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Trace element variations in mussels' shells from continent to sea: The St. Lawrence system, Canada

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Abstract :

Rare Earth Elements (REE) and several trace elements abundances in mussel's shells collected along the St. Lawrence River, the Estuary, and the Gulf of St. Lawrence (EGSL) reveal coherent chemical variations, with a sharp contrast between freshwater and seawater bivalves. In freshwater mussel's shells, Rare Earth Elements and Y (REY) patterns are rather flat. Their Mn and Ba concentrations are higher than those of EGSL mussel shells, which are much richer in Sr. Shale-normalized REY abundances in mussel's shells from the EGSL show positive anomalies in La and Y and well-marked negative anomalies in Ce, reflecting those of seawater. Prince Edward Island shells show light REE depletion relative to PAAS, positive La and Y anomalies, and negative Ce anomalies. Our data confirm the lack of detectable Gd pollution in the St. Lawrence River and in the EGSL, as well as Pb pollution at the mouth of the Saguenay Fjord and near Rimouski.

Highlights

► Freshwater and seawater mussel's shells display distinct trace elements concentrations and rare earth elements patterns. ► Trace elements and rare earth elements in shells reflect their concentration in water. ► No Gd pollution was detected in mussel's shells from the St. Lawrence River, Estuary and Gulf. ► Mussel's shells may be used as tracers for local pollution in heavy metals.

Keywords : Rare earth elements, Trace elements, Estuary, Bivalve, Shell, Environmental proxy, Pollution

1. Introduction

Bivalves' shells ability to record physicochemical water changes in fresh (e.g. Merschel & Bau, 2015), estuarine (e.g Gillikin et al., 2006) and seawater (e.g Ponnurangam et al., 2016, Akagi et al., 2017 ; Le Goff et al., 2019) has made them useful bioarchives. Mussels are sessile filter-feeding species ubiquitous in diverse aquatic environments and have been used as ecological bioindicators for decades (Goldberg, 1975; Beyer et al., 2017), as they are able to monitor specific pollution such as heavy metals (Puente et al., 1996) or trace elements (Vander Putten et al., 2000). More recently, their ability to record Rare Earth Elements and Yttrium (REY) signatures in soft tissues (Wang et al., 2022) and shells (Ponnurangam et al., 2016; Wang et al., 2020; Barrat et al., 2022 Castro et al., 2023) have made them effective proxies of this particular geochemical group. Specific speciation of trace elements and REY in water and their partition in carbonate shells can be used to monitor trace element and REY environmental behavior (e.g., Le Goff et al. 2019).

The St. Lawrence is a complex system (Fig. 1) that extends over more than 1200 km, encompassing the St. Lawrence River, the St. Lawrence Estuary, and St. Lawrence Gulf

(EGSL). The St. Lawrence River is the primary drainage outflow of the Great Lakes Basin. According to the estuary definition given by Pritchard (1967), the estuary section extends from Québec city to Pointe-des-Monts, where the estuary opens to the Gulf. Its magnitude and specificities such as the seasonality dominated by an ice-covered winter have makes it a particularly relevant site to study large scale processes.

This study assesses the Rare Earth Elements (REE) and other few trace elements (Ba, Cu, P, Mn, Pb, Sr, