

Article

Rare Earth Elements in Shells of Black Sea Molluscs: Anomalies and Biogeochemical Implications

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Abstract: Rare earth elements (REE) are a class of increasingly used high-tech product components and new emerging environmental pollutants, which are accumulated, in particular, in marine biota. In this study, REE contents were estimated in shells of several molluscs common in the Black Sea. The summed REE contents in mollusc shells decreased in the following order of species: *Magallana gigas* = *Anadara kagoshimensis* > *Flexopecten glaber ponticus* ≥ *Rapana venosa* > *Mytilus galloprovincialis*, ranging from 0.46 to 1.9 mg·kg^{−1}. Canonical analysis of principal coordinates allowed for the correct identification of species based on the REE composition in no fewer than 67% of the samples. The mollusc shells were anomalously enriched in Sc, Y, La, Eu and Tb, most likely due to anthropogenic contamination. The Y/Ho ratios in all samples were represented by two fit values: 23.2 (chondritic) and 67.6 (superchondritic, mainly associated with *A. kagoshimensis*). A new universal relationship linking the contents of three light and heavy REE in Black Sea mollusc shells was proposed: $Ce^{0.3}Er^{0.7}/Yb = 2.00 \pm 0.46$ (mean ± standard deviation).

Keywords: trace elements; ICP-MS; *Magallana gigas*; *Anadara kagoshimensis*; *Flexopecten glaber ponticus*; *Rapana venosa*; *Mytilus galloprovincialis*



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1. Introduction

The last few decades have witnessed a boost in the research on rare earth elements (REE) in various fields, including environmental, life and Earth sciences. REE are a group of metals that includes lanthanides (f-block elements with atomic numbers from 57 to 71), scandium and yttrium [1,2], which demonstrate very similar chemical behaviour due to their ordinary trivalent state. REE have been extensively studied in geochemistry, serving as indicators of the terrestrial or marine provenance of rocks and suspended matter [3–6], as a proxy for redox conditions in paleogeography and paleoceanography [7–14], or as tracers of water masses and their circulation [15–21].

REE are widely used in many technical products such as permanent magnets, light emitting diodes and lasers, fluorescent tube phosphors and nickel–metal hydride batteries [22]. They have found increasing applications in high-tech devices like liquid crystal displays and smartphones. Particularly dependent on REE are components of clean energy technologies, e.g., wind turbines, electric vehicles and solar cells [23–25]. REE are elements of growing importance for manufacturing novel efficient catalysts and metal alloys with enhanced mechanical, anticorrosive and ignition-resistant properties [26–29]. In agriculture, REE have long been known to have a positive effect on the growth and quality of crops and to increase their resistance to diseases. These elements have also been used as a feed additive for livestock, poultry and farmed fish [30–34] and proposed as growth promoters for domestic animals [35–37]. REE also find applications in medicine and biology [38,39],

with the best-known ones being in foodstuff authentication, as scintillators in medical imaging and as contrast agents (Gd) in magnetic resonance imaging.

As demand for high-tech products grows, the use of REE is expected to expand and increase significantly [40,41]. Consequently, the widespread use of rare earth elements will lead to their growing release into the environment. Under the influence of atmospheric precipitation, especially at acidic pH, they are continuously washed out from the soil, solid waste landfills and mines, forming REE pollution foci, which involve aquatic areas [3,42–48]. Unlike the effects of heavy metals, whose toxicity has been widely studied, the effects of REE on the marine environment have received relatively little attention [49,50], and there is virtually no information on the macro-scale consequences of REE pollution in the marine environment [51].

It has been established that rare earth elements from seawater bind strongly to calcite, substituting Ca^{2+} ions [52]. A similar mechanism of calcium replacement could be expected in the shells or skeletons of marine calcifiers since they intensively use calcium from seawater in the biomineralization process to form internal or external skeleton structures made up largely of CaCO_3 . REE distribution was studied in marine biogenic carbonate skeletons of microbialites [53–55], corals [56–61] and foraminifera [62–65] in relation to their environment. There are a number of studies on the accumulation of REE in freshwater and marine molluscs in their natural habitat [4,66–81] and on REE effects on molluscs exposed to these metals in laboratory conditions [82–89]. In some studies [68,78], it was found that the REE composition of shells of bivalves matched that of seawater, which implied the possibility of using shells as biomonitors of REE pollution in the marine environment. However, this observation was not confirmed in other works [76,90], in which most REE in mussel shells were shown to originate from particulate matter and no accurate estimates of REE in water were possible using the REE contents in shells.

In analogy to rocks and geological formations, mollusc shells were proposed as REE archives of redox conditions in the mollusc habitat. Pronounced positive europium anomalies as reducing environment indicators were detected in the shells of deep-sea mussels from hydrothermal vents [71,91].

In most of the studies of carbonate sediments, the measured REE contents normalized by the Post-Archaean Australian Shale (PAAS) values are well below 1 [6,53,67,71,72,91], which implies weak bioconcentration of REE in carbonate rocks and may introduce ambiguity in relation to the rock weathering and anthropogenic contamination contributions, as well as processes related to specific enrichment or depletion of a certain group of REE in shells. This discrepancy highlights the problem of appropriate normalization when studying REE distribution in natural objects [92,93].

In the present study, we estimate the REE contents in shells of five molluscs, common in the coastal area of the Black Sea and sampled from the same site. This information allows for finding regularities and anomalies of REE accumulation in the mollusc shells under study; in particular, using local normalization and assessing the mollusc shells as potential biomonitors and sources of REE.

2. Materials and Methods

2.1. Sampling Area and Sampled Molluscs

In this work, four bivalves and one gastropod species were sampled in autumn in the area of a mollusc farm located between the entrances to Karantinnaya and Sevastopol Bays on the southwestern coast of Crimea ($44^{\circ}37'13.4''$ N, $33^{\circ}30'13.6''$ E, Figure 1). The bivalves included: the ark clam *Anadara kagoshimensis* (Tokunaga, 1906), the scallop *Flexopecten glaber ponticus* (Bucquoy, Dautzenberg and Dollfus, 1889), the Mediterranean mussel *Mytilus galloprovincialis* Lamarck, 1819 and the Pacific cupped oyster *Magallana* (= *Crassostrea*) *gigas* (Thunberg, 1793). The gastropod species was the veined rapa whelk *Rapana venosa* (Valenciennes, 1846). Two species—*F. glaber ponticus* and *M. galloprovincialis*—are indigenous to the Black Sea whereas the other molluscs are native species in waters of East Asia and were introduced into the Black Sea in different periods of the 20th century. These are the

common and most abundant mollusc species collected in the same conditions of the mollusc farm environment; three of them (*M. galloprovincialis*, *M. gigas* and *R. venosa*) are popular and commercially valuable seafood [74] and the scallop and the ark clam are potentially important species [94,95] in the Black Sea aquaculture. No other gastropod species of a similar size, availability and commercial value as *R. venosa* have been detected in this area.

