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Rare earth elements as new biogeochemical proxies in deep-sea mussels

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Abstract :

We report on the abundances of REE in a comprehensive suite of shells of deep-sea chemosynthetic mussels from hydrothermal vents and cold seeps. Except for mussel shells from oceanic hydrothermal sites that often show extremely pronounced Eu anomalies ((Eu/Sm)sn = 2–200), and abundances for this element that can occasionally exceed 200 ng/g, REE concentrations are usually low and typically between 10−4 and 10−3 times the shale reference.

In addition to exhibiting commonly high Eu anomalies, mussel shells from hydrothermal vents are depleted in light-REE and heavy-REE compared to reference shales (e.g., Pr/Sm)sn < 1, (Tb/Yb)sn = 1–6). These features are inherited from hydrothermal fluid. Mussel shells from cold seeps have very different REE concentrations, which also reflect the compositions of the waters they filter: their (Eu/Sm)sn ratios are much lower (<2) and are much less heavy-REE fractionated ((Tb/Yb)sn = 0.5–2.7). Furthermore, the REE distributions show a clear dichotomy between thiotrophic and methanotrophic mussels. The latter show marked enrichments in light-REE and even sometimes La enrichments much larger than those classically observed in deep-sea waters, leading to huge positive La anomalies (La/La* > 10). These light-REE enrichments are likely related to REE-dependent methanol dehydrogenase enzymes used by the symbionts that these mussels host in their gills. These data show that REE chemistry is a promising tool to study chemosynthetic faunas living near hydrothermal vents or cold seeps. Furthermore, REE chemistry, coupled with stable isotopes, should reveal the footprint of aerobic methanotrophy in carbonates formed in cold seeps, but also potentially in ancient sediments.

Highlights

► Mussel shells from hydrothermal vents show large Eu anomalies. ► REE patterns of thiotrophic and methanotrophic mussel shells are different. ► Shells of methanotrophic mussels exhibit distinctive LREE enrichments and often, large positive La anomalies. ► REE chemistry is a promising tool to study chemosynthetic faunas.

Keywords : Rare earth elements, Bivalve, Shell chemistry, Hydrothermal system, Cold seep, Methanotrophy

1/ Introduction

Over the last fifty years, rare earth elements (REEs) have become one of the most studied groups of elements by geochemists, finding applications in all fields, from the petrogenesis of rocks, terrestrial or not, to the origin of the first condensed solids in the solar system, through rock dating and isotope tracing (e.g., Henderson, 1984). In marine geochemistry, REEs and their isotopes have been also extensively studied since they allow, among other things, the characterization of the different water masses composing the oceans and their circulation (e.g., Elderfield, 1988). For decades, it has been assumed that these elements do not participate in any biochemical cycle and therefore that their distributions at the Earth's surface are not impacted by life. Nature is certainly more complex. Notable biological effects of the REEs have been observed in plants, and REEs are even used as fertilizers (Tommasi et al., 2021). Furthermore, some species can accumulate large amounts of these elements, as exemplified by the fern *Dicranopteris linearis* (Ozaki et al., 1997). More recently, it was established that light REEs are vital for aerobic methanotrophic and methylotrophic bacteria that play an essential role in global carbon cycling (e.g., Pol et al., 2014; Semrau et al., 2018; Cotruvo, 2019). Methanotrophic bacteria first convert methane to methanol, which is subsequently degraded into formaldehyde using Ca-dependent (MxaF type) or REE-dependent (XoxF type) methanol dehydrogenase enzymes (Skovran *et al.*, 2011). Ramachandran and Walsh (2015) and Taubert et al. (2015) have shown that XoxF type enzymes are more frequently used by marine bacteria. These recent findings clearly indicate the ability of micro-organisms to fractionate and redistribute REE, emphasizing the importance of life in the REE cycling in Earth's surface environments. For instance, there is growing evidence that bacterial activity and chemosynthetic ecosystems can influence the REEs distribution in seawater, at least locally. During the blowout of the Deepwater Horizon well (Gulf of Mexico), the depletion of light REE in a submerged plume of methane-rich water was explained by an uptake of these elements by methanotrophic bacteria (Shiller et al., 2017). More recently, light REE depletions were observed in seawater from the Sargasso Sea, at depths between approximately 200 and 500 m, ascribed to the activity of methanotrophic or methylotrophic microorganisms (Meyer et al., 2021). Therefore, methanotrophic bacteria, at least those using enzymes containing REEs, display distinctive REE distributions, as do animals living in symbiosis with them.

Within this scope, deep-sea fauna associated with black smokers and cold seeps are ideal targets to evaluate the distinctive chemical signatures developed by organisms. In these environments, reduced sulfur compounds, methane and/or hydrogen fuel primary productivity sustained by the symbiotic bacteria that form here the basis of the trophic web (Cavanaugh et al., 1981, 1987; Felbeck, 1981; Childress et al., 1986; Petersen et al., 2011), which are vital for many thiotrophic or methanotrophic animals. Recently, two investigations of chemosynthetic fauna have provided direct support for an active consumption of light-REE associated with aerobic microbial oxidation of methane at cold seeps. Bayon et al. (2020a) determined trace element abundances along a one-meter-long chitin tube of a siboglinid worm (*Escarpia southwardae*) collected at the Regab pockmark (Congo margin), identifying distinctive light REE enrichments that were attributed to methanotrophic activity in the branchial plume region of the worm. Additionally, similar light-REE enrichments were found in the gills of methanotrophic mussels collected at seeps from the South China Sea, but not in thiotrophic clams or mussels from the same sites (Wang et al., 2020). Because gills are the organs hosting the methanotrophic symbionts in mussels, Wang et al. (2020) proposed that these light-REE enrichments were related to aerobic methanotrophy. In that latter study, other soft tissues and the shell of studied methanotrophic mussels, while displaying lower light-REE abundances, also show higher positive La anomalies relative to seawater or pore water.

Rare earth element data for deep-sea shells are still sparse. To date, mussels from only three hydrothermal vent fields (Bau et al., 2010) and two cold seeps (Wang et al., 2020) have been investigated. Here we present a comprehensive review for the distribution of REE in mussel shells from deep-sea chemosynthetic environments, which combine previously published literature data (Bau et al., 2010; Wang et al., 2020) and new results obtained on a suite of deep-sea mussels from both submarine methane seeps and hydrothermal vents (Fig. 1). The aim of this study was to further investigate the factors influencing the REE distribution in marine mollusks and assess the degree to which REE abundances in shells can be used to monitor the activity of methanotrophic symbiotic bacteria.

2/ Sampling

Forty-five mussel shells belonging to ten different species were analyzed here, of which nine reside in the genus *Bathymodiolus*. Application of DNA analyses to newly discovered species has led to the assignment of the intensively studied *Bathymodiolus*

childressi to the genus *Gigantidas* (Xu et al., 2019). Twenty-five shell samples, belonging to nine species of *Bathymodiolus*, were sourced from the Scripps Institution of Oceanography Benthic Invertebrate Collection (SIO-BIC) in La Jolla (California, USA). Our sampling includes both thiotrophic and methanotrophic species. Descriptive data for each sample (site, depth, species, museum catalog number, etc.) are given in Supplementary Table 1.

2.1/ Hydrothermal vents

We analyzed three shells from three different sites in the Pacific Ocean for this study, which complement the dataset obtained by Bau et al. (2010) on thiotrophic mussels from the Mid-Atlantic Ridge. Two mussels (*Bathymodiolus thermophilus*) originate from the East Pacific Rise (SIO-BIC M16462) and the Rose Garden vent field (SIO-BIC M8223) located east of the Galápagos Islands, which was among the first submarine hydrothermal sites discovered (e.g., Corliss and Ballard, 1977). The third shell (*Bathymodiolus septemdierum*; SIO-BIC M15353) comes from the Nifonea vent field (Schmidt et al., 2017), located within the caldera of a large shield-type volcano of the Vate Trough, a young extensional rift in the New Hebrides back-arc (Vanuatu, SW Pacific).

2.2/ Cold seeps

We analyzed samples from seven seeps located in three different regions: the Gulf of Mexico, the western margin of Costa Rica, and Melanesia.

The Gulf of Mexico seeps (Brine Pool, Bush Hill, and West Florida Escarpment) have been extensively studied both geologically and biologically (Paull et al., 1984, 1985; Martens et al. 1991; Chanton et al., 1993), and were the basis for seminal observations on chemoautrophic life, including the demonstration of methane-based symbiosis between animals and intracellular bacteria (Childress et al., 1986). The mussels of these sites are particularly well characterized, and the reader is referred to the numerous papers concerning in particular their symbionts or their isotopic compositions allowing analysis of their diet (e.g., Duperron et al., 2007; Macavoy et al., 2008; Riekenberg et al., 2018; Feng et al., 2018). Twenty *Gigantidas childressi* shells from Brine Pool and Bush Hill, and one *Bathymodiolus heckerae* shell from West Florida Escarpment (SIO-BIC M8018), were analyzed. *Gigantidas childressi* is associated with only one type of methanotrophic symbionts, and consumes primarily methane. The metabolism of *Bathylomodius heckerae*, predominantly

methanotrophic, is however potentially much more complex as its gills harbor a greater diversity of symbionts, including one methanotrophic, one methylotrophic, and two thiotrophic polytypes (Duperron et al., 2007). However, $\delta^{13}C$ values of these mussels confirm that seep hydrocarbons represent the dominant carbon source in their soft tissues (Cavanaugh et al., 1987; Paull et al., 1989; Duperron et al., 2007).

