

Calibration of the oxygen isotope ratios of the gastropods *Patella candei crenata* and *Phorcus atratus* as high-resolution paleothermometers from the subtropical eastern Atlantic Ocean

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ABSTRACT

The oxygen isotope composition ($\delta^{18}\text{O}$) recorded in shells of the gastropods *Patella candei crenata* and *Phorcus atratus* from the Canary Islands (27–29°N) potentially provide invaluable high-resolution paleoclimatic data. However, because these two species have never been studied isotopically, it is necessary to calibrate and validate this approach by using live-collected specimens that can be compared to present-day climate data. For *P. candei crenata*, live organisms were collected at 15-day intervals for nearly one year (between 2011 and 2012) from the rocky-intertidal coast of SE Tenerife along with sea surface temperatures (SST) and seawater $\delta^{18}\text{O}$ values. The $\delta^{18}\text{O}$ values of the last growth episode along the shell growth margin, representing the conditions when organisms were collected, illustrate that *P. candei crenata* $\delta^{18}\text{O}$ values were $1.3 \pm 0.2\text{‰}$ higher than expected values from isotopic equilibrium. This finding resulted in estimated SST $5.7 \pm 0.6\text{ °C}$ lower than observed values. This offset or “vital effect” is uniform and predictable, and therefore can be corrected by subtracting 1.3‰ from the measured shell $\delta^{18}\text{O}$ value. Adjusted temperatures from the shell coincided with observed SST in the study area. Therefore, *Patella candei crenata* shells are reliable repositories of SST data, in agreement with other species of *Patella* from higher latitudes. For *Phorcus atratus*, a live specimen was analyzed isotopically along shell-growth direction. The intrashell $\delta^{18}\text{O}$ values showed the entire range of measured SST in the region without an apparent “vital effect”, in correspondence with other *Phorcus* species from the Mediterranean. Both *Patella candei crenata* and *Phorcus atratus* are common components of archaeological and Pleistocene-Holocene paleontological sites across the Canary Archipelago. This study suggests that well-preserved shells of these two taxa retrieved from ancient settings have the capacity to serve as excellent high-resolution paleotemperature archives for the tropical/subtropical eastern Atlantic region.

1. Introduction

Numerous paleoclimatic proxies have been intensively developed, calibrated and validated over the past several decades for the marine (e.g., sea sediment cores, corals) and terrestrial (e.g., ice cores, lake cores, tree rings, speleothems) realms. Most of these proxies, however, track paleoclimatic information at the multi-annual, annual, or single-season temporal scale. Additionally, most of them focus on localities from mid- to high-latitude regions (Berglund et al., 1994; Biondi et al., 2001; Charles et al., 1996; Dansgaard et al., 1984; Dorale et al., 1992; Duplessy et al., 1981; Morellón et al., 2008; Oeschger et al., 1984; van der Bilt et al., 2015). Even though these and many other records have provided important information about different aspects and scales of

past climate systems, proxies that generate high-resolution data, at monthly-submonthly scale, are preferred for generating a more informed picture of ancient climate change (Dorale et al., 1992; Hallmann et al., 2009). These kinds of high-resolution paleoclimatic datasets are still rare in low-latitude regions. Sclerochronology, or the study of the physical and chemical features in accretionary hard structures (Andrus, 2011), is probably the best proxy to generate the highest resolution paleoclimate data. The majority of marine mollusc species precipitate their shells in isotopic equilibrium with the local seawater (Epstein et al., 1951; Epstein et al., 1953; Grossman and Ku, 1986; Jones et al., 1989; Jones et al., 1984). Thus, the oxygen isotope value ($\delta^{18}\text{O}$) of these accretionary carbonate layers can be used to infer seawater $\delta^{18}\text{O}$ signatures and sea surface temperature (SST) at the time of shell

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formation, assuming one of those variables can be held constant (Epstein et al., 1951; Epstein et al., 1953; Friedman and O'Neil, 1977; Grossman and Ku, 1986; Tarutani et al., 1969). This approach has been intensively applied since the 1950s at mid-latitude regions of the Northern Hemisphere (~30–60°N), especially using bivalves (Helama and Hood, 2011; Schöne and Fiebig, 2009; Wang et al., 2013) and, to a lesser degree, gastropods (Abell, 1985; Curtis et al., 1996). To our knowledge, high-resolution paleoclimatic datasets using marine mollusc shells around the tropical/subtropical eastern Atlantic Ocean have not been generated in paleoclimatic studies.

A large portion of the world's population lives in subtropical to tropical coastal regions, and yet there is a distinct lack of study regarding how seasonality, climate, and SST affect those areas. Climate fluctuations can influence geopolitics, population migration, resource acquisition, economics, and ecosystems, which have huge impacts on humans and non-humans alike. Macaronesia and North Africa are part of the Mediterranean biodiversity super-hotspot (Myers et al., 2000) and are both particularly understudied regions with respect to high-resolution (seasonal-submonthly) climate reconstructions. Therefore, it would benefit from a high-resolution climate map to aid in the production of comprehensive conservation and human development plans that respond to climate's pivotal role in generating ecological, geopolitical, economic, and social change.

The rocky intertidal, fast-growing gastropods of the genus *Patella* Linnaeus 1758 have been investigated isotopically as paleotemperature archives at mid- to high-latitude regions, ranging from the Loosen Islands, Norway to Scotland, Northern Spain, and Gibraltar (between ~70° and ~36°N) (Fenger et al., 2007; Ferguson et al., 2011; Surge et al., 2013; Wang et al., 2012), as well as South Africa (Shackleton, 1973; Cohen and Tyson, 1995). Species of this genus appear to be ideal candidates for seasonal paleoclimatic studies because many of them grow rapidly and continuously year-round (Fenger et al., 2007). In addition, species of *Phorcus* Risso, 1826 have been validated as credible paleothermometers in the Mediterranean area (Colonese et al., 2011; Colonese et al., 2009; Mannino et al., 2007; Mannino et al., 2008; Prendergast et al., 2013). However, none of these studies have so far targeted tropical/subtropical (< 30°N) regions. The Canary Islands are a subtropical (27–29°N) volcanic and oceanic Spanish archipelago rich in the “Black Limpet”, *Patella candei crenata* d'Orbigny 1840 and the “Topshell”, *Phorcus atratus* Wood, 1828 across modern ecosystems and archaeological/paleontological records (Mesa-Hernández, 2007; Navarro et al., 2005). These archaeological and paleontological shells may function as a powerful tropical/subtropical high-resolution paleoclimatic archive. However, before ancient shells can be used for paleoclimate reconstructions, modern specimens must be isotopically analyzed and compared to present-day climate data and therefore, quantitatively assess the utility of these gastropods as a viable repository of climate information at the local scale. This study calibrates and validates two abundant rocky intertidal species from the Canary Islands, *Patella candei crenata* and *Phorcus atratus*, as high-resolution paleothermometers using live-collected specimens and relevant climatic parameters. The results are compared to other studies at higher latitudes and illustrate how these two proxies can be used for future paleoclimatic inferences in the region.

