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1 Does trace element composition of bivalve shells record ultra-high
2 frequency environmental variations?
3

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31 **Abstract**

32 Saint-Pierre and Miquelon (SPM) is a small archipelago where instrumental measures based
33 on water column velocity and temperature profiles compiled comprehensive evidence for
34 strong near-diurnal (25.8h) current and bottom temperature oscillations (up to 11.5°C) which
35 is possibly the largest ever observed — at any frequency — on a stratified mid-latitude
36 continental shelf. The main objective of our study was to identify if *Placopecten magellanicus*
37 can record on its shell these high frequency environmental variations. To this end, we have
38 tried to identify proxies for water temperature and food availability through development of
39 a new ultra-high resolution LA-ICPMS analyses method capable of resolving shell surface
40 elemental composition with a 10 µm resolution. This method was applied on two shell
41 fragments, both representing the third year of growth and 2015 annual growth period,
42 respectively coming from two environmentally contrasted sites, more (30 m depth) or less (10
43 m depth) affected by high frequency thermal oscillations. Our results strongly suggest a
44 relationship between phytoplankton biomass and barium incorporation into *P. magellanicus*
45 shells at both sites. Even if *P. magellanicus* might present a physiological control of magnesium
46 incorporation, the shape of the two Mg/Ca profiles seems to illustrate that temperature also
47 exerts a control on magnesium incorporation in *P. magellanicus* shells from SPM. While U/Ca
48 and Mg/Ca profiles show a strong positive correlation for 30 m site shell, suggesting that
49 uranium incorporation in *P. magellanicus* shell is at least partially temperature dependent.
50 The absence of such correlation for 10 m site shell suggests differences in uranium
51 environmental availability or in *P. magellanicus* biomineralization between these two sites.
52 The resolution of this new analytical method raises questions about such data interpretation
53 related to *P. magellanicus* growth dynamics and physiology or individual scale based
54 environmental measurements.

55

56 **Keywords:** Ultra-high resolution LA-ICPMS; *Placopecten magellanicus*; shell chemistry; trace
57 elements; environmental change; bivalve; environmental proxies; North Atlantic; Saint-Pierre
58 and Miquelon; Coastal Trapped Wave.

59 **1. Introduction**

60 Saint-Pierre and Miquelon (SPM) is a small archipelago at the confluence of major oceanic
61 currents, marking the boundary between the North Atlantic Ocean subtropical and subpolar
62 gyres. However, SPM archipelago hydrodynamics is poorly known and its physic observations
63 (sensor deployments) only began very recently. In this context, instrumental measurements
64 based on water column velocity and temperature profiles compiled comprehensive evidence
65 for strong near-diurnal (25.8h) current and bottom temperature oscillations (up to 11.5°C)
66 from July to October between 10 and 80m depth. This feature is possibly the largest ever
67 observed, at any frequency, on a stratified mid-latitude continental shelf (Lazure *et al.*, 2018).
68 The extremely unstable physical nature of this sub-tidal environment associated with the
69 presence of poikilothermic organisms represents a true ecological paradox, making this site a
70 relevant place to study benthic organism responses to chronic thermal variations.

71 Biogenic carbonate with recognizable periodic growth bands, such as bivalve molluscs can
72 incorporate minor and trace elements into their shells, in amounts depending on their
73 concentrations in the environment and on the physical and biological properties of the
74 surrounding seawater. However, bivalve shell biomineralization is a complex process, subject
75 to strong physiological and kinetic effects related to metabolism, growth rates, ontogenetic
76 age, shell mineralogy, crystal fabrics and organic matrix (e.g. Carré *et al.*, 2006; Freitas *et al.*,
77 2008; Freitas *et al.*, 2009; Freitas *et al.*, 2016; Klein *et al.*, 1996; Lazareth *et al.*, 2013; Lorens
78 and Bender, 1977; Schöne *et al.*, 2013; Shirai *et al.*, 2014). Owing to their wide geographic
79 distribution, economic importance, rapid growth rates, and the presence of annual growth
80 lines on their shell, pectinid bivalves (aka. scallops) offer good opportunities to document past
81 environmental conditions (Chauvaud *et al.*, 1998). The occurrence of a clearly visible annual
82 banding pattern on the upper valve of the Atlantic sea scallop, *Placopecten magellanicus*, and
83 the presence of this species in SPM over a wide bathymetric gradient (5 to 80 m), make this
84 species a good candidate to track high-frequency past environmental changes - reflected as
85 variations in the shell geochemical properties – at extremely high temporal resolution.

86 Spatially-resolved geochemical analysis of biogenic carbonates deposited between two
87 accurately dated growth lines can be performed with a wide set of methods, such as laser
88 ablation inductively coupled mass spectrometry (LA-ICPMS), secondary ion mass
89 spectrometry (nanoSIMS) or electron micro probe analyser (EMPA). Because of its potential

90 for rapid and accurate high-resolution *in situ* trace element analysis at relatively low cost and
91 minimal sample preparation requirements, LA-ICPMS has become a routine analytical tool in
92 a wide area of research applications (Warter and Müller, 2017).

93 As bivalve growth rates have often been related to environmental variables such as food
94 availability or water temperature (Ballesta-Artero *et al.*, 2017; Butler *et al.*, 2010; Marali and
95 Schöne, 2015; Witbaard *et al.*, 1997) and because of the importance of these two parameters
96 to track environmental and ecological changes, we then understand the interest to track and
97 calibrate elemental proxy records of these two variables. For example, some authors
98 proposed that magnesium to calcium ratios (Mg/Ca) can be used to record water temperature
99 (Ullmann *et al.*, 2013, Bougeois *et al.*, 2014), while there are many reports of strong vital
100 effects in bivalve shells for this element (Lorrain *et al.*, 2005, Wanamaker *et al.*, 2008, Surge
101 and Lohmann, 2008). Uranium-to-calcium ratio has also been suggested as a proxy for
102 temperature in shallow-water corals (Min *et al.*, 1995; Shen and Dunbar, 1995) and in
103 planktonic foraminiferal carbonates (Yu *et al.*, 2008). Some authors also found a pH effect on
104 U/Ca ratios in both inorganic aragonite and calcite (Kitano and Oomori, 1971; Chung and
105 Swart, 1990). Indeed, U/Ca ratios in calcium carbonate are negatively correlated with pH and
106 $[\text{CO}_3^{2-}]$, because in aqueous solutions the carbonate ion complexes with the uranyl ion (UO_2^{2+})
107 at higher pH (Langmuir, 1978), therefore less uranium is available to be incorporated in shell
108 carbonate. Regarding U/Ca ratio on mollusc shells, Frieder *et al.* (2014) demonstrated that
109 U/Ca varies as a function of pH in shells of living larvae in *Mytilus californianus* and *Mytilus*
110 *galloprovincialis*. More recently, Zhao *et al.* (2018) demonstrated by measuring U/Ca ratio on
111 *Mya arenaria* shells exposed to $p\text{CO}_2$ -enriched environments the existence of efficient
112 regulatory mechanisms to tightly control the pH at the site of calcification of this species. .
113 Ba/Ca profiles in bivalve shells are typically characterized by a flat background signal
114 interrupted by sharp peaks. Background level has been suggested to be linked with salinity
115 (Gillikin *et al.*, 2006, 2008). As for peaks, many authors suggested a synchronization with
116 phytoplankton blooms (e.g. Elliot *et al.*, 2009; Lazareth *et al.*, 2003; Stecher *et al.*, 1996;
117 Thébault *et al.*, 2009; Vander Putten *et al.*, 2000). Building on the work of Stecher and Kogut
118 (1999), Thébault *et al.* (2009) proposed two main hypotheses to explain the peaks: (1)
119 ingestion of barite originating from assemblages of recently dead diatoms or (2) adsorption of
120 barium onto iron oxyhydroxides associated with diatoms frustules.

