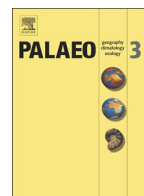




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## Assessing elemental ratios as a paleotemperature proxy in the calcite shells of patelloid limpets

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## ABSTRACT

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  $\delta^{18}\text{O}_{\text{shell}}$  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  $\delta^{13}\text{C}$  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 ( $^{18}\text{O}/^{16}\text{O}$ ) 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  $\delta^{18}\text{O}$  values and temperature,

where increases in temperature result in a decrease in carbonate  $\delta^{18}\text{O}$  values. Such studies depend on the ability to constrain the  $\delta^{18}\text{O}$  value of seawater ( $\delta^{18}\text{O}_{\text{water}}$ ) for accurate paleotemperature calculations. Freshwater inputs to coastal environments influence  $\delta^{18}\text{O}_{\text{water}}$  values making it difficult to constrain  $\delta^{18}\text{O}_{\text{water}}$  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  $\delta^{18}\text{O}$  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

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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  $\delta^{18}\text{O}$ -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  $\delta^{18}\text{O}$  values record the full range of SST in the Mediterranean, although shells without a clear  $\delta^{18}\text{O}$ -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  $\delta^{18}\text{O}$ -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  $\delta^{18}\text{O}$  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  $\delta^{18}\text{O}$  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).

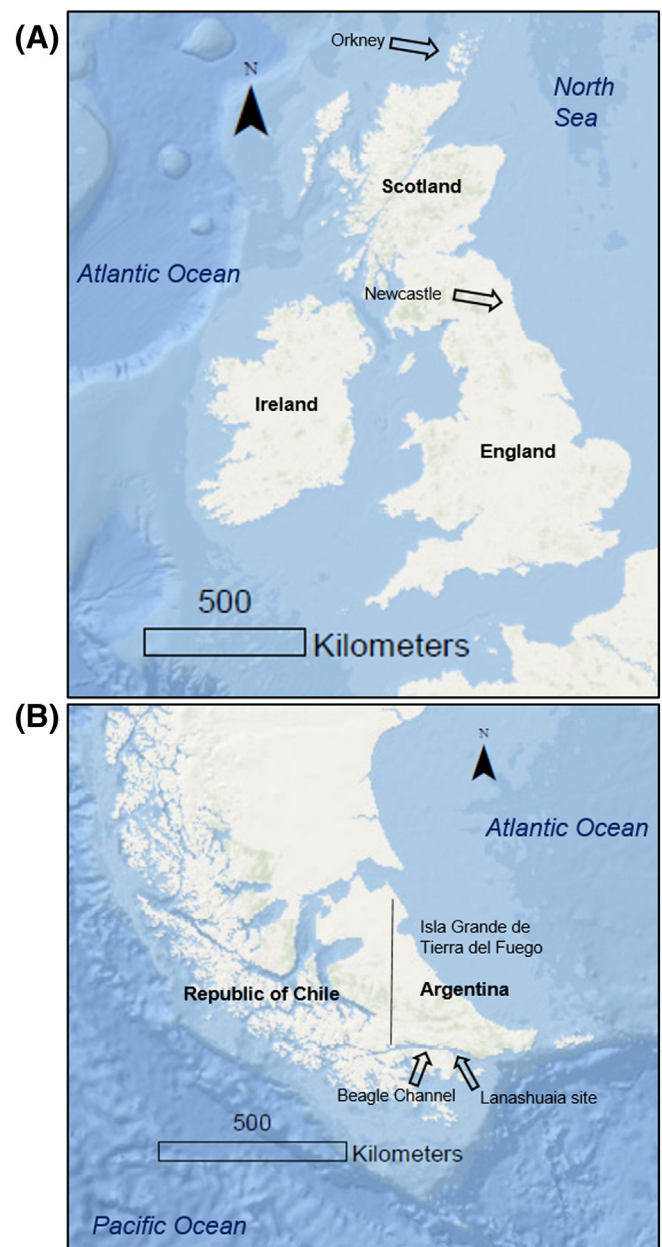
Li/Ca ratios in calcite foraminifera have been investigated as a proxy for temperature, calcification rate, and carbonate ion concentration (Delaney et al., 1985; Hall and Chan, 2004; Marriott et al., 2004; Hathorne and James, 2006). Although Li/Ca ratios increase in planktonic and benthic foraminiferal 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  $\delta^{18}\text{O}_{\text{shell}}$  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.

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