Rebuttal (2) for Mouchi et al.: 'Rare Earth Elements in oyster shells: provenance discrimination and potential vital effects'

General comments.

The authors have improved their manuscript and substantiated their conclusions with the inclusion of modern specimens of *O. edulis* from an additional site.

However, I think that the introduction and discussion are missing some important information on REEs in seawater and biogenic carbonate material that would help to assess whether the chosen method is suitable or not. The authors should consider the following:

- Zaky et al (2015) highlighted that strict cleaning procedures were required in order to reproduce seawater-like REE patterns in brachiopod analyses. They checked this by reporting the distribution coeffecients. I accept that Mouchi and co-authors want to use a rapid sample processing approach in their study but this should be assessed more thoroughly. If the kDs are widely different from other mollusc studies, then it may be the method rather than the specimens themselves that are causing the similarities between disparate groups.

Response: We thank the reviewer for his/her time on our manuscript. We however disagree regarding the concerns about the potential contamination of our specimens for two reasons:

- Zaky et al. (2015) tested different procedures for solution-based ICP-MS measurements and indeed highlighted the benefit of both extensive physical and chemical cleaning prior dissolution of the sample and analysis due to surface contaminants. The physical cleaning they suggest precisely aims at exposing internal (preserved and uncontaminated) shell areas. We however perform our analyses by LA-ICP-MS on internal, preserved sections of the shells. We precisely indicated this in our initial manuscript L. 151-154: "thick sections (approx. 750 µm thick) were manufactured to expose the preserved internal structures (Figure 2), in order to perform geochemical analyses on this protected region, away from shell surface organic or chemical contaminants. An extensive chemical cleaning of the section surfaces, as advised by Zaky et al. (2015), was not performed as the analytical surface was preserved from any external contaminants over the history of the shell."
- Also, if it were indeed contaminants that are causing the similarities between *O. edulis* groups of various geographic origin, we would have the same observation for *C. gigas* groups, especially those collected on the same sites than *O. edulis* specimens. On the contrary, although all specimens have been prepared in an identical fashion, the *C. gigas* specimens show a region-specific REE composition, and the *O. edulis* have systematically the same REE composition whatever the region of origin, even for specimens of both species from the same sites. If the method was inadequate, it would be for all observations, which is not the case. We are therefore strongly confident about our method.

Minor comments

Some specific comments are listed below.

Line 37. Unfortunately, I don't have access to the Jouanneau et al paper but from the abstract, they measured REE in sediments, rather than seawater. From the sentence beginning in line 35, it sounds like the authors wish to compare this with studies that reconstruct REE compositions in seawater. Did Jouanneau et al. measure the sediment transported by the river, or did they measure a seawater signal? This needs to be made clear because the REE composition of river water undergoes major changes upon reaching the estuary (see work of Sholkovitz especially), so it would be incorrect to say that the dissolved fraction on the continental shelf reflects the composition of contributor rivers. **Our sentence was indeed misleading. We removed this sentence.**

Line 180. Do you have a reference for the BCR-2 reference material where the composition is listed?

The reference of Jochum et al. (2005) was already indicated in Appendix B, in which we indicate our measurements and the expected values. We have nevertheless added this reference in the manuscript.

Lines 223-224. The start of the sentence is overly complicated. Consider simplifying this to "The Y/Ho ratios in the present study (Figure 3) do not....".

Lines 228, 233, 244 and 235. Look again at the connectors used at the beginning of the sentences in order to highlight whether something is the same as or different from the observation in the previous sentence. It is hard to decipher what is reported here, especially with the very long bracketed sections.

We did our best to find better connectors. We hope it is clearer now.

Lines 307-309. I agree with this sentence and would point out that as a result, it is not accurate to say that 'strong vital effects' are responsible for the Y/Ho ratios in the oysters (line 285). It is not known whether this is a 'vital effect' or just "passive" incorporation into the shell.

"Passive" incorporation could be at play for only one of the two species. We consider as 'vital effects' this difference of chemical incorporation in the shell between species. We have however agreed to follow the reviewer's suggestion to be less specific in the conclusion.

All other corrections required from the reviewer have been made:

Lines 18 – 20. This sentence should be divided into two in order to make more sense. E.g. "Here, we present a dataset of 297 measurements of REE and Y abundances by LA-ICP-MA from two oyster species (*Crassostrea gigas* and *Ostrea edulis*). We measured a total of 49 oyster specimens from six locations in France (Atlantic Ocean and Mediterranean Sea)." Line 26. Remove "and are not adapted for *O. edulis* as this is a repeat of the information in the previous sentence.

Line 29. Replace "form a group gathering" with "are a group of". Also, add "The" to the start of the sentence.

Line 30. There are important exceptions to the statement that the REE have similar properties and chemical behavior – what about Ce and Eu?

Line 30. Remove 'the' before atmospheric fallout.

Line 33. The end of the sentence appears to be missing. Complexation with what?

Line 38. Remove "from REE", as Y isn't a REE and this sentence makes sense without saying this.

Lines 45-47. It is incorrect to say that the "seawater" composition of REE and Y is recorded in carbonate materials, as it is always altered during uptake/adsorption (e.g. Osborne et al., 2017).

Lines 55-57. This relates to the previous comment – the REE composition recorded in carbonates (not just corals) is altered during uptake/adsorption.

Line 64. Intraspecific variations and potential seasonal fluctuations in what exactly?

Line 72. Is "British Channel" the international name for this stretch of water? I know it as the "English Channel".

Line 81. "in" the shells.

Line 85. "is" the most commonly found.

Line 87. Move "respectively" to the end of the sentence.

Lines 89-91. No need to capitalize western, northern, north etc.

Line 90. "Its surface area is approximately...". Also, remove "The" at the beginning of the next sentence.

Line 96. Amongst "these". Either "a" rearing experiment, or "the rearing experiment of Lartaud et al.....".

