Rare earth elements and yttrium in suspension-feeding bivalves (dog cockle, *Glycymeris glycymeris* L.): accumulation, vital effects and pollution

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Abstract :

Rare earth element (REE) and Y (REY) concentrations were determined in soft tissues and shells prepared from 9 to 93 years old dog cockles sampled alive from a marine site in NW Brittany, France. The concentrations shown by the different soft tissues and shells are extremely variable ranging from 9.10^{-5} to 10^{-1} x PAAS. The mantle is the organ with the highest concentrations, while the feet, the adductor muscles and the digestive glands display the lowest ones. Relative to the masses of the different organs, we show that the shell concentrates more than 85% of the REY contained in an animal, and the mantle, which represents less than 0.5% of the total animal mass (on a dry basis), contains 10% of the total REY. Organs accumulate REY throughout the life of the animal. REY concentrations in soft tissues increase by more than one order of magnitude in 90 years. The shells mirror the REY abundances of the mantle but are slightly less light-REE enriched than the latter. Furthermore, shells as well as feet and adductor muscles show a striking correlation between animal age and Ce/Ce* ratios. Ce/Ce* ratios evolve from 0.8 for animals aged ~10 years to 1 for the oldest, with most of the variation during the first 25 years, indicating that Ce also accompanies biochemical reactions probably related to the growth or maturity of the animals.

Soft tissues also show extremely variable positive Gd anomalies (Gd/Gd*= 1.04 - 1.94) which indicate environmental pollution by Gd based contrast agents (GBCA) used in medical imaging. Anomalies tend to be more important for organs poor in REY (like muscles and digestive glands). Low excesses of Gd, on the order of 1-3 ng/g (on a dry basis), account for these anomalies. There is no correlation between

the age of the animals and the amount of anthropogenic Gd or Gd/Gd* ratios suggesting that GBCAs do not accumulate in the bivalve body on a long-term basis.

1/ Introduction

The rare earth elements (REE), to which yttrium is often added (REY), are widely used in Earth Sciences. These elements are particularly useful, because of their geochemical coherence, to study a multitude of processes ranging from the formation of the first condensed solids in the solar system, to planetary differentiation, and to the formation and evolution of the different envelopes constituting our planet (e.g., Henderson, 1984). They are also studied in Marine Sciences for example, to characterize oceanic water masses and their circulation (e.g., Elderfield, 1988; Grenier et al., 2018). Over the last decades, these elements have become critical for industry, and the world demand is now growing exponentially. Therefore, some of them (e.g., La, Sm, Gd; Kulaksiz and Bau, 2013) are at present emerging pollutants whose consequences on the environment and the various living species, in particular aquatic species, are the subject of a growing number of studies (e.g., Chen et al., 2000; Hanana et al., 2017; Martino et al., 2018).

Bivalves are excellent indicators of environmental pollution and have been actively studied for this purpose for several decades (e.g., Goldberg, 1986; Ma et al., 2019). Their ability in recording REY pollution is well established, as their shells show positive anomalies in La, Sm or Gd when exposed to these pollutants (e.g., Merschel and Bau, 2015; Le Goff et al., 2019; Valdés-Vilchis et al., 2021). In order to better understand the impact of REY on these animals, there are still many fundamental questions that need to be specifically addressed, that have been little or not addressed in the literature. First, the origin of the REY they contain remains debated. The marine waters in which they live are obvious sources (e.g., Ponnurangam et al., 2016; Saitoh et al., 2018), but their contributions are not necessarily dominant compared to those of the particulate matter these animals filter (Akagi and Edanami, 2017; Ma et al., 2019), and possibly that of the organic matter they digest.

Moreover, the possibility that these elements can participate to marine biogeochemical cycles has never been considered for heterotrophic mollusks. More generally, for a long time, scientists considered that REYs were not involved in any biochemical cycle, thus explaining the very low REY concentrations measured in living organisms. Consequently, these elements have been largely ignored in biology, and for the same reasons, the contribution of (micro)biological activity to the REY cycles at the Earth's surface has been totally neglected by geochemists. About ten years ago, biochemists have shown that these elements, in particular light REEs, were widely used by methanotrophic or methylotrophic microorganisms (Pol et al.,

2014; Semrau et al., 2018; Cotruvo, 2019) to degrade methanol to formaldehyde by using methanol dehydrogenase lanthanoenzymes. As some of such microorganisms live in symbiosis with mollusks or worms, the enzymatic activity fractionates REE in these animals, some of whose organs may display distinctive REE patterns (Wang et al., 2020; Bayon et al., 2020; Barrat et al., 2022). In heterotrophic animals, this type of enzymatic functions is of course absent, but REY may follow other metals in biochemical cycles. Thus, organs or shells also could exhibit REY signatures inherited from biological processes. Finally, it is not known how REY are distributed within a heterotrophic bivalve, how these elements are transferred from one organ to another, and whether they accumulate in some of them during the life of the animals. Data have been published on the REY contents of their whole soft tissues, but to our knowledge, an inventory of the contributions of the different organs has never been made.

In order to address these issues, we chose the dog cockle (*Glycymeris glycymeris*, L.), a common bivalve from coastal coarse sediment subtidal habitats of Europe and North Africa, who can live up to two centuries (Ramsay et al., 2000; Reynolds et al., 2010). Due to its longevity and large size (up to 80 mm), its easily determinable annual growth increments, and of course its abundance, this species can be considered as an excellent sclerochronological bioarchive (Brocas et al., 2013; Royer et al., 2013; Featherstone et al., 2017). We have analyzed the REY concentrations of the organs of the dog cockles of various ages, sampled in one typically marine site, in order to discuss the REY distributions in the shell and five different tissues (feet, adductor muscles, gills, digestive glands, mantle), the accumulation processes, the recording of pollution (Gd) but also the vital effects that can be detected. We will also briefly discuss the sources of REY in bivalves.

2/ Sampling and analytical procedures

Bivalves were collected on July 2019 at a water depth of 5 m by a scuba diver on the northwest coasts of Brest, close to the cliffs of Brenterc'h (48.394069°N, -4.778582W). The sampling site was chosen because of the lack of riverine influence on water salinity at the sea bottom (Figure S1), as well as because its environmental setting has not evolved during the last hundreds of years. Among the forty live individuals of various sizes that were collected on a surface of a few square meters, sixteen were selected to cover the whole size range in the population then stored 3 days in a fridge before processing.

In order to estimate the relative proportions of the different organs and shell on a dry basis, we dissected six individuals to collect gills, mantle, adductor muscles, foot and the digestive gland. All organs were dehydrated in an oven at 60°C for 48 hours, then weighed. For chemical analyses, organs were sampled by dissecting pieces of soft tissues and shell from the same individual. Soft tissues were then rinsed with deionized water to remove residual seawater and impurities, and freeze-dried at -20°C for 48 hours. Shells were scraped with a steel blade to remove periostracum, soft tissues, and sediments, rinsed with deionized water and dried. We sampled only the most recent part of the shell: fragments located within less than 5 mm of the margin were handpicked after shell was broken.

The determination of the REE and Y abundances follows the procedure designed by Barrat et al. (2020) for carbonates, and already used for soft tissues by Wang et al. (2020). Results are given in Table S-1. For each sample, about 150-250 mg were spiked with a solution of pure Tm and digested in a Teflon beaker by HNO_3 (carbonate), or by HNO_3/H_2O_2 (soft tissue). REEs have been separated and concentrated before analysis using ion-exchange chromatographic columns loaded with about 1 ml DGA resin (Barrat et al., 1996, 2020). 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 (Barrat et al., 2016). Results on two carbonate standards (CAL-S and BEAN) obtained during the sessions are compared with literature values and given in Table S-1. Based on standards, the precisions (RSD) for abundances and element ratios are better than 3 %. The reader is referred to previous papers where our routine sequence for carbonates (Barrat et al., 2020), calibration, isobaric interference corrections and calculations of concentrations with the Tm spike have been extensively described, and results for many international standards were reported (e.g., Barrat et al., 1996, 2012, 2016, 2020; Charles et al., 2021).

We use for the normalisation of the concentrations, 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: $La_{sn}* = Pr_{sn}^3/Nd_{sn}^2$, $Ce_{sn}* = Pr_{sn}^2/Nd_{sn}$, $Gd_{sn}* = Tb_{sn}^2/Dy_{sn}$.

The determination of the age of the shells were conducted at the sclerochronology platform of the LEMAR Laboratory. Valves were mounted on PVC cubes with quick drying

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two-part epoxy resin (Royer et al., 2013). Depending on the shell, one or two 1-mm thick sections were cut from each valve perpendicular to the growth lines along the axis of maximum growth. Samples were sectioned with a low-speed precision saw. These sections were ground and polished down to a thickness of 240 μm, and annual growth increments were counted, allowing determination of the age of the individuals in July 2019, when they were sampled.

