

Uranium in aragonitic marine bivalve shells

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ABSTRACT

Uranium concentrations in foraminiferal and coral skeletons track oceanic $[\text{CO}_3^{2-}]$ and can be useful as a proxy of ocean acidification, but this pH proxy is yet to be investigated in bivalves. Two *Saxidomus giganteus* shells from the industrialized Puget Sound (WA, USA) and one from the more pristine Kodiak Island (AK, USA) were sampled through ontogeny for U/Ca using laser ablation inductively coupled mass spectrometry. All three shells show a similar pattern of seasonal U/Ca cycles during the first six years of life, followed by a sharp decrease to below the detection limit for the remainder of the clams life (10–20 years), consistent with a biological or ontogenic forcing (vital effect). However, analyses along a growth-line (carbonate formed at the same time) show a decrease in U/Ca from the outside of the shell toward the inside, consistent with diagenesis. Clearly U/Ca is not under environmental control in these aragonite shells, but the cause of the variability is not currently clear.

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1. Introduction

Uranium to calcium ratios have been suggested as a proxy of oceanic $[\text{CO}_3^{2-}]$ in aragonitic shallow and deepwater corals (Min et al., 1995; Shen and Dunbar, 1995; Anagnostou et al., 2011) and calcitic foraminifera (Russell et al., 2004). Shallow water corals also show a strong temperature control on skeletal U/Ca ratios (Min et al., 1995; Shen and Dunbar, 1995). Studies have also found a pH effect on U in both inorganic aragonite and calcite (Kitano and Oomori, 1971; Chung and Swart, 1990). U/Ca ratios in calcium carbonate are negatively correlated with pH and $[\text{CO}_3^{2-}]$ because in aqueous solutions the carbonate ion complexes with the uranyl ion (UO_2^{2+}) (Langmuir, 1978), therefore at higher pH less U is available to be incorporated in shell carbonate. However, this relationship has never been tested in mollusk shells.

Carbon dioxide emissions from burning fossil fuels decrease ocean pH and reduce the availability of $[\text{CO}_3^{2-}]$. Ocean acidification is a major concern threatening calcifiers around the world (Feely et al., 2004; Fabry, 2008; Doney et al., 2009). Recently, estuarine acidification has also become a concern due to potential impacts on larval and adult mollusks (Gazeau et al., 2007, 2010; Miller et al., 2009; Talmage and Gobler, 2010). In order to predict the impact of increasing pCO_2 emissions on estuarine mollusks, it is important to understand how mollusks dealt with past pCO_2 variability. Experiments can be designed based on our best predictions of past and future pCO_2 variations (e.g., Gazeau et al., 2007, 2010; Miller et al., 2009;

Talmage and Gobler, 2010), but natural populations are both better acclimated to changes that take place over several generations and have to cope with other environmental stressors in addition to acidification. Experimental acclimation time can alter the outcomes of acidification impacts on calcifiers (see Krief et al., 2010). Therefore, it would be ideal to have a proxy of past estuarine acidification to ascertain how natural mollusk populations were impacted.

There are few studies on uranium in bivalve shells. Several papers dealing with U-series dating have reported strong diagenetic trends in fossil and recent shells (e.g., Kaufman et al., 1971, 1996; McLaren and Rowe, 1996; Labonne and Hillaire-Marcel, 2000), but these were generally low-resolution studies (integrating large amounts of shell and thus time). Understanding uranium incorporation into bivalve shells may also help refine the application of U-series dating mollusk shells, which would provide an archive with unprecedented resolution for samples older than the ^{14}C -dating range. Only a few studies investigated high-resolution temporal variability of U/Ca in bivalve shells. Price and Pearce (1997) studied aragonite marine cockle shells (*Cerastoderma edule*) and related their uranium concentrations to granite weathering and industrial effluents. Markich et al. (2002) analyzed U/Ca ratios in aragonite freshwater mussel shells and found the shells to be archival indicators of uranium pollution from a copper–uranium mine in tropical northern Australia, but they did not discuss potential pH impacts of the acid effluent on U/Ca ratios. Studies investigating U/Ca in bivalve shells as a potential acidification proxy are lacking.