121 The main objective of our study was to identify whether the calcitic shell of *P. magellanicus*
122 can record the high frequency (25.8 h) environmental variations observed in SPM. To this end,
123 we have developed a new ultra-high resolution LA-ICPMS analytical method in order to
124 investigate skeletal trace element concentration with a 10 μm resolution. Results of our
125 investigation can contribute to a better understanding of environmental and physiological
126 mechanisms associated to sub daily environmental variations on ions incorporation into fast
127 growing marine bivalve shells.

128 **2. Materials and Methods**

129 **2.1 Sample collection**

130 Two live *P. magellanicus* were collected in September 2016 from Saint-Pierre Bay (Saint-Pierre and
131 Miquelon – NW Atlantic) respectively at 10 m and 30 m depth (Figure 1). Both individuals were
132 in their fourth year of growth. The deepest location consisted in a homogeneous substrate,
133 made of compacted and stable fine sand. At the shallowest one, the substrate was more
134 heterogeneous and consisted of a mixture of gravels, pebbles, and rocks with a seaweed
135 cover. Soft tissues were removed immediately after collection. Both shells were carefully
136 cleaned with freshwater to remove adherent sediment and biological tissues before sample
137 preparation.



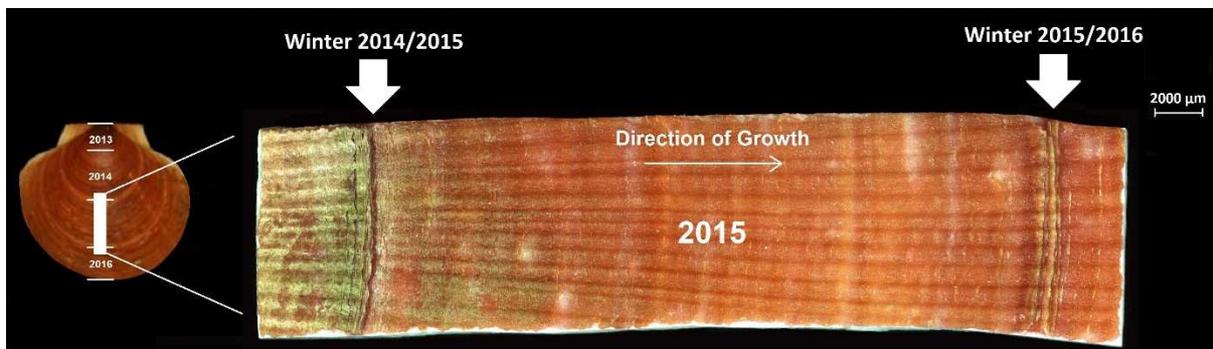
138
139 **Figure 1:** (A) Location of Saint-Pierre and Miquelon archipelago. (B) Satellite image of *P.*
140 *magellanicus* sampling sites (red dots) in Saint-Pierre Bay.

141 **2.2 Environmental monitoring**

142 Annual thermal profiles at 10 m and 30 m discussed were derived from Lazure *et al.* (2018)
143 study. To refine our vision of thermal variations on the two collection sites (Figure 1), three multi-
144 parameter probes measuring temperature every 5 minutes were deployed at 8 m, 12 m and
145 30 m depth, between 28/08/2017 and 15/09/2017. The 2015 monthly satellite chlorophyll *a*
146 measurements were downloaded from the GlobColour website (<http://hermes.acri.fr>) and
147 are weighted monthly averages of single-sensor products (SeaWiFS/MERIS/MODIS/VIIRS/N
148 merged chlorophyll concentrations) over the area 46.6–47.3°N / 56.0–56.6°W (i.e., waters
149 surrounding the SPM archipelago within ca. 30 km).

150 **2.3 Sample preparation**

151 All micro-chemical analyses were performed on *P. magellanicus* upper valves. Indeed, the
152 lower valves might have been contaminated as a result of a prolonged contact with the
153 sediment. For each individual, a fragment of shell of ca. 3.5 cm x 1 cm was cut with a diamond
154 saw, including the axis of maximal growth (Figure 2).



155
156 **Figure 2:** Example of one *P. magellanicus* fragment used for LA-ICPMS analyses. White arrows
157 indicate annual shell growth lines positions defining 2015 increment.

158 All ultra-high resolution LA-ICPMS analyses were performed on these two shell portions.
159 These fragments represent, for each individual, the third year of growth corresponding to
160 2015 annual growth periods. The outer shell layer was ultrasonically cleaned with deionized
161 water to remove organic matter and sediment particles. In addition, before LA-ICPMS
162 analyses, the outer shell layer of each sample was chemically cleaned with a 15 seconds acetic
163 acid (10 %) bath, soaked in deionized water during 10 seconds, and left to air dry in the LA-
164 ICPMS clean room.

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2.4 Ultra-high resolution fs-LA-ICPMS analysis

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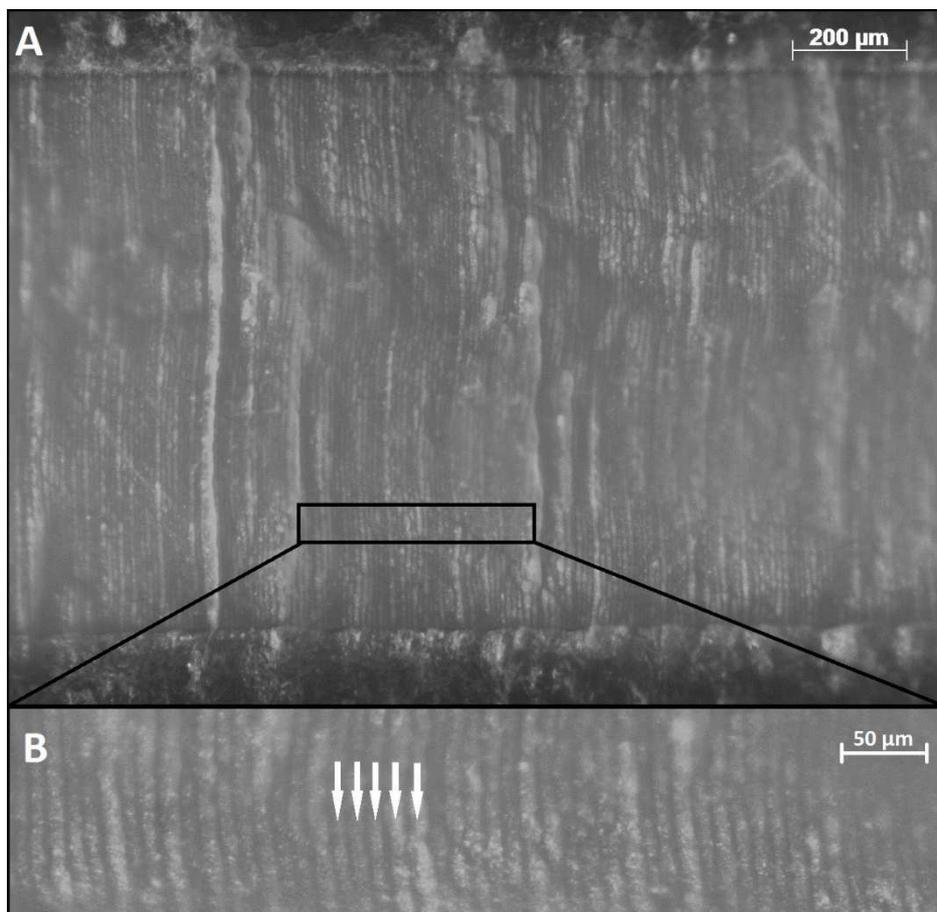
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A UV high-repetition-rate femtosecond laser ablation (fs-LA) system (Nexeya SA, Canejan, France) was employed (Pulse duration: 360fs; wavelength: 257 nm). Each ICPMS measurement point represents an ablation transect with a 1-mm long arcuate trajectory, parallel to the ventral margin, made by fast round trips of a 10 μm spot (Figure 3). All transects were adjacent in order to analyse the whole “2015 annual period of growth” for the two individuals. The area, covered by a 1 mm x 10 μm transect is equivalent to the area covered by a 110 μm diameter round spot.



