

Strontium, magnesium, and barium incorporation in aragonitic shells of juvenile *Arctica islandica*: Insights from temperature controlled experiments



Alan D. Wanamaker Jr.^{a,*}, David P. Gillikin^b

^a Iowa State University, Department of Geological and Atmospheric Sciences, Ames, IA 50011, USA

^b Union College, Department of Geology, Schenectady, NY 12308, USA

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ABSTRACT

In order to constrain spatial and temporal temperatures and environmental conditions in the North Atlantic Ocean during the Holocene, high-resolution (seasonal to annual) marine proxies with excellent chronological constraints are needed. The long-lived ocean quahog, *Arctica islandica*, which has the potential to provide a precise annually-dated record, via crossdating techniques, is a fairly well-developed and tested marine proxy archive. In particular, oxygen isotopes derived from *A. islandica* shell carbonate have provided a wealth of information on marine climate and ocean circulation dynamics, however, shell-derived oxygen isotopes are influenced by both the isotopic source water signature (covarying with salinity) and seawater temperature. If seawater isotopic signature is not known, temperature reconstructions become challenging. Thus, an independent technique to estimate past seawater temperatures is highly desired, however based on previous studies on adult and juvenile clams, the utility of elemental ratios in *A. islandica* shell material as environmental proxies remains questionable. To further evaluate the influence of seawater temperature on elemental and isotopic incorporation during biomineralization, *A. islandica* shells were grown at constant temperatures under two regimes during a 16-week period from March 27 to July 21, 2011 at the Darling Marine Center in Walpole, Maine. Individual juvenile clams were stained with calcein and cultured at 10.30 ± 0.30 °C for six weeks. After this, the clams were again stained with calcein and cultured at 15.00 ± 0.40 °C for an additional 9.5 weeks. Average salinity values were 30.20 ± 0.70 and 30.70 ± 0.70 in the first and second phases of the experiment, respectively. Continuous sampling within and across the temperature conditions (from 10.30 °C to 15.00 °C) coupled with the calcein markings provided the ability to place each sample into a precise temporal framework and to establish exact average growth rates for the shells sampled. After accounting for changes in the isotopic composition of seawater, oxygen isotopes from one sampled shell effectively recorded seawater temperatures during the study and also gave confidence to the temporal fit of the data. Elemental ratios (Sr/Ca, Mg/Ca, Ba/Ca) from five aragonitic shells were determined via laser ablation inductively coupled plasma mass spectrometry. Sr/Ca and Mg/Ca data showed little coherence with temperature during the culture experiment, including the rapid 5 °C increase in seawater temperature. However, Ba/Ca ratios showed an inverse relationship with seawater temperatures although this relationship was noisy. Additionally, salinity interactions were present during the 15.00 °C treatment, further highlighting complex incorporation of elements during biomineralization. Incorporation of Sr, Mg, and Ba were strongly and variably impacted by growth rates. Combined, the results from these culture experiments demonstrate that Sr/Ca, Mg/Ca, Ba/Ca ratios in juvenile *A. islandica* shell material are dominated by physiological processes and thus not reliable as environmental proxies.

1. Introduction

High-resolution (seasonal to annual) marine archives that can be absolutely-dated (i.e., without error) are needed to better constrain spatial and temporal temperatures and other environmental conditions in the North Atlantic Ocean during the Holocene. The marine bivalve *Arctica islandica* is a key archive for high-resolution paleoceanography

(see Schöne, 2013 and Wanamaker et al., 2016 for recent reviews) because of its extreme longevity (Schöne et al., 2005a; Wanamaker et al., 2008a; Butler et al., 2013), it forms annual increments in its aragonitic shell (Thompson et al., 1980; Witbaard et al., 1994; Scourse et al., 2012), populations show synchronous gaping activity (Ballester-Artero et al., 2017) and growth (Marchitto et al., 2000; Butler et al., 2009, 2013; Marali and Schone, 2015; Mette et al., 2016). Because shell

* Corresponding author.

E-mail address: adw@iastate.edu (A.D. Wanamaker).

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growth is synchronous within populations, crossdating (Black et al., 2016) is possible yielding an error-free chronology similar to dendrochronology (Fritts, 1971). The absolutely-dated growth chronology can then serve as a template for geochemical sampling. Thus far, light stable isotopes (carbon and oxygen) and radiocarbon (^{14}C) data have provided useful information on oceanographic conditions, seawater temperature seasonality, carbon dynamics, and ocean circulation (Weidman and Jones, 1993; Weidman and Jones, 1993; Schöne et al., 2005a, 2005b, 2011a; Wanamaker et al., 2008b, 2011, 2012; Mette et al., 2016; Reynolds et al., 2016, 2017). Despite the potential of *A. islandica* records in modern and ancient climates, an independent and reliable method to isolate seawater temperature changes from isotopic source water effects (e.g., Wanamaker et al., 2008b) in the shell carbonate remains elusive, although some progress at the microstructural scale (i.e., crystallographic orientation) is promising (Milano et al., 2017). While clumped isotope thermometry in mollusks (Henkes et al., 2013; Eagle et al., 2013) may prove useful for reconstructing the relatively small late Holocene seawater temperatures (compared to glacial/interglacial climates) in the coming years as methodological advancements help reduce errors (better signal-to-noise ratio), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) techniques offer the potential to rapidly measure element-to-calcium ratios in biogenic or skeletal carbonates at a very high spatial and thus temporal resolution allowing researchers to evaluate the potential proxies of environmental conditions.

Element-to-calcium ratios in some biogenic or skeletal carbonates have proven to be reliable proxies of seawater temperature, providing an independent method to estimate marine conditions. Although there has been demonstrated success in using Sr/Ca or Mg/Ca ratios in foraminifera, corals, and coralline algae to estimate past seawater temperatures (e.g., Nurnberg et al., 1996; Beck et al., 1992; DeLong et al., 2007; Hetzinger et al., 2009) very little consistent progress has been demonstrated with element-to-calcium ratios in mollusks, despite substantial efforts (e.g., Klein et al., 1996a, 1996b; Vander Putten et al., 2000; Lazareth et al., 2003; Takesue and van Geen, 2004; Gillikin et al., 2005; Lorrain et al., 2005; Freitas et al., 2005, 2006; Carré et al., 2006; Wanamaker et al., 2008c; Elliot et al., 2009; Thebault et al., 2009; Schöne et al., 2011b; Schöne, 2013; Yan et al., 2013; Poulain et al., 2015; Füllenbach et al., 2015, 2017; Marali et al., 2017a).

Studies investigating the usefulness of Mg/Ca and Sr/Ca ratios from natural populations in juvenile and adult shells of the bivalve *A. islandica* as environmental proxies have been conflicting, often illustrating complex heterogeneities in element-to-calcium ratios at the micrometer scale (e.g., Eplé, 2004; Foster et al., 2008, 2009; Toland et al., 2000; Schöne et al., 2010; Schöne et al., 2011b; Schöne, 2013; Shirai et al., 2014; Füllenbach et al., 2017). Hart and Blusztajn (1998) reported a Sr/Ca temperature calibration on one *A. islandica* shell as a footnote in their paper. Their calibration is difficult to assess because they do not show any data aside from a regression equation. Since then, however, both Sr/Ca and/or Mg/Ca in *A. islandica* shells have been difficult to match to seawater temperature (Foster et al., 2008, 2009; Schöne et al., 2010, 2011b; Liu et al., 2015; Marali et al., 2017a). The lack of a consistent relationship between environmental conditions and Mg/Ca or Sr/Ca ratios in *A. islandica* shells is likely due to physiological processes during biomineralization (e.g., Foster et al., 2009). However, very few “culture” experiments have been conducted on *A. islandica* to evaluate the incorporation of elements and their isotopes into the shell with highly constrained growing conditions (e.g., Beirne et al., 2012; Hippler et al., 2013). Such experiments have the potential to isolate contributing factors (temperature, salinity, food availability and quality, growth rates, etc.) during biomineralization that are beyond thermodynamic controls. For example, Gillikin et al. (2006) grew mussels (*Mytilus edulis*) and determined that shell Ba/Ca ratios closely tracked water Ba/Ca ratios. Wanamaker et al. (2008c) conducted a similar study on this species, but altered temperature and salinity and showed that Mg/Ca ratios are not a robust recorder of seawater

temperature. Similarly, Poulain et al. (2015) raised aragonitic Manila clams (*Ruditapes philippinarum*) at a constant temperature but modified salinity while keeping seawater Mg/Ca and Sr/Ca ratios constant and found that shell Mg/Ca and Sr/Ca ratios were highly variable, while shell Ba/Ca ratios closely tracked changes in water Ba/Ca ratios.

Barium-to-calcium ratios in both aragonitic and calcitic mollusk shells usually show a fairly invariable background interrupted with sharp peaks (Gillikin et al., 2006, 2008; Marali et al., 2017b). The flat background has been correlated with water Ba/Ca ratios, while the peaks often remain unexplained (Gillikin et al., 2006), although some have claimed that these are due to spring phytoplankton blooms (Stecher et al., 1996; Vander Putten et al., 2000; Lazareth et al., 2003; Thebault et al., 2009). Marali et al. (2017b) demonstrated that Ba/Ca signatures in *A. islandica* shells strongly covary regionally (for example, Iceland, Faroe Islands, Irish Sea, Gulf of Maine), likely reflecting some sort of environmental driver. Inorganic aragonite precipitation experiments have shown Ba/Ca partitioning coefficients to be inversely related to temperature (Dietzel et al., 2004; Gaetani and Cohen, 2006). In cultured aragonitic corals (*Favia fragum*), Ba/Ca partitioning coefficients also varied inversely with seawater temperature (Gonneea et al., 2017); however, additional environmental effects (upwelling, fresh-water input) or physiological parameters may also influence Ba/Ca ratios in corals (Allison and Finch, 2007; Gonneea et al., 2017).