Line 98. "their stay at this site"

Line 99. Move "respectively" to the end of the sentence.

Line 106. "consists of", "to a lesser extent".

Line 113. Remove "of" before 14.

Line 114. "the hydrology is a balance between"

Lines 117-118. It is unclear what "likely extended to 60 km far from the pool" means.

Line 129. Please add some references to this statement.

Line 135. "is comprised of" rather than "is constituted by".

Line 155. "as in any"

Line 163. "Only the Leucate". First occurrence of the abbreviation "CL". This needs to be defined in line 162.

Line 176. It is unclear what "different year periods" means. Do you mean seasons?

Line 179. "prior to".

Line 184. "made" rather than "executed".

Line 195. What is the "it" at the start of the sentence? The cophenetic correlation?

Line 198. Replace "performed from" with "of".

Line 202. "The idea of the t-SNE method is to..."

Line 223. It doesn't make sense to say that something is commonly used as a "potential" provenance proxy.

Line 242. You need to define what you mean by "dispersion" i.e. what you plot in figure 4 (abundance relative to Y).

Line 245. It is more usual to say "middle" REE.

Line 247. "the Mod_LEU_Cgig group"

Line 251. Replace "particularity" with "feature" or "pattern".

Lines 265 and 267. This sentence is overly complicated. Simplify by removing "it appears that", "on the one hand" and "on the other hand".

Lines 276 and 277. "and other REE" is vague – can you be more specific? You want to emphasize that the heavy REE have lower bioavailability. (Gd is a middle REE).

Line 291. "in providing" rather than "to provide".

Lines 314-322. This seems an overly long explanation. It would be simpler to say that the Gd anomaly is only seen in the modern C. gigas specimens at two locations because they are the only coastal regions with a major city in the watershed, and then that it is not seen in the *O*. *edulis* specimens from these locations.

Lines 322-324. This statement needs some references.

Line 324. "discriminate between".

Line 243. The last part of the sentence doesn't make sense.

Lines 345-346. It isn't possible to generalize to "other oyster species" as only one other was tested. It is more accurate to say that "intraspecific vital effects prevent its application in *O. edulis*, whose specimens..."

Lines 348-349. The last two sentences can be omitted.

Line 351. Again, it is not possible to say whether these are 'vital effects' or not. It would be more accurate to say that there are many factors that affect the incorporation of REEs into oyster shells.

Line 354. "in identifying"

Line 355. "is ineffective"

Line 357. "Reconstruction of the provenance"

Rare Earth Elements in oyster shells: provenance discrimination and potential vital effects

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Abstract. Rare Earth Elements (REE) and yttrium in seawater originate from atmospheric fallout, continental weathering, and transport from rivers, as well as hydrothermal activity. Previous studies reported the use of REE and Y measurements in biogenic carbonates as a means to reconstruct these surface processes in ancient times. As coastal seawater REE and Y concentrations partially reflect those of nearby rivers, it may be possible to obtain a regional fingerprint of these concentrations from bivalve shells for seafood traceability and environmental monitoring studies. Here, we present a dataset of 297 measurements of REE and Y abundances by LA-ICP-MS from two species (*Crassostrea gigas* and *Ostrea edulis*). We

- 20 measured a total of 49 oyster specimens from six locations in France (Atlantic Ocean and Mediterranean Sea). Our study reports that there is no significant difference in concentrations from shell parts corresponding to winter and summer periods for both species. Moreover, interspecific vital effects are reported from specimens from both species and from the same locality. REE and Y profiles and t-distributed Stochastic Neighbour Embedding processing (t-SNE; a discriminant statistical method) indicate that REE and Y measurements from *C. gigas* shells can be discriminated from one locality to another, but
- 25 this is not the case for *O. edulis*, which presents very similar concentrations in all studied localities. Therefore, provenance studies using bivalve shells based on REE and Y have to be first tested for the species, Other methods have to be investigated to be able to find the provenance of some species such as *O. edulis*.

1 Introduction

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Rare Earth Elements (REE) are a group of 15 elements (La to Lu) with similar electronic configuration of the atoms, similar properties and chemical behavior (Elderfield, 1988), with the exceptions of Ce and Eu, which present multiple oxidation states. The main sources of REE in seawater are atmospheric fallout (Elderfield & Greaves, 1982; De Baar et al., 1983) and riverine input through continental weathering (Goldstein et al., 1984; Frost et al., 1986), as well as hydrothermal activity (Olivarez &

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Owen, 1991). In addition to these various sources, the concentrations of REE in seawater are impacted by adsorption processes of REE to mineral surfaces and complexation with organic ligands, especially near the ocean surface (Sholkovitz et al., 1994; Schijf et al., 2015).

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Reconstruction of REE compositions of seawater is generally used to provide information on past continental weathering, tectonic activity, and water mass circulation (Greaves et al., 1991; Censi et al., 2004; Haley et al., 2005; Piper & Bau, 2013). Moreover, specific elemental ratios, such as Y/Ho, have been investigated as potential provenance proxies. Indeed, although the average Y/Ho value is equivalent to that of chondritic meteorites and mid-ocean-ridge basalts (MORB; Jochum et al., 1986;