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Figure 3: Post ablation picture of a 1.5 mm *P. magellanicus* section showing ca. 150 femtosecond laser ablation transects (A). Zoom on a small fraction of them, each white arrow points to a laser ablation transect (B). The visible lines represent ridges generated during the laser ablation process.

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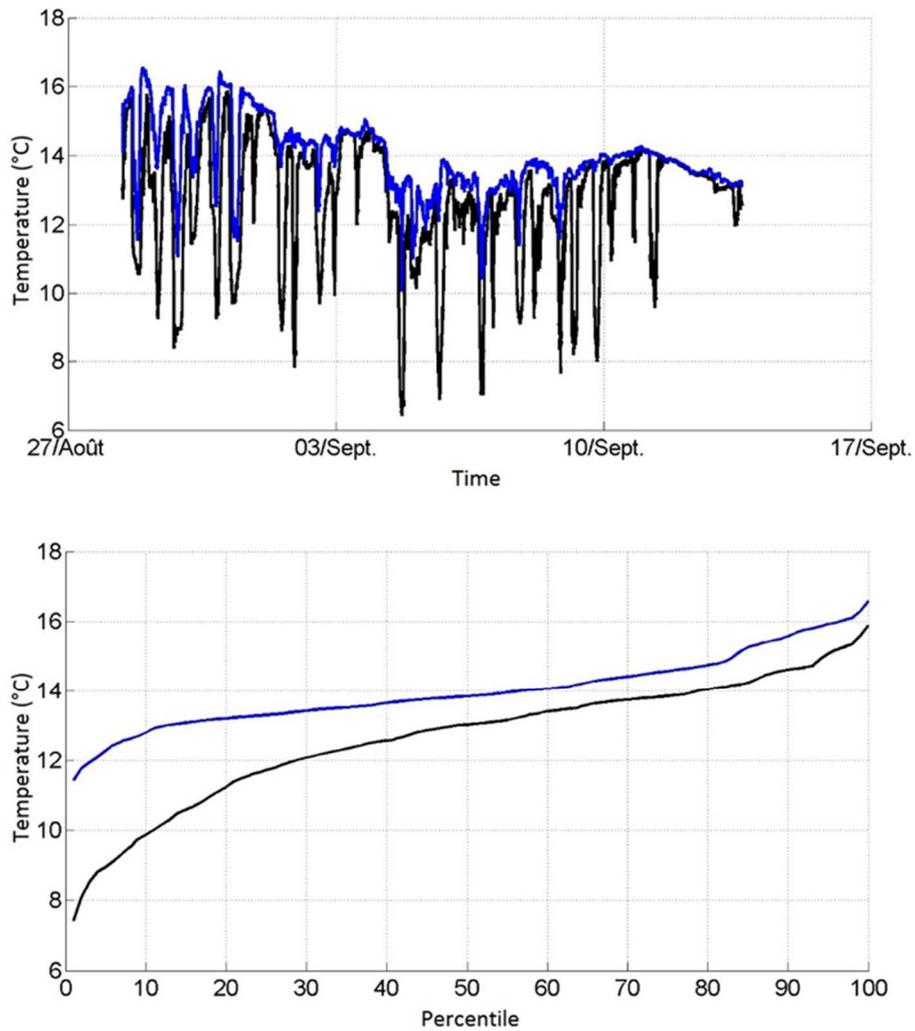
Outer shell layers were analysed for Mg/Ca, Ba/Ca and U/Ca ratios using a high-resolution inductively coupled plasma mass spectrometer fitted with a jet interface (Element XR, Thermo

180 Scientific, USA). A helium gas stream carried ablated material to the HR-ICP-MS (carrier gas
181 flow rate 0.68 L.min⁻¹). Elemental ratios were quantified by monitoring ⁴³Ca, ²⁴Mg, ¹³⁸Ba, and
182 ²³⁸U. Calcium was used as an internal standard. Elements were standardized to calcium based
183 on the stoichiometry of calcium carbonate (388 000 µgCa.g⁻¹ outer shell layer), assuming 100
184 % CaCO₃: Mg/Ca (µg.g⁻¹), Ba/Ca (µg.g⁻¹) and U/Ca (µg.g⁻¹). Quantification of trace elements in
185 otoliths was achieved by external calibration using both carbonate pellets FEBS-1 (Barats et
186 al., 2007) and 2 NIST glass standards (610, 612) to ensure the best accuracy. Each standard
187 was analysed three times before and after each session with the laser to account for drifting
188 during the day. The limits of detection (µg.g⁻¹ in shells) achieved in this study were 0.08, 0.01
189 and 0.002 for ²⁴Mg, ¹³⁸Ba, and ²³⁸U, respectively. They were based on a 3σ criterion, where
190 σ is the standard deviation of the mean blank count for each isotope. All the elemental
191 concentrations in the outer shell layer were above the detection limits.