This study aims to quantify the incorporation of magnesium (Mg), strontium (Sr), and barium (Ba) into the shell aragonite of juvenile *A. islandica* clams cultured under controlled temperature conditions. A major goal of this work is to establish if the element-to-calcium ratios are consistently reflecting seawater temperature conditions, or whether physiological processes dominate the incorporation of the elements. The results from this study are compared and integrated with previous work on adult *A. islandica* shells from field collections. The goal of this portion of the work is to determine if the physiological influences noted here on Mg/Ca, Sr/Ca, and Ba/Ca ratios in juvenile shells can (or should) be transferred to adult clams. In other words, are the mechanisms of elemental incorporation similar or different for juvenile and adult specimens? Additionally, we utilize the oxygen isotope signatures in shell material to constrain biomineralization processes during the culture experiment (such as the time it takes for the shell geochemistry to respond to the sudden 5 °C increase in seawater temperature) and to further evaluate the utility of this thermometry tool.

2. Materials and methods

2.1. Collection and transplantation to flow-through seawater tanks

A commercial quahog fishing vessel, F.V. three of A Kind, was employed on November 21, 2009 to collect live *A. islandica* via a bespoke commercial dredge in the Gulf of Maine. Samples were collected from a depth of 82 m at 44°26'9.829"N, 67°26.0'18.045"W off Jonesport, Maine. Animals were transported to the Darling Marine Center (University of Maine, Orono) in Walpole, Maine and placed in flow-through seawater tanks (see Beirne et al., 2012 for additional details) until the beginning of the experimental period. These clams (< 1 year old) were exposed to ambient salinity, temperature, and food conditions only.

2.2. Transfer to the experimental tank and experimental design

A total of 50 juvenile (~3 year; initial shell height based on 30 individuals = 36.14 ± 3.18 mm; maximum = 43.15 mm; minimum = 26.46 mm) *A. islandica* were grown in a muddy sediment (collected from the local estuary) in a temperature-controlled environment at the Darling Marine Center in Walpole, Maine, USA. The Darling Marine Center is located adjacent to the tidally-influenced Damariscotta River estuary. Animals were grown during the spring and early summer of 2011 (March 27 to July 21, 2011) under two temperature settings

(10.30 °C ± 0.20 and 15.00 °C ± 0.30; Tidbit® temperature logger ± 0.20 °C). Prior to the experiment (3/21/2011 to 3/26/2011) ambient seawater temperature and salinity were 3.58 ± 0.08 °C and 30.96 ± 0.03 respectively. Ambient seawater from −10 m was pumped into the flowing seawater labs, where the water flow was adjusted (average of 6 l per min) and the water was heated (using two 800 W titanium heaters) or cooled (using ambient seawater) in a 200-liter tank to maintain the desired temperature. Seawater was then pumped (Quiet One 3000) into a 500-l holding tank (121.92 cm × 129.92 cm × 45.72 cm) at the same flow rate, which housed the clams (Fig. S1). The tank water turnover rate was once (500 l) per ~83 min and seawater was returned to the Damariscotta River estuary via an established outflow at the Darling Marine Center.

Average salinity values were 30.20 ± 0.70 and 30.70 ± 0.70 (Hydrolab® MiniSonde ± 0.20) in the first and second phases of the experiment, respectively. Prior to the start of the growth experiment, individuals were immersed and marked with a biomarker stain, calcein, for 48 h according to methods outlined by Beirne et al. (2012). The clams (N = 30) were exposed to 10.30 °C seawater for 47 days (March 27 to May 12, 2011), then briefly removed from the growth experiment and re-marked with calcein stain. These animals, plus an additional 20 clams, were reintroduced/introduced to the growth experiment and exposed to 15.00 °C seawater for 69 days (May 14 to July 21, 2011). The clams were only exposed to ambient food during the entire experiment. Average linear shell growth for the original 30 clams was determined by digital calipers (± 0.10 mm) after both temperature treatments. Exact average growth rates (± 1.00 μm) for each part of the experiment were determined by calcein marks for the five randomly selected shells reported in this study, which were photographed and measured (details below). On July 21, 2011, all animals were harvested. The soft tissues were removed and the intact valves were rinsed and air-dried. Samples were then shipped to Iowa State University.

2.3. Seawater chemistry

Sr/Ca and Mg/Ca ratios of seawater are assumed to be constant based on conservative mixing principles (Broecker and Peng, 1982). This assumption is further supported from empirical evidence presented by Wanamaker et al. (2008c) during a similar study that was also conducted at the Darling Marine Center. Wanamaker et al. (2008c) reported seawater values for Mg/Ca = 5.01 ± 0.18 (mmol/mol) and Sr/Ca = 8.09 ± 0.17 (mmol/mol), and these seawater ratios remained fairly stable over a four month experiment (July through October 2003). Additionally, average salinity values were above 30 during this study. The authors are not aware of any time-series of Ba/Ca ratios of seawater at the Darling Marine Center, or the nearby region, although

Ba/Ca values in seawater are generally expected to follow salinity in an inverse fashion (e.g., Gillikin et al., 2006). Further, Gillikin et al. (2008) provide context regarding Ba cycling and bivalves, while Horner et al. (2015) provide a comprehensive review of Ba cycling in the marine environment.

2.4. Shell preparation, imaging and sampling

Five shells (TC1, TC2, TC3, TC6, TC7) were sectioned along the maximum growth axis (see Mette et al., 2016) with a Buehler IsoMet low speed saw producing 3–4 mm thick sections. Thick sections were lightly sanded with decreasing grit-size silicon carbide grinding paper (Buehler; P120, P400, P800), rinsed in deionized water, air-dried, and finally imaged in reflected and UV light using a Olympus BX-53 compound petrographic microscope with a 17MP Peltier-cooled camera with Prior computer-controlled stage. These images, which illustrated the calcein marks, were used to determine exact average growth rates for the shells sampled (corresponds to linear growth rates) for the two phases of the experiment and to guide sampling (Fig. 1). Although daily/weekly growth rates were possibly variable within each phase of the experiment, the calcein marks only allowed for average growth rates (in mm/week) to be determined. All shells were sampled for geochemical analysis in the outer shell layer (outer sublayer) along the ventral margin from the sectioned material (Fig. 1; see Schöne, 2013 for an example).

2.5. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

Five shells were sampled every 250 μm from the most recent growing edge prior to the experiment (Fig. 1). Element-to-calcium ratios were determined by laser ablation (LA) along growth transects using inductively coupled mass spectrometry (LA-ICP-MS) in the Geochemistry Laboratory at Union College as described in Gillikin and Dehairs (2013). The system is comprised of a CETAC LSX-213 frequency quintupled Nd:YAG laser (λ = 213 nm) coupled to a Perkin Elmer Elan 6100 DRC ICP-MS. Helium was used as the carrier gas (600 ml/min), which was mixed with argon after the ablation cell (800 ml/min). Spot size was set to 50 μm and a 15 s pre-ablation was used for gas blank corrections. Laser energy was set to 100% and the laser shot frequency was 10 Hz with a burst count of 600. The isotopes ²⁶Mg, ⁴³Ca, ⁸⁶Sr, and ¹³⁸Ba were monitored and data were reduced using the LA-ICP-MS data reduction program Iolite (<https://iolite-software.com/>). ⁴³Ca was used as the internal standard and was assumed to be 40% by mass. The NIST612 glass standard was used for calibration (values from Pearce et al., 1997) and the USGS MACS-3, a pressed carbonate pellet, (values

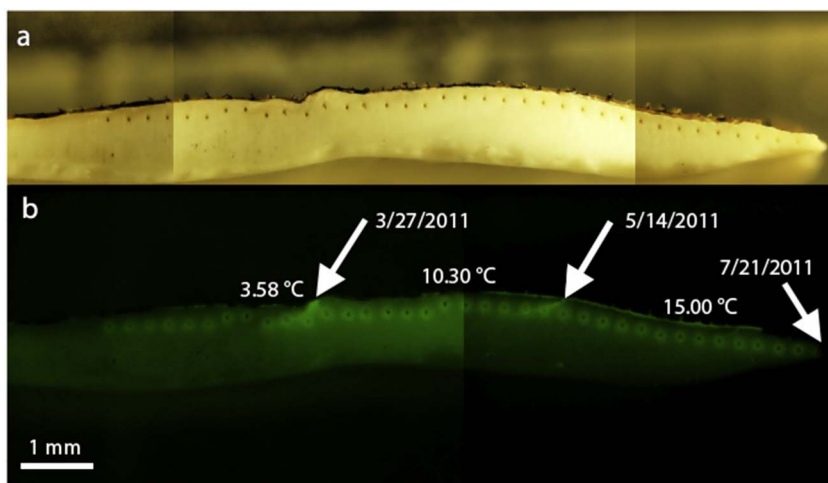


Fig. 1. Photomosaic images of sectioned shell TC3 (magnification = 2 ×) in reflected light (a) and UV light (b). Laser ablation holes (spaced every 250 μm) are illustrated in (a) and the two calcein marks (with respective dates: b) separate the different shell portions grown under different seawater temperature conditions (ambient marine 3.58 °C and ambient laboratory culture at 10.30 °C and 15.00 °C). All shells were harvested on 7/21/2011.

from USGS, 2011) was used to check the calibration. Relative standard deviations on all analyses of the MACS-3 standard were < 6.5% and were within 10% of the recommended value (N = 25), which suggests a robust LA-ICP-MS calibration and excellent reproducibility.