Due to the increasing emissions of fossil fuel CO_2 coupled with increased nutrient loading to coastal areas leading to increased aquatic respiration and subsequent acidification (see Feely et al., 2010), in addition to direct industrial U effluent, we expect live collected shells to show an increase in U/Ca ratios through time. Here we test this

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hypothesis on shells of the butter clam (*Saxidomus giganteus* DeShayes, 1839) collected from the industrial Puget Sound (Washington, USA) and the more pristine Old Harbor (Kodiak Island, Alaska, USA). Oxygen isotope data from these shells has been presented in Gillikin et al. (2005a, b), which shows that the Puget Sound shells lived for approximately 10 years while the shell from Kodiak Island lived for about 20 years.

2. Materials and methods

Two living clams were collected from the same area (within ~10 m of each other; shells B1 and B2) in Puget Sound, near Carkeek Park, North Seattle, WA, USA (N47°42'45" W122°22'46") on 18 September 2001 (see Gillikin et al., 2005a and b for more details) and one clam was collected from Old Harbor, Kodiak Island, Alaska, USA (N57°10'57" W153°18'14") on 28 June 2003 (shell OH1; see Gillikin et al., 2005b for more details). A photo of these shells is presented in Gillikin et al. (2008). In Puget Sound, the substrate was gravelly mud, and the tidal height was about 30 cm above mean lower low water. Puget Sound salinities range from 21 to 30 and temperatures from 7 °C to 17 °C, while Old Harbor salinities range from 18 to 32 and temperatures from 0 to 13 °C (see Gillikin et al., 2005b). Gillikin et al. (2005b) have shown that *S. giganteus* precipitate aragonite shells and that the shells used in this study are 100% aragonite (i.e., there has been no recrystallization to calcite). Sections of the shells were cut with a diamond saw along the axis of maximal growth, rinsed with deionized water, air-dried and mounted on microscopic slides.

Two laser ablation Inductively Coupled Mass Spectrometer (LA-ICP-MS) systems were used in this study. High-resolution profiles along the entire growth axes were obtained using a Fisons-VG frequency quadrupled Nd-YAG laser ($\lambda = 266$ nm) coupled to a Fisons-VG PlasmaQuad II + mass spectrometer. Details of LA-ICP-MS operating conditions can be found in Lazareth et al. (2003) and Gillikin et al. (2006). ^{43}Ca was used as the internal standard and was considered to be 40% by mass; ^{238}U was monitored for U concentrations. Gas blank intensities were recorded every 10th sample. Approximately after every 50th sample, two standards (NIST 610, values from Pearce et al. (1997), and the USGS MACS1, values from S. Wilson, USGS, unpublished data, 2004) were analyzed five to six times each. Calibration (including gas blank subtraction, ^{43}Ca normalization, and drift correction) was performed offline following Toland et al. (2000). The U/Ca detection limit was calculated to be 0.004 $\mu\text{mol/mol}$. For this study, the laser was shot directly in the holes of the isotope sampling reported in Gillikin et al. (2005a). Samples were taken from the middle of the outer shell layer, avoiding the outermost part of the shell, which is in contact with the water.

To determine U/Ca variations from the external part of the shell to the internal part, a CETAC LSX-213 frequency quintupled Nd:YAG laser ($\lambda = 213$ nm) coupled to a Perkin Elmer Elan 6100 DRC ICP-MS was used (ThO/Th ratios were less than 0.5%). Helium was used as the carrier gas (600 mL/min), which was mixed with argon after the ablation cell (800 mL/min). A spot size of 50 μm was used with the laser set at 10 Hz and 600 burst counts. As above ^{43}Ca and ^{238}U were monitored. A 15 s pre-ablation was used for gas blank corrections (i.e., the shutter was closed). Calibration was performed using the NIST 612 (values from Pearce et al., 1997). The USGS standard MACS-3 was used to check the calibration, which suggests a robust LA-ICP-MS calibration and good reproducibility ($[\text{U}] = 1.55 \pm 0.04$ ppm, $n = 6$ on two analytical days; recommended value = 1.52 ± 0.04 ppm, USGS, 2011; $\text{U/Ca} = 0.65 \pm 0.02$ $\mu\text{mol/mol}$). Data was reduced using GeoPro software (CETAC). Four transects from the outer to inner shell were analyzed: two toward the umbo region (oldest shell material), where one progressed perpendicular from the outside of the shell (starting as close to the edge as possible, in an area without clearly visible growth lines) to the inside, the other following a pronounced growth

line. Two transects were also analyzed toward the growing edge, perpendicular to the external shell surface. This LA-ICP-MS system was also used to check the data collected from the 266 nm laser; 18 analyses were taken near the umbo and five shots were taken near the growing edge.