Cold seeps at the continental margin offshore Costa Rica harbor a varied fauna (Sahling et al., 2008; Levin et al., 2012, 2015), including mytilid species whose distribution shows some stratification with water depth (McCowin et al., 2020): *Bathymodiolus billschneideri* (~1400–1900 m), *B. earlougheri* (~1000–1900 m), and *B. nancyschneiderae* (1000–1100 m). Furthermore, *Bathymodiolus thermophilus,* a thiotrophic mussel typically encountered at hydrothermal vents along the Galápagos Rift Zone and the East Pacific Rise (e.g., Kenk and Wilson, 1985), has been also identified in this area (McCowin et al., 2020). These four species are all thiotrophic (Levin et al., 2012; Brzechffa and Goffredi, 2021). A total of twenty shells from three seeps (Jaco Scar, Mound 12, and Parrita Seep) were analyzed (SIO-BIC specimens listed in Table S-1).

Two mussel shells (*Bathymodiolus edisonensis*, SIO-BIC M18361; and *B. anteumbonatus*, SIO-BIC M15360) from a cold seep in the vicinity of Edison Seamount (New Ireland Basin, Melanesia, Herzig et al., 1998) complement our sampling of methane seep mollusks. Mussels from this location have been described by von Cosei and Janssen (2008), but to the best of our knowledge, the nature of their symbionts and their isotopic compositions are unknown. The abundance of methane at these sites (Herzig et al., 1998), as well as the similarities of these shells to *Gigantidas childressi* from Gulf of Mexico, strongly suggest that they are methanotrophic (von Cosei and Janssen, 2008).

3/ Analytical procedures

Periostracum was removed from the shells by scraping using a clean steel blade. The determination of the REE abundances follows the procedure designed by Barrat et al. (2020). About 150-200 mg of shell were precisely weighted, spiked with Tm, and dissolved with HNO_3. REE and Y were separated using ion-exchange chromatographic columns loaded with about 1 ml DGA resin. The measurements were performed on a Thermo Scientific ELEMENT XR™ spectrometer located at the "Pôle Spectrométrie Ocean", Institut

Universitaire Européen de la Mer (IUEM), Plouzané (France). The reader is referred to previous papers where our analytical methodology for carbonate samples (Barrat et al., 2020), calibration, isobaric interference corrections and calculation of concentrations based on Tm addition are extensively described, and in which reference values for many international rock standards are reported (e.g., Barrat et al., 1996, 2012, 2016; Charles et al., 2021).

Measured REE concentrations were normalized to the Post Archean Australian Shale (PAAS; Pourmand et al., 2012), adjusted to standard results obtained in our laboratory (Barrat et al., 2020). The La, Ce, and Gd anomalies were calculated using the La/La*, Ce/Ce*, Gd/Gd* ratios, where X* is the extrapolated concentration for a smooth PAAS-normalized REE pattern and X_{sn} is the concentration of element X normalized to PAAS: $La_{sn}^* = Pr_{sn}^3/Nd_{sn}^2$, $Ce_{sn}^* = Pr_{sn}^2/Nd_{sn}$, $Gd_{sn}^* = Tb_{sn}^2/Dy_{sn}$. Replicate measurements obtained for two carbonate standards (CAL-S and BEAN) during the analytical sessions are given in Supplementary Table 1, together with reference values from the literature. The precision (RSD) on measured abundances and elemental ratios was generally better than 3 %. Note that there is no analytical bias between the REE concentrations presented here and those obtained by Wang et al. (2020), which were obtained using the same procedure in our laboratory; or those from Bau et al. (2010) obtained at Jacobs University (Bremen), which are also of very high quality. However, Y concentrations obtained in Bremen on different standards (e.g., Bau et al., 2010, 2014, 2018) were systematically lower than those obtained in Brest (e.g., Barrat et al., 2012, 2020, Charles et al., 2021). This calibration bias was corrected here by multiplying all Y concentrations obtained by Bau et al. (2010) by 1.10.

4/ Results

Sixty-six shell analyses were obtained here (supplementary Table 1), greatly increasing the number of available data for deep-sea mussels. These shells are very poor in REEs. Only rarely did concentrations of an element exceed 100 or 200 ng/g (e.g. Eu for some samples from hydrothermal vents). PAAS-normalized REY patterns from the available data set (Bau et al., 2010; Wang et al., 2020 and this work) are given in Figures 2-5 and provide an overview of the diversity of compositions of these shells.

4.1/ Hydrothermal vent mussels

As shown by Bau et al. (2010), the shells of hydrothermal vent mussels have REY patterns showing large positive Eu anomalies, inherited from hydrothermal fluids (Fig. 2). In this regard, the shells analyzed here are no exception. The East Pacific shells show identical patterns (Fig. 2b), except for Eu, with the EPR sample having an Eu-anomaly similar to those from Logatchev (Fig. 2a) and the Rose Garden sample similar to those from Golden Valley (Fig. 2c) obtained by Bau et al. (2010). Both samples are also marked by positive Y and negative Ce anomalies that are unquestionably the fingerprint of seawater. Two samples of the same shell from Nifonea were analyzed and the results are almost identical, suggesting a homogeneity of the latter (Fig. 2e). The patterns obtained show positive Eu anomalies lower than for the two other samples from Pacific, as well as negative anomalies in Ce and positive in Y quite pronounced. These patterns are similar to those of Lilliput (Fig. 2b). The less pronounced Eu anomalies here could be explained by the composition of hydrothermal fluids, whose Eu anomalies are much lower than those of typical oceanic hydrothermal fluids (Schmidt et al., 2017), but also by a more important contribution of ambient seawater than for the other sites.

4.2/ Cold seep mussels

4.2.1/ Thiotrophic mussels

Only three thiotrophic mussel shells from the China Sea (Site F, Fig. 1) had been analyzed before this study (Wang et al., 2020). Here we studied a much larger series of such mussels collected from three sites located in western Costa Rica. Four species of mussels were analyzed. For these three sites, whatever the species considered, the REY-patterns are quite similar (Fig. 3), and comparable in abundance and shape to those of *Bathymodiolus aduloides* collected in the China Sea (Fig. 4 b). Unlike shells from hydrothermal sites, these shells display low $(Eu/Sm)_{sn}$ ratios (=1.21-1.92). The shape of their REY patterns resembles those of marine carbonates (e.g., Northdurft et al., 2004). The patterns are characterized by marked negative Ce anomalies (Ce/Ce*= 0.34-0.77 for Costa Rica samples, and 0.77-0.81 for China Sea samples) and positive Y anomalies (Y/Ho= 51-80 for Costa Rica samples, and 50-64 for China Sea samples). They also display positive anomalies in La (La/La*=1.9-3.0) in the range of seawater values, and apparent positive anomalies in Gd (Gd/Gd*=1.1-1.37).

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246 **4.2.1/ Methanotrophic mussels**

247 The two *Bathymodiolus* shells from the Edison Seamount display lower REE than the
248 *Gigantidas* from the China Sea (Wang et al., 2020), but their patterns show quite similar
249 characteristics (Fig. 4). Two fragments per shell were analyzed, and the results are very
250 consistent, suggesting that both shells do not show marked heterogeneities for REE and Y. As
251 expected, they show positive anomalies in Y (Y/Ho=59.8-69.5) and negative in Ce
252 (Ce/Ce*=0.39-0.46), but also striking La anomalies (La/La*= 7.9-11.9). Wang et al. (2020)
253 previously showed that the shells of methanotrophic mussels from the China Sea display
254 exceptionally high positive anomalies in La (La/La*=2.5-5.1). Those measured in Edison
255 Seamount shells are even higher, and to the best of our knowledge, represent the most
256 pronounced La anomalies ever measured to date in natural environments not affected by
257 emerging micropollutants. In addition, these shells also show apparent anomalies in Gd
258 (Gd/Gd*=1.26-1.77).