2.6. Isotopic analyses

2.6.1. Seawater oxygen isotopes

Seawater was collected five times during the experiment. These samples were measured for oxygen isotopic composition using a ThermoFinnigan Delta Plus XL isotope ratio mass spectrometer (IRMS) in the Department of Geological and Atmospheric Sciences at Iowa State University. Seawater (0.5 ml) was pipetted into a 12 ml Labco Exetainer® vial, capped and then flushed for 60 s with a 1% CO₂ and He mixture. Samples equilibrated (without phosphoric acid) at 24 °C for approximately 18 h. Seawater analyses were measured using a Gas Bench, with an automated sampler (CombiPal), coupled to the IRMS. International isotopic standards (VSMOW, OH-3) were used as reference materials to place samples on the international scale, Vienna Standard Mean Ocean Water (VSMOW). The analytical uncertainty was ± 0.12‰ (2 standard deviations). The measured oxygen isotopic values were then compared to predicted oxygen isotope values using the isotope/salinity mixing line for the western Gulf of Maine developed by Whitney et al. (2017; see supplementary materials) (Eq. (1)).

$$\delta^{18}\text{O}\text{‰} = (\text{Salinity} \times 0.20) - 7.79 \quad (1)$$

2.6.2. Shell aragonite oxygen isotopes and thermometry

Shell TC2 was microdrilled (Mercantek) every 500 µm, yielding ~200 µg of calcium carbonate powder for isotopic analyses. Shell oxygen isotope analyses were performed on a ThermoFinnigan Delta Plus XL IRMS, in the Department of Geological and Atmospheric Sciences at Iowa State University. Carbonate analyses were measured using a Gas Bench, with an automated sampler (CombiPal), coupled to the IRMS. International isotopic standards used were NBS-18, and NBS-19. At least one standard was run for every five samples analyzed on the Gas Bench. Powdered carbonate samples were placed in a low temperature oven (~50 °C) to remove any atmospheric moisture and then placed in a 12 ml Labco Exetainer® vial, capped and flushed with ultrapure helium gas. 100 µl of > 95% phosphoric acid was then injected into the vial, and the carbonate sample was allowed to react with the acid in the heating block of the GasBench at 34 °C for approximately 18 h. All carbonate isotope values are reported relative to the

international standard Vienna PeeDee Belemnite (VPDB). Analytical uncertainty (2 standard deviations) was ± 0.14‰ for oxygen for all samples presented here. The long-term reproducibility of this mass spectrometer is ± 0.18‰ (2 standard deviations) for oxygen.

Using the modified Grossman and Ku (1986) aragonite transfer function (Eq. (2)); for details regarding the modification, see Dettman et al., 1999; Gonfiantini et al., 1995), shell oxygen isotope values and predicted seawater oxygen isotopic composition (Eq. (1)) were used to compare actual seawater temperatures versus predicted seawater temperatures. Three-day averages of salinity/oxygen isotopic composition of seawater and temperature were used to represent the time averaging from sampling.

$$T(^{\circ}\text{C}) = 20.60 - 4.34 \times (\delta^{18}\text{O}_{\text{aragonite}} - (\delta^{18}\text{O}_{\text{water}} - 0.27)) \quad (2)$$

2.7. Determination of statistical significance for environmental interactions

Relationships were considered to be statistically significant when p-values were 0.05 or lower using the two-tailed approach; p-values were calculated via Graph Pad Software (<http://www.graphpad.com/quickcalcs/pvalue1.cfm>) by inputting Pearson correlation values (r) and the degrees of freedom (N-2).

3. Results

3.1. Environmental conditions

For the six days prior to the experiment (3/21/2011 to 3/26/2011) average daily ambient seawater temperature and salinity were 3.58 ± 0.08 °C and 30.96 ± 0.03 respectively (Fig. 2). In the first phase of the experiment, the average daily seawater temperature and salinity were 10.30 ± 0.20 and 30.20 ± 0.70 , respectively from March 27 to May 12, 2011 (47 days). In the second phase of the experiment, the average daily seawater temperature and salinity were 15.00 ± 0.30 and 30.70 ± 0.70 , respectively from May 14 to July 21, 2011 (69 days) (Fig. 2).

Predicted seawater oxygen isotopic composition based on measured salinity (hourly averages) and Eq. (1) are shown in Fig. 3. The actual seawater oxygen isotopic values are from discrete sampling times and thus better compared to hourly rather than daily averages. In all cases, measured seawater oxygen isotopic composition is within daily-predicted ranges. Greater variability in hourly salinity occurred in the first phase of the experiment. This increased variability is consistent with

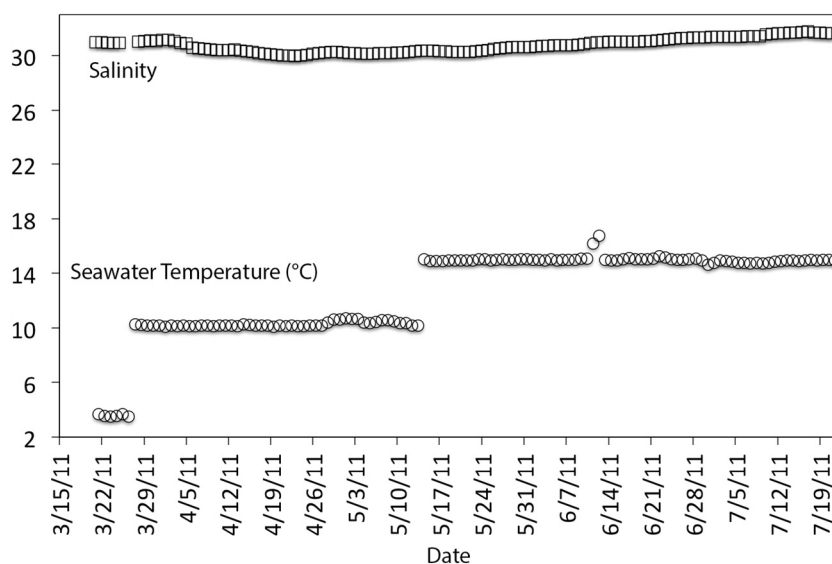


Fig. 2. Daily averages of seawater salinity (open squares) and temperature (open circles) conditions during the experiments are shown.

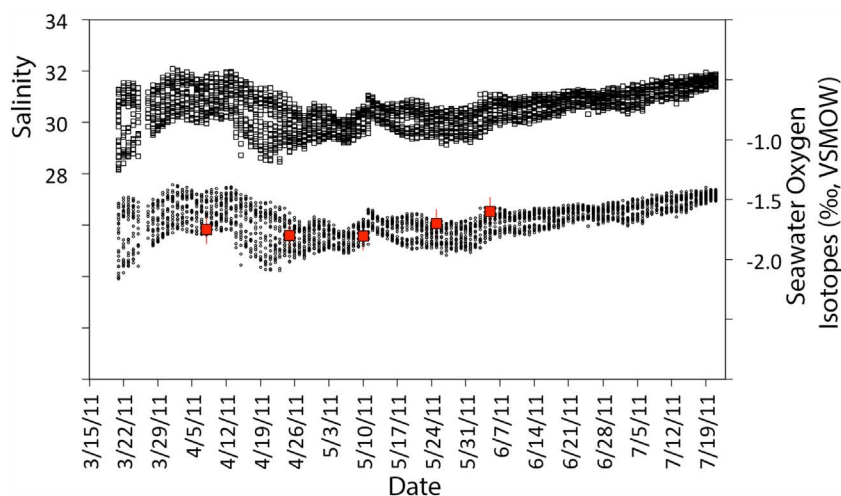


Fig. 3. Hourly salinity (open squares; left y-axis) and calculated oxygen isotopic composition of seawater (open circles; right y-axis) using Eq. (1) (Whitney et al., 2017) are shown. Measured oxygen isotopic values of seawater (red squares; right y-axis) are also shown for comparison. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Summary of shell growth data (N = 5) is shown for each temperature treatment.

Shell ID	Temperature (°C)	Salinity	Growth (mm)	Growth rate (mm/week)
TC1	10.30	30.20	4.30	0.64
TC2	10.30	30.20	3.06	0.46
TC3	10.30	30.20	3.25	0.48
TC6	10.30	30.20	3.75	0.56
TC7	10.30	30.20	4.50	0.67
TC1	15.00	30.70	4.00	0.41
TC2	15.00	30.70	3.33	0.34
TC3	15.00	30.70	3.75	0.38
TC6	15.00	30.70	1.75	0.18
TC7	15.00	30.70	4.25	0.43

more variable coastal salinity values during the snowmelt season in Maine (Fig. 3).