- 45 Taylor & McLennan, 1988), it has been shown that Y/Ho fractionates in sediment particles, not only in seawater with depth, but also probably in waterbodies from watersheds (rivers and estuaries), whose composition has been modified depending on the weathered continental rocks (Bau et al., 1995; Nozaki et al., 1997; Prajith et al., 2015). The Y/Ho ratios in estuaries could therefore exhibit different values according to the regional inputs related to the mineralogical variability in continental covers. It has been demonstrated that the seawater composition in REE and yttrium is at least partially recorded in carbonate materials,
- 50 such as ooids (Li et al., 2019), brachiopod shells (Zaky et al., 2015, 2016), foraminifera tests (Osborne et al., 2017), and coral skeletons (Sholkovitz & Shen, 1995). In addition, the anthropogenic REE contamination of the Rhine River (Germany) has been demonstrated by the shell composition of freshwater mussels (Merschel & Bau, 2015). The reconstruction of the REE and Y fingerprints in a coastal environment from mollusk shells could therefore be useful, not only to monitor potential contaminations from anthropic activities (Le Goff et al., 2019), but also as a provenance proxy for quality control of cultured
- 55 organisms prior to human consumption (Bennion et al., 2019; Morrison et al., 2019). Indeed, public interest is rising regarding the origin of food due to various reasons including decreased confidence in the quality and safety of remote food supply (Kelly et al., 2005; Gopi et al., 2019). The geographic origin of seashells can also be of interest in archaeology, since mollusk shells can be unearthed sometimes very far from the nearest shoreline (Bardot-Cambot, 2014), in order to rebuild historic trade routes. Seafood traceability is therefore important for both modern and archaeological contexts. However, 'vital effects'
- 60 (compositional shifts between inorganic and biogenic carbonate due to metabolic activity; Urey et al., 1951) have been reported to alter this regional fingerprint of REE between species (Akagi et al., 2004); therefore, a feasibility study needs to be conducted on mollusks before any extended seafood traceability perspective is considered.

To this end, REE and Y measurements have been performed by laser-ablation inductively-coupled mass spectrometry (LA-ICP-MS) on modern and archaeological oyster shells from various French localities. The aim of this study is to assess the

- 65 interspecific effects using specimens from two edible species: the flat oyster Ostrea edulis (Linnaeus, 1758), commonly found in antique sites but still found on modern shores, and the cupped oyster Crassostrea gigas (Thunberg, 1793), which first appeared on the French coastline during the 20th century. Multiple measurements were performed on each of the specimens to evaluate the intraspecific variations, in particular regarding the potential seasonal fluctuations of rainfall intensity, weathering, and rate of river flows, A recent statistical method, the t-SNE, standing for "t-distributed Stochastic Neighbour Embedding"
- 70 (van der Maaten & Hinton, 2008), is introduced as an attempt to discriminate the nine oyster groups of the study, in order to highlight significant interspecific and inter-regional differences between REE incorporations.

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2. Material and methods

2.1 Modern-day settings and specimens

80 2.1.1 Baie des Veys (Normandy)

The Géfosse area, in Baie des Veys (Normandy, France), is currently used as a commercial oyster farm location. This open sea area is characterized by a semidiurnal tidal range of 8 m from the <u>English</u> Channel and an overall siltation due to weaker ebb than flow, inducing a poor resuspension of sediment particles (Le Gall, 1970). The Baie des Veys is recharged in freshwater by the Isigny Channel, formed by the Vire and Aure rivers, and the Carentan Channel, constituted of the Douve and the Taute

- 85 rivers, which drain a large part of the Bessin plain and the Cotentin. The watershed comprises limestone as well as basalt, acidic and alkaline metavolcanic rock and diorite (Baize et al., 1997). Respective flows of the Isigny and Carentan Channels are 19 m³ s⁻¹ and 33 m³ s⁻¹, these rates having no significant impact on the salinity of the shoreline (Sylvand, 1995). Oyster specimens from this locality were gathered during a previous rearing experiment conducted between 2005 and 2006 (Lartaud et al., 2010a, 2010b; Mouchi et al., 2013). Although these specimens have been transplanted in several localities
- 90 during their lives (for details, see Lartaud et al., 2010a), the part of the shells analyzed in the present study is restricted to that corresponding to their Baie des Veys stay. This period is recognized in the shells owing to *in vivo* chemical labeling performed during the rearing experiment (Huyghe et al., 2019). Both *Crassostrea gigas* (n=5) and *Ostrea edulis* (n=5) specimens from this locality and having shared the same breeding location, have been considered (Figure 1, Table 1, Appendix A). *Crassostrea gigas* was recently renamed *Magallana gigas* by Salvi and Mariottini (2016); however, as this genus change is still debated
- 95 (Bayne et al., 2017) and *C. gigas* is the most commonly found occurrence in the literature, this paper refers to this species by using its original genus name. As modern specimens, these are referred to as Mod_BDV_Cgig and Mod_BDV_Oedu groups in this paper for *C. gigas* and *O. edulis*, respectively.

2.1.2 Marennes-Oléron bay (Charente-Maritime)

The Marennes-Oléron bay is located on the Atlantic Ocean coast of France. It is bordered by the Oléron island on the western
side, and opens to the Atlantic on its northern and southern borders. Its surface area is approximately 180 km². Atlantic seawater
runs through the bay from North to South (Dechambenoy et al., 1977). In the area, the tidal range is 5 m with a semi-diurnal
rhythm. The large watershed covers 10,000 km² of land and comprises Cenozoic river deposits, limestones, and clays
(Bourgueil et al., 1968, 1972; Platel et al., 1977, 1978; Bambier et al., 1982; Hanztpergue et al., 1984; Mourier et al., 1989).
The bay is recharged in freshwater by two rivers, the Charente (North side), with a 36 m³.s⁻¹ flow, and the Seudre (South side)
whose flow is 30 times less important (Soletchnik et al., 1998).

