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Investigation of Li/Ca variations in aragonitic shells of the ocean quahog *Arctica islandica*, northeast Iceland

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[1] Interannual and intra-annual variations in lithium-to-calcium ratio were investigated with high temporal resolution in the aragonitic outer shell layer of juvenile *Arctica islandica* (Mollusca; Bivalvia) collected alive in 2006 off northeast Iceland. Li/Ca_{shell} ranged between 7.00 and 11.12 μmol mol^{-1} and presented well-marked seasonal cycles with minimum values recorded at the annual growth lines; a general pattern was a progressive increase in Li/Ca_{shell} from March to May, followed by a plateau in June and a decrease down to minimum values in July–August. Li/Ca_{shell} was correlated with $\delta^{18}O_{shell}$-derived temperature, but the strength of this relationship was weak ($r^2 < 0.25$ and $p < 0.05$). It covaried significantly with microgrowth increment width and with the discharge from one of the closest rivers. Seasonal variations of Li/Ca_{shell} in *A. islandica* may most likely be explained (1) by calcification rate and/or (2) by significant river inputs of Li-rich silicate particles flowing to the sea as soon as snow melts. In the first case, Li/Ca_{shell} may be a useful proxy for addressing seasonal variations of growth rate in bivalves that lack discernable microgrowth patterns. Abrupt decreases of Li/Ca_{shell} may, in turn, help identify growth retardations due to harsh environmental conditions. Alternatively, if Li/Ca_{shell} variations are linked to particulate Li inputs by rivers, this could be a new proxy for the intensity of mechanical weathering of Icelandic basalts, with interesting perspectives for the reconstruction of frequency and intensity of past jökulhlaups (subglacial outburst floods). Further works, including experimental studies, are needed to test these hypotheses.

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1. Introduction

[2] During the past sixty years, a large number of studies have focused on the use of elemental concentrations in marine sediment cores as proxies for past variations of environmental parameters. These parameters include, among others, temperature (proxies: Mg/Ca, Sr/Ca), alkalinity (Ba/Ca), dissolved inorganic carbon concentration (Cd/Ca), ocean circulation (Cd/Ca, Nd, Hf, Pb), biological productivity ($BaSO_4$, Pa/Th, Be/Th, U) and sedimentation rate (^{230}Th, ^{210}Pb, ^{231}Pa/^{230}Th) (for thorough reviews, see *Wefer et al.* [1999] and *Henderson* [2002]). However, the temporal resolution of such paleoceanographic reconstructions is low, generally coarser than decades. Therefore, efforts have been made to assess the potential of elemental content in marine biogenic carbonates, especially bivalve mollusk shells, as high-resolution proxies for environmental conditions [e.g., *Stecher et al.*, 1996; *Vander Putten et al.*, 2000; *Thébault et al.*, 2009].

[3] Bivalve shells grow by accretion of calcium carbonate crystals, either in the form of calcite, aragonite, or both depending on the species [*Pannella and McClintock*, 1968]. Shell growth, however, does not occur continuously over a day, or over a year; instead, growth ceases periodically, on ultradian (several growth stops during a single day), circatidal (semidiurnal, ~12.4 h), circadian (solar day, ~24 h), circalunidian (lunar day, ~24.8 h), or annual time scales [*Schöne*, 2008]. These growth stops result in the formation of so-called growth lines, which are enriched in organic matter and separate growth increments that represent equal time slices. These periodic growth lines can therefore be used to assign precise calendar dates to each successive increment of accreted shell material. This characteristic gives bivalve shells an outstanding potential for the high-resolution reconstruction of paleoenvironmental conditions, especially through geochemical analyses. For example, skeletal oxygen isotope composition (δ^{18}O) of many bivalve species (including scallops, mussels, and clams) has been extensively used since the pioneering work of *Epstein et al.* [1953] to infer paleotemperature variations, sometimes with an accuracy of less than 1°C [*Chauvaud et al.*, 2005; *Thébault et al.*, 2007].

[4] In the past decade, the elemental composition of bivalve shells has also been increasingly used for paleoenvironmental reconstructions. Bivalve shells are not exclusively made of $CaCO_3$. Aside from Ca, a number of minor and trace elements are also incorporated within the shell during its formation, either in an interstitial location within the crystal lattice or as carbonates (substitution for Ca^{2+} [*Okumura and Kitano*, 1986]), or even within the organic matrix [*Lingard et al.*, 1992], which can represent up to 5% of the shell dry weight [*Marin and Luquet*, 2004]. The incorporation of these elements is known to be partly controlled by various environmental parameters, either physical (temperature, salinity), chemical (seawater elemental concentration, metallic contamination), or biological (primary production). Physiology, however, also exerts an important control on the chemical composition of bivalve shells [*Schöne*, 2008].

[5] Microanalytical techniques (e.g., laser ablation coupled to an ICP-MS system = LA-ICP-MS [*Craig et al.*, 2000]) allow the accurate measurement of tens of elements archived in biogenic carbonates within a few seconds. Their abiding improvement considerably increases the probability of discovering new paleoenvironmental proxies. With the exception of a few studies [e.g., *Lindh et al.*, 1988; *Carriker et al.*, 1996; *Dick et al.*, 2007] however, most investigations on the geochemical composition of bivalve shells have only dealt with a few elements (mainly Sr, Mg, Ba, and some trace metals including Mn, Pb, Zn, and Cd).

[6] Lithium is a trace element that (1) is easily measurable using mass spectrometers, (2) has been demonstrated to present an interesting potential as a paleoceanographic proxy in some marine biogenic carbonates [*Delaney et al.*, 1985, 1989; *Hall and Chan*, 2004; *Marriott et al.*, 2004a, 2004b;

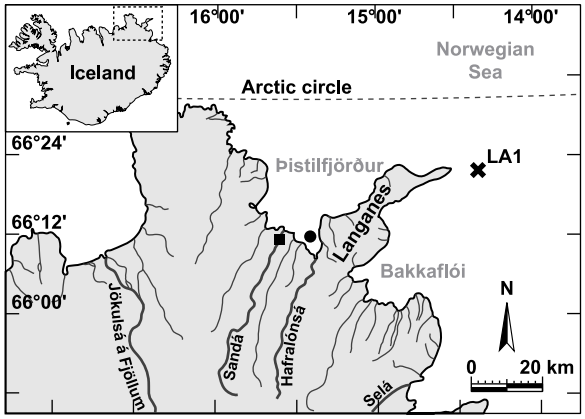

Figure 1. Map of northeastern Iceland showing Langanes Peninsula between Þistilfjörður and Bakkaflói. *Arctica islandica* specimens were collected by dredging in Þistilfjörður at 30 m water depth (black dot). Temperature and salinity data used in this paper were measured off Langanes Peninsula by the Marine Research Institute of Reykjavik (CTD station LA1, 20 m water depth, black cross). Seasonality of freshwater inputs in Þistilfjörður were assessed using river discharge data collected at Sandá River gauging station (black square).