192 **3. Results**

193 **3.1 Environmental parameters:**

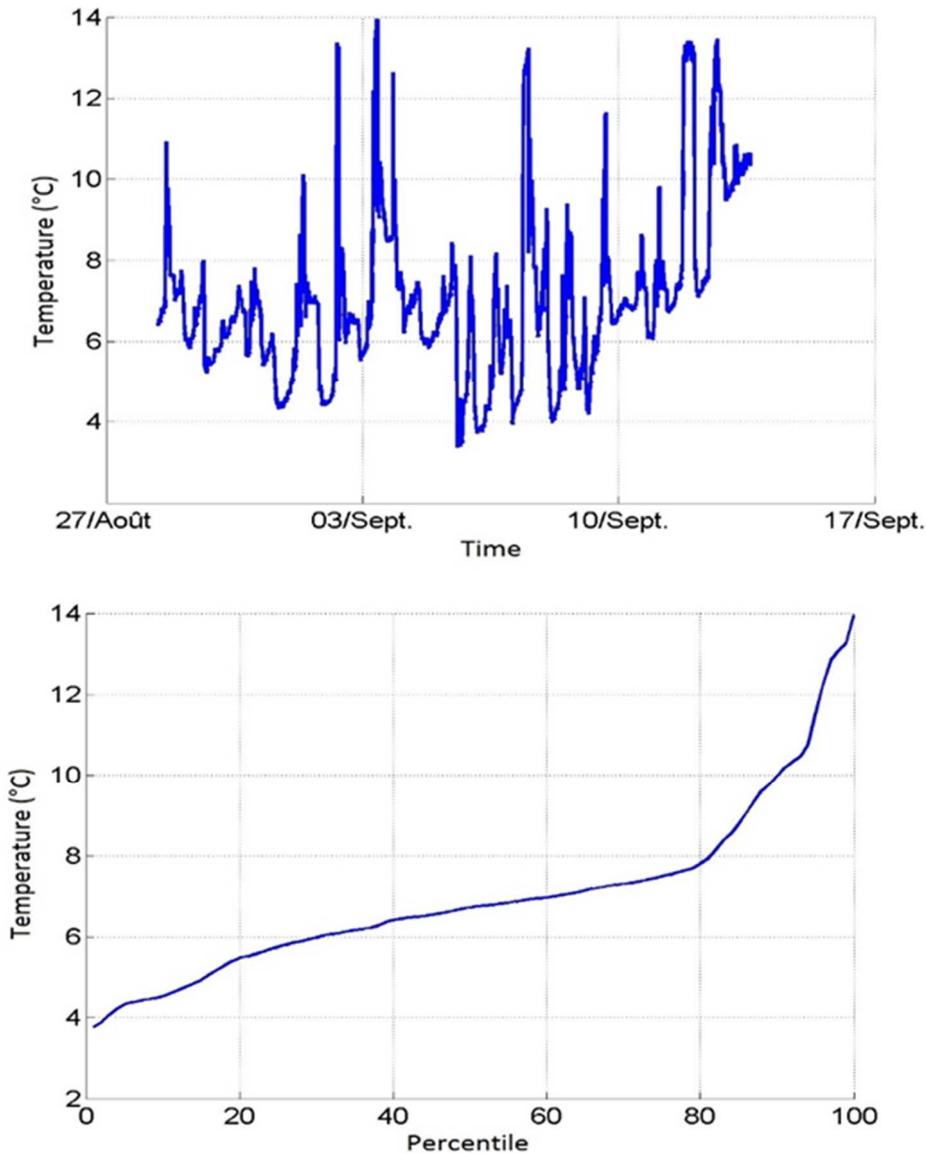
194 Around 10 m depth, the temperature varied from 2 °C in May to a maximum of 16 °C in early
195 September and then decreased to 8 °C in November. At this depth, seawater temperature
196 presents a classic seasonal cycle with cold water intrusions (Figure 4). During the first two
197 weeks of September at 8 m and 12 m in Saint-Pierre Bay, temperature showed high-frequency
198 variations with cold water incursions leading to 4°C (8m) to 6°C (12m) amplitudes (Figure 4).
199 Along these two weeks, temperatures were 70% of the time above 12 °C (Figure 4).



200

201 **Figure 4:** End of August and first two weeks of September 2017 time series of seawater
 202 temperatures at 8 m and 12m depth (blue and black) (top graphic). Percentile distribution of
 203 these temperatures at 8 m and 12m depth (blue and black).

204 At 30 m depth, the temperature annual profile was radically different (Figure 5). Seawater
 205 temperature baseline is mainly cold over the year, showing low seasonal amplitudes.
 206 However, during the stratified period, temperatures showed high-frequency variations whose
 207 amplitude increased with sea-surface temperature. During the first two weeks of September
 208 (Figure 5), oscillations were the largest in term of amplitude, reaching nearly 10°C. Along these
 209 two weeks, temperatures were 80% of the time below 8 °C (Figure 5).

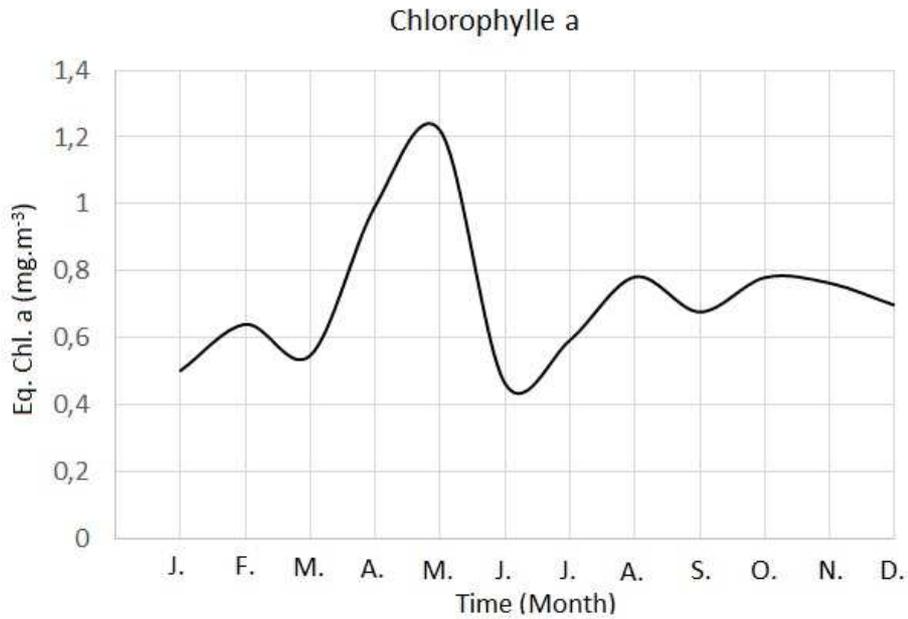


210

211 [Figure 5](#): End of August and first two weeks of September 2017 time series of seawater
 212 temperatures at 30m depth (top graphic). Percentile distribution of these temperatures
 213 during these two weeks.

214

215 Monthly mean satellite chlorophyll *a* concentrations ranged from 0.46 to 1.22 mg.m⁻³ (Figure
 216 6). The annual time series-exhibited a background level around 0.7 mg.m⁻³, with one major
 217 peak in April - May 2015.



