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Geochemical and Crystallographic Study of *Turbo Torquatus* (Mollusca: Gastropoda) From Southwestern Australia

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Key Points:

- Different mineralogy between gastropod shells of a same species depending on SST
- Elemental concentrations found in *T. torquatus* shell are mainly biologically controlled
- These findings support the proposal of an active selective elemental pathway across the mantle

Supporting Information:

- Supporting Information S1

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Abstract Shells of the marine gastropod *Turbo torquatus* were sampled from three different locations along the Western Australian coastline, namely Marmion Lagoon (31°S), Rottnest Island (32°S), and Hamelin Bay (34°S). Marmion Lagoon and Rottnest Island have similar sea surface temperature ranges that are ~1°C warmer than Hamelin Bay, with all sites influenced by the warm southward flowing Leeuwin Current. The shells were characterized using crystallographic, spectroscopic, and geochemical analyses. Shell mineral composition varies between the three sites suggesting the influence of sea surface temperature, oxygen consumption, and/or bedrock composition on shell mineralogy and preferential incorporation and/or elemental discrimination of Mg, P, and S. Furthermore, *T. torquatus* was found to exert control over the incorporation of most, if not all, the elements measured here, suggesting strong biological regulation. At all levels of testing, the concentrations of Li varied significantly, which indicates that this trace element may not be a suitable environmental proxy. Variation in Sr concentration between sites and between specimens reflects combined environmental and biological controls suggesting that Sr/Ca ratios in *T. torquatus* cannot be used to estimate sea surface temperature without experimentally accounting for metabolic and growth effects. The mineral composition and microstructure of *T. torquatus* shells may help identify sea surface temperature variations on geological time scales. These findings support the previously hypothesized involvement of an active selective pathway across the calcifying mantle of *T. torquatus* for most, if not all, the elements measured here.

1. Introduction

The precipitation of biogenic carbonate represents a sink for carbon in the oceans and is a major process in the global carbon cycle (Barker et al., 2003). The study of modern and fossilized remains of calcifying organisms plays an important role in building an understanding of present day perturbations associated with global change (Cuif et al., 2011). A large number of studies have focused on reconstructing paleoclimate and paleoceanographic conditions using geochemical data sets, notably stable isotope records ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) from fossilized and modern mollusks and corals (e.g., (Brachert et al., 2016; Carré et al., 2013; Charles et al., 1997; McConnaughey & Gillikin, 2008; Urban et al., 2000; Weidman & Jones, 1994). Documenting oceanic changes combined with their impact on marine calcifiers is critical for elucidating the consequences of past and present climatic changes and predicting future change.

Biogenic calcification is controlled to a large extent by organic macromolecules that govern many properties of the biominerals such as crystal size, texture, crystallographic orientation, chemical properties of the biogenic crystals, and mechanical strength (e.g., Lowenstam & Weiner, 1989; Sun & Bhushan, 2012; J. Wang et al., 2012). The calcification process requires an active or passive system for supplying essential ions to the calcification site and maintaining the supersaturated conditions needed for mineral precipitation (e.g., Cuif et al., 2011). The environmental limitations regulating the supply systems underlying gastropod calcification may determine the relative survival of marine calcifiers in the face of global change. Assessing the potential for resilience requires a better understanding of trace element incorporation with regards to the chemical composition of seawater and climate reconstructions from CaCO_3 records. Equilibrium-based thermodynamic models (Kinsman & Holland, 1969) or kinetically controlled inorganic partitioning (Gaetani & Cohen,

Figure 1. Location of the three sampling sites: Hamelin Bay, Rottnest Island, and Marmion Lagoon along the Western Australian coastline and location of the Leeuwin Current (LC) and Capes Current (CC). Base satellite images were sourced from Ahoy Map Maker®.

2006) form the basis for paleoclimatic reconstructions (Finch & Allison, 2007). However, biological regulation confounds these models. The biological or “vital effect” is a time-independent offset from theoretical/experimental equilibrium and thermodynamics controlled by physiological processes. Many organisms exert a certain level of control on CaCO_3 precipitation as identified in previous studies of foraminiferans (e.g., Bentov & Erez, 2006), corals (e.g., Marshall, 1996; Tambutté et al., 1996), bivalves (e.g., Kennedy et al., 1969), gastropods (e.g., Nehrke & Nouet, 2011; Yao et al., 2010), and bryozoans (e.g., Loxton et al., 2014). As a consequence, it is essential to consider biological controls in the use of biogenic materials as proxies for environmental reconstruction (e.g., Austin & James, 2008, and references therein).

Most molluscan studies have focused on bivalves at the expense of gastropods, despite the broad global distribution of Gastropoda. The focus is here on *T. torquatus* (Mollusca: Gastropoda) in an attempt to increase the pool of geochemical proxies for paleoceanographic studies in Western Australia, and possibly Australia as a whole, by using a particularly common gastropod. Using Turbinid shells as paleoceanographic proxies could prove useful considering the wide geographical distribution of this family (shallow to deep waters, tropics to polar regions; Williams et al., 2008). Furthermore, Turbinidae are often found in shell middens around the world (e.g., Attenbrow, 1992; Cann et al., 1991; Erlandson et al., 2011; Lasiak, 1991; Schneider & Egan, 2016) and, in addition to their archeological value in providing social and dietary knowledge on the indigenous people, these shells could provide information regarding the environmental conditions at the time.

Turbo torquatus were sampled from three separate localities along the southwestern coast of Australia (Figure 1) to determine the level of biological control over the structure, size, and morphology of the CaCO_3 crystals precipitated and the incorporation of trace elements within the shell. These characteristics were compared between three study sites to examine whether variation in shell microstructure and composition may have been influenced more strongly by geographical (environmental) factors and/or biological factors. These findings add to the limited data available on molluscan shell geochemistry from the southwestern coastal regions of Australia and provide further insights into the use of these mollusks as proxies for reconstructing marine climates globally.

2. Materials and Methods

2.1. Study Sites

Large specimens of *T. torquatus* were collected from three different locations in southern Western Australia: Hamelin Bay ($34^{\circ}14'S$, $115^{\circ}01'E$); Rottnest Island ($32^{\circ}00.5'S$, $115^{\circ}30.1'E$); and Marmion Lagoon ($31^{\circ}50'S$, $115^{\circ}42'E$; WSG84, Figure 1). Average shell height was 76.3 ± 0.6 mm in Rottnest Island, 75.3 ± 1.5 mm in Marmion Lagoon, and 75.3 ± 1.2 mm in Hamelin Bay. Hamelin Bay is located between Cape Leeuwin and Cape Naturaliste where the coastline is dominated by exposures of granite gneisses (Wilde, 1999) with small limestone islands (e.g., Hamelin Island). Rottnest Island is located approximately 18 km west of Fremantle port (Perth area) and, at 1,900 ha, is the largest in a chain of limestone islands along the continental shelf (Prince, 1995). The Rottnest coastline is characterized by alternating of rocky headlands and sandy bays, fringed with offshore reefs and rocky platforms. Marmion Lagoon is located approximately 25 km north of Perth. Much like Rottnest Island, the reefs in Marmion Lagoon form a series of offshore limestone ridges (Wernberg et al., 2003). *T. torquatus* is found in abundance at all three sites. Rottnest Island and Marmion Lagoon have typical Mediterranean weather patterns, with mild, wet winters and hot, dry summers, with some temperature moderation by the surrounding waters (Prince, 1995). Hamelin Bay has more temperate climate conditions with higher rainfall, moderate temperatures, and moderate changes between summer and winter (Table 1).

