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Trace elements in bivalve shells: how “vital effects” can bias environmental studies.

by

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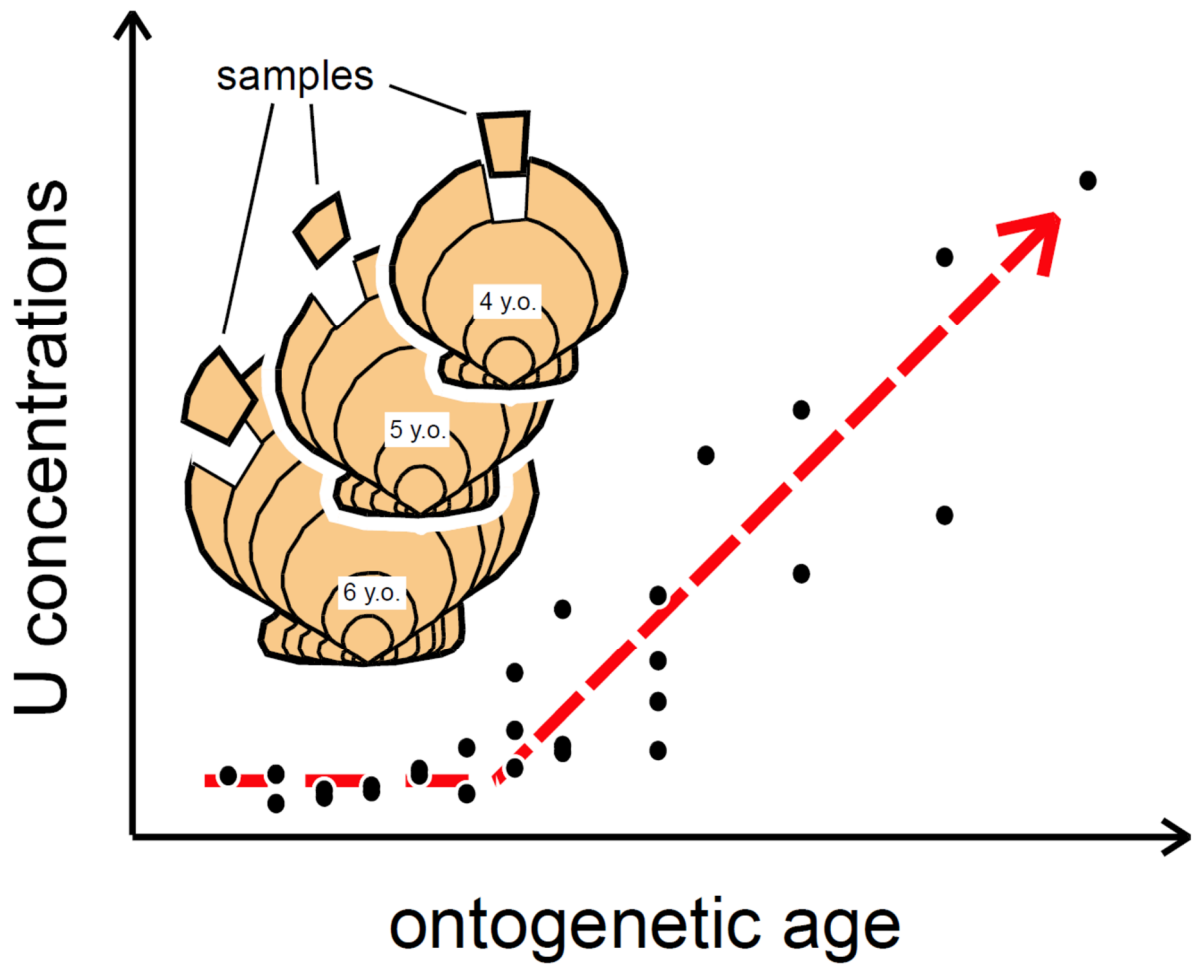
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24 Graphical abstract:

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30 **Highlights**

31 • Trace elements in shells of giant scallops were determined.

32

33 • Rare earth elements, Y, copper, uranium and barium show two-step trends, with a turning
34 point at 8 y.o.

35

36 • Metabolic processes control the behavior of these trace elements.

37

38 • The knowledge of metabolic effects on trace elements will improve geographic tracking
39 processes of shellfish.

40

41 • Shells are valuable archives of bivalve metabolism.

42

43 **Abstract**

44

45 We report on the concentrations of rare earths (REE), Y, Mg, Mn, Cu, Zn, Sr, Ba, Pb
46 and U in a series of wild scallops (*Placopecten magellanicus*) collected alive on the same day
47 in Saint Pierre et Miquelon (a French archipelago located south of Newfoundland) and
48 ranging in age from 2 to about 20 years. We analyzed representative fragments from the entire
49 last annual shell growth increment of each animal to assess changes in trace element
50 incorporation with age.

51 No correlation with the age of the animals was obtained for Sr and Mn concentrations,
52 which are quite variable from one individual to another, even of similar age. On the other
53 hand, for REE, Y, Cu, Zn, Ba and U, the concentrations measured in the last annual growth
54 increment formed by animals aged 2 to 7 years are similar. From 8 years of age, the
55 concentrations of these elements increased very strongly (for example for Yb, almost by an
56 order of magnitude between 8 and 20 years of age), and possibly with some variation between
57 individuals of the same age. Two elements show a different behavior: Mg concentrations in
58 the shell margins increase continuously with the age of the animals; Pb concentrations are
59 scattered but seem to decrease with the age of the animals.

60 This turning point in the behavior of the elements from 8 years of age coincides with
61 major metabolic changes, since at this age wild *P. magellanicus* from Newfoundland reduce
62 their growth, in favor of gamete production. Our results demonstrate that metabolic activity of
63 the animals largely controls the incorporation of many trace elements into the shells. These
64 results demonstrate that the age of the animals must be taken into account when their shells
65 are used to study pollution or (paleo) environmental condition.

66

67 **Key words:** sclerochronology, bivalve, shell, rare earth elements, trace elements,
68 *Placopecten*, environmental proxy

69

70

71 **1/ Introduction**

72 The chemistry of trace elements in biogenic carbonates has been an extremely active
73 field of research for the last 60 years. It is generally accepted that the composition of these
74 minerals is largely controlled by the physicochemical properties of the water where they
75 formed. Indeed, seminal works on corals for example, have shown that seawater temperatures
76 are well deduced from Sr/Ca ratios (e.g. among many others, Smith et al., 1979; McCulloch et
77 al., 1994; Reynaud et al., 2007). Thus, it is generally thought that biogenic carbonates could
78 be excellent proxies and have the potential to provide long-term environmental records.
79 Considerable effort has been put into studying other biogenic carbonates such as foraminifera,
80 fish otoliths, and bivalve shells (e.g., Rosenthal et al., 1997; Bath et al., 2000; Eggins et al.,
81 2003; Immenhauser et al., 2016). The behavior of other elements has been evaluated to trace
82 also temperature (e.g., Dodd, 1965; Hart and Blusztajn 1998; Elliot et al., 2009; Liu et al.,
83 2021), salinity (e.g., Gillikin et al., 2006), pH (e.g., Frieder et al., 2014; Norrie et al., 2018;
84 Zhao et al., 2017), dissolved oxygen (Schöne et al., 2022), and even phytoplankton dynamics
85 (e.g., Elliot et al., 2009; Thébault et al., 2009; Thébault and Chauvaud, 2013; Poitevin et al.,
86 2020, 2022; Fröhlich et al., 2022).

87 Despite initially promising results suggesting, for example, that water temperature and
88 salinity could be inferred from Sr/Ca or Ba/Ca ratios in mussel shells, respectively (e.g.,
89 Dodd, 1965; Gillikin et al., 2006), the ability of trace elements in bivalve shells to be used as
90 environmental proxies is still debated. While it is certain that incorporation of trace elements
91 by shells is partly controlled by environmental parameters, internal biological effects are also
92 important, and are of variable magnitude depending on the species involved. Calibration
93 attempts performed on several species (e.g., *Ruditapes philippinarum* by Poulain et al., 2015,
94 *Perna canaliculus* by Norrie et al., 2018, *Arctica islandica* by Wanaker and Gillikin, 2019) as
95 well as systematic study of trace element distributions in shells (e.g., Schöne et al., 2011,
96 2023 among many others), have shown that physiological processes are determinant at least
97 for some elements. However, these biological effects are poorly understood, and ontogenetic
98 trends have only rarely been determined (e.g., for REE in *Glycymeris glycymeris*, Barrat et al.,
99 2022b).

100 The goal of this study was to evaluate the effect of bivalve age on the incorporation of
101 trace elements in their shells, and to investigate if consistent ontogenetic trends can be

102 obtained. We selected a common pectinid species from the Atlantic coasts of North America,
103 *Placopecten magellanicus* (Gemlin, 1791). This species is particularly well suited to our
104 study, since its calcitic shells have a very high growth rate in the first few years, with marked
105 growth streaks that make them easy to age (e.g., Poitevin et al., 2020). Furthermore, shells are
106 large (up to 16 cm) and consequently very easy to prepare.

107

108 **2/ Sampling and analytical procedures**

109 Twenty-seven *P. magellanicus* were selected and collected alive in the same station, by
110 a scuba diver on february 6, 2022 in Saint Pierre Bay (46.713706°N, -56.157593W) at a water
111 depth of 22 m (Fig. 1).