3.2. Shell growth

Based on digital caliber measurements, the average shell growth (N = 30) during the first phase of the experiment was 2.4 mm with a growth rate of 0.36 mm/week. The average shell growth during the second phase of the experiment was 3.2 mm with a growth rate of 0.33 mm/week. Exact average shell growth and growth rates for the five shells sampled for geochemistry are shown in Table 1. During the 10.30 °C experiment growth rates (N = 5) ranged from 0.46 to 0.67 mm/week with an average of 0.56 ± 0.09 mm/week. During the 15.00 °C experiment growth rates (N = 5) ranged from 0.18 to 0.43 mm/week with an average of 0.35 ± 0.10 mm/week. Exact average growth rates were 1.60 times higher at 10.30 °C compared to 15.00 °C and this difference is statistically significant based on a paired Student's *t*-test.

3.3. Shell oxygen isotopes and predicted seawater temperature

Shell $\delta^{18}\text{O}_{\text{aragonite}}$ values, from shell TC2, prior to and during the experiments are shown in Fig. 4. The lowest value occurred in shell portions (2.04‰) prior to the experiment. $\delta^{18}\text{O}_{\text{aragonite}}$ values decreased (note reverse scale) to 0.50 ± 0.06 ‰ and remained relatively steady during the 10.30 °C experiment. $\delta^{18}\text{O}_{\text{aragonite}}$ values further decreased to -0.62 ± 0.25 ‰ during the 15.00 °C experiment. Evidence of time averaging during sampling is apparent at the transition to 10.30 °C and 15.00 °C. These samples were not used in the above averages.

Calculated seawater temperatures based on shell TC2 $\delta^{18}\text{O}_{\text{aragonite}}$ values using measured salinity and Eqs. (1) and (2) are also shown in Fig. 4. To account for time averaging during shell sampling, a 3-day

salinity average was chosen for these temperature estimates.

3.4. Shell elemental incorporation

3.4.1. Seawater temperature effects

Element-to-calcium ratios, Sr/Ca, Mg/Ca, Ba/Ca, for five sampled shells (TC1, TC2, TC3, TC6, TC7) prior to and during the experiments are shown in Figs. 5, 6, and 7. Sr/Ca, Mg/Ca, and Ba/Ca data versus seawater temperature illustrate the impact, or lack of impact, of seawater temperature on incorporation of elements into the shell (see bi-plots in Figs. 5–7). Sr/Ca data show no relationship with seawater temperature ($r^2 = 0.02$; $p = 0.1200$) and Mg/Ca data show a very weak positive relationship ($r^2 = 0.05$; $p = 0.0064$) with temperature that is statistically significant. Ba/Ca data show a fairly strong inverse relationship ($r^2 = 0.56$; $p < 0.0001$) with temperature that is statistically significant. Dates are shown in Figs. 5–7 when clams were handled. In particular, Mg/Ca ratios were elevated after handling. When five elevated Mg/Ca ratio values are removed after handling on 5/8/2011 and 6/21/2011, the relationship does not change much ($r^2 = 0.06$; $p = 0.0070$) (see Supplementary Fig. S2).

3.4.2. Seawater salinity effects

Across both temperatures, Sr/Ca data show no relationship with seawater salinity ($r^2 < 0.01$; $p = 0.8500$) (Fig. 8a) and Mg/Ca data show a moderate positive relationship ($r^2 = 0.19$; $p < 0.0001$) with salinity that is statistically significant (Fig. 8b). After five elevated Mg/Ca ratio values are removed after handling on 5/8/2011 and 6/21/2011 (two values from TC3, two values from TC6, one value from TC7), the relationship improves substantially ($r^2 = 0.33$; $p < 0.0001$) (see Supplementary Fig. S3). Ba/Ca ratios do not yield a statistically significant relationship ($r^2 = 0.02$; $p = 0.1030$) with salinity (Fig. 8c).

Element-to-calcium data were regressed against salinity for the 10.30 °C and 15.00 °C treatments discretely to further evaluate possible salinity effects. At 10.30 °C Sr/Ca data were not related to salinity ($r^2 = 0.015$; $p = 0.1600$) (Fig. 9a), however a weak, statistically significant, salinity interaction at 15.00 °C was present ($r^2 = 0.13$, $p < 0.0001$) (Fig. 9b). At 10.30 °C, Mg/Ca data are not related to salinity ($r^2 < 0.001$; $p = 0.7600$) (Fig. 9c), whereas a moderate relationship ($r^2 = 0.21$; $p < 0.0001$) exists for 15.00 °C (Fig. 9d). Ba/Ca data were weakly related to salinity in the 10.30 °C treatment ($r^2 = 0.036$; $p = 0.0290$) (Fig. 9e). In the 15.00 °C treatment, salinity was related to Ba/Ca ratios ($r^2 = 0.21$; $p < 0.0001$) (Fig. 9f).

3.4.3. Growth rate effects

Exact average growth rates for the five sampled shells were compared to element-to-calcium ratios across both temperatures together

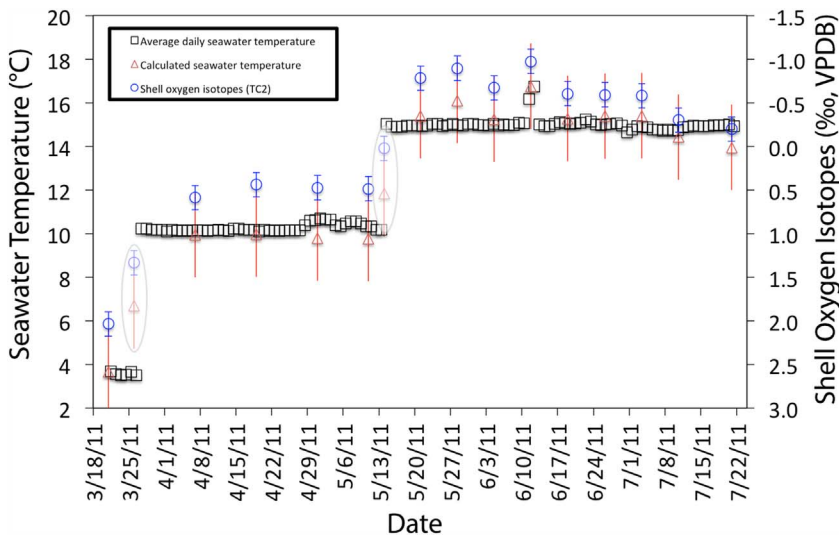


Fig. 4. Average daily seawater temperature data (open squares; left y-axis) and measured shell oxygen isotopic values from shell TC2 (blue circles; right y-axis and note reversed scale) are shown. Calculated seawater temperature (red triangles; left y-axis) using Eqs. (1) and (2) are also illustrated. Uncertainty estimates are described in the text. Two temperature transition shell isotope values (shown with ellipses) were not used in assessing oxygen isotope equilibrium with ambient seawater. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

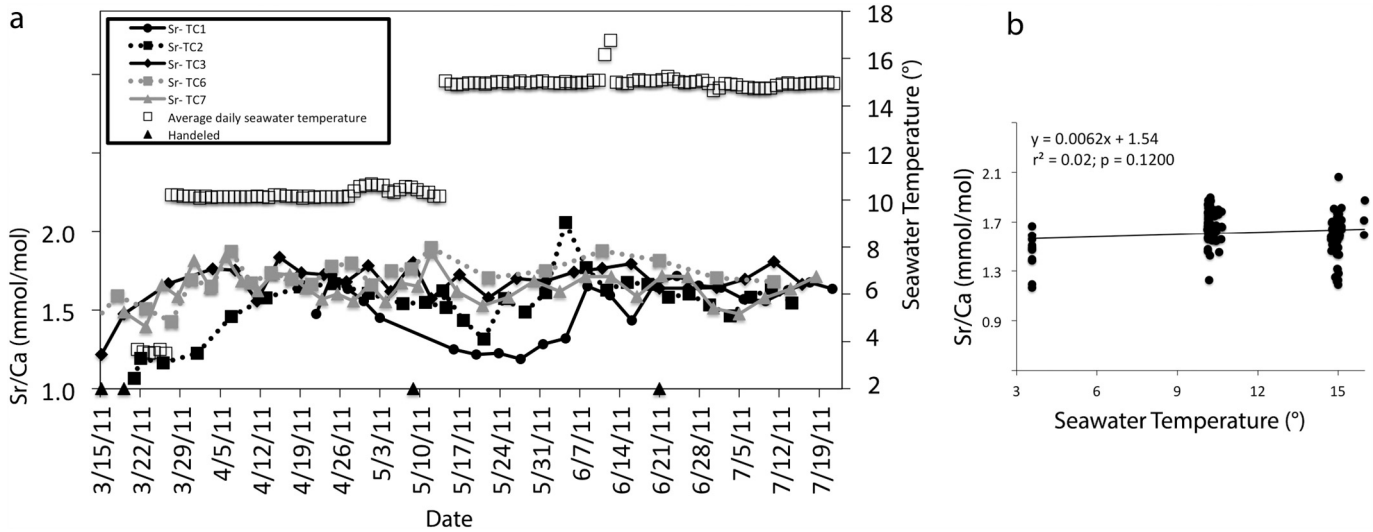


Fig. 5. Average daily seawater temperature data (open squares) and shell Sr/Ca ratios from five different clams (a). Biplot of Sr/Ca data versus average daily seawater temperature is also shown (b). The dates in which the clams were handled are noted with black triangles (a).