Table 1

Weather Average for Marmion Lagoon, Rottnest Island, and Hamelin Bay (Australian Bureau of Meteorology, www.bom.gov.au)

	Mean maximum temperature (°C)	Mean minimum temperature (°C)	Mean maximum rainfall (mm)	Mean minimum rainfall (mm)
Marmion Lagoon	30.7 (February)	9.6 (July)	149.5 (July)	6.6 (February)
Rottnest Island	27.3 (February)	12.3 (July)	113.6 (July)	10.3 (December)
Hamelin Bay	23.4 (February)	11.3 (July)	183.8 (July)	15.5 (February)

The sample sites are linked by oceanic currents that influence offshore Western Australia as a whole (Leeuwin Current and the Capes Current: Figure 1). The Leeuwin Current is a warm, low salinity, surface current that flows south-southeast along the continental shelf (Pearce, 1991; Pearce & Pattiaratchi, 1999; Pearce et al., 2006). The Capes Current is a cold, high salinity, coastal current that flows westward along the southwestern Australian coast (Cresswell & Golding, 1980; Pearce, 1991; Pearce & Pattiaratchi, 1999; Pearce et al., 2006). Hamelin Bay sea surface temperature (SST) varies from 17.3°C to 19.5°C in winter (August) and 19.6°C to 24.4°C in summer (February). Marmion Lagoon and Rottnest Island have a similar SST range of 18.6°C–20.2°C in winter (August) and 20.6°C–25.9°C in summer (February) (<http://www.bom.gov.au/oceanography/forecasts> [Australian Bureau of Meteorology, 2016]). The Leeuwin Current has a greater influence at Hamelin Bay compared to Marmion Reef (Smale & Wernberg, 2009) and the intensity of the Capes Current is greater between the capes resulting in well-mixed waters (Pearce & Pattiaratchi, 1999). Marmion Lagoon and Rottnest Island present more stratified waters in comparison (Pearce & Pattiaratchi, 1999). The salinity and temperature differences between sites have thermodynamic implications for the precipitation of biogenic calcium carbonate (Lowenstam & Weiner, 1989). A number of species living in warm waters form different minerals compared to those formed by their colder water counterparts (Lowenstam & Weiner, 1989) and temperature may further influence shell trace element and stable isotopic compositions (e.g., Schöne et al., 2011; Sossian et al., 2006). Shell trace element concentration can also be studied with regards to salinity changes in very low-salinity waters (e.g., Dodd & Crisp, 1982).

2.2. Species and Sample Preparation

T. torquatus belongs to the Turbinidae family which include both predominantly shallow and deep water clades with genera distributed globally from the poles to the tropics (Williams et al., 2008). For this study, three specimens of *Turbo* (*Ninella*) *torquatus* Gmelin, 1791 ("heavy turban shell") were collected alive from each of the three localities. *T. torquatus* (Mollusca: Gastropoda: Turbinidae) shells have a variegated cream, pink to reddish brown color, highly conspiral large and thick walled (Figure 2). Their width is greater than their height (90–200 mm across) and they possess a circular calcareous operculum. They are found on rocky intertidal platforms amongst the seagrass on which they feed (Atlas of Living Australia, 2016). The shells are composed of nacreous aragonite on the inner layer (IL1, Figure 3) and prismatic calcite on the outer layer (OL, Figure 3). A second inner layer (prismatic) is visible in older whorls (OWs) only (IL2, Figure 3) and shows a different structure/orientation to IL1. Mollusk shells also contain an important organic fraction of 0.1 – 5 wt% (Mann, 2001), the organic matrix, which functions to mediate biomineralization (Weiner et al., 1984). The fraction of organic macromolecules varies depending on the microstructure, and nacre commonly has a higher organic content (Marin et al., 2012).

T. torquatus shells were manually cleaned of organic material (e.g., animal tissue, epiphytes, algae) and rinsed with fresh water. The shells were then soaked in sodium hypochlorite (12.3 vol%) for approximately 12 h, thoroughly rinsed with Milli-Q water and air dried. For X-ray diffraction (XRD) analysis, shell powder was sampled along the outer lip of the aperture (Figure 2, inner and OL as bulk, ~13 cm²) using a hand-held dental drill. Fifty milligrams of fine powder was mixed with ~10 mg of CaF₂ (~20% by weight) and mounted on a low X-ray background holder according to the settings described in the supporting information (Table S1). Shells were then cut along the central axis or columella, fixed in Styrene[®] polymer and mounted on a glass slide with Epoteck[®] 301 epoxy glue before being trimmed and polished to a thickness of 30 μm. These thin-sectioned samples were used for petrographic observations, confocal Raman microscopy, laser ablation inductively coupled plasma-mass spectrometry (LA ICP-MS) (Figure 3), and electron probe micro analysis (EPMA).

Figure 2. Photograph of *T. torquatus* shell, (a) top view and (b) tilted umbilical view. Crustose coralline algae (bleached) cover the top whorls of the shell. Red box (a) indicates where shell powder was sampled for XRD analyses.

Certain cleaning methods used for the removal of organic matter have been reported to alter the elemental and crystallographic composition of mollusk shell (e.g., *A. islandica*; Krause-Nehring et al., 2011). Among the cleaning methods tested, sodium hypochlorite, as used in this study, has the least effect on structure and composition (Nategaal et al., 2012). Leaving the samples untreated may potentially lead to measuring trace elements from uncertain origins such as from epiphytes or other external contaminants. Cleaning the samples using sodium hypochlorite minimizes the organic contamination with the minimum effect on structure and composition. This cleaning method does not remove intracrystalline organic molecules but the fraction of these molecules (0.001% to 0.01% by weight of biomineral) is negligible in the present context (Penkman et al., 2008).

2.3. Powder XRD (pXRD) Analysis

A PANalytical Empyrean diffractometer was used to perform XRD analysis of bulk powdered shell material (bulk inner and OL). The instrument was operated at 40 kV and 40 mA (Cu K α radiation and Ni Beta filter) and a PANalytical PixCel position sensitive detector. Instrumental settings can be found in S1. Corundum NIST (676a, Certificate number 382200) and calcium fluoride (CaF₂) were used as primary external and secondary internal standards. The amount of secondary standard was determined by analyzing various CaF₂:sample ratios. No major variations were observed between ratios tested therefore 20% weight of CaF₂ was chosen. CaF₂ (lattice parameters $a = b = c = 5.4661$ (2) Å, and $\alpha = \beta = \gamma = 90^\circ$) is an ideal internal calcium standard because its diffraction peaks do not interfere with those of the various CaCO₃ mineral phases.

The Inorganic Crystal Structure Database (ICSD) and the International Centre for Diffraction Data (ICDD) databases were used to identify the different mineral phases present in the samples. Phase quantification and lattice parameter determination was carried out using the Rietveld refinement method (Rietveld, 1969) and the Coherently Scattering Domain (CSD) size (i.e., crystallite size) was calculated using the Scherrer equation applied to the dominant reflections of calcite and aragonite (Cullity, 1978). Both the Rietveld refinement and the Scherrer calculation were software automated (version 3.0e of Panalytical HighScore Plus[®] software).

