Trace elements in bivalve shells: How "vital effects" can bias environmental studies

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Abstract :

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

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

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

Graphical abstract
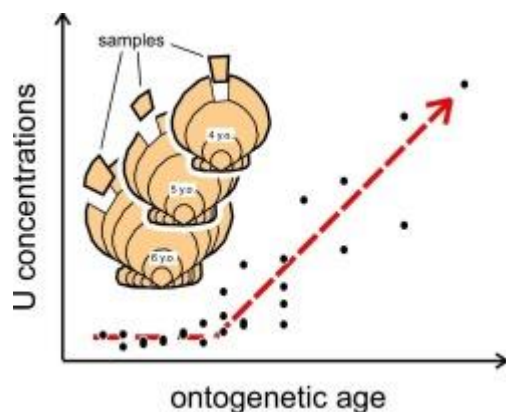
Highlights

► Trace elements in shells of giant scallops were determined. ► Rare earth elements, Y, copper, uranium and barium show two-step trends, with a turning point at 8 y.o. ► Metabolic processes control the behavior of these trace elements. ► The knowledge of metabolic effects on trace elements will improve geographic tracking processes of shellfish. ► Shells are valuable archives of bivalve metabolism.

1/ Introduction

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

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

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

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

2/ Sampling and analytical procedures

Twenty-seven *P. magellanicus* were selected and collected alive in the same station, by a scuba diver on february 6, 2022 in Saint Pierre Bay (46.713705°N, -56.157593W) at a water depth of 22 m (Fig. 1).

The age of the mollusks was determined directly by counting the "winter marks" deposited during spring growth restart. The sampling comprises one 2 y.o. individual, two 3 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. individuals, one 12 y.o. individual, two 14 y.o. and 17 y.o. individuals, and one 20 y.o. individual.

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

Trace element concentrations were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using well-established procedures (e.g., Barrat et al., 2012, 2016). Each sample was spiked with a solution of pure Tm (Barrat et al., 1996) and digested in a Teflon beaker by HNO_3. REEs and Y have been separated and concentrated before analysis using ion-exchange chromatographic columns loaded with about 1 ml DGA-Normal resin (DN-B50-S, 50-100 μm, produced by Triskem®) following the procedure developed by

Barrat et al. (2020). For other elements (Mg, Mn, Cu, Zn, Sr, Ba, Pb, U), an aliquot of the sample solution containing the equivalent of 4 mg of sample was dried and the residue was taken up in 4 ml of 2.5% HNO_3 before analysis (e.g., Wang et al., 2019). The measurements were performed on a Thermo Scientific ELEMENT XR™ spectrometer located at the "Pôle Spectrometrie Ocean", Institut Universitaire Europeen de la Mer (IUEM), Plouzané. Each solution was analyzed in triplicate, and the results were averaged. Results on two carbonate standards (CAL-S and BEAN) obtained during the sessions are compared with literature values in Table S1. Based on standards, the precisions (RSD) for concentrations and element ratios are better than 3 %.

For the normalisation of the concentrations, we use the Post Archean Australian Shale (PAAS) average obtained by Pourmand et al. (2012), adjusted to standard results obtained in our laboratory (Barrat et al., 2020). The La, Ce, and Gd anomalies are calculated using the La/La*, Ce/Ce*, Gd/Gd* ratios, where X* is the extrapolated concentrations for a smooth PAAS-normalised REE pattern and X_{sn} is the concentration of element X normalised to 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, 2023).

3/ Results

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

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

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

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

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

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

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

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

4/ Discussion

There is no doubt that the composition of the nutrients, the water and possibly the fraction of sediment that the bivalves ingest, imprints some of their chemical signatures into shells, and explains possible differences observed between shells of the same species collected from distant sites. All the bivalves studied here were caught on the same day on the same site, at the same depth. The shell samples we analyzed, were all formed during the same period (i.e., the year 2021), under the same conditions: same water temperatures, salinity, dissolved O_2 level, pH, composition, the same nutrients and the same access to food for all animals. Therefore, none of these factors, although they may have significant effects on shell composition (e.g., Steinhardt et al., 2016), can be the cause of the observed differences in concentration between these shells. However, the relationships between the trace element concentrations (e.g., REY, Ba, U or Cu) and ontogenetic ages, demonstrate that a major change occurs in the life of *P. magellanicus* when they reach about 8 years old. Examination of the growth curve (Fig. 3a) shows that it is around this age that growth slows down. To have a picture of the growth rate, or of the calcification rate, we have opted for the calculation of the mass of shell formed per year. This mass increment is easy to estimate. MacDonald (1986) showed that the total mass of shells of a given wild *P. magellanicus* from Newfoundland can be deduced from its height (see Table 1 in MacDonald (1986)). For a bivalve whose growth is described by von Bertalanffy's law, the annual increment is calculated directly as the difference between the estimated shell masses at ages n and n-1. A bell curve is obtained, and displays indeed a maximum for 7-8 years old (Fig. 3b).

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

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

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

In the last 60 years, it has been repeatedly suggested that the incorporation of trace elements into bivalve shells is potentially controlled by salinity (Ba, e.g., Gillikin et al., 2006), temperature (Mg, Sr, e.g., Dodd, 1965; Hart and Blusztajn 1998; Elliot et al., 2009; Liu et al., 2021), pH and $[CO_3^{2-}]$ (Na and U, e.g., Frieder et al., 2014; Norrie et al., 2018; Zhao et al., 2017), dissolved oxygen (Mn, Schöne et al., 2022), or even the phytoplankton dynamics (e.g. Ba, Li, e.g., Elliot et al., 2009; Thébault et al., 2009; Thébault and Chauvaud, 2013; Poitevin et al., 2020, 2022; Fröhlich et al., 2022). Although it is certainly the case that all of these factors can contribute to behavior of trace elements in shells, data obtained over the last decades have shown a very high complexity of the chemical signal they recorded. Moreover,

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

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

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

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

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

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

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

5/ Conclusions

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

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

Appendix A. Supplementary materials.

