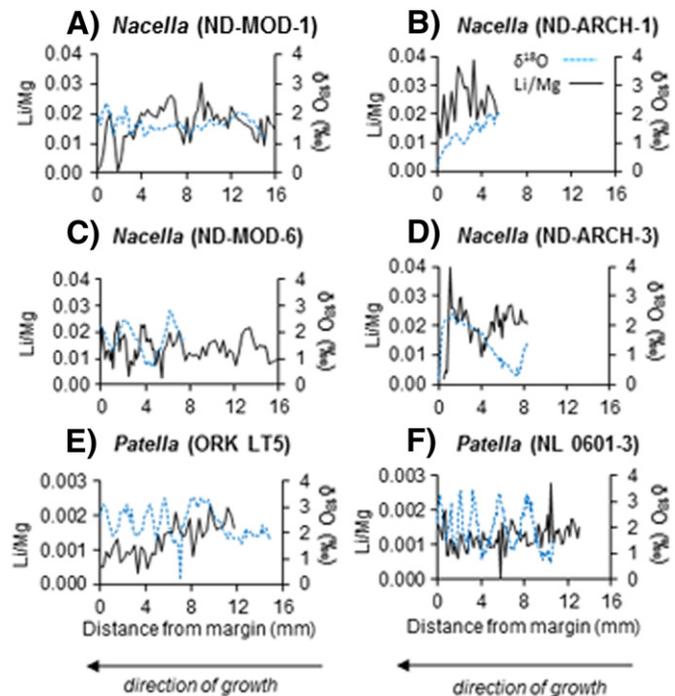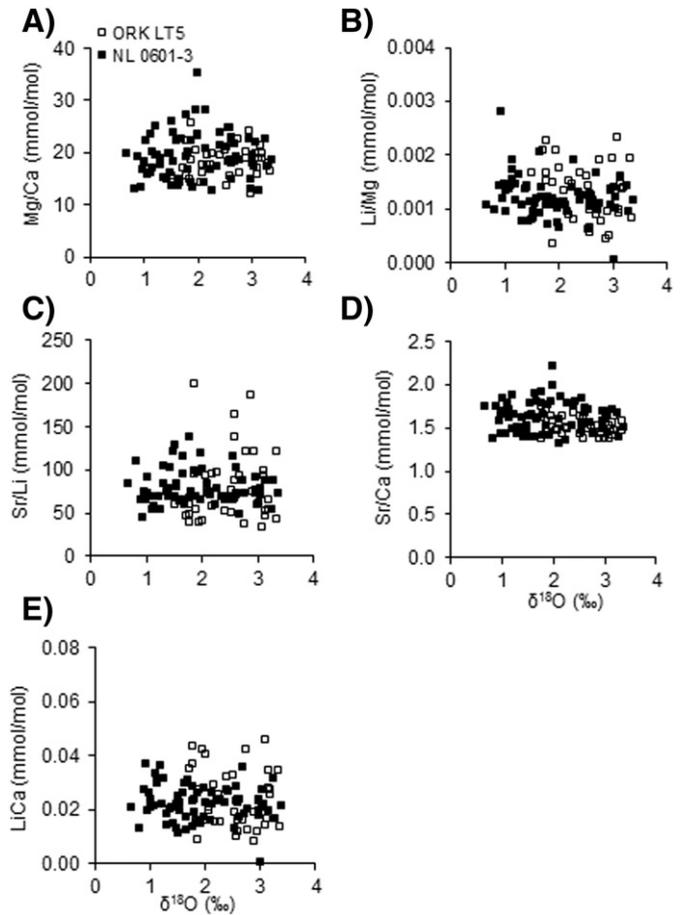
Fig. 11. A–E. Elemental ratio-δ18O relationships for modern *Patella vulgata* limpet shells.

temperature, therefore, it is reasonable to compare elemental ratios to shell δ18O values to evaluate whether elemental ratios record variations in temperature (Figs. 11, 12). Thus, it is clear that the elemental ratios do not follow the expected sinusoidal variation in SST. Furthermore, salinity variations are not likely to influence Mg, Sr, and Ca concentrations in the water because Mg/Ca and Sr/Ca are conservative at salinities above 10 psu (Dodd and Crisp, 1982; Lazareth et al., 2003). Since study sites are fully marine, salinity variations are not expected to significantly affect the Mg/Ca and/or Sr/Ca at either site.