All samples analyzed here were indexed to the orthorhombic symmetry system for aragonite and the hexagonal system for calcite. XRD provides detailed quantitative data and confocal Raman microscopy provides crystallographic maps of the samples, for this reason both methods were used here in conjunction.

2.4. Confocal Raman Microscopy (CRM)

CRM uses intense monochromatic light (here infrared laser) to irradiate samples and trigger molecular vibrations producing highly specific Raman spectra reflecting molecular structure and chemical structure. Differences between crystalline form and different polymorphs of CaCO₃ can be identified by shifts in the intensity and position of particular peaks (Nehrke & Nouet, 2011). The spectral peaks caused by the unit cell symmetry of the crystals and the carbonate ions (CO₃²⁻) of aragonite and calcite can overlap. The

Figure 3. Photographs montage of *T. torquatus* in thin section. White dashed line indicates coiling axis (arrow shows direction of growth) and red box and insert show sample location of CRM and LA ICP-MS sampling with suture between BW and OW highlighted with blue dashed line: three parallel transects shown by white spots with red outlines (white laser spots were sampling tests). Yellow box indicates location targeted for EPMA, IL1: first inner (nacreous) layer, IL2: second (prismatic) inner layer, OL: outer (prismatic) layer. IL2 is only present in OWs.

differentiation between the two polymorphs is done using their shared CO_3^{2-} vibration modes along the lower end of the spectrum, $50\text{--}1,200\text{ cm}^{-1}$.

CRM was undertaken on thin-sectioned gastropod shells to provide key information about the crystallographic structure of CaCO_3 . A WITec Raman alpha300 RA+ coupled with diode infrared laser module (785 nm) and 20X objective (numerical aperture 0.4) was used to perform the analyses. The work was performed in reflection mode whereby scattered light is collected through a $100\text{ }\mu\text{m}$ detection fiber connected to a UHTS 300 spectrometer equipped with a 300 lines/mm grating. Full Raman spectra at each imaging pixel were obtained using a thermoelectrically cooled camera with back-illuminated CCD chip. The first-order Raman peak of silicon ($520.2\text{ rel. cm}^{-1}$) was used to optimize alignment and signal intensity before each analysis. Large area scans with the accumulation of three to five spectra to minimize error ($\pm 1\text{ rel. cm}^{-1}$) and integration time of $0.1\text{--}0.05\text{ s}$ were used to collect spectral data. Two spectral ranges were measured: $0\text{--}1,600$ and $1,600\text{--}3,000\text{ rel. cm}^{-1}$; the second range was explored in an attempt to detect organic functional groups (C-H or C=O) within crystalline structures.

2.5. EPMA

Wavelength dispersive spectrometry (JEOL 8530 Hyperprobe) with five tunable wavelengths was used to acquire quantitative chemical maps from thin sections. Calibration conditions were 40° take-off angle, 15 kV beam energy, and 20 nA beam current. The beam was defocused to 2 μm and the following crystals were used: pentaerythritol for Ca K α , S K α , and Sr L α ; thallium acid phthalate for Na K α and Mg K α . The standards used for instrument calibration were barite (for S K α); calcite (for Ca K α); celestite (for Sr L α); periclase (for Mg K α); and jadeite (for Na K α). On peak counting, times were 20 s and mean atomic number background corrections were used throughout (Donovan & Tingle, 1996). Results from the standardization are an average of three points and detection limits ranged from 0.008 wt% for S K α to 0.010 wt% for Mg K α to 0.049 wt% for Sr L α . The Armstrong/Love Scott algorithm was used for ZAF matrix correction (Armstrong, 1988). Probe Image[®] software was used for quantitative elemental map acquisition. Beam current, dwell time and pixel dimensions are, respectively, 80 nA, 40 ms, and 4 $\times$ 4 μm . CalImage[®] and Surfer[®] software were used for data reduction and image processing. Elemental mapping was done on the thin sections and targeted the body whorl (BW) of the shell to capture its typical composition (Figure 3).

2.6. Laser Ablation ICP-Mass Spectrometry

Thin sections were analyzed using a Resonetics RESolution M-50A-LR incorporating a Compex 102 excimer laser coupled with an Agilent 7700s quadrupole ICP-MS. Two cleaning pulses followed by background analysis preceded the spot ablation of the samples (30 s, 7 Hz repetition rate, 75 μm beam and 5 J cm⁻² laser energy). Flow rates were tuned for a ThO/Th < 0.5% to minimize oxide polyatomic interferences. Ultrahigh purity He (350 mL min⁻¹) and N₂ (3.8 mL min⁻¹) were flushed through the sample cell and the plasma carrier gas used was high-purity Ar. Elemental concentrations were calculated using ⁴³Ca and the stoichiometric Ca content for calcite/aragonite (40.4%). The primary reference standard for data reduction and drift correction was NIST 612 and carbonate pellet MACS-3 was analyzed as a secondary reference material. Standard blocks were run after every 20 unknown samples. The mass spectra were reduced using Iolite[®] (Armstrong, 1988; Paton et al., 2011).

Samples were analyzed for 16 elements ⁷Li, ²⁴Mg, ²⁸Si, ³¹P, ³⁴S, ⁴³Ca, ⁴⁴Ca, ⁵²Cr, ⁵⁵Mn, ⁵⁶Fe, ⁶³Cu, ⁶⁶Zn, ⁷⁵As, ⁸⁸Sr, ¹¹¹Cd, ¹³⁸Ba, and ²⁰⁸Pb (supporting information Figure S1). Si was used as a tracer, to detect whether the laser perforated the samples and intercepted to the glass slide. Trace element profiles were measured across two shells of *T. torquatus* from each sample site. Laser spots were organized in two parallel transects where the BW joins the OW, with an intermediate transect undertaken to verify compositional consistency (Figure 3).

3. Results

To address the lack of data concerning the growth rate of the *T. torquatus*, the shells were dated assuming a growth rate of 1.29 cm yr⁻¹ following Wernberg et al. (2008) and Foster et al. (1999). This growth rate corresponds to that of *Turbo sarmaticus*, a homologous species to *T. torquatus*. Using this growth rate, the shells were estimated to be 5.9 $\pm$ 0.1 years old on average old when collected.

3.1. Shell Mineral Composition

The powder sampling targeted the lip of the shells and, therefore, represents the last deposited material. The results rely on the assumption that the powder sampled represents the same snapshot in time in each individual (assuming similar daily growth rates). Examination of powder XRD patterns show that all the shells analyzed are a composite of CaCO₃ polymorphs. Diffraction peaks in the samples were matched with two crystallographic phases in the ICSD database (Figure 4), aragonite and calcite. CaF₂ was added as an internal standard (~20% weight of sample) and precalibrated against NIST 767a Alumina Standard Reference Material. Rietveld refinement was applied in order to obtain phase quantification for each sample (Figure 5). The Rietveld refinement yielded R-Bragg factor (goodness of fit/refinement) averaging 3.16 $\pm$ 0.16 for aragonite and 2.13 $\pm$ 0.22 for calcite. Both factors <5, which indicates a good refinement. The samples from both Rottneest Island and Marmion Lagoon are predominantly composed of aragonite (average of 94.4% for Rottneest Island and 92.0% for Marmion Lagoon, excluding standard) with minor calcite (average of 5.5% for Rottneest Island and 7.8% for Marmion Lagoon, excluding standard). In contrast, Hamelin Bay samples are calcite dominated: average of 77.1% calcite and 23.6% aragonite (excluding standard, Figure 5).