112 The age of the mollusks was determined directly by counting the "winter marks"
113 deposited during spring growth restart. The sampling comprises one 2 y.o. individual, two 3
114 y.o., 4 y.o., 5 y.o., 6 y.o., 7 y.o. individuals, three 8 y.o. and 9 y.o. individuals, four 11 y.o.
115 individuals, one 12 y.o. individual, two 14 y.o. and 17 y.o. individuals, and one 20 y.o.
116 individual.

117 Soft tissues were removed immediately after collection, and the shells were rinsed with
118 tap water, then dried. The margins of the left valves were gently cleaned with a Dremel™
119 rotary tool equipped with a steel brush, to remove periostracum, soft tissue remnants, and
120 sediments, then rinsed with deionized water and dried. From each shell, a fragment of the
121 margin was cut which sampled the entire width of the last annual growth increment. These
122 fragments weighed between 100 to 350 mg (Fig. 2), and were all formed by scallops during
123 the year 2021. It is important to note that Pectinid shells have different microstructures, for
124 example between the upper and lower parts, with trace element concentrations that may differ
125 (e.g. Thorn et al., 1995; Freitas et al., 2009). The samples we have collected and analyzed do
126 not allow us to discuss the effect of microstructure on measured composition. They are only
127 representative of the bulk carbonate synthesized by the animal during the last year of its life.

128 Trace element concentrations were determined by Inductively Coupled Plasma Mass
129 Spectrometry (ICP-MS) using well-established procedures (e.g., Barrat et al., 2012, 2016).
130 Each sample was spiked with a solution of pure Tm (Barrat et al., 1996) and digested in a
131 Teflon beaker by HNO₃. REEs and Y have been separated and concentrated before analysis
132 using ion-exchange chromatographic columns loaded with about 1 ml DGA-Normal resin
133 (DN-B50-S, 50-100 µm, produced by Triskem®) following the procedure developed by

134 Barrat et al. (2020). For other elements (Mg, Mn, Cu, Zn, Sr, Ba, Pb, U), an aliquot of the
135 sample solution containing the equivalent of 4 mg of sample was dried and the residue was
136 taken up in 4 ml of 2.5% HNO₃ before analysis (e.g., Wang et al., 2019). The measurements
137 were performed on a Thermo Scientific ELEMENT XR™ spectrometer located at the “Pôle
138 Spectrometrie Ocean”, Institut Universitaire Europeen de la Mer (IUEM), Plouzané. Each
139 solution was analyzed in triplicate, and the results were averaged. Results on two carbonate
140 standards (CAL-S and BEAN) obtained during the sessions are compared with literature
141 values in Table S1. Based on standards, the precisions (RSD) for concentrations and element
142 ratios are better than 3 %.

143 For the normalisation of the concentrations, we use the Post Archean Australian Shale
144 (PAAS) average obtained by Pourmand et al. (2012), adjusted to standard results obtained in
145 our laboratory (Barrat et al., 2020). The La, Ce, and Gd anomalies are calculated using the
146 La/La*, Ce/Ce*, Gd/Gd* ratios, where X* is the extrapolated concentrations for a smooth
147 PAAS-normalised REE pattern and X_{sn} is the concentration of element X normalised to
148 PAAS: $La_{sn}^* = Pr_{sn}^3/Nd_{sn}^2$, $Ce_{sn}^* = Pr_{sn}^2/Nd_{sn}$, $Gd_{sn}^* = Tb_{sn}^2/Dy_{sn}$. (e.g., Barrat et al., 2022a,
149 2023).

150

151 **3/ Results**

152 Heights of the 27 selected shells ranged between 4.2 and 17.1 cm, with corresponding
153 ages between 2 to about 20 years at the time of capture (Fig. 3). The age of the largest
154 specimen (20 y.o.) is uncertain, and we do not exclude the possibility that this shell could be
155 older. The size of the other shells as a function of age is well explained by the von Bertalanffy
156 growth equation with a maximum shell height of 15.5 cm.

157 Trace element concentrations in the Placopecten shells we analyzed are extremely
158 variable (Table S1).

159 *REE and Y (REY)* - The REY concentrations in shells were low and highly variable,
160 and ranged between 7.8×10^{-5} and 2.5×10^{-3} times the shale reference (Fig. 4). The shapes of
161 the REY patterns were similar to those of previously analyzed coastal shellfish (e.g.,
162 Ponnurangam et al., 2016; Le Goff et al., 2019; Wang et al., 2020; Barrat et al., 2022b). They
163 display positive La (La/La*=1.48-2.11), Gd (Gd/Gd*=1.01-1.28) and Y (Y/Ho=44-68)
164 anomalies, and negative Ce anomalies (Ce/Ce*=0.34-0.62), which represent conspicuous
165 features of seawater and marine-derived materials such as biogenic carbonates (e.g., Webb

166 and Kamber, 2000). Although the shapes of the patterns were quite similar, the variations of
167 some ratios, such as Ce/Ce*, Y/Ho, but also (Tb/Lu)_{SN} (=1.1-3.2), were significant. Some of
168 these ratios, such as (Tb/Lu)_{SN}, are correlated with REY concentrations (Fig. S1). A
169 contribution from terrigenous sediments might be considered. However, this explanation is
170 not tenable since, if it were the case, a sedimentary input would flatten the REY patterns and
171 erase all the anomalies, especially for the most REY-rich samples. Furthermore, it should be
172 emphasized that the most REY-rich margins were taken from the oldest animals, and that
173 striking relationships are obtained in REY vs. ontogenetic age diagrams (Fig. 5). These show
174 that REY concentrations are stable until the animals reach the age of 7-8 years. After that, the
175 concentrations increase very substantially: these increases vary by a factor of 3.7 (e.g., Pr, Nd)
176 to 7 (e.g., Lu) between the samples taken from the shell margins of the oldest animals and
177 those taken from the 2 to 7 years old animals. For element ratios, changes with the age of the
178 animals were also observed, but are less clear than with the concentrations (Fig. S2). For
179 example, (Tb/Lu)_{SN} ratios decrease with the age of the animals. On the other hand, Ce
180 anomalies show a lot of dispersion potentially masking a possible increase of the Ce/Ce* ratio
181 from 2 to 8-10 years.

182 *Ba, Cu, U and Zn* (Fig. 6-8) - For these four elements, similar behaviors to REY were
183 observed, i.e., large concentration ranges and variations in two age periods. From 2 to 8 years
184 of age, concentrations were low and did not show a relationship with age. From 8 years
185 onwards, the concentrations increased very strongly. Such trends are particularly striking for
186 Ba, U, and Cu, but with a higher scattering of analyses around the trends for animals older
187 than 8 years. For Zn, the dispersions were more marked, but the two stages were clearly
188 apparent

189 *Pb* (Fig. 6c) - Pb concentrations ranged from 0.037 to 0.726 µg/g. Apart from two
190 outliers, the concentrations decreased with the age of the animals. An evolution in two stages
191 as above would be plausible, but cannot be confirmed given the dispersion of the data.

192 *Mg* (Fig. 6a) - Concentrations of this element varied from 267 to 1155 µg/g, and
193 increased from 2 to 20 years of age without a marked change at 8 years. As before, however,
194 there was a little more dispersion around the trend for individuals over 8 years old.

195 *Sr and Mn* (Fig. 6b and 8a) – These two elements showed significant variation (Mn =
196 0.43 – 2.99 µg/g, Sr = 571 - 1212 µg/g), but no trend with animal age was observed.

197

198 **4/ Discussion**

199 There is no doubt that the composition of the nutrients, the water and possibly the
200 fraction of sediment that the bivalves ingest, imprints some of their chemical signatures into
201 shells, and explains possible differences observed between shells of the same species
202 collected from distant sites. All the bivalves studied here were caught on the same day on the
203 same site, at the same depth. The shell samples we analyzed, were all formed during the same
204 period (i.e., the year 2021), under the same conditions: same water temperatures, salinity,
205 dissolved O₂ level, pH, composition, the same nutrients and the same access to food for all
206 animals. Therefore, none of these factors, although they may have significant effects on shell
207 composition (e.g., Steinhardt et al., 2016), can be the cause of the observed differences in
208 concentration between these shells. However, the relationships between the trace element
209 concentrations (e.g., REY, Ba, U or Cu) and ontogenetic ages, demonstrate that a major
210 change occurs in the life of *P. magellanicus* when they reach about 8 years old. Examination
211 of the growth curve (Fig. 3a) shows that it is around this age that growth slows down. To have
212 a picture of the growth rate, or of the calcification rate, we have opted for the calculation of
213 the mass of shell formed per year. This mass increment is easy to estimate. MacDonald (1986)
214 showed that the total mass of shells of a given wild *P. magellanicus* from Newfoundland can
215 be deduced from its height (see Table 1 in MacDonald (1986)). For a bivalve whose growth is
216 described by von Bertalanffy's law, the annual increment is calculated directly as the
217 difference between the estimated shell masses at ages n and $n-1$. A bell curve is obtained, and
218 displays indeed a maximum for 7-8 years old (Fig. 3b).