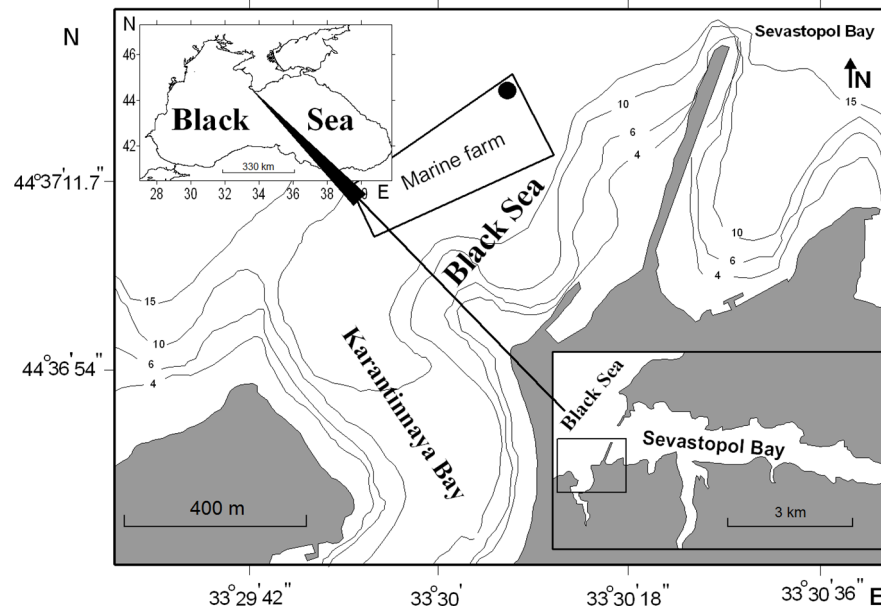


Figure 1. Map of the coastal area and marine farm encompassing the sampling site (black dot).

The mussel *M. galloprovincialis* ($n = 7$) with a shell length of 54.1 ± 2.9 mm was sampled randomly from rope collectors on the farm at a depth of 2–3 m. The bivalves *A. kagoshimensis* ($n = 10$) and *F. glaber ponticus* ($n = 7$) with shell sizes of 38.8 ± 5.1 mm and 30.5 ± 1.0 mm, respectively, were collected from nylon cages suspended on farm ropes equipped with weights and floats. Based on the shell size, the age of these molluscs was assessed to be in the range of 1.5–2.5 years. The oyster *M. gigas* ($n = 7$) with a shell length of 90.7 ± 10.3 mm was also taken from the cages, where it had been reared from spat for 4–5 years. The gastropod *R. venosa* ($n = 10$) with a shell height of 84.7 ± 4.8 mm was collected by scuba divers from the seafloor under the mollusc farm. Its age was estimated at 3–5 years. The black dot in the sampling site map (Figure 1) approximately corresponds to the sea floor area involved in the sampling of the gastropod, with the spatial dispersion in the sampling of the bivalves being much smaller. The temperature during sampling was 21.4 °C at the collectors and 19.0 °C at the seafloor. Sex and gonadal ripening stages in the molluscs were not determined.

2.2. Analytical Sample Preparation

The molluscs were delivered to the laboratory in plastic buckets filled with seawater within one hour after the sampling. The mollusc shells were thoroughly cleared from attached algae, epifauna and mineral residues under seawater using a brush and a knife. Then, bivalve shells were opened with a knife and the rapa whelk shells were broken. After removing the soft tissues, the shells were rinsed with deionized water, blotted with filter paper and dried in an oven at 105 °C. The dried shells were ground in a mortar to pieces smaller than 0.5 mm in size, and 0.2 g samples of each crushed shell were weighed out in triplicate.

For the shell sample digestion, analytical-grade nitric acid was additionally purified by sub-boiling distillation in an acid purification system DST-1000 (Saville, Eden Prairie, MN, USA) and the acid distillate was added to the digestion tubes in a proportion of 3 mL

per 100 mg of sample. PTFE-capped digestion tubes containing the samples and digestion medium aliquots were placed in an autoclave and heated at 2 bar for 1.5 h.

To find an optimum dilution factor that was high enough to eliminate the calcium matrix effect, a digested sample of an *A. kagoshimensis* shell was diluted with deionized water to factors ranging from 100 to 2000 mL·g⁻¹ and the concentration of the lightest and most abundant REE (Sc) was measured in the diluted sample. The dilution factor was assumed optimal if the calculated Sc content in the sample between two successive dilutions dropped by less than 10%. In our measurements, it was found to be about 1000 mL·g⁻¹, and all digested samples were diluted to this level.

2.3. ICP-MS Analysis

The REE concentrations were measured on a quadrupole ICP-MS instrument PlasmaQuant[®] MS Elite (Analytik Jena, Jena, Germany). The plasma argon flow was 9 L·min⁻¹, the sampling depth was 7 mm and the RF power was 1.25 kW. The dwell time for each element was 50 ms. A collisional reaction interface (CRI) was additionally enabled to ensure the absence of polyatomic interferences. Gaseous hydrogen (40 mL·min⁻¹) was the skimmer gas in the CRI. However, the higher sensitivity was in the CRI 'off' mode, and only the measurements in this mode were taken into account in the REE quantitation.

The calibration curves were obtained using a blank solution (extrapure nitric acid diluted with deionized water to approximately the same concentration as in the samples) and multielement standards IV-ICPMS-71A, D (Inorganic Ventures, Christiansburg, VA, USA) diluted to the concentrations 0.005, 0.01, 0.05, 0.1 and 0.5 µg·L⁻¹. The coefficients of determination R^2 for all calibration curves were not smaller than 0.999.

As no internal standard was used in the measurements, the signal drift was taken into account by resloping (measuring the apparent concentration in the standard solution) and linear piecewise correction after every tenth sample. Following each resloping, the capillary and nebulizer were rinsed with a minimum of ten times their volume of blank solution, which was sufficient to restore the REE signals to the background levels.

In the measurements, the following nuclides were involved: ⁴⁵Sc, ⁸⁹Y, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb and ¹⁷⁵Lu. The limits of detection (LOD) of REE in this method were below 0.03 ng·L⁻¹ [96], which corresponds to LOD < 0.03 µg·kg⁻¹ on a shell weight basis. The quality control of the analysis was ensured by measuring REE in the certified reference material BCR-670 (Institute for Reference Materials and Measurements, Geel, Belgium), from which 0.1 g samples were digested according to the above-mentioned procedure and diluted to a factor of 500 mL·g⁻¹. The certified and measured values and recovery rates are given in Supplementary Table S1.

2.4. Statistical Analysis

Differences in the REE contents among the molluscs were tested in PAST 4.14 [97] using one-way ANOVA followed by Tukey's HSD pairwise test unless variances were significantly inhomogeneous according to Levene's test. Otherwise, Welch's ANOVA (F test) was applied with the post hoc pairwise Games–Howell test [98] run in Matlab 8.2.0 (MathWorks, Natick, MA, USA). Boxplots were created in Matlab using the *boxplot* function.