The lattice parameters (*a*, *b*, *c*) generated by Rietveld refinement and post-Scherrer calculation differ from geological reference materials (5% uncertainty, Table 2) for all phases identified, which is consistent with

Figure 4. X-ray diffraction pattern extracted from samples from all three sites: Hamelin Bay (BG), Rottneest Island (RI), and Marmion Lagoon (ML). CaF₂ diffraction peak ($\sim 29.2^\circ\theta$) is used to calibrate samples. Diffraction patterns were offset from each other arbitrarily (relative scale). (1) Aragonite, (2) calcite, and (3) CaF₂.

crystallographic studies on a number of mollusks species (Pokroy et al., 2006). They reveal peak shifts in all *Turbo* samples analyzed here (Table 3). The Miller indices of the peaks targeted are (111), (102), (201), and (122) for aragonite and (104), (018), (116) for calcite.

All samples show distortion along the *a* and *b* axes in the aragonite lattice but no common trend can be found in calcite, with the exception of a generalized shrinking of the calcite lattice in samples from Hamelin Bay (Figure 6). Positive/negative shifts and distortions, as seen in ML_02, ML_03, HB_01, and HB_02, indicate axial distortion as opposed to generalized distortion, nevertheless, the highest amount of strain is found in the calcite lattice of samples from Rottneest Is. (RI_01) and Marmion Lagoon (ML_01). Lattice distortion is controlled by ionic substitution, which in turn depends on the environmental concentrations and physiological control applied to incorporation/substitution (Brečević et al., 1996).

Figure 5. Crystallographic phase quantification extracted from X-ray diffraction measurements on powdered samples from *T. torquatus* from Rottneest Island (RI_01, _02, _03), Marmion Lagoon (ML01, _02, _03), and Hamelin Bay (HB_01, _02, _03). CaF₂ was added as internal precalibrated standard.

Crystallite size (i.e., CSD, Table 4) calculated from width at half height using the Sherrer equation on four diffraction peaks for aragonite (hkl: (111), (102), (201), and (122)) and three peaks for calcite (hkl: (104), (116), and (018)) reveals that aragonite and calcite crystallites here are nanocrystals < 100 nm. Average aragonitic crystallites (64 nm) are larger than their calcitic crystallites (26.9 nm) across all sites (Table 4).

Table 2

Lattice Parameters (Å) of Aragonite After Rietveld Refinement and Other Reference Materials for Comparison^a

Origin		a	b	c
<i>This study</i>				
HB_01	Biogenic: <i>T. torquatus</i> (Hamelin Bay)	5.7513	4.9646	7.9688
HB_02	Biogenic: <i>T. torquatus</i> (Hamelin Bay)	5.7524	4.9642	7.9727
HB_03	Biogenic: <i>T. torquatus</i> (Hamelin Bay)	5.7523	4.9650	7.9652
RI_01	Biogenic: <i>T. torquatus</i> (Rottneest Is.)	5.7413	4.9563	7.9529
RI_02	Biogenic: <i>T. torquatus</i> (Rottneest Is.)	5.7310	4.9490	7.9608
RI_03	Biogenic: <i>T. torquatus</i> (Rottneest Is.)	5.7378	4.9543	7.9457
ML_01	Biogenic: <i>T. torquatus</i> (Marmion L.)	5.7503	4.9634	7.9671
ML_02	Biogenic: <i>T. torquatus</i> (Marmion L.)	5.7507	4.9636	7.9666
ML_03	Biogenic: <i>T. torquatus</i> (Marmion L.)	5.7527	4.9653	7.9640
<i>Pokroy et al. (2007)^b</i>				
ICSD-98-015-7993	Mineral: Morocco	5.7420	4.9630	7.9680
JCPDS-41-1475	Mineral	5.7439	4.9623	7.9680
ICSD-98-015-7994	Biogenic: <i>P. canaliculus</i>	5.7520	4.9670	7.9640
ICSD-98-015-7992	Biogenic: <i>A. tuberculata</i>	5.7480	4.9650	7.9640
ICSD-98-015-7995	Biogenic: <i>S. decorus persicus</i>	5.7530	4.9690	7.9590
ICSD-98-015-7996	Biogenic: <i>S. decorus persicus</i> (Bleached)	5.7430	4.9630	7.9640
ICSD-98-015-7997	Biogenic: <i>S. decorus persicus</i> (Annealed)	5.7530	4.9690	7.9610
<i>De Villiers (1971)^c</i>				
ICSD-98-001-5194	Mineral: Nevada	5.7400	4.9670	7.9670
<i>Bragg (1925)^d</i>				
ICSD-98-005-6090	Mineral: Hungary	5.7300	4.9500	7.9550
<i>External standard</i>				
NIST 676a Alumina	Synthetic powder	4.7593	4.7593	12.992
<i>Internal standard</i>				
CaF2	Synthetic powder	5.4664	5.4664	5.4664

^a*Perna canaliculus*: marine bivalve; *Acanthocardia tuberculata*: marine bivalve; *Strombus decorus persicus*: marine gastropod. ^bJCPDS: data file 41 – 1475, Joint Committee on Powder Diffraction Standards (Keller et al., 1989). ^cXRD from single crystal CaCO₃—Nevada. ^dXRD from single crystal CaCO₃—Hungary.

Table 3
Peak Shift ($2^\circ\theta$) Measured for Specific Peaks (hkl) of Aragonite and Calcite Using X-Ray Diffractometry^a

Phase	h	k	l	RI_01	RI_02	RI_03	ML_01	ML_02	ML_03	HB_01	HB_02	HB_03
Aragonite	1	1	1	-0.068	-0.037	0.093	-0.013	0.004	0.022	0.007	0.003	0.059
Aragonite	1	0	2	-0.054	-0.024	0.109	-0.009	0.011	0.034	0.013	0.010	0.073
Aragonite	2	0	1	-0.099	-0.067	0.055	-0.041	-0.025	-0.011	-0.022	-0.032	0.026
Aragonite	1	2	2	-0.064	-0.035	0.086	-0.009	0.008	0.023	0.008	0.003	0.057
Calcite	1	0	4	0.011	0.033	0.126	0.021	0.049	0.065	0.067	0.057	0.131
Calcite	0	1	8	0.154	0.108	0.165	0.140	0.080	0.104	0.089	0.069	0.156
Calcite	1	1	6	0.032	0.061	0.015	0.011	0.066	0.073	0.099	0.082	0.169

^aRottne Island: RI_01, RI_02, and RI_03; Marmion Lagoon: ML_01, ML_02, and ML_03; Hamelin Bay: HB_01, HB_02, and HB_03.