To assess the similarity between the two *S. giganteus* shells from Puget Sound, the profiles need to be fit to a common timescale. For this purpose, the $\delta^{18}\text{O}$ profiles, obtained from former studies on these shells (Gillikin et al., 2005a), were used. High-resolution profiles of shell $\delta^{18}\text{O}$ often show a clear annual periodic signal, reflecting the seasonal temperature variation. Using the relation between $\delta^{18}\text{O}$ and temperature, shell layers were assigned intra-annual dates. This was achieved by using the phase demodulation method of De Ridder et al. (2004). More details can be found in Gillikin et al. (2005a). Considering that the elemental analyses were perfectly aligned with $\delta^{18}\text{O}$ analyses (see Gillikin et al., 2005b), the fitting of the $\delta^{18}\text{O}$ profiles allows a direct comparison of elemental profiles between the two shells (the profiles of shell B1 was fit to shell B2). Oxygen isotope data from shell OH1 are from Gillikin et al. (2005b). Due to the annual periodic signal, oxygen isotope profiles also allow year and season of growth to be determined (being that time of death is known).

Sections of shells B1 and B2 were imaged with a Zeiss EVO50XVP scanning electron microscope (SEM; 15 kV). Images were taken from the outer prismatic shell layer in the umbo region as well as at the growing edge region of both shells. Shell pieces were manually broken to expose crystal structure and were carbon coated for analyses.

3. Results

All three shells exhibit seasonal cycles in U/Ca, which decreased below the detection limit after about 6 years of growth (Fig. 1). Shells from Puget Sound that grew at the same time show similar U/Ca profiles generally following inverted $\delta^{18}\text{O}_{\text{shell}}$ values, with minimal values in winter (close to the detection limit) and maximal in spring (as high as 1.1 $\mu\text{mol/mol}$, or ~2.6 ppm). However, this pattern is variable between years and shells; for example the winter near 46 mm shell growth is characterized by high U/Ca ratios. U/Ca in all three shells decreases below the detection limit after about 6 years of growth (despite OH1 being twice as old).

Analyses with the 213 nm laser confirm the results of the 266 nm laser. The analysis was not in the same exact position, so small differences can be expected. Nevertheless, both lasers show higher U/Ca ratios toward the umbo region and U/Ca values below the detection limit toward the growing tip of the shell (Fig. 1).

LA-ICP-MS transects from the outside to the inside of the shell (perpendicular to the outer surface in cross-section) near the growing edge of the shell show no change across the shell and remain below the detection limit for both transects (data not shown). The LA-ICP-MS transects near the umbo region both showed high U/Ca ratios toward the exterior shell edge (external environment), decreasing toward the inner edge (where the animal lived). The perpendicular transect, which started very close to the external surface of the shell shows a high U/Ca value (~1.0 $\mu\text{mol/mol}$) that quickly decreases toward the inside of the shell (Fig. 2). The transect following the growth line starts off lower than the perpendicular transect (similar to the low U/Ca values seen at growth lines in Fig. 1) and also decreases to below the detection limit at the inside of the shell (Fig. 2).

pH data were obtained from the Washington State Department of Ecology Environmental Information Management website (<http://www.ecy.wa.gov/eim>). Monthly data (taken in triplicate) from station PSB003, approximately 10 km from the clam collection site were available for the period the clams grew in Puget Sound (1991–2001). As pH has a large seasonal fluctuation due to respiration and photosynthesis, only data from the months when these clams produce most of their shell (July, August and September; Gillikin et al., 2005a) was investigated. All three months showed a clear decrease in pH through time (Fig. 3).