The bay hosts 30 km² of aquaculture domains, amongst <u>these</u> oysters. This site was also used during <u>a</u> rearing experiment (Lartaud et al., 2010a, 2010b): both *C. gigas* (n=3) and *O. edulis* (n=3) shells parts analyzed in the present study refer to the shell portions corresponding to their stay <u>at</u> this site, highlighted by *in vivo* labels. These two groups are referred to as Mod_MO_Cgig and Mod_MO_Oedu_for *C. gigas* and *O. edulis* specimens, respectively. Supprimé: British

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2.1.3 Tès (Arcachon basin)

The Arcachon basin is a lagoon of 156 km² on the French Atlantic coastline. The area is subdivided into a subtidal zone and an intertidal zone with a semidiurnal tidal range of 3 m, where the studied oysters grew. Freshwater is provided from a watershed of 4,138 km² by three main channels, the Eyre, the Porge and the Landes, as well as twenty-six other streams and local groundwater, for a total supply of 1,340 million m³ freshwater per year (Lamour & Balades, 1979; Auby et al., 1994). The largest part of this watershed consists <u>of</u> Cenozoic river deposits, with, to a lesser extent, limestone, clay (Dubreuilh & Bouchet, 1992), and some iron oxide deposits historically used as building material (Gourdon-Platel & Maurin, 2004). *Crassostrea gigas* specimens (n=8; Figure 1, Table 1) from this locality originate from the same rearing experiment as those that were placed at Baie des Veys and measurements were restricted to the parts of the shells corresponding to the period spent at this locality (Lartaud et al., 2010a). These specimens are referred to as Mod_TES_Cgig.

2.1.4 Leucate (Aude)

The Salses-Leucate lagoon is located on the southwestern French Mediterranean coast. It corresponds to a shallow coastal basin 14 km long and 5 km wide, separated from the Mediterranean Sea by a sandy barrier interrupted by three narrow marine inlets. The average water depth is 1.7 m and the hydrology is a balance between entrance of marine waters from the Mediterranean Sea, supply of groundwater discharges from two main karstic springs with flows of 3 x 10⁵ m³ d⁻¹ and 2 x 10⁵ m³ d⁻¹, respectively (Fleury et al., 2007), and rainfall of approximately 500 mm y⁻¹ restricted to the fall and spring periods. The superficial watershed covers 162 km² but the total area including the karstic waters is not yet known accurately, likely extended to 60 km inland far from the shore (Salvayre, 1989; Ladagnous & Le Bec, 1997), with karstic waters penetrating Jurassic and Cretaceaous limestone and dolomite. While tidal range is restricted, seawater level changes in the lagoon are controlled by

145 strong northwesterly winds, regularly exceeding 10 m s⁻¹ (Rodellas et al., 2018). *Crassostrea gigas* oysters (n=5; Figure 1, Table 1) originate from a wild brood stock in the vicinity of the local oyster farming area. We were not able to collect reliable *O. edulis* specimens from the Mediterranean Sea shoreline for comparison, as only aquaculture specimens of *C. gigas* are now available here. Specimens from this group are referred to as Mod_LEU_Cgig.

2.2 Archaeological sites and specimens

150 2.2.1 Lyon, Auvergne-Rhône-Alpes

In the area of the Fourvière hill of Lyon city, where remains of a building were tentatively identified as a sanctuary to the goddess Cybele, a pit was filled by food wastes which included around 200 valves of the flat oyster *O. edulis* (Bardot-Cambot, 2013). Absolute dating of this pit is currently being re-evaluated, and is approximated to the beginning of the current era or during the 1st century CE. The provenance of these oysters is debated (Bardot-Cambot, 2013). Two groups of animals, one

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160 originating from the Mediterranean Sea coastline and the other from the Atlantic Ocean coastline, were identified based on morphometric measurements and associated mollusc shells (Bardot-Cambot, 2013). Six *O. edulis* specimens were selected from the first group (later referred to as Anc_CYB1_Oedu group) and seven more from the second group (Anc_CYB2_Oedu group) for the preservation quality of their umbo (Figure 1, Table 1).

2.2.2 La Malène, Occitany

165 This medieval site (circa the 6th century CE) is located on top of a cliff and is <u>comprised of the remains of a fortified</u> construction (Schneider & Clément, 2012). This *castrum* corresponds to one of the last antique sites where oysters were consumed by the elite, with supposedly spatially-restricted commercial travel (Bardot-Cambot & Forest, 2014). Still, the shells found in a dump, along with other proofs of the high social status of the occupants (such as golden currency and silver nails; Schneider & Clément, 2012), had been transported for over 120 km from the Mediterranean Sea. This origin is certified because some valves are fixed on valves of *Flexopecten glaber*, which is endemic to the Mediterranean Sea. Six *O. edulis* specimens were selected for the preservation quality of their umbo (Figure 1, Table 1). As ancient specimens, those are referred to as

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(Figure 1)

Anc_MAL_Oedu.

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(Table 1)

2.3 Sample preparation

All specimens were mechanically cleaned from any epibiont and were selected according to the preservation state of their 180 umbo region. The umbo was cut from the rest of the shell and embedded in Huntsman Araldite 2020 epoxy resin. Longitudinal thick sections (approx. 750 µm thick) were manufactured to expose the preserved internal structures (Figure 2), in order to perform geochemical analyses on this protected region, away from shell surface organic or chemical contaminants. An extensive chemical cleaning of the section surfaces, as advised by Zaky et al. (2015), was not performed as the analytical surface was preserved from any external contaminants over the history of the shell. However, the influence of organic matter 185 occluded in the crystal lattice cannot be discarded, as in any LA-ICP-MS work on biominerals.

(Figure 2)

All sections were observed under cathodoluminescence using a Cathodyne-OPEA cold cathode at ISTeP, Sorbonne Université (Paris, France). Observation settings were 15-20 kV and 200-400 µA mm⁻², at a pressure of 0.05 Torr. Areas potentially affected by diagenesis or damaged were identified in order to avoid any analysis of these regions by LA-ICP-MS. In addition, cathodoluminescence (CL) observations were used to define seasonal calibration of the umbo, according to Langlet et al. (2006) and Lartaud et al. (2010a). Only Leucate specimens did not have seasonal calibration as the CL signal was uniform and
nearly absent for these specimens. A second seasonal calibration method from Kirby et al. (1998), based on a sclerochronological record on the ligamental area in the form of external convex and concave bands, was attempted. Unfortunately, umbos from Leucate specimens did not exhibit the necessary curved surface to conduct such a study. Consequently, measurement data from Leucate specimens were removed from the dataset used for the study of seasonal contrasts of the REE and Y fingerprints.