3/ Results

The sixteen selected shells have major growth axes ranging from 41 to 80 mm, and were aged from 9 to 93 years at the time of capture (Fig. 1). Concentrations of Rare Earths and yttrium in the different organs are given in supplements. The PAAS normalized REY patterns are drawn in Figure 2. Abundances are generally low and rarely exceed 1 µg/g for the most abundant measured elements (Y, La, Ce, and Nd). The abundances of all these elements are extremely variable, spanning about 3 orders of magnitude (from 9.10^{-5} to 10^{-1} x PAAS). Several important observations emerge and will be the basis of the discussions in this paper:

-*The REY patterns of all the organs are similar* (Fig. 2). Taken apart the anomalies for La, Ce, Eu, Gd, and Y, they are rather flat for light REE ($Pr_{sn}/Sm_{sn} = 0.76$ to 1.51) and display a variable depletion for heavy REE ($Tb_{sn}/Lu_{sn} = 1.10$ to 3.97). They all show positive Y ($Y_{sn}/Ho_{sn} = 1.24$ to 2.10 or Y/Ho=37-72), La ($La/La* = 1.52$ to 2.00), Eu ($Eu_{sn}/Sm_{sn} = 1.15$ to 1.53), and Gd ($Gd/Gd*=1.02$ to 1.94) anomalies and sometimes negative Ce anomalies ($Ce/Ce* = 0.8$ to 1.1). Regardless of the REY abundances in the different organs, the element ratios are at first glance similar (Fig. 3). However, we note that some of the mantle samples are more light-REE enriched than the other samples, and that shells are on average less enriched in light REE than the soft tissues, pointing to biological effects on the REY distributions in the organs.

- *Terrigenous sediments do not contribute to the REY balance in organic matter or shells.* In the NW of Brittany, these sediments have regular REY distributions comparable to those of the PAAS (e.g., sample # 45 in Bayon et al., 2015). The involvement of such sedimentary particles would have largely flattened the shape of the REY patterns, and would have masked any anomalies (La, Ce, Gd, and Y) displayed by the various organs.

- *REE are heterogeneously distributed in bivalves, being more concentrated in some organs.* For samples for which most organs were analyzed, the mantle is systematically the richest in REE, then the gills, which are also much richer than the foot, adductor muscles, and digestive

gland. Abundances in the shells are generally intermediate between those of the gills and those of the feet and muscles.

- *The dog cockle accumulates these elements over their lifetime*. The REY patterns unambiguously show that the organs of the oldest individual have the highest REE concentrations.

- *Shells lack noticeable Gd anomalies* (Gd/Gd*=1.02-1.09), but the soft tissues with the lowest REE abundances display striking ones (Gd/Gd*=1.04-1.94).

4/ Discussion

4.1/ Sources of REY in dog cockles

Since the bivalves analyzed in this study were collected from a small area of a few square meters in a marine environment, it is not surprising that shapes of the obtained REY patterns are not very different. The positive Y, La, and negative Ce anomalies have already been widely described in marine shells (e.g., Bau et al., 2010; Ponnurangam et al., 2016; Akagi and Edanami, 2017; Le Goff et al., 2019; Wang et al., 2020). These marine signatures raise the issue of the origin of REE and Y in filter-feeding bivalves in general, and in coastal ones in particular. For example, the positive Y anomalies in both soft tissues and shells, are very similar to those in local coastal seawater (Fig. 4) and may suggest that REY dissolved in seawater are essentially the source of these elements in bivalves (e.g., Ponnurangam et al., 2016; Saitoh et al., 2018). However, even in a strictly marine environment, seawater cannot be considered as the sole source of REY contained in coastal filter-feeding bivalves, especially dog cockles which are heterotrophic and live within the surficial layer of sediments. One must necessarily consider the contribution of pore waters and water at the sediment interface, which may have different REY distributions from seawater (e.g., Elderfield and Sholkovitz, 1987; Haley et al., 2004). Obviously, it is necessary to consider in addition to the REEs contained by the different waters in contact with the bivalves, those contained in the suspended sediments (Akagi and Edanami, 2017) and in the nutrients (organic matter) ingested by these animals. Their respective contributions must at present be discussed:

- Although suspension-feeding bivalves are efficient at sorting what they ingest (e.g., Jørgensen, 1981), some sediment may be absorbed along with their nutrients. These sediment particles are on the order of 10^7 times richer in REE than local coastal water (Freslon et al.,

2011), and, if assimilated, their contribution could easily dominate the budget for these elements in heterotrophic bivalve as proposed by Akagi and Edanami (2017). These authors showed that a non-negligible proportion of the REEs in sediments are well dissolved with different acids, but the acids used by these authors (HF, HCl, HNO$_3$, acetic acid) are certainly much too strong to be considered as analogues of the solutions that circulate in the digestive system of bivalves. The pH in the digestive system of bivalves and many other types of mollusks are just weakly acidic (pH ≈ 5, e.g., Yonge, 1925; Wallace et al., 1981; Walker et al., 1996). Under these conditions, and even with long transit times of the order of one day or more, it is questionable that the sedimentary particles ingested by the animals could release a significant fraction of their REY during the digestion process.

- Sedimentary organic matter may contain substantial amounts of these elements, and hence could play a role in the biogeochemical cycling of REY associated with bivalves. Freslon et al. (2014) determined the concentrations of REEs bound to organic matter contained in sediments deposited at different settings (rivers, estuaries, oceans, methane-seepage areas). Concentrations of REE ranging from 16 to 342 µg/g have been measured in organic matter contained in estuarine and oceanic sediments, which makes it an important source of REEs in marine food chains. Such mature organic matter can be absorbed with other nutrients by suspension-feeding bivalves, and can be readily assimilated by these animals. It should therefore be considered as a possible source of the REY contained in bivalves. While additional results would be needed to determine the origin of the REY in bivalves, we suggest that their nutrients should be considered as a major source of the REYs they contain, in addition to seawater, pore water, and sediments.

4.2/ REY repartition in dog cockles' organs

Our results demonstrate the very high heterogeneity of REY distribution within dog cockles. The feet, adductor muscles and digestive glands are poor in REY (Fig. 2), while the mantles and gills are not (Fig. 2). If we calculate the contributions of the different organs according to their relative proportions (Table S2 and Fig. 5), it appears that the shell, which represents about 94 % of the mass on a dry basis, contains about 85 % of the total REY found in an animal. The majority of the remaining REY are contained in the mantle. While this organ represents only 0.5 % of the mass of the animals, and 10 % of the mass of soft tissues, it contains nearly 70 % of the REY outside the shell. With the gills, which represent the same proportion

of soft tissue, about 80% of the REY are contained in about 20% of the soft tissues. This heterogeneity obviously raises the question of the cycle of REY in the organism of these animals, and of their transfers from one organ to another. The ionic radii of the REY (REE^{3+} and Y^{3+}) are quite close to that of Ca^{2+} (1.14 Å), and it is logical to assume that these elements may behave similarly in the organism (e.g., Bertini et al., 2003). Calcium is transferred from the digestive gland to the mantle (e.g., Cheng, 1981). Thus, it is not surprising that the digestive gland is poor in REY, and that the mantle is enriched in REY, since this organ builds the shell, where most of the REY contained by the animal end up. Similarly, the muscle fibers (actins) of the adductor muscles and feet also use Ca (Marston and Smith, 1985), but in much lower amounts than the mantle. Therefore, these organs are neither important sinks for Ca nor for REY. Finally, the enrichment of REY in gills is at first glance more surprising. However, much higher levels of light REE were found in the gills of methanotrophic mussels, but these enrichments were related to the enzymatic activity of the symbionts they contain (Wang et al., 2020). In the case of dog cockles, such an explanation is not tenable since they are not associated with methanotrophic organisms. Interestingly, Ca is essential for the function of *Mytilus* gill cilia (Murakami and Machemer, 1982; Stommel and Stephens, 1985), and the same must be true for the gills of other bivalves such as dog cockles. It is tempting to suggest that the REY enrichments observed here in the gills are related to Ca and the activity of these organs.

4.3/ REY accumulation in dog cockles

The concentrations of certain minor or trace elements (e.g., Sr, Ba, Mg, Na, Li) in shells have been studied previously by many teams in order to use shells as paleoenvironmental archives (Stecher et al., 1996; Gillikin et al., 2006; Thebault and Chauvaud, 2013; Marali et al., 2017). Some of these studies have revealed compositional variations that could be related to the ontogenetic age of the animals rather than to environmental parameters (e.g., Eliott et al., 2009; Schöne et al., 2011; Gillikin and Dehairs, 2013). Here our approach is different from those previously developed. To discuss the accumulation of REEs in the animals, and detect possible ontogenetic trends, we will not read the chemical signal recorded in a given shell since its birth, but will compare the concentrations in the soft tissues and shell margins of animals of various ages.