Hathorne and James, 2006; *Montagna et al.*, 2006], and (3) has surprisingly not yet been analyzed in bivalve shells. One of the first studies dealing with Li/Ca ratios in marine biogenic carbonates suggested that this ratio in foraminiferal calcite was partly controlled by the Li/Ca ratio of the growing medium [*Delaney et al.*, 1985]. This was later confirmed by *Hathorne and James* [2006] who demonstrated that Li/Ca in foraminifera could be used to reconstruct past changes in the Li/Ca ratio of seawater, which could be interpreted in terms of continental silicate weathering rate. Several studies have also highlighted significant inverse relationships between temperature and Li/Ca in foraminifera [*Hall and Chan*, 2004; *Marriott et al.*, 2004a], in calcitic brachiopods [*Delaney et al.*, 1989], in coralline aragonite [*Marriott et al.*, 2004b; *Montagna et al.*, 2006], and in inorganic calcite [*Marriott et al.*, 2004b]. It has finally been suggested that the main factor controlling Li incorporation in foraminifera is not temperature but calcification rate [*Hall and Chan*, 2004; *Marriott et al.*, 2004a]. Because calcification rate may be a function of CO_3^{2-} concentration in the oceans, it has been suggested that the Li/Ca ratio in foraminifera could be a potential proxy of past atmospheric CO_2 [*Hall and Chan*, 2004].

[7] Here, we present for the first time Li/Ca records in bivalve mollusk shells. We have focused on juvenile ocean quahogs *Arctica islandica* (Linnaeus, 1767) collected alive in 2006 off the coast of northeast Iceland, probably one of the last pristine ecosystems in the North Atlantic. *A. islandica* has all the characteristics necessary for paleoceanographic reconstructions. First, it produces circadian and annual growth patterns in its aragonitic shell [*Schöne et al.*, 2005a]. Second, it holds the longevity record for bivalves and may in fact be the longest-lived noncolonial animal, living up to 4 centuries [*Schöne et al.*, 2005b; *Wanamaker et al.*, 2008a]. Third, it exhibits a broad biogeographic distribution centered around Iceland, inhabiting the continental shelves on both sides of the North Atlantic, in Europe from the Barents Sea to the Bay of Cadiz in Spain, and in North America from Newfoundland to Cape Hatteras [*Thorarinsdóttir and Jacobson*, 2005]. Fourth, this species has been intensively studied for its anatomy, behavior, physiology, biology, and ecology [*Witbaard*, 1997]. And finally, several studies have already highlighted that shells of *A. islandica* provide multiproxy records of environmental variables. Changes in environmental parameters are recorded in variations of growth rates [*Marchitto et al.*, 2000; *Schöne et al.*, 2003, 2005b], stable isotope composition [*Weidman et al.*, 1994; *Schöne et al.*, 2004, 2005a, 2005b, 2005c; *Wanamaker et al.*, 2008b] and trace element concentrations [*Epplé*, 2004; *Toland et al.*, 2000; *Liehr et al.*, 2005].

[8] The aims of this paper are (1) to analyze the behavior of Li/Ca in *A. islandica* aragonitic shells (interannual and intra-annual variability) using variations of the oxygen isotope composition of these shells as chronological checks, (2) to review the different processes that may explain the temporal variations of this ratio, and (3) to assess if Li/Ca could be a promising addition to the arsenal of proxies already used in bivalve shells.

2. Materials and Methods

2.1. Study Area

[9] Our study site is located in Þistilfjörður (northeast Iceland; 66°10.751′N, 15°21.296′W), 1 km off the southwestern edge of Langanes Peninsula and 3 km away from Hafralónsá estuary (Figure 1). Hafralónsá and Sandá are the two main rivers flowing into Þistilfjörður. Catchments of these

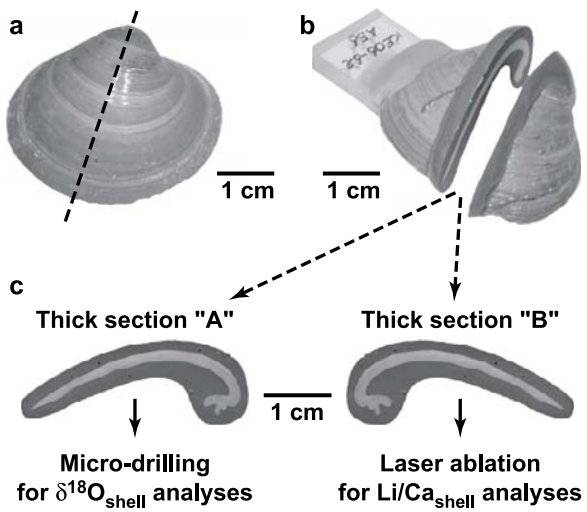

Figure 2. Preparation of *Arctica islandica* shells for geochemical analyses. (a) Right valve of *Arctica islandica*. The axis of maximum growth was identified on shells as the largest distance between the umbo and the ventral margin (dashed line). (b) After mounting on a Plexiglas cube and embedding in metal-epoxy resin, left valves were cut along the axis of maximum growth using a low-speed saw. (c) Two "mirroring" sections were cut in each shell, one for isotopic analyses (thick section "A") and the other one for Li/Ca determination (thick section "B").

two nonglacial rivers are composed of old basaltic rocks (>3.1 million years of age). Water depth at our study site is 30 m and the substrate mainly consists of sand and silt sediments. Hydrographic conditions off north Iceland largely depend on the physical characteristics of the East Icelandic Current, which, in turn, depend on the eastward transport of Greenland Polar Water by the East Greenland Current and the northward transport of Irminger Atlantic Water by the North Irminger Current [*Hopkins*, 1991]. No environmental survey has ever been conducted in Þistilfjörður because of its isolated situation in this remote part of Iceland. The closest site where environmental data are available is located 50 km northeastward of our study site, off the northeastern part of the Langanes Peninsula (Langanes Austur LA1, 66°22N, 14°22W (Figure 1)). Environmental conditions at LA1 are also mainly controlled by the relative intensities of the East Icelandic Current and the North Irminger Current. Temperature and salinity are measured at this location at a depth of 20 m by the Oceanographic Group of the Marine Research Institute of Reykjavik using a CTD profiler (data available at http://www.hafro.is/Sjora/). This data set indicates that water temperature is lowest in February–March (mean [2000–2006] = 2.8°C; σ = 0.9°C) and reaches a maximum in August (7.9°C; σ = 0.8°C). Over the same period, salinity variations ranged between 34.4 and 34.8. These temperature and salinity values are similar to those measured at 20–30 m water depth in two other fjords in North Iceland: Reykjarfjörður [*Andrews et al.*, 2001] and Ísafjörður [*Astthorsson*, 1990]. From early May to the end of August, somewhat lower salinities (<34) can be observed near the surface in Icelandic fjords because of meltwater runoff from the land. However, these low salinities are restricted to the top 10 m of the water column [*Astthorsson*, 1990; *Andrews et al.*, 2001]. Therefore, temperature and salinity data measured at 20 m depth at LA1 likely reflect those of our study site at 30 m depth.