Table S-1 contains all the data obtained during the course of this study.

Supplementary figures contains Figures S-1 and S-2

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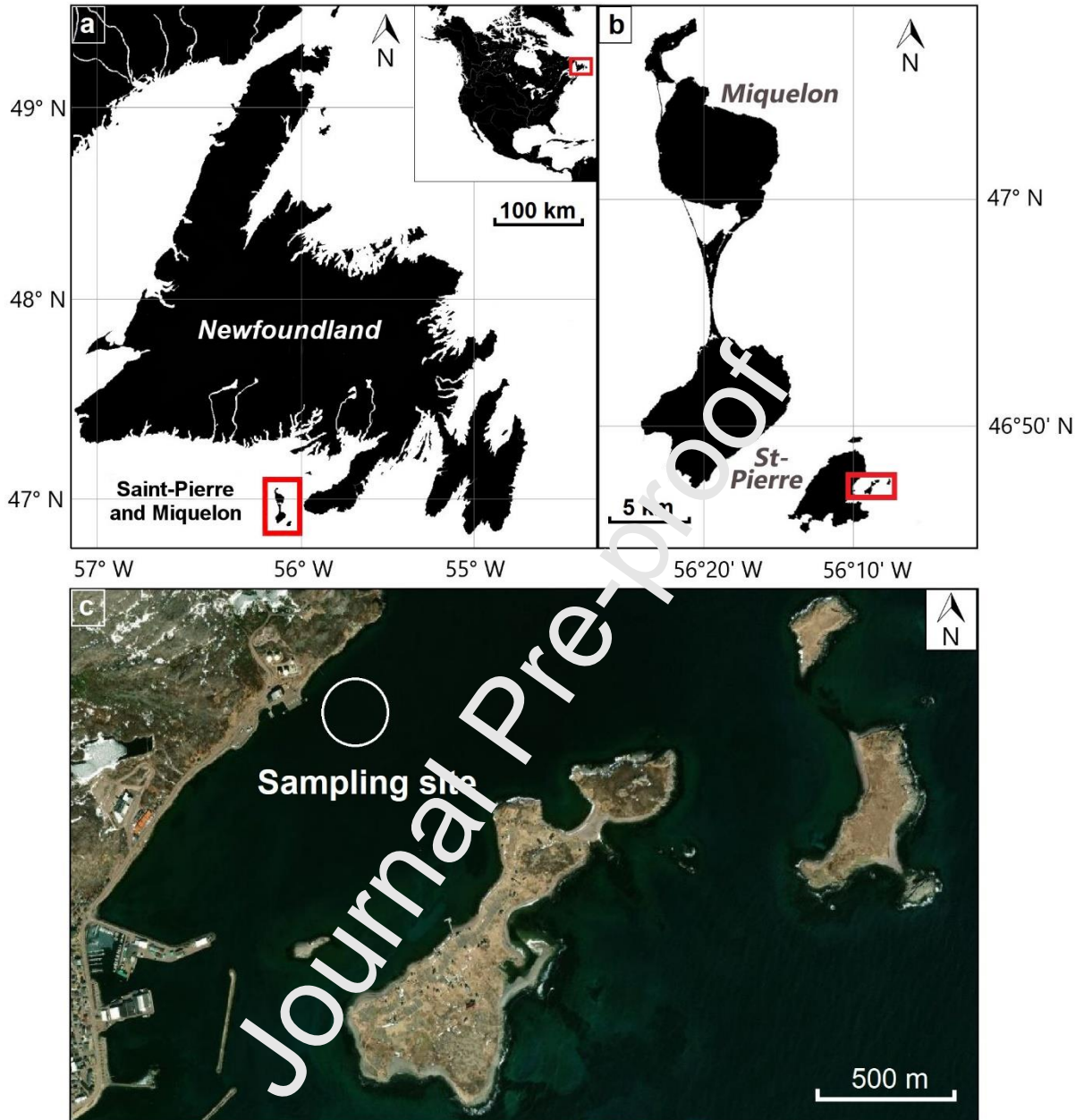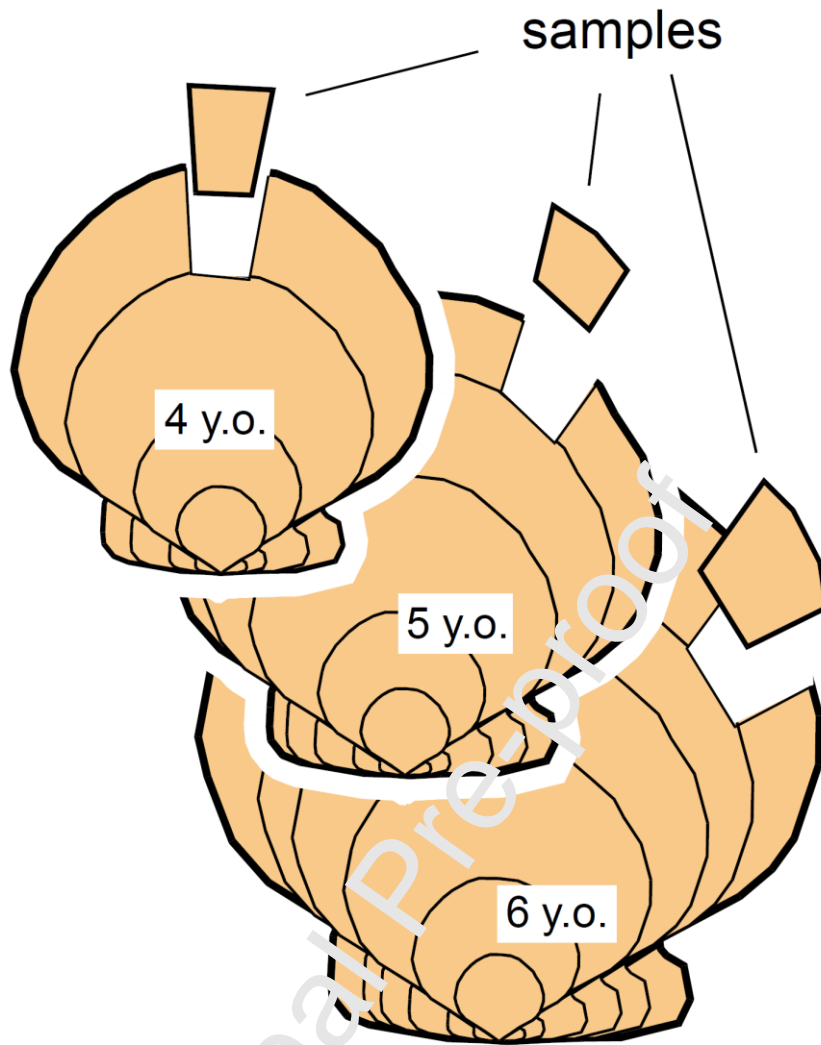Figure 1. Location of Saint Pierre and Miquelon (a) and of the sampling site (b and c).