Multivariate analyses were performed in PRIMER 6.1.16 and PERMANOVA+ 1.0.6 [99,100]. Prior to the analyses, the data were logarithm-transformed. For the ordination methods—principal component analysis (PCA) and canonical analysis of principal coordinates (CAP)—the log-transformed data were Z-standardized and Euclidean distance was used as the similarity measure. In CAP, species identity was the group factor, and the number of permutations in the hypothesis testing was 999. The fundamentals for both multivariate ordination techniques are briefly outlined in the Supplementary Materials to [75]. For the agglomerative hierarchical cluster analysis (CLUSTER function), no standardization was applied, and the unweighted pair-group average was chosen as the clustering algorithm.

3. Results

3.1. REE Contents

The molluscs were placed in the following order according to the REE sum decrease in their shells: *A. kagoshimensis* = *M. gigas* > *F. glaber ponticus* ≥ *R. venosa* > *M. galloprovincialis*. Both the ark clam shells and oyster shells contained $1.91 \text{ mg} \cdot \text{kg}^{-1}$ REE (Table 1). At the same time, the oyster shells were richer in all REE except Sc, while the ark clam shells were enriched only in Sc, whose high content compensated for the lower levels of the other elements. Shells of the scallop *F. glaber ponticus* contained more Sc than those of *R. venosa*, but were depleted in Ce and Nd, with the other REE being at comparable levels in the shells of these two molluscs. The lowest REE contents were observed in shells of the mussel *M. galloprovincialis*. Thus, in terms of abundance of most of REE except Sc, the shells of the bivalves under consideration can be arranged in the following order: *M. gigas* > *A. kagoshimensis* > *F. glaber ponticus* > *M. galloprovincialis* (Table 1, Figure S1).

Table 1. Median (min–max) of the Al and REE contents in shells of the Black Sea molluscs (in $\mu\text{g} \cdot \text{kg}^{-1}$). ΣREE denotes the sum of medians. The different superscript letters denote the significance of differences in mean REE contents in the shells: ^a < ^b < ^c. BDL = below detection limit.

	<i>A. kagoshimensis</i>	<i>F. glaber ponticus</i>	<i>M. galloprovincialis</i>	<i>M. gigas</i>	<i>R. venosa</i>
Al	3.3×10^5 (1.2×10^5 – 4.7×10^5)	1.0×10^5 (4.6×10^4 – 4.1×10^5)	3.2×10^4 (2.9×10^4 – 7.1×10^4)	3.9×10^5 (2.2×10^5 – 8.0×10^5)	1.7×10^5 (5.8×10^4 – 4.3×10^5)
Sc	1043 (278–1387) ^a	316 (270–488) ^a	245 (224–336) ^b	599 (505–966) ^b	137 (BDL–330) ^c
Y	204 (92–340) ^a	119 (92–150) ^b	56 (48–63) ^c	229 (133–407) ^{ab}	117 (69–215) ^{ab}
La	252 (135–491) ^a	224 (75–3039) ^{ab}	70 (30–241) ^b	370 (129–538) ^a	228 (52–583) ^{ab}
Ce	201 (58–282) ^a	78 (12–121) ^b	39 (38–55) ^b	318 (150–720) ^a	153 (74–293) ^a
Pr	24 (8.7–34) ^a	11 (3.9–14) ^b	4.1 (2.1–7.5) ^b	36 (17–89) ^a	13 (6.0–31) ^{ab}
Nd	91 (38–140) ^a	39 (15–55) ^{bc}	18 (11–24) ^c	161 (90–379) ^a	78 (24–119) ^{ab}
Sm	21 (7.8–28) ^a	9.3 (3.3–11) ^b	3.5 (0.9–7.9) ^b	35 (17–95) ^a	12 (4.3–32) ^{ab}
Eu	17 (8.1–24) ^{ab}	9.4 (4.3–11) ^b	12 (6.0–18) ^{ab}	24 (14–39) ^a	5.2 (BDL–9.6) ^b
Gd	21 (8.5–31) ^a	9.6 (3.4–13) ^b	3.1 (1.3–6.4) ^b	36 (16–84) ^a	13 (6.9–32) ^{ab}
Tb	2.7 (0.9–5.5) ^b	1.6 (0.8–4.3) ^b	0.9 (0.3–3.6) ^b	10.4 (4.5–19) ^a	1.6 (1.1–5.8) ^{ab}
Dy	16 (6.5–22) ^a	9.0 (3.5–11) ^b	2.7 (1.9–6.7) ^b	33 (20–77) ^a	11 (7.2–25) ^{ab}
Ho	2.9 (1.0–5.0) ^a	1.8 (0.7–4.1) ^a	0.8 (0.2–4.5) ^a	7.9 (2.2–16) ^a	2.5 (1.8–6.0) ^a
Er	8.4 (2.9–13) ^{ab}	5.3 (2.9–6.8) ^{bc}	2.4 (1.3–6.2) ^c	21 (8.8–53) ^a	9.0 (3.4–16) ^{ab}
Tm	1.2 (0.4–2.0) ^b	1.3 (0.11–3.7) ^{ab}	1.2 (1.0–4.5) ^{ab}	2.5 (2.0–4.8) ^a	3.8 (2.1–5.7) ^{ab}
Yb	5.9 (3.1–9.4) ^{ab}	4.4 (2.6–6.1) ^{ab}	1.8 (0.71–5.3) ^b	18 (5.6–32) ^a	7.6 (3.4–12) ^{ab}
Lu	0.86 (0.45–2.0) ^b	1.4 (0.12–4.6) ^{ab}	1.4 (1.2–4.4) ^{ab}	2.6 (1.3–4.4) ^a	2.6 (1.5–4.5) ^{ab}
ΣREE	1913	840	461	1903	792

3.2. Multivariate Analysis of the REE Data

Cluster analysis of the log-transformed REE contents in the samples (Figure 2) shows that the elements are divided into two main groups, which can be referred to as the groups of major and minor REE. Major REE include Sc, Y, La, Ce and Nd. The group of minor REE, in turn, is also split into two big clusters, one of which contains the least abundant REE: Tb, Ho, Tm and Lu. The contents of major REE are typically in the order of hundreds of $\mu\text{g} \cdot \text{kg}^{-1}$ while the least abundant REE are characterized by the levels of a few $\mu\text{g} \cdot \text{kg}^{-1}$.

Principal component analysis (Figure 3a) shows that principal component 1 (PC1) accounts for 69.1% of the total variation in the REE contents. Projections of vectors of all the variables (element contents) on the PC1 axis have the same sign, demonstrating that PC1 is associated with the overall degree of REE accumulation. Expectedly, the scores of *M. galloprovincialis* shells (poorest REE accumulator) and *M. gigas* shells (best REE accumulator) are maximally apart and are located in opposite directions from the origin. Principal component 2 (PC2) explains 12.9% of the total variation and is attributed mainly to the selectivity in concentrating specific REE. For example, projections of vectors of Sc, Tm and Lu onto this axis have opposite signs. The Sc vector points toward the scores of *A. kagoshimensis* shells, which proved to contain the highest levels of Sc. On the other hand, the vectors of Tm and Lu are oriented mainly towards the scores of *R. venosa*, which has the highest contents of these scattered REE.