Four filters were applied to each Raman spectrum to target different phases or reveal particular features of the shell (Figures 7 and 8): (1) Σ peak area of aragonite (centered on 209 rel. cm^{-1}), (2) Σ peak area of calcite (centered on 282 rel. cm^{-1}), (3) center of mass/weighted width (Full Width at Half Maximum [FWHM]) of ν_1 (centered at 1,085 rel. cm^{-1}) highlighting crystallinity and order, and (4) Σ peak area of the tail of the spectrum targeting fluorescence (centered on 1,450 rel. cm^{-1}). Peak intensities at 152 rel. cm^{-1} (translational mode T) and 209 rel. cm^{-1} were also ratioed (PIR) to distinguish crystal orientation variations (filter 5). The scan range of the laser was increased to 3,000 rel. cm^{-1} in order to detect the presence of organic compounds (Nehrke & Nouet, 2011), e.g., -CH groups, but no features characteristic of these groups were found.

Filters 1 and 2 confirm the presence of aragonite and calcite in the shells of *T. torquatus*. Mg-calcite can be identified by the increasing FWHM and peak shift of peak ν_4 (714 rel. cm^{-1} toward ~ 738 rel. cm^{-1})

Figure 6. Lattice distortion presented as $\Delta a/a$, $\Delta b/b$, and $\Delta c/c$ for nine specimens of *T. torquatus* from Rottne Is., Marmion Lagoon, and Hamelin Bay (three specimens per site) for aragonite (compared to mineral aragonite, ICSD 98-015-7993; Pokroy et al., 2007) and calcite (compared to mineral calcite, ICSD 98-008-6161; Sitepu et al., 2005). Negative distortions indicate shrinking, and positive distortions indicate stretching.

Table 4

Aragonite and Calcite Average Crystallite Size (CSD) Per Sample Site ($n = 3$ at Each Site) in Nanometer, Estimated Using the Sherrer Equation (With $K = 0.9$) on Four Diffraction Peaks of Aragonite, (111), (102), (201), and (122) and Three Peaks for Calcite (104), (018), and (116)

Sample ID	Peak (hkl)	
	Aragonite	Calcite
Rottneest Is.	71.2	25.3
Marmion Lagoon	63.4	22.2
Hamelin Bay	57.4	33.2

(Bischoff et al., 1985), however, no Mg calcite was observed suggesting that Mg^{2+} substitution in calcite was not sufficient to create a change in peak position or shape. Filter 3 shows that disorder and low crystallinity (bright color) is evenly spread across the sample area with sharp variations in the prismatic layer of the OW (Figure 8, right side of image). According to our observations, the prismatic layer (IL2, Figure 3) appears to have been deposited later, as the animal grew and extended its BW because it is not present in the last deposited part of the shell. Organic components (indicated by fluorescence measured by the filter centered on $1,450 \text{ rel. cm}^{-1}$) are most pronounced at the suture of the BW and the OW, and also in the nacreous layer. Crystal orientation is consistent throughout the nacreous layer of both whorls but is significantly different in IL1 of the older BW (right) and IL2 (Figure 8e).

3.2. Elemental Composition

Elemental maps showing concentrations of Ca, Mg, Sr, S, and Na were obtained by EPMA for one shell from each location (Figure 9). Totals are between 97% and 100%, however, Mg, Sr, and S are mostly below instrument detection limits. Sulphur is elevated in one sample (ML_02; $\sim 0.26 \text{ wt\%}$) where an organic-rich layer marks the suture between two whorls. Higher Ca wt% was found in prismatic layers of the shell. Sodium is layered in HB_02 map 2 and in ML_02 with higher concentrations usually corresponding to lower Ca wt%. Average Na concentrations are between 0.55 and 0.65 wt% with peaks at 0.8 wt%.

Laser ablation ICP-MS was performed on two whorls: the BW and that directly joined to it (OW, Figure 3, standard results in S2). Using the *T. sarmaticus* growth rate, the *T. torquatus* specimens were estimated to be 5.9 ± 0.1 years old (shell size of $75 \pm 1.1 \text{ mm}$ in average), and, using that same growth rate, the OW material sampled was estimated to be have been deposited when the shells were 3 ± 0.1 years old (shell size of $38 \pm 7 \text{ mm}$ on average). Sixteen elements were measured by LA ICP-MS along three transects on two specimens from each sample location. Each transect is a cross section of the BW and OW (Figure 3). Sixteen elemental contents were measured by LA ICP-MS along three transects on two samples from each sample location. Each transect is a cross section of the BW and OW (Figure 3). Of these 16 elements, based on review of elemental geochemistry of mollusks and their relevance in term of proxies for environmental parameters (Immenhauser et al., 2016), the most useful elements are Li, Mg, S, Ca, P, Sr, Ba, and Pb (normalized to calcium).

Overall, elemental concentrations are not significantly different between the OW and the BW (Table 5). They are broadly similar at all sites with some notable variations. Samples with the highest average Ca concentration are from Marmion Lagoon and those with the lowest average from Hamelin Bay. Rottneest Island samples have the highest average concentration of Li, and lowest average concentrations of Sr, S, Mg, Ba,

Table 5

LA ICP-MS Results (2σ) for Two Specimens (Average of Three Transects) of *T. torquatus* From Rottneest Island (RI(1), RI(2)), Marmion Lagoon (ML(1), ML(2)), and Hamelin Bay (HB(1), HB(2)), Averaged Over Three Transects for the BW and OW

		Li/Ca		Mg/Ca		P/Ca		S/Ca		Sr/Ca		Ba/Ca		Pb/Ca	
		($\mu\text{mol/mol}$)	2σ	(mmol/mol)	2σ	(mmol/mol)	2σ	(mmol/mol)	2σ	(mmol/mol)	2σ	($\mu\text{mol/mol}$)	2σ	($\mu\text{mol/mol}$)	2σ
RI_01	OW	7.69	0.32	0.27	0.03	0.01	0.00	0.59	0.07	1.35	0.05	0.23	1.04E-05	0.004	1.59E-07
RI_01	BW	6.83	0.75	0.26	0.04	0.05	0.02	0.77	0.05	1.47	0.05	0.30	2.41E-05	0.005	1.15E-06
RI_02	OW	8.06	1.17	0.29	0.04	0.01	0.02	0.61	0.16	1.53	0.23	0.31	5.05E-05	0.006	2.72E-06
RI_02	BW	9.09	6.18	0.29	0.04	0.07	0.21	0.51	0.52	1.40	0.43	0.35	4.42E-04	0.007	5.93E-06
ML_01	OW	5.96	3.15	0.37	0.13	0.02	0.02	0.68	0.32	1.49	0.22	0.37	2.80E-04	0.009	6.23E-06
ML_01	BW	6.05	0.39	0.31	0.06	0.04	0.05	0.85	0.02	1.67	0.06	0.59	6.05E-04	0.030	6.95E-05
ML_02	OW	9.78	6.00	0.39	0.12	0.03	0.02	0.72	0.30	1.12	0.20	0.20	3.00E-04	0.003	6.23E-06
ML_02	BW	8.41	8.00	0.39	0.05	0.04	0.04	0.74	0.01	1.21	0.06	0.22	6.00E-04	0.003	6.95E-05
HB_01	OW	6.19	0.26	0.27	0.04	0.06	0.07	0.89	0.08	1.51	0.01	0.32	1.37E-05	0.010	5.43E-07
HB_01	BW	6.75	1.88	0.23	0.00	0.01	0.00	0.55	0.04	1.48	0.11	0.26	2.67E-05	0.007	7.65E-07
HB_02	OW	4.04	0.32	0.17	0.01	0.01	0.01	1.26	0.05	1.43	0.05	0.31	1.60E-05	0.012	2.56E-06
HB_02	BW	8.07	1.21	0.44	0.12	0.03	0.02	0.95	0.10	1.58	0.17	0.36	1.18E-04	0.009	5.17E-06