2. Materials and methods

2.1. Geographical, climatic and geological setting

The Canary Islands are a subtropical Spanish archipelago located in the Atlantic Ocean, ~90 km from the Moroccan coastline, between 27°37' and 29°25' N and 13°20' and 18°10' W per the WSG84 coordinate system (Fig. 1A). The climate is characterized by low-moderate rainfall (200–700 mm/yr) and mild air temperatures (18–24 °C) throughout the year (Herrera et al., 2001). These islands are mountainous and exhibit a large variety of climate zones due to a confluence of factors including

elevation and geospatial orientation on the island (Bueno and Carta, 2006). They are also surrounded by the Canary Current, a cold, south-moving derivative of the Gulf Stream, which maintains the dry and mild climate (Herrera et al., 2001). The annual oscillation of the Inter-tropical Convergence Zone (ITCZ) affects the islands, bringing Saharan dust in the summer months—May through November—and keeping precipitation low (Izquierdo et al., 2011). The islands are volcanic in origin, with the oldest subaerial rocks dating to ~23 Ma from the easternmost Fuerteventura island (van den Bogaard, 2013).

The island targeted in this study, Tenerife (Fig. 1B), is the largest island of the archipelago by both elevation (3718 m) and land area (2030 km²) (Ancochea et al., 2003; Herrera et al., 2001). All samples in this study were collected from the port of the city Puertito de Güímar, located on the southeast coast of the island (28°17'41" N, 16°22'26" W), ~20 km southwest of the island capital of Santa Cruz (Fig. 1B). Coarse, basaltic, black sand beaches and boulders that give way to a rocky intertidal region characterize the coastline of Puertito de Güímar.

2.2. Ecology and morphology of *Patella candei crenata*

Patellid gastropods (Gastropoda: Patellidae) are slow moving to stationary browsers that inhabit the rocky intertidal to infratidal region, stretching geographically along most coastlines from Europe and Africa to New Zealand (Branch, 1972). *Patella* feed on algae, lichens, and diatoms, and accordingly, are strongly zoned vertically and geographically to reduce competition for food (Branch, 1972). When stationary, *Patella* resides on a home base scar, to which the limpet will return after browsing for food (Branch, 1972). This stationary behavior makes these organisms excellent candidates for isotope sclerochronological analyses to infer climatic profiles from a discreet location (Fenger et al., 2007).

The genus *Patella* is characterized by a concave/cap-shaped, elliptical shell with a subcentrally located apex and iridescent interior (Fig. 1E). The external surface of the shell is rarely smooth and instead usually characterized by radiating lirae (ridges) and concentric growth rings from the apex to the growth margin (Fig. 1D) (Wang et al., 2012). *Patella* shells precipitate calcite at their shell margins. Much of the shell is calcite but crossed lamellar aragonite layers are present near the myostracum where the organism attaches to the shell (Surge et al., 2013; Fenger et al., 2007; MacClintock, 1967).

In warm temperate zones, such as along the Iberian Peninsula, the shells have been observed to slow their growth rates in the summer (warmer) and winter (colder) months, whereas in higher latitudes of the cold temperate zone growth rates decline during the winter (Gutiérrez-Zugasti et al., 2017; Wang et al., 2012). Fenger et al. (2007) and Surge et al. (2013) report that SST is the major control producing prominent annual growth checks in *Patella* shells.

Several *Patella* species inhabit in the Canary Islands, including *P. candei crenata*, *P. rustica*, *P. aspera*, *P. candei* and *P. piperata* (Bergasa et al., 2007; Côte-Real et al., 1996; Navarro et al., 2005). Of these, *P. candei crenata*, *P. rustica*, *P. piperata*, and *P. aspera* are abundant in the present intertidal region of all seven islands of the archipelago (Navarro et al., 2005; Ramírez et al., 2008). *Patella candei* has been shellfished to local extinction in all regions of the archipelago except near the island of Fuerteventura (Navarro et al., 2005). Navarro et al. (2005) documented *Patella* distributions across the entire archipelago and found that *P. rustica* was the most prevalent species across the archipelago, followed by *P. candei crenata* and then *P. aspera*. *Patella candei crenata* was found at 44% of the 25 field sites investigated by Navarro et al. (2005). Of these three abundant patellid species throughout the Canaries, *P. candei crenata* is the largest, with an average size of 25.3–42.3 mm along the axis of maximum growth, compared to *P. rustica* (16.6–20.8 mm) and *P. aspera* (18.1–30.2 mm) (Navarro et al., 2005; Ramírez et al., 2008). The present study focuses on the largest species, *P. candei crenata*, a species that dominates most archaeological shell middens across the archipelago and has not been previously