259 Different REY patterns were obtained for mussels from the Gulf of Mexico (Fig. 5):

260 -The patterns of *Gigantidas* shells from Brine Pool and Bush Hill show distinctive
261 light REE enrichments, moderate negative Ce anomalies, variable Gd anomalies
262 (Gd/Gd*=0.88-1.53), as well as usual seawater-like positive Y anomalies (Y/Ho=43.8-72.5).
263 Their La anomalies (La/La*=1.73-2.70) are not as high as those discussed above, being
264 comparable to typical marine values. Mussels from these two sites display similar REE
265 concentrations, showing that the brines at Brine Pool do not affect the REE composition of
266 shells. Note that the mussels at this site do not live in direct contact with the brines but within
267 at ~10-cm-thick layer of seawater immediately overlying the brine pool or the surficial
268 sediment at the pool edge. However, a sample from Brine Pool (BP7a) stands out from other
269 shells by displaying higher heavy REE contents. We analyzed a second fragment from the
270 same shell (BP7b), and obtained results that are closer to the rest of studied samples,
271 suggesting that the first sub-sample may have been contaminated by impurities. Alternatively,
272 the range of shell composition could be larger than suggested by the other samples.

273 -Two fragments of the same *Bathymodiolus heckerae* shell from the West Florida
274 Escarpment were analyzed, with identical results (Fig. 5c). The corresponding patterns are
275 different from those of other methanotrophic mussels. They do not show notable enrichments
276 in light REE like those obtained from the Brine Pool or Bush Hill *Gigantidas*, nor large

positive La anomalies like the methanotrophic mussels from China Sea or Melanesia. Their La/La* (=2.35-2.40) are in the range of seawater values. They are similar to those of thiotrophic mussels (e.g., those from Costa Rican seeps, Fig. 3), with similar negative Ce and positive Y anomalies (Ce/Ce*=0.39-0.41) and positive Y (Y/Ho=55.2-56.3).

5/ Discussion

5.1/ REE characteristics of hydrothermal *versus* cold seep mussels

Notable differences are apparent between the REE concentrations of mussel shells from hydrothermal vents and those from cold seeps. Bau et al. (2010) showed that mussel shells living in the vicinity of Atlantic hydrothermal vents exhibit characteristic REY patterns, with large positive Eu anomalies [$(Eu/Sm)_{sn}$ up to 5, and >2 in most cases], which are inherited from hydrothermal fluids. The analyses obtained here confirm this observation, showing that all shells from submarine hydrothermal vents display positive Eu anomalies. In contrast, significant positive Eu anomalies are totally absent in shells from cold seeps (Fig. 6), which exhibit $(Eu/Sm)_{sn}$ ratios with little variability (between 1.1 to 1.9). Furthermore, 'hydrothermal' shells show much more variable and generally much higher REE concentrations than those from cold seeps, as illustrated by the histograms of Sm concentrations (Fig. 7). Their patterns also sometimes show enrichments in middle REE compared to heavy REE, which can be quantified with $(Tb/Yb)_{sn}$ ratios frequently exceeding 2 (Fig. 8). These mid-REE enrichments, combined with presence of significant positive Eu anomalies, reflect the contribution of hydrothermal fluids with REY distributions very different from seawater abundances (Bau and Dulski, 1999; Douville et al., 1999, Schmidt et al., 2007, 2017; Craddock et al. (2010) ; Cole et al., 2014), with no evidence for any presumed biological effect.

5.2/ Differences between thiotrophic and methanotrophic mussels at cold seeps

At cold seeps, the REE distributions in mussel shells appear, at least in part, to reflect some characteristics of the surrounding water that they filter (Fig. 8, Fig. 9). Thiotrophic mussels have REE ratios falling in the range of seawater and pore water values. Some samples, however, have slightly higher $(Tb/Sm)_{sn}$ ratios than pore waters, but we do not consider this discrepancy to be very significant since the fluid composition at the sites where our shells originate is not known. As for the mussels from hydrothermal sites, there is no evidence for measurable imprint of any biochemical process involving REE for these animals.

309 The situation is quite different for methanotrophic mussels. While their heavy-REE
310 ratios are similar to those for seawater or pore waters (Fig. 8), light-REE abundances depart
311 substantially from both seawater and pore water values (Fig. 9). They are, in most cases,
312 much more enriched in light-REE than waters, but also more than oil that can be present in
313 some seeps like those of the Gulf of Mexico (Smrzka et al., 2019). As mentioned above,
314 Wang et al (2020) showed that the shells of methanotrophic mussels at methane seeps from
315 the South China Sea display high La anomalies relative to nearby thiotrophic mussel species,
316 clams and seawater. The decoupling of La from other trivalent REE at cold seeps has been
317 interpreted as reflecting the enzymatic activity of associated methanotrophic symbionts, hence
318 indicating aerobic methanotrophy. The new data obtained in this study provide further support
319 to this hypothesis. First, the thiotrophic mussel shells are not particularly enriched in light-
320 REE, and do not show positive La anomalies exceeding usual seawater values, confirming
321 that the enzymatic activity of their symbionts has no notable effect on these elements. On the
322 other hand, the REY patterns obtained for methanotrophic mussel shells are much more
323 variable than those associated with thiotrophic species. Light REE provide a clear-cut
324 separation between most thiotrophic and methanotrophic mussels (Figs. 8 and 9). Except for
325 one sample that will be discussed later, methanotrophic mussels show light-REE enrichments
326 (illustrated by $(Pr/Sm)_{sn}$ or $(Pr/Nd)_{sn}$ ratios, Figs. 8 and 9) commonly accompanied by even
327 more pronounced La enrichments (illustrated by the ratios $(La/Nd)_{sn}$ and La/La*, Fig. 9). The
328 range of measured light-REE enrichments or La anomalies cannot be explained by local or
329 environmental factors because it far exceeds the range of values known for sediments and
330 marine waters (e.g., Fig. 8 and 9). In agreement with Wang et al. (2020), these enrichments
331 are most likely related to the enzymatic activity of methanotrophic symbionts hosted by the
332 gills of these mussels. It is logical to link them to the degradation of methane to methanol and
333 then to formaldehyde, since REE-dependent (XoxF type) methanol dehydrogenase enzymes
334 are used by these organisms (e.g., Skovran et al., 2011; Semrau et al., 2018; Cotruvo et al.,
335 2019). The large variability of REY patterns obtained for methanotrophic shells suggests that
336 the use of light-REE by these organisms differs from one species to another. For example,
337 some animals generate very large La anomalies in their shells (e.g., *Gigantidas platifrons*
338 from China Sea or *Bathymodiolus* from Edison Seamount), whereas others display only light
339 REE enrichments, with La anomalies similar to those in seawater (e.g., *Gigantidas childressi*
340 from Gulf of Mexico). These differences, which are extremely marked, necessarily reflect
341 different needs in light-REE for the enzymatic activity of these animals. It should be noted,
342 however, that the transfer of these elements from the gills (which are the seat of symbiont

activity) to the mantle (which synthesizes the shell) has never been considered until now, and that REE fractionation during this transfer cannot be ignored.

One sample, a *Bathymodiolus heckerae* shell from the West Florida Escarpment (Gulf of Mexico), differs from all other methanotrophic mussel shells analyzed to date (Wang et al., 2020 and this study) in that it lacks significant light REE enrichment, and has an anomaly in La within the range of conventional marine values. This sample even shows REE distributions very similar to those of thiotrophic mussel shells (Fig. 5c). Note that these particular REE signatures associated with *Bathymodiolus heckerae* cannot be related to analytical artefacts because two separate shell fragments were analyzed, both returning similar results (Supplementary Table 1). Clearly, the symbionts of this mussel did not require light-REE to degrade methane. It is logical to assume that they do not use REE-dependent (XoxF type) methanol dehydrogenase enzymes, but rather Ca-dependent (MxaF type) methanol dehydrogenase enzymes. However, only one shell of this species was available for our study. It would be appropriate at this stage to analyze other samples from this site, and obviously to identify the enzymes used by the mussel symbionts of this species.

5.3/ Gd anomalies in mussels from cold seeps

An unexpected result of our study concerns the presence of marked positive Gd anomalies in many cold seep shells (Fig. 10), whereas those from hydrothermal vents show a much narrower range of Gd/Gd* values.

Gd anomalies are a common feature of REE sorption in the presence of strong solution complexation, for example with carbonate (dominant in the ocean) or with organic ligands (e.g., Quinn et al., 2006; Christenson and Schijf, 2011). Gd/Gd* ratios on the order of 1.2 are typically encountered in the marine environment. The cold seep mussels investigated here typically display Gd/Gd* ratios exceeding 1.2. We are confident that these anomalies do not correspond to analytical artifacts resulting from biased correction of interferences produced by Ce and Pr oxides. Our procedure effectively corrects for these interferences (e.g., Charles et al., 2021), and the results obtained on standards during the course of the study demonstrate the quality of our analyses (Supplementary Table 1). Moreover, these anomalies were confirmed through multiple measurements of different fragments of the same shells, and cannot possibly relate to inappropriate normalization values, because similar Gd/Gd* values are calculated by normalizing abundances to other shale references or to chondrites (e.g.,

Barrat et al., 2012; Bau et al., 2018, not shown). We are also confident that measured Gd excesses in this study were not caused by an artefact related to the calculation of Gd anomalies. Here, Gd anomalies have been calculated by extrapolating Gd* using Tb and Dy concentrations, but similar results are obtained when Gd* is interpolated between Sm and Tb (not shown).