[10] The seawater oxygen isotope composition of our study site was measured on 17 August 2006 ($\delta^{18}O_{water}$ = −0.58‰ VSMOW; Salinity = 34.58). Seasonal variations in $\delta^{18}O_{water}$ are expected given the salinity variations around the Langanes Peninsula but coefficients of the local $\delta^{18}O_{water}$–salinity relationship are unknown. The $\delta^{18}O_{water}$ and salinity values were measured off northwest Iceland in October 1998 (65.98–68.72°N; 22.98–29.25°W; depth = 10–30 m) in the framework of the VEINS Program (Variability of Exchanges In the Northern Seas; data compiled by *Schmidt et al.* [1999]). These data indicate that, over the salinity range 32–35, we can expect a lowering of the $\delta^{18}O_{water}$ values of 0.68‰ for every unit decrease in salinity. Given (1) $\delta^{18}O_{water}$ and salinity values measured on 17 August 2006 at our study site and (2) the slope of the $\delta^{18}O_{water}$–salinity relationship derived from the VEINS Program, we can expect seasonal variations of $\delta^{18}O_{water}$ at our study site of between −0.7 and −0.4‰ VSMOW over the salinity range 34.4–34.8.

2.2. Shell Sampling and Preparation

[11] Two specimens of *Arctica islandica* were collected alive on 17 August 2006 by dredging on our study site in Þistilfjörður, at a depth of 30 m. Both specimens (ICE06–6.2-A55 and ICE06–6.2-A56, hereafter simply named A55 and A56) were juveniles with a shell height of 33.0 and 31.2 mm, respectively (shell length of 40.0 and 37.4 mm, respectively (Figure 2a)). We chose young specimens because *A. islandica* grows fairly rapidly during early ontogenetic stages [*Jones*, 1983; *Weidman et al.*, 1994; *Jones*, 1998; *Kilada et al.*, 2007] and young shells

therefore provide the highest temporal resolution in carbonate records.

[12] Immediately after dredging, the soft parts were discarded and the right and left valves kept frozen until analysis. The left valves of shells A55 and A56 were gently rinsed with deionized water and air dried. Each valve was mounted on a Plexiglas cube using a two-part methacrylat glue (plastic welder, Gluetec GmbH and Co. KG, Germany) and embedded in a two-part metal-epoxy resin (Wiko, Germany) to strengthen the shell and to avoid shell fracture during sawing (Figure 2b). Two immediately adjacent, 2.6 mm thick sections were cut from each valve perpendicular to the growth lines along the axis of maximum growth using a low-speed precision saw (Isomet 1000, Buehler Ltd., Illinois, United States) equipped with a 0.4 mm thick diamond-coated blade cooled and kept wet using deionized water (Figure 2c). These "mirroring" sections were then mounted on glass slides, manually ground with ~12 μm and 8 μm SiC powder, and polished with 1 μm Al_2O_3 powder to visualize the internal growth patterns. Thick sections were ultrasonically rinsed with deionized water between each grinding/polishing step to remove any adhering grinding powder. Thick section "A" was used for isotopic analyses and thick section "B" for trace elemental analyses. Once geochemical analyses were done, these thick sections were cleaned with ethanol before being etched in the so-called Mutvei's solution for 25 min at 37–40°C in order to resolve interannual and intra-annual growth lines and increments (see *Schöne et al.* [2005d] for a detailed description of this method). Finally, the sections were gently rinsed with deionized water and air dried. Micro-growth increment width was subsequently measured using the image analysis software Panopea (© 2004 Peinl and Schöne). High-resolution photographs of these four sections were taken using a Nikon Coolpix 995 digital camera attached to a Wild Heerbrugg M3Z stereozoom microscope. Photo stitching software (Photoshop Elements 2.0) was then used to assemble the 25–30 photographs taken for each section into a single, high-resolution picture.

2.3. Isotopic Analyses

[13] The oxygen isotope ratio ($^{18}O/^{16}O$) of marine biogenic carbonate is controlled by temperature and the oxygen isotope composition of the seawater from which it precipitates [*McCrea*, 1950; *Epstein et al.*, 1953]. Therefore, shells of our two *A. islandica* specimens were sampled for isotopic analyses in order to reconstruct variations in the bottom water temperatures these animals experienced during their life. Aragonite samples (48 and 50 samples on shells A55 and A56, respectively) were collected in thick sections "A" using a micro-drill (Minimo C121, Minitor Co. Ltd., Japan) equipped with a 0.3 mm tungsten carbide drill bit (model H52.104.003, Gebr. Brasseler GmbH and Co. KG, Germany). Samples were taken in the outer shell layer along an axis running from the ventral margin and toward the youth portions of the shells. Holes drilled in these sections were ~350 μm in diameter. Aliquots of shell aragonite weighing between 38 and 125 μg (mean = 80 μg) were analyzed at the University of Frankfurt using an automated Gas Bench II carbonate device interfaced with a Thermo Finnigan MAT 253 isotope ratio mass spectrometer. Shell isotopic data are expressed in conventional delta (δ) notation [*Epstein et al.*, 1953] relative to the VPDB standard. The in-house standard used was a Carrara marble ($\delta^{18}O_{Carrara}$ = −1.74‰ VPDB) calibrated against NBS19. The isotopic value used for this calibration was $\delta^{18}O_{NBS19}$ = −2.20‰ VPDB (for more details, see *Fiebig et al.* [2005]). Repeated analyses of this standard yielded a reproducibility (1σ) of 0.07‰ VPDB.

[14] To temporally align aragonite samples taken between two annual growth lines, we compared the temperature reconstructed from our $\delta^{18}O_{shell}$ records (hereafter referred as $T_{\delta 18O}$) with seasonal variations of seawater temperature measured at 20 m depth at station LA1. To this end, we used the empirically determined paleothermometry equation of *Grossman and Ku* [1986, equation 1]. A modification of this equation was, however, required as their water values were reported in VSMOW minus 0.27‰ [*Hut*, 1987]. Once corrected, their equation translates to:

$$T_{\delta 18O} = 19.43 - 4.34\left(\delta^{18}O_{shell} - \delta^{18}O_{water}\right) \quad (1)$$

where $T_{\delta 18O}$ is seawater temperature (in °C) reconstructed from $\delta^{18}O_{shell}$, and $\delta^{18}O_{shell}$ and $\delta^{18}O_{water}$ are the oxygen isotope composition of aragonite and water expressed in ‰ relative to the VPDB and VSMOW standards, respectively. We used an average $\delta^{18}O_{water}$ value of −0.55‰ VSMOW. In order to estimate the uncertainty on $T_{\delta 18O}$, i.e., half the difference between upper and lower bounds, we applied the following formula using (1) the uncertainty in $\delta^{18}O_{shell}$ value given by

Table 1. LA-ICP-MS Operating Conditions

Parameter	Value
Laser: New Wave Research UP-213	
Crystal	Nd:YAG
Wavelength	213 nm
Laser mode	Q-switched
Laser power	0.2 mJ
Repetition rate	10 Hz
Pit diameter	80 μm
Ablation time	60 s
Background	60 s
ICP-MS: Agilent 7500ce	
RF power	1200 W
Plasma gas flow	15 L min^{-1}
Auxiliary gas flow	1 L min^{-1}
Carrier gas flow	0.65 L min^{-1}
Optional gas flow	75% He
Acquisition mode	pulse counting
Acquisition time	120 s
Dwell time	10 ms

IR-MS (ε_{IRMS} = ±0.07‰) and (2) the estimated range of $\delta^{18}O_{water}$ (min. = −0.7‰; max. = −0.4‰):

$$\text{Uncertainty} = 4.34 \times \left(2\varepsilon_{IRMS} + \delta^{18}O_{water\,max.} - \delta^{18}O_{water\,min.}\right)/2 \quad (2)$$

This resulted in an absolute uncertainty on $T_{\delta 18O}$ of ±0.95°C.