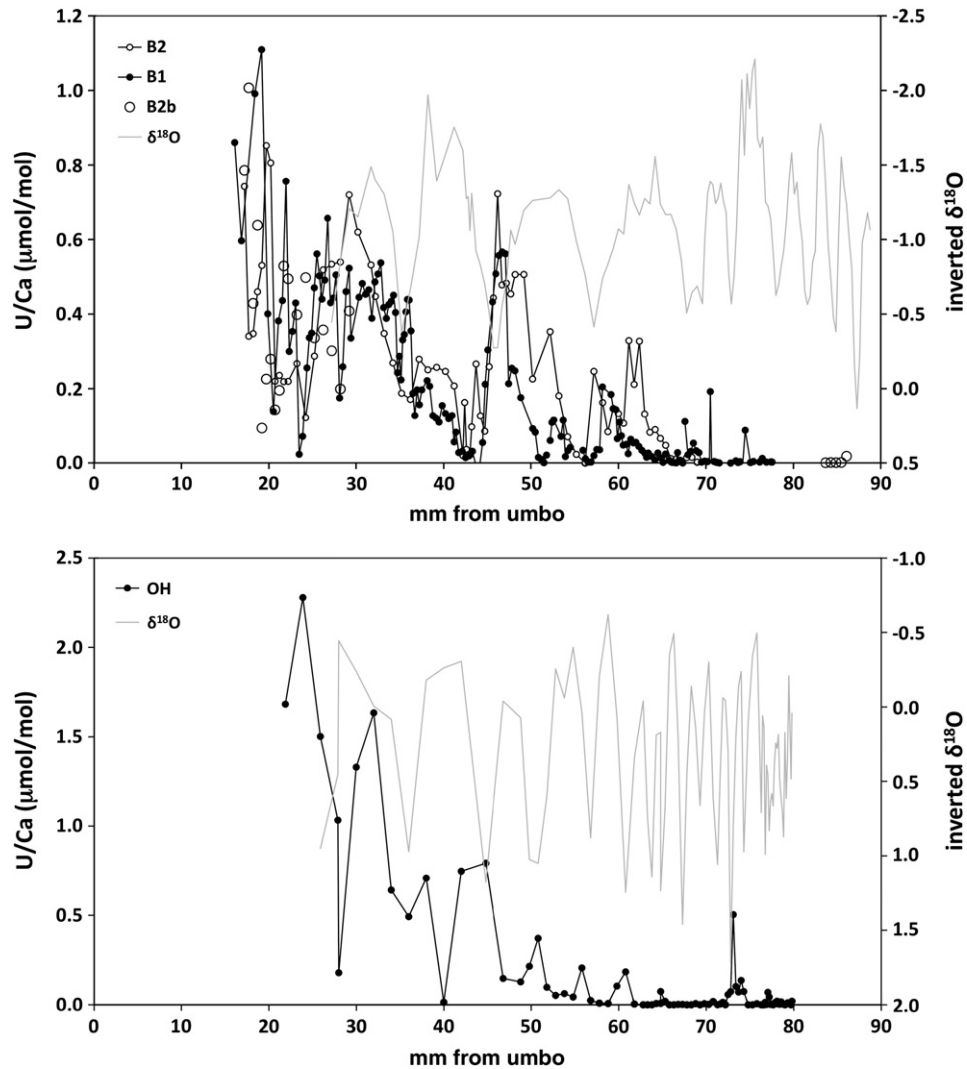


Fig. 1. U/Ca ratios in two *S. giganteus* shells from Puget Sound (WA, USA; top) (B1 and B2) and from Old Harbor, Kodiak Island (AK, USA; bottom) (OH). Data are fit to shell B2 using oxygen isotopes (see Gillikin et al., 2005a,b). Data labeled as B2b are analyses carried out using the 213 nm laser (see Materials and methods). Thin gray line is the oxygen isotope profile (in ‰), inverted to give an approximation of temperature and thus seasonality.

A linear regression between year and pH resulted in a slope of -0.036 ($R^2 = 0.53$; with data from 1999 removed because they were up to 0.5 pH units lower than all other data).