219 It has often been assumed that shell growth rate may exert a strong influence on trace
220 element incorporation (e.g., Pilkey and Goodell, 1963; Dodd, 1965; Stecher et al., 1996;
221 Takesue and van Geen, 2004). However, while correlations have been observed between
222 concentrations and daily growth rates (e.g., Lorrain et al., 2005), this is not systematic for all
223 species (e.g., Gillikin et al., 2005). For *P. magellanicus*, yearly growth rates do not have any
224 control over variations in element concentrations. If we take for example Ba, Cu, U, or REE,
225 the concentrations are homogeneous from 2 to 7 years while growth rates strongly vary. The
226 variations in concentration are high only for older animals. It should be noted that the annual
227 mass increase of the shells of these individuals can be similar to that of younger ones (for
228 example, the same annual increase at 5 y.o. as at 14 y.o.), but presents very different
229 concentrations. Thus, variations in shell growth rate (at the scale of one year) cannot account
230 for the change in trace element behavior recorded by the shell. Alternatively, and more likely,

231 the sharp changes in trace element behavior, as well as the slowdown in shell growth, are the
232 consequences of a major metabolic turning point over the lifetime of *P. magellanicus*. Indeed,
233 in wild *P. magellanicus* from Newfoundland older than 8 years, somatic tissues continue to
234 grow with a proportional increase in gamete production (MacDonald, 1986). Work is now
235 needed to identify precisely the metabolic reactions involved and their impact on trace
236 element concentrations. This work is beyond the scope of this study.

237 "Vital effects" or "biological controls" on the behavior of trace elements in bivalve
238 shells have already been extensively reported. Previous studies involved other shellfish
239 species, and the elements analyzed were mainly Mn, Mg, Sr, and Ba. REEs and U were rarely
240 determined for this purpose (Gillikin and Dehairs, 2013, Barrat et al., 2022b). Elemental
241 behavior that could be very different from those reported here, have been observed, as
242 exemplified for *Arctica islandica*, which is among the most studied species due to its extreme
243 lifespan and its large size (e.g., Butler et al., 2013). The available data for this species show an
244 increase in Sr concentrations with the age of the animals that contrasts to *P. magellanicus*
245 (e.g., Schöne et al., 2011, 2023 and references therein). Increases in B, Mg and Ba, and
246 decreases in Pb with age have also been observed by these authors. The ontogenetic trends,
247 when present, are not necessarily similar from one species to another. For example, for the
248 dog cockles (*Glycymeris glycymeris*), REE concentrations in shells initially increase during
249 the first 25-30 years of the animal's life then remain at a constant level during the following
250 decades (Barrat et al., 2022b). During the early stage, increases in REE concentrations in dog
251 cockles are also accompanied by a reduction of Ce anomalies. Such changes in concentrations
252 recorded in the shells, reflect quite closely the changes in concentrations of these elements in
253 the soft tissues. They are certainly the consequence of major metabolic changes during the life
254 of these animals (Barrat et al., 2022b).

255 In the last 60 years, it has been repeatedly suggested that the incorporation of trace
256 elements into bivalve shells is potentially controlled by salinity (Ba, e.g., Gillikin et al., 2006),
257 temperature (Mg, Sr, e.g., Dodd, 1965; Hart and Blusztajn 1998; Elliot et al., 2009; Liu et al.,
258 2021), pH and $[\text{CO}_3^{2-}]$ (Na and U, e.g., Frieder et al., 2014; Norrie et al., 2018; Zhao et al.,
259 2017), dissolved oxygen (Mn, Schöne et al., 2022), or even the phytoplankton dynamics (e.g.
260 Ba, Li, e.g., Elliot et al., 2009; Thébault et al., 2009; Thébault and Chauvaud, 2013; Poitevin
261 et al., 2020, 2022; Fröhlich et al., 2022). Although it is certainly the case that all of these
262 factors can contribute to behavior of trace elements in shells, data obtained over the last
263 decades have shown a very high complexity of the chemical signal they recorded. Moreover,

264 experimental work has reinforced the idea that in addition to the set of factors previously
265 mentioned, metabolic processes are also involved (e.g., Poulain et al., 2015; Norrie et al.,
266 2018; Wanamaker and Gillikin, 2019), which could even be for some elements essential
267 factors controlling their concentrations. Examination of Sr or Mg concentrations recorded by
268 *A. islandica* shells throughout the life of these animals (e.g., Fig. 4 in Schöne et al., 2011)
269 clearly show age-related trends, with variations around these trends being interpreted by
270 environmental effects. In order to have a chance to deconvolute the chemical signal recorded
271 by the shells and eventually constrain environmental factors and their variations, it seems
272 essential to have the most precise idea possible of the metabolic behavior of trace elements for
273 the bivalve species studied, and this at all stages of the life of these animals. The protocol that
274 we have applied for the REE in *G. glycymeris* (Barrat et al., 2022b), and here in *P.*
275 *magellanicus* for a larger number of elements, could be easily generalized to the species
276 studied by the other teams, and in particular *A. islandica*, the most studied of them.

277 If we transpose the ontogenetic trends we have obtained, to what would be recorded by
278 a single scallop placed in the same conditions from the age of 2 years to 20 years, we could
279 read in its shell a history in two stages, with a turning point at 8 years. A geochemist trying to
280 reconstruct it and ignoring the metabolic changes of this bivalve, could logically imagine that
281 it lived in an environment with homogeneous conditions during the first 8 years of its life,
282 followed by a clear change in conditions that would have to be interpreted (salinity,
283 temperature, etc...). The increase in Ba concentrations observed after 8 years could be
284 ascribed to a drastic change in primary production, and U variations to huge pH variations, or
285 to pollution... This is obviously not the case. Knowledge of these ontogenetic trends allows us
286 to avoid these errors, and even to better select the samples to be studied, depending on the
287 questions asked. Our observations (this work and Barrat et al., 2022b) allow us to suggest the
288 following recommendations:

289 -In the case of establishing chemical time series, the results obtained on several shells can be
290 combined in order to cover as long a period as possible. In order to avoid detrending
291 calculations that may introduce artifacts and the removal of long-term environmental trends,
292 we recommend using data only for those portions of the shells for which the corrections are
293 the smallest possible. In the case of *P. magellanicus*, portions of shells formed by animals
294 older than 8 years should be excluded. For *G. glycymeris*, portions formed by animals
295 younger than 30-40 years, for which the ranges of variation of the elements are very large
296 (Barrat et al., 2022b), should not be retained.

297 - A sudden increase in the concentrations of an element recorded in a shell is not necessarily
298 the mark of pollution. It could simply be explained by a change of trace element behavior
299 linked to metabolic reactions, as illustrated here by Cu, Zn or U ontogenetic trends. For such
300 an increase to be interpreted in terms of pollution, it is necessary that this observation be
301 confirmed by similar and synchronous increases recorded in the shells of individuals of very
302 different ages. Moreover, in order to compare the concentration levels of a given element
303 from one shell to another, the age parameter must necessarily be taken into account. In the
304 case of *Placopecten magellanicus*, one can indifferently analyze either the shell margin of
305 individuals less than 8 years old, or the whole shell (provided, of course, that all surfaces are
306 perfectly cleaned before grinding): both types of samples will give similar results. For older
307 scallops, the results obtained from the whole shell and the margin will diverge significantly,
308 since the trace element concentrations in the portion of the shell formed after 8 years may be
309 very different from that formed before. Indeed, the curve given in figure 3b allows to
310 calculate that for a 15-year-old individual, about 45% of the valve mass formed between 8
311 and 15 years of age. As an example, we estimate the La concentration of the same shell using
312 the La vs. age curve (Fig. 5a). The La concentration of its margin is about 70 ng/g while the
313 average concentration in the shell is only about 40 ng/g.

314 - When studying chemical variations recorded in the shells of fossil species, metabolic effects
315 obviously cannot be ignored. As a first step, we recommend obtaining results similar to those
316 presented here, on present-day species comparable to those studied, before any discussion of
317 the chemical variations recorded in fossil shells. If possible, the analysis of a few fossil shells
318 from individuals of very different ontogenetic ages, taken strictly from the same layer, can
319 help to assess vital effects and confirm interpretations.

320 - Trace element chemistry has the potential to track the geographic origin of bivalves
321 (cockles, mussels or king scallops, e.g. Ricardo et al., 2017 ; Morrison et al., 2019 ; Del Rio-
322 Lavín et al., 2022), and to provide tools for tackling frauds. Our results show that the
323 concentrations of certain elements in the shells formed at the same time in the same location
324 could vary by an order of magnitude depending on the age of the animals. This observation is
325 important because potentially it would permit a significant improvement in the procedures for
326 geographic tracking. Indeed, if we know the ontogenetic trends of the commercialized
327 species, we can select the individuals of the most discriminating age class to characterize their
328 origin. For example, *P. magellanicus* being a species of important economic interest, one can
329 imagine the possibility of tracing the different production sites, by targeting the determination

330 of trace elements on individuals of age lower than 8 years. Coupling these data with C, N and
331 O isotopes would obviously improve the accuracy of determining the geographic origin of
332 these bivalves.

333

334 **5/ Conclusions**

335 Variations in concentrations of minor or trace elements in mollusk shells are
336 frequently determined today, in order to trace environmental variables or the imprint of
337 pollution, among other factors, that may have been recorded. However, this environmental
338 signal is superimposed on metabolic signals, which are poorly understood. This lack of
339 knowledge limits the interpretation of chemical data in terms of environmental evolution or
340 pollution tracing. This study presents a simple method to determine the metabolic signals
341 recorded by trace element concentrations in the shell of bivalves by reducing the contribution
342 of variations produced by environmental factors. Applied to *Placopecten magellanicus*, we
343 show that the concentrations of trace elements incorporated in the shell change dramatically
344 when the animal reaches 8 years old. The concentrations of REE, U, Ba, Cu for example, are
345 stable from 2 to 8 years of age, then increase steadily until 20 years of age. This turning point
346 at 8 y.o. corresponds to a slowing down of the growth of the shell of the animals, which
347 accompanies a major metabolic change (e.g., MacDonald, 1986).