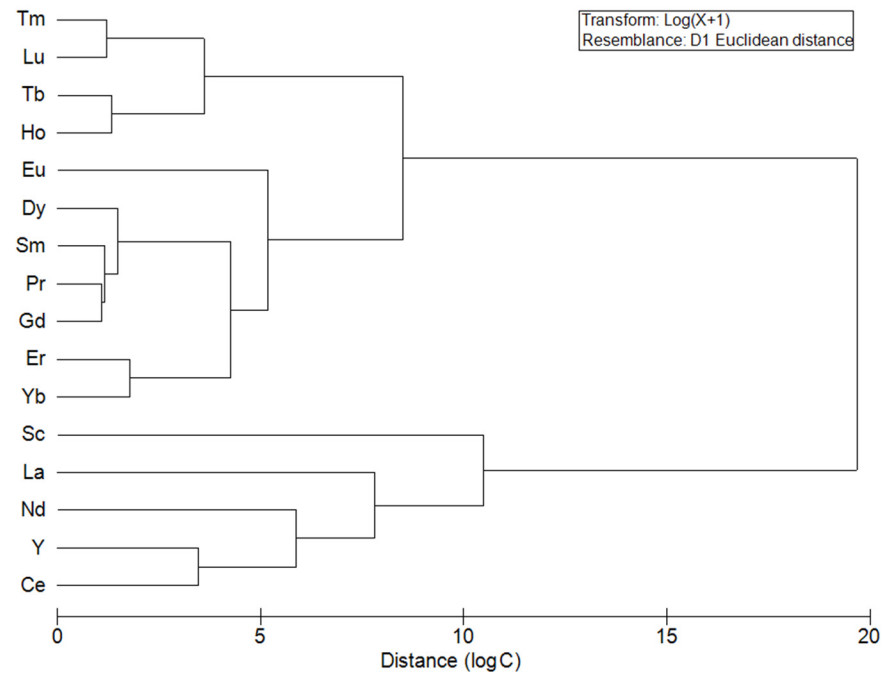


Figure 2. Dendrogram of resemblances in the log-transformed REE contents in Black Sea mollusc shells.

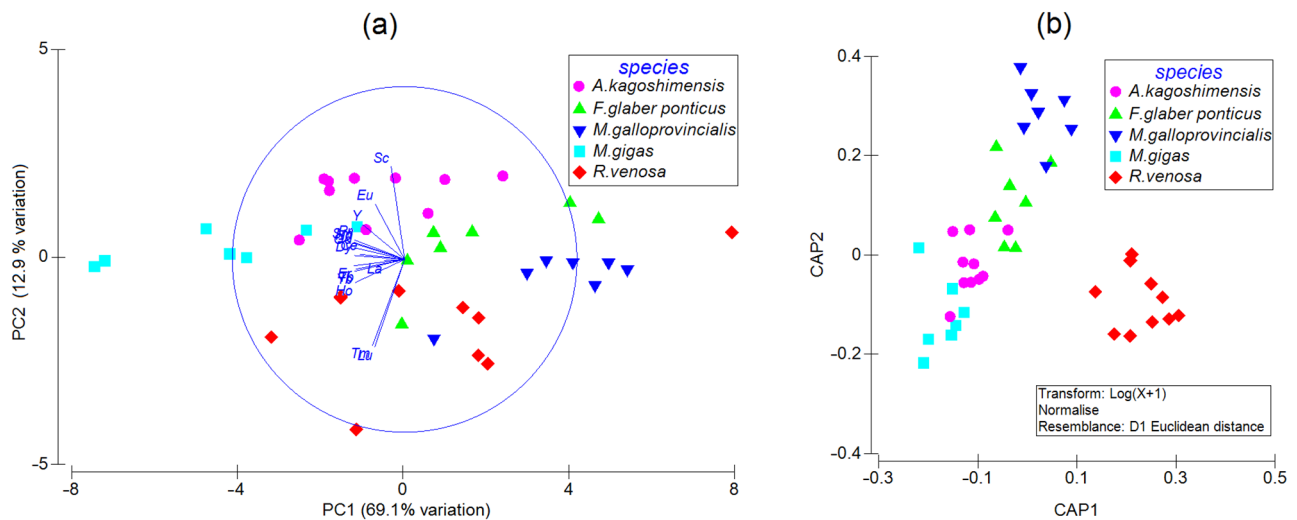


Figure 3. Multivariate ordination analyses of REE contents in mollusc shells: (a) principal component analysis (PCA) and (b) canonical analysis of principal coordinates (CAP).

Canonical analysis of principal coordinates (Figure 3b), which aims to separate groups of observations as far as possible using REE measurements, shows almost perfect separation of the data for *R. venosa* from those related to the bivalve species. The separation of the data related to the bivalves is also considerable though not ideal. The CAP statistics for the matrix product trace is $tr(\mathbf{Q}_m^T \mathbf{H} \mathbf{Q}_m) = 2.929$, $p < 0.001$, and for the principle eigenvalue, it is $\delta_1^2 = 0.938$, $p < 0.001$, which suggests significant separation among groups. The cross-validation based on the jackknifing technique (leave-one-out assignment of observations to groups) shows a total misclassification error of 15%, which is associated mainly with the scallop and oyster shells (67% and 71% of correct classification, respectively).

3.3. REE Enrichment, Anomalies and Characteristic Ratios

The contribution of other sources than natural weathering to the element abundance can be estimated using enrichment factors (EF):

$$EF = (REE/Al)_S / (REE/Al)_B \quad (1)$$

where the subscript “S” stands for “sample” (in the present context, mollusc shell) and “B” denotes the normalization divisor related to the background element levels. In the EF calculation, reference element content is used to account for the overall degree of weathering from primordial rocks. A reference element for the sampling area must be conservative, i.e., it must originate almost exclusively from Earth’s crust. In the literature [101–103], several elements have been suggested as reference elements. In the present work, as in numerous studies [104–108], aluminium (Al) is adopted in this role. As normalization values, we use the data from Late Pleistocene sediments, the oldest sedimentary material available in this area, from the adjacent Sevastopol Bay [109].

The enrichment factors for REE in the mollusc shells (Equation (1)) are shown in Figure 4a. The local normalization results in values < 1 for most of the enrichment factors. The monotonous decline of EF for Sc, La and Y to the background levels in all the molluscs indicates the decreasing external contamination with these elements. In addition, instead of smooth REE profiles, some REE demonstrate pronounced peaks in shells of all the molluscs (Eu, Tb) or some of them (Tm, Lu). These peaks may indicate either positive REE anomalies or inappropriate normalization, and they are also visible in the normalized REE contents (Figure 4b):

$$REE_N = (REE)_S / (REE)_B \quad (2)$$

where the subscripts denote the same as in Equation (1).