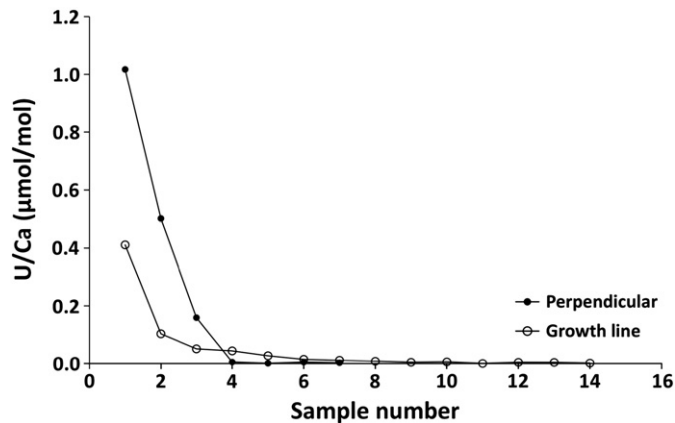


Fig. 2. Transects from the outer shell (starting at sample number 1) toward the inner shell of the region near the umbo of shell B2. One transect follows a prominent growth line (shell precipitated at the same time), whereas the other is approximately perpendicular to the outer layer (crossing time).

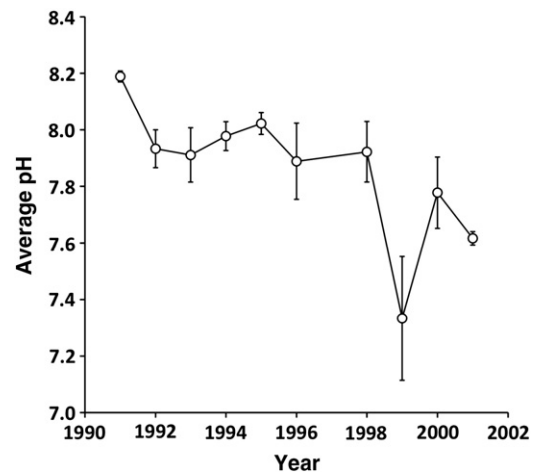


Fig. 3. Three-month average pH (July, August, and September; the months of maximal shell growth) in Puget Sound at station PSB 003 (see Gillikin et al., 2005a, b, c for station location). Error bars represent standard deviation. Data are the average of three replicates taken on one day in each of the three months. The linear regression mentioned in the text excludes data from 1999. pH data are from the Washington State Department of Ecology Environmental Information Management website (<http://www.ecy.wa.gov/eim>).

SEM images show clear indications of borings in both the prismatic regions closer to the umbo (both shells) as well as the region closer to the growing edge (shell B2 only) (Fig. 4). Several of the borings in the shell can be seen in cross-section showing how they perforate the shells of the living animals.

4. Discussion

Uranium to calcium ratios in *S. giganteus* shells are clearly not controlled by pH (or $[\text{CO}_3^{2-}]$). We expect pH to decrease over the life of these bivalves due to both acidification from CO_2 equilibrium with the atmosphere and from increased respiration from nutrient run off (cf. Feely et al., 2010). Indeed, pH at a nearby station in Puget Sound (PSB003) shows a drop of 0.036 pH units per year during the time the clams lived (Fig. 3). This should lead to an increase in shell U/Ca ratios throughout the life of these bivalves. We see the opposite, a decrease in shell U/Ca ratios through time (Fig. 1). U concentrations in estuaries are generally conservative with salinity with low U in fresher waters (e.g., Chen et al., 1986; Strady et al., 2009), but salinity at these sites has not steadily decreased during the lives of these bivalves (Gillikin et al., 2005b) and water U pollution is not expected to have changed dramatically over this time period, therefore U concentrations in the water are not likely the cause of the variability. Two viable hypotheses that can explain this pattern are that 1) U/Ca ratios are controlled by biological effects (vital effects) or 2) U/Ca ratios are an early (in vivo) diagenetic signal affecting the older part of the shell first.