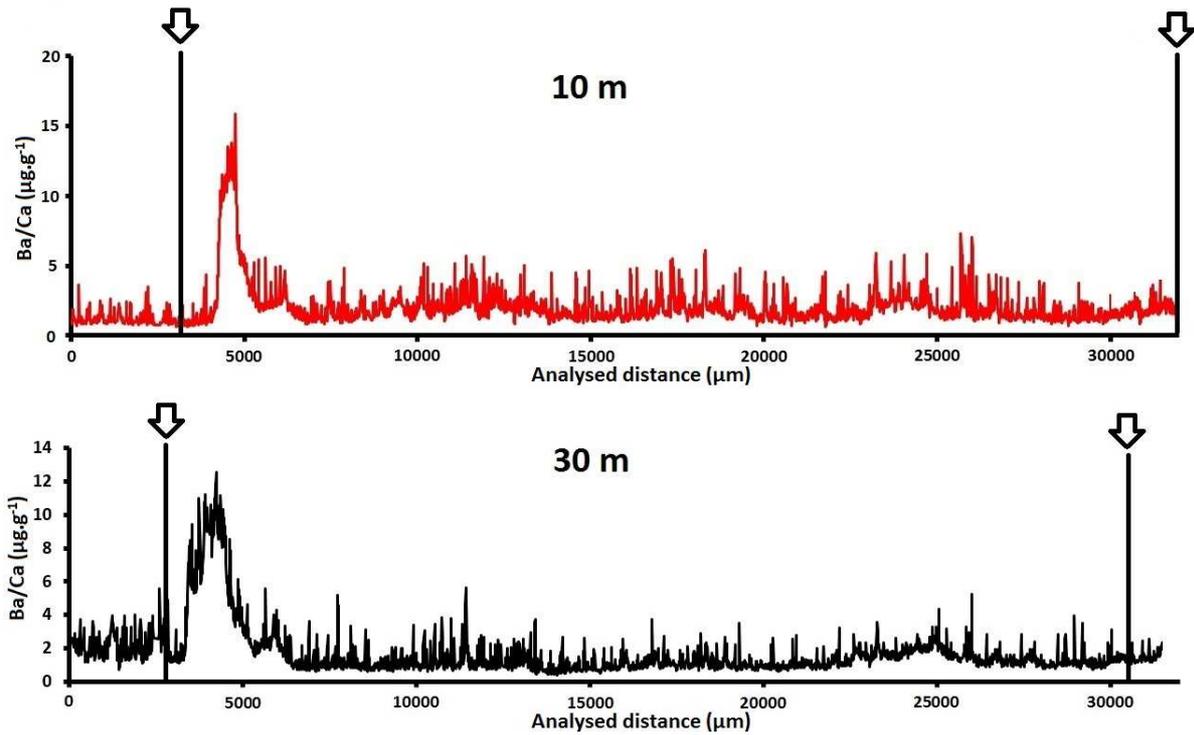
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219 [Figure 6: Monthly satellite equivalent chlorophyll a \(mg.m⁻³\) measurements over the year](#)
 220 [2015.](#)

221

222 **3.2 Ba/Ca ratio profiles in the shell carbonates**

223 Outer shell layer Ba/Ca ratios ranged from 0.61 to 15.71 $\mu\text{g.g}^{-1}$ at 10 m and from 0.43 to 12.54
 224 $\mu\text{g.g}^{-1}$ at 30 m (Figure 7). Both series have the same profile with one major peak occurring
 225 respectively 370 μm and 830 μm after the “winter 2014/2015” growth line. The main Ba/Ca
 226 peak covers 1370 and 2220 μm of shell at 10 and 30 m, respectively. A secondary smaller
 227 Ba/Ca peak occurred immediately after the first one, covering respectively 1230 and 1160 μm
 228 at 10 and 30 m. Ba/Ca baseline was the same for the two time-series (around 1.5 $\mu\text{g.g}^{-1}$).



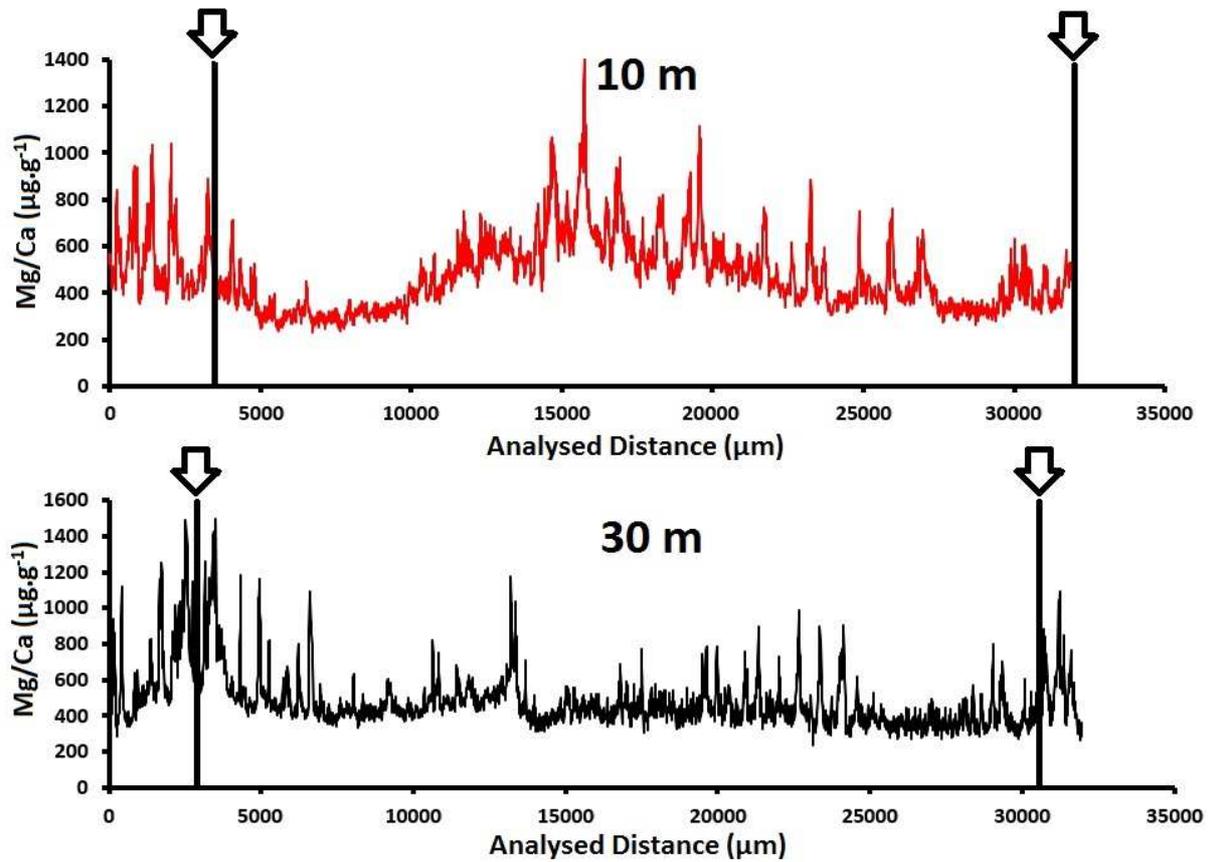
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230 [Figure 7: Ba/Ca \(\$\mu\text{g.g}^{-1}\$ \) series at 10 m \(red curve\) and 30 m \(black curve\). Vertical lines](#)
 231 [placed under the arrows indicate the position of winter shell growth lines.](#)

232

233 3.3 Mg/Ca ratio profiles

234 Outer shell layer Mg/Ca ratios ranged from 232 to 1408 $\mu\text{g.g}^{-1}$ at 10 m and from 233 to 1495 $\mu\text{g.g}^{-1}$
 235 at 30 m (Figure 8). At 10 m, Mg/Ca profile followed a sinusoidal pattern with stronger high
 236 frequency variations between 15 000 and 25 000 μm (top and decreasing phase, Figure 8). At
 237 30 m depth, the Mg/Ca profile was radically different with a globally flat profile between the
 238 two growth lines and high frequency variations mainly between 15000 and 25000 μm (Figure
 239 8).