2.4. Li/Ca$_{shell}$ Analyses

[15] Li/Ca ratios were analyzed in thick sections "B" using LA-ICP-MS at the University of Mainz. An Agilent 7500ce quadrupole ICP-MS (Agilent Technologies Inc., California, United States) coupled to a UP-213 laser ablation system (New Wave Research, California, United States) was used with the parameters listed in Table 1. Aragonite samples (n = 332 in each shell) were ablated in the outer shell layer from the ventral margin toward the youth portions of the shells at a constant distance from the shell surface (400 μm). The diameter of the laser spots was 80 μm and the distance between the centers of two successive spots was 100 μm (i.e., 20 μm between edges of two successive spots). During acquisition, signal intensities were recorded for ^{7}Li, ^{43}Ca and ^{44}Ca. The intensity of the isotope of interest was systematically normalized against the ^{43}Ca signal (internal standard) in order to correct for laser beam energy drift, focus variation at the sample surface, and ICP-MS detection drift [see *Pearce et al.*, 1997]. The glass reference material NIST SRM 612 was used as a calibration standard with the values of *Pearce et al.* [1997]. Precision (degree of reproducibility) and accuracy (degree of veracity) of the applied method were controlled by repeated analyses of the glass reference material NIST SRM 614 (Li concentration value taken from *Kurosawa et al.* [2002]). For each shell, the sequence of analyses was as follows: (NIST612) $_{\times 2}$ + shell $_{\times 2}$ + (shell $_{\times 15}$ + NIST614 + shell $_{\times 15}$ + NIST612) $_{\times 11}$ + NIST612. Data processing (including instrumental drift correction and normalization) was performed using GLITTER v.4 software (Macquarie Research Ltd., Australia [*Van Achterbergh et al.*, 2001]), following the methods of *Longerich et al.* [1996].

[16] Li/Ca detection limit at the 99% confidence level was calculated by GLITTER using Poisson counting statistics and was 0.243 μmol mol^{-1}. Repeated measurements of NIST SRM 614 (n = 22) yielded a precision of 1.9% (% RSD). Accuracy was extremely good with a Li concentration value in NIST SRM 614 of 1.687 ± 0.007 μg g^{-1} compared with the recommended value of 1.69 ± 0.026 μg g^{-1} (means ± standard errors).

2.5. Statistical Analyses

[17] Two different statistical tests were used to compare the means of two independent samples: Student's t test (large samples: $\min(n_1, n_2) \geq 30$) and Mann-Whitney U test (small samples: $\min(n_1, n_2) < 30$). An analysis of covariance (ANCOVA; α = 0.05) was used to test whether there were significant differences between the slopes of the least squares linear regressions (Li/Ca$_{shell}$ versus $T_{\delta 18O}$) calculated for each of the two shells. Homogeneity of residual variances was tested with Bartlett's test (α = 0.01). No data were excluded. All statistical analyses were performed according to *Scherrer* [1984].

3. Results

3.1. Profiles of $\delta^{18}O_{shell}$

[18] In each shell, $\delta^{18}O_{shell}$ profile showed cyclical oscillations in phase with the main growth lines that were revealed after the immersion of shell sections in Mutvei's solution (Figure 3). This confirms the annual periodicity of these growth lines. Seven main growth lines were observed in both shells, suggesting that both specimens settled on the seafloor in 1999. Isotopic data covered four full years of growth (2002–2005) and the beginning of year 2006.