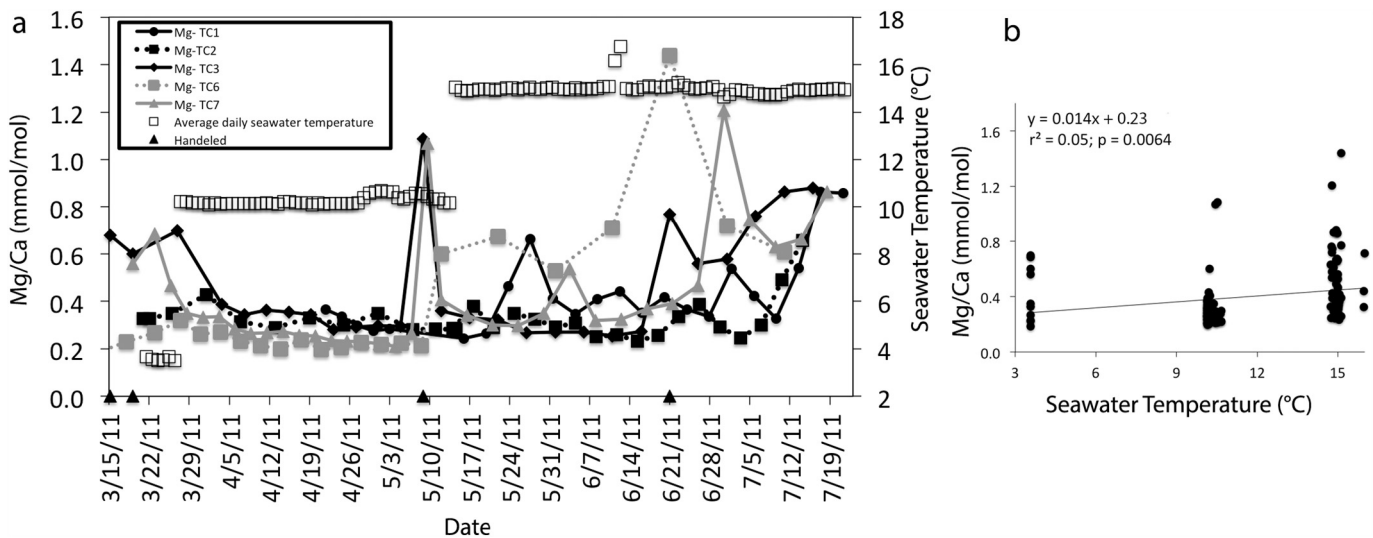


Fig. 6. Average daily seawater temperature data (open squares) and shell Mg/Ca ratios from five different clams (a). Biplot of Mg/Ca data versus average daily seawater temperature is also shown (b). The dates in which the clams were handled are noted with black triangles (a).

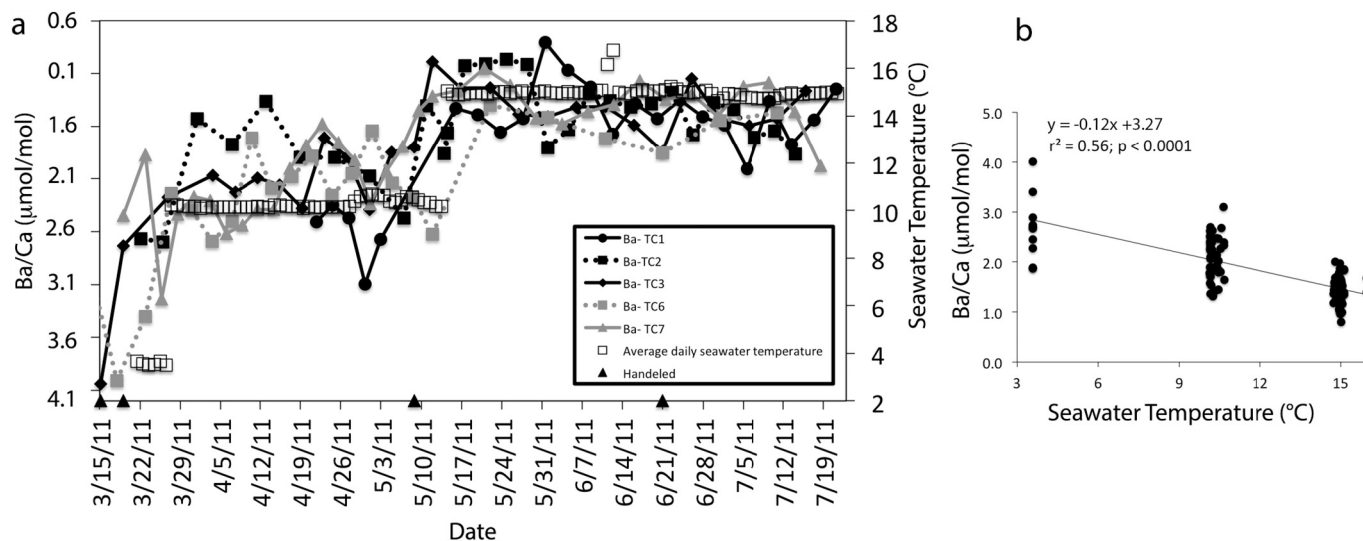


Fig. 7. Average daily seawater temperature data (open squares) and shell Ba/Ca ratios from five different clams (a; note the inverted scale for Ba/Ca ratios). Biplot of Ba/Ca data versus average daily seawater temperature is also shown (b). The dates in which the clams were handled are noted with black triangles (a).

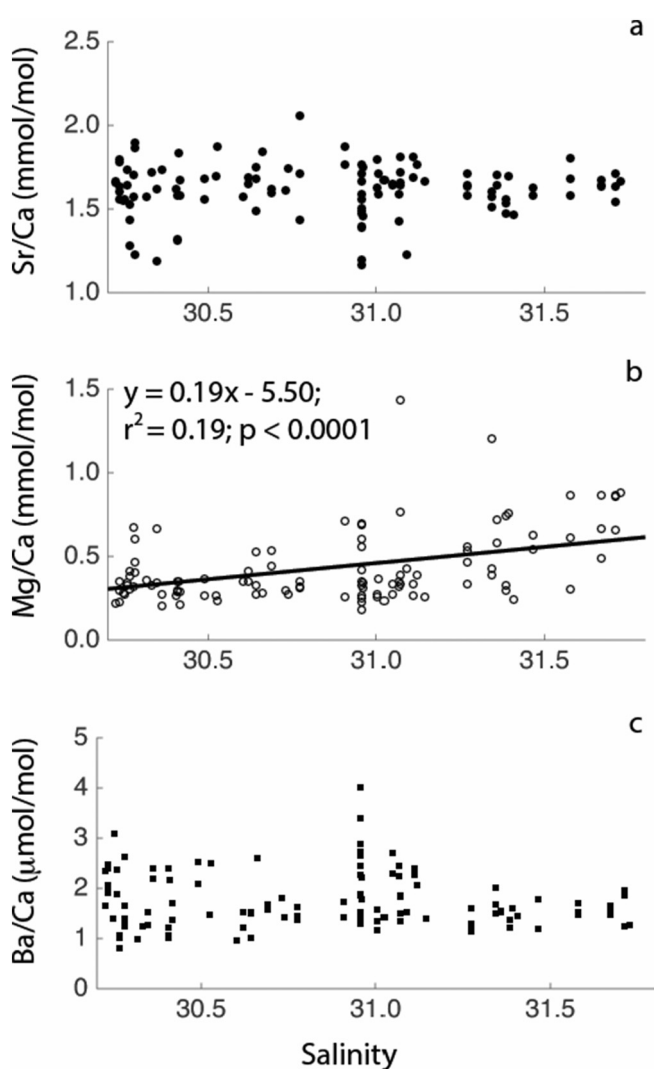


Fig. 8. Sr/Ca (a), Mg/Ca (b), and Ba/Ca (c) ratios versus salinity throughout the culture experiments are shown. Mg/Ca versus salinity yields a statistically significant relationship (b).

(10.30 °C and 15.00 °C combined) and for each temperature alone (Fig. 10, panels a–i). For both temperatures, Sr/Ca data were inversely related to growth rates ($r^2 = 0.20$; $p = 0.1919$), but this relationship is not statistically significant (Fig. 10a). In the 10.30 °C treatment, Sr/Ca ratios are not related to growth rates ($r^2 = 0.01$; $p = 0.8729$) (Fig. 10b), and the apparent inverse relationship ($r^2 = 0.61$; $p = 0.1197$) in the 15.00 °C treatment is not statistically significant (Fig. 10c). Mg/Ca data across both temperatures were statistically significant and inversely correlated with temperature ($r^2 = 0.58$; $p = 0.0107$) (Fig. 10d), however, when Mg/Ca ratios are regressed for each temperature treatment alone, no statistically significant relation between growth rates and temperature exist ($r^2 = 0.07$; $p = 0.6727$ for 10.30 °C; $r^2 = 0.47$; $p = 0.1973$ for 15.00 °C) (Fig. 10e, f). Ba/Ca ratios and growth rates were positively related and statistically significant for both temperatures combined ($r^2 = 0.46$; $p = 0.0305$) (Fig. 10g). In the 10.30 °C treatment, growth rates were positively correlated with temperature ($r^2 = 0.73$; $p = 0.0681$) (Fig. 10h) but this was not quite statistically significant. At 15.00 °C, growth rates and temperature were strongly inversely related ($r^2 = 0.95$; $p = 0.0062$) and statistically significant (Fig. 10i).