Positive Gd anomalies have been measured in mollusk shells living in waters polluted by Gd-based contrast agents (GBCA) used for medical imaging by magnetic resonance (e.g., Merschel and Bau, 2015; Ponnurangam et al., 2016; Akagi and Edanami, 2017; Le Goff et al., 2019). Even if this pollution is now common in coastal waters worldwide, it is highly unlikely that anthropogenic Gd pollution affects the deep sea at which our samples were collected. We tentatively propose that these Gd anomalies are the result of either biological fractionation or that they reflect the composition of the water filtered by the mussels. Since Gd anomalies are present in the shells of both thiotrophic and methanotrophic animals, they are probably not the result of any specific enzymatic activity related to nutritional symbiosis. It is possible that cold seep mussels fractionate Gd for an undiscovered use in other biological functions. One may wonder why these anomalies are not ubiquitous features of bivalve shells, including in thiotrophic species encountered at hydrothermal vents, where mussel shells lack the marked Gd anomalies. As an alternative, Gd anomalies could be inherited from water filtered by mussels. Recently, Möller et al. (2021) reported high Gd/Gd* ratios in natural, uncontaminated, spring waters and hypersaline waters (e.g., Dead Sea). Gd/Gd* ratios close to 1.7 or higher are unknown in seawaters and oceanic hydrothermal fluids. What about methane-rich fluids from cold seeps? There are limited REE data for methane-rich fluids at cold seeps (e.g., Himmler et al., 2013; Lemaitre et al., 2014). However, some of their characteristics can be inferred from the composition of the carbonates they deposit (e.g., Smrzrka et al., 2020; Bayon et al., 2020a). To date, it has not been convincingly shown that cold seeps carbonates can exhibit such anomalies, making it more than hypothetical that they are present in cold seeps fluids. The origin and significance of the Gd anomalies observed in cold seeps mussel shells is not yet understood.

6/ Conclusions and perspectives

In this study, we compared REE abundances in deep-water mussel shells from various hydrothermal and cold seep systems worldwide, confirming that animals living at

hydrothermal sites display compositional shell characteristics of surrounding fluids such as positive Eu anomalies (Bau et al., 2010). The REE distribution in bivalve shells at submarine methane seeps provides a window into the enzymatic activity of associated symbionts. Unlike thiotrophic mussels, methanotrophic species whose symbionts use light-REE to degrade methane, show characteristic light-REE enrichments in their shells. Our results confirm that only methanotrophic mussels display distinctive positive La anomalies, but selective La enrichments are not systematic to all species analyzed. The degree of light REE enrichment in shells probably depends on the distribution pattern of hosted symbionts and associated enzymatic activities, suggesting regional variability. For instance, only shells from western Pacific sites displayed strong positive La anomalies in this study. At this stage, it is unclear whether this characteristic relates to the presence of specific symbiont lineages. Future investigations of other mussel species from additional sites combined with symbiont characterization will be required to address this issue. In future studies, REE concentrations in abyssal mussel shells could be used to distinguish methanotrophic from thiotrophic species, hence serving as tools for identifying their general enzymatic pathway. This novel approach could be also applied to the sedimentary record and the investigation of fossil shells in ancient seep deposits, providing of course that diagenesis or any other post-depositional processes have not modified their REE abundances. Overall, these findings open up important multidisciplinary perspectives in biology, Earth and environmental sciences, requiring further improvements in our understanding of the REE biogeochemistry and inventory in organisms, and their role in enzymatic activities and metabolic pathways. Additional work will be also needed to assess the impact of life on REE cycling in the ocean, something that has been largely overlooked until now. Our new data reinforce the idea that methanotrophic organisms, at least those using REE-based enzymes, can leave a distinctive chemical fingerprint in rocks, in particular in methane-derived carbonates at cold seeps. Some of these authigenic carbonates contain organic-rich aragonitic cements exhibiting high light-REE enrichments (Zwicker et al., 2018). So far, these cements have been interpreted as fossil biofilms (Hagemann et al., 2013), but it is very tempting to see here the imprint of aerobic methanotrophic activity. Finally, we draw the attention of the large geochemical community studying ancient marine sedimentary formations of Precambrian age, to the interest of carrying out detailed investigations coupling REE to other conventional biogeochemical proxies such as stable isotopes in order to detect the emergence of aerobic methanotrophy on Earth.

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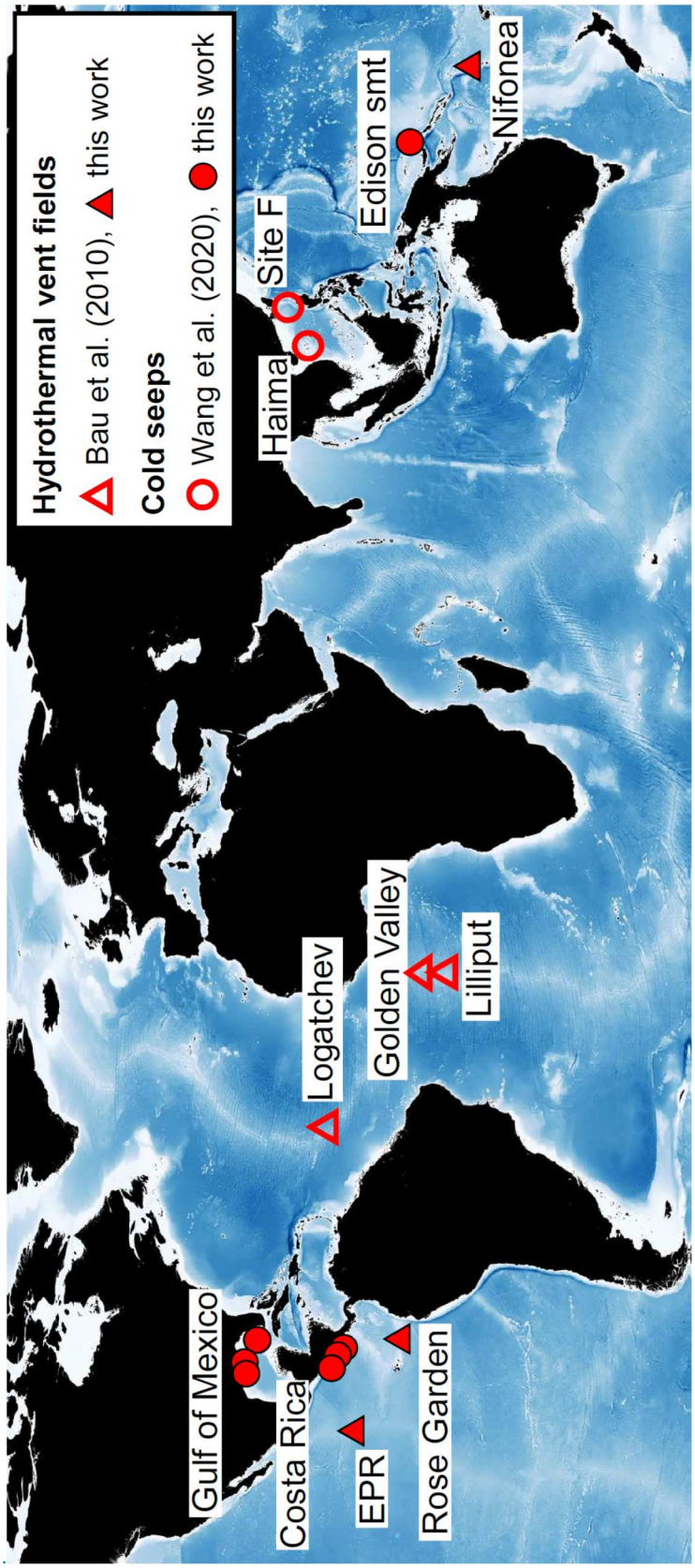

Figure 1. World map and location of the hydrothermal vents and cold seeps where mussels have been analyzed for REE and Y abundances (Bau et al., 2010; Wang et al., 2020; this study).