348 In order to increase the quality of the chemical time-series obtained on mollusks, it is
349 essential to know these metabolic signals to have better constraints on the environmental
350 forcing. However, data comparable to those we have obtained here on *P. magellanicus* are
351 still lacking on all the long-lived species whose trace element chemistry is studied for this
352 purpose. On the other hand, it should be noted that before being environmental records, shells
353 are first valuable archives of their own metabolism. Therefore, trace elements in bivalves have
354 the potential to become a new tool for biochemists to understand the metabolism of these
355 animals, as already shown for the REE in the chemosynthetic deep-sea mussels (Wang et al.,
356 2020; Barrat et al., 2022a).

357

358

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364

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366 References

- 367
368 Barrat J.A., Keller F., Amossé J., Taylor R.N., Nesbitt R.W., Hirata T. (1996) Determination of rare earth
369 elements in sixteen silicate reference samples by ICP-MS after Tm addition and ion exchange separation.
370 *Geostandards Newsletter* **20**, 1, 133-140.
- 371 Barrat J.A., Zanda B., Moynier F., Bollinger C., Liorzou C., and Bayon G. (2012) Geochemistry of CI
372 chondrites: Major and trace elements, and Cu and Zn isotopes. *Geochim. Cosmochim. Acta* **83**, 79-92.
- 373 Barrat J.A., Dauphas N., Gillet P., Bollinger C., Etoubleau J., Bischoff A., Yamaguchi A. (2016) Evidence from
374 Tm anomalies for non-CI refractory lithophile element proportions in terrestrial planets and achondrites.
375 *Geochim. Cosmochim. Acta*, **176**, 1-17.
376
- 377 Barrat J.A., Bayon G., Wang X., Le Goff S., Rouget M.L., Gueguen B., Ben Salem B. (2020) A new chemical
378 separation procedure for the determination of rare earth elements and yttrium abundances in carbonates by ICP-
379 MS. *Talanta* **219**, 121244.
380
- 381 Barrat J.A., Bayon G., Carney R.S., Chauvaud L. (2022a) Rare earth elements as new biogeochemical proxies in
382 deep-sea mussels. *Chem. Geol.*, <https://doi.org/10.1016/j.chemgeo.2022.121102>.
383
- 384 Barrat J.A., Chauvaud L., Olivier F., Poitevin P., Bayon G., Ben Salem D. (2022b) Rare earth elements and
385 yttrium in suspension-feeding bivalves (dog cockle, *Glycymeris glycymeris* L.): accumulation, vital effects and
386 pollution. *Geochim. Cosmochim. Acta* **339**, 12-21.
387
- 388 Barrat J.A., Bayon G., Lalonde S. (2023) Calculation of cerium and lanthanum anomalies in geological and
389 environmental samples, *Chem. Geol* **615**, <https://doi.org/10.1016/j.chemgeo.2022.121202>.
390
- 391 Bath G.E., Thorrold S.R., Jones C.M., Campana S.E., McLaren J.W., Lam J.W.H. (2000) Strontium and barium
392 uptake in aragonitic otoliths of marine fish. *Geochim. Cosmochim. Acta* **64**, 1705-1714.
393
- 394 Butler P. G., Wanamaker A. D. Jr., Scourse J. D., Richardson C. A., and Reynolds D. J. (2013). Variability of
395 marine climate on the North Icelandic Shelf in a 1357-year proxy archive based on growth increments in the
396 bivalve *Arctica islandica*. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **373**, 141–151.
397
- 398 Del Rio-Lavín A., Weber J., Molkentín J., Jiménez E., Artetxe-Arrate I., Pardo M.A. (2022) Stable isotope and
399 trace element analysis for tracing the geographical origin of the Mediterranean mussel (*Mytilus*
400 *galloprovincialis*) in food authentication. *Food Control* **139**, 109069.
- 401 Dodd J.R. (1965) Environmental control of strontium and magnesium in *Mytilus*. *Geochim. Cosmochim. Acta*
402 **29**, 385-398.
403
- 404 Eggins S, De Deckker P, Marshall J. (2003) Mg/Ca variation in planktonic foraminifera tests: implications for
405 reconstructing palaeo-seawater temperature and habitat migration. *Earth Planet. Sci. Lett.* **212**, 291-306.
- 406 Elliot M., Welsh K., Chilcott C., McCulloch M., Chappell J., Ayling B. (2009) Profiles of trace elements and
407 stable isotopes derived from giant long-lived *Tridacna gigas* bivalves: potential applications in paleoclimate
408 studies. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **280**, 132–142.
409
- 410 Freitas P.S., Clarke L.J., Kennedy H., and Richardson C.A. (2009) Ion microprobe assessment of the
411 heterogeneity of Mg/Ca, Sr/Ca and Mn/Ca ratios in *Pecten maximus* and *Mytilus edulis* (bivalvia) shell calcite
412 precipitated at constant temperature. *Biogeosciences* **6**, 1209-1227.
413
- 414 Frieder C.A., Gonzalez J.P., Levin L.A. (2014) Uranium in larval shells as a barometer of molluscan ocean
415 acidification exposure. *Environ. Sci. Technol.* **48**, 6401–6408.
416
- 417 Fröhlich L., Siebert V., Walliser E.O., Thébault J., Jochum K.P., Chauvaud L., Schöne B.R. (2022) Ba/Ca
418 profiles in shells of *Pecten maximus* – a proxy for specific primary producers rather than bulk phytoplankton.
419 *Chem. Geol.* **593**, 120743

420 Gillikin, D.P., Lorrain A., Navez J., Taylor J.W., André L., Keppens E., Baeyens W., and Dehairs F. (2005),
421 Strong biological controls on Sr/Ca ratios in aragonitic marine bivalve shells. *Geochem. Geophys. Geosyst.*, **6**,
422 Q05009, doi:10.1029/2004GC000874.
423

424 Gillikin D.P., Dehairs F., Lorrain A., Steenmans D., Baeyens W., André L. (2006) Barium uptake into the shells
425 of the common mussel (*Mytilus edulis*) and the potential for estuarine paleo-chemistry reconstruction. *Geochim.*
426 *Cosmochim. Acta* **70**, 395-407.
427

428 Gillikin D.P., Dehairs F. (2013) Uranium in aragonitic marine bivalve shells. *Palaeogeogr. Palaeoclimatol.*
429 *Palaeoecol.* **373**, 60-65.
430

431 Hart S., Blusztajn J. (1998) Clams as recorders of ocean ridge volcanism and hydrothermal vent field activity.
432 *Science* **280**, 883-886.
433

434 Immenhauser A., Schöne B.R., Hoffmann R., Niedermayr A. (2016) Mollusc and brachiopod skeletal hard parts:
435 intricate archives of their marine environment. *Sedimentology* **63**, 1-59.
436

437 Le Goff S., Barrat J.A., Chauvaud L., Paulet Y.M., Gueguen B., Ben Salem D. (2019) Compound-specific
438 recording of gadolinium pollution in coastal waters by great scallops. *Scientific Reports* **9**, 8015.
439

440 Liu C., Yan H., Wang G., Zhao L., Hu Y., Zhou P., Luo F., Yang H., Dodson J. (2021) Species specific Sr/Ca-
441 $\delta^{18}\text{O}$ relationships for three Tridacnidae species from the northern South China Sea. *Chem. Geol.* **584**, 120519.
442

443 Lorrain A., Gillikin D.P., Paulet Y.M., Chauvaud L., Le Mercier A., Navez J., André L. (2005) Strong kinetic
444 effects on Sr/Ca ratios in the calcitic bivalve *Pecten maximus*. *Geology* **33**, 965-968.
445

446 MacDonald B.A. (1986) Production and resource partitioning in the giant scallop *Placopecten magellanicus*
447 grown on the bottom and in suspended culture. *Mar. Ecol. Prog. Ser.* **34**, 79-86.
448

449 McCulloch M.T., Gagan M.K., Mortimer G.E., Chivas A.R., Isdale P.J. (1994) A high-resolution Sr/Ca and $\delta^{18}\text{O}$
450 coral record from the Great Barrier Reef, Australia, and the 1982-1983 El Niño. *Geochim. Cosmochim. Acta* **58**,
451 2747-2754.
452

453 Morrison L., Bennion M., Gill S., Graham, C.T. (2019). Spatio-temporal trace element fingerprinting of king
454 scallops (*Pecten maximus*) reveals harvesting period and location. *The Science of the Total Environment* **697**,
455 134121.

456 Norrie C.R., Dunphy B.J., Ragg N.L.C., Lundquist C.J. (2018) Ocean acidification can interact with ontogeny to
457 determine the trace element composition of bivalve shell. *Limnology and Oceanography Letters* **3**, 393-400.
458

459 Pilkey O.H., Goodell H.G. (1963) Trace element in recent mollusc shells. *Limnol. Oceanogr.* **8**, 137-148.
460

461 Poitevin P., Chauvaud L., Pécheyran C., Lazure P., Jolivet A., Thébault J. (2020) Does trace element
462 composition of bivalve shells record ultra-high frequency environmental variations? *Marine Environmental*
463 *Research* **158**, 104943.
464

465 Poitevin P., Roy V., Galbraith P.S., Chaillou G. (2022) Insights into coastal phytoplankton variations from 1979
466 to 2018 derived from Ba/Ca records in scallop shells (*Chlamys islandica*) from a fishing ground in the northern
467 Gulf of St. Lawrence. *Marine Env. Res.* **181**, 105734.