200 2.4 Geochemical analyses

Chemical analyses were carried out by LA-ICP-MS at ISTE (University of Lausanne, Switzerland). Measurements were performed using an Element XR (ThermoScientific) ICP-MS coupled with a RESOlution 193 nm ArF excimer ablation system equipped with an S155 two-volume ablation cell (Australian Scientific Instruments). A pulse repetition rate of 20 Hz and an on-sample energy density of 4 J cm⁻² were used. Pre-ablation of spots was first conducted in order to clean the surface of potential contaminants that could possibly be introduced during the sanding and polishing of the samples. The analytical spots

- 205 potential contaminants that could possibly be introduced during the sanding and polishing of the samples. The analytical spots were 200 µm in diameter. Ablation was performed on the areas of each sample section corresponding to winter and summer periods (according to the cathodoluminescence seasonal calibration). This protocol allows the REE and Y incorporation to be compared at different <u>seasons</u> throughout the life of the oysters (Figure 2c), with the exception of Leucate specimens, which did not exhibit seasonal cathodoluminescence signals. Sections from Leucate specimens were analysed at random positions
 210 over the umbo region instead. Multiple measurements were performed on each section to avoid bias from potential internal variability. Repeated measurements of NIST SRM 612 prior to and following each 15-samples analytical series were used for external standardisation. Accuracy was checked against measurements of the BCR-2 basalt reference material from USGS according to the GeoReM preferred values (Jochum et al., 2005). Relative standard deviation from 22 measurements of BCR-2 was always better than 2.8% for all REE and Y. Measured and expected values are indicated in Appendix B. Measured
- 215 elements were La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Y, and Ca as the internal standard. Data reduction was performed using the LAMTRACE software (Jackson, 2008). A total of 297 measurements were made.

2.5 Data processing

Data processing was conducted using the Matlab software (MathWorks, www.mathworks.com, v. R2017a). None of the measured elements exhibit a normal distribution (Kolmogorov-Smirnov test): the distribution is right-skewed, at larger element
abundances. To facilitate further statistical treatment of such data, they need to be transformed to normality, for which several mathematical transforms can be used. Here, we use the cubic root transform (Chen & Deo, 2004). Seasonal differences (from the seasonal age models from cathodoluminescence) were estimated by hierarchical cluster analyses of 30 measurements from *C. gigas* specimens (n=5) and 41 measurements from *O. edulis* specimens (n=5) from Baie des Veys, and 24 measurements from *C. gigas* specimens (n=3) and 13 measurements from *O. edulis* specimens (n=3) from Marennes-Oléron (Appendix C).

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For both species, two methods for calculating cluster distances were tested, (i) unweighted average distance and (ii) "Ward" inner squared distance. A cophenetic correlation coefficient has been calculated, as it is the linear correlation coefficient between the distances obtained from the cluster tree and the original distances (in the multivariate space). This coefficient is an indicator of the accuracy of the distances (estimated on the tree) to faithfully represent the dissimilarities among the observations. Multivariate analysis of variance (MANOVA) was used to compare the REE and Y fingerprints obtained from

measurements of *C. gigas* and *O. edulis* from Baie des Veys, against the null hypothesis that both datasets belong to the same population. Kruskal-Wallis tests were performed to compare the Y/Ho ratios of multiple groups, against the null hypothesis that all groups belong to the same population. A recent statistical method, the t-SNE (t-distributed Stochastic Neighbour
Embedding; van der Maaten & Hinton, 2008), was used to compare and classify the multivariate dataset (exact Euclidean method). The idea of the t-SNE method is to embed high-dimensional data points in low dimensions in a way that respects similarities between points. Nearby data points in the high-dimensional space correspond to nearby embedded low-dimensional points (MathWorks, www.mathworks.com, v. R2017a).

240 3 Results

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3.1 Comparisons of the inter- and intra-specific seasonal record

Firstly, heavy REE (Tm, Yb, Lu) and Hf were usually not detected (below 0.1 ng g^{-1}) in all the specimen groups, and were therefore removed from the dataset. Secondly, measurements from the Baie des Veys and Marennes-Oléron specimens allow for inter- and intra-specific comparisons, as they were performed on specimens from both *C. gigas* and *O. edulis* species. Data

- 245 collected at the different seasons for each species did not show any significant difference in the incorporation of REE and Y between winter and summer. For Mod_BDV_Oedu, records from both winter (n=25) and summer (n=16) in *O. edulis* shell samples are mixed together, without clustering samples with respect to seasons (Appendix C); in addition, the cophenetic correlation coefficients are 0.92 and 0.76 for average and Ward methods, respectively, which emphasizes the quality of the classification. Results are similar for Mod_BDV_Cgig shells (n=19 and n=11 for winter and summer, respectively; Appendix
- 250 C), with cophenetic correlation coefficients of 0.76 and 0.69 for average and Ward methods, respectively. Equivalent results are found for Mod_MO_Cgig (cophenetic correlation coefficients of 0.75 and 0.74 for average and Ward methods, respectively) and Mod_MO_Oedu (cophenetic correlation coefficients of 0.94 and 0.87 for average and Ward methods, respectively; Appendix C). However, a comparison between *C. gigas* and *O. edulis* (inter-specific comparison) clearly exhibits significant differences for both winter (MANOVA, p-value = 1.10⁻⁸) and summer (MANOVA, p-value = 2.10⁻⁵) periods
- 255 between the two species. Therefore, C. gigas and O. edulis seem to record differently their respective seasonal signals.