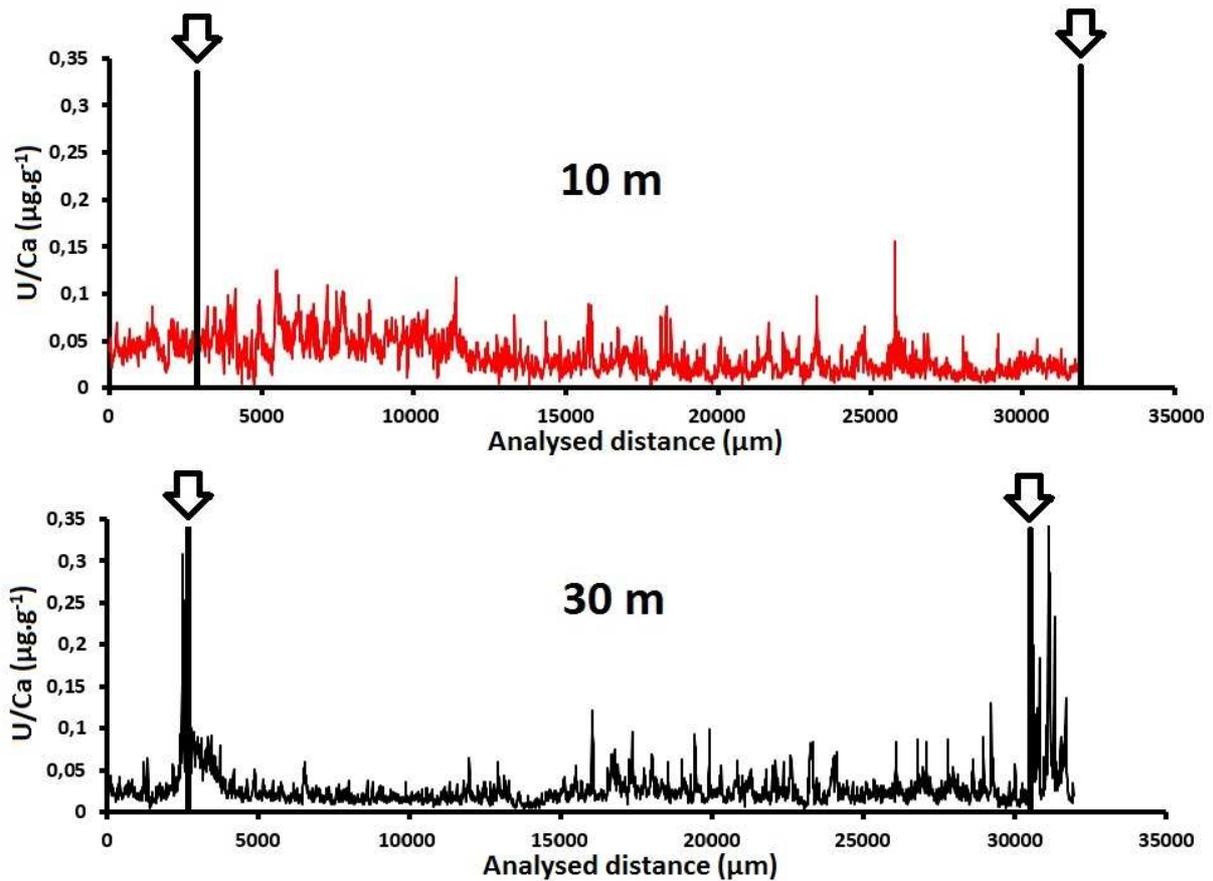
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241 [Figure 8](#) : Mg/Ca ($\mu\text{g}\cdot\text{g}^{-1}$) series at 10 m (red curve) and 30 m (black curve). Vertical lines
 242 placed under the arrows indicate the position of shell growth lines.

243

244 3.4 U/Ca ratio profiles

245 Outer shell layer U/Ca ratios ranged from 0.003 to 0.16 $\mu\text{g}\cdot\text{g}^{-1}$ at 10 m and from 0.004 to 0.36 $\mu\text{g}\cdot\text{g}^{-1}$
 246 at 30 m (Figure 9). At 10 m depth, U/Ca time series had a relatively flat pattern with high-
 247 frequency variations all along the profile. At 30 m depth, U/Ca profile was close to Mg/Ca one. So
 248 we decided to compare those profiles in the next paragraph.



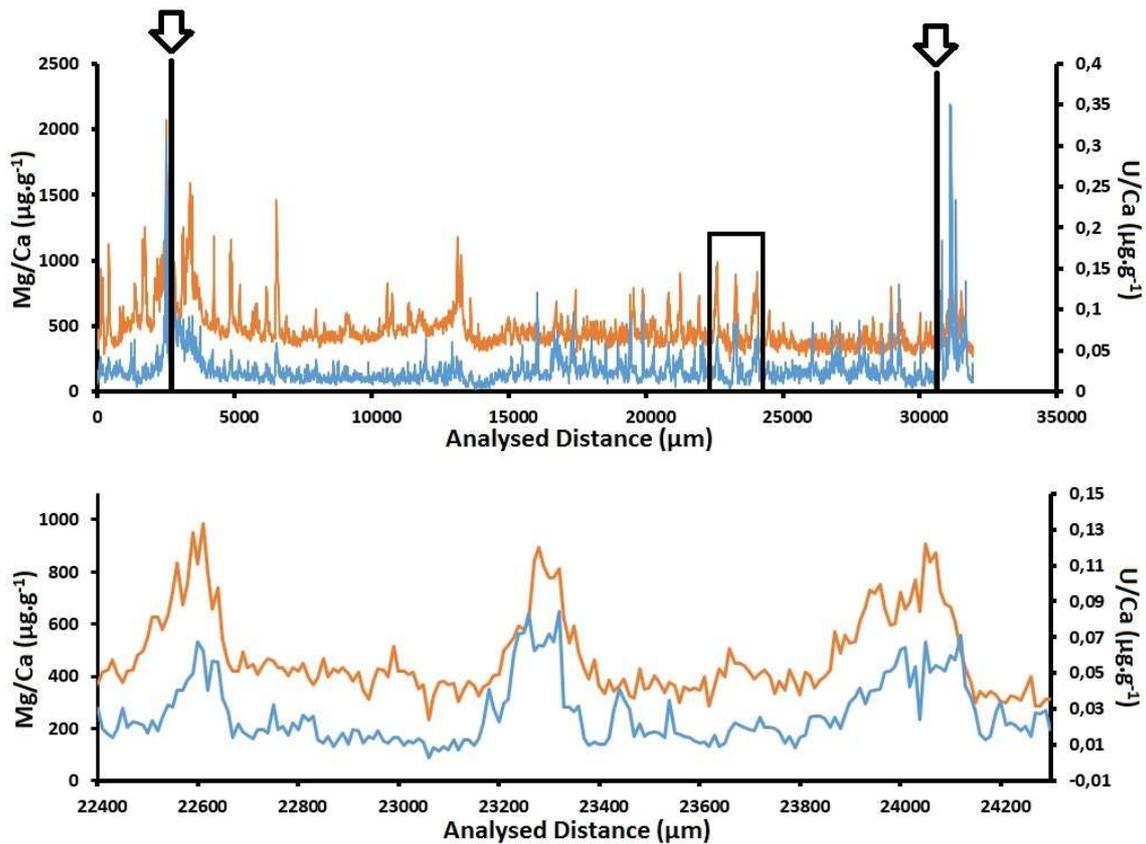
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250 [Figure 9](#): U/Ca ($\mu\text{g}\cdot\text{g}^{-1}$) series at 10 m (red curve) and 30 m (black curve). Vertical lines placed
 251 under the arrows indicate the position of shell growth lines.