Patella vulgata from this study do not show the significant Mg/Ca-SST correlation observed in *P. caerulea* (Schifano and Censi, 1986; Ferguson et al., 2011) and *P. rustica* (Ferguson et al., 2011) from previous studies. For instance, Ferguson et al. (2011) were able to reconstruct SST within ~4 °C using Mg/Ca ratios in *P. caerulea* and *P. rustica* from the Mediterranean Sea, although they did report some inconsistencies in the Mg/Ca-SST relationship. Shells with no clear correlation between δ18O and Mg/Ca values were excluded from their SST reconstruction, suggesting that Mg/Ca ratios are unpredictable as a paleotemperature proxy. While the absolute Mg/Ca ratios measured in this study are comparable to those from Ferguson et al. (2011) (about 11 to 30 mmol/mol), our samples exhibit the enigmatic breakdown of this Mg/Ca-SST relationship that was observed in one shell from the aforementioned study.

While the cause of this breakdown in Mg/Ca-SST in limpet shells is unknown, we consider habitat heterogeneity and changes in life habit as potential causes. Differences in growth patterns between studies may explain this disparity between *P. vulgata* from the UK, which grow slowly during winter and rapidly during early summer (Blackmore, 1969; Baxter, 1982; Fenger et al., 2007), and other *Patella*

Fig. 10. Shell Li/Mg ratios and δ18O values for *N. deaurata* (A-D) and *P. vulgata* (E, F). The blue dashed line indicates δ18O values and the black solid line indicates Li/Mg values. Note that time and growth is from right to left.
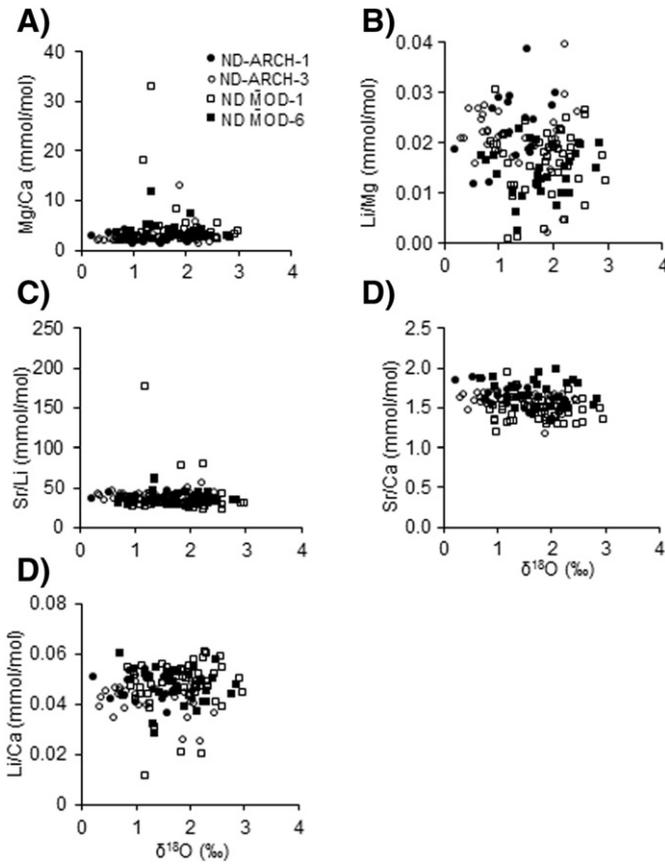
Fig. 12. A–E. Elemental ratio- δ^{18}O relationship for modern *Nacella deaurata* limpet shells. Shells ND 1 and ND 3 are archaeological, and ND MOD-1 and ND MOD-6 are modern.
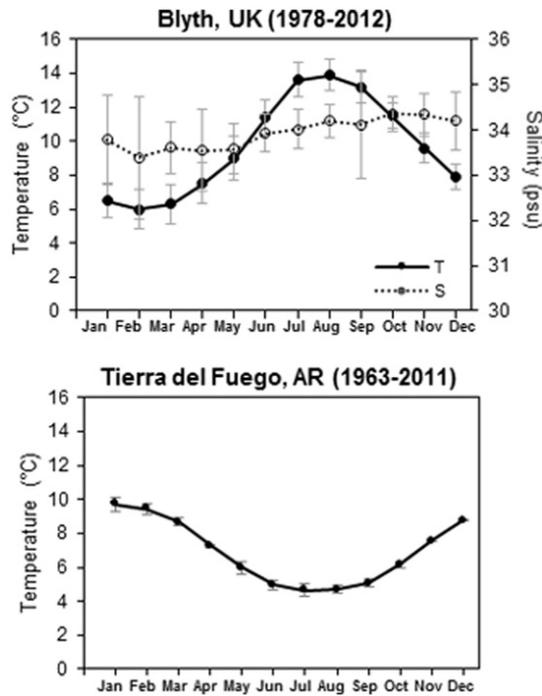
Fig. 13. Average monthly temperature and salinity profiles from (A) Blythe, UK (near Newcastle) compiled from the National Power and CEGB (www.cefas.co.uk) from 1978 to 2012 and (B) average monthly temperatures from the Beagle Channel, AR, compiled from Gordillo et al. (2015) and sources referenced within, from 1963 to 2011.