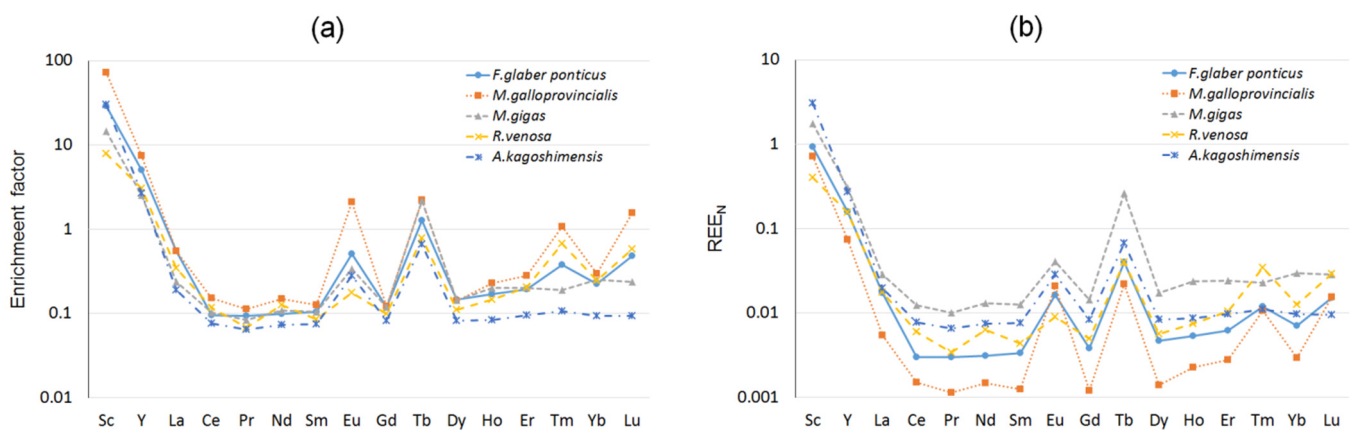


Figure 4. (a) REE enrichment factors (Equation (1)) and (b) abundances in mollusc shells normalized by the contents in a reference material (Late Pleistocene sediments, Equation (2)).

It is reasonable to associate the peaks for Sc—La, Eu and Tb with the positive anomalies of these elements due to external pollution since they are observed in all mollusc shells. This idea is supported by the calculation of anomalies of the respective elements using different formulas (Table 2). The lanthanum anomaly (δLa) was calculated from Equations (3) and (4) [48,93,110]:

$$\delta La_1 = La_N / (3Pr_N - 2Nd_N) \quad (3)$$

and

$$\delta La_2 = La_N / \left(Pr_N^3 / Nd_N^2 \right). \quad (4)$$

Table 2. REE anomalies (3)–(9) and averaged characteristic ratios for mollusc shells.

	<i>A. kagoshimensis</i>	<i>F. glaber ponticus</i>	<i>M. galloprovincialis</i>	<i>M. gigas</i>	<i>R. venosa</i>
δLa_1	4.17	6.51	12.23	7.61	- *
δLa_2	3.90	6.45	8.16	4.94	17.61
δCe_1	1.39	1.07	1.91	1.79	11.49
δCe_2	1.36	1.07	1.73	1.62	3.19
δEu_1	3.60	4.57	17.01	3.05	1.92
δEu_2	3.69	4.43	16.20	2.98	1.92
δTb	8.04	9.53	16.93	16.66	7.53
Y/Ho	82.73	81.64	93.63	35.84	43.02
Ce/Nd	2.20	2.02	2.14	1.98	1.96
Pr/Sm	1.12	1.17	1.18	1.04	1.03
Nd/Er	7.29	7.56	7.80	8.67	10.90
Nd/Yb	8.86	10.06	8.81	10.21	15.57
$\text{Ce}^{0.3}\text{Er}^{0.7}/\text{Yb}$	2.02	1.96	1.89	2.09	2.09
$\text{La}_\text{N}/\text{Yb}_\text{N}$	2.04	2.44	1.84	0.96	1.41
$\text{Nd}_\text{N}/\text{Er}_\text{N}$	0.76	0.51	0.53	0.55	0.61
$\text{Nd}_\text{N}/\text{Yb}_\text{N}$	0.77	0.44	0.50	0.44	0.51
$\text{Ce}_\text{N}^{0.3}\text{Er}_\text{N}^{0.7}/\text{Yb}_\text{N}$	0.90	0.90	0.87	0.96	0.93

* Negative value.

The cerium anomaly (δCe) was found from Equations (5) and (6) [92,93,110]:

$$\delta\text{Ce}_1 = \text{Ce}_\text{N} / (2\text{Pr}_\text{N} - \text{Nd}_\text{N}) \quad (5)$$

and

$$\delta\text{Ce}_2 = \text{Ce}_\text{N} / \left(\text{Pr}_\text{N}^2 / \text{Nd}_\text{N} \right). \quad (6)$$

For the calculation of the europium anomaly (δEu), Equations (7) and (8) were applied [92,110]:

$$\delta\text{Eu}_1 = \text{Eu}_\text{N} / (\text{Sm}_\text{N} \times \text{Gd}_\text{N})^{1/2} \quad (7)$$

and

$$\delta\text{Eu}_2 = 4\text{Eu}_\text{N} / (3\text{Sm}_\text{N} + \text{Dy}_\text{N}). \quad (8)$$

Terbium anomaly was calculated as follows:

$$\delta\text{Tb} = \text{Tb}_\text{N} / (\text{Gd}_\text{N} \times \text{Dy}_\text{N})^{1/2}. \quad (9)$$

No equations for Sc and Y anomalies are readily available from the literature as these are the elements from Periodic Table periods other than Period 6 containing lanthanides and thus do not have reference elements to compare with. In Equations (3)–(9), the notations REE_N designate the same as in Equation (2), i.e., the corresponding REE contents in shells normalized by their contents in the reference material (Late Pleistocene sediments). The formulas for the REE anomaly calculation were chosen such that they did not involve contents of elements that were suspected to be anomalously distributed [92,93]. For example, unlike the formulations in many widely accepted approaches [8,9,45,93,104], the cerium anomaly relationships used did not include La content, which was itself anomalous in the present study.

From the Table 2 data, the lanthanum and europium anomalies are positive in all mollusc shells. The Ce anomaly in *R. venosa* shells is positive, too, but there are no pronounced cerium anomalies in the shells of the bivalves.

The Y/Ho ratios (Table 2), which are used in the literature to ascertain the predominantly marine or terrestrial origin of REE in aquatic objects [53], demonstrate both high superchondritic (82–94) and nearly chondritic values (36–43). The separation of the Y/Ho ratios into the two categories is more clearly seen in the Ho–Y plots for individual samples (Figure 5). Unlike the averaged ratios, the observations are best fitted with the lines char-

acterized by the slopes of 23.2 and 67.6. The line with a slope of 67.6 fits most of the data for *A. kagoshimensis*, while the line with a slope of 23.2 fits most of the data for *M. gigas*, *M. galloprovincialis* and *R. venosa*. Interestingly, some Y/Ho ratio results for *F. glaber ponticus*, *R. venosa* and *A. kagoshimensis* can be fitted with the superchondritic (steeper) line, whereas the other observations related to the same mollusc species are better approximated with the chondritic fit line.