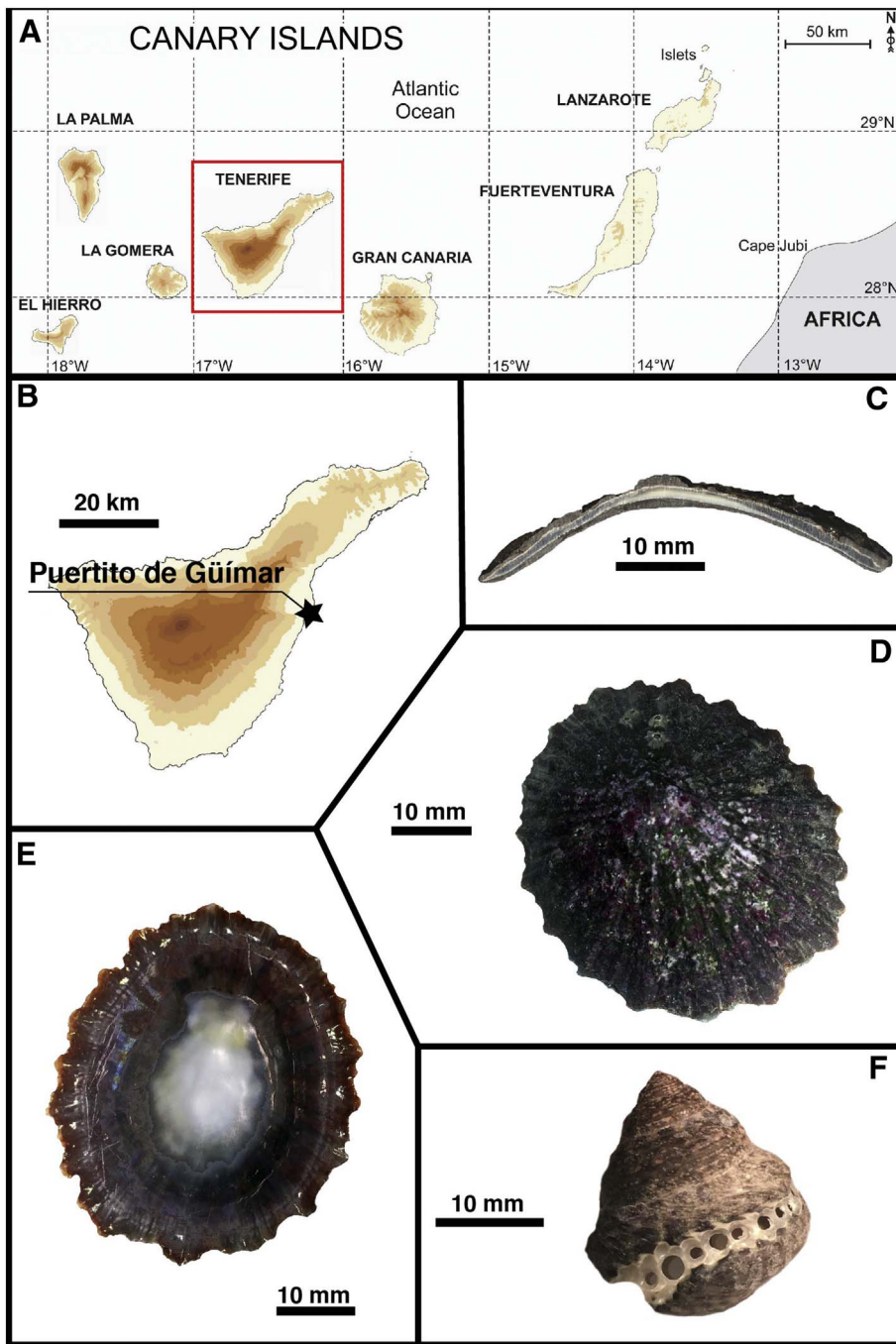


Fig. 1. A) Geographical setting of the Canary Archipelago near the coast of Morocco, NW Africa. B) Geographical location of the field site at Puertito de Güímar. C) Bisected *Patella candei crenata* shell to show the layered calcium carbonates—Calcite (dark brown/grey) and Aragonite (white). D) Dorsal view of *Patella candei crenata*. E) Ventral view of *Patella candei crenata*. F) *Phorcus atratus* with the first several samples removed to illustrate ~1 mm sample methodology. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

analyzed isotopically.

Patella candei crenata has undergone several taxonomic name changes over time, and other synonymized names include *P. chlorostica* Gmelin, 1791, *P. crenata* Gmelin, 1791, *P. tenuis* Gmelin, 1791, *P. gomesii* Drouet, and 1858, *P. teneriffae* Mabilbe, 1888. In recent years, this organism has been synonymized under the *P. candei* name with two subspecies, *P. candei crenata* and *P. candei candei*. However, significant debate still exists over whether or not the morphological differences between the subspecies merit distinct classifications. In this paper, we use *Patella candei crenata* following Riera et al. (2016).

2.3. Ecology and morphology of *Phorcus atratus*

Phorcus Risso, 1826, formerly known as *Osilinus*, is a genus of marine gastropods that commonly inhabit the rocky intertidal to

infratidal region of coastlines in the Mediterranean basin, Persian Gulf, and northeastern Atlantic stretching as far south as Senegal (Donald et al., 2012; Prendergast et al., 2013). They are prosobranch gastropods that use their radula to “brush off” and consume algal films in the rocky intertidal zone (Granado and Caballero, 2001; Steneck and Watling, 1982). *Phorcus* is relatively stationary, with a strong foot to keep it in place even in strong currents. Their shells are dominantly composed of aragonite with an outer calcite layer coating the shell. They form by precipitating new growth onto the aperture shell lip. Regional studies in the Mediterranean have shown that *Phorcus* grow continuously through the year tracking the full range of SST (Colonese et al., 2011; Colonese et al., 2009; Mannino et al., 2007; Mannino et al., 2008; Prendergast et al., 2013).

Phorcus atratus (Wood, 1828) has an imperforate conical shell with eroded apical whorls. The shell looks like a spinning top; hence, the

common name “Topshell”. The coloration is purple-black with several spiraling rows of white spots or sometimes zigzag white stripes and a base that is generally stripped with white (Fig. 1F). Adult topshells have 5–6 whorls, with 2 carinae that give the ultimate whorl a squared-off appearance. The central columella is short (17–23 cm height), and the aperture is oblique. The total diameter ranges between 16 and 19 mm (Tryon, 1889). The present study focuses on *P. atratus*, a species that is present and often abundant in archaeological shell middens across the archipelago and has never investigated isotopically.

3. Field sampling methods

3.1. *Patella candei crenata*

Fifty-one specimens of *P. candei crenata* were collected every 15th day for 17 consecutive collection dates, between July 2011 and April 2012. These specimens were alive at the time of their harvest, therefore, their collection day corresponds with date of death. The body tissue was removed from the shell, and the shells were mechanically cleaned with distilled water and soft brushes to remove detrital contaminants.

Additionally, sea surface water samples and in-situ SST were recorded at the time of limpet collection. Water samples were collected in plastic 12 ml vials, immediately sealed, and preserved in a refrigerator (~4 °C) to prevent evaporation until laboratory analysis. SST was measured using an aquatic digital thermometer with a remote probe having an accuracy of ~0.5 °C for temperatures between (–10° to 50 °C).

3.2. *Phorcus atratus*

Although we planned to collect specimens of *P. atratus* every 15th day, as for *P. candei crenata* above, we rarely found them during field sampling times, probably due to the intensive exploitation of the species by today’s Canary Island inhabitants. The few specimens encountered were collected alive and sacrificed the same day; therefore, the day of collection also corresponds with date of death. One shell was selected for intra-shell isotopic analysis along shell growth direction.