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3.2 The Y/Ho ratio as a provenance proxy

The Y/Ho ratio is commonly used as a provenance proxy (Bau et al., 1995; Prajith et al., 2015). The Y/Ho ratios in the present 260 study (Figure 3) do not display significant differences between the four localities for modern C. gigas specimens (Kruskal-Wallis, p-values = 0.70 between groups Mod_TES_Cgig and Mod_LEU_Cgig, 0.95 between groups Mod_TES_Cgig and Mod_BDV_Cgig, 0.98 between groups Mod_TES_Cgig and Mod_MO_Cgig, 1.00 between groups Mod_LEU_Cgig and Mod_BDV_Cgig, 0.31 between groups Mod_LEU_Cgig and Mod_MO_Cgig, and 0.57 between groups Mod_BDV_Cgig and Mod_MO_Cgig). Also, all O. edulis modern and archaeological specimens from the other localities, except Anc_CYB2_Oedu, 265 are similar to each other (Kruskal-Wallis, p-values = 0.98 between groups Anc CYB1 Oedu and Anc MAL Oedu, 0.99 between groups Anc_CYB1_Oedu and Mod_BDV_Oedu, 1.00 between groups Anc_CYB1_Oedu and Mod_MO_Oedu, 1.00 between groups Anc MAL Oedu and Mod BDV Oedu, 0.97 between groups Anc MAL Oedu and Mod MO Oedu, and 0.97 between groups Mod_BDV_Oedu and Mod_MO_Oedu) but are different from C. gigas shells (Appendix D). Moreover, a significant difference between modern C. gigas and O. edulis shells from the same localities (Baie des Veys and Marennes-270 Oléron) is also reported (Appendix D). However, the Anc_CYB2_Oedu group does not share the homogeneity of other modern and ancient O. edulis populations. On the contrary, the ratios measured in O. edulis specimens from this group are not significantly different from the ones obtained in modern C. gigas specimens (Kruskal-Wallis, p-values = 0.97, 0.26, 0.48 and 1.00, when compared with specimens from Mod_TES_Cgig, Mod_LEU_Cgig, Mod_BDV_Cgig and Mod_MO_Cgig, respectively).

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(Figure 3)

3.3 REE incorporation in shells

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For all the specimens, a gradual decrease in REE dispersion (*i.e.*, amplitude of values relative to Y) is generally observed with their increasing atomic number (Figure 4). Indeed, several groups can be identified with light REE (e.g., Pr and Sm), such as the C. gigas groups. On the contrary, middle REE (e.g., Dy and Er) distributions appear similar for all groups, with the exception of the Mod_LEU_Cgig group whose measurements are isolated from those of the other groups. The REE median profiles (normalized to the Post-Archean Australian Shales; McLennan, 1989) also present similar trends of middle REE (from Gd to Er) for most groups (Figure 5), except for the Mod_LEU_Cgig group, which exhibits lower abundances than the other 285 groups for all REE. However, light REE are generally substantially depleted in C. gigas specimens compared to modern and ancient O. edulis groups (approx. one order of magnitude difference). The only exceptions are La and Ce in C. gigas shells from Baie des Veys (Mod_BDV_Cgig), which present values in the range of those from modern and ancient O. edulis

specimens. This pattern of enriched Ce (and to a lesser extent, La) is not shared by O. edulis specimens from this same locality

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(Mod_BDV_Oedu). Although these two elements have similar abundances for both species in this locality, all the other REE abundances are different.

305 (Figure 4)

(Figure 5)

Results from the entire dataset (*i.e.*, 297 measurements and 12 elements per measurement) are compared in Figure 6 using tSNE. Some groups are well identified by this method, such as the Mod_LEU_Cgig and Mod_BDV_Cgig groups (Mediterranean Sea and British Channel coastlines). Both Mod_MO_Cgig and Mod_TES_Cgig groups, originating from the Atlantic Ocean coastline, appear as one unique group by t-SNE, with a restricted dispersion. The modern and ancient *O. edulis* groups are however not discriminated by t-SNE and present a substantially larger dispersion than the Atlantic Ocean's *C. gigas* groups. In this sample set, Anc_CYB1_Oedu, Mod_MO_Oedu and Mod_BDV_Oedu groups are relatively similar in terms of
range of distribution, and Anc_CYB2_Oedu and Anc_MAL_Oedu specimens share similarities; but the five groups remain

poorly differentiated.

(Figure 6)

320 4 Discussion

In both studied species, the decrease in the range of variation of REE abundances with the increasing atomic number (except for Tm, Yb, Lu, and Hf, which were not quantified in the shells) can be explained by the increased affinity of heavy REE for complexation in seawater, as it has been demonstrated in previous studies (Cantrell & Byrne, 1987; Byrne & Kim, 1990; De Baar et al., 1991). As these elements are trapped into complexed forms or ligands, their bioavailability in seawater is strongly

- 325 reduced, limiting their insertion in the oyster ionic pumps leading to the mineralisation locus. These bioavailability restrictions of REE have already been demonstrated in the freshwater mussel *Corbicula fluminea* for Gd (Merschel & Bau, 2015) and <u>heavy REE in *Mytilus edulis* (Ponnurangam et al., 2016)</u>. Another explanation can be advanced regarding the technique used. LA-ICP-MS device analyses both the mineral and organic phases ablated from the biomineral without the possibility to assess their relative proportions. Although the mean proportion of organic compounds in oyster shells is limited (<0.5% for *C. gigas*;
- 330 Mouchi et al., 2016), it is known that organic REE abundances are depleted in heavy REE (Freslon et al., 2014). The decreasing abundance with the increasing atomic number may then be caused by protein and polysaccharide contents. Only extensive cleaning for solution-based ICP-MS analyses would be able to remove entirely the organic molecules before measurements, but this would not fit the fast REE assessment from a large number of specimens we aimed to conduct in this study.