252

253 **3.5 U/Ca and Mg/Ca comparison at 30m depth:**

254 At 30 m depth, U/Ca and Mg/Ca profiles presented a strong positive correlation ($N = 3135$, $r =$
 255 0.62 , $p < 0.001$) (Figure 10). A closer examination of this relationship on a shorter time window
 256 (i.e. three high frequency cycles, between $22400 \mu\text{m}$ and $24250 \mu\text{m}$) revealed an even stronger
 257 correlation ($N = 186$, $r = 0.77$, $p < 0.001$).



258

259 **Figure 10:** U/Ca ($\mu\text{g}\cdot\text{g}^{-1}$) (blue curve) and Mg/Ca ($\mu\text{g}\cdot\text{g}^{-1}$) (orange curve) series at 30 m. Vertical
 260 lines placed under the arrows indicate the position of shell growth lines. The graph below
 261 represents a close-up on three peaks (black box in the upper graph).

262 **4. Discussion**

263

264 This paper presents the first chemical analyses performed on *P. magellanicus* shells. Regarding
 265 the temporal resolution (25.82 h) of the environmental phenomena we wanted to track, it
 266 was necessary to develop a new analytical method. Our novel approach using ultra-high
 267 resolution fs-LA-ICPMS enables trace element analyses in bivalve shells with a 10- μm
 268 resolution. This study gave us first insights about *P. magellanicus* ability to record high-
 269 frequency environmental variations within its shell.

270 **4.1 Barium**

271 The high degree of similarity between the two Ba/Ca profiles suggests that the occurrence of
 272 Ba/Ca peaks was controlled by one or multiple common environmental factors. The pattern

273 of these two Ba/Ca profiles is similar to those observed in cross sections of other bivalve
274 species (e.g., Gillikin *et al.*, 2008; Stecher *et al.* 1996; Vander Putten *et al.*, 2000). This confirms
275 the hypothesis which suggests that the choice of analyzing the shell surface or the outer shell
276 layer in cross sections do not have significant influence on Ba/Ca records in shells. In this
277 section, we will discuss several hypotheses to explain temporal variability of Ba/Ca in *P.*
278 *magellanicus* shell. Background levels of Ba/Ca time-series in bivalve shells have been
279 suggested to record salinity variations (e.g. Gillikin *et al.*, 2006). There is generally a linear
280 inverse relationship between seawater salinity and dissolved barium concentrations (Coffey
281 *et al.*, 1997; Gillikin *et al.*, 2006). However, variability in seawater dissolved barium
282 concentrations as a source for the Ba/Ca peaks in *P. magellanicus* from SPM is highly unlikely.
283 Indeed, SPM islands, due to their offshore status, are not subjected to major riverine inputs
284 and associated variations in salinity (Poitevin *et al.*, 2018). Salinity usually ranges from 31.3 to
285 32.2 PSU (see Figure 4 in Poitevin *et al.*, 2018) without a clear seasonal trend and, therefore,
286 cannot explain Ba/Ca peaks measured in the shells. Many authors suggested a close
287 relationship between these Ba/Ca peaks and phytoplankton blooms (e.g. Elliot *et al.*, 2009;
288 Lazareth *et al.*, 2003; Stecher *et al.*, 1996; Thébault *et al.*, 2009; Vander Putten *et al.*, 2000).
289 In our study, the high similarity of chlorophyll *a* concentration (Figure 6) and Ba/Ca (Figure 7)
290 profiles strongly suggest a relationship between phytoplankton biomass and barium
291 incorporation into *P. magellanicus* shells. Indeed, the occurrence of this bloom, in May 2015,
292 seems to be consistent with the starting of *P. magellanicus* annual growth from other
293 Canadian regions (Chute *et al.* 2012; Kleinman *et al.*, 1996). Elevated levels of suspended
294 barite (BaSO₄) have been suggested to be linked with oceanic diatoms primary productivity
295 (Dehairs *et al.*, 1991). Most of the barium released by diatoms after a bloom is labile and only
296 a minor fraction eventually forms barite crystals (Ganeshram *et al.*, 2003). Therefore, if labile
297 barium, either in phytoplankton or released into the dissolved phase, was the cause of the
298 Ba/Ca peaks, these peaks should form near the end of the bloom or very shortly thereafter
299 (Gillikin *et al.*, 2008). Considering the absence of daily growth lines in *P. magellanicus*, we
300 cannot conclude about chlorophyll *a* and Ba/Ca peaks timing. Finally, the two Ba/Ca profiles
301 exhibited a double peak, with a first large amplitude one and a smaller second peak. This
302 observation has also been made in *P. maximus* Ba/Ca profiles (Gillikin *et al.*, 2008). One
303 explanation for this double peak proposed in this study is based on Ganeshram *et al.* (2003).
304 They found that barite formation can take several weeks to reach its maximum after the

305 beginning of phytoplankton decay. Barite may be formed at the sediment surface and be
306 ingested by *P. magellanicus* several weeks after the phytoplankton bloom ends.

307 These observations on Ba/Ca incorporation in *P. magellanicus* shell from SPM imply a real
308 need for complementary information related to local *P. magellanicus* growth dynamics and
309 physiology. It would also be crucial to get insights about the nature and the quantity of benthic
310 and pelagic primary production over the year and along a bathymetric gradient.