4. Laboratory analytical methods

4.1. *Patella candei crenata*

A Dremel® 4000 Dental Drill was used to collect carbonate powder from the last growth line of three shells per collection date. Care was taken to sample the growing edge representing the most recent growth increment, and broken edges were avoided.

The carbonate powder samples were transferred into a 6 ml exetainer™ for δ¹⁸O analysis at the University of Kentucky using the Gasbench II™ peripheral device attached to a Finnigan Delta Plus XL continuous flow isotope ratio mass spectrometer (CF-IRMS). Samples were digested at 25 °C over 24 h using anhydrous phosphoric acid according to established procedures. NBS 19 international standard (δ¹⁸O = –2.2‰ VPDB) was used to calibrate analyses and assess analytical and experimental precision. Analytical uncertainty was ± 0.1‰ based on the repeated measurement of standards and samples throughout a run.

SST was calculated from shell δ¹⁸O values using the calcite equilibrium equation for calcite and water from Friedman and O’Neil (1977) modified from Tarutani et al. (1969):

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

where α is the fractionation factor between calcite and water, and T is temperature in Kelvin. The relationship between α and δ is:

$$\alpha = (\delta_{\text{calcite}} + 1000)/(\delta_{\text{water}} + 1000) \quad (2)$$

where δ is presented in VSMOW (Vienna Standard Mean Ocean Water)

(Fenger et al., 2007). Conversion between VPDB (Vienna Pee Dee Belemnite) and VSMOW is conducted using the equation reported by Coplen et al. (1983) and Gonfiantini et al. (1995):

$$\delta^{18}\text{O}_{(\text{VSMOW})} = (\delta^{18}\text{O}_{(\text{VPDB})} - 30.91)/1.03091 \quad (3)$$

The magnitude of seasonal variation of seawater δ¹⁸O values in the Canary Islands was determined by measuring local water samples collected at the time of shell collection. Samples were analyzed using a Picarro device at the University of Kentucky. Analytical uncertainty was ± 0.1‰ based on the repeated measurement of international standards VSMOW and SLAP (Standard Light Antarctic Precipitation) throughout the run. Analytical uncertainty corresponds to a possible error of 0.5 °C per the equation by Friedman and O’Neil (1977).

4.2. *Phorcus atratus*

After mechanical cleaning, the outer calcitic layer of the selected *P. atratus* shell was removed in order to access the aragonitic layers below. Sample growth lines are easier to determine in the aragonitic layer, which is why this is the section of the shell chosen for isotopic analysis (Colonese et al., 2009; Prendergast et al., 2013). The last deposited growth increment (near the shell lip) was drilled first using a Dremel® 4000 handheld dental drill. A series of points every ~1 mm were drilled along the direction of whorl, perpendicular to the direction of growth (Fig. 1F). A total of 41 carbonate samples were milled from these points, culminating near the protoconch. As for *P. candei crenata* above, all milled carbonate powder samples were transferred into a 6 ml exetainer™ for δ¹⁸O analysis at the University of Kentucky using the same equipment, procedures, and standard described above.

The calculated temperature from the shell δ¹⁸O values were performed using the following aragonite equilibrium equation for aragonite and water determined by Grossman and Ku (1986), with a correction by Dettman et al. (1999) to convert from VSMOW to VPDB scales:

$$T(^{\circ}\text{C}) = 20.6 - 4.34(\delta^{18}\text{O}_{\text{Aragonite}}(\text{VPDB}) - (\delta^{18}\text{O}_{\text{Water}}(\text{VSMOW}) - 0.27)) \quad (4)$$

The δ¹⁸O values of shell aragonite were not adjusted to accommodate differences in acid fractionation factors for calcite and aragonite because the paleotemperature equation used—Grossman and Ku, 1986—assumes no difference in acid fractionation factors between the calcium carbonate polymorphs (Füllenbach et al., 2015). Analytical uncertainty is 0.1‰, which corresponds to a possible error of 0.4 °C per the equation by Grossman and Ku (1986) (Prendergast et al., 2016).

5. Results

5.1. Present-day seasonal climate

The temperature of the water collected in situ between 20 July 2011 and 15 March 2012 ranged from 23.0 °C to 18.1 °C, with an average value of 21.0 ± 1.7 °C (n = 17) (Fig. 2A; Table 1). In contrast, there was almost no variation in the δ¹⁸O values of the coastal seawater throughout the year (Fig. 2B; Table 1). Measured seawater δ¹⁸O values ranged from 1.0‰ in November 2011 to 0.6‰ in March 2012, with an average of 0.8 ± 0.1‰ (n = 17). Measured seawater samples illustrate that the δ¹⁸O values of the water does not vary seasonally (Fig. 2B).

5.2. Last growth-episode δ¹⁸O values of *Patella candei crenata*

The δ¹⁸O values along the growing edge of *P. candei crenata* shells varied through seasons following a sinusoidal trend (Fig. 3A). The lowest value was 0.1‰ for a limpet collected on September 15, 2011. The highest value was 1.9‰ from an individual gathered on March 3,

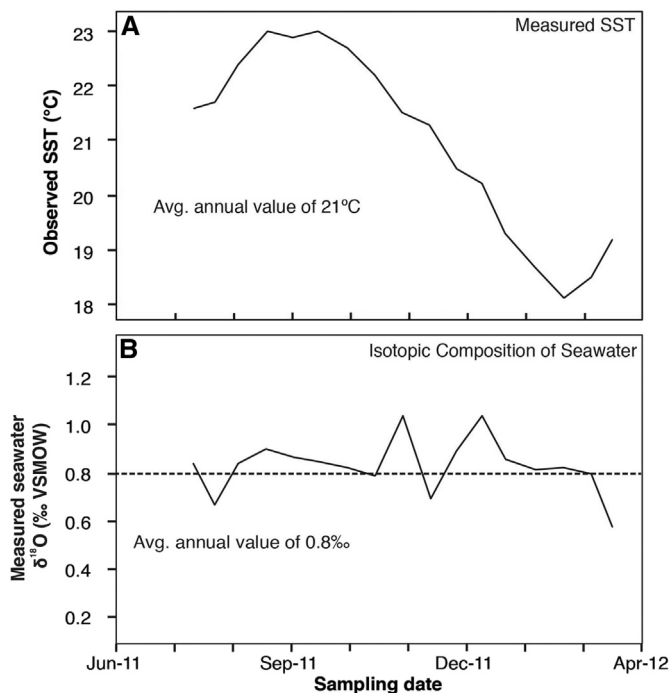


Fig. 2. A) Local measured sea surface temperatures (SST) of Puertito de Güimar collected with a digital thermometer every 15 days between June 2011 and March 2012. B) Local seawater $\delta^{18}\text{O}$ values (in VSMOW scale) from samples collected every 15 days between June 2011 and March 2012.