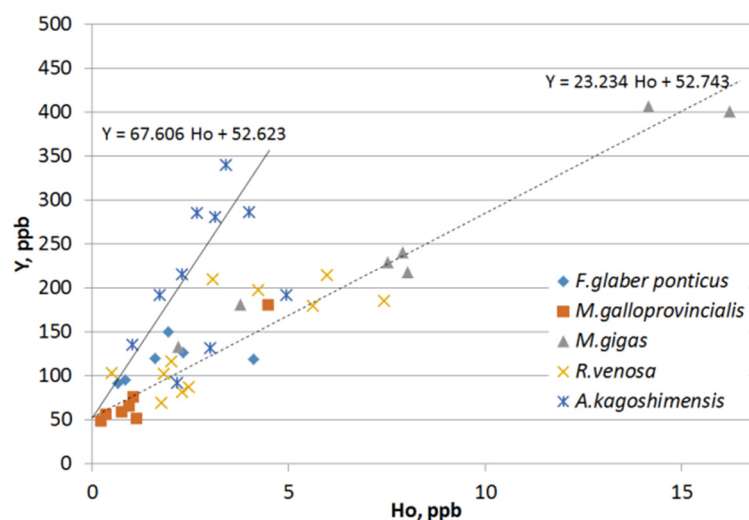


Figure 5. Mollusc shell Ho vs. Y contents demonstrating two different Y/Ho ratio patterns.

There are REE ratios that turn out to be very uniform across the species, e.g., $Ce/Nd = 2.06 \pm 0.11$ and $Pr/Sm = 1.11 \pm 0.07$ (mean $\pm$ SD). The same holds for the ratios of the normalized values: $Ce_N/Nd_N = 0.98 \pm 0.05$ and $Pr_N/Sm_N = 0.85 \pm 0.05$. However, these are the ratios of the neighbor elements whose atomic numbers differ by 2. The ratios of light and heavy REE contents with greater atomic number differences, e.g., Nd/Er or Nd/Yb [53], prove to be much less even.

To find a relationship linking heavy and light REE in shells of all the molluscs under study, a factor C was sought for three REE components in the form:

$$C = HREE^k REE^{1-k} / LREE \text{ or } C = HREE / (LREE^k REE^{1-k}) \quad (10)$$

where HREE is the heavy REE content, LREE is the light REE content and k is some constant. This operation was performed by trying out all possible REE combinations and finding the minimal standard deviation among the mean values for the molluscs. The best found combination was: $Ce^{0.3}Yb^{0.7}/Er = 2.01 \pm 0.09$, or $Ce_N^{0.3}Yb_N^{0.7}/Er_N = 0.92 \pm 0.04$ (mean $\pm$ SD). It is worthwhile noting that across a diversity of Black Sea molluscs, C obviously represents some narrow, and likely not normal, distribution rather than a fixed constant.

4. Discussion

4.1. REE Contents

The highest REE values in mollusc shells were found in the thiotrophic clams *Calypotogena* sp. from Nankai Trough, Pacific Ocean [79]. Interestingly, the lowest REE levels in this region were detected in a mollusc of the same genus from the South China Sea, which may be due to the different geochemical environment of these molluscs. Shells of the deep-sea mussels *Bathymodiolus adulaoides*, which host symbiotic methanotrophic bacteria containing REE as enzyme cofactors [91], had REE levels an order of magnitude higher than those in shells of the blue mussel *Mytilus edulis* [79], which does not host any chemotrophic symbionts (Table 3).

Table 3. REE contents ($\mu\text{g}\cdot\text{kg}^{-1}$) in shells of molluscs from different areas of the World Ocean: min–max.

	<i>Bivalves, Gastropod *</i>	<i>Bivalves</i>	<i>Glycymeris glycymeris</i>	<i>Placopecten magellanicus</i>	<i>Chemotrophic mussels</i>	<i>Bathymodiolus spp.</i>	<i>Chemotrophic mussels</i>	<i>Mytilus edulis</i>	<i>Mytilus edulis</i>
	N Black Sea	Tokyo Bay	NW France Coast	Newfoundland, Atlantic	Deep Pacific and Atlantic	Mid-Atlantic Ridge	E Asia Pacific	NW France Coast	North Sea
	This Study	[76]	[78]	[77]	[91]	[71]	[79]	[79]	[68]
Sc	134–945	–	–	–	–	–	–	–	–
Y	55–259	–	36–357	12–78	6.9–94	10–116	3.6–62	6.0–24	–
La	95–319	19.6–104.3	26–175	19–103	13–97	8.5–153	5.4–1474	5.7–66	8.0–15
Ce	43–424	27.7–209	26–206	7.8–58	3.2–66	8.9–205	10–2487	4.9–64	7.6–13
Pr	4.7–50	2.07–27.2	4.2–26	2.3–12	0.8–12	1.8–27	1.2–224	0.8–6.8	1.3–2.5
Nd	18–219	6.5–121	17–106	8.8–50	2.4–44	7.5–100	4.7–814	3.6–34	5.4–11
Sm	4.0–47	0.750–27.0	3.6–20	1.5–8.9	0.4–9.0	1.5–24	0.7–128	0.7–7.1	1.2–2.5
Eu	8.4–25	0.135–4.62	0.9–5.1	0.3–1.9	0.10–55	0.5–296	0.2–31	0.17–1.6	0.3–0.7
Gd	3.8–48	0.97–31.5	4.7–27	1.8–10	0.6–14	1.7–24	0.9–139	1.0–7.8	2.1–3.8
Tb	1.3–12	0.114–4.44	0.6–3.7	0.2–1.3	0.06–1.7	0.2–3.0	0.1–19	0.1–1.0	0.2–0.5
Dy	3.7–43	0.790–28.0	3.4–21	1.1–7.9	0.4–8.4	1.4–14	0.6–102	0.5–5.2	1.2–2.4
Ho	1.4–8.5	0.191–6.03	0.7–4.5	0.2–1.7	0.10–1.9	0.3–2.4	0.1–18	0.09–1.0	0.2–0.4
Er	2.9–27	0.692–18.1	1.6–12	0.5–4.3	0.3–5.6	0.7–6.3	0.3–41	0.2–2.6	0.5–1.0
Tm	1.2–3.1	0.109–2.20	–	–	–	–	–	–	–
Yb	2.5–18	0.537–12.7	0.8–6.6	0.3–2.9	0.2–4.9	0–4.5	0.23–23	0.09–2.2	0–0.6
Lu	0.93–2.7	0.102–1.83	0.1–0.9	0.03–0.4	0.04–0.73	0–0.8	0.03–3.0	0.012–0.34	0.03–0.1

* Min and max values are taken from the median values for each species under study.