468 Ponnurangam, A., Bau, M., Brenner, M., Kochinsky, A. (2016) Mussel shells of *Mytilus edulis* as bioarchives of
469 the distribution of rare earth elements and yttrium in seawater and the potential impact of pH and temperature on
470 their partitioning behavior. *Biogeosciences* **13**, 751-760.

471 Poulain C., Gillikin D.P., Thébault J., Munaron J.M., Bohn M., Robert R., Paulet Y.M., Lorrain A. (2015) An
472 evaluation of Mg/Ca, Sr/Ca, and Ba/Ca ratios as environmental proxies in aragonite bivalve shells. *Chem. Geol.*
473 **396**, 42-50.
474

475 Pourmand, A., Dauphas, N., Ireland, T.J. (2012) A novel extraction chromatography and MC-ICP-MS technique
476 for rapid analysis of REE, Sc and Y: Revising CI-chondrite and Post-Archean Australian Shale (PAAS)
477 abundances. *Chem. Geol.* **291**, 38-54.

478
479 Reynaud S., Ferrier-Pagès C., Meibom A., Mostefaoui S., Mortlock R., Fairbanks R., Allemand D. (2007) Light
480 and temperature effects on Sr/Ca and Mg/Ca ratios in the scleractinian coral *Acropora* sp. *Geochim. Cosmochim.*
481 *Acta* **71**, 354-362.

482 Ricardo F., Pimentel T., Génio, L., Calado R. (2017). Spatio-temporal variability of trace elements fingerprints
483 in cockle (*Cerastoderma edule*) shells and its relevance for tracing geographic origin. *Scientific Reports* **7**, 3475.

484 Rosenthal Y., Boyle E.A., Slowey N. (1997) Temperature control on the incorporation of magnesium, strontium,
485 fluorine, and cadmium into benthic foraminiferal shells from Little Bahama Bank: Prospects for thermocline
486 paleoceanography. *Geochim. Cosmochim. Acta* **61**, 3633-3643.

487 Schöne B.R., Zhang Z., Radermacher P., Thebault J., Jacob D.E., Nunn E.V., Maurer A.-F. (2011) Sr/Ca and
488 Mg/Ca ratios of ontogenetically old, long-lived bivalve shells (*Arctica islandica*) and their function as
489 paleotemperature proxies. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **302**, 52–64.

490
491 Schöne B.R., Huang X., Jantschke A., Mertz-Kraus R., Zettler M.L. (2022) High-resolution reconstruction of
492 dissolved oxygen levels in the Baltic Sea with bivalves – a multi-species comparison (*Arctica islandica*, *Astarte*
493 *borealis*, *Astarte elliptica*). *Frontiers in Marine Science* **9**, 820731.

494 Schöne B.R., Marali S., Jantschke A., Mertz-Kraus R., Butler P.G., Fröhlich F. (2023) Can element chemical
495 impurities in aragonitic shells of marine bivalves serve as proxies for environmental variability? *Chem. Geol.*,
496 <https://doi.org/10.1016/j.chemgeo.2022.121215>

497
498 Steinhardt J., Butler P.G., Carroll M.L., Hartley J. (2016) The Application of Long-Lived Bivalve
499 Sclerochronology in Environmental Baseline Monitoring. *Front. Mar. Sci.* **3**, 176. doi:
500 10.3389/fmars.2016.00176

501
502 Smith S.V., Buddemeier R.W., Redalje R.C., Houck J.E. (1979) Strontium-calcium thermometry in coral
503 skeletons. *Science* **204**, 404-407.

504
505 Stecher H.A., Krantz D.E., Lord C.J., Luther G.W., Bock K.W. (1996) Profiles of strontium and barium in
506 *Mercenaria mercenaria* and *Spisula solidissima* shells. *Geochim. Cosmochim. Acta* **60**, 3445–3456.

507
508 Strasser C. A., Mullineaux L.S., Walther, B.D. (2008). Growth rate and age effects on *Mya arenaria* shell
509 chemistry: Implications for biogeochemical studies. *J. Exp. Mar. Bio. Ecol.*, 355, 153–163.

510
511 Takesue R.K., van Geen A. (2004) Mg/Ca, Sr/Ca, and stable isotopes in modern and Holocene *Protothaca*
512 *staminea* shells from a northern California coastal upwelling region. *Geochim. Cosmochim. Acta* **68**, 3845-3861.

513
514 Thébault J., Chauvaud L. (2013) Li/Ca enrichments in great scallop shells (*Pecten maximus*) and their
515 relationship with phytoplankton blooms. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **373**, 108–122.

516
517 Thorn K., Cerrato R.M., and Rivers M.L. (1995) Elemental distributions in marine bivalve shells as measured by
518 synchrotron X-ray fluorescence. *The Biological Bulletin* **188**, 57-67, <https://doi.org/10.2307/1542067>.

519
520 Thébault J., Chauvaud L, L’Helguen S, Clavier J., Barats A., Jacquet S., Pécheyran C., Amouroux D. (2009)
521 Barium and molybdenum records in bivalve shells: Geochemical proxies for phytoplankton dynamics in coastal
522 environments? *Limnol. Oceanogr.* **54**, 1002–1014

523
524 Wanamaker A.D., Gillikin D.P. (2019) Strontium, magnesium, and barium incorporation in aragonitic shells of
525 juvenile *Arctica islandica*: insights from temperature controlled experiments. *Chem. Geol.* **526**, 117–129.

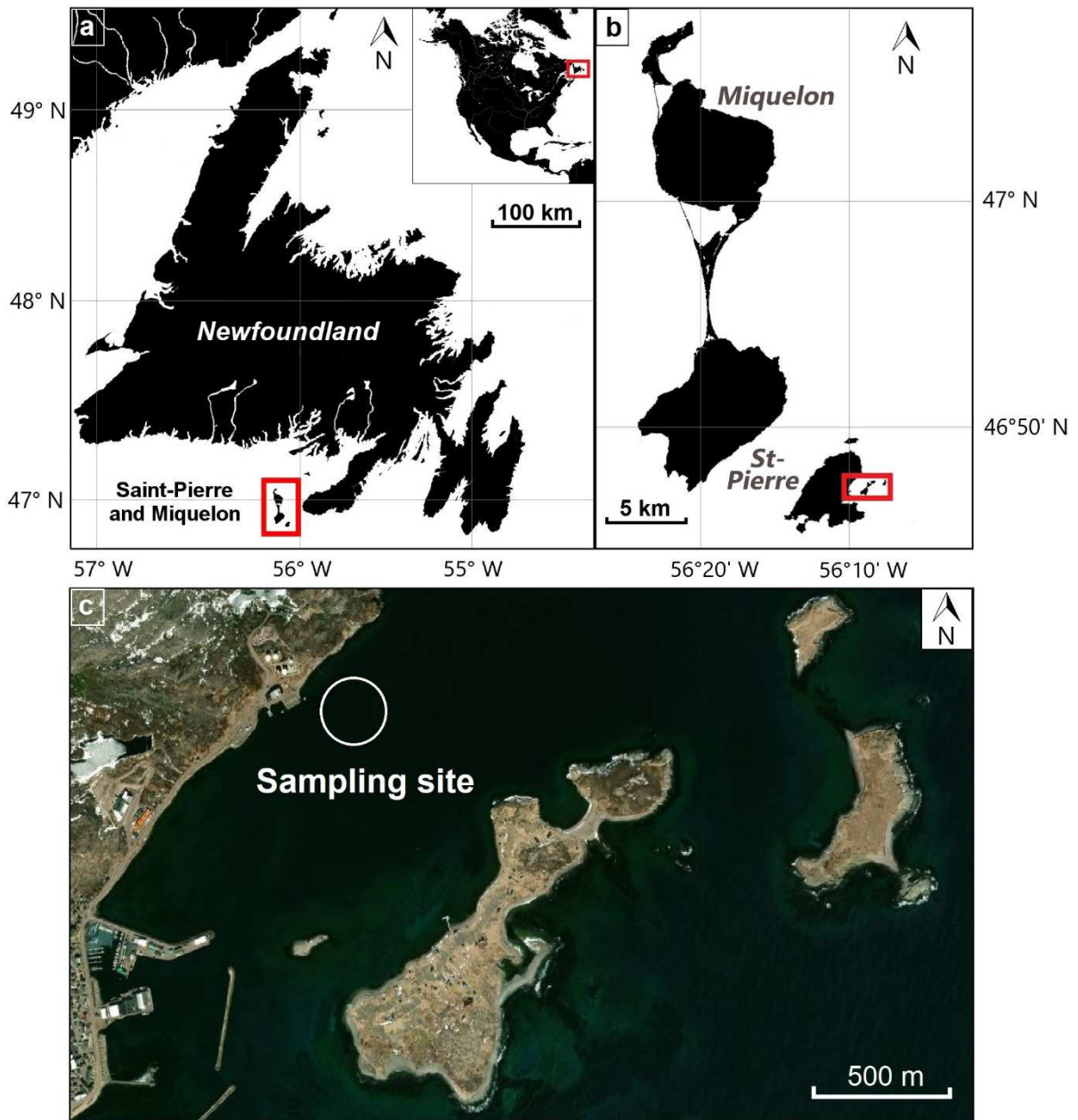
526
527 Wang X., Bayon G., Kim J.H., Lee D.H., Kim D., Guéguen B., Rouget M.L., Barrat J.A., Toffin L., Dong F.
528 (2019) Trace element systematics in cold seep carbonates and associated lipid compounds. *Chem. Geol.*,
529 doi.org/10.1016/j.chemgeo.2019.119277

530
531 Wang X., Barrat J.A., Bayon G., Chauvaud L., Feng D. (2020) Lanthanum anomalies as fingerprints of
532 methanotrophy. *Geochem. Persp. Let.* **14**, 26–30.