Table 1

Observed sea surface temperatures (SST) and measured seawater $\delta^{18}\text{O}$ values for each sampling date ($n = 17$) between June 2011 and March 2012.

Sampling date	Measured SST ($^{\circ}\text{C}$)	Seawater $\delta^{18}\text{O}$ ‰ (VSMOW)
20-Jul-11	21.6	0.8
1-Aug-11	21.7	0.7
15-Aug-11	22.4	0.8
31-Aug-11	23.0	0.9
15-Sep-11	22.9	0.9
29-Sep-11	23.0	0.9
16-Oct-11	22.7	0.8
1-Nov-11	22.2	0.8
16-Nov-11	21.5	1.0
2-Dec-11	21.3	0.7
17-Dec-11	20.5	0.9
1-Jan-12	20.2	1.0
14-Jan-12	19.3	0.9
31-Jan-12	18.7	0.8
16-Feb-12	18.1	0.8
3-Mar-12	18.5	0.8
15-Mar-12	19.2	0.6

2012 (Table 2). The oxygen isotope offset between shell and seawater $\delta^{18}\text{O}$ values ($\delta^{18}\text{O}_{\text{shell-seawater}}$) negatively correlates with instrumentally observed SST ($R^2 = 0.91$), with a larger isotopic offset during cooler seasons (Fig. 3B), as observed in other mollusc studies (Epstein et al., 1953).

5.3. Intrashell $\delta^{18}\text{O}$ values of *Phorcus atratus*

Intrashell $\delta^{18}\text{O}$ values of the live-collected *Phorcus atratus*, ranging from the shell margin to near the apex showed a quasi-sinusoidal trend (Fig. 4A). The lowest value was 0.5‰ at 28 mm from the lip, and the highest value was 1.7‰ at 16 mm from the lip (Table 3).

The calculated SST from the intrashell $\delta^{18}\text{O}$ values of *Phorcus atratus* also follow a quasi-sinusoidal trend, with a maximum temperature of 22.9 $^{\circ}\text{C}$ at 25 mm from the shell lip and a minimum temperature of

17.9 $^{\circ}\text{C}$ at a distance of 16 mm (Fig. 4B). The lowest temperature value corresponds to the maximum $\delta^{18}\text{O}$ value of the shell. This quasi-sinusoidal trend in both the $\delta^{18}\text{O}$ and the calculated SSTs shows a full year of SST variability and therefore, relatively continuous growth across all seasons. Each consecutive millimeter from the shell margin, therefore, represents approximately 1/40th of a year (~ 9 days), showing that this intrashell sampling method provides at least fortnightly (~ 14 day) resolution with which to study SST variability.

6. Discussion

6.1. Growing edge $\delta^{18}\text{O}$ values of *Patella candei crenata*

The shell-edge $\delta^{18}\text{O}$ values of *P. candei crenata* follow a predictable sinusoidal pattern and are primarily influenced by seasonal variations in SST. However, an offset is detected when measured shell-edge $\delta^{18}\text{O}$ values are compared to calculated $\delta^{18}\text{O}$ values assuming isotopic equilibrium (Fig. 3C; Table 2). The observed offset ranges from $+1.1 \pm 0.1\text{‰}$ to $+1.7 \pm 0.1\text{‰}$, with an average offset of $+1.3 \pm 0.1\text{‰}$ (Table 2). Calculated SST from the shell are therefore 5.7 ± 0.6 $^{\circ}\text{C}$ cooler than measured SST (Fig. 3D). A similar offset in magnitude and direction has been observed in other *Patella* species (Cohen and Tyson, 1995; Fenger et al., 2007; Ferguson et al., 2011; Shackleton, 1973). This offset from isotopic equilibrium between measured and expected values is best explained by a vital effect, and the observed vital effect is consistent across all shells throughout the year. A vital effect can be defined as any biochemical or metabolic process that results in a deviation of the stable isotope ratios from expected values at isotopic equilibrium (Lowenstein and Epstein, 1954; Wefer and Berger, 1991). The vital effect phenomenon is the topic of ongoing research, and many different hypotheses have been put forth to explain this process (Fenger et al., 2007).

Carbonate precipitation in disequilibrium may cause isotopic offsets in mollusc species (Wefer and Berger, 1991; Wefer and Killingley, 1980). In molluscs, shell precipitation is believed to occur in the space between the mantle and the shell, known as the extrapallial space (EPS). Oxygen and carbon atoms are likely brought into the EPS through CO_2 diffusion through the mantle cavity or through HCO_3^- and CO_3^{2-} undergoing active transport across the epithelium of the mantle (Wheeler, 1992). Ongoing research on the biomineralization process has illuminated many complex and interrelated processes at work in the creation of molluscan shell material. Some molluscs seem to construct their shells using a hydrophobic silk gel, a very acidic aspartic acid that is rich in protein, and is initiated during an amorphous precursor phase from which biomineral crystals form (Addadi et al., 2006). Different molluscs precipitate their shells using a variety of mechanisms that change from organism to organism, and sometimes even change throughout the life cycle of one organism. In this study, we are focusing on shells that exhibit indeterminate growth, and therefore continue adding shell material to the leading edge/shell margin as well as thickening over time.