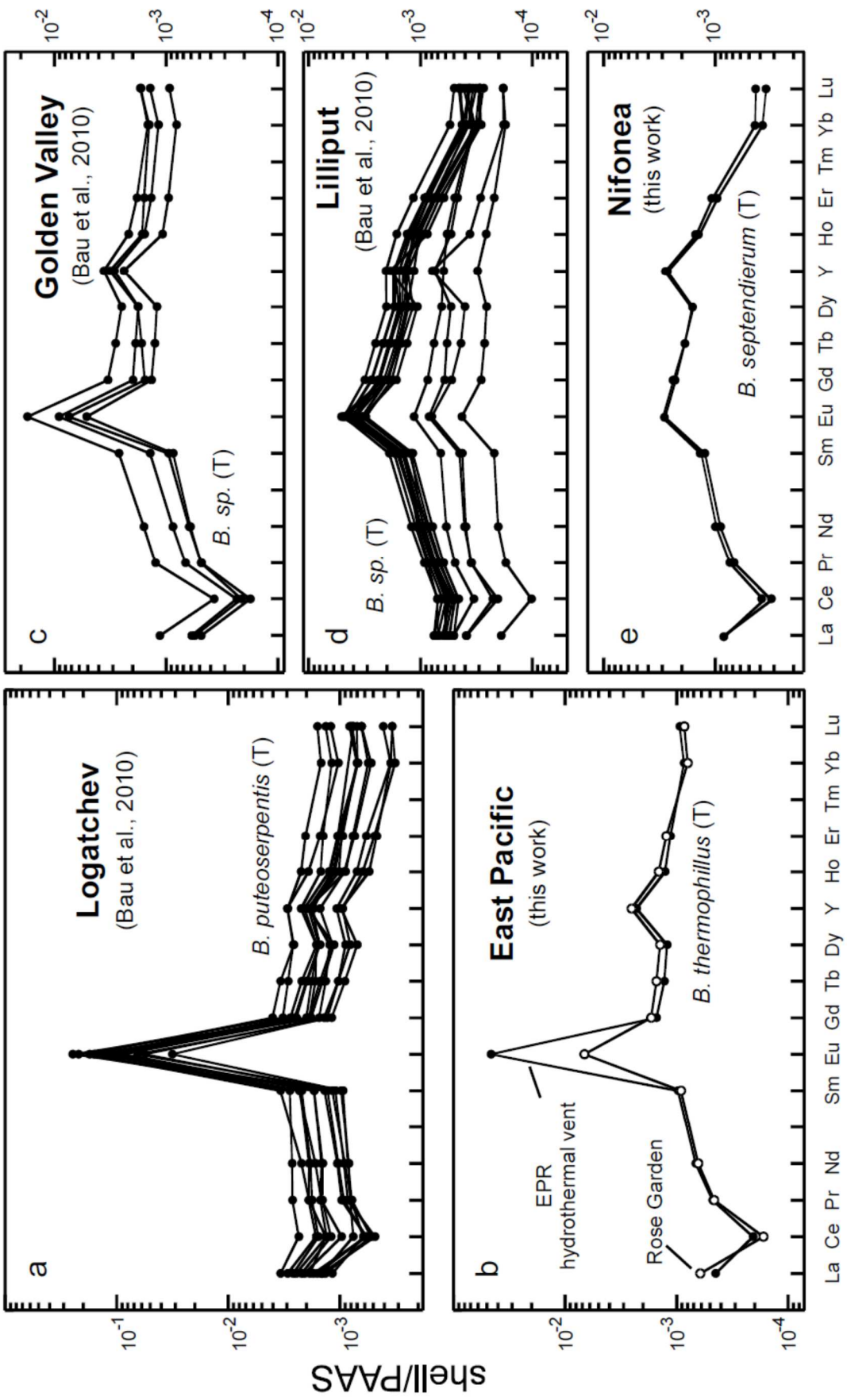

Figure 2. PAAS-normalized REY patterns for shells of thiotrophic (T) mussels from hydrothermal vents.

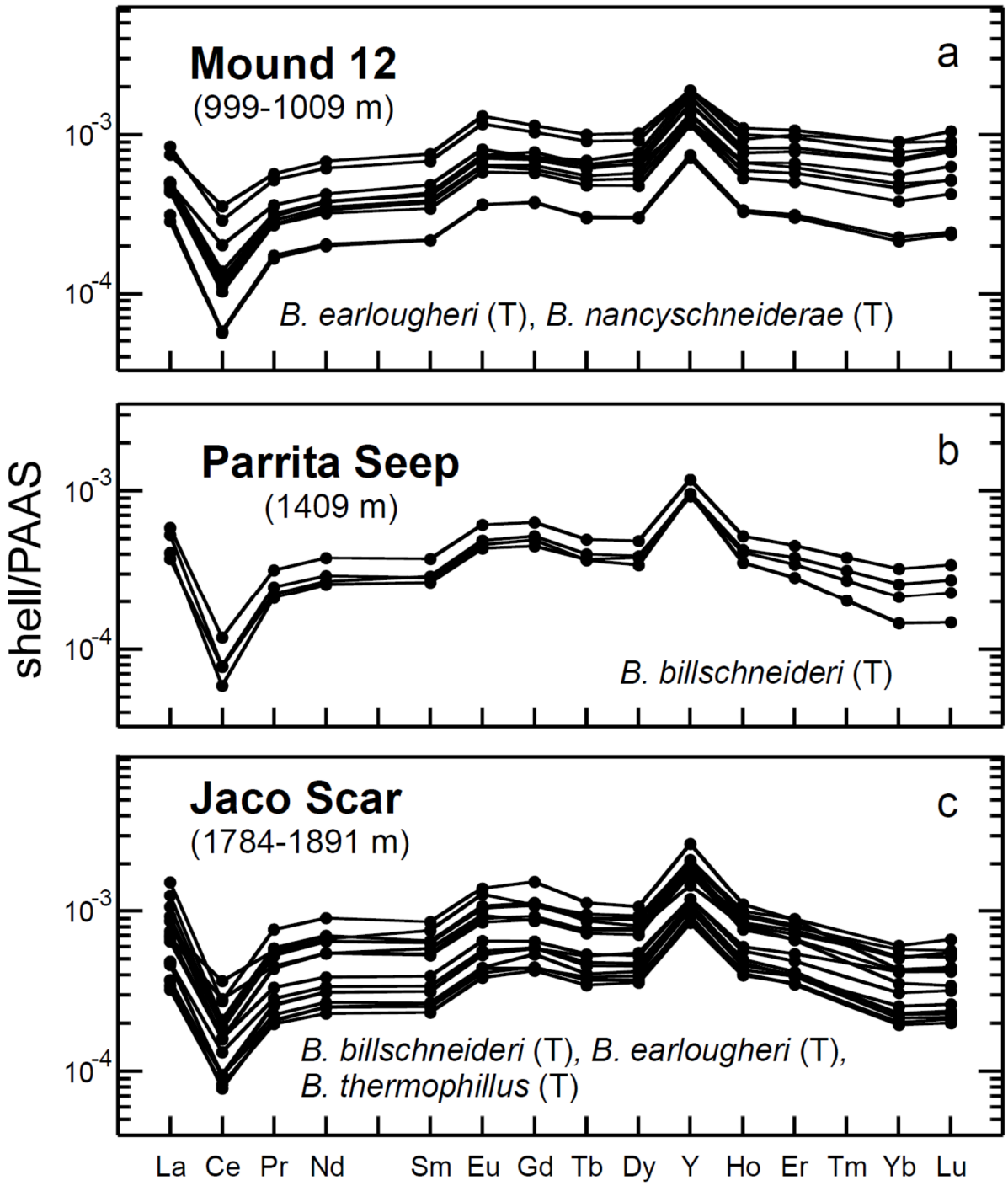

Figure 3. PAAS-normalized REY patterns for mussel shells from vents located west of Costa Rica. Here, all the mussels are thiotrophic (T).