Biological processes (vital effects) are reported to control several elemental systems in bivalve shells (Klein et al., 1996; Purton et al.,

1999; Gillikin et al., 2005b, 2005c; Carré et al., 2006), sometimes with a strong ontogenic decrease in concentrations, often correlated with growth rate (e.g., Gillikin et al., 2005b; Lorrain et al., 2005; Carré et al., 2006). In fact, these same shells exhibit strong ontogenic decreases in Sr/Ca ratios (Gillikin et al., 2005b) and subtle ontogenic decreases in Ba/Ca ratios (Gillikin et al., 2008). This would seem to also apply to U/Ca ratios, with the highest shell U/Ca ratios in spring when the fastest growth rates would occur. Indeed, Gabitov et al. (2008) found that U/Ca increased at higher crystal growth rates in inorganic aragonite, similar to what we observed in these shells. However, biological or crystal growth rate effects should be equal in carbonate being precipitated at the same time (i.e., along growth lines). Therefore, elemental ratios should be approximately similar along growth lines, while we found a strong decrease along the growth line closer to the umbo of the shell (Fig. 2), indicating these effects do not control U/Ca in these shells. Other elements (Sr, Ba, and Pb) monitored along this same growth line did not show a trend in concentrations (data not shown) indicating they are being deposited under similar conditions along the growth line (which is presumably being deposited at the same time). Similar results have also been reported for another bivalve species (for Sr/Ca and Ba/Ca; Lazareth et al., 2013). Moreover, using winter $\delta^{18}\text{O}_{\text{shell}}$ values to mark annual growth, it is apparent that between 57 and 68 mm of shell growth U/Ca ratios are low despite similar or even lower growth during the previous growth years between 27 and 57 mm where U/Ca is high (Fig. 1, top). Therefore, there is not a direct link between shell growth rate and U/Ca ratios. An alternative hypothesis is that crystalline bound organic matter might be sequestering uranium. However, we expect higher organic content toward the growing edge of the shell and at growth lines (see Schöne, 2008),