533

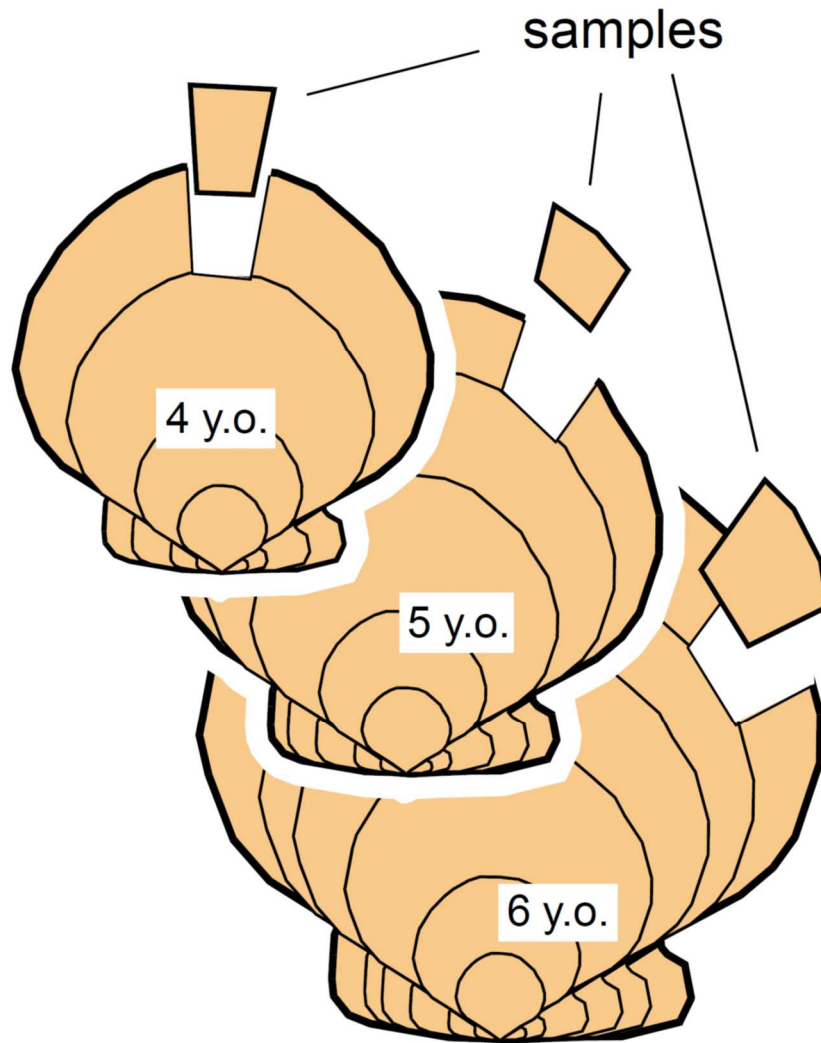
- 534 Webb G.E., Kamber B.S. (2000) Rare earth elements in Holocene reefal microbialites: a new shallow seawater
535 proxy. *Geochim. Cosmochim. Acta* **64**, 1557-1565.
536
- 537 Zhao L., Schöne B.R., Mertz-Kraus R. and Yang F. (2017) Sodium provides unique insights into
538 transgenerational effects of ocean acidification on bivalve shell formation. *Sci. Total Env.* **577**, 360-366.
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Figure 1. Location of Saint Pierre and Miquelon (a) and of the sampling site (b and c).



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553 Figure 2. Diagram illustrating the shell sampling strategy. Live *Placopecten* of different ages
554 (here 4 to 6 y.o.) were caught at the same site and prepared on the same day. The shells were
555 brushed to remove any adhering particles, and a fragment sampling the entire width of the last
556 annual growth increment was taken. These samples were therefore all formed under the same
557 conditions (temperature, food, etc.), during the same period, but the ages of the animals are
558 not the same.