In shells that precipitate through CO_2 diffusion, kinetic fractionation can occur during the diffusion process, preferentially incorporating the lighter isotopes in the biomineralization process, generally resulting in a lower $\delta^{18}\text{O}$ value relative to the environment. But in the case of *P. candei crenata*, this offset is higher (i.e., more positive) relative to expected values, suggesting the vital effect is unlikely to be initiated in the biomineralization process, and therefore we exclude kinetic fractionation as a cause for the observed vital effect. Some other proposed causes of higher shell $\delta^{18}\text{O}$ values relative to expected values include: (1) metabolic isotope effects in which the biomineralization process utilizes respired CO_2 ; (2) shell deposition during changes in the pH of the ambient seawater (McConnaughey, 1989a, 1989b); (3) precipitation of the shell during evaporative conditions (Schifano and Censi, 1983); or (4) an undetermined internal process of ^{16}O transport out of the calcification process (Land et al., 1977). In general, however, the

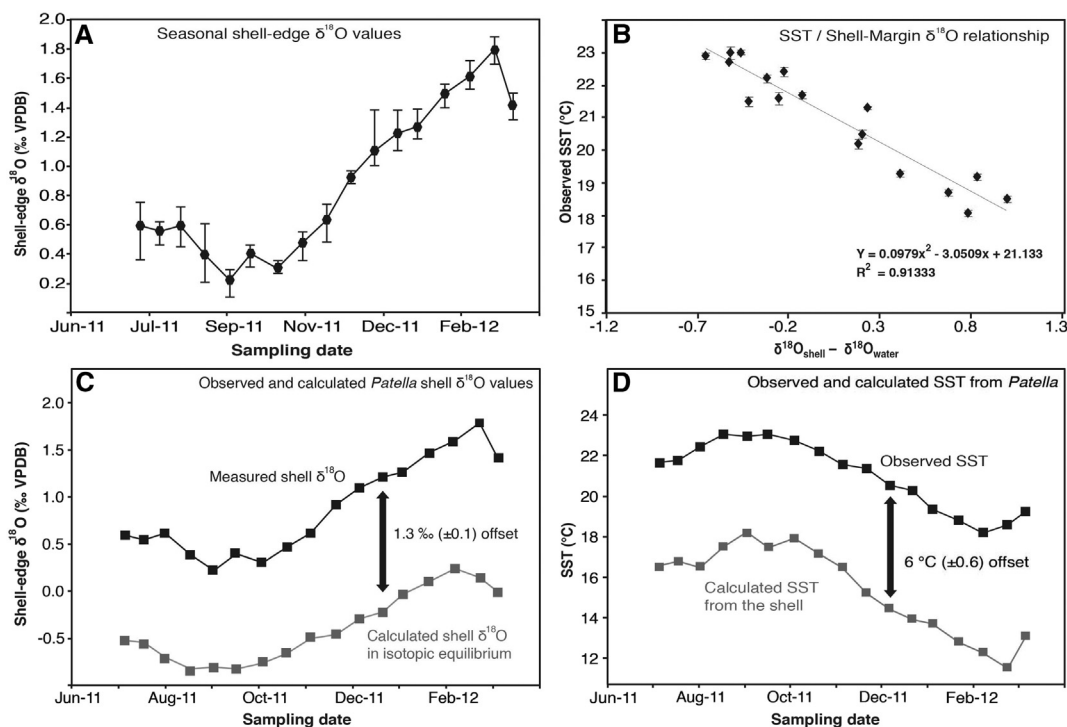


Fig. 3. A) Measured shell-margin $\delta^{18}\text{O}$ values of *Patella candei crenata* collected 17 times between June 2011 and March 2012 at Puerto de Güímar, Tenerife Island. Dots represent the average $\delta^{18}\text{O}$ value from three different shells collected the same date while whiskers denote the range of values. B) Observed SST plotted against the isotopic offset between shell and seawater $\delta^{18}\text{O}$ values. Dots depict the average value of three *Patella* shells collected the same date while whiskers represent 1-sigma standard deviation. C) Comparison of measured shell $\delta^{18}\text{O}$ values with expected shell $\delta^{18}\text{O}$ values assuming isotopic equilibrium. D) Comparison of observed SST with calculated SST from *Patella* shells.

Table 2

Calculated sea surface temperatures (SST) from *Patella candei crenata* shell-margin $\delta^{18}\text{O}$ values.

Sampling date	Average shell margin $\delta^{18}\text{O}$ ‰ (VPDB) (3 shells/date)	SD	Corrected shell margin $\delta^{18}\text{O}$ (– 1.3‰)	Calculated SST (°C)
20-Jul-11	0.6	0.2	– 0.7	22.3
1-Aug-11	0.6	0.1	– 0.7	22.5
15-Aug-11	0.6	0.1	– 0.7	22.2
31-Aug-11	0.4	0.2	– 0.9	23.3
15-Sep-11	0.2	0.1	– 1.1	24.1
29-Sep-11	0.4	0.1	– 0.9	23.2
16-Oct-11	0.3	0.0	– 1.0	23.7
1-Nov-11	0.5	0.1	– 0.8	22.9
16-Nov-11	0.6	0.1	– 0.7	22.2
2-Dec-11	0.9	0.0	– 0.4	20.8
17-Dec-11	1.1	0.1	– 0.2	20.0
1-Jan-12	1.2	0.1	– 0.1	19.4
14-Jan-12	1.3	0.1	0.0	19.2
31-Jan-12	1.5	0.1	0.2	18.2
16-Feb-12	1.6	0.1	0.3	17.7
3-Mar-12	1.8	0.1	0.5	16.9
15-Mar-12	1.4	0.1	0.1	18.6

understanding of the specific mechanisms that result in the ^{18}O -enrichment of biomineralized calcite in *P. candei crenata* are not well understood and warrant additional study.

The first hypothesis, utilization of respired CO_2 in the biomineralization process, is not supported by the data because previous studies of other calcareous organisms note that this would cause a depletion, not enrichment, of ^{18}O , which is not observed in our study (Fenger et al., 2007; McCrea, 1950; Spero and Lea, 1996; Swart, 1983). The second hypothesis, pH changes in the ambient seawater, is also not supported by the data as most studies involving pH-related changes also observe depletion of the target isotope, not enrichments

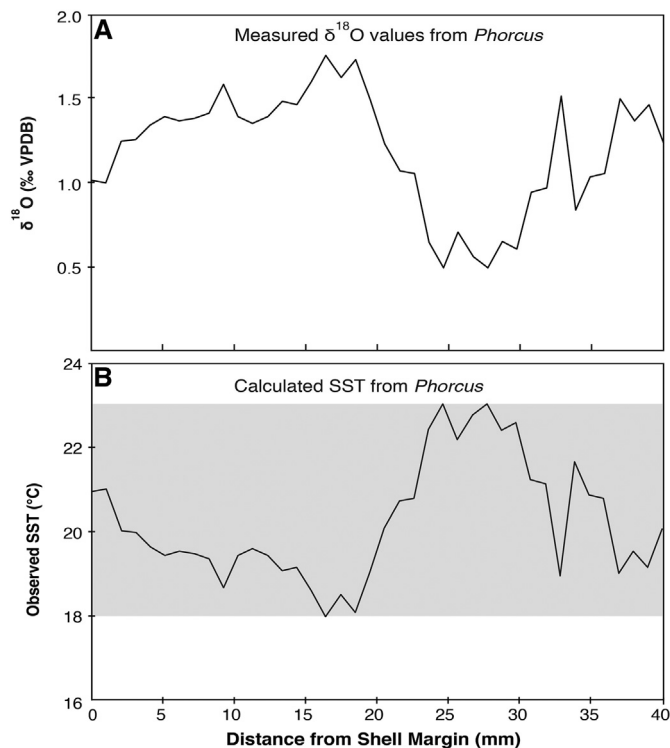


Fig. 4. A) Shell $\delta^{18}\text{O}$ values from carbonate aliquots taken every ~ 1 mm from the growth margin to near the apex of *Phorcus atratus*. B) Calculated sea surface temperatures (SST) from *Phorcus atratus* using the equation by Grossman and Ku (1986). The grey box represents the range of temperatures observed in the Canary Islands for one year prior to the collection of the analyzed specimen.