Figure 2. Diagram illustrating the shell sampling strategy. Live *Placopecten* of different ages (here 4 to 6 y.o.) were caught at the same site and prepared on the same day. The shells were brushed to remove any adhering particles, and a fragment sampling the entire width of the last annual growth increment was taken. These samples were therefore all formed under the same conditions (temperature, food, etc.), during the same period, but the ages of the animals are not the same.
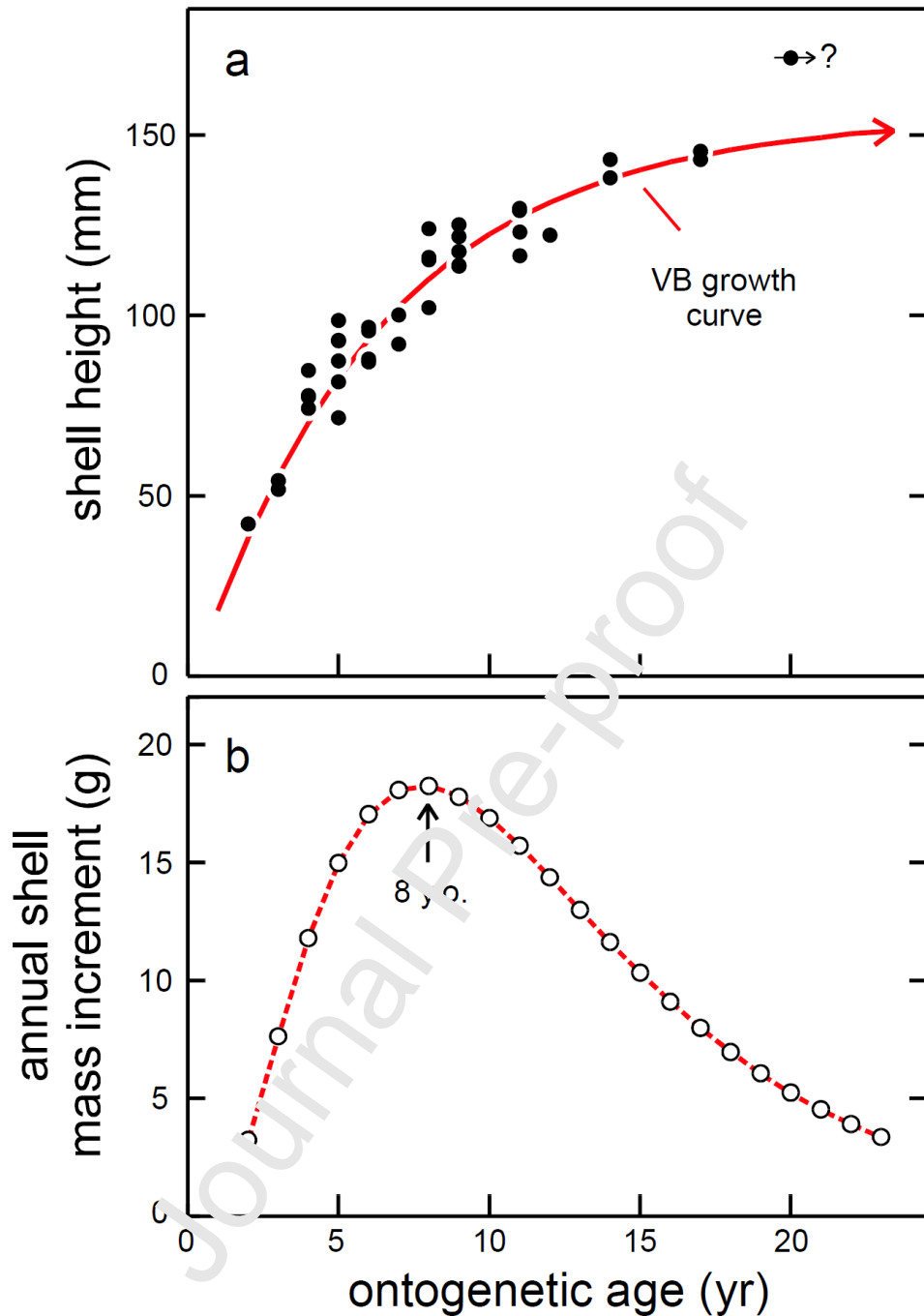