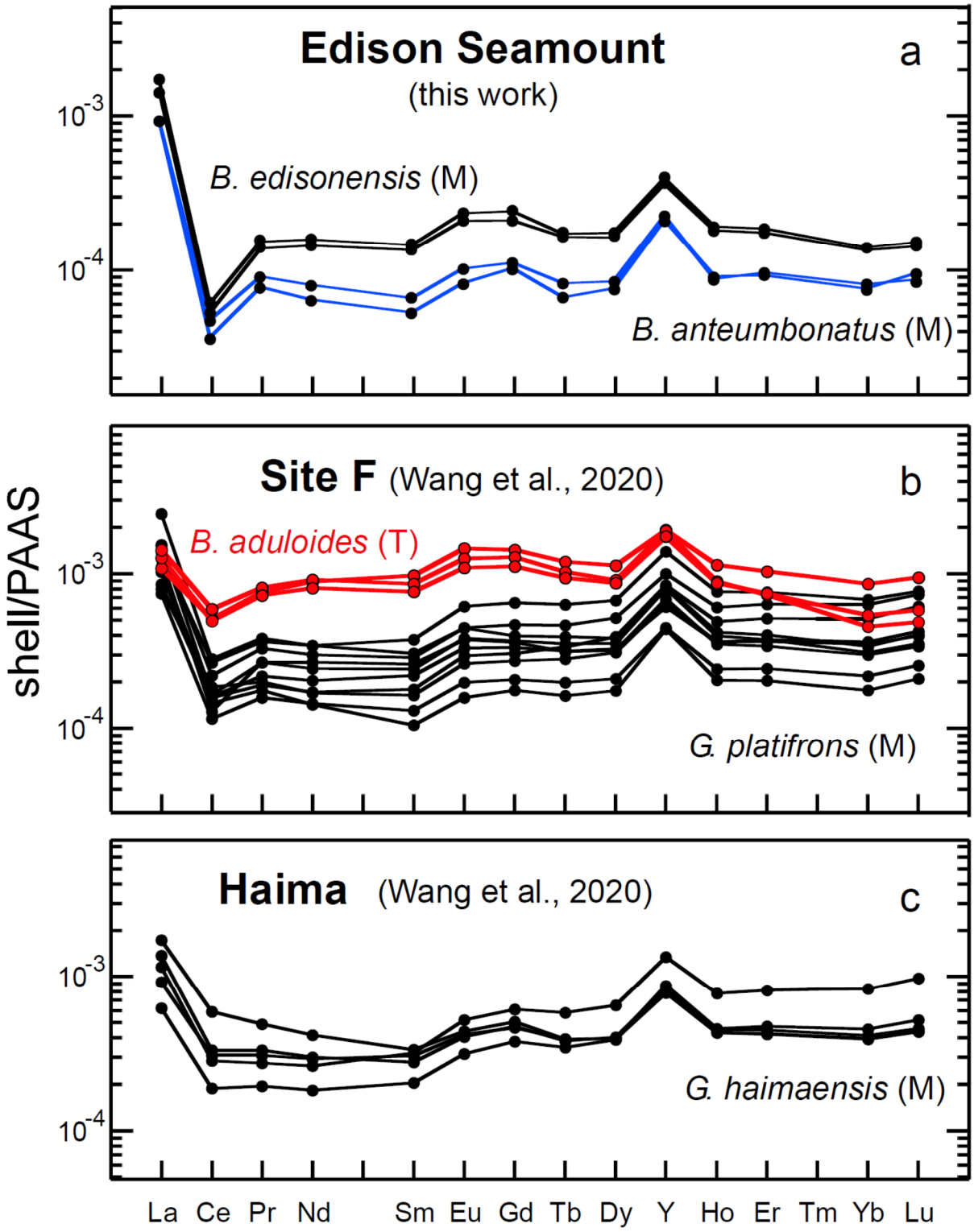

Figure 4. PAAS-normalized REY patterns for mussel shells from cold seeps located in the China Sea (site F and Haima, Wang et al., 2020), and from Edison Seamount (this work). *Bathymodiolus aduloides* mussels are thiotrophic (T). The others are methanotrophic (M).

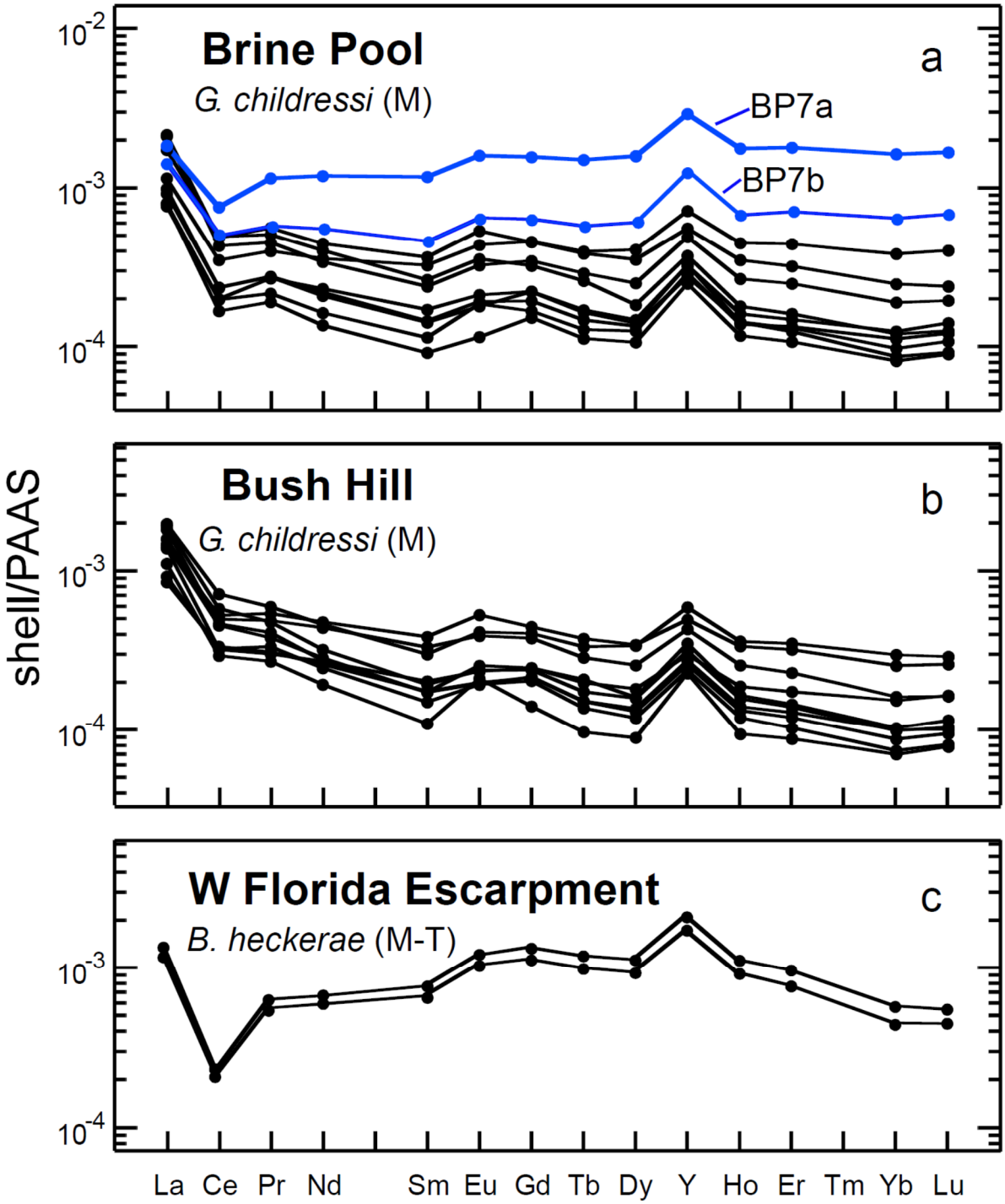

Figure 5. PAAS-normalized REY patterns for mussel shells from the Gulf of Mexico (M: methanotrophic; T: thiotrophic).