The REY patterns show directly that the oldest individuals have the highest concentrations (Fig. 2). Since the ages of the animals studied have been determined, it is

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possible to discuss more precisely the accumulation of REY in the organisms. We specifically prepared the feet and adductor muscles for this purpose, as they were large enough to be easily analyzed even in the smallest individuals, we had available. As shown in Figure 6, La abundances vary by an order of magnitude between the youngest (9 years old) and oldest (93 years old) samples, i.e. over a period of 84 years. For even younger samples, the trends point to even lower concentrations, suggesting that the concentration ranges could easily vary by 2 or more orders of magnitude over the lifetime of these bivalves. Similar trends were obtained for other REY (not shown).

The few data we have obtained suggest identical trends for the gills, but also for the mantle. This can be discussed with the data obtained on the shells. We did not analyze the whole shells but we specifically analyzed the margin portion of the valves, i.e. one of the most recent areas formed by the mantle. Of course, the very last millimeters of the shells do not correspond to exactly the same duration for each of them, but for simplicity, we will assume that all fractions are contemporaneous and formed during a short period ending in 2019, the year of sampling. All the studied animals lived in the same place, and were collected on the same day. They feed on the same organic matter sources, filtering the same water. What distinguishes the sampled bivalves here is their size, thus their age. The mantle in the presence of extrapalleal fluid directly synthesizes the shell. The REY concentrations of this type of fluids have never been determined, but they must be quite comparable, at least in order of magnitude, to those of the seawater or pore water in which the animals were living. Thus, the contribution of the extrapalleal fluid is certainly insignificant compared to those of the mantle, which consequently controls the REY contained in the shell (the mantle is about 10^5-10^6 times richer in REY than seawater). Compared to the mantles, the shells are 5 to 30 times poorer in REY, and systematically less enriched in light REE (Fig. 7). It demonstrates that the transfer of REE from the mantle to the shell changes their relative proportions. The increase in REY concentrations in the shell margins with the age of the individuals is similar to the trends observed for the feet and adductor muscles, and is likely the consequence of accumulation of these elements in the mantle during the life of the animals. Thus, although most of the REY that pass through the animals end up in the shell, the output of REY from the mantle is probably less than the flux of these elements that this organ receives.

During the life of the animal, the mantle will become enriched in light REE since the shell it forms is less enriched in light REE than the latter [$(La/Sm)_{shell} < (La/Sm)_{mantle}$]. Consequently, the composition of the shell synthesized by the animal will evolve with time: as an illustration,

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the carbonates formed when the animal is 60 years old will also be more enriched in light REE than those formed during the youth of the animal. Such a trend is indeed possible, but is partially masked by the scattering of the data (Fig. 8). We investigated whether other element ratios evolved with the age of the animals, but we did not find a clear trend except for Ce anomalies (Fig. 9). The variations of Ce/Ce* ratios recorded during the life of the animals are very substantial (> 20 %). Ce/Ce* ratios range from 0.8 for the shell margin of the youngest animals to about 1 for the oldest. The feet and adductor muscles display the very same trend.

The Ce anomaly quantified by the Ce/Ce* ratio is a parameter that has received considerable interest from geochemists, especially those working on the chemistry of REY in waters and their mineral precipitates. Cerium has two possible valences in water (Ce^{3+} and Ce^{4+}), and is considered a powerful proxy for redox conditions in natural environments (e.g., German and Elderfield, 1990; German et al., 1991; Bau et al., 1997; Wallace et al., 2017; Bellefroid et al., 2018). Decoupling of cerium from other trivalent REYs is frequently the result of oxidative scavenging of this element by Fe and Mn hydroxides in aqueous environments (Bau and Koschinsky, 2009). The observation of variations in the Ce/Ce* ratio correlated with the age of the dog cockles is astonishing.

It could be proposed that this range of Ce anomalies results from a mixing of two components: an endmember dominated by a marine signature, characterized by a negative Ce anomaly, and another one devoid of Ce anomaly. The first endmember could correspond to seawater and nutrients it contained, sucked and filtered by animals. As the animals live buried in the sediment, at the interface with seawater, we can logically propose that the second endmember corresponds to pore water. The relationships displayed by Figure 9, would then indicate that the contribution of pore water is more and more important as the animal grows. This interpretation is unfortunately not tenable. Indeed, young animals filter much smaller volumes of water than larger animals, and would therefore be much more sensitive to the contribution of pore water. An adult dog cockle (with a shell height of about 6-7 cm), on the other hand, aspires about 60 l of seawater per day (Savina and Pouvreau, 2004) and is in contact with only a very small volume of pore water, which is difficult to estimate (probably of the order of a few cm³). The lowest Ce/Ce* ratios should be measured in the oldest shellfish, and Ce/Ce* ratios close to 1 in the youngest animals, the opposite of what is observed. We conclude that the involvement of pore water cannot explain the variations of Ce/Ce* ratios in dog cockles.

Note that all analysed animals in this study were collected on the same day at a spatial scale of only few square meters. The water filtered by the animals, as well as all other inputs (nutrients, sediments) were certainly the same for all animals during the formation of the shell margins. It is impossible that these variations are the result of variations in the environment since the shell margins are contemporary. Moreover, the similarity of the trends obtained for both the soft tissues and the shells (Fig. 9) demonstrate that the observed signal is biological, and that the shells reflect it very closely. These variations are necessarily linked to specific biochemical reactions that remain to be identified. The shape of the trends indicates that these reactions occur during the first 25 years or so of life and are probably related to the growth or maturity of the dog cockles. At present, we can only speculate on the cause of these variations. One possibility is that they are produced in response to enzymatic changes related to the oxidative stress that accompanies maturity and aging of the animals. Indeed, Abele et al. (2008) reported such changes for another long-lived bivalve species, the ocean quahog (*Arctica Islandica* L.). The abundances of catalase, citrate synthase and gluthatione change significantly during the life of these animals, with interestingly two main periods: one before 25-30 years with a striking drop in gluthatione concentrations in the gills and mantle, and the other after (30-192 years old) where the concentrations of this enzyme remain low. It is extremely tempting to link the behavior of some trace elements including Ce in dog cockles to a similar enzymatic activity, which has yet to be investigated.

This observation is very promising. To our knowledge, this is the first time that variations in the Ce/Ce* ratios are so clearly linked to a biological process. At this stage, it is important to verify if similar behavior of this element is observed with other species, and to understand its precise biochemical meaning. In any case, our observations suggest that variations in the Ce/Ce* ratios may be sometimes biological, and this may also have implications for the interpretation of geochemical data.

4.4/ Gd pollution

The soft tissue samples analyzed here, with the notable exception of gills and mantles, which show the highest REY concentrations, display very significant Gd anomalies. Gd/Gd* ratios as high as 2 were even measured for some REY-poor soft tissues (Fig. 10). These anomalies are the footprint of Gd pollution resulting from the use of Gd based contrast agents (GBCA) in medical imaging since the late 1980s (e.g., Ognard et al., 2020). This pollution was

first detected in German rivers (Bau and Dulski, 1996), and later in the rivers or coastal waters of all heavily populated regions where medical activity is important (e.g., Nozaki et al., 2000; Kulaksiz and Bau, 2007; Hatje et al., 2016). The aquatic fauna obviously records this pollution, and shells often show marked Gd anomalies (e.g., Merschel and Bau, 2015; Ponnurangam et al., 2016; Akagi and Edanami, 2017; Le Goff et al., 2019). Here, Gd anomalies and Gd excesses of Gd ($\Delta Gd=Gd-Gd*$) are most pronounced in the tissues displaying the lowest REE abundances, and are well explained by relatively low amounts of anthropogenic Gd, of the order of 3 ng/g at most (Fig. 10). The higher the REE concentrations, the lower the Gd anomaly will be for a given ΔGd value. The mantles are the organs for which the detection of pollution is the most difficult due to their REE abundances. The shells that they produce do not show marked Gd anomalies either, illustrating again that they reflect the REE features of the mantle fairly well.