Among the most avid accumulators of REE among aqueous animals are the freshwater molluscs, e.g., *Dreissena* spp. and *Corbicula* sp. [66,80], whose shells can contain up to several $\text{mg}\cdot\text{kg}^{-1}$ of REE. Bivalves from the Atlantic basin are the poorest in REE although the accumulation in the most long-lived Atlantic species critically depends on their age [77,78]. The intermediate REE levels are observed in the present study in shells of molluscs from the Black Sea (Table 3). The most likely reason for such an order in REE accumulation is the increase in salinity and pH from riverine to oceanic water. Higher salinity and alkalinity decrease the ability of invertebrates to accumulate REE, e.g., La [88,111]. At the same time, the mixing of freshwater rich in dissolved and colloidal REE with seawater causes colloid coagulation and REE fractionation that drastically decreases their abundance and bioavailability in the particulate form [112,113]. The Black Sea water is intermediate in salinity (18 psu) with respect to the river and oceanic water, and thus, the REE accumulation by Black Sea molluscs is expectedly intermediate, too.

At the sampling site in the Black Sea, the highest REE contents were noted in shells of the cultivated oyster *M. gigas*. This may be caused by the older age of this mollusc, which can accumulate trace elements in shells throughout its life like other bivalves [77,78,114]. The highest scandium (Sc) content in shells of the clam *A. kagoshimensis* may be due to the high specific area of the ribbed shells of this mollusc, given the fact that scandium among all REE forms the most stable complexes with carbonates [115]. It is worthwhile noting that the rapa whelk *R. venosa*, although being a benthic animal, either does not capture these elements from sediments [116] or does not deposit them in its shell, as it turns out to be poorer in REE than the bivalve shells.

4.2. Multivariate Analysis

The cluster analysis of the rare earth element abundances can separate the group of the major REE from the minor ones. The major REE include Sc, Y, La, Ce and Nd. This division differs from the common classification of REE as light and heavy ones, and it highlights, to some extent, the shell enrichment in the first light REE and yttrium. This is a typical pattern of the REE division in organisms from the northern Black Sea, and the group of the major REE can also include praseodymium (Pr) provided it is abundant enough in the samples [117].

Principal component analysis applied to standardized element contents in tissues of Black Sea organisms usually associates principal component 1 with the overall element contamination in the environment [75,118,119]. As this method seeks to maximize the dispersion along principal coordinates, it can discriminate between samples with sufficiently different element abundances. However, PCA demonstrates only moderate success in identifying separate groups of marine organisms based on a specific group criterion [73,75,119–122], as also seen in Figure 3a. There exist special methods of multivariate analysis, such as linear discriminant analysis (LDA) and canonical analysis of principal coordinates (CAP), that are best suited for this purpose. These methods have been used for the accurate tracking of sampling locations of a number of molluscs [75,123–128], and CAP proved to be superior, compared to LDA, in the correct classification of the locations [75]. In the present work, it is shown that mollusc species can also be successfully identified based on the REE contents in their shells. Particularly impressive is the separation of the gastropod data from those of the bivalves (Figure 3b). Although this technique is not perfectly accurate in the correct classification of some bivalve species samples, its discriminating power can be improved by including other elements in the CAP analysis and increasing the number of samples.

4.3. REE Enrichment, Anomalies and Characteristic Ratios

The REE enrichment factors mainly below 1 suggest that the Late Pleistocene sediments are more enriched in REE than mollusc shells, suggesting the absence of REE accumulation in shells. However, the EF are of the order of or above 0.1, which are much higher than

those normalized by the PAAS values, indicating more adequate normalization by the contents in the ancient sediment.

The anomalies demonstrated by Sc, Y, La, Eu and Tb are likely the result of anthropogenic contamination. For example, the Sc, Y, La and Tb anomalies were observed in the sediments of Kazachya Bay [117], a water area in the vicinity of the sampling site. It is tempting to attribute the Eu anomaly to the reducing organic matrix of the extrapallial fluid that mediates the shell growth [66–68,71,78]. However, no such anomaly has been observed in the shells of any other molluscs unless they were in contact with the reducing environment of abyssal hydrothermal vents [71,91]. Another argument against the natural origin of the Eu anomaly in the mollusc shells is the absence of concomitant negative Ce anomaly in the samples. Negative Ce anomaly in reducing conditions occurs much more frequently in nature, when the insoluble product of cerium (3+) oxidation, CeO_2 , is not formed and accumulated. The positive Eu anomaly typically occurs when the reduced Eu^{2+} ion substitutes for Ca^{2+} in the calcium-rich solid matrices.

The observed Eu enrichment cannot either be a measurement artefact, e.g., due to the interference of $^{137}\text{Ba}^{16}\text{O}^+$ from the matrix, since: (1) the use of CRI yielded comparable results; (2) the measurements in the reference material did not show appreciable deviations from certified values; and (3) the anomaly of Tb, which has no matrix interferences, demonstrated commensurate values with the Eu anomaly (Figure 4a). The positive Eu and Tb anomalies were also observed in airborne particulate matter in Tokyo (Japan) and were attributed to the anthropogenic pollution from the high-tech waste such as the out-of-use cathode-ray tubes, luminescent tube phosphors and magneto-optical disks [129].

In shells of *M. galloprovincialis*, *R. venosa* and *F. glaber ponticus*, one can notice positive anomalies of the most scattered heavy REE—Tm and Lu (Figure 4). It is not very likely that they are associated with anthropogenic REE pollution since not all the molluscs demonstrate these anomalies. It is plausible that they are due to specific dietary preferences. For example, the diet of the two bivalves showing anomalous Tm and Lu peaks, in the absence of intensive microalgal development in the autumn, may include detrital material, which is characterized by relatively flat REE patterns [6,53]. As a result, the heavy REE profile becomes flattened, too, and the normalized values for the bivalves and the gastropod preying on them (Figure 4) are enriched in the least abundant rare earth elements, Tm and Lu. Dietary contents of *M. gigas* and *A. kagoshimensis*, which exhibit no Tm and Lu anomalies, may differ from those of the other molluscs so that *M. gigas* demonstrates only a gradual increase in the normalized values for heavy REE and there is virtually no increase at all in *A. kagoshimensis* shells.

It is noteworthy that shells of the oyster *M. gigas* do not show enrichment in light REE (La) compared to heavy REE (Yb) whereas shells of the other molluscs were 1.5–2.5 times more enriched in La ($\text{La}_\text{N}/\text{Yb}_\text{N}$, Table 2). The same pattern was observed for oysters from other water areas [72,76]. This may indicate either a very specific REE composition of feed items in the diet of the oyster resembling the element composition of ancient rocks, or specific evolutionary mechanisms maintaining a conservative REE composition in the oyster (shell) throughout millions of years.