from the Mediterranean, which grow slowly during the summer (Schifano and Censi, 1986). Variations in microhabitat may potentially impact elemental ratios in limpets as well. A previous study found that *P. vulgata* living in sheltered versus exposed shores are exposed to differing food supply, grazing activity, dessication stress, and predation (Jenkins and Hartnoll, 2001). For instance, grazing at sheltered shores is <50% of that at exposed shores, although the cause of this dissimilarity is debated (see Jenkins and Hartnoll, 2001). Nevertheless, Jenkins and Hartnoll (2001) showed that limpets at comparable densities from sheltered and exposed shores exhibit no significant difference in growth rate despite occupying disparate habitats. More broadly, the difference between limpets inhabiting subtidal and intertidal environments may influence the incorporation of trace elements into shells. Limpets living in subtidal environments experience constant submersion and higher food availability than those from intertidal environments (Willmer et al., 2005). The Mg/Ca-SST relationship appears to differ between subtidal *P. caerulea* (Schifano and Censi, 1986), intertidal *P. rustica, P. caerulea* (Ferguson et al., 2011), and *P. vulgata* from this study. Furthermore, Schifano and Censi (1986) found that the Mg/Ca-SST in *Patella* changes seasonally, showing a stronger correlation ($R^2 = 0.99$) during warm temperatures, although the annual correlation is significant as well ($R^2 = 0.82$).

Strontium to calcium ratios are variable among individuals that grew at the same location, therefore, we suggest that Sr/Ca ratios in our specimens are do not appear to be governed by environmental controls. Previous studies reasoned that shell Sr/Ca ratios may be related to calcification temperature (Dodd, 1965), kinetic effects (e.g., Carpenter and Lohmann, 1992; Lorens, 1981), biological processes, and/or salinity (see Lorrain et al., 2005 for a review). However, due to the lack of Sr/Ca-SST correlation (Figs. 11, 12) and no apparent ontogenetic trends (Fig. 7), temperature and metabolism do not appear to be controlling the Sr/Ca ratios in *N. deaurata* and *P. vulgata*. Unfortunately, the mechanism of Sr^{2+} incorporation into the shell is still not well understood and is likely controlled by multiple mechanisms. It is likely that Sr/Ca ratios are primarily under biological control, although further research is needed to assess how biology affects the process of Sr^{2+} incorporation from the water column, through the body, and ultimately into the shell (Gillikin et al., 2005). When the Sr/Ca partition coefficient deviates significantly from 1, Gillikin et al. (2005) suggest controls on Sr/Ca ratios within the shell are controlled by biological processes. The analysis of water Sr/Ca ratios may shed light on the degree of biological controls on shell Sr/Ca ratios.