Figure 7. Typical Raman spectrum from *T. torquatus*. (a) Blue boxes correspond to filters applied to the data: filter 1 (Σ peak area) centered at 209 rel. cm^{-1} (width = 36.6 rel. cm^{-1}), filter 2 (Σ peak area) centered at 282 rel. cm^{-1} (width = 66.3 rel. cm^{-1}), filter 3 (center of mass, weighted width) centered at 1,085 rel. cm^{-1} (width = 36.6 rel. cm^{-1}), and filter 4 (Σ peak area) centered at 1,450 rel. cm^{-1} (width = 600 rel. cm^{-1}). The blue dashed box, filter 5, encapsulated filter 1 and a filter centered at 152 rel. cm^{-1} (Σ peak area, width = 36.6 rel. cm^{-1}) to represent their calculated peak intensity ratio (PIR). (b) The blue and red spectra show the intensity differences seen at 152 and 209 rel. cm^{-1} . Each filter measured peak area, except filter 3, which measured FWHM, and produces a qualitative map. Filter 1 targeted the aragonite phases, and filter 2 targeted calcite. Filter 3 by measuring variation in FWHM represents crystallinity and order. Filter 4 by targeting the tail of the spectrum shows fluorescence because peaks related to organics tend to show beat in the tail of the spectrum. The PIRs (filter 5) show changes in crystal orientation (aragonite crystallites).

and Pb. Hamelin Bay samples have the highest average concentrations of Sr, S, Pb, and Ba, and Marmion Lagoon samples have the highest average concentrations of Mg and P. Marmion Lagoon samples also have the highest Mg/Ca ratios and Rottneest Island the lowest on average (0.468 and 0.287 mmol/mol, respectively). Across all sites, the average Li/Ca ratio is 7.18 $\mu\text{mol/mol}$, Mg/Ca 0.385 mmol/mol, P/Ca 0.058 mmol/mol, S/Ca 0.94 mmol/mol, Sr/Ca 1.468 mmol/mol, Ba/Ca 0.366 $\mu\text{mol/mol}$, and Pb/Ca 0.0088 $\mu\text{mol/mol}$.

Statistical analysis of the LA ICP-MS data revealed a number of significant correlations (p -values ≤ 0.05 ; Table 6). To account for nested variables, a three-level nested ANOVA-VCA was performed with multiple transects nested within multiple individuals (shells) nested within multiple locations (level 1: location, level 2: location:shells, level 3 location:shell:transect). Lithium concentration is significantly different at all three nested levels (location $p = 0.01$, location:shell $p = 0.03$ and location:shell:transect $p = 0.003$). Conversely, Mg and S concentration are not significantly different at all three nested levels (location $p = 0.09$, location:shell $p = 0.69$ and location:shell:transect $p = 1$). The variation in the concentration of P and Li are statistically significant at the third level (location:shell:transect, $p = 0.045$ and $p = 0.003$, respectively); Ca, Ba, and Pb at the second level (location:shell $p = 0.01$, $p = 0.002$, and $p = 0.007$ respectively), and Sr at the first level (location $p = 0.001$) and second level (location:shell $p = 0.007$) (Table 6). This indicates that the Li and Sr concentrations within the shells change between sites in contrast to Mg, P, S, Ca, Ba, and Pb concentrations. Furthermore, the concentration of Li, Ca, Sr, Ba, and Pb are significantly different from one shell to another whereas concentrations of Mg, P and S are similar. Lithium and P concentrations also vary between transects within each shell analyzed.

4. Discussion

4.1. Crystal Composition

Peak shift is considered to indicate ionic substitution, which can induce lattice strain, or act to relieve it. Positive peak shifts in calcite (0.011–0.165 cm^{-1}) in all samples indicate that partial substitution of Mg^{2+} for Ca^{2+} is widespread. Negative peak shift observed in two samples from Rottneest Island and one sample from Marmion Lagoon (RI_01, RI_02, and ML_01) indicate substitution of Sr^{2+} for Ca^{2+} in aragonite (Table

Figure 8. Images extracted from filters applied to the Raman spectrum (see Figure 7) from *T. torquatus* (ML_02) from Marmion Lagoon. Scale bar: 660 μm . Color scale: bright colors correspond to high intensities (high CCD counts) and dark colors correspond to low intensities (low CCD counts). (a) Arrows indicate location of suture plane (blue dashed line) where (left) BW joins (right) older world. Filter 1: aragonite, Filter 2: calcite, Filter 3: crystallinity and order, Filter 4: fluorescence, and Filter 5: PIR. IL1: first inner (nacreous) layer; IL2: second inner (prismatic) layer.

3). Locally, some samples also show Mg^{2+} substitution in aragonite (e.g., RI_03, HB_03). All the other samples (ML_02, ML_03, HB_01, and HB_02) show negative peak shifts on the (201) peak of aragonite but positive shifts along all other peaks measured (Table 3). This suggests that the shells at all three localities are composed of aragonite and calcite with Mg^{2+} substitution below 4 mol% as defined for high Mg-calcite (Azmy et al., 2011; Chave, 1954; Long et al., 2014). Differences in SST reportedly play a role in varying the proportion of calcite and aragonite formed by a number of organisms (Chave, 1954; Lowenstam, 1954) with warmer SST promoting the formation of aragonite and cooler SST favoring the precipitation of calcite. This relationship has been documented for a wide range of organisms such as foraminifera, sponges, corals, echinoids, asteroids, ophiuroids, crinoids, annelids, mollusks, cephalopods, decapods, ostracods, and calcareous algae (e.g., Chave, 1954; Lowenstam, 1954). Shell mineralogy was more recently reported to vary along a latitudinal gradient with decreasing oxygen consumption of the animal (Ramajo et al., 2015). Here the samples from the coolest, southernmost location (Hamelin Bay) exhibit a high calcite (with Mg^{2+}) content (HB_01 77.1%, HB_02 61.4%, HB_03 64.2%, Figure 5) although the SST in Hamelin Bay are only cooler than the other two sites by $\sim 1^\circ\text{C}$. A study of SST in the region of Marmion Lagoon and Hamelin Bay revealed complex temperature patterns with higher daily average minimum SST in Hamelin Bay compared to Marmion Lagoon (Smale & Wernberg, 2009). This is likely due to the observation that the warm Leeuwin Current flows 18 km offshore from the coast along the Perth-Marmion area, whereas it comes closer inshore around Cape Naturaliste and Cape Leeuwin where the shelf break is closer to shore (Figure 1; Smale & Wernberg, 2009). Although small, the SST difference between the sites could