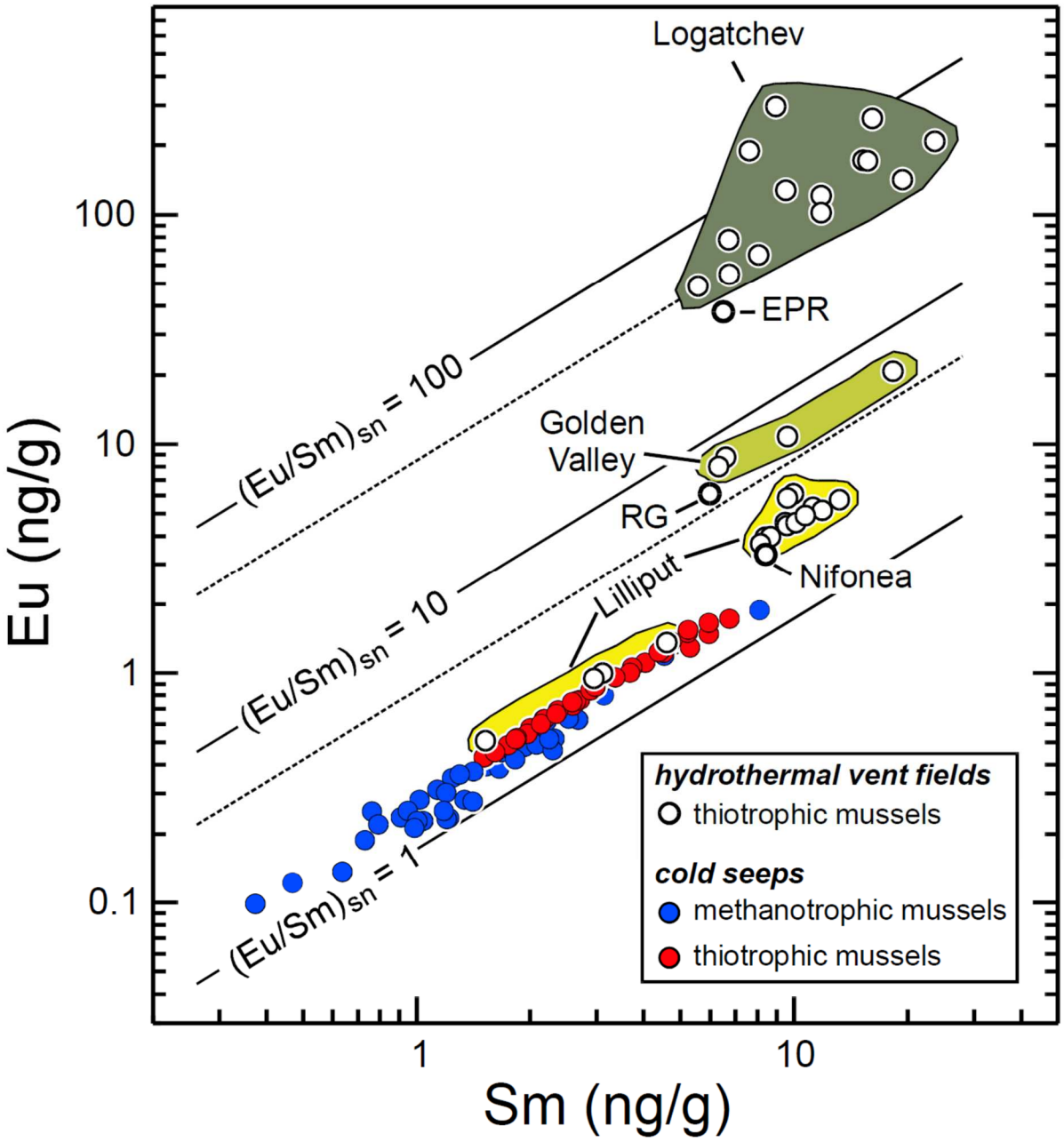

Figure 6. Eu vs. Sm plot for mussel shells from hydrothermal vents and cold seeps (data from Bau et al., 2010, Wang et al., 2020, and this study).

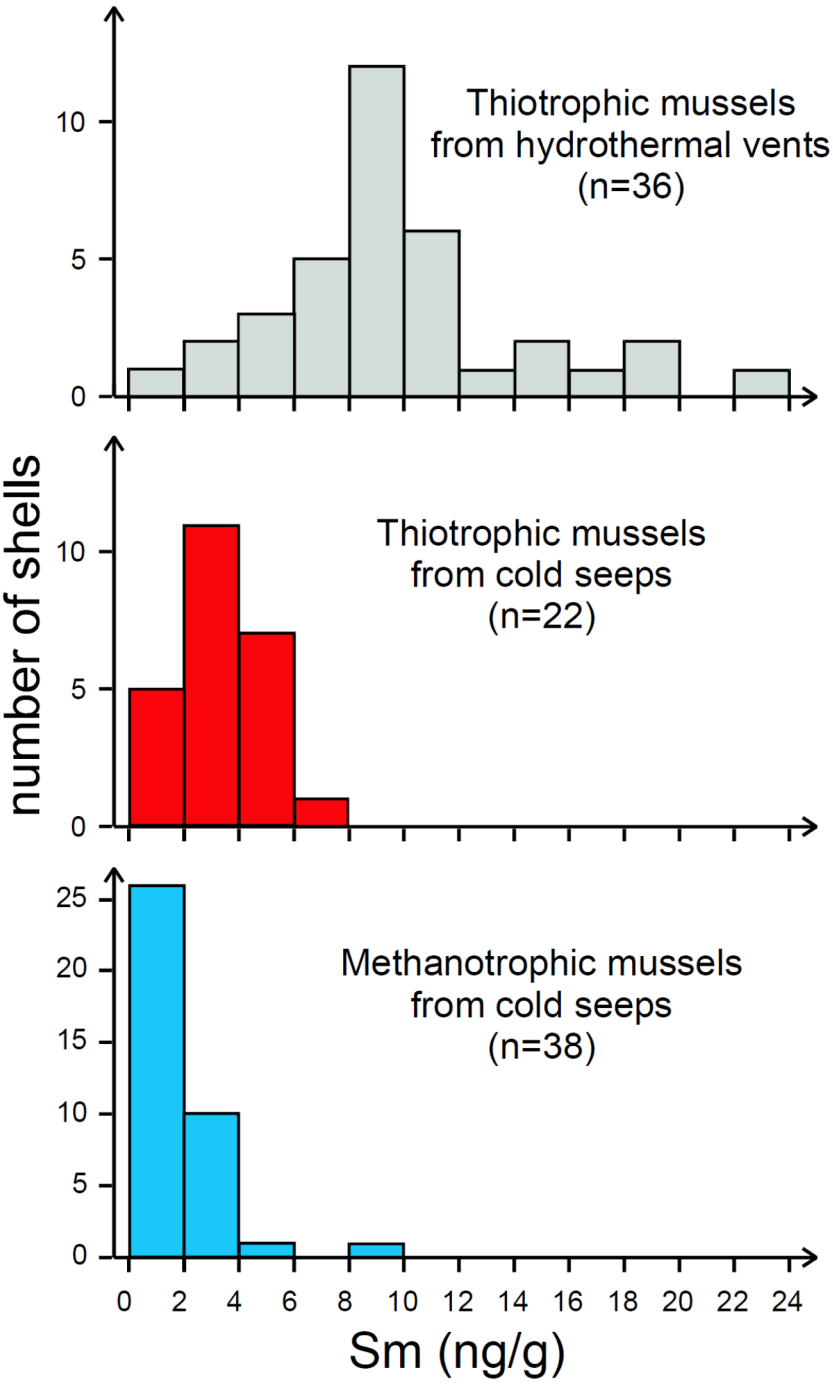

Figure 7. Histograms of Sm abundances in mussel shells from hydrothermal vents and cold seeps (data from Bau et al., 2010, Wang et al., 2020, and this study). When two fragments of the same shell were analyzed, we used their average here.

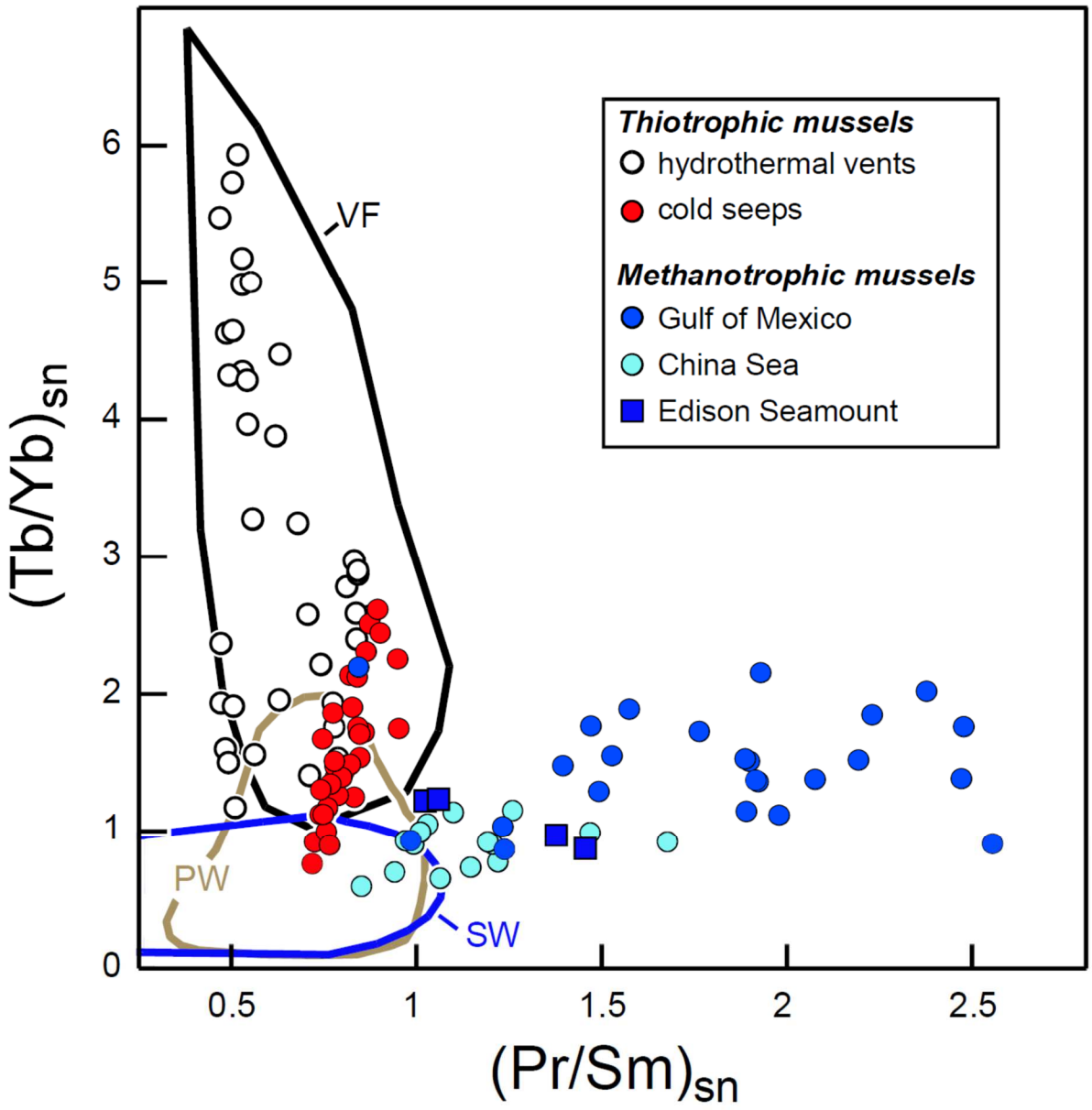

Figure 8. $(Tb/Yb)_{sn}$ vs. $(Pr/Sm)_{sn}$ plot for mussels shells (data from Bau et al., 2010, Wang et al., 2020, and this study). Fields for seawater (SW), pore waters (PW) and vent fluids (VF) are drawn from a database of results of the literature (see Bayon et al. (2020b) for the references for seawaters and pore waters, and Bau and Dulski (1999, Douville et al. (1999), Schmidt et al. (2007, 2017), Craddock et al. (2010), and Cole et al. (2014) for vent fluids).