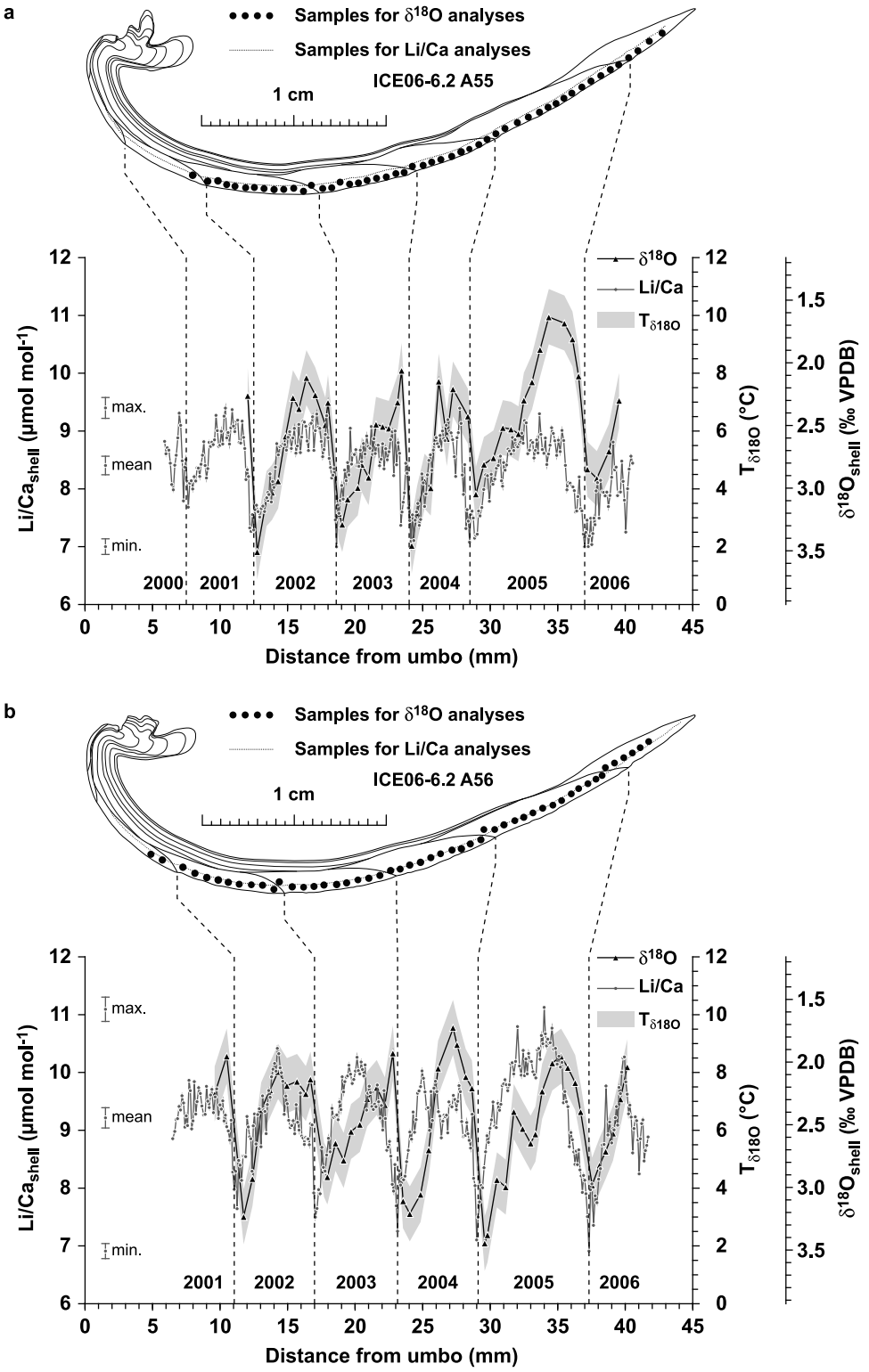

Figure 3. Temporal variations (2000–2006) of Li/Ca_{shell} ratio (gray circles), $\delta^{18}O_{shell}$ (black triangles; inverted scale), and $\delta^{18}O_{shell}$-derived seawater temperature ($T_{\delta 18O}$, gray area) measured in *Arctica islandica* shells. (a) Specimen A55. (b) Specimen A56. Error bars on the left side of each plot correspond to $Li/Ca_{min.}$ ± 1RSD, Li/Ca_{mean} ± 1RSD, and $Li/Ca_{max.}$ ± 1RSD, with RSD = 1.9% (precision given by 22 measurements of NIST SRM 614). Vertical dashed lines represent the annual growth lines revealed in shell cross sections and are used to identify the different years of growth. Also presented are digitized cross sections of the two specimens, showing annual growth lines in outer and inner shell layers, and location of aragonite samples taken for isotopic and elemental analyses.

Table 2. Annual Amplitudes of $\delta^{18}O_{shell}$ and $T_{\delta 18O}$ of Specimens A55 and A56 Over the Period 2002–2006[a]

		$\delta^{18}O_{shell}$ (‰VPDB)		$T_{\delta 18O}$ (±0.95°C)	
Year	Shell	Minimum	Maximum	Minimum	Maximum
2002	A55	2.12	3.51	1.8	7.8
	A56	2.08	3.23	3.0	8.0
2003	A55	2.06	3.29	2.8	8.1
	A56	1.93	2.92	4.4	8.7
2004	A55	2.15	3.46	2.0	7.7
	A56	1.73	3.21	3.1	9.5
2005	A55	1.64	3.05	3.8	9.9
	A56	1.96	3.45	2.1	8.5
2006	A55	–	2.92	4.4	–
	A56	–	2.98	4.1	–

[a] $T_{\delta 18O}$ were calculated using equation (1) using a mean $\delta^{18}O_{water}$ value of −0.55‰. The uncertainty in temperature reconstruction from $\delta^{18}O_{shell}$ is ±0.95°C.

[19] $\delta^{18}O_{shell}$ values ranged from 1.64 to 3.51‰ in shell A55 and from 1.73 to 3.45‰ in shell A56. Annual minima ranged from 1.64 to 2.15‰, whereas annual maxima varied between 2.92 and 3.51‰ (Table 2). Seasonal $\delta^{18}O_{shell}$ cycles were strongly right skewed with minimum/maximum values occurring shortly before/after the annual growth lines (Figure 3).

[20] These $\delta^{18}O_{shell}$ values were converted into temperature ($T_{\delta 18O}$) using equation (1) and a $\delta^{18}O_{water}$ value of −0.55‰ (Figure 3). Annual minimum temperatures recorded by the shells ranged from 1.8 to 4.4°C (mean [2002–2006] = 3.1°C; σ = 1.0°C (Table 2)). Mean annual minima in shells A55 (3.0°C) and A56 (3.3°C) were not significantly different from each other (Mann-Whitney U = 8.5, $n_1 = n_2 = 5$, $p > 0.05$). Annual maximum temperatures recorded by the shells ranged from 7.7 to 9.9°C (mean [2002–2005] = 8.5°C; σ = 0.8°C (Table 2)). Mean annual maxima in shells A55 (8.4°C) and A56 (8.7°C) did not differ significantly (Mann-Whitney U = 5, $n_1 = n_2 = 4$, $p > 0.05$).

[21] The offsets between $T_{\delta 18O}$ and T_{LA1} (0.3°C and 0.6°C for average annual minima and maxima, respectively) are within the ±0.95°C uncertainty on $T_{\delta 18O}$, so it is reasonable to assume that the whole annual range of seawater temperature was recorded by the shells.

3.2. Li/Ca_{shell} Profiles

[22] For both specimens, Li/Ca_{shell} profiles showed cyclical variations with minimum values recorded exactly at the annual growth lines (Figure 3). A general tendency of the seasonal Li/Ca_{shell} variations was a progressive increase after the annual line, followed by a plateau and then a decrease down to minimum values. Maximum Li/Ca_{shell} values tended to occur earlier during the growing season than $\delta^{18}O_{shell}$ minima (i.e., before temperature maxima (Figure 3)).

[23] Li/Ca_{shell} ranged from 7.00 to 9.40 μmol mol^{-1} in shell A55 (mean = 8.37 μmol mol^{-1} (Figure 3a)) and from 6.91 to 11.12 μmol mol^{-1} in shell A56 (mean = 9.23 μmol mol^{-1} (Figure 3b)). Mean Li/Ca_{shell} ratio was significantly higher in shell A56 than in shell A55 (t test t = 16.87, $n_1 = n_2$ = 332, $p < 0.01$).

[24] Annual minimum values ranged from 7.00 to 7.29 μmol mol^{-1} in shell A55 (mean [2001–2005] = 7.16 μmol mol^{-1}; σ = 0.12 μmol mol^{-1}), and from 7.10 to 7.64 μmol mol^{-1} in shell A56 (mean [2002–2005] = 7.44 μmol mol^{-1}; σ = 0.23 μmol mol^{-1} (Table 3)). Mean annual minima in shells A55 and A56 did not differ significantly (Mann-Whitney U = 3, n_1 = 5, n_2 = 4, $p > 0.05$).

[25] Annual maxima ranged from 9.08 to 9.40 μmol mol^{-1} in shell A55 (mean [2001–2005] = 9.30 μmol mol^{-1}; σ = 0.13 μmol mol^{-1}), and from 10.03 to 11.12 μmol mol^{-1} in shell A56 (mean [2002–2005] = 10.46 μmol mol^{-1}; σ = 0.22 μmol mol^{-1} (Table 3)). Mean annual maximum in shell A56 was significantly higher than in shell A55 (Mann-Whitney U = 0, n_1 = 5, n_2 = 4, $p < 0.05$).

[26] As a consequence, mean annual amplitude in shells A55 (2.14 μmol mol^{-1}) and A56 (3.02 μmol mol^{-1}) were significantly different (Mann-Whitney U = 0, n_1 = 5, n_2 = 4, $p < 0.05$). Annual amplitude ranged from 2.01 to 2.32 μmol mol^{-1} in shell A55, and from 2.76 to 3.63 μmol mol^{-1} in shell A56 (Table 3).