explain the phases ratios, or this could be a result of metabolic activity (oxygen consumption) as seen along the Chilaen coast by Ramajo et al. (2015). The concentration of Mg in food and the nearby bedrock could also influence the shell mineralogy by facilitating calcite precipitation in Hamelin Bay and thereby explaining the high calcite content in shells from Hamelin Bay associated with high ionic substitution of Mg^{2+} , minimizing shrinkage of the aragonite lattice along the *c* axis compared to the other samples. In contrast to Rottneest Island and Marmion Lagoon, which are located in the coastal exposures of the Pleistocene Tamala Limestone and Holocene bioclastic-quartz sands (e.g., Lipar & Webb, 2014), Hamelin Bay's headlands expose gneisses of the Neoproterozoic–Early Cambrian Leeuwin Complex (Collins, 2003, and references therein). More specifically, the exposures in the region of Hamelin Bay are dominated by felsic gneisses (garnet-biotite and hornblende-biotite types; Wilde 1999) which could provide a ready source of Mg cations through dissolution of the ferro-magnesian mineral components. From a purely crystallographic point of view, the Mg^{2+} substitution in calcite is also synonymous with enhanced mechanical properties (Long et al., 2014; Moureaux et al., 2010; R. Z. Wang et al., 1997) which suggests *T. torquatus* shells from Hamelin Bay may be stronger than their northern counterparts. It is also important to note that the Leeuwin coast is subject to high energy, heavy swells and these environmental conditions also contrast with the sample areas to the north.

Mineralogy is affected by salinity variations only when salinity is very low (Lowenstam, 1954) and discharge of submarine groundwater has been reported in Marmion Lagoon, resulting in a visible salinity front in the lagoon in calm conditions (Johannes & Hearn, 1985). This phenomenon has received limited study in recent years but the different crystallographic ratios measured in samples from Marion Lagoon and Rottneest Island do not suggest the shifts in salinity were large enough to affect the aragonite:calcite ratio (Figure 5). The observation that Mg/Ca ratios from Marmion Lagoon are not significantly different to the other sites (although Mg concentration has been linked to salinity (Dodd & Crisp, 1982)) further suggest that Mg/Ca ratios in the shells of *T. torquatus* were not affected by the salinity in Marmion Lagoon.

Figure 9. Typical Electron Probe Micro-Analysis elemental map of *T. troquatus* (sample RI_02) from Rottnest Island: totals, Ca concentration, Mg concentration, Na concentration, and S concentration. Sr concentration was below detection limit and is not presented here. (Detection limits for samples—from RI and ML: Na 0.1 wt%, Mg 0.094 wt%, S 0.076 wt%, Ca 0.13 wt%, Sr 0.47 wt%; and from HB: Na 0.045 wt%, Mg 0.053 wt%, S 0.028 wt%, Ca 0.066 wt%, Sr 0.88 wt%).

In terms of crystallite size (CSD), Hamelin Bay samples were shown to precipitate smaller aragonite crystallites and larger calcite crystallites resulting in lattice distortion. Although the axial distortion found in aragonite in all samples is typical of biogenic CaCO_3 , the distortion found in calcite in all Hamelin Bay samples means the calcite lattice is compressed (Figure 6). This distortion and strain may result from the incorporation of trace elements in the crystal lattice and/or the interaction between organic macromolecules and mineral crystallites (Pokroy et al., 2007). Finch and Allison (2007) reported that calcite and aragonite require a large degree of relaxation to allow the substitution of Mg^{2+} for Ca^{2+} . Strontium ion (Sr^{2+}) substitution causes a weak dilation of structure in aragonite but causes significant dilation in calcite. Although Mg/Ca ratios are very similar between sites, samples from Rottnest Island show no Mg^{2+} substitution for Ca compared to Hamelin Bay samples. This suggests that the Mg cation is incorporated on the surface of the crystal structure in samples from Rottnest Island rather than within the lattice of the crystal (i.e., ionic substitution). Regarding samples from Marmion Lagoon, strain and distortion suggest elemental substitution, however this is not corroborated by the phase quantification or the elemental composition (Mg and Sr particularly) suggesting a more complex, yet unknown, complex interplay of factors.

4.2. Chemical Composition

Lithium and Sr concentrations in *T. troquatus* shells are significantly different between sites indicating chemical differences in seawater between Marmion Lagoon, Rottnest Island, and Hamelin Bay. The SST are warmer in Marmion Lagoon and Rottnest Island (particularly in winter) due to the influence of the Leeuwin Current (Pearce & Pattiaratchi, 1999; Smale & Wernberg, 2009) which has thermodynamic implications for CaCO_3 precipitation as discussed above. Furthermore, although groundwater seeps have been reported in Marmion Lagoon (Johannes & Hearn, 1985), Sr and Mg concentrations only reflect salinity changes at very low salinities ($<8\text{‰}$; Dodd & Crisp, 1982) so the differences in Li and Sr concentrations between sites is most likely due to SST or the availability of Li and Sr in the seawater.

Ca, Li, Sr, Ba, and Pb concentrations are significantly different between shells (within sites) implying a biological or physiological effect associated with each specimen. Even shells from Marmion Lagoon and Rottnest Island, which are geographically close to each

other and might be expected to have similar seawater properties, manifest significantly different concentrations of Ca, Li, Sr, Ba, and Pb. In addition to the influence of SST on the concentration of Sr mentioned above, Sr/Ca ratios have been reported to vary with growth rate and/or metabolism (e.g., Austin & James, 2008; Gillikin et al., 2005b) potentially explaining part of the Sr concentration variation. Ba/Ca ratios are typically associated with environmental parameters, namely rainfall, nutrients, and salinity (e.g., Gillikin et al., 2005c, 2006; Gröcke & Gillikin, 2008; Poulain et al., 2015) this is not consistent with our findings for *T. troquatus*, which show that Ba/Ca ratios vary from one shell to another even within specimens from the same site. Pb/Ca ratios are also typically associated with environmental factors (anthropogenic lead pollution; Gillikin et al., 2005a), whereas in the case of *T. troquatus*, Pb concentration appears to be controlled by the gastropod animal because the only significant difference found in Pb/Ca ratios was between individuals. Li/Ca ratios can be associated with growth rate in relation to environmental conditions as demonstrated for aragonitic shells of the ocean quahog *Arctica islandica* (e.g., Thébault et al., 2009). Growth rate variations due to ontogeny or environmental conditions could explain the significant difference in Li/Ca ratios found

Table 6
Visual Representation of Three-Level Nested ANOVA (top) and F Ratios and p-Values of Nested ANOVA

Location Level 1		Rottneest Island (RI)			Marmion Lagoon (ML)			Hamelin Bay (HB)		
Shell Level 2		RI_01 RI_02 RI_03			ML_01 ML_02 ML_03			HB_01 HB_02 HB_03		
Transect Level 3		T1 T2 T3			T1 T2 T3			T1 T2 T3		
				Level 1			Level 2			Level 3
Li	F ratio			13.997			8.088			5.113
	p-value			0.015			0.033			0.003
Mg	F ratio			2.628			0.557			0.024
	p-value			0.098			0.699			1.000
P	F ratio			0.317			0.270			1.086
	p-value			0.376			0.730			0.045
S	F ratio			2.688			0.097			0.060
	p-value			0.068			0.994			1.000
Ca	F ratio			0.269			3.490			0.200
	p-value			0.802			0.019			1.000
Sr	F ratio			5.803			6.718			1.209
	p-value			0.047			0.002			0.121
Ba	F ratio			2.534			1.111			1.120
	p-value			0.122			0.002			0.068
Pb	F ratio			3.552			4.080			0.113
	p-value			0.062			0.008			1.000

between *T. torquatus* specimens and between sites, and the significant difference in Ca concentration between specimens (e.g., Rosenberg, 1973, and references therein).