Figure 3. (a) Variation in shell height with age in *P. magellanicus* collected in Saint Pierre. The growth curve was fitted using the von Bertalanffy (VB) growth equation with a maximum shell height of 155 mm. (b) annual shell mass increment during the life of an animal whose size follows the Von Bertalanffy equation. The annual shell mass increment is calculated using the shell weight vs. height determined by MacDonald (1986) for wild *P. magellanicus* from Newfoundland.
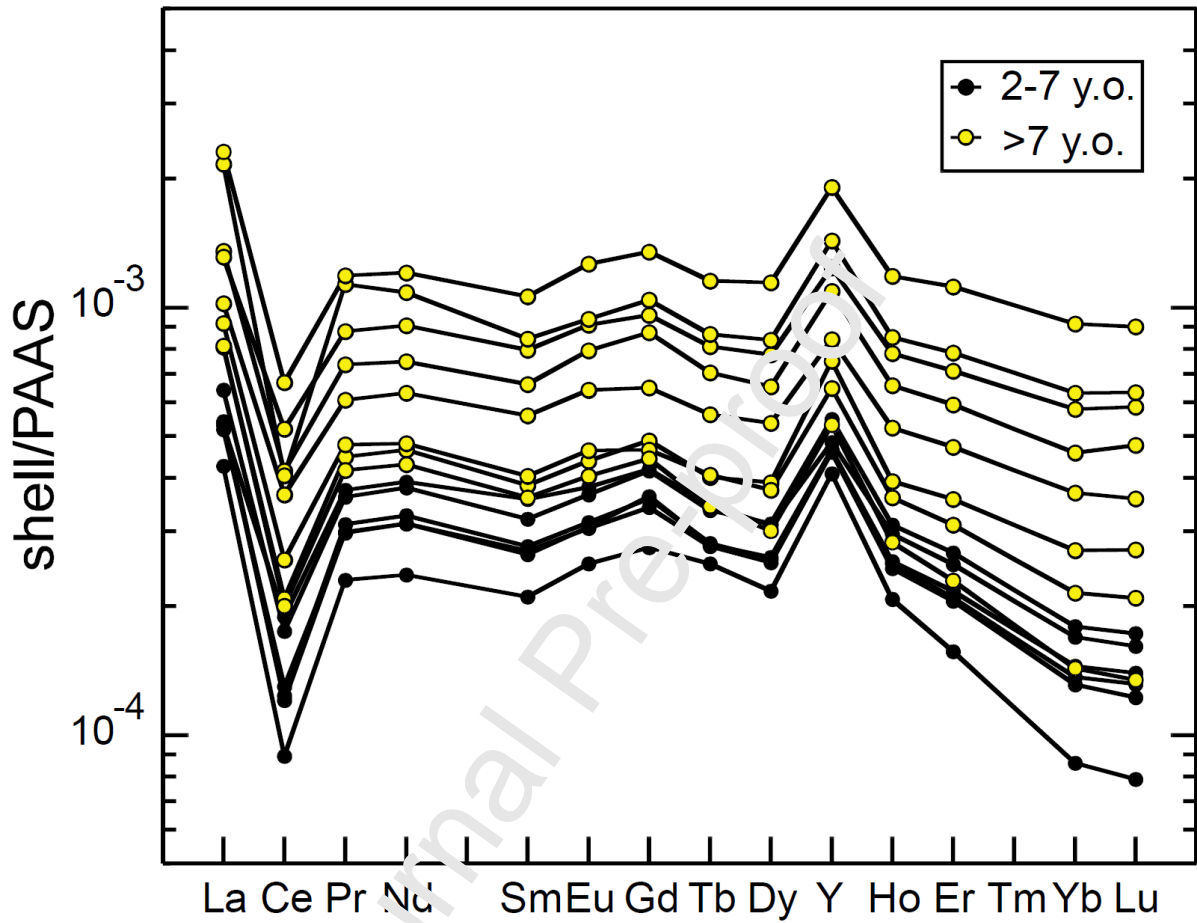
Figure 4. PAAS-normalized REY patterns of selected shells of *P. magellanicus* (last annual growth increment) from Saint Pierre.
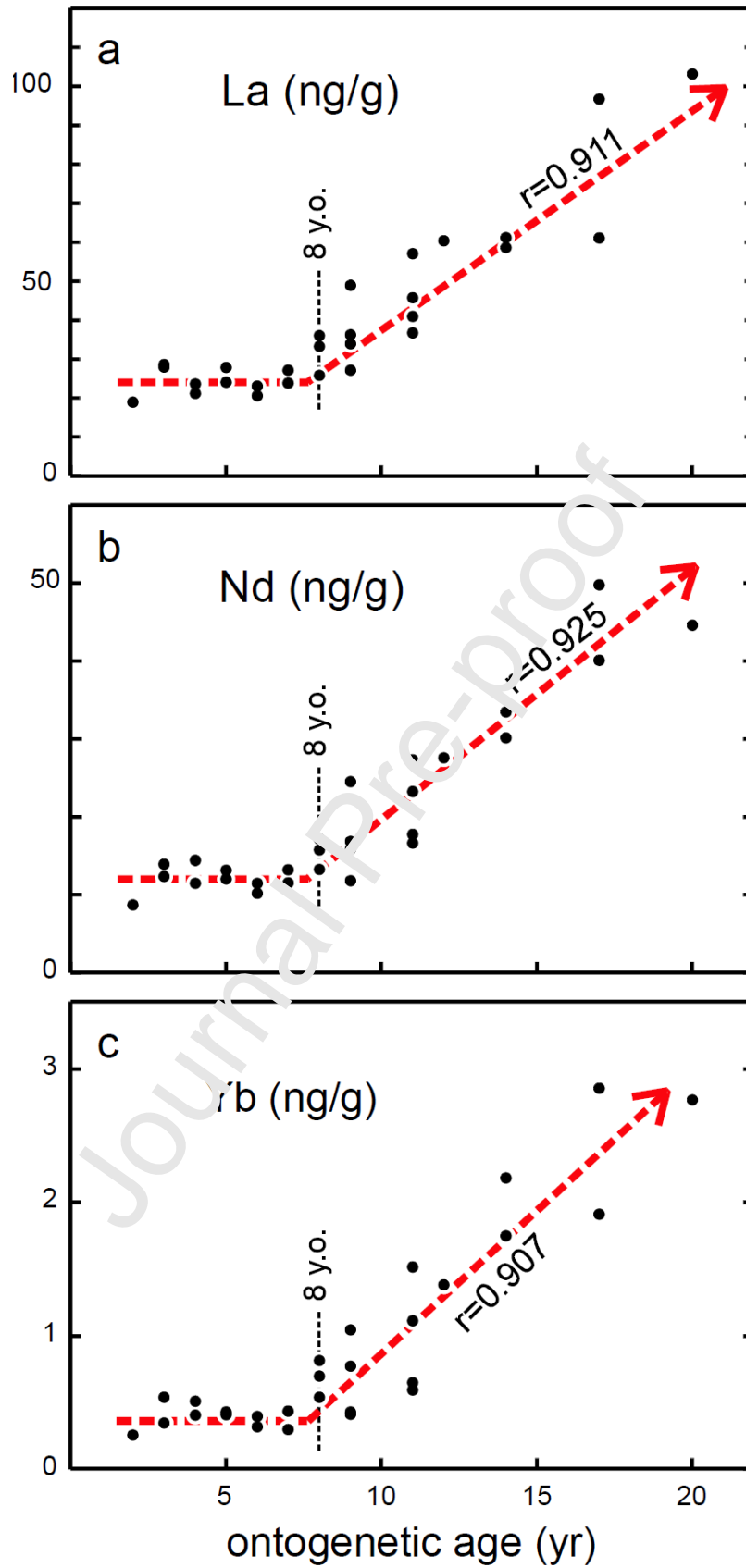