Recently, Li^+ has gained attention as an element that may be a useful paleotemperature proxy in biological carbonates (Delaney et al., 1985; Hall and Chan, 2004; Marriott et al., 2004; Hathorne and James, 2006; Thébault et al., 2009; Thébault and Chauvaud, 2013). The Li/Ca ratios from this study are comparable to values reported for *Pecten maximus* ranging from ~0.01 to 0.100 mmol/mol (Thébault and Chauvaud, 2013). Modern and archaeological Li/Ca ratios in *N. deaurata* from Tierra del Fuego are comparable, generally ranging from 0.03 to 0.06 mmol/mol (Fig. 8A-D). Likewise, inter-individual variation was low in *P. vulgata* from the UK. This finding suggests that shell Li/Ca ratios are under environmental control; however, seasonal fluctuations in shell Li/Ca ratios are difficult to distinguish (Fig. 8). While previous studies suggest that higher SST increases the amount of Li^+ incorporated into *Cerastoderma edule* (Füllenbach et al., 2015), there is no evidence of this effect in *N. deaurata* or *P. vulgata*. For *P. vulgata*, there is a decrease in Li/Ca with ontogeny in ORK LT5 ($R^2 = 0.68$) and NL 0601-3 ($R^2 = 0.31$). Therefore, changes in metabolism and/or growth rate with ontogeny may be influencing Li^+ incorporation into the shell.

Archaeological and modern *N. deaurata* shells show similar elemental ratio-SST relationships (Fig. 12). This may suggest that while the controls on limpet shell elemental ratios (Mg/Ca, Sr/Ca, Li/Ca, Sr/Li, Li/Mg) are not temperature-dependent, they likely have not changed significantly over time.

5. Conclusion

Elemental ratios (e.g., Mg/Ca, Sr/Ca, Li/Ca, Sr/Li, Li/Mg) are not reliable recorders of paleotemperature in patelloid limpets. Although our results exhibit the breakdown in the Mg/Ca-SST relationship presented by Ferguson et al. (2011), they are consistent with the assessment made by Foster and Chacko (1995) that the incorporation of Mg in *Patella vulgata* are insensitive to changes in environmental conditions. While the cause of enigmatic breakdowns in Mg/Ca-SST in limpet shells is unknown, it may be the result of localized differences in habitat between limpets.

Sr/Ca ratios varied among individuals growing at the same location, which suggests that Sr/Ca ratios are not likely dominated by environmental controls. The lack of Sr/Ca-SST correlation and no apparent ontogenetic trends suggest that temperature and metabolism do not appear to be controlling the Sr/Ca ratios in *N. deaurata* and *P. vulgata*. Conversely, inter-individual variations in Li/Ca were low in *P. vulgata* from the UK suggesting that shell Li/Ca ratios may be under environmental control, although they lack clear seasonal fluctuations in shell Li/Ca ratios as would be expected for a SST proxy (Fig. 8). For *P. vulgata*, there is a decrease in Li/Ca with ontogeny in both ORK LT5 ($R^2 = 0.68$) and NL 0601-3 ($R^2 = 0.31$). Therefore, changes in metabolism and/or growth rate may influence Li^+ incorporation into the shell. Further research is necessary to establish the controls on elemental ratios in limpet shells.

Considering the variability in elemental profiles between individuals growing in the same location and the lack of any ontogenic trends or any other discernable trends, we suggest that elemental incorporation into limpet shells are governed by a plethora of factors resulting in large inter-individual differences. However, we were able to rule out growth-rate and other ontogenic effects as have been observed in bivalves (e.g., Purton et al., 1999; Gillikin et al., 2005; Lorrain et al., 2005). Similar to bivalves (Poulain et al., 2015), limpet shell elemental ratios seem to be under strong physiological control.

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