311

312 **4.2 Magnesium**

313 In bivalve shells, the relationship between seawater temperature and Mg/Ca ratio is still
314 subject to controversy. Some authors proposed that Mg/Ca ratios can be used to record water
315 temperature (e.g., Bougeois *et al.*, 2014; Lazareth *et al.*, 2003; Mouchi *et al.*, 2013; Surge and
316 Lohmann, 2008; Ullmann *et al.*, 2013), while there are many reports of strong vital effects in
317 bivalve shells for this element (e.g., Elliot *et al.*, 2009; Lorrain *et al.*, 2005, Wanamaker *et al.*,
318 2008,). In this study, we can hardly discuss the importance of vital effects on trace elements
319 incorporation into *P. magellanicus* shell. Indeed, our analyses were only carried out on one
320 year of growth (ontogenetic and calendar) and one individual per site. The only thing we can
321 say about physiological control of Mg incorporation in *P. magellanicus* shell is based on Mg/Ca
322 level. In this study, the mean Mg/Ca ratio ($\sim 500 \mu\text{g}\cdot\text{g}^{-1}$ corresponding to $\sim 2\text{mmol}\cdot\text{mol}^{-1}$) of the
323 calcitic outer shell layer of *P. magellanicus* corresponds to a low value compared to other
324 calcitic mollusc shells (Lazareth *et al.*, 2007 and references therein). Given the absence of
325 sclerochemical studies about trace element incorporation in *P. magellanicus* shells, we can
326 only try to explain these low Mg concentrations relying on studies based on other calcitic
327 bivalves with low Mg/Ca concentrations. For example, Lorens and Bender (1977) suggested
328 that *Mytilus edulis* biologically regulates the amount of Mg entering the extrapallial fluid to
329 produce low-Mg calcite. Perhaps a similar process occurs in *P. magellanicus*, suggesting a
330 physiological control of Mg incorporation that could obscure Mg/Ca and seawater
331 temperature relationship. This confirms the need for additional investigations on
332 biomineralization, e.g. through experiments in controlled environments, in order to better
333 understand trace elements incorporation in *P. magellanicus* shell. However, the shape of the
334 two Mg/Ca profiles tend to highlight kind of a temperature control on magnesium

335 incorporation in our shells. At 10 m, the sinusoidal pattern of Mg/Ca ratio may reflect the
336 seasonal seawater temperature annual cycle at 10 m depth. While at 30 m, the Mg/Ca profile
337 presents a relatively flat baseline with high-frequency variations, which could mirror the
338 seawater seasonal temperature trend, namely showing low seasonal amplitudes with high-
339 frequency variations (Lazure *et al.*, 2018). Other studies also point to the non-systematic
340 relationship between Mg/Ca ratio and SST. From a one year study of *M. edulis* growth, Vander
341 Putten *et al.* (2000) observed a positive correlation between Mg/Ca and SST only during
342 spring. Small-scale variations in Mg concentrations in *M. edulis* calcite have also been shown
343 to derive from Mg being concentrated along the margins of calcite prisms (Rosenberg *et al.*,
344 2001). Indeed, the absence of interannual growth lines on the *P. magellanicus* shell is
345 problematic to convert analysed distances in time. That is why enhance our knowledge on *P.*
346 *magellanicus* growth dynamics along this bathymetric gradient in SPM would help us decipher
347 physiological and environmental effects on trace element incorporation in *P. magellanicus*
348 shell calcite. In addition, the lack of high frequency environmental data limits our ability to
349 fully interpret our results and confirms the interest to set up a high frequency observatory
350 along this bathymetric gradient.

351

352 **4.3 Uranium**

353 In our study, U/Ca and Mg/Ca profiles show a strong positive correlation in shells collected at
354 30 m (N=3135, $r=0.62$, $p<0.001$) (Fig. 10). However, this is not the case for the shallowest shells
355 for which no significant correlation could be found. These results suggest that (i)
356 environmental uranium availability for *P. magellanicus* are not the same between the two
357 sites and/or (ii) that physiological differences between *P. magellanicus* from 10 m and 30 m
358 sites could lead to differential incorporation of uranium in shells.

359 Since (i) we do not have information about *P. magellanicus* physiological differences between
360 these two depths, and (ii) only few studies previously investigated U/Ca ratio as a potential
361 paleo environmental proxy in bivalve shells (Frieder *et al.*, 2014; Gillikin and Dehairs, 2012;
362 Zhao *et al.*, 2018), it seems difficult to draw conclusions about the kind of processes
363 influencing uranium incorporation in *P. magellanicus* shells.

364 To our knowledge, U/Ca ratio as a paleo environmental proxy has been studied for the first
365 time in mollusc shell by Gillikin and Dehairs (2012). In this study the authors tried to investigate
366 U/Ca in *Saxidomus gigantea* shell as a potential acidification proxy and concluded that U/Ca
367 may not reflect environmental variability and did not function as a paleo-pH proxy. More
368 recently, Zhao *et al.* (2018) also found virtually unchanged U/Ca values in *Mya arenaria* shells
369 with increasing seawater $p\text{CO}_2$ up to 2900 μatm . However, in the same study the authors
370 found a significant increase in U/Ca ratio in shells with the increase in seawater $p\text{CO}_2$ at 6600
371 μatm . These findings reveal the existence of certain compensatory mechanisms by which this
372 species may partially mitigate the impact of high environmental $p\text{CO}_2$ on shell formation
373 through modifying the calcifying fluid chemistry to maintain its pH homeostasis (Zhao *et al.*,
374 2018). These conclusions lead us to consider *P. magellanicus* physiological responses induced
375 by the repeated thermal variations occurring at the 31m site and their impact on the calcifying
376 fluid pH of this species. Considering our study purpose and resolution, it seems difficult to
377 conclude about U/Ca as a potential acidification proxy in *P. magellanicus* shell, especially as
378 we do not have pH measurements on our study sites. Uranium-to-calcium ratios have also
379 been suggested as a proxy for temperature in shallow water corals (e.g., Min *et al.*, 1995; Shen
380 and Dunbar, 1995) and in planktonic foraminiferal carbonates (e.g., Yu *et al.*, 2008). In our
381 study, the positive correlation between U/Ca and Mg/Ca profiles in the shell collected at 30 m
382 would support this hypothesis. However, this correlation does not hold anymore at 10 m,
383 suggesting that variations in uranium bioavailability differs between our two sites. Indeed,
384 microorganisms have the ability to adsorb radionuclides/metals through extracellular binding
385 involving physical adsorption, ion exchange, complexation and precipitation (Acharya *et al.*,
386 2009). They also sequester the metal ions by passive/active transport to the interior of the
387 cell, followed by its accumulation. Microbial cells have been shown to reduce, oxidize, adsorb,
388 accumulate and precipitate uranium (Fredrickson *et al.*, 1999; Macaskie *et al.*, 2000). So
389 differences in microbial communities between the two sites, related to the nature of the
390 habitat or to depth, could lead to changes in environmental uranium availability and finally to
391 shell U/Ca ratios.

392 **5. Conclusion**

393 Our novel approach using ultra-high resolution fs-LA-ICPMS enables trace element analyses in
394 bivalve shells with a 10- μm resolution. This study gave us first insights about *P. magellanicus*
395 ability to record high-frequency environmental variations within its shell at a sub-hourly scale.

396 From an analytical point of view, it would be interesting to continue this study by applying this
397 new analytical technique to more individuals. This would allow us to discuss about inter-
398 individual variability within those two sites. Moreover, combining this approach with nano-
399 SIMS $\delta^{18}\text{O}$ measurements (temperature proxy) would help us to get insights about the
400 temperature control of Mg and U incorporation in shells.

401 In terms of data interpretation, these results also confirm a real need for complementary
402 information. Some of them should be related to *P. magellanicus* intra-annual growth
403 dynamics. Indeed, in this study the absence of visible intra-annual growth lines visible on *P.*
404 *magellanicus* shells hindered the temporal alignment of our microchemical data. Others must
405 concern *P. magellanicus* physiological responses and their impacts on the calcifying fluid
406 chemistry of this species. All these additional studies will require multiple high frequency
407 environmental data continuously recorded at an individual scale within those two sites.

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