Figure 5. La (a), Nd (b) and Yb (c) concentrations vs. ontogenetic age for the margins of the *P. magellanicus* valves (last annual growth rind) from Saint Pierre. The correlation coefficients calculated with individuals older than 8 years are given next to the trends.
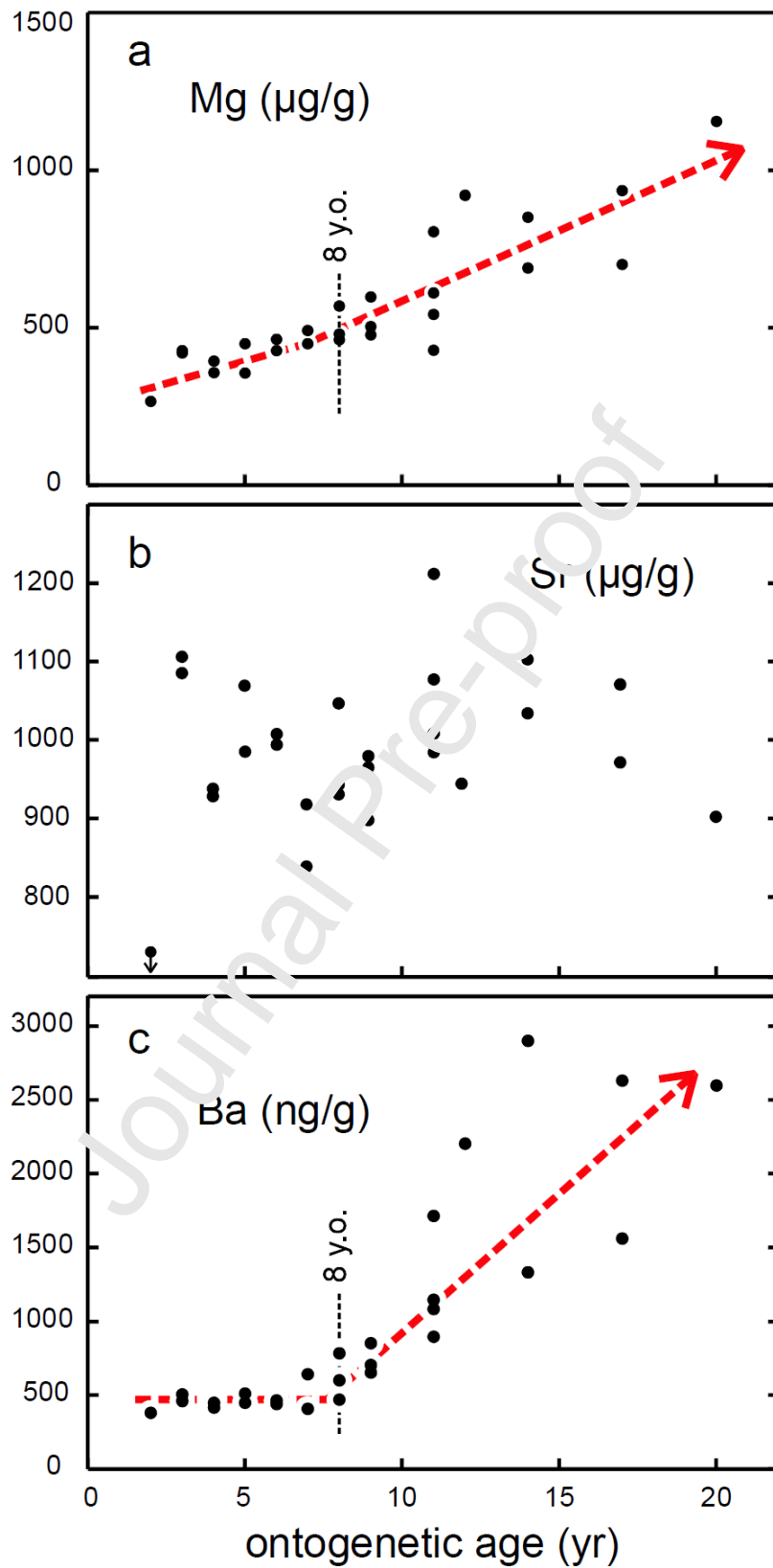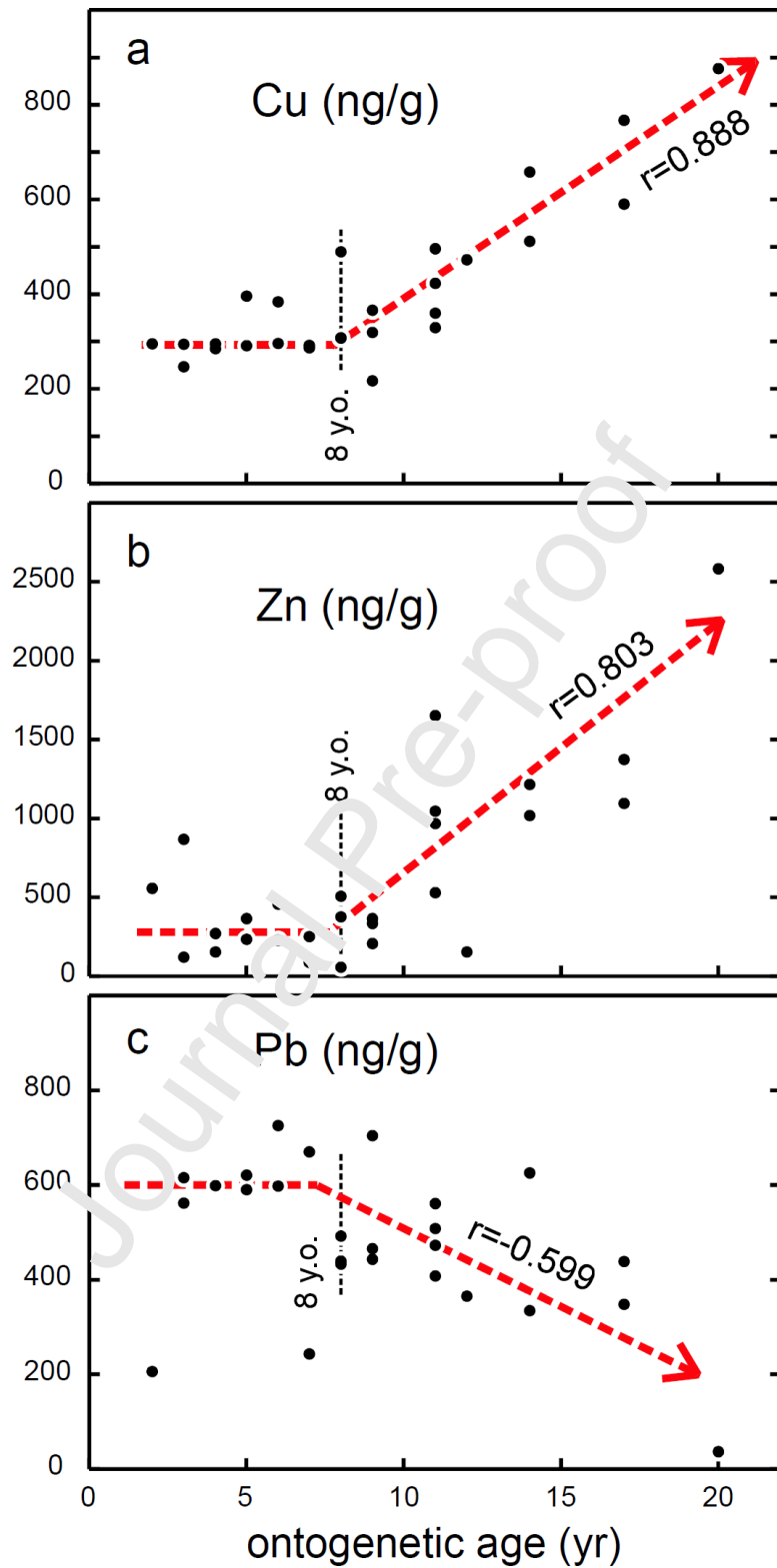
Figure 6. Mg (a), Sr (b) and Ba (c) concentrations vs. ontogenetic age for the margins of the *P. magellanicus* valves (last annual growth rind) from Saint Pierre. The correlation coefficients calculated with individuals older than 8 years are given next to the trends.