Soft tissues do not show specific anthropogenic Gd accumulation correlated with the age of the individuals: foot or muscle analyses do not show a systematic increase in Gd/Gd* ratios (or ΔGd, not shown) with sample age (Fig. 11). This result is surprising since the positive Gd anomalies measured in soft tissues show indisputably that the region is polluted in Gd. Since bivalve soft tissues are capable of fixing GBCA-derived gadolinium (Perrat et al., 2017), and that the annual consumption of GBCA in Brittany as in France is growing exponentially (Chazot et al., 2020), significant accumulations of anthropogenic Gd in the tissues of older individuals were expected. Gd speciation may explain this apparent contradiction. If Gd is in the form of Gd^{3+} ions, the soft tissues will easily retain them (Henriques et al., 2019). This is the case for geogenic Gd, which behaves like other REY in soft tissues. If anthropogenic Gd is still chelated inside the bivalve (i.e., the GBCA molecules are not destroyed), its ability to be accumulated for long times is unknown. Experimental works exposing mollusks to GBCAs for long periods followed by depuration, are needed to assess the ability of bivalve soft tissues to permanently accumulate GBCA. Gd speciation is an important parameter, which should not be forgotten during these experiments. Indeed, two types of GBCA molecules were used since 1985: linear GBCA that are banned by the European Union since 2017 (European Medicines Agency, 2017), and macrocyclic GBCA. Le Goff et al. (2019) showed that high Gd/Gd* ratios or high ΔGd recorded in scallop shells were specifically related to the use of linear GBCA. The lack of notable Gd excesses in shells of dog cockles and the lack of significant accumulation of anthropogenic Gd in the oldest tissues, may simply be explained by the fact that linear GBCA

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were virtually no longer in use by the time the animals were caught, and that GBCA do not accumulate *permanently* in organisms.

5/ Conclusions

The analyses obtained on the dog cockles collected in Brenterc'h, have shown that:

- REY are not evenly distributed in a bivalve. Here, about 85% of the REY are contained in the shells. In soft tissues, REY are contained mainly in the mantle (which secretes shells), and in the gills. The transfers of REY from one organ to another are probably related to those of Ca.

- The organs and shells formed by older individuals are much richer in REY than those of younger ones. REY accumulate in the soft tissues during the lifetime of the bivalves. Our sampling indicates that concentrations increase by an order of magnitude from age 9 to 93. Younger individuals certainly have much lower concentrations, implying much greater variation in concentrations over the life of the dog cockles.

- The REY contained in the dog cockles are fractionated by the biological activity. Two effects are particularly clear. First, secretion of the shell by the mantle promotes the introduction of heavy REE into the carbonate. Consequently, the mantle tends to be enriched in light REE throughout the bivalve's life. Secondly, the shells, as well as the soft tissues, have Ce/Ce* ratios that increase significantly during the first 20-25 years of the life of animals. This evolution is probably related to chemical reactions that accompany the growth or maturity of these bivalves.

- Although the dog cockles lived in an environment contaminated with Gd from contrast agents used in magnetic resonance imaging, soft tissues do not show age-controlled accumulation of anthropogenic Gd. The data suggest that when anthropogenic Gd is still chelated, it is not permanently fixed in soft tissues.

These observations have important implications for pollution studies. Filter-feeding bivalves may have excess Gd in their shells or soft tissues, but these excesses do not necessarily reflect accurately the extent of that pollution. In agreement with Le Goff et al. (2019), shells show anomalies in Gd, especially if the pollutants were linear GBCAs. As these products are now banned in the European Union and less used than before in the rest of the world, the use

of shells as proxies for macrocyclic GBCA pollution is more questionable. For pollution by non-chelated REY, bivalves remain potentially excellent proxies. However, we draw the attention of analysts in future studies to take into account the age of the individuals analyzed, since concentrations in both soft tissues and shells also depend on this parameter.

These observations also have more fundamental implications on the behavior of REY in organisms, since they demonstrate that these elements can be fractionated by biological activity. The evolution of Ce/Ce* ratios recorded by both soft tissues and shells is particularly striking in this respect. In addition to its precise meaning in the metabolisms of bivalves, which remains to be determined, this observation demonstrates that this ratio is not necessarily related to the redox conditions of the environments in which the organisms live. We draw the attention of geochemists who use these ratios in sedimentary carbonates or fossils to the fact that this ratio can also be affected by purely biological processes.