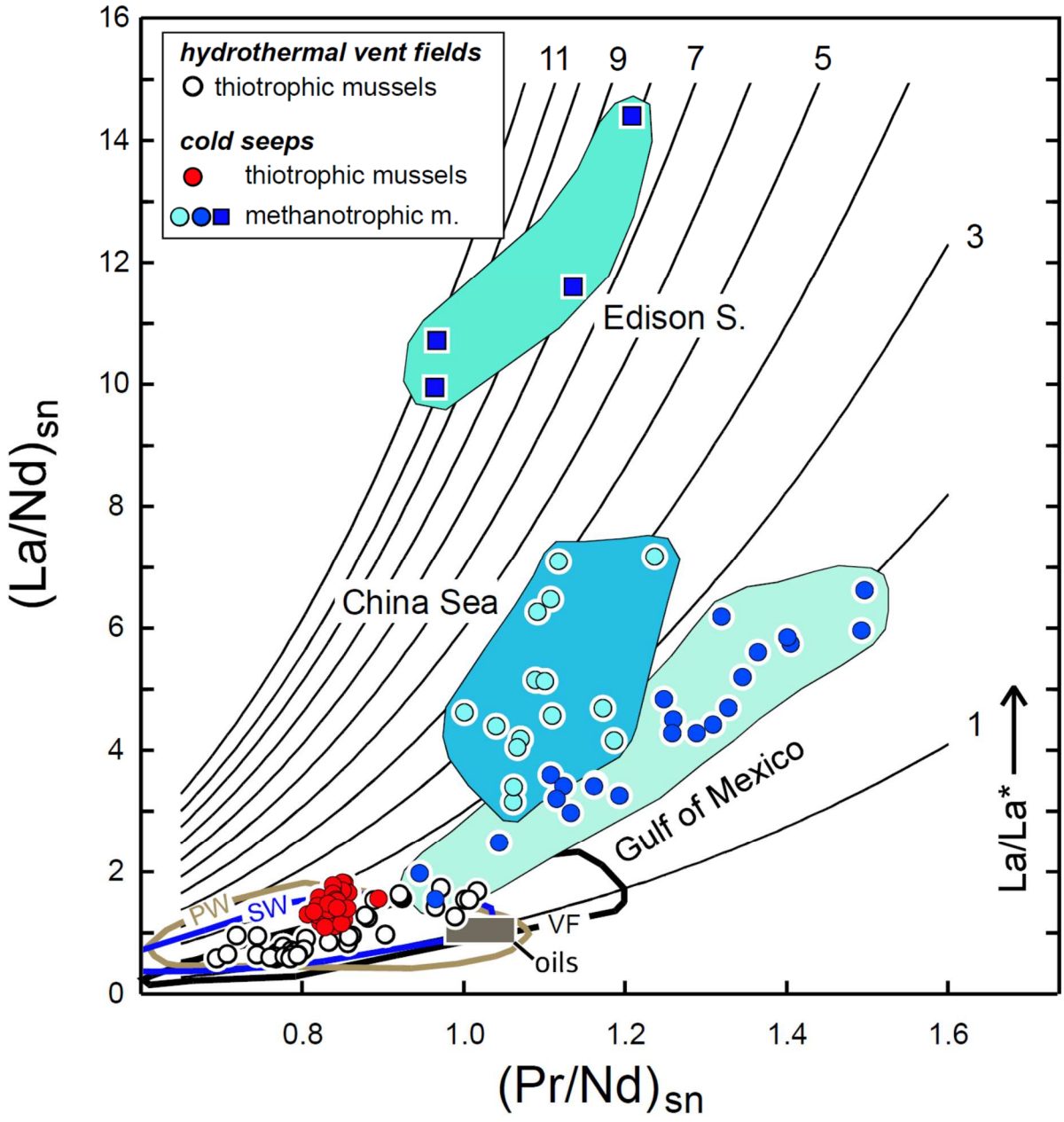

Figure 9. $(La/Nd)_{sn}$ vs. $(Pr/Nd)_{sn}$ plot for mussels (data from Bau et al., 2010, Wang et al., 2020, and this study). Fields for seawater (SW), pore waters (PW) and vent fluids (VF) are drawn from a database of results of the literature (see figure 8 for the references). Oils from seeps from the southern Gulf of Mexico are shown for comparison (Smrzka et al., 2019).

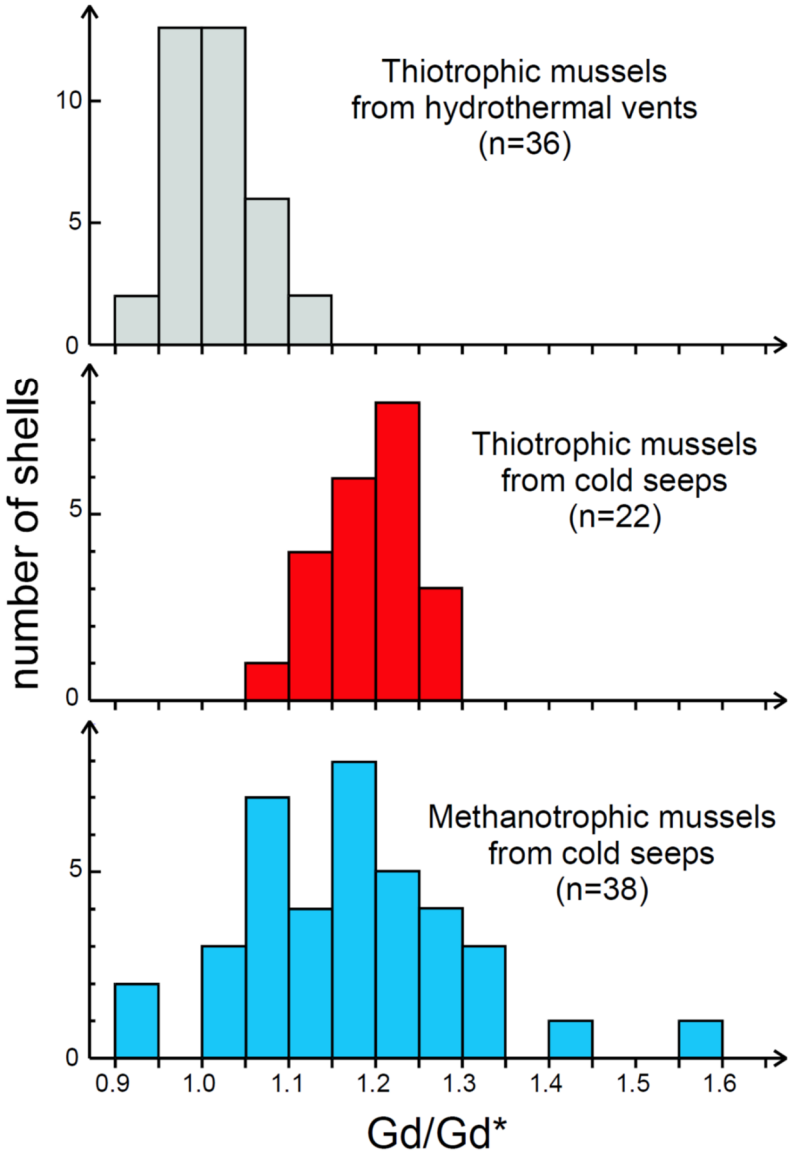

Figure 10. Histograms of Gd/Gd* ratios in mussels shells from hydrothermal vents and cold seeps (data from Bau et al., 2010, Wang et al., 2020, and this study). When two fragments of the same shell were analyzed, we used their average here.