Figure 7. Cu (a), Zn (b) and Pb (c) concentrations vs. ontogenetic age for the margins of the *P. magellanicus* valves (last annual growth rind) from Saint Pierre. The correlation coefficients calculated with individuals older than 8 years are given next to the trends.
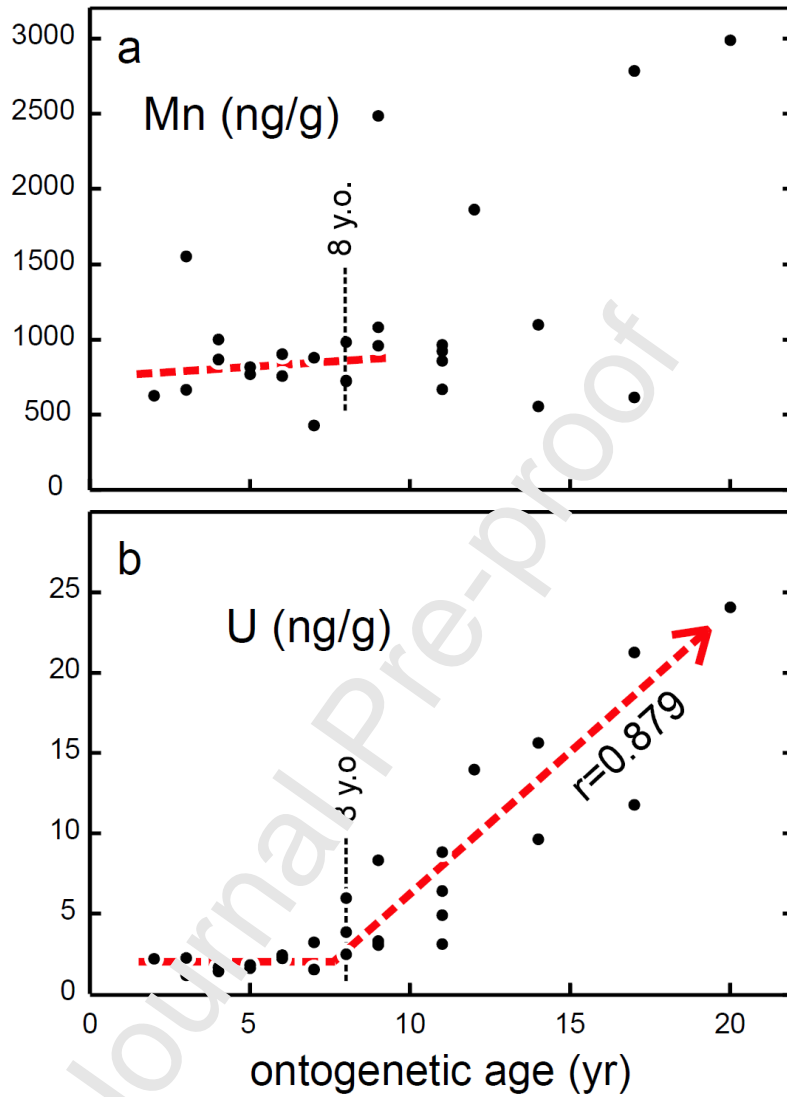
Figure 8. Mn (a) and U (b) concentrations vs. ontogenetic age for the margins of the *P. magellanicus* valves (last annual growth rind) from Saint Pierre. The correlation coefficient calculated with individuals older than 8 years is given next to the trend in Fig. 8b.