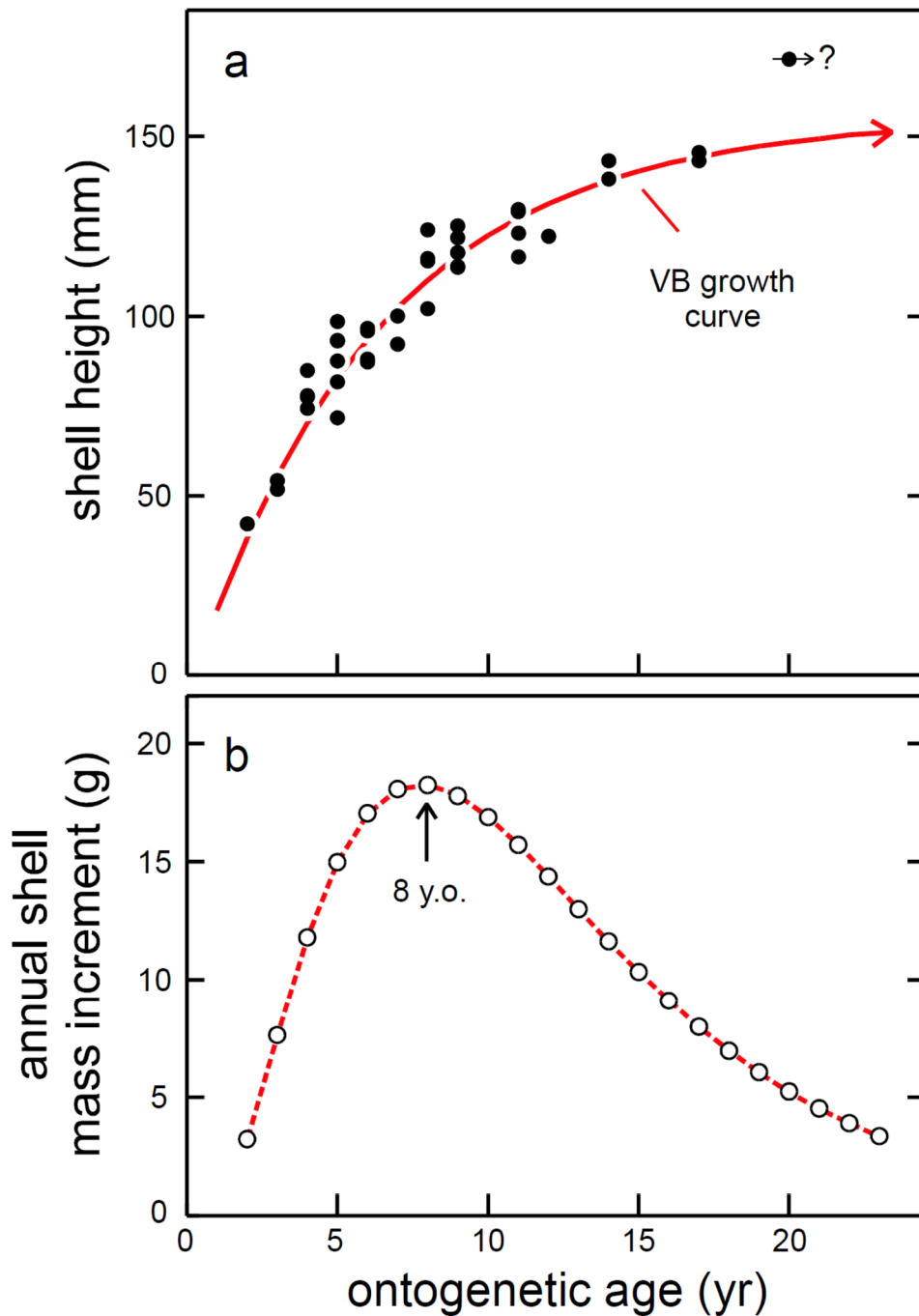
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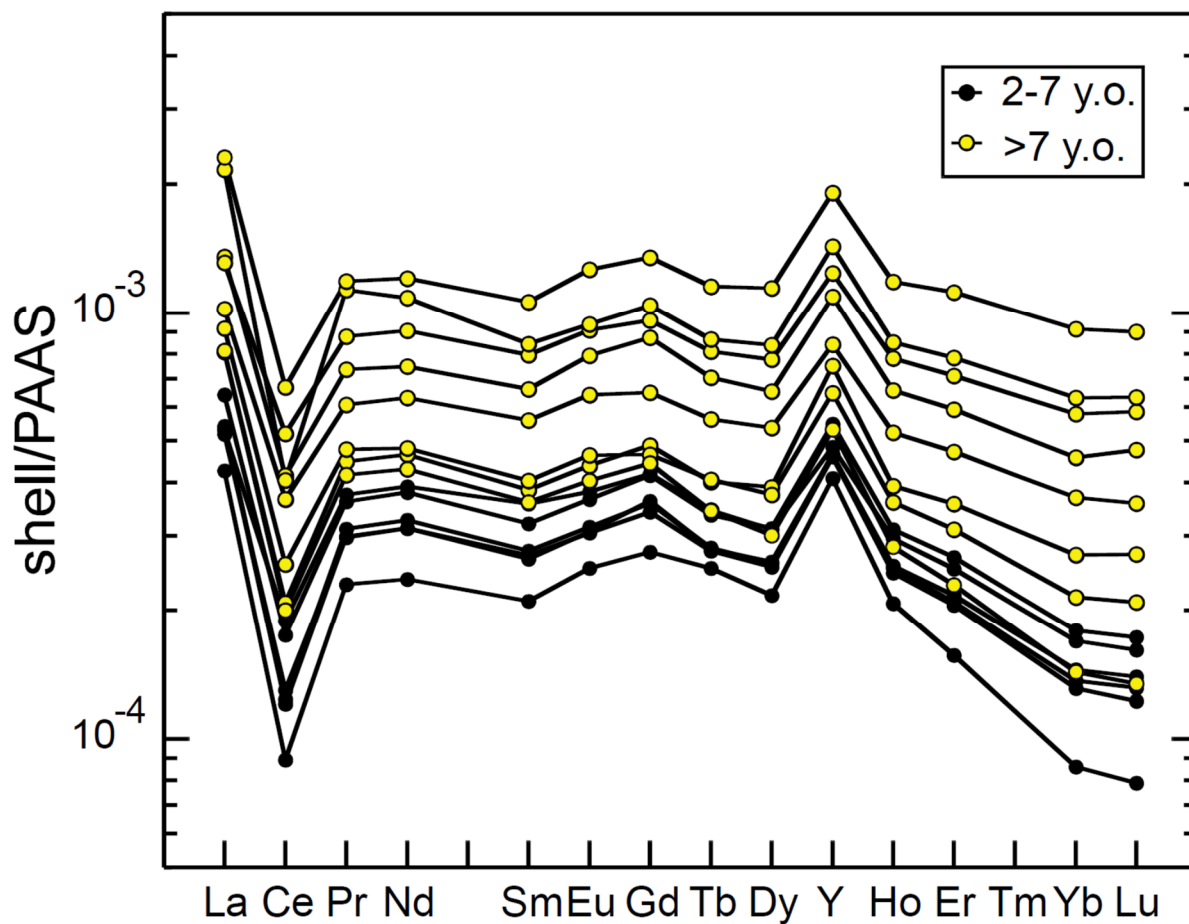
566 Figure 3. (a) Variation in shell height with age in *P. magellanicus* collected in Saint Pierre.
 567 The growth curve was fitted using the von Bertalanffy (VB) growth equation with a
 568 maximum shell height of 155 mm. (b) annual shell mass increment during the life of an
 569 animal whose size follows the Von Bertalanffy equation. The annual shell mass increment is
 570 calculated using the shell weight vs. height determined by MacDonald (1986) for wild *P.*
 571 *magellanicus* from Newfoundland.
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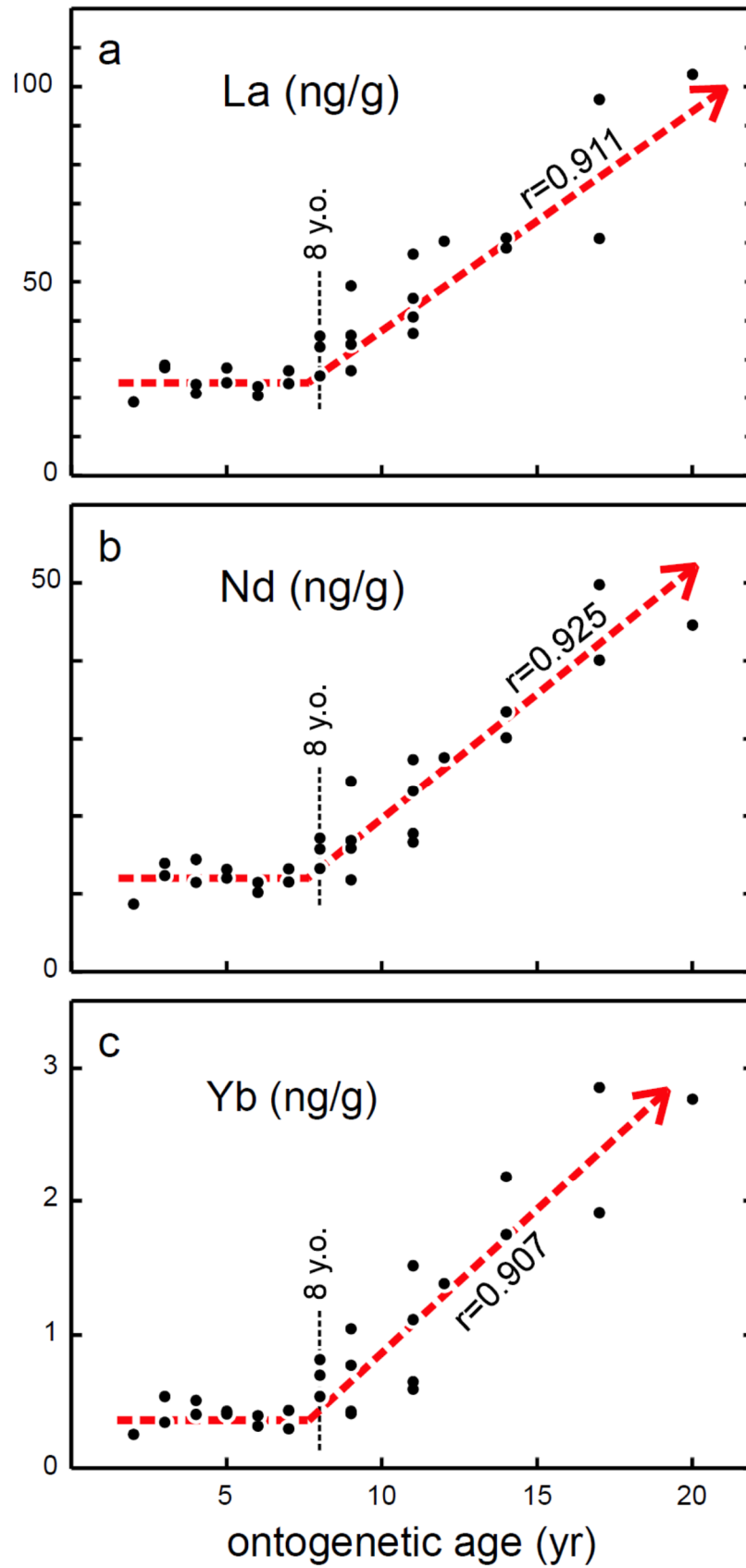
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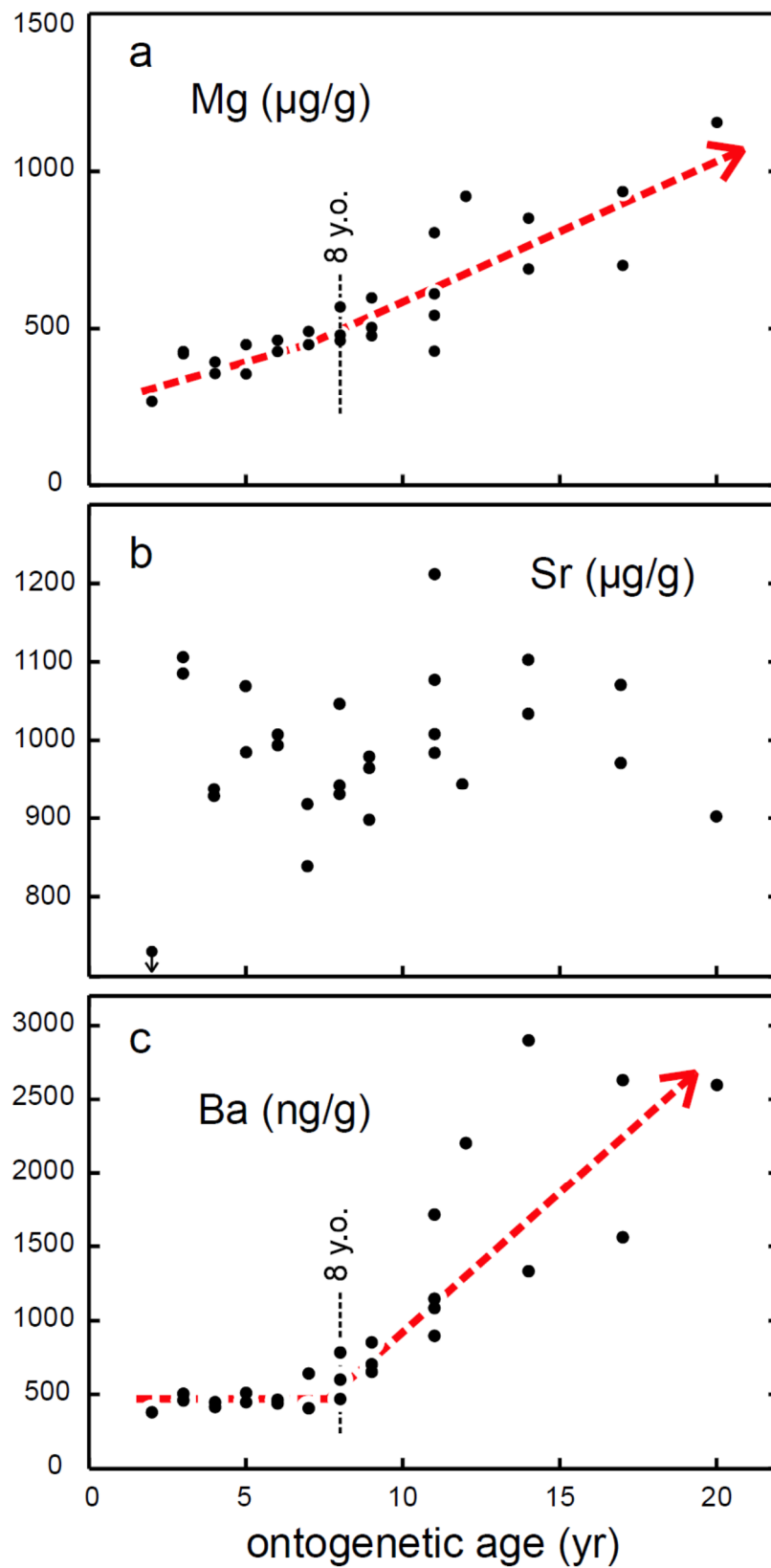
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Figure 4. PAAS-normalized REY patterns of selected shells of *P. magellanicus* (last annual growth increment) from Saint Pierre.