4. Discussion

4.1. Oxygen isotopes

In general, $\delta^{18}\text{O}_{\text{aragonite}}$ values reflect seawater temperatures and the changes in seawater temperature in a consistent manner (Fig. 4; note inverse scale). Utilizing the salinity record (Fig. 2) during the experiments and Eq. (1), $\delta^{18}\text{O}_{\text{aragonite}}$ values were transformed into seawater temperature estimates using Eq. (2). When considering the propagated random uncertainties ($[a^2 + b^2 + c^2]^{1/2}$, where a, b, and c are the three error sources) for seawater temperature estimates, one must consider the uncertainty in Eqs. (1) and (2) and the analytical uncertainty for $\delta^{18}\text{O}_{\text{aragonite}}$ measurements. In terms of temperature, Eq. (1) has an uncertainty of ± 1.26 °C based on the root mean squared error [RMSE] of 0.29‰ calculated using data from Whitney et al. (2017). Eq. (2) has an uncertainty of ± 1.38 °C (based on RMSE of all aragonite data and associated temperature model of Grossman and Ku, 1986). Finally, the analytical uncertainty in the $\delta^{18}\text{O}_{\text{aragonite}}$ measurements from this study is ± 0.60 °C (based on the 2 standard deviation uncertainty of 0.14‰). These combined uncertainties translate to a total error of ± 1.96 °C at

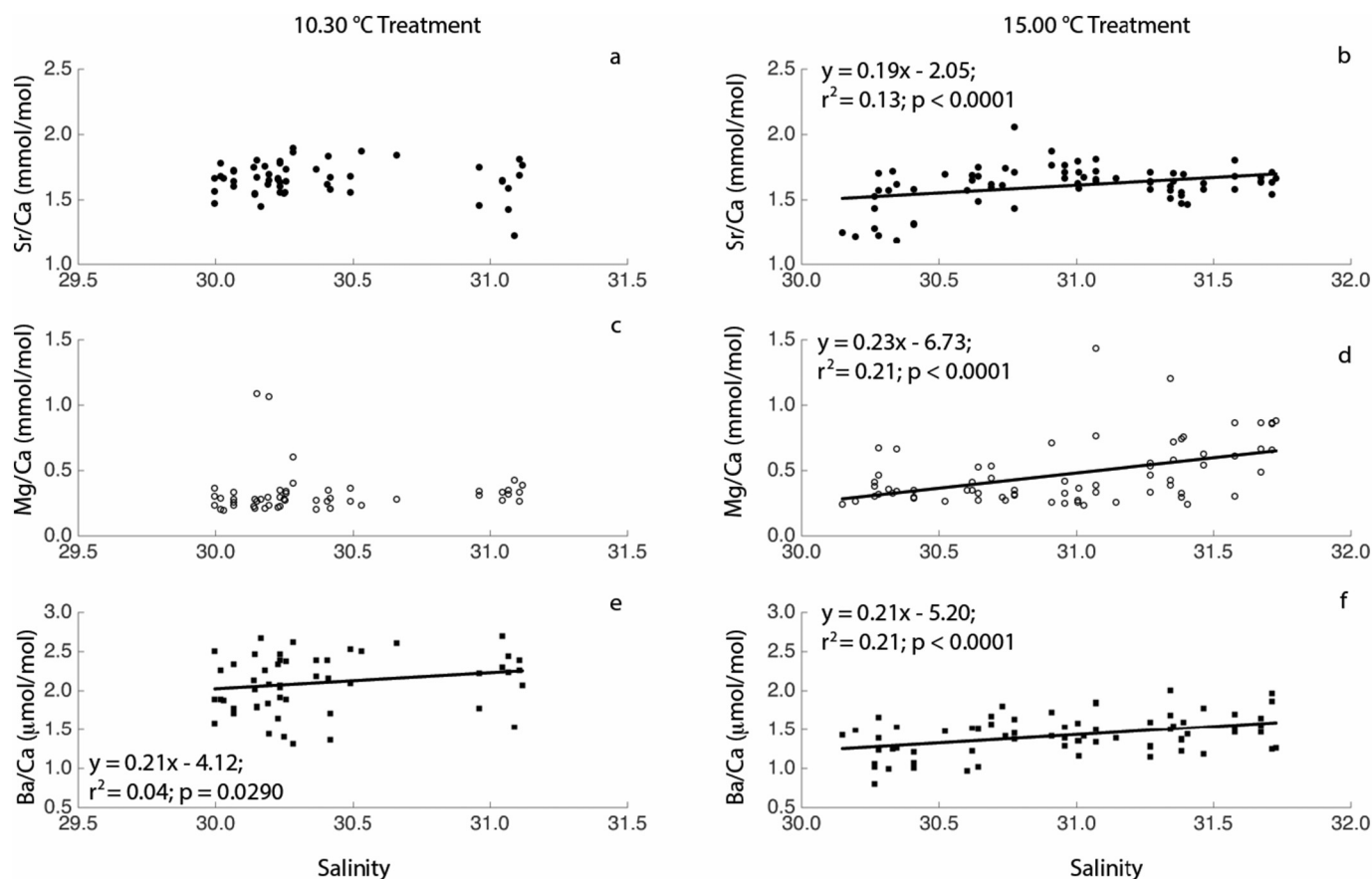


Fig. 9. Element to calcium ratios versus salinity for each temperature treatment are shown. Sr/Ca ratios, 10.30 °C treatment (a) and 15.00 °C treatment (b); Mg/Ca ratios, 10.30 °C treatment (c) and 15.00 °C treatment (d); Ba/Ca ratios, 10.30 °C treatment (e) and 15.00 °C treatment (f). Regression lines and associated equations are shown for statistically significant relationships (b, d, e, f).

the 95% confidence interval. After considering the total error (± 1.96 °C), every temperature estimate matches the actual temperature with the exception of two “transition” values (Fig. 4). Although it is encouraging that *A. islandica* appear to incorporate shell oxygen isotopes in equilibrium with ambient seawater, perhaps the largest benefit of showing the time-series of $\delta^{18}\text{O}_{\text{aragonite}}$ is that they illustrate the time it takes to respond to the experimental conditions in terms of biomineralization. Effectively, shell TC2 responded to the abrupt changes in temperature in a matter of days after considering the impacts of time averaging during sampling (Fig. 4). This result becomes more important in terms of biomineralization rates and processes when you consider the variable elemental incorporation noted in this study.

As noted by Mette et al. (this issue) geochemical replication is highly desired in such records, thus additional work with substantially more individual clams (e.g., Wanamaker et al., 2006, 2007) would be required to robustly demonstrate that *A. islandica* consistently incorporates oxygen into the shell carbonate in oxygen isotope equilibrium with ambient seawater. With that said, additional evidence using salinity data and salinity/isotope mixing lines as a surrogate for $\delta^{18}\text{O}_{\text{water}}$ conditions (Weidman and Jones, 1993; Mette et al., this issue) suggest that *A. islandica* deposit shell oxygen isotopes in equilibrium with ambient seawater.

It should also be noted that Grossman and Ku (1986) digested their aragonite samples at 50 and 60 °C, while our digestion temperature was 34 °C. Such a difference in digestion temperatures would likely cause an isotopic offset of $\sim 0.05\text{‰}$ in oxygen. However, because the samples were corrected based on isotopic standards that also were digested at the same temperatures (50 °C, 60 °C, and 34 °C), it is assumed that this potential effect is neutralized. Additionally, like Grossman and Ku (1986), we did not take into account the different fractionation factors

between our aragonite samples and the calcite standards (NBS-19 and NBS-18) that were used in this study (cf. Füllenbach et al., 2015). Therefore, we argue that a direct comparison of our isotopic data to the Grossman and Ku (1986) aragonite equation is valid.

4.2. Element-to-calcium ratios

Because of the experimental design used in this study, multiple potential physiological interactions could be isolated and examined. The results of this temperature-controlled, culture-based study strongly illustrate that Sr and Mg incorporation into the aragonitic shell material of *A. islandica* are controlled by physiological factors (or vital effects) rather than environmental controls. Although only data from juvenile clams are presented here, these results are consistent with other *A. islandica* studies that included adult specimens (Foster et al., 2008, 2009; Schöne et al., 2011b; Marali et al., 2017a). As shown by Marali et al. (2017b) Ba/Ca ratios in adult and juvenile *A. islandica* shells from specific populations show synchronous changes. Compared to Mg and Sr, Ba incorporation was more consistent among the shells studied here. A possible mechanism that may explain the regional synchronous Ba incorporation in *A. islandica* shells noted by Marali et al. (2017b) and the work presented here is variable growth rates. If regional Ba incorporation into *A. islandica* shells were related to growth rates, that would explain why both increment widths and Ba/Ca ratios can be used in crossdating (e.g., Black et al., 2016; Marali et al., 2017b). Although shell Ba/Ca ratios were strongly and inversely related to seawater temperature in this study, growth rate and salinity effects confound this signal and point to physiological controls during Ba incorporation. Hence, using Ba/Ca ratios in *A. islandica* as a paleothermometer or a paleosalinity proxy do not look promising.