Supplementary Material

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

by

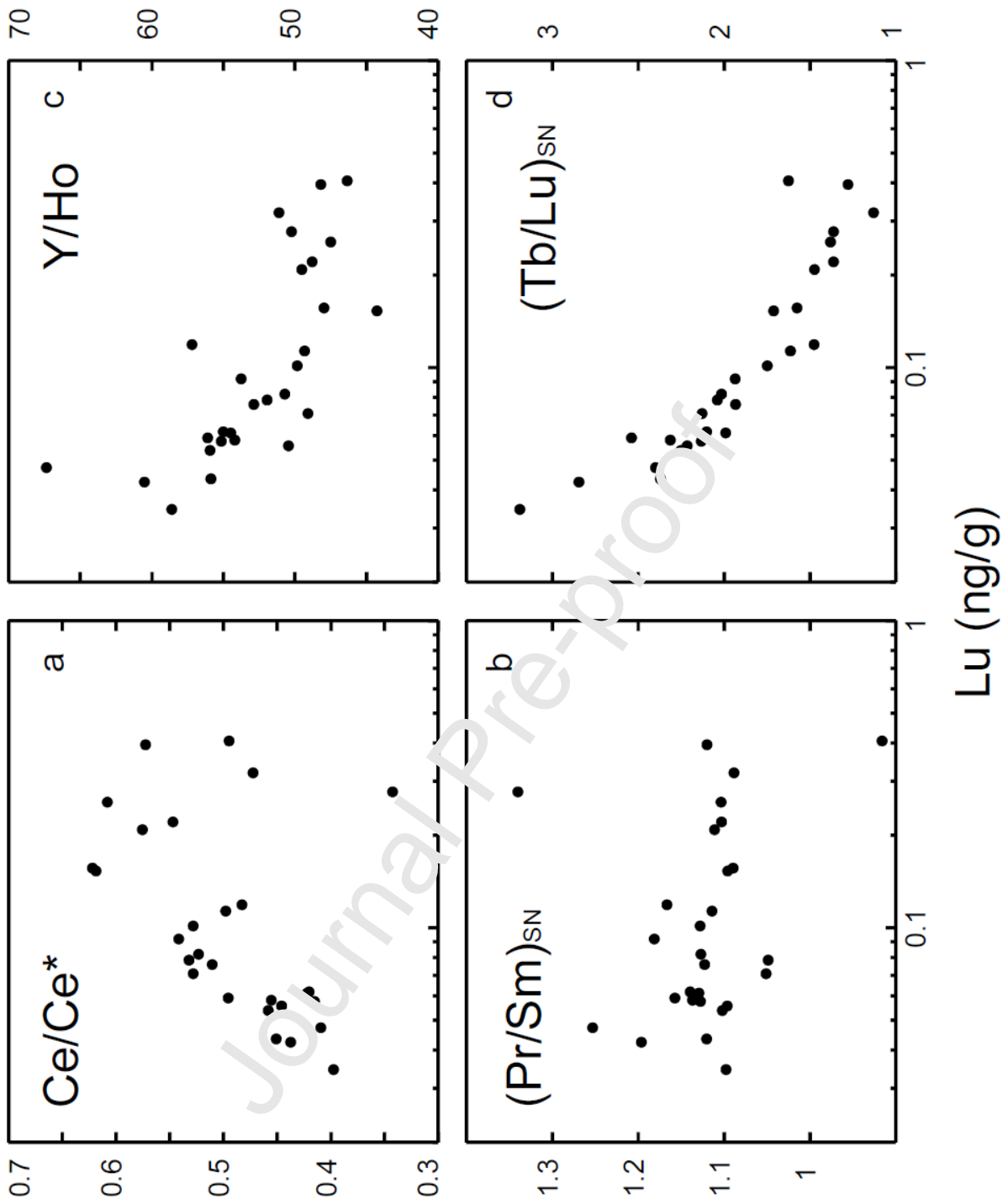Jean-Alix Barrat, Laurent Chauvaud, Fréderic Olivier, Pierre Poitevin, Marie-Laure Rouget