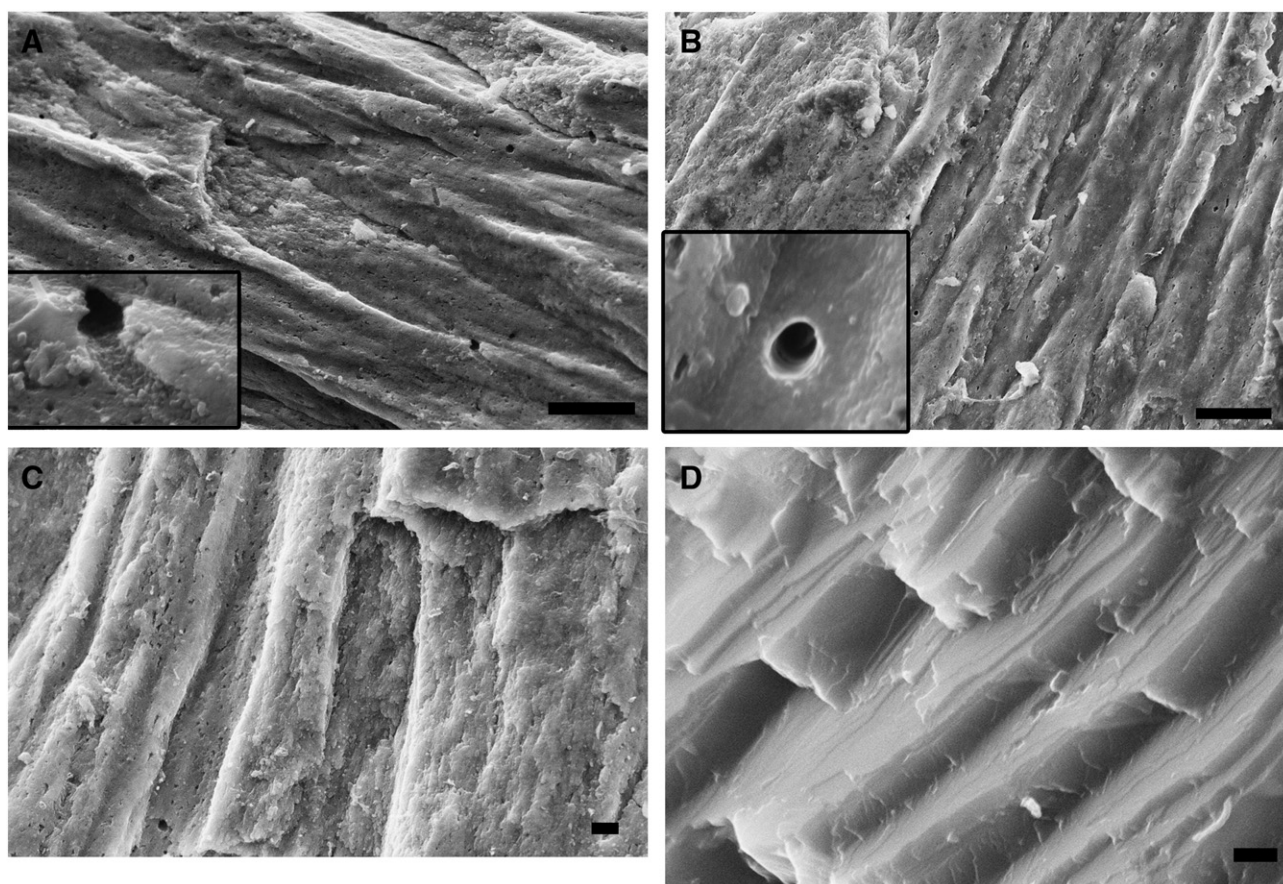


Fig. 4. Scanning electron images of A) shell B2, outer prismatic layer toward the umbo of the shell showing many micro-borings (inset shows a close up of one), B) shell B2, outer prismatic layer toward the growing tip of the shell also showing many micro-borings (inset shows a close up of one), C) shell B1, outer prismatic layer toward the umbo of the shell showing many micro-borings, and D) shell B1, outer prismatic layer toward the growing tip of the shell also showing pristine unbored prisms. Scale bars, A, B = 10 μm , C = 2 μm , D = 1 μm .

where U/Ca ratios are typically low. The discussion above would indicate that biological or kinetic effects are not the main forcing on U/Ca ratios in these shells, but that diagenesis is first impacting the exterior part of the older shell (that closer to the umbo).

The impact of early (in vivo) digenesis on high-resolution mollusk shell geochemistry has received little attention (Kaufman et al., 1996; Labonne and Hillaire-Marcel, 2000; Lazareth et al., 2013). Kaufman et al. (1996) studied U concentrations in bivalve shells and found U to decrease from the exterior of the shell to the interior in both living and fossil shells, but did not investigate high-resolution trends along the growth axis (through time) or along growth lines (shell precipitated at the same time). They instead ground off large quantities of shell material in sequential layers from the outer shell to the inner shell, covering about two thirds of the shell surface (Kaufman et al., 1996). Nevertheless, our data seem to support this trend, with the older shell material (toward the umbo) having higher U/Ca ratios (Fig. 1) and the exterior of the shell also having the highest concentrations along the growth line (Fig. 2). The shell sections toward the umbo also have been heavily bored by micro-organisms (probably fungal, see Glover and Kidwell, 1993; Fig. 4), which would increase porosity and promote diagenesis (cf. Kaufman et al., 1996; Labonne and Hillaire-Marcel, 2000). The older part of the shell is sitting deeper in reducing sediments and likely is exposed to porewaters with higher U/Ca ratios (e.g., Chaillou et al., 2002; Sundby et al., 2004). The longer this region of the shell sits in these conditions, with increased porosity in the shell caused by micro-borers, the more likely it will take up more U (cf. Swart and Hubbard, 1982). However, there are some inconsistencies with the U/Ca profiles being solely the result of diagenesis.