Table 3

Intrashell samples from a live-collected *Phorcus atratus* and the calculated temperature (°C) from each sample.

Sample ID	Intra-shell $\delta^{18}\text{O}$ ‰ (VPDB)	Distance from lip (mm)	Calculated SST (°C)
Pho-lip	1.0	1	20.9
Pho-1	1.0	2	21.0
Pho-2	1.2	3	20.0
Pho-3	1.2	4	19.9
Pho-4	1.3	5	19.6
Pho-5	1.4	6	19.4
Pho-6	1.3	7	19.5
Pho-7	1.3	8	19.4
Pho-8	1.4	9	19.3
Pho-9	1.5	10	18.6
Pho-10	1.4	11	19.4
Pho-11	1.3	12	19.5
Pho-12	1.4	13	19.4
Pho-13	1.4	14	19.0
Pho-14	1.4	15	19.1
Pho-15	1.5	16	18.6
Pho-16	1.7	17	18.0
Pho-17	1.6	18	18.5
Pho-18	1.7	19	18.1
Pho-20	1.4	20	19.0
Pho-21	1.2	21	20.0
Pho-22	1.1	22	20.7
Pho-23	1.0	23	20.7
Pho-24	0.7	24	22.3
Pho-25	0.5	25	22.9
Pho-26	0.7	26	22.1
Pho-27	0.6	27	22.7
Pho-28	0.5	28	22.9
Pho-29	0.7	29	22.3
Pho-30	0.6	30	22.5
Pho-31	0.9	31	21.2
Pho-32	1.0	32	21.1
Pho-33	1.5	33	18.9
Pho-34	0.8	34	21.6
Pho-35	1.0	35	20.8
Pho-36	1.0	36	20.7
Pho-37	1.4	37	19.0
Pho-38	1.3	38	19.5
Pho-39	1.4	39	19.1
Pho-apex	1.2	40	20.0

(McConnaughey, 1989b). Additionally, there is no indication of dramatic pH shifts in the seawater during the time of shellfish collection. The third hypothesis presented above, biomineralization during evaporative conditions, primarily applies to organisms that live in microhabitats with enhanced evaporation processes, such as tide pools (Fenger et al., 2007). The *Patella candei crenata* collected for this study were collected from rocky intertidal areas without tide pools. Although desiccation of sub-aerially exposed organisms in the intertidal region during low tide could potentially affect ^{18}O in intertidal molluscs, this would likely result in a variable offset in the shell ^{18}O values as is expected that some organisms may be exposed longer than others (Fenger et al., 2007).

The fourth hypothesis above, which states that it is an internal process in which ^{16}O is transported out of the shell during the biomineralization process, is not disproven by this study, and could be tested using analysis of living organisms in laboratory conditions. This study can, however, support that the vital effect observed in *Patella candei crenata* from the Canary Islands is due to an ^{18}O enrichment occurring within the biomineralization process, but probably not related to CO_2 respiration. A possible explanation for this is enrichment of ^{18}O in the EPS, which could be tested in subsequent studies through analysis of EPS during shell-growth. This study, however, notes that the vital effect is due to an unspecified internal process, and not likely due to enrichment or depletion of ambient seawater.

The observed vital effect in *P. candei crenata* is constant year-round,

Table 4

Calculation of the degree of vital effect (i.e., offset between expected and measured shell $\delta^{18}\text{O}$ values).

Sampling date	Average shell $\delta^{18}\text{O}$ ‰ (VPDB)	Measured SST (°C)	Expected shell $\delta^{18}\text{O}$	Vital effect
20-Jul-11	0.6	21.6	-0.5	-1.1
1-Aug-11	0.6	21.7	-0.6	-1.1
15-Aug-11	0.6	22.4	-0.7	-1.3
31-Aug-11	0.4	23.0	-0.8	-1.2
15-Sep-11	0.2	22.9	-0.8	-1.0
29-Sep-11	0.4	23.0	-0.8	-1.2
16-Oct-11	0.3	22.7	-0.8	-1.1
1-Nov-11	0.5	22.2	-0.7	-1.1
16-Nov-11	0.6	21.5	-0.5	-1.1
2-Dec-11	0.9	21.3	-0.5	-1.4
17-Dec-11	1.1	20.5	-0.3	-1.4
1-Jan-12	1.2	20.2	-0.2	-1.5
14-Jan-12	1.3	19.3	0.0	-1.3
31-Jan-12	1.5	18.7	0.1	-1.4
16-Feb-12	1.6	18.1	0.2	-1.4
3-Mar-12	1.8	18.5	0.2	-1.7
15-Mar-12	1.4	19.2	0.0	-1.4

and therefore can be accounted for. If all shell $\delta^{18}\text{O}$ values are corrected by -1.3‰ , the offset between calculated and measured SSTs is $0.0 \pm 0.8\text{ °C}$ (Table 4). Because the isotopic offset is predictable and can be taken into account, *P. candei crenata* serves as a credible and consistent repository of paleotemperature data with an approximate error of $\pm 0.8\text{ °C}$. This error includes the both analytical uncertainty and variability in shell $\delta^{18}\text{O}$ values. The variation of seawater $\delta^{18}\text{O}$ is not included, as this study assumes a constant year-round $\delta^{18}\text{O}_{\text{water}}$ of 0.8‰ . If variation in seawater $\delta^{18}\text{O}$ were included, the additional variability would span an additional 1.8 °C range ($\pm 0.9\text{ °C}$), resulting in a total error of $\pm 1.7\text{ °C}$. Other studies of the genus *Patella* have reported errors of ranging from $\pm 0.4\text{ °C}$ to $\pm 2.7\text{ °C}$ (Cohen and Tyson, 1995; Gutiérrez-Zugasti et al., 2017; Prendergast et al., 2016; Surge et al., 2013; Wang et al., 2012).