The ratio Y/Ho is considered an important indicator of marine/terrestrial contributions and a provenance proxy for marine biota [3,53,67]. For the oceanic molluscs, its mean value is 55.0 ± 9.3 [71,77,78,91]. For the freshwater molluscs [66], it is lower, 34.8 ± 5.9 , due to the terrestrial origin that yields values closer to that of the Upper Continental Crust (25) or chondrites (28). In the present work, we singled out two groups of samples with the chondritic (23.2) and superchondritic, i.e., marine, Y/Ho ratios (67.6). The latter was predominantly associated with shells of *Anadara kagoshimensis*, which feeds almost exclusively on marine microalgae. The other bivalves seem to be not selective in food preferences and consume the most abundant particulate matter of terrestrial origin, most likely detritus, which is carried from the coast by currents and whose element composition makes an imprint on the REE contents in shells. The linear fits intersect near zero Ho concentration

at a Y content equal to $52.6 \mu\text{g}\cdot\text{kg}^{-1}$, which is the lowest possible Y level accumulated by all the molluscs due to anthropogenic contamination.

The commonly used ratio of a light and a heavy REE, Nd/Yb, applied to mollusc shells from the Crimean coast demonstrates rather strong dispersion. There exists no more precise ratio of two such elements. A correlation linking the contents of three REE, one of which is a light REE and another one is a heavy REE, was proposed in the form: $\text{Ce}^{0.3}\text{Yb}^{0.7}/\text{Er} = 2.01 \pm 0.09$. For the pooled samples from the Black Sea, $\text{Ce}^{0.3}\text{Yb}^{0.7}/\text{Er} = 2.00 \pm 0.46$. For all the data on mollusc shell REE from the literature, this correlation is $\text{Ce}^{0.3}\text{Yb}^{0.7}/\text{Er} = 1.89 \pm 0.52$ (mean $\pm$ SD). This pooled sample (Figure 6) does not originate from the normal distribution (according to the Shapiro–Wilk test, $p = 1.58 \times 10^{-8}$) as it has a rather heavy right tail. The upper points in Figure 6 mainly represent the samples of abyssal methanotrophic mussels [79,91], which are rich in light REE that are used by their symbiotic bacteria as enzyme cofactors.

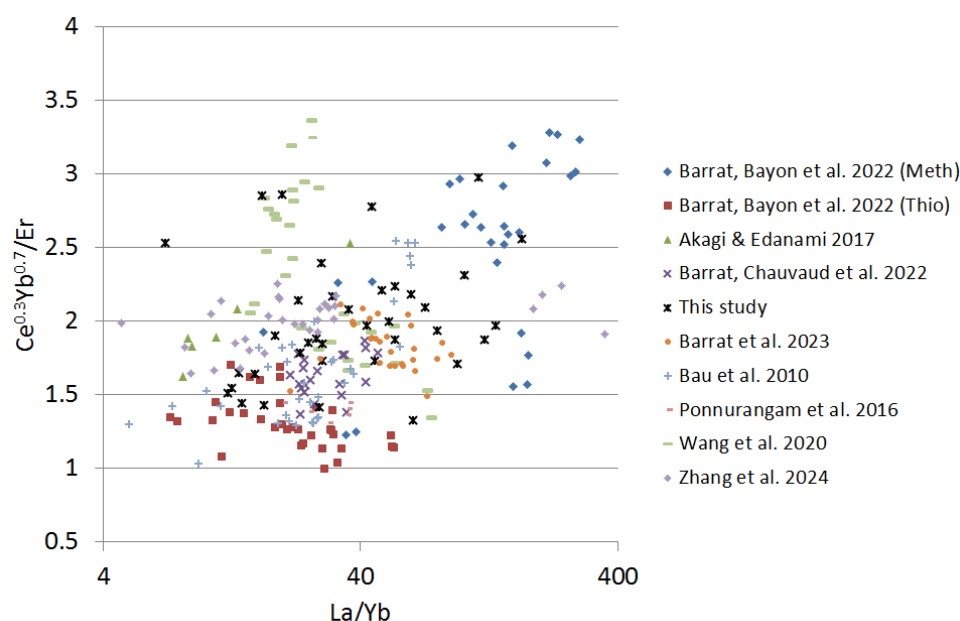


Figure 6. The relationship $\text{Ce}^{0.3}\text{Yb}^{0.7}/\text{Er}$ plotted against the La/Yb ratio for shells of different molluscs from the World Ocean [66,68,71,76–79,91]. Meth = methanotrophic and Thio = thiotrophic symbiont mussels.

5. Conclusions

The REE contents have been estimated in the shells of four bivalves (*Magallana gigas*, *Anadara kagoshimensis*, *Flexopecten glaber ponticus* and *Mytilus galloprovincialis*) and one predatory gastropod (*Rapana venosa*) sampled at the same site on the Black Sea coast of Crimea. The total REE abundance in the shells has been found to decrease in the following order of species: *Magallana gigas* = *Anadara kagoshimensis* > *Flexopecten glaber ponticus* $\geq$ *Rapana venosa* > *Mytilus galloprovincialis*. The Black Sea mollusc shells have proven to be moderate REE accumulators, lying in the REE accumulation ability between oceanic and freshwater mollusc shells.

Canonical analysis of principal coordinates has demonstrated that mollusc species can be identified from the information on REE contents in their shells with a probability no smaller than 67%. The discrimination between the bivalve and gastropod species according to this method is almost perfect.

The calculated enrichment factors normalized by the REE contents in the local Late Pleistocene sediments have allowed the detection of some REE anomalies in the shells. In particular, the Sc, Y, La, Eu and Tb anomalies have been associated with the anthropogenic contamination of the marine environment. The characteristic Y/Ho ratios in the samples have been proven to follow two different patterns: superchondritic Y/Ho = 67.6 mainly for

shells of *A. kagoshimensis*, and chondritic Y/Ho = 23.2 for shells of the other molluscs. This difference has been attributed to the different dietary preferences of the molluscs.

The best correlation linking contents of three REE, one light and two heavy, has been obtained by minimizing the standard deviation: $Ce^{0.3}Yb^{0.7}/Er = 2.00 \pm 0.46$ for all samples under study. For all data available from the literature, this correlation reads: $Ce^{0.3}Yb^{0.7}/Er = 1.89 \pm 0.52$. The distribution of the $Ce^{0.3}Yb^{0.7}/Er$ values is not symmetric and has a heavy tail to the right-hand side.

The largest sum of REE in the shells of the Black Sea molluscs (*M. gigas* and *A. kagoshimensis*) is $1.9 \text{ mg} \cdot \text{kg}^{-1}$, a value almost twice as high as the total REE content in the seagrass wrack from Crimean coasts that was considered as a potential source of REE in the future [117]. Thus, edible molluscs' shells that have been traditionally treated as waste turn out to be not only informative biogeochemical archives but also a useful biomaterial [130] with a number of valuable properties, one of them being the accumulation of rare earth elements to the levels of a few ppm.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/jmse12050713/s1>, Figure S1: Boxplots of the rare earth element contents in shells of five molluscs from the Black Sea coast of Crimea; Table S1: Element contents in the certified reference material BCR-670: mean $\pm$ 95% confidence interval (in $\text{mg} \cdot \text{kg}^{-1}$ d.w.); recovery rates as 100%·Observed/Certified; and relative errors as 100%·(Observed – Certified)/Certified.

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Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

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