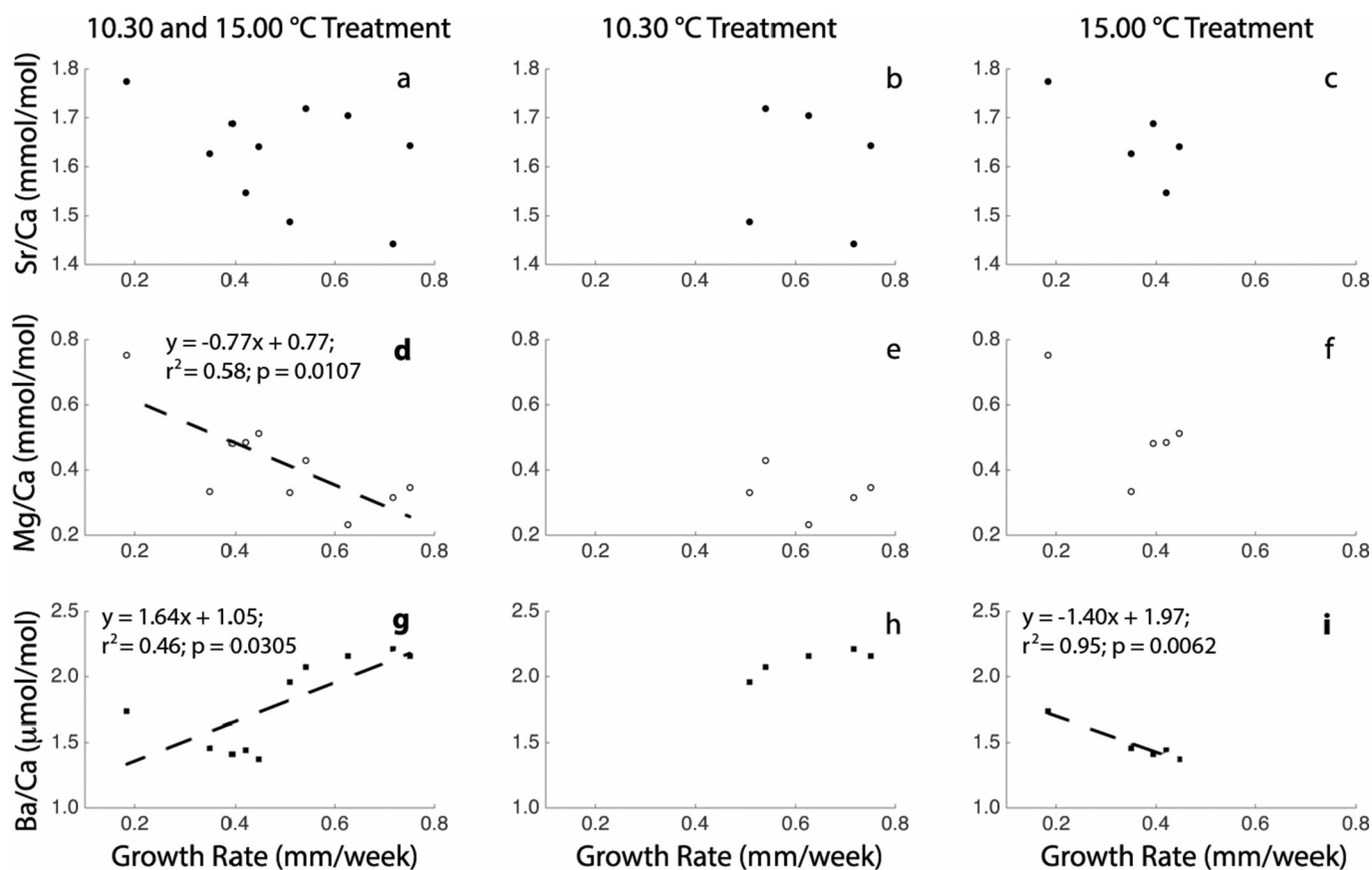


Fig. 10. Growth rate effects on element to calcium ratios by each temperature treatment are shown. Sr/Ca ratios, 10.30 and 15.00 °C treatments combined (a); 10.30 °C treatment (b) and 15.00 °C treatment (c); Mg/Ca ratios, 10.30 and 15.00 °C treatments combined (d); 10.30 °C treatment (e) and 15.00 °C treatment (f); Ba/Ca ratios, 10.30 and 15.00 °C treatments combined (g); 10.30 °C treatment (h) and 15.00 °C treatment (i). Statistically significant correlations are shown in bold with dashed regression lines (d, g, i; see text for additional details).

4.2.1. Sr/Ca ratios

The data from five shells sampled in this study clearly illustrate that seawater temperature is not a contributing factor of Sr incorporation during biomineralization. Despite a sudden increase in temperature of 5 °C in May 2011, Sr/Ca ratios did not change accordingly like $\delta^{18}\text{O}_{\text{aragonite}}$ shell values. In fact, average Sr/Ca ratios across the 10.30 °C and 15.00 °C treatments were not statistically different (Fig. 5). A salinity interaction was present in the higher temperature (15.00 °C) treatment but not at the lower temperature (10.30 °C) (Fig. 9). The differential temperature response in shell Sr/Ca ratios as a function of salinity also indicates a physiological response. Because *A. islandica* is a cool-water bivalve (Dahlgren et al., 2000) these clams were likely thermally stressed at 15.00 °C compared to 10.30 °C, which may explain the response to salinity at higher temperatures. Although strong correlations with growth rate have been reported for other veneroids (Purton et al., 1999; Gillikin et al., 2005), Sr/Ca variability in this study was not related, in a statistically significant manner, to growth rates (Fig. 10).

4.2.2. Mg/Ca ratios

Similar to Sr, Mg incorporation into the aragonitic shells of *A. islandica* was not primarily related to seawater temperature (Fig. 6). Only about 5% of the Mg/Ca variability can be explained by seawater temperature. However, strong growth rate effects, explaining ~58% of variance in Mg/Ca ratios, dominated Mg incorporation (Fig. 10). Additionally, a fairly strong salinity interaction at 15.00 °C was present. Similar to Sr, a relationship between salinity and Mg/Ca ratios at 15.00 °C likely resulted from the clams being thermally stressed (Fig. 9). After handling the clams (dates indicated on the bottom of Fig. 6), a sudden increase in shell Mg/Ca ratios was obvious in the majority of the

clams. This result was an evident stress response to being handled; thus handling or other disturbances such as predation attempts may need to be considered if Mg/Ca ratios suddenly change (i.e., spike) in *A. islandica* (and perhaps other mollusk) shells. Lorens and Bender (1980) noted a similar response in Mg/Ca ratios *Mytilus edulis* after being handled. Combined, the Mg/Ca data presented here unequivocally demonstrate that Mg incorporation in *A. islandica* shells is controlled by physiology and not the environment.

4.2.3. Ba/Ca ratios

Consistent with other empirical studies using aragonitic biogenic/skeletal carbonates (Gonneea et al., 2017) and inorganic aragonite (Dietzel et al., 2004; Gaetani and Cohen, 2006), Ba/Ca ratios were inversely related to seawater temperature (Fig. 7). Although > 50% of the Ba/Ca variability can be explained by seawater temperature, this relationship was noisy. In other words, much of the Ba/Ca data overlapped among the different temperature conditions. Nevertheless, this strong relationship does suggest a thermodynamic influence on Ba incorporation in *A. islandica* shells. With that said, very strong and variable growth rate effects were noted on Ba/Ca ratios (Fig. 10). When considering both temperature treatments, a little less of the variance (46%) can be explained by growth rates compared to the seawater temperature effects (56%). Interestingly, in the 15.00 °C treatment, Ba/Ca ratios are inversely related to growth rates while they are positively related under both lower temperature treatments. Although the growth rate effect at 15.00 °C is very strong ($r^2 = 0.95$; $p = 0.0062$) and statistically significant, caution should be used because of the small sample size used here ($N = 5$; degrees of freedom = 3) compared to the entire dataset ($N = 10$; degrees of freedom = 8). A weak yet statistically significant salinity interaction was present at 10.30 °C while a

moderate relationship between salinity ($r^2 = 0.21$; $p < 0.0001$) and Ba/Ca ratios was obvious in the 15.00 °C treatment (Fig. 9). Consistent with Sr and Mg, Ba incorporation in the 15.00 °C treatment showed a fairly strong salinity interaction. Taken together, these data suggest a strong biological/physiological interaction between Ba incorporation and salinity when temperatures are elevated. This further illustrates the complex elemental incorporation during biomineralization.

Gillikin et al. (2008) noted elevated background Ba/Ca ratios in the younger portions in the aragonitic clams *Saxidomus gigantea*, likely reflecting an ontogenetic effect. Similar to the results of Marali et al. (2017b) for *A. islandica* shells, Gillikin et al. (2008) demonstrated that two contemporaneous *S. gigantea* clams from Puget Sound had nearly identical background Ba/Ca ratios throughout ontogeny and very similar peaks (timing and magnitude) which generally occurred seasonally. The synchronicity of Ba/Ca peaks in bivalve shells at the regional scale suggests an external environmental driver. However, it is interesting to note that the timing and magnitude of the Ba/Ca peaks noted by Gillikin et al. (2008) did not match local *chlorophyll a* dynamics very well, and Marali et al. (2017b) reported variable results linking shell Ba/Ca ratios to regional primary productivity data. Although it is thought that Ba/Ca peaks in bivalve shells are related to primary productivity (e.g., Stecher et al., 1996; Vander Putten et al., 2000; Lazareth et al., 2003), it is obvious that additional environmental and/or biological controls complicate the singular interpretation of Ba/Ca peaks as a primary productivity proxy. Alternatively, Ba transport from seawater and food may be delayed due to potentially intermediate storage of Ba in amorphous calcium carbonate (ACC) vesicles. Incorporation of Ba may then not occur simultaneously with a phytoplankton bloom, but with a lag.