The seasonal variation in shell margin $\delta^{18}\text{O}$ values correlates closely with measured year-round temperatures year-round, which supports that *P. candei crenata* grows continuously throughout the year without noticeable growth cessation. This finding contrasts with *Patella* species found at higher latitudes, most notably *P. vulgata*. In the case of *P. vulgata*, the optimal growth temperature is exceeded during winter or summer, and therefore, there is a slowdown or cessation of growth in those season as indicated by prominent annual growth checks (Fenger et al., 2007).

Because the genus *Patella* is endemic to the Atlantic Ocean, most of the studies regarding this genus have focused on Europe (Fenger et al., 2007; Ferguson et al., 2011; Surge et al., 2013) with the notable exception of archaeological studies in South Africa (Cohen and Tyson, 1995; Shackleton, 1973). In the calibration study of *Patella vulgata* collected near Newcastle-upon-Tyne, United Kingdom ($\sim 55^\circ\text{N}$), Fenger et al. (2007) reported a predictable offset of $+1.01\text{‰}$. Gutiérrez-Zugasti et al. (2017) reported an offset of $+0.38\text{‰}$ in specimens of *Patella vulgata* from northern Spain, while Ferguson et al. (2011) reported a predictable offset of $+0.72\text{‰}$ in shells of *P. rustica* and *P. caerulea* collected near Gibraltar ($\sim 36^\circ\text{N}$). This last offset value was observed as well by Prendergast and Schöne (2017) in *P. caerulea* from eight sites in the eastern Mediterranean nations of Israel, Croatia, Libya, Tunisia, Turkey and Malta. Shackleton (1973) and Cohen and Tyson (1995) reported a similar offset ($+0.7\text{‰}$) in shells of *P. tabularis* from archaeological and modern sites in South Africa. All published studies of *Patella* have shown that this genus is a credible repository of paleotemperature information; however, the positive offset from expected equilibrium values appears to be species-specific. Geographic position relative to low- and high-tide could perhaps impact vital effects, as this position changes the period during which the organism is sub-aerially

exposed at low-tide, and may result in desiccation stress induced ^{18}O enrichment. This would likely result in a variable vital effect—not observed in this study—however is a potential ongoing research study into constraining the vital effect in the Canary Islands.

Shell $\delta^{18}\text{O}$ values suggest that *P. candei crenata* grows its shell continuously throughout the year. It is possible, however, that growth rates may be slower during summers than during winters, as documented in *P. vulgata* from the warm temperate zone of the east Atlantic (Surge et al., 2013). *P. vulgata* from the northern coast of Spain exhibited increased growth in spring, while growth slowed in both summer and winter (Gutiérrez-Zugasti et al., 2017). We will test for slow-down/cessation in a future study by analyzing a high-resolution intrashell time series of *P. candei crenata* from the Canary Islands. Such a high-resolution, seasonal-scale record will also allow us to confirm lifespan estimates based on local ecological studies (Navarro et al., 2005; Ramírez et al., 2008).

6.2. Intrashell $\delta^{18}\text{O}$ values of *Phorcus atratus*

Predicted SST from intrashell $\delta^{18}\text{O}$ values of *Phorcus atratus* are within the range of measured SST in the study locale. This finding suggests that the shell carbonate is precipitated throughout the year, with no significant cessation of shell growth. In contrast to *Patella*, *Phorcus atratus* precipitates its shell in isotopic equilibrium with the local seawater with no apparent offset from equilibrium. The close correlation of calculated and instrumentally measured SSTs indicates that variations in SST should be the primary control of the seasonal variations in shell $\delta^{18}\text{O}$ values. The distribution of $\delta^{18}\text{O}$ values also shows four distinct seasons, indicating that the measured *Phorcus atratus* specimen has a life span of at least one year. The close correlation of measured (23.0–18.0 °C) and predicted temperatures from the *Phorcus* shell (22.9–17.9 °C) demonstrates that the calculated temperature range is within the boundaries of the measured SST throughout the year, and thus, this species serves as a reliable indicator of seasonal temperature variability with an instrumental error of ± 0.4 °C.

This result is consistent with other published work involving species of the same genus from the Mediterranean (Colonese et al., 2011; Colonese et al., 2009; Mannino et al., 2007; Mannino et al., 2008; Prendergast et al., 2013). The most recent study by Prendergast et al. (2013) focuses on the final growth margin of *Phorcus turbinatus*, a endemic species to the Mediterranean. Prendergast et al. (2013) documented a high correlation between measured and expected SST values from the shell margin ($R^2 > 0.9$) with no observed vital effect or offset, consistent with *P. atratus* from the Canary Islands. Mannino et al. (2007) produced a high-resolution, intrashell record of *P. turbinatus* to determine season of harvest. Their shells were collected from archaeological sites in Grotta dell'Uzzo, Sicily and recorded seasonal-scale fluctuations of SST spanning at least two years of growth. The longevity of the organism combined with the abundance in the rocky intertidal of the past and present and the lack of a vital effect all support the utility of *Phorcus* as a useful paleoclimate proxy and recorder of human collecting activity. The present study conducted in the Canary Islands expands this useful proxy archive to low-latitude regions and new archaeological sites.

7. Conclusions

Patella candei crenata and *Phorcus atratus* from the Canary Archipelago are a valuable cache of climate data as they both grow shell throughout the year, tracking the full range of SST in their shell $\delta^{18}\text{O}$ values. While calculated SST from the *Phorcus atratus* shell overlaps with measured SST, the $\delta^{18}\text{O}$ values from *Patella candei crenata* exhibit a positive isotopic offset of +1.3‰ from expected equilibrium values. Because this offset is constant and predictable, however, it can be taken into account, providing calculated growth temperatures that match

measured local SSTs within an error of ± 0.8 °C.

These results are promising for developing high-resolution paleotemperature reconstructions through the Holocene, as *Patella candei crenata* and *Phorcus atratus* were extensively harvested by aboriginal pre-Hispanic peoples in the Canary Islands for the last 2500 years as evidenced by their abundance in shell middens across the archipelago. This establishes a baseline for useful studies regarding variations in magnitude of seasonality, season of shellfish harvest, and mean annual temperature fluctuations in the Canary Islands and, by extension, Northwest Africa and other comparable regions.

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