Figure S1. Ce/Ce* (a), (Pr/Sm)$_{SN}$ (b), Y/Ho (c) and (Tb/Lu)$_{SN}$ (d) ratios vs. Lu concentrations for the margins of the *P. magellanicus* valves (last annual growth rind) from Saint Pierre.
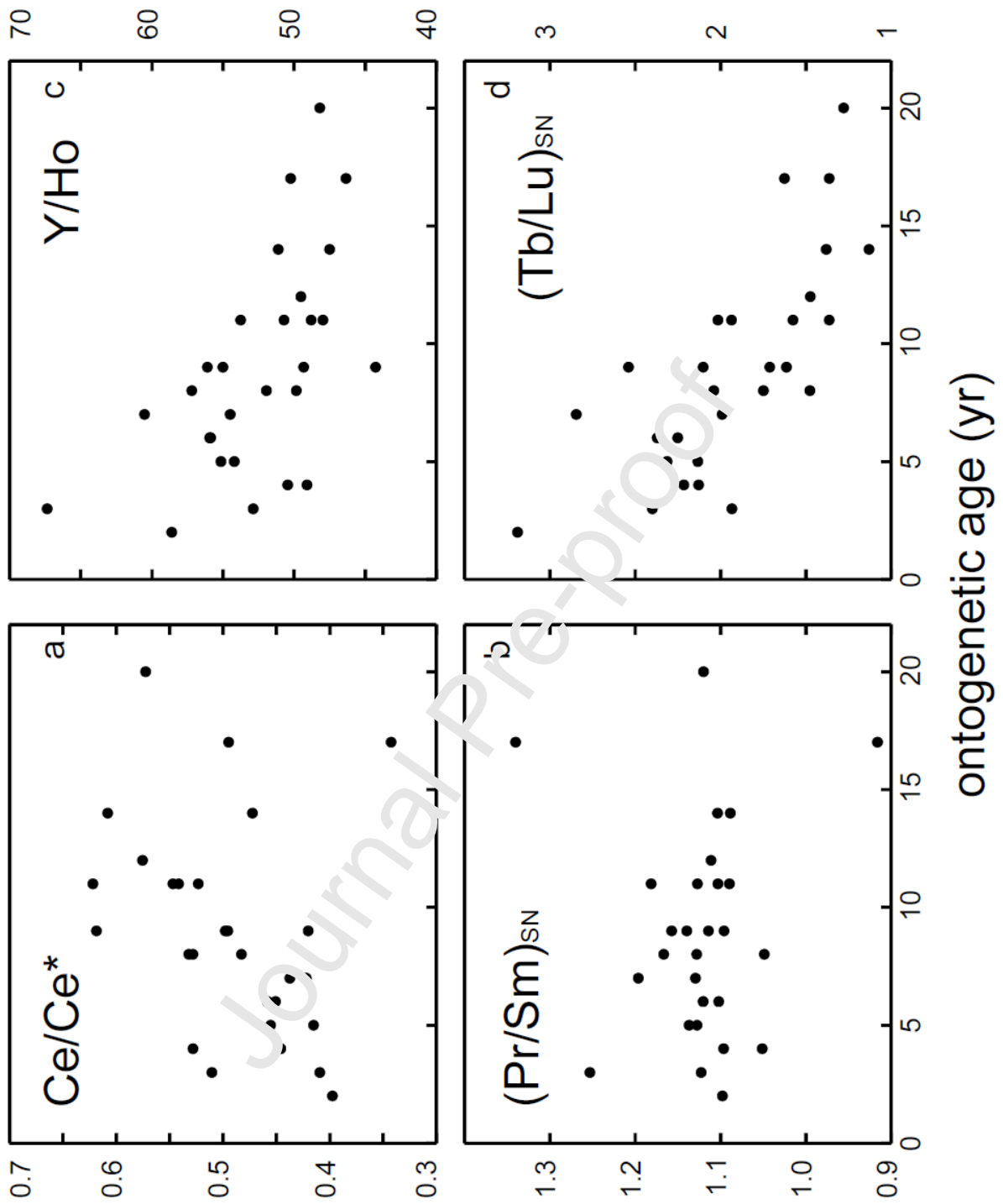
Figure S2. Ce/Ce* (a), $(Pr/Sm)_{SN}$ (b), Y/Ho (c) and $(Tb/Lu)_{SN}$ (d) ratios vs. ontogenetic age for the margins of the *P. magellanicus* valves (last annual growth rind) from Saint Pierre.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

• Trace elements in shells of giant scallops were determined.

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

• Metabolic processes control the behavior of these trace elements.

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

• Shells are valuable archives of bivalve metabolism.