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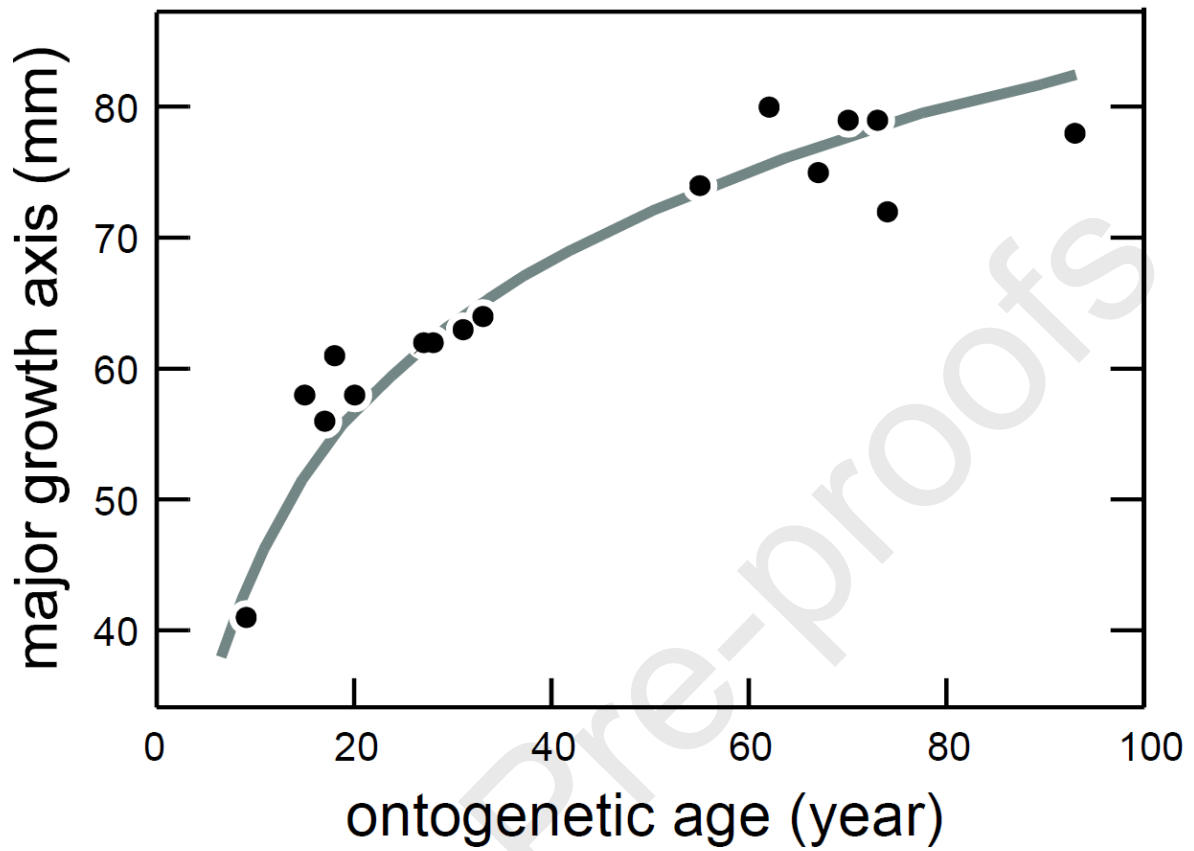
Figure 1. Major growth axis (mm) vs. age (year) for dog cockles sampled in June 2019 close to the Brenterc'h cliffs.
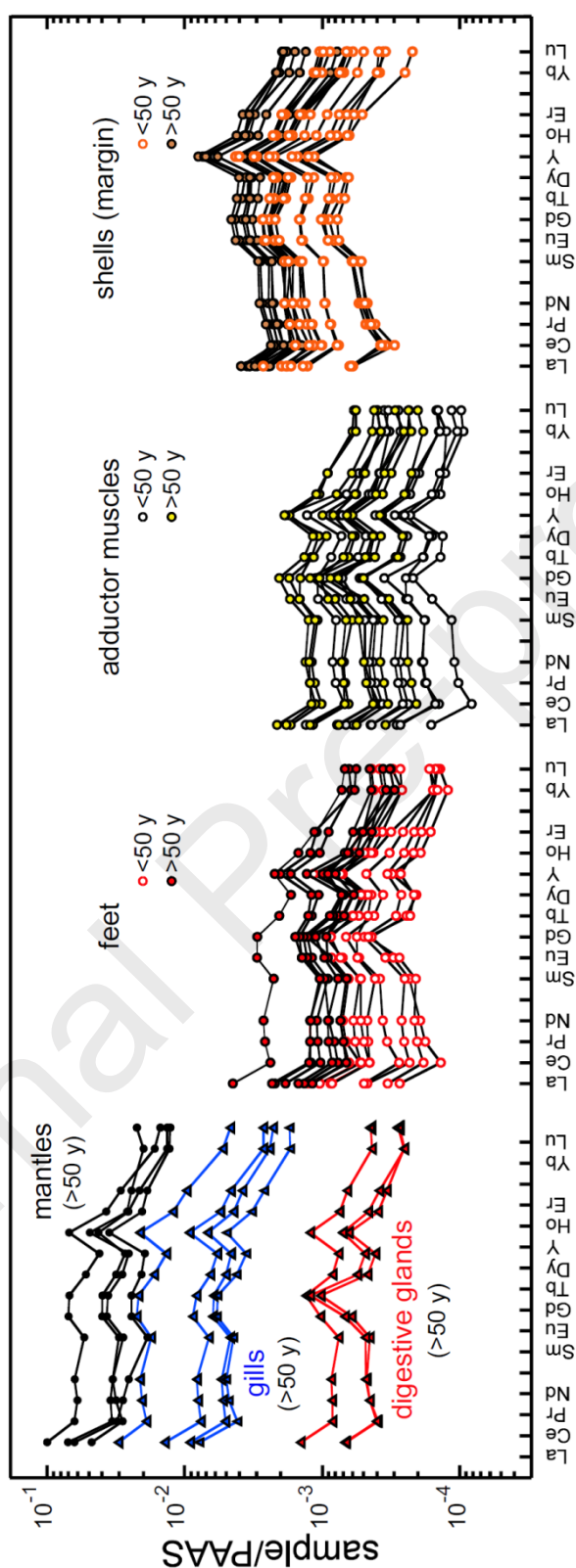
Figure 2. PAAS-normalized REY patterns of the soft tissues and shells of the dog cockles originating from Brenterc'h site. Only the mantles, gills and digestive glands of the largest specimens (> 50 years old) were prepared and analyzed.
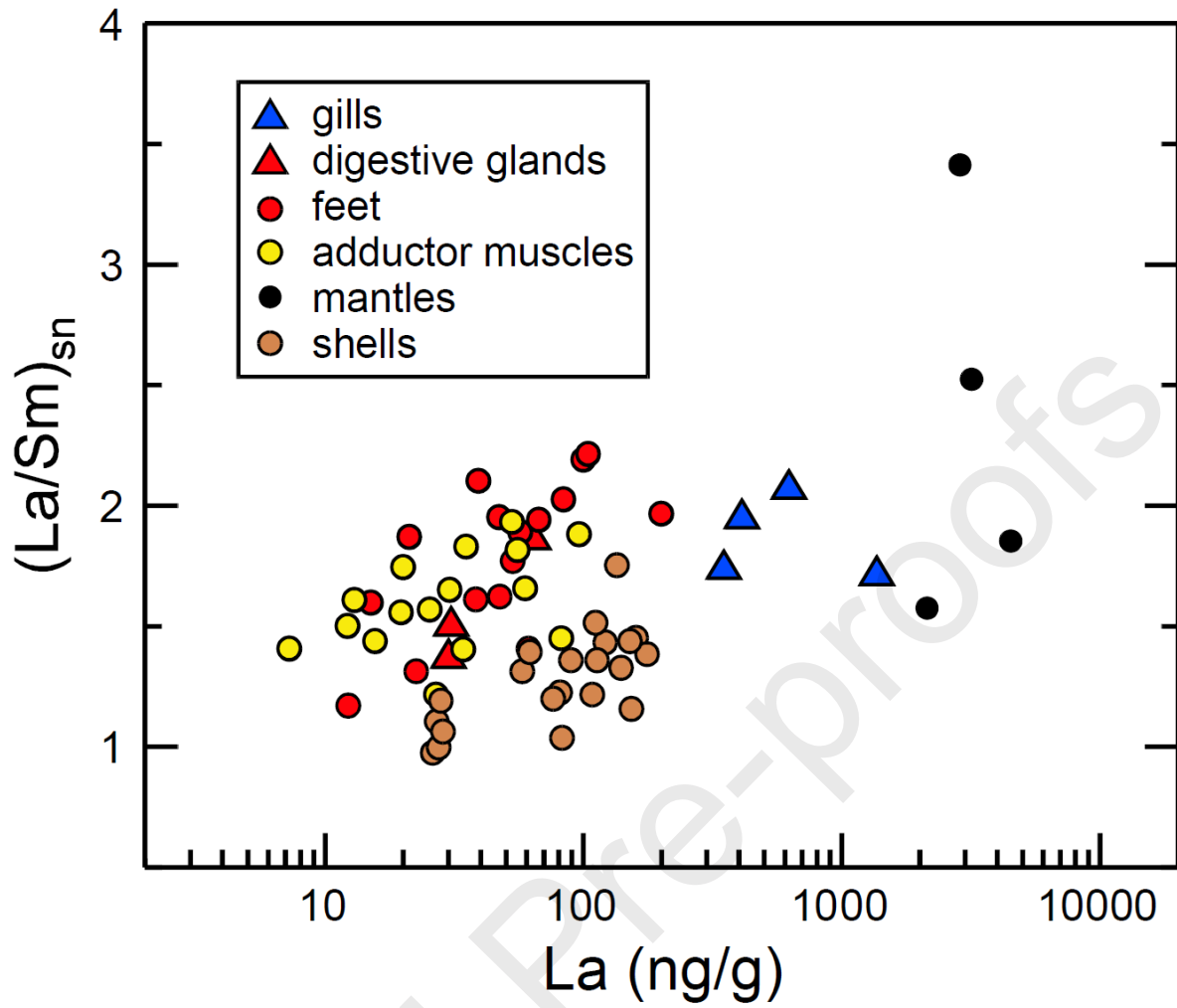
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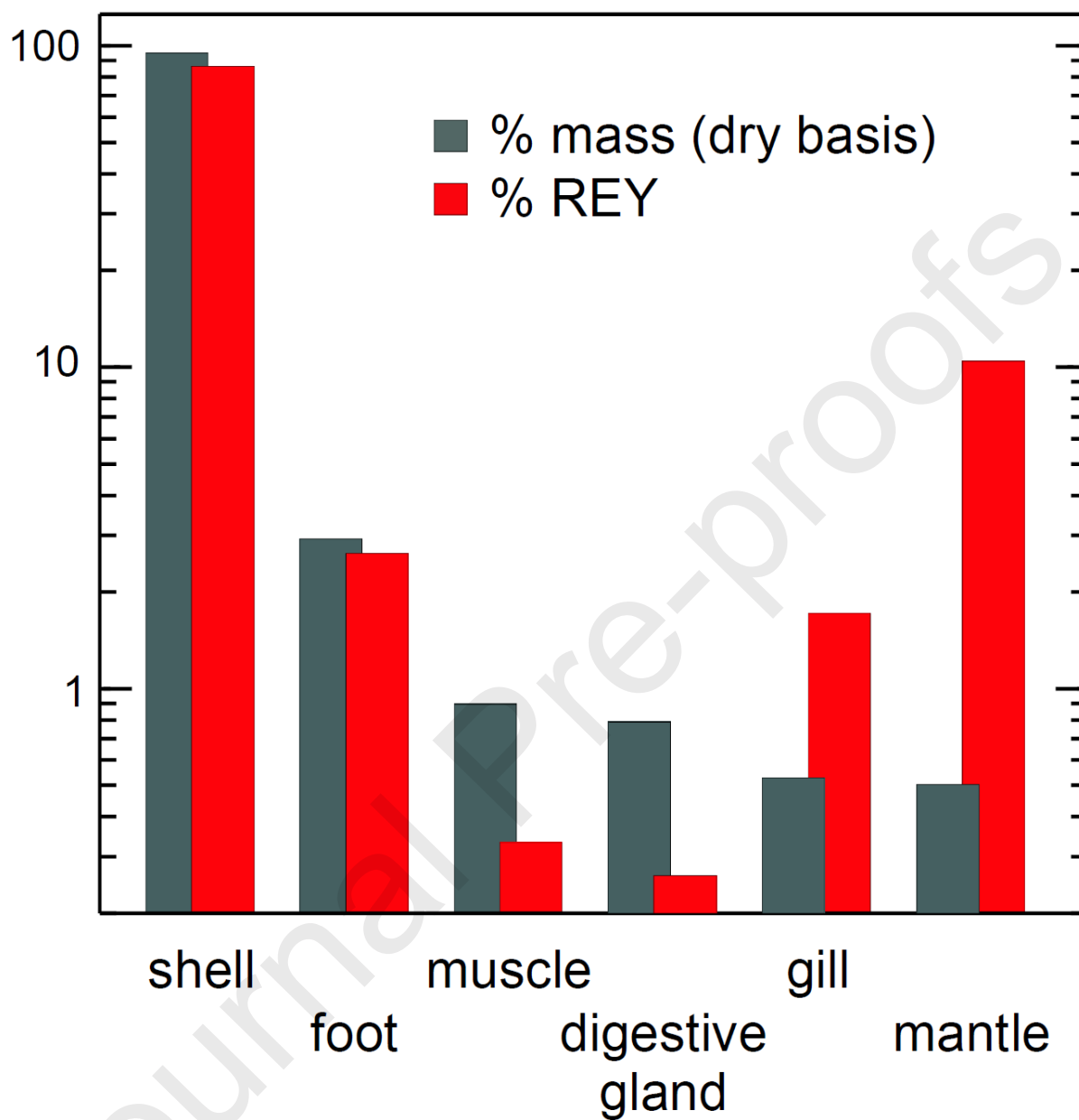Figure 3. $(La/Sm)_{sn}$ vs. La (ng/g) plot for the soft tissues and shells of the dog cockles originating from Brenterc'h site.