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In this study, the Y/Ho ratios, which are usually proposed as a provenance proxy (Bau et al., 1995; Prajith et al., 2015), are 340 affected by strong vital effects for both oyster species, potentially due to the decrease in REE abundance with increasing atomic number. In addition, significant differences between species from the same locality are also reported. Hence, the Y/Ho ratio generally does not depend on the original location (Figure 3). Consequently, Y/Ho should not be used directly as a provenance proxy (at least from LA-ICP-MS data collected on biogenic carbonates), or with extreme caution after having discarded any

345 specific variation of Ho, other Y/REE ratios have been tested as alternative provenance proxies using lighter REE (Figure 4). Y/La, Y/Ce, Y/Pr and Y/Nd were all unsuccessful in providing identification of locality groups and also present similar values for all modern and ancient *O. edulis*. For Y/La and Y/Ce ratios, *C. gigas* specimens from Baie des Veys were identical to all modern and ancient *O. edulis* specimens, while for Y/Pr and Y/Nd ratios, *C. gigas* specimens from Baie des Veys were identical to all *C. gigas* specimens from the other localities. Overall, Y/REE ratios appear unsuccessful for provenance discrimination.

potential vital effect. As the decreased REE abundance with increasing atomic number discussed above prevents a locality-

- 350 Measurements performed on Baie des Veys and Marennes-Oléron specimens (Mod_BDV_Cgig and Mod_BDV_Oedu, as well as Mod_MO_Cgig and Mod_MO_Oedu) have been used to study the incorporation of REE inside a single species, in order to evaluate its intraspecific variation. Contrary to the models performed for different temperatures on the mussel *Mytilus edulis* (Ponnurangam et al., 2016), the seasonal conditions do not have any impact on the REE incorporation, neither for *O. edulis* nor *C. gigas* shells (in the range of 5-20 °C; Table 1). Other parameters than temperature and pH, used by Ponnurangam et al.
- 355 (2016), are probably in effect, which lowers the impact of temperature on REE incorporation. This observation implies that any part of a shell can be sampled without necessarily having to define a temporal calibration of the umbo. However, REE abundances fluctuate widely within a single specimen, and the "local fingerprint" of these elements needs to be clarified and based on multiple measurements performed on each of several specimens. These intra-individual fluctuations cannot be due to seasonally-controlled environmental factors, such as temperature, precipitations or plankton blooms. However, a potential
- 360 source of REE for oysters can be the porewater or resuspended sediment (Haley et al., 2004; Crocket et al., 2018), and therefore, the relative abundances may fluctuate without precise temporal cyclicity. The reasons for these intra- and inter-specific vital effects remain unknown. Indeed, as far as we know, no study has ever

shown evidence or suspicion of the use of REE in metabolic processes that could induce an effective filter of these elements between seawater and the extrapallial cavity where shell mineralization occurs. Nevertheless, it has been reported that REE,

365 or other unsuspectedly useful elements, are indeed used by organisms in specific environmental settings; an example is provided by diatoms in Zn-depleted conditions, where Zn is used as a co-factor of carbonic anhydrase (Lee et al., 1995). Another example is given by methanotrophic archaea, which use Cd, a toxic element, as a co-factor of methanol dehydrogenase (Pol et al., 2014).

Incorporation of REE differ between both studied species. Not only *C. gigas* shells present different REE profiles between 370 groups (unlike those of *O. edulis*), but also the Gd positive anomaly, a characteristic of modern coasts under pressure of anthropic activities (Bau & Dulski, 1996; Nozaki et al., 2000; Le Goff et al., 2019), is observed solely for "modern" *C. gigas* specimens from Mod_BDV_Cgig, Mod_MO_Cgig and Mod_TES_Cgig groups (Figure 5), which correspond to the only Supprimé: to Supprimé: e

- 375 watersheds with major cities. The Gd anomaly is neither visible in modern C. gigas from Mod_LEU_Cgig, nor in modern O. edulis, The systematically low abundances of REE in the Leucate shells can also be explained by the regional geology (Ladagnous & Le Bec, 1997), as watersheds of the other localities of C. gigas specimens present substratum types with higher REE contents than karsts (e.g., such as basalts; Baize et al., 1997). The dispersion of measurements using t-SNE seems to be ineffective to discriminate between Mod_MO_Cgig and Mod_TES_Cgig groups. Both these groups are located on the Atlantic
- 380 Ocean coastline of France, and both respective watersheds comprise the same rock types (*i.e.*, mainly limestones and some clays and river deposits). One could therefore expect a similar riverine water REE content. Overall, these species-specific characteristics indicate that *C. gigas* can be used as a sentinel species regarding REE pollution of coastal waters. On the contrary, we cannot confirm that *O. edulis* is a proper candidate for such studies.
- Several reasons for these interspecific differences can be advanced. It is known that oysters can be selective in their diet, composed mainly of diatoms (Yonge, 1928; Paulmier, 1971) of a specific size range, and preferentially digest specific species of diatoms over others (Shumway et al., 1985; Cognie et al., 2001). If food is a source of REE, it may be possible that each oyster species does not feed on the same prey, which can present different abundances of these elements. Aquarium experiments reported different ingestion rates in the 5-15 µm algal size range between these oyster species (Nielsen et al., 2017), but there is no indication on the REE content of the food. Alternatively, *O. edulis*, which exhibits generally higher
- 390 abundances of REE (nearly one order of magnitude higher for light REE, except for La and Ce for Mod_BDV_Cgig specimens; Figure 5), could present a higher bioaccumulation of these elements in its soft tissues (and eventually shell) compared to *C. gigas*. Ong et al. (2013) presented trace element measurements from soft tissues of both species from the Baie de Quiberon (Brittany, France) indicating that soft tissues of *O. edulis* contain generally less Cu and Zn but more Cd and Pb than those of *C. gigas*. Such species-specific bioaccumulation and incorporation differences could also be in effect for REE. Finally, it is
- 395 possible to explain the higher abundance of light REE in O. edulis shells compared to C. gigas by suggesting that O. edulis ingests more clay particles. As heavy REE are trapped in complexed form in seawater, mainly light REE must be available for adsorption on clay particles, and eventually integrate the forming carbonate shell.