[27] Li/Ca_{shell} in both shells was statistically correlated with the $\delta^{18}O_{shell}$-derived temperature ($p <$ 0.05 for both specimens (Figure 4)). An ANCOVA showed no significant difference between slopes of the two linear regressions (Bartlett's test: B_C = 5.52, df = 1; ANCOVA: F = 0.02, df = 1 and 95). The strength of these correlations was, however, extremely weak with determination coefficients ranging from 0.11 (shell A56) to 0.25 (shell A55). The difference in intercept values (∼1 μmol mol^{-1}) reflects the difference in annual maxima between shell A56 and shell A55.

[28] The comparison of Li/Ca_{shell} variations with daily shell growth rates was difficult because we were unexpectedly unable to resolve microgrowth

Table 3. Annual Minima, Maxima, and Amplitude of Li/Ca_{shell} Values of Specimens A55 and A56 Over the Period 2001–2005

Year	Shell	Minimum Li/Ca_{shell}	Maximum Li/Ca_{shell}	Annual Amplitude
2001	A55	7.26	9.40	2.13
	A56	–	–	–
2002	A55	7.29	9.29	2.01
	A56	7.64	10.42	2.77
2003	A55	7.00	9.08	2.08
	A56	7.50	10.26	2.76
2004	A55	7.08	9.39	2.32
	A56	7.10	10.03	2.92
2005	A55	7.15	9.30	2.15
	A56	7.50	11.12	3.63

structures over the whole shell sections despite etching with Mutvei's solution. Nevertheless, 22 groups of 3–5 microgrowth increments were quite clearly revealed in the A56 shell portion formed in 2004. The average increment width in each of these 22 batches was calculated and plotted with the A56 Li/Ca_{shell} record for year 2004 (Figure 5a). Although the number of increment data was limited, our data showed that Li/Ca_{shell} covaried with microgrowth increment width, which ranged from 24 to 28 μm near the annual lines to 43 μm in the first half of the 2004 growing season (average = 32.3 μm). A simple linear regression indicated that microgrowth increment width explained 53% of the Li/Ca_{shell} variability in shell A56 ($p < 0.001$ (Figure 5b)). Note that all geochemical and shell growth data obtained on specimens A55 and A56 can be retrieved in the auxiliary material.[1]

4. Discussion

4.1. Seasonal Timing of Geochemical Records in Shells

[29] The present study is the first to investigate Li/Ca records in bivalve shells. Li/Ca_{shell} seasonal variations in our two *Arctica islandica* specimens were well marked, presenting a 1.3- to 1.6-fold range over a given growing season (Figure 3). The interannual variability between ontogenetic ages 3 to 8 was far less pronounced than intra-annual variability. Combined analyses of Li/Ca_{shell} and $\delta^{18}O_{shell}$, and reconstruction of seawater temperature from $\delta^{18}O_{shell}$ allowed us to estimate the seasonal timing of Li/Ca_{shell} variations.

[30] $T_{\delta 18O}$ variations (average annual range = 3.1–8.5°C) showed that the whole annual range of seawater temperature (2.8 to 7.9°C at 20 m depth at LA1) was recorded by the shells (Table 2). This implies that *A. islandica* shells did not stop growing because of thermal stress. Conversely, the position of the annual growth breaks between minimum and maximum $\delta^{18}O_{shell}$ (i.e., between maximum and minimum temperatures, recorded in August and March, respectively) suggests that shells stopped growing between September and February. The average microgrowth increment width measured in shell A56 was 32.3 μm at ontogenetic age 6, i.e., similar to the value calculated by *Schöne et al.* [2005a] for North Sea specimens (31.5 μm at ontogenetic age 4). This suggests that shell growth lasted ~185 days to achieve the 5.96 mm width of the 2004 annual increment. This result supports the hypothesis of an ~6 month growth break between September and February. As minimum temperatures were recorded by $\delta^{18}O_{shell}$, shells did not stop growing because of harsh winter conditions. *Schöne et al.* [2005a] showed that *A. islandica* specimens from the North Sea stopped growing from early September to mid-November and described this growth break as a spawning biocheck. In Iceland, *A. islandica* spawning activity peaks in June–July, whereas gametogenesis occurs from January to May [*Thorarinsdóttir*, 2000]. Therefore, the annual growth breaks found in our specimens cannot be attributed to reproductive activity. Moreover, our specimens were likely juveniles as in Icelandic waters, only 10% of *A. islandica* of 40 mm shell length are mature [*Thorarinsdóttir and Jacobson*, 2005]. Therefore, the origin of these annual growth breaks remains unclear. Their investigation, however, is far beyond the goals of this paper. The most important point is that the timing of the growing season determined by $T_{\delta 18O}$ variations allowed us to conclude that Li/Ca_{shell} increases from March to May, i.e., right after the annual line, stays roughly stable in June, and then decreases in July–August.

4.2. Processes Potentially Involved in Li/Ca_{shell} Seasonal Variations

[31] The shape of Li/Ca_{shell} variations is very similar in shells A55 and A56 and as such this ratio likely responds to environmental variations or to variations of a physiological process synchronized within a given population by genetic and/or exogenous factors. Based on published literature on Li/Ca ratios in $CaCO_3$ structures, the following

[1] Auxiliary materials are available at ftp://ftp.agu.org/apend/gc/2009gc002789.

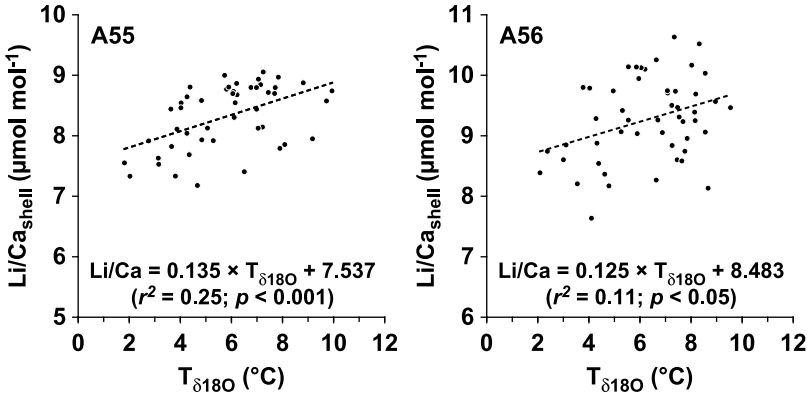

Figure 4. Correlations between $\delta^{18}O_{shell}$-derived seawater temperature ($T_{\delta 18O}$) and Li/Ca_{shell} ratio in shells A55 (n = 48) and A56 (n = 50).

parameters may provide plausible hypotheses to explain the Li/Ca_{shell} variations in *A. islandica*: temperature, calcification rate, and Li/Ca ratio in seawater. Their potential influence on the shell geochemistry will be discussed in light of the evidence presented here. A fourth hypothesis will also be put forward: the influence of suspended Li-rich particles originating from the mechanical weathering of basaltic rocks.