Organic matter in carbonates is known to promote diagenesis (recrystallization) in shells (e.g., Glover and Kidwell, 1993). If diagenesis were the reason for elevated U/Ca ratios via uranium enrichment from the sediments, then high U/Ca would be expected at organic rich growth lines, where we find lower shell U/Ca ratios. We also do not expect diagenesis to cause a seasonal cycle in U/Ca as is seen in these shells. Moreover, if micro-borings led to an increased porosity and subsequent diagenesis we would expect to find heavy borings toward the shell region close to the umbo (where U/Ca is high) and no borings toward the growing tip (where U/Ca is below the detection limit). We do find this scenario in shell B1, but the growing tip of shell B2 is heavily bored (Fig. 4) and we also found evidence of micro-borings in the inner layer of the growing tip of shell B1. Therefore there is no correlation between U/Ca ratios and micro-borings. A final problem with the diagenesis hypothesis is that the OH1 shell is ~20 years old, but only shows elevated U/Ca during the first 6 years of life (Fig. 1, bottom), the same amount of time the ~10-year-old shells from Puget Sound show elevated U/Ca ratios (Fig. 1, top). In addition, the two shells from Puget Sound show very similar annual and ontogenetic patterns, which would not be expected from diagenesis. If diagenesis was steadily causing U to increase in these shells as they sit in the mud, then we would expect the older shell to show elevated shell U/Ca over more shell than the younger shells (e.g., perhaps over the first 16 years of growth). Therefore, diagenesis does not explain all the U/Ca patterns we see in these shells.

It is clear that whatever the cause for the variation in shell U/Ca, these clams are strongly regulating U uptake into their shells. If we use the detection limit of the LA-ICP-MS (0.004 $\mu\text{mol/mol}$) as the U/Ca value for the region of the shell near the growing tip (Fig. 1) and a water U/Ca value of 1.28 $\mu\text{mol/mol}$ for seawater (Shen and Dunbar, 1995), we calculate a partition coefficient ($D_U = [\text{U/Ca}]_{\text{shell}}/[\text{U/Ca}]_{\text{water}}$) of 0.003. Considering U/Ca values near the umbo region reach 1 $\mu\text{mol/mol}$, a D_U of 0.78 is obtained. The D_U calculated for the growing tip region is more than 1000 times lower than that for corals (0.95; Swart and Hubbard, 1982). Even higher D_U values have been reported for sclerosponge aragonite ($D_U = 2.98$; Rosenheim et al., 2005) and inorganic aragonite precipitates ($D_U = 1.8$ to 9.8; Meece and Benninger, 1993). It should be noted that this is an oversimplified calculation

because uranium exists as several complexes in seawater and it is not certain which is incorporated into the skeleton (see Swart and Hubbard, 1982; Reeder et al., 2000; Russell et al., 2004; Rosenheim et al., 2005). In addition, U/Ca will certainly change in an estuarine setting (river water typically contains less U; Palmer and Edmond, 1993; Strady et al., 2009). Nevertheless, these estimations allow a first approximation of the partition coefficient into bivalve shell aragonite.

With the data at hand we cannot determine what controls the U/Ca in these shells. However, the fact that the 20-year old shell (OH1) and the 10-year old shells (B1 and B2) both only show elevated U/Ca in the first 6 years of life, the presence of borings in the low U/Ca shell regions, and the U/Ca minima at organic rich growth lines suggest it is not entirely a diagenetic signal. Perhaps U incorporation is not similar along the entire growth line and U is controlled by biological processes. Non-continuous calcification (spatially heterogeneous skeletal formation) along a single growth surface has been noted in corals (Houlbrèque et al., 2009), and therefore may be possible in bivalves. To test this hypothesis, shells from young (e.g., <6 year old) living individuals need to be analyzed. If their shells contain low U/Ca ratios toward the umbo region, then the signal in these older shells is likely to be diagenetic; however, if the young shells have elevated U/Ca ratios, then it is likely biological (i.e., the elevated U is not from the shell sitting in the mud for many years). This could assist with studies attempting to utilize U series dating in bivalve shells. To date, bivalve shells are considered to be open systems and not appropriate for U-series dating (Kaufman et al., 1971, 1996; McLaren and Rowe, 1996; Burgess et al., 2010). Several authors have shown that shells take up uranium through time (Kaufman et al., 1971, 1996), but these shells have not been investigated at a high-resolution. Clearly more work is needed to understand U uptake in bivalve shells. Our results illustrate that U uptake in aragonitic bivalve shells may not be as straightforward as previously thought. This study also illustrates that shells cannot serve as simple tracers of environmental uranium contamination without detailed examination of biological and/or diagenetic effects.

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