In any case, this study shows that t-SNE can be used on REE and Y measurements from *C. gigas* shells to identify regions of origin of specimens from this species. However, it appears that intraspecific vital effects prevent its efficiency in *O. edulis*,

400 whose specimens exhibit the same fingerprint for several localities of origin. For this reason, we cannot confirm or refute a different origin of the two populations of the Cybèle archaeological specimens (Anc_CYB1_Oedu and Anc_CYB2_Oedu) with these elements

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Supprimé: In the latter, this may be due to the fact that (i) most of the freshwater input in the Leucate area originates from karsts and (ii) the watershed does not include any major city

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5 Conclusions

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Multiple types of vital effects and/or other factors on REE incorporation in *C. gigas* and *O. edulis* oyster shells have been highlighted in this study. Intraspecific variations in REE abundances are significant but not related to seasonal fluctuations. A gradual decrease in REE incorporations with increasing atomic numbers has been observed, and it appears that heavy REE are

less discriminant than light REE in identifying the various studied groups. The Y/Ho ratio, previously reported as a proxy for provenance studies, is ineffective in oyster shells. Finally, interspecific variations underline the ability of t-SNE procedure to correctly separate C. gigas specimens of various regions of origin but not O. edulis specimens, which also implies that only C. gigas can be used as a monitor species of light REE pollution. Reconstruction of the provenance of oyster specimens will therefore have to be performed separately for each studied species, as regional geochemical fingerprints of the shells appear to be species-dependant. In order to be able to identify the regions of origin of species affected by strong vital effects (such as O. edulis), it is necessary to investigate other chemical elements as potential provenance proxies. Moreover, an increased efficiency in identifying the locality (and not only the region) of origin of C. gigas specimens could be achieved by also measuring other elements than REE.

430 6 Data availability

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The data used in this manuscript have been deposited on the Zenodo data repository (Mouchi et al., 2019).

7 Author contribution

VM conceived the study, VM, CG and AU performed the data analysis, VF and FL provided specimens, VM and EV performed statistics and data processing. VM, CG, MdR, LE, EV and FL interpreted the results. VM wrote the manuscript with contributions from all authors.

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8 Competing interests

The authors declare that they have no conflict of interest.

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Group	Specie s	Locality of origin	Coordinates	Age	Annual temperature range	Annual salinity range (PSU)	Number of specimens	Number of measurements
Mod_BD V_Cgig	C. gigas	Géfosse, Baie des Veys (Normandy)	49°23.11 N, 01°06.05 W	Modern	5-20°C	30-34	5	30
Mod_BD V_Oedu	O. edulis	Géfosse, Baie des Veys (Normandy)	49°23.11 N, 01°06.05 W	Modern	5-20°C	30-34	5	41
Mod_M O_Cgig	C. gigas	Marennes- Oléron, Charente Maritime (Atlantic Ocean)	45°52.23 N, 01°10.60 W	Modern	5-26°C	24-38	3	24
Mod_M O_Oedu	O. edulis	Marennes- Oléron, Charente Maritime (Atlantic Ocean)	45°52.23 N, 01°10.60 W	Modern	5-26°C	24-38	3	13
Mod_TE S_Cgig	C. gigas	Tès, Arcachon (Atlantic Ocean)	44°40.01 N, 01°08.18 W	Modern	5-26°C	25-35	8	58
Mod_LE U_Cgig	C. gigas	Leucate, Aude (Mediterranean pond)	42°52.48 N, 03°01.50 W	Modern	2-32°C	26-42	5	14
Anc_CY B1_Oedu	O. edulis	Unknown	Unknown	20-30 CE	Unknown	Unknown	6	44
Anc_CY B2_Oedu	O. edulis	Unknown	Unknown	20-30 CE	Unknown	Unknown	7	30
Anc_MA L_Oedu	O. edulis	Unknown	Unknown	6 th c. CE	Unknown	Unknown	6	43

Table 1: Specimen groups and information on their respective localities. Temperature and salinity ranges at Marennes-Oléron, Tès and Baie des Veys are from Lartaud et al. (2010b), and at Leucate from Andrisoa (2019).



655 Figure 1: Map of the localities of modern (squares) and archaeological (stars) specimens. Coordinates of the modern sites are indicated in Table 1.



growth direction

Figure 2: Typical archaeological *Ostrea edulis* (a) and modern *Crassostrea gigas* (b) specimens. The umbo region (c) is cut following the dashed white line. Laser ablation craters (200 µm in diameter) are indicated by circles (on c). Multiple measurements have been performed on each shell, in both winter and summer parts. Red and blue circles represent measurements corresponding to summer and winter periods, respectively, based on cathodoluminescence.



Figure 3: Boxplots of Y/Ho ratios for all groups. The letters on top of the boxes (a and b) identify the significant differences between groups from Kruskal-Wallis tests. Note that for the same locality at Baie des Veys (BDV) and Marennes-Oléron (MO), the Y/Ho ratios are significantly different depending on the species considered (*C. gigas* and *O. edulis* groups). Grey bars represent median values, the lower and higher large black bars represent the 25th and 75th percentiles, respectively, and the lower and higher small black bars represent the minimum and maximum values not considered as outliers, respectively. Outliers are represented by grey crosses.



670 Figure 4: Gradual decrease of REE abundances in oyster shells according to the REE atomic number, presented against Y. Values are expressed in cubic root of abundances (in μg.g⁻¹) to approach normality. Measurements from *C. gigas* and *O. edulis* are indicated with crosses and filled circles, respectively.



Figure 5: REE median profiles for all groups of oyster specimens. *Crassostrea gigas* groups are symbolized with dashed lines and continuous lines for *O. edulis* groups. Seawater profiles of the Atlantic Ocean (van der Flierdt et al., 2012) and the Mediterranean Sea (Censi et al., 2004) are indicated for comparison. Values are normalized to Post-Archean Australian Shales (PAAS) according to McLennan (1989).



Figure 6: Visualization of shell group partitioning using t-SNE applied to all REE and Y measurements as variables. Crosses and large dots refer to *C. gigas* and *O. edulis*, respectively.