Phosphorus concentrations vary from one transect to the other but overall these variations remain nonsignificant at the specimen and site level. These differences might reflect the composition of the organic fraction within the shell where organic matrix composition may vary between sulphur or phosphorus dominated (e.g., Borbas et al., 1991; Crenshaw, 1982; Reddy, 1977; Shirai et al., 2014; Wheeler & Sikes, 1984), resulting in different P concentrations between transects without affecting the overall concentration variation between specimen and site.

Both Li and Sr appear to be affected by a combination of environmental and biological/physiological parameters owing to the fact that statistical testing revealed significant differences in Li/Ca and Sr/Ca ratios between locations and individuals. The Sr/Ca ratio in corals and foraminifera is commonly used as proxy for SST (e.g., Austin & James, 2008, and references therein); however, no clear direct relationship was found here. Sr/Ca ratios in mollusks have been reported to vary with growth rate and/or metabolism (e.g., Austin & James, 2008; Gillikin et al., 2005b; Lorrain et al., 2005; Poulain et al., 2015). These findings are consistent with studies on a number of bivalve species (e.g., Pannella & MacClintock, 1968, and references therein; Schöne et al., 2002, 2003; Schwartzmann et al., 2011). Studies on the effect of mineralogy, salinity and temperature on Li/Ca, and the Li isotopic composition of nonbiogenic CaCO₃ compared to biogenic CaCO₃,

have concluded that there is limited biological control on Li incorporation into biogenic CaCO_3 (Marriott et al., 2004). Our findings suggest a combination of biological (metabolism and growth rate) and environmental parameters, whereby environmental fluctuations and differences between sites drives the significant. This explains the significant difference in Li/Ca found between individuals and transects in the present study. Marriott et al. (2004) also reported a strong increase in Li/Ca with salinity in calcite but not in aragonite. Marmion Lagoon shells show the lowest Li/Ca ratios, 0.0015 mmol/mol, across the LA ICP-MS transects, with peaks at ~ 0.01 mmol/mol. Freshwater discharge has been noticed in Marmion Lagoon and shells from this site are aragonite dominated so no particular increase would be expected based on Marriott et al.'s (2004) results. The Li/Ca peaks found may be explained by the small calcite fraction present in the shells (3–11%). Given that the 75 μm laser beam diameter was larger than the average crystallite size (64 nm for aragonite and 26.9 nm for calcite), the La ICP-MS results will reflect the average composition of multiple crystals of aragonite and calcite. Peaks in spot traverses might represent an area of the shell dominated by calcite. Although some level of control (biological and environmental) is indicated by the Li/Ca ratios, the statistically determined significant difference between individuals and between transects suggests that the Li/Ca ratio is not a well-defined proxy for environmental parameter reconstructions in the case of *T. torquatus*. It seems too many factors affect the incorporation of Li in *T. torquatus*.

The Mg and S concentration in *T. torquatus* shells show no significant difference between sites, individuals or transects, which suggests their incorporation is biologically mediated at the species level. This is consistent with the findings of Shirai et al. (2014). Harris (1965) reported that Mg concentration in mollusk shell material is controlled principally by the mineralogy of the shell and hence geographical location has little control on shell composition. Here there is no significant difference in Mg concentration between shells or sites but the shells from Hamelin Bay have a distinct mineralogy (calcite dominated) compared to shells from the other sites. The variation of Mg/Ca ratios between geographical location is indirectly linked to environmental factors; geographical location affects the Mg concentration through thermodynamics applied to biogenic precipitation which should have resulted in significantly different Mg/Ca ratios between shells from different locations.

Mineralogy, along with temperature and salinity, are described as secondary to kinetics and/or metabolic processes in influencing the concentration of Sr in mollusk shells (Harris, 1965). Furthermore, Sr/Ca ratios are described as biologically mediated because of the correlation found between Sr/Ca, S/Ca and microstructure (Shirai et al., 2014). Here, Sr concentration is significantly different between individuals and between sites, which supports a combination of environmental and biological influences. Variations in environmental conditions influence shell properties, such as mineralogy or growth rate, which in turn affect the incorporation of Sr into the shells of *T. torquatus* through preferential incorporation/discrimination, for example. Significant differences were found only at the individual level for Ca, Ba, and Pb content, suggesting that the incorporation of these elements in the shell material is also biologically mediated and specific to each individual through particular growth rates and metabolism. The concentration of these elements does not vary significantly between sites.

Carré et al. (2006) demonstrated the presence of an active selective elemental pathway and Zhao et al. (2017) showed the competition along the same pathway between Ca, Mn, Cu and Pb, independently to the transport pathway of Mg, Sr and Ba. The biological control found here on Ca, Mg, P, S, Sr, Ba, and Pb concentrations in *T. torquatus* shells supports the postulation of an active selective pathway through the calcifying mantle. The concentration of Li is too variable for any conclusions to be drawn about an active pathway for this element.

5. Conclusions

Shells of the gastropod *Turbo torquatus* analyzed using crystallographic and geochemical techniques (pXRD, CRM, EPMA, and LA ICP-MS) reveal a composite mineralogy and suggest that a combination of controlling factors influenced their geochemical composition. The shells from Rottneest Island and Marmion Lagoon are principally composed of aragonite with a small calcitic fraction whereas the samples from Hamelin Bay are calcitic with a small aragonitic fraction. SST affects the aragonite:calcite ratio with differences as low as 1°C changing the dominant phase from aragonite in “warmer” locations (Marmion Lagoon and Rottneest Island) to calcite in the “cooler” location (Hamelin Bay). Although the level of Mg^{2+} substitution is below 4 mol %, all three sites show signs of ionic substitution. Ionic substitution in all shells appears to

follow preferential incorporation were Sr^{2+} is preferentially incorporated into the bulk aragonite and Mg^{2+} into the bulk calcite. The similar concentration of Mg between aragonite- and calcite-dominated shells shows Mg^{2+} can also be incorporated on the crystal surface. The lattice distortions found here are consistent with other studies on biogenic CaCO_3 .

T. torquatus was found to exert control over the incorporation of all elements tested (with the possible exception of Li) but in different ways. Elemental analyses reveal Li concentration is too highly variable to be used as a proxy for environmental parameters. Magnesium and S concentrations in the shells are biologically mediated at the species level and, therefore have limited value as an environmental proxy, but may have utility as a physiological proxy if future work can calibrate its relation to metabolic activity. Calcium, Ba, and Pb concentrations in the shells are also biologically mediated but at the individual level, implying the effect of growth rate and metabolism is different in each individual. The Sr/Ca ratio seems to be the best proxy for environmental properties, particularly SST, but controlled experiments need to be undertaken to more precisely identify the biological effect involved during the precipitation of the shells.

The dominant biological control, independent of environmental variations (e.g., no significant difference in elemental concentrations between geographical locations) found in *T. torquatus* supports the proposal of an active selective elemental pathway across the calcifying mantle.

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