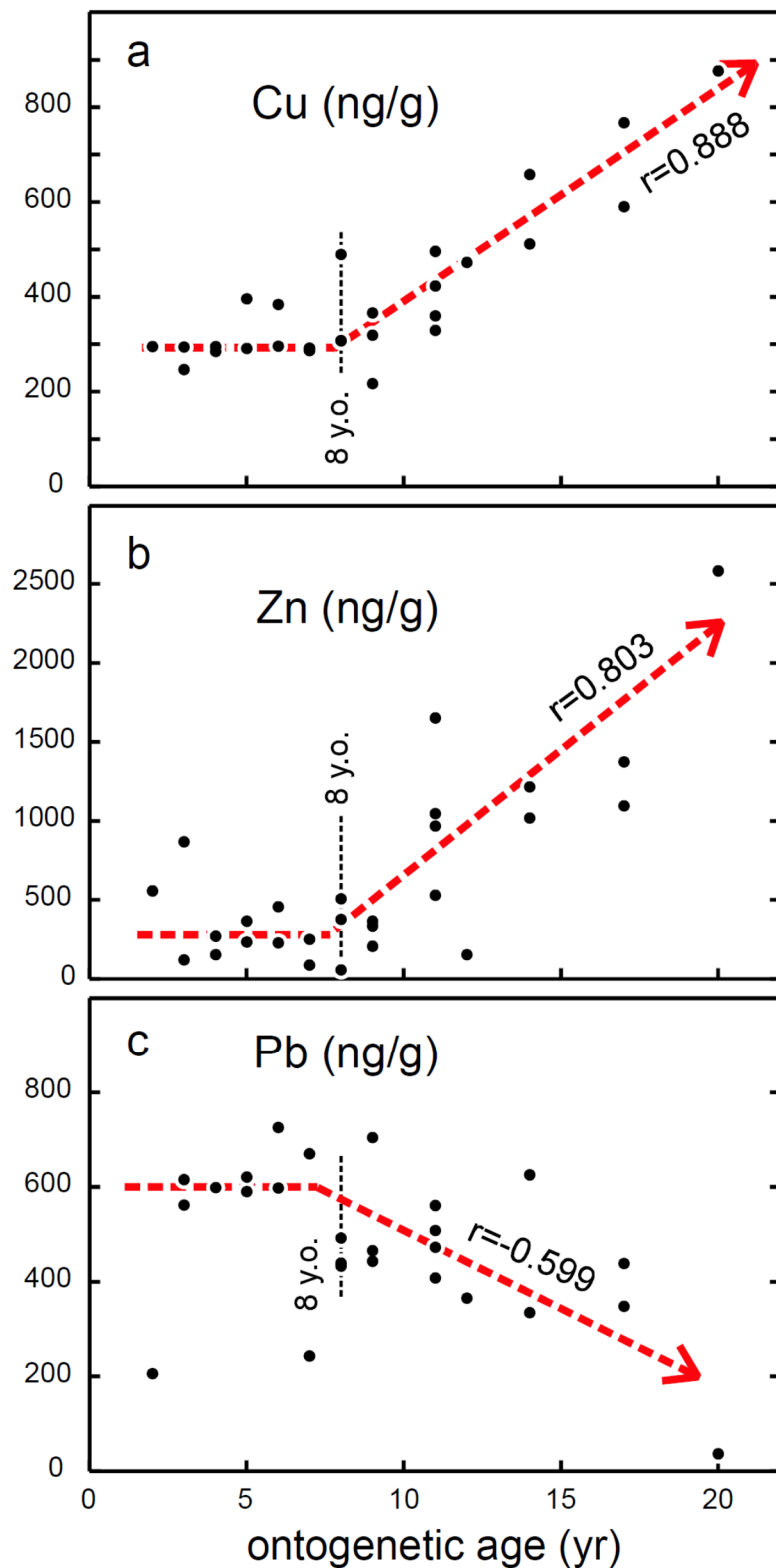
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590 Figure 5. La (a), Nd (b) and Yb (c) concentrations vs. ontogenetic age for the margins of the
 591 *P. magellanicus* valves (last annual growth rind) from Saint Pierre. The correlation
 592 coefficients calculated with individuals older than 8 years are given next to the trends.



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595 Figure 6. Mg (a), Sr (b) and Ba (c) concentrations vs. ontogenetic age for the margins of the
 596 *P. magellanicus* valves (last annual growth rind) from Saint Pierre. The correlation
 597 coefficients calculated with individuals older than 8 years are given next to the trends.

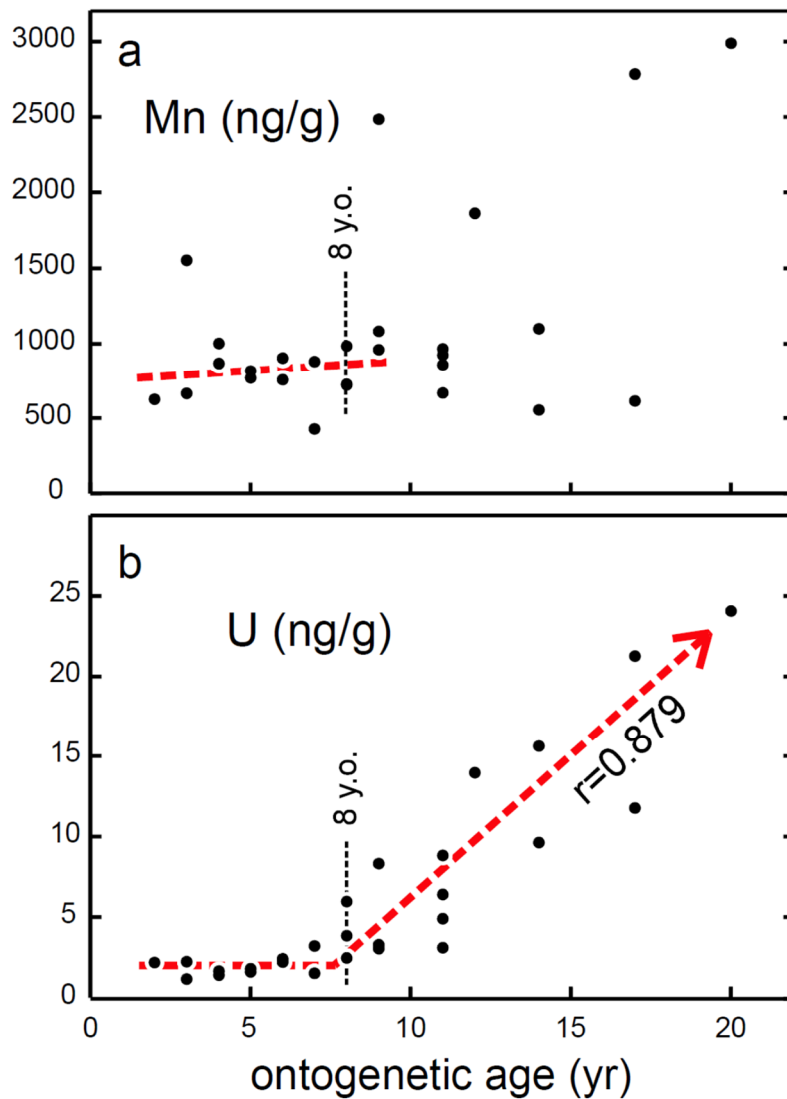


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600 Figure 7. Cu (a), Zn (b) and Pb (c) concentrations vs. ontogenetic age for the margins of the
 601 *P. magellanicus* valves (last annual growth ring) from Saint Pierre. The correlation
 602 coefficients calculated with individuals older than 8 years are given next to the trends.

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Figure 8. Mn (a) and U (b) concentrations vs. ontogenetic age for the margins of the *P. magellanicus* valves (last annual growth rind) from Saint Pierre. The correlation coefficient calculated with individuals older than 8 years is given next to the trend in Fig. 8b.