Figure 4. Ho vs. Y plot for the soft tissues and shells of the dog cockles originating from Brenterc'h site.

Figure 5. Distribution of REY in the organs of dog cockles analyzed compared to their proportions in mass (on a dry basis). See supplementary Table 2 for the data and calculations.
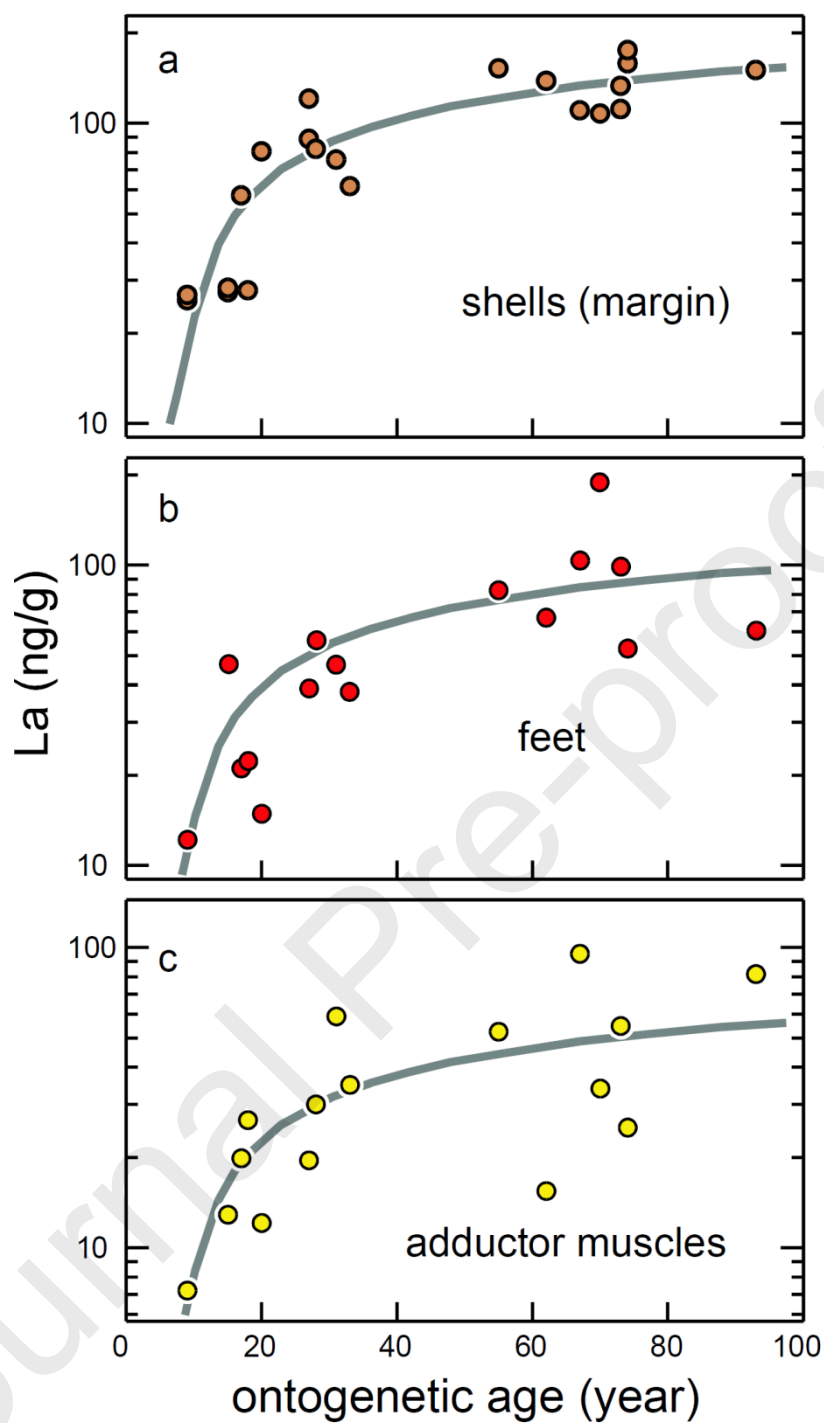
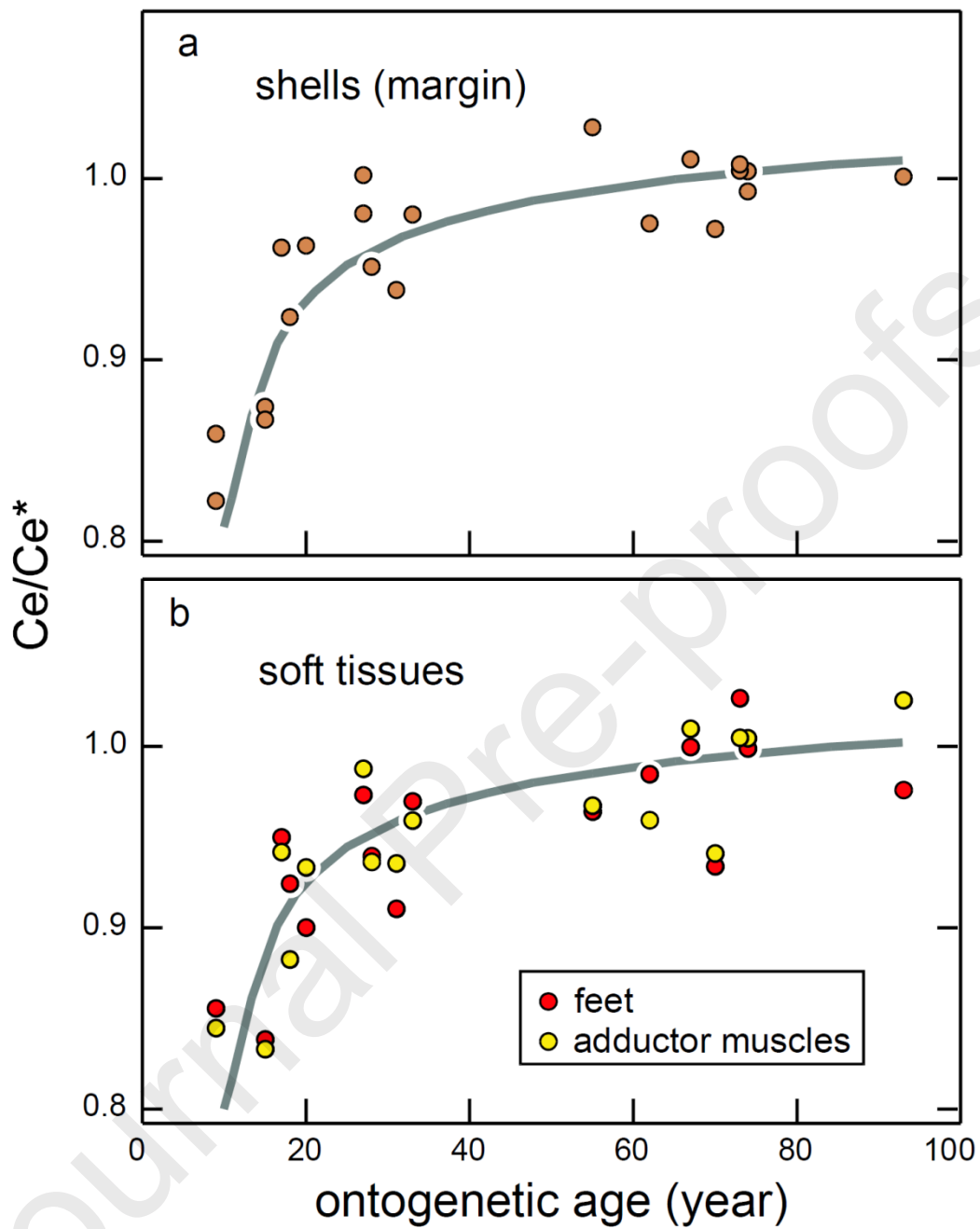Figure 6. La abundances (ng/g) in the margins of the valves (a), in the feet (b) and in adductor muscles (c) prepared from the dog cockles from Brenterc'h, vs. age (year).