4.2.1. Temperature

[32] Several studies have found a significant inverse relationship between Li/Ca in $CaCO_3$ structures and temperature in coralline aragonite [*Marriott et al.*, 2004b; *Montagna et al.*, 2006], in foraminiferal calcite [*Hall and Chan*, 2004; *Marriott et al.*, 2004a], in calcitic brachiopods [*Delaney et al.*, 1989], and in inorganic calcite [*Marriott et al.*, 2004b]. We also found relationships with temperature in *A. islandica* aragonitic shells but these were positive, not negative (Figure 4). Unlike these previous studies, our findings agree with thermodynamic calculations predicting that Li concentration in $CaCO_3$ structures should decrease with decreasing temperature [*Hall and Chan*, 2004]. According to *Okumura and Kitano* [1986], Li is incorporated in the crystal structure of aragonite in substitution of Ca, leading to the formation of lithium carbonate (Li_2CO_3) crystals. *Smith et al.* [1971] showed that the solubility of Li_2CO_3 increases with decreasing temperature. In other words, crystallization of Li_2CO_3 becomes easier as temperature rises (an almost linear relationship between 0 and 30°C [*Smith et al.*, 1971]). Although statistically significant ($p < 0.05$), the strength of our temperature-Li/Ca_{shell} relationships is extremely weak ($0.11 < r^2 < 0.25$). The weakness of this relationship is particularly obvious for the 2003 Li/Ca_{shell} record in shell A56 where an important offset can be seen between Li/Ca_{shell} and $\delta^{18}O_{shell}$ (Figure 3b). Our findings suggest that if temperature-dependent solubility of Li_2CO_3 really plays a role on Li/Ca_{shell} in *A. islandica*, this influence is extremely weak.

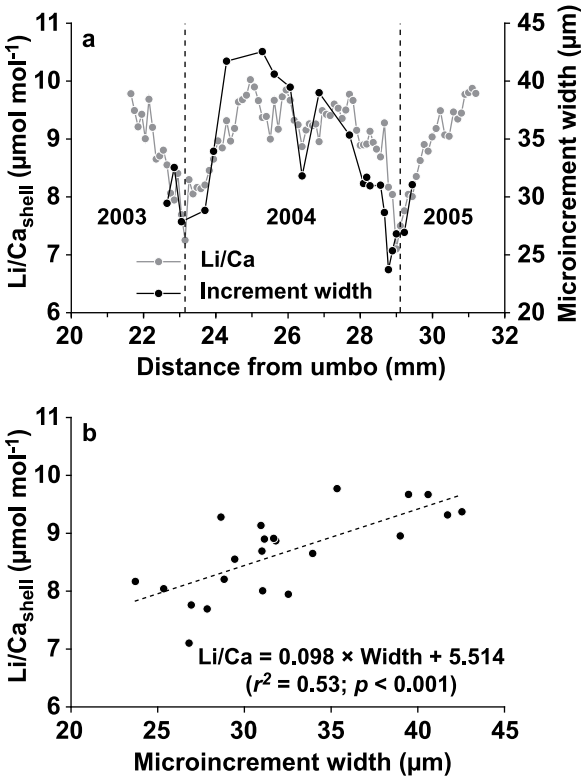

Figure 5. (a) Li/Ca_{shell} profile (gray circles) and microgrowth increment width (black circles) measured during the 2004 growing season in shell A56. (b) Simple linear regression performed between Li/Ca_{shell} and microgrowth increment width in shell A56 (n = 22).

4.2.2. Calcification Rate

[33] Many authors have suggested that the main factor controlling Li incorporation in foraminiferal calcite could be calcification rate, which may itself correlate partly with temperature [*Delaney et al.*, 1985; *Hall and Chan*, 2004; *Marriott et al.*, 2004a]. According to *Carré et al.* [2006], crystal growth rate strongly influences incorporation of Sr, Ba, Mn, and Mg in aragonitic shells of two Peruvian bivalve species (*Mesodesma donacium* and *Chione subrugosa*). However, they did not investigate Li/Ca_{shell} ratios. Our own results seem to support these findings. Indeed, we found a relatively strong relationship between microgrowth increment width and Li/Ca in *A. islandica* shells (Figure 5). Although microgrowth increment width represents the dorso-ventral linear extension of the shell per unit time and may slightly differ from the absolute calcification rate (see *Gillikin et al.* [2005] for elaboration), our results suggest that Li/Ca_{shell} may increase as a direct response of increasing calcification rate. Another argument in favor of this hypothesis is the difference observed in the range of Li/Ca variations in shells A55 and A56; although these two specimens appeared to have grown at an equivalent annual rate from 1999 to 2006, it can be assumed that A56 reached higher daily growth rates in summer than A55, explaining the difference in annual Li/Ca_{shell} maxima between these two shells. The mechanisms involved in these vital effects are unknown and any discussion on that subject would be highly speculative due to the scarcity of studies dealing with the formation of Li_2CO_3 crystals within aragonitic structures. Identification of these mechanisms would require biomineralization and/or inorganic precipitation experiments.

4.2.3. $Li/Ca_{seawater}$

[34] *Delaney et al.* [1985] and *Hathorne and James* [2006] suggested that Li/Ca ratio in calcitic foraminifera was directly controlled by the Li/Ca of the growing medium. Could possible variations of $Li/Ca_{seawater}$ over *A. islandica* growing season have an influence on the shell geochemistry? Li is essentially conservative in seawater with an almost constant concentration of 26 μmol L^{-1} and a $Li/Ca_{seawater}$ ratio of ~2310 μmol mol^{-1} [*Li*, 2000]. It has no significant involvement in biological activity or scavenging by particles [*Stoffyn-Egli and Mackenzie*, 1984]. Given the long residence times of Li (1.5 million years [*Huh et al.*, 1998]) and Ca (1 million years [*Broecker and Peng*, 1982]), the Li/Ca ratio of the global ocean has probably not changed over the Holocene [*Hall and Chan*, 2004]. The two major sources of Li to the ocean are (1) high-temperature basalt-seawater reactions and (2) river input from the weathering of continental crust [*Hoefs and Sywall*, 1997]. In hydrothermal systems near the mid-ocean ridges, Li is leached from oceanic basalts at temperatures >250°C [*Hoefs and Sywall*, 1997]. Although the mid-Atlantic ridge runs right through Iceland, it is unlikely that such high temperatures could be reached at shallow coastal locations. Moreover, it is hardly conceivable that Li leaching from this ridge would follow a seasonal pattern; it is rather roughly constant throughout the year. Therefore, high-temperature hydrothermal circulation can certainly not explain Li/Ca_{shell} seasonal variations.