4.3. The use of element-to-calcium ratios in bivalves as environmental proxies

The substitution of Sr and Mg for Ca into the crystal lattice of calcium carbonate during precipitation has been shown to follow environmental parameters (and thermodynamic properties) in abiogenic materials (e.g., Kinsman and Holland, 1969; Katz, 1973; Mucci and Morse, 1983; Mucci, 1987; Oomori et al., 1987; Zhong and Mucci, 1989; Dietzel et al., 2004). Thus, testing if this holds true in biogenic/skeletal carbonates is extremely appealing. A central tenant for using element-to-calcium ratios as environmental proxies relies on the proxy archive to incorporate elements through the extra pallial fluid (EPF) from the ambient environment and biomineralize those elements in a passive fashion. In other words, if the organism uses any of these elements for their physiology and function it is likely that the element-to-calcium ratios will be altered. If the degree to which an organism, in this case a bivalve, modifies the calcifying environment (Wheeler, 1992) is variable throughout its lifetime, then the reliability of such a proxy will likely be low. Because elemental uptake can occur via food or from diffusion through the mantle epithelia and then end up in the EPF/extra pallial space (EPS; Wheeler, 1992; Gillikin et al., 2006), any storage or detoxification of certain elements in ACC vesicles could potentially alter incorporation into the shell carbonate. Perhaps more importantly, organic macromolecules in the EPS may control how much a certain element is incorporated into the shell. The very low Sr/Ca and Mg/Ca ratio values in the aragonitic shells compared to ambient seawater support this idea. Hence there must be a mechanism to remove Mg and Sr from the EPS. Until the elemental compositions of the EPS can be readily measured, our collective understanding of these processes will be somewhat limited. However, a recent study by Zhao et al. (2017) on elemental incorporation into freshwater bivalve shells (*Corbicula fluminea*) has provided some mechanistic advances in this area. Specifically, these authors tested the impacts of increasing dissolved Ca^{2+} concentrations in water on uptake and incorporation of Ba, Sr, and Mg into shell material. Zhao et al. (2017) concluded that Ca^{2+} transport mechanisms do not control the Ba, Sr, and Mg incorporation

into the shell material because these values were unaltered despite doubling the Ca^{2+} levels in the water. Thus other mechanisms for elemental partitioning between ambient water and the shells must be considered.

In this study, when seawater temperature was relatively warm for *A. islandica* (15.00 °C), the elemental incorporation response to salinity was substantially different compared to the lower temperature treatment (10.30 °C). We assert that this result necessitates reason for caution when working with natural populations of bivalves (and other biological proxies). This is because it is often assumed that the proxy behaves (in this case- elemental incorporation) in a similar fashion across all environmental conditions, which clearly is not the situation for many bivalve species. This result further illustrates the need for experimental culture work to isolate and examine potential physiological effects during biomineralization across a range of naturally-occurring environmental conditions.

In most of the studies that have investigated the use of element-to-calcium ratios, especially Mg/Ca and Sr/Ca ratios, in bivalves as marine environmental proxies, the result has been fairly similar: elemental incorporation is dominated by physiological effects and does not reflect environmental conditions in a consistent manner (e.g., Toland et al., 2000; Eplé, 2004; Gillikin et al., 2005; Lorrain et al., 2005; Carré et al., 2006; Lazareth et al., 2003; Wanamaker et al., 2008c; Foster et al., 2008, 2009; Schöne et al., 2010; Schöne et al., 2011b; Schöne, 2013; Poulain et al., 2015; Marali et al., 2017a). The results presented here further support this notion. Although Ba/Ca ratios in bivalves have shown some promise to track salinity (Gillikin et al., 2006, 2008) and that these signatures can be regionally synchronous (Marali et al., 2017b), the Ba/Ca results from this study further highlight the strong physiological overprinting of Ba incorporation during biomineralization in *A. islandica*.

4.4. Limitations of this study and generalizing results from juvenile to adult clams

Although some notable progress was made in this study documenting the elemental and isotopic incorporation into the aragonitic shell material of juvenile *A. islandica* clams several notable limitations are worth considering. The experimental design did not include measuring the elemental composition of seawater through time, which would likely explain some of the variability noted here in shell elemental ratios. Additionally, we did not quantify the elemental composition of food in this experiment. It is therefore possible that the elemental signature of the food had noticeable impacts on the trace and minor impurities in the shell material. Further, the reliance on the salinity/isotope mixing line used here (Whitney et al., 2017) on assessing oxygen isotope equilibrium for *A. islandica* somewhat qualifies this positive result. It would have been better to measure the weekly oxygen isotope composition in seawater samples when assessing isotope equilibrium fractionation. Also, as noted by Mette et al. (this issue) replication with two or three shells, rather than just one for oxygen isotopes, would yield improved statistical confidence.

A major challenge in culture studies is to produce (grow) enough shell material to sample under highly controlled conditions that mimic the natural world. Such calibration studies are expensive and require substantial resources, including people hours. Because of these limitations, juvenile specimens are routinely used because growth rates are much higher compared to adults. Because *A. islandica* can live for several centuries or more, growth rates in older adults (> 100 years) are generally too low for relatively short (< 1 year) culture studies (which are generally more economically feasible). Workers are then left with the following question. Are the mechanisms of elemental and isotopic incorporation similar or different for juvenile and adult specimens? There is an emerging body of literature that indicates that *A. islandica* clams exhibit a fairly substantial vital effect during early ontogeny (first 20 years or so) during incorporation of stable carbon

isotopes (for a review, see Reynolds et al., 2017). However, there is no evidence of an age-related vital effect during oxygen isotope incorporation into the aragonitic shells of *A. islandica* (Schöne et al., 2005a; Wanamaker et al., 2008b; Schöne, 2013; Reynolds et al., 2016). Until similar culture experiments are conducted on sexually mature *A. islandica* adults that grow reasonably fast (maybe 30 to 50 year old clams), we must consider field studies from natural populations to determine if the results from juveniles reported here are potentially transferable to adults. Recently, Marali et al. (2017a) measured the Ba/Ca, Sr/Ca, and Mg/Ca ratios from juvenile and adult portions of *A. islandica* shells from the Gulf of Maine (N = 3), Iceland (N = 1), and the Isle of Man (N = 3). In general, Ba/Ca ratios between shells from the Gulf of Maine and Isle of Man were highly reproducible (also see Marali et al., 2017b) and did not show any age-related trends. For these same shells, Mg/Ca and Sr/Ca ratios in the Gulf of Maine showed no age-related trends, while two out of three shells from the Isle of Man showed a slight increase in Mg/Ca and Sr/Ca ratios through time. One shell from the Isle of Man did not show an age-related trend. These results generally suggest that elemental incorporation is fairly similar in juvenile and adult specimens. However, Schöne et al. (2011b) also studied the Sr/Ca and Mg/Ca ratios of four *A. islandica* shells collected from Iceland. Interestingly, all of these shells showed an age-related increase in both Sr/Ca and Mg/Ca ratios through time. Based on the findings by Marali et al. (2017a), the Sr/Ca and Mg/Ca ratios from both juvenile and adult portions of *A. islandica* shells had little coherence with seasonal or annual changes in seawater temperature through time. In this regard, the results from this study are consistent with the results reported by Marali et al. (2017a) between adult and juvenile specimens. Although it is very difficult to confidently address potential differences in elemental incorporation among juvenile and adult specimens of *A. islandica*, there is ample evidence that Mg/Ca and Sr/Ca ratios in *A. islandica* shells, regardless of ontogenetic stage, do not reliably record ambient seawater conditions. Although we recommend using caution when generalizing results from juvenile culture studies to adult specimens, it appears that the physiologic effects noted in this study also impact adult *A. islandica* populations from natural settings.

5. Conclusions

In the temperature-controlled culture experiments conducted here, Sr/Ca and Mg/Ca ratios from five shells exhibited little coherence with seawater temperature. Ba/Ca ratios showed a strong, statistically significant, inverse relationship with seawater temperature, but pronounced and variable growth rates effects coupled with salinity interactions confounded this effect. A salinity interaction (salinity was correlated with element-to-calcium ratio) was noted in Sr, Mg, and Ba incorporation in the 15.00 °C treatment, which was likely a result of thermal stress associated with relatively warm temperatures for *A. islandica*. Growth rate effects were obvious in Mg and Ba incorporation but not Sr in the *A. islandica* shells sampled. The results from this study further support that elemental incorporation in bivalve shell material tends to be dominated by physiological processes (vital effects) rather than mediated/controlled by thermodynamic processes like oxygen isotopes. Oxygen isotopes from one shell closely tracked seawater temperature throughout the treatments, and based on the assumptions made in this study, *A. islandica* precipitated its shell oxygen isotopes in equilibrium with ambient seawater. Additionally, oxygen isotopes provided a tool to quantify biomineralization response times to changing seawater temperatures, which were on the order of days. The findings from these culture experiments demonstrate that Sr/Ca, Mg/Ca, Ba/Ca ratios in juvenile *A. islandica* shell material are not reliable environmental proxies due to strong physiological controls during biomineralization. Additional work is needed to better quantify if the effects documented in juvenile specimens here can be directly applied to adult clams.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemgeo.2018.02.012>.

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