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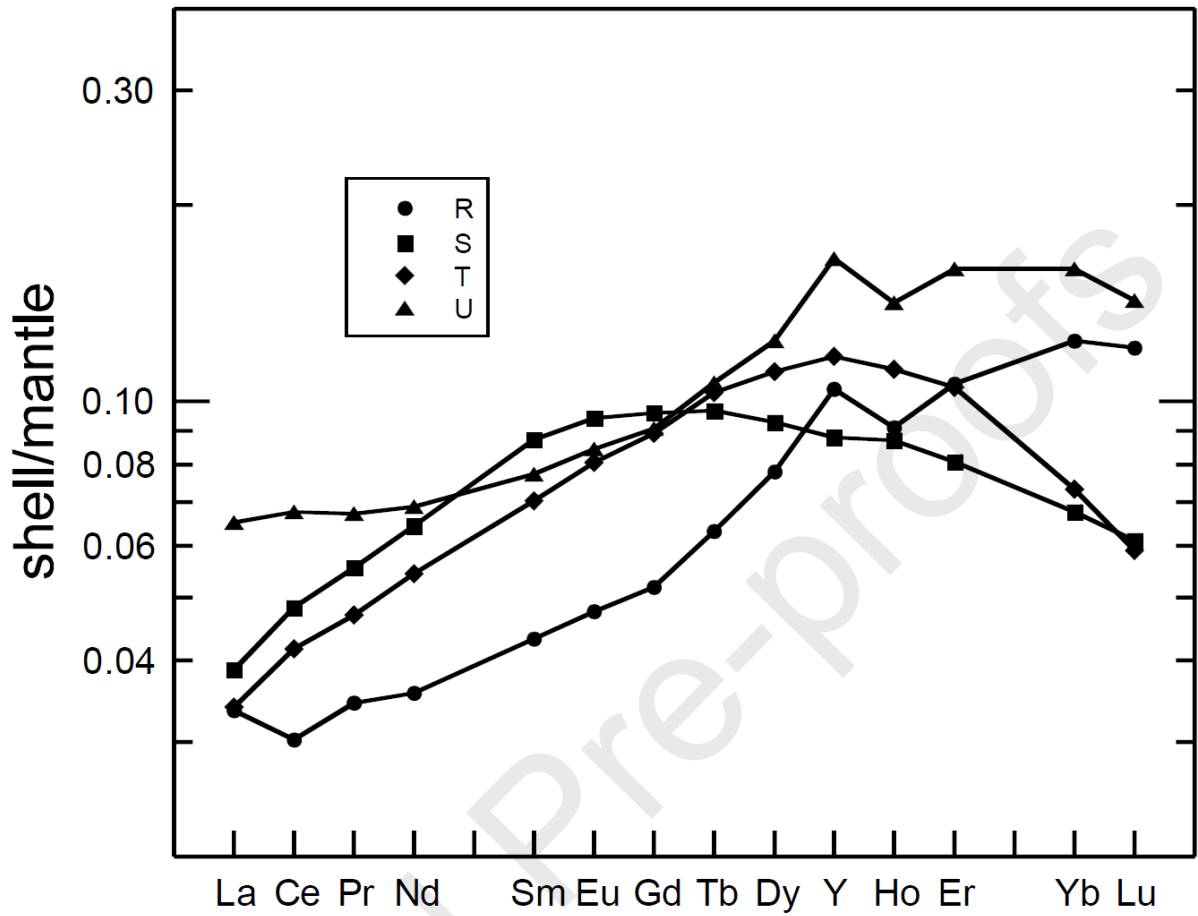
Figure 7. Apparent partition coefficients between shell (margin) and mantle for the dog cockles originating from Brenterc'h site (samples R, S, T, U in supplementary Table 1).
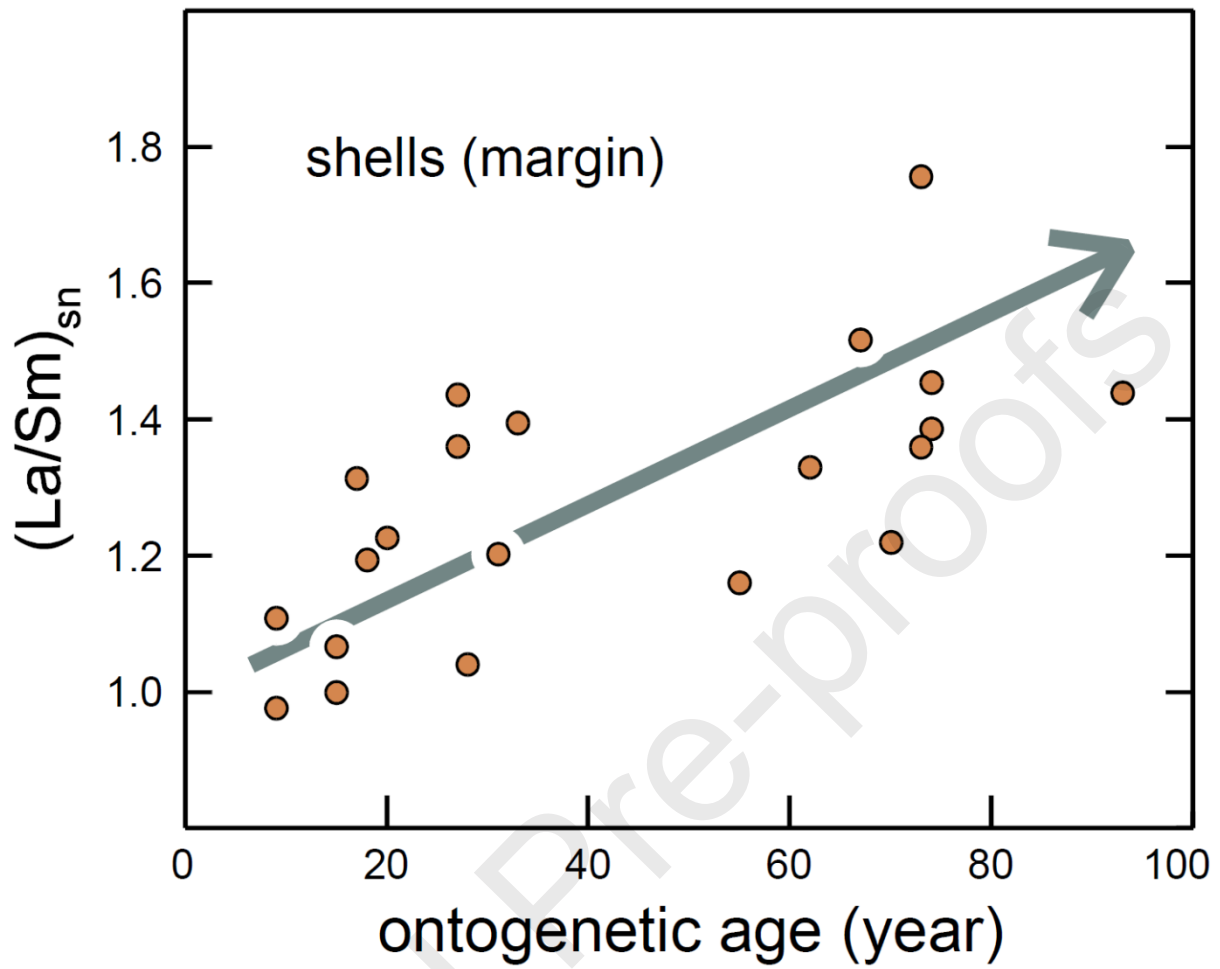
Figure 8. (La/Sm)$_{sn}$ vs. ontogenetic age for shells (margin) of the dog cockles originating from Brenterc'h site.