[35] Seasonal variations of riverine inputs may, however, have a local influence on Li/Ca ratios in coastal waters. Intensities of chemical and mechanical weathering of silicate rocks like basalts are usually expressed in terms of fluxes of dissolved and suspended materials, respectively [*Gislason et al.*, 2009]. *Gislason et al.* [2009] found a relationship between air temperature and chemical weathering rate in 8 northeastern Iceland river catchments. Air temperature in Iceland starts increasing in March and reaches maxima in July. Intensity of chemical weathering may therefore follow the same general pattern as Li/Ca_{shell}. *Pogge von Strandmann et al.* [2006] analyzed the chemical composition of 25 Icelandic rivers in September 2003 and August 2005 and found an average dissolved Li concentration of 87.5 nmol L^{-1} (range: 1.54–1250 nmol L^{-1}) and a Li/Ca_{river} ratio ranging from 31 to 2461 μmol mol^{-1} (average = 563 μmol mol^{-1}). This dissolved Li concentration range is similar to that measured by *Vigier et al.* [2009] in the major Icelandic rivers (range: 3–317 nmol L^{-1}; average = 86.5 nmol L^{-1}). These values may be slightly higher in July, i.e., at the annual air temperature maximum. According to *Delaney et al.* [1985], a 1.8- to 2.6-fold increase of the average $Li/Ca_{seawater}$ ratio is necessary to observe a 1.3- to 1.6-fold increase of Li/Ca in calcitic foraminifera. This relationship can probably not be applied to *A. islandica* shells because of their aragonitic structure. Nevertheless, it highlights that $Li/Ca_{seawater}$ must increase significantly to induce a 1.3- to 1.6-fold increase of Li/Ca in biogenic carbonates. Given that the maximum Li/Ca_{river} ratio measured by *Pogge von Strandmann et al.* [2006] was only 1.1-fold higher than $Li/Ca_{seawater}$, seasonal variations of basalt chemical weathering and dis-

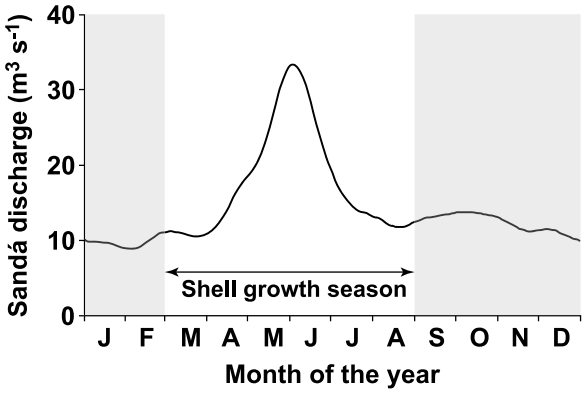

Figure 6. Long-term smoothed daily averages of Sandá River discharge (data obtained from the Hydrological Service of the Icelandic National Energy Authority). Maximum discharge is recorded in May and June, i.e., in the middle of *A. islandica* shell growth season.

solved Li flux can hardly explain the full variability of Li/Ca_{shell} in *A. islandica*.

4.2.4. Suspended Li-Rich Basaltic Particles

[36] A fourth hypothesis could be put forward to explain Li/Ca_{shell} seasonal variations: the possible influence of weathered basaltic particles carried by rivers. Seasonal variations of Sandá River discharge were obtained from the Hydrological Service of the Icelandic National Energy Authority (http://www.os.is/ (Figure 6)). These data show that discharge roughly follows the same seasonal pattern as Li/Ca_{shell}, with values ranging from $\sim$10 m^3 s^{-1} in fall and winter to $\sim$35 m^3 s^{-1} in June (long-term average). Could these variations in river discharge induce large changes in the flux of suspended particles? *Gislason et al.* [2009] described and quantified a direct relationship between river discharge and mechanical weathering (expressed as suspended inorganic material (SIM) flux) in 8 river catchments in northeast Iceland. Depending on which of their 8 discharge-SIM flux equations is used for calculation, the 350% seasonal increase in river discharge would induce a 350 to 4900% increase in SIM flux over a year. Therefore, high loads of suspended basaltic particles probably flow to the sea with Icelandic rivers as soon as the snow melts, reaching a peak roughly at the same time as the Li/Ca_{shell} annual maximum. These river particles have a high Li content (several ppm [*Pogge von Strandmann et al.*, 2006]), $\sim$1 order of magnitude larger than in shells. Although the freshwater inputs likely flow as a thin surface layer ($\sim$10 m thickness [cf. *Astthorsson*, 1990; *Andrews et al.*, 2001]), it is likely that suspended material carried by rivers can cross the halocline and settle on the seafloor, thus modifying the chemistry of bottom waters. Consequently, these Li-rich particles may significantly increase Li/Ca_{shell}, either directly (if ingested, transferred to the internal fluids, and then incorporated within the shell during biomineralization) or indirectly if they weather after deposition on the seafloor. This hypothesis could be tested in further studies through analyses of the lithium isotope composition of *A. islandica* shells. SIM originating from the weathering of basaltic material has a very low δ^7Li value ($\delta^7Li_{SIM} = -1.3$ to 7.5‰ in Icelandic rivers [*Pogge von Strandmann et al.*, 2006]) in comparison to seawater ($\delta^7Li_{seawater}$ = 32‰ [*Huh et al.*, 1998]). If indeed Li incorporation in shells is linked to Li-rich particle inputs by rivers, then shell aragonite must have a δ^7Li several per mil lighter than seawater.

4.3. Conclusions

[37] Lithium is likely incorporated in *A. islandica* aragonitic shells as lithium carbonate Li_2CO_3; that is, Li^+ substitutes for Ca^{2+} at the site of calcification in the extrapallial fluid. Several explanations could account for the observed seasonal variations in Li/Ca ratio in shells:

[38] 1. The significant positive relationship found between $\delta^{18}O_{shell}$-derived temperature and Li/Ca_{shell} suggests that seasonal Li/Ca_{shell} variations could be linked to increasing solubility of Li_2CO_3 with decreasing temperature in the extrapallial fluid. However, the strength of this relationship is so weak that temperature-dependent solubility of Li_2CO_3 cannot possibly be the main factor controlling Li/Ca_{shell} variations;

[39] 2. Given the strong and significant positive relationship found between Li/Ca_{shell} and micro-growth increment width, Li/Ca_{shell} may partly be controlled by variations in calcification rate. As this rate is also partly controlled by temperature, it is difficult to make conclusions about the exact importance of Li_2CO_3 solubility in Li/Ca_{shell} variations;

[40] 3. Sandá river discharge and Li/Ca_{shell} presented an intriguing similarity in their seasonal variations. As soon as snow melts in spring, mechanical weathering of basaltic rocks gains intensity due to the increased river discharge, leading to a massive flow of Li-rich silicate particles into the ocean. This phenomenon reaches a peak at the same time as Li/Ca_{shell}. We therefore

suggest that this massive input of Li could be trapped in the shell, thus impacting Li/Ca_{shell}.

[41] If indeed Li/Ca_{shell} is mainly controlled by calcification rate, then this ratio may be useful to address seasonal variations in growth rate of bivalve species in which daily growth increments and lines are not easily discernable. In turn, abrupt decreases of Li/Ca_{shell} may be helpful to identify growth retardations, for instance related to the occurrence of toxic phytoplankton blooms in coastal ecosystems. Alternatively, if Li/Ca_{shell} in *A. islandica* is controlled by river inputs of Li-rich silicate particles, it may then be used a proxy for the intensity of mechanical weathering of Icelandic basaltic rocks. This could have exciting perspectives, e.g., to get a better insight about the frequency and intensity of past jökulhlaups (subglacial outburst floods). It may also be interesting to analyze the geochemical composition of recent *A. islandica* shells from the southeast coast of Iceland, where a huge jökulhlaup flowed under the Vatnajökull glacier in 1996 because of the subglacial eruption of the Grímsvötn Volcano. In any event, it is clear from our work that further studies, including δ^7Li_{shell} analyses and experiments under controlled conditions, are needed to better understand Li/Ca_{shell} variations in bivalve shells and to determine if this could be a useful proxy for paleoecological reconstructions.

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