Figure 9. Ce/Ce* in the margins of the valves (a), in the feet and in adductor muscles (b) prepared from the dog cockles from Brenterc'h, vs. age (year).
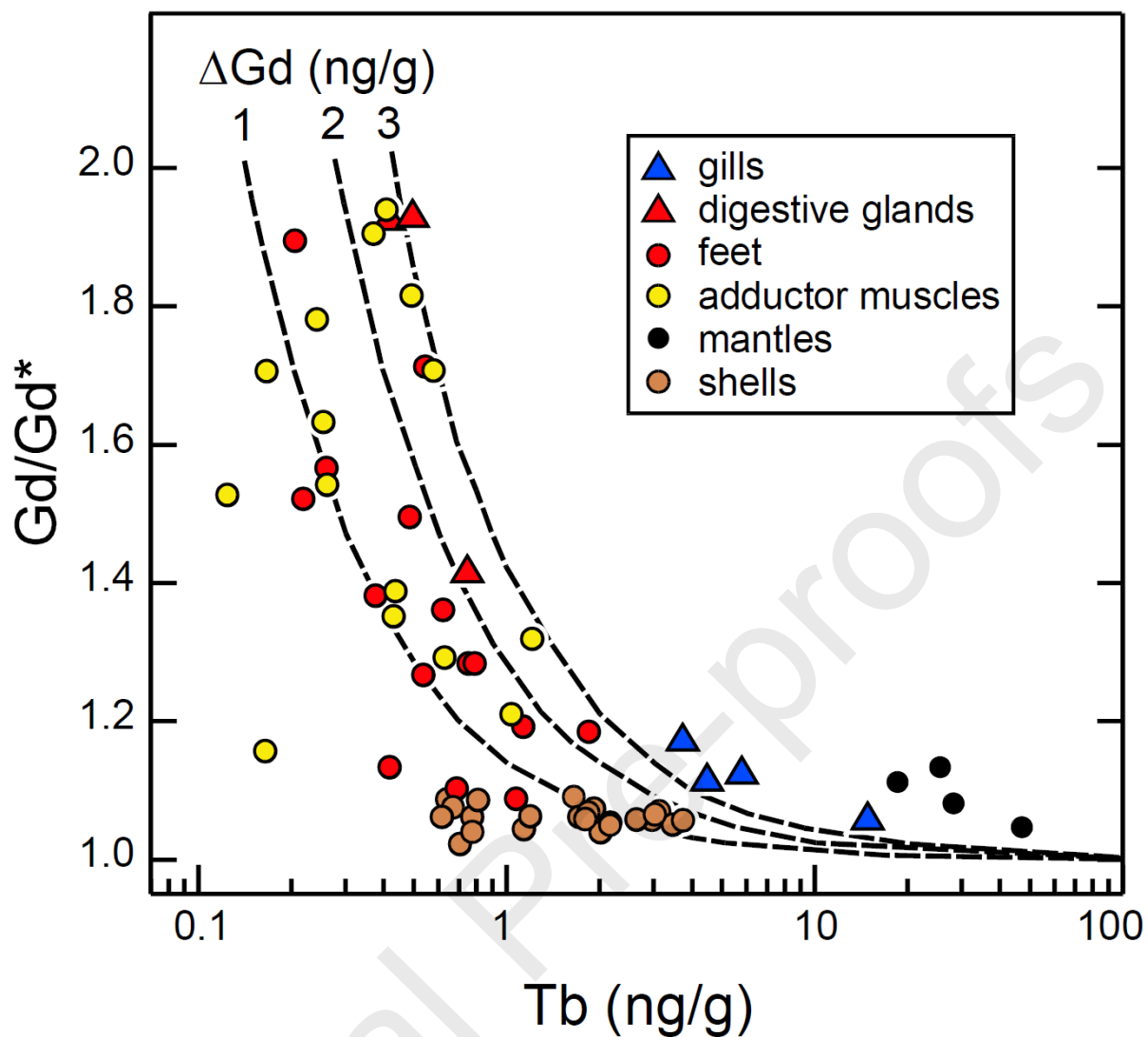
Figure 10. Gd/Gd* vs. Tb plot for the soft tissues and shells of the dog cockles from Brenterc'h. The curves corresponding to ΔGd=1, 2 and 3 ng are calculated assuming a Gd*/Tb = 7 (ng/ng) corresponding to a typical sample of soft tissue with no Gd anomaly.
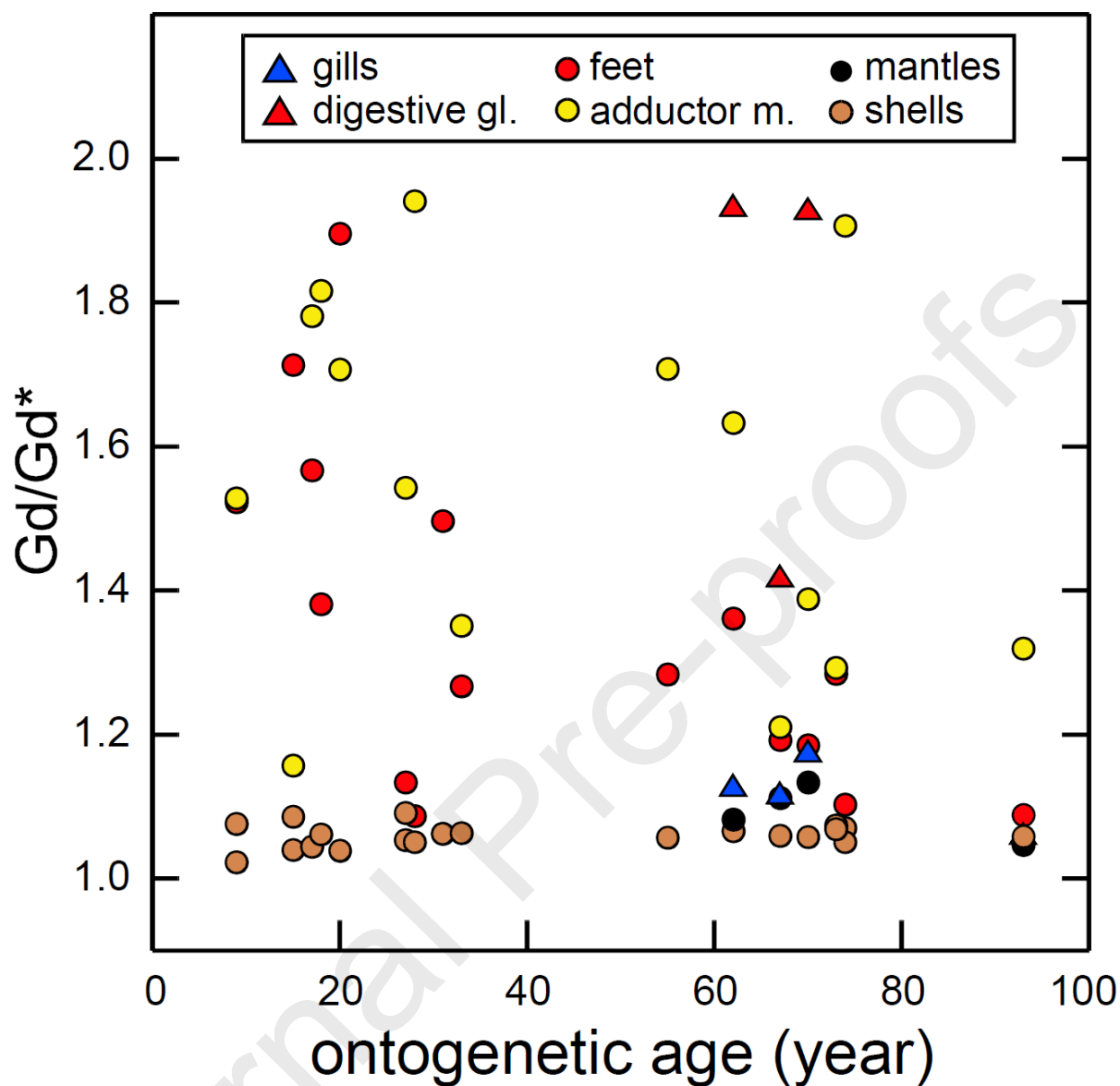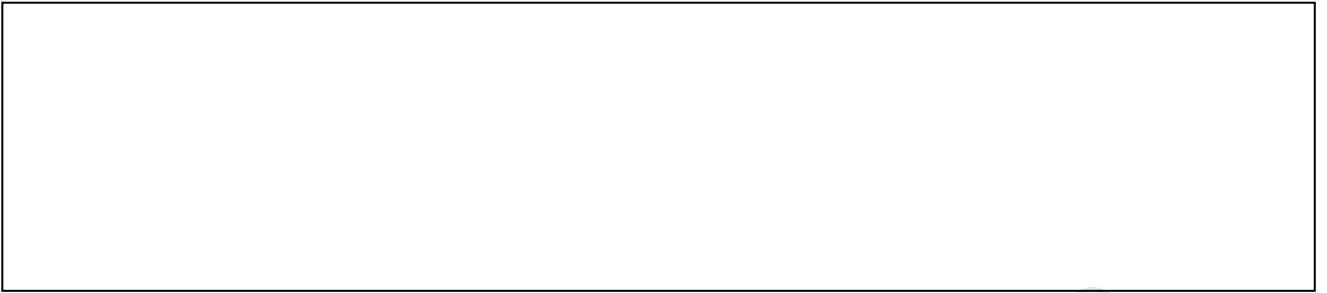
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Figure 11. Gd/Gd* in the margins of the valves, and in soft tissues prepared from the dog cockles originating from Brenterc'h site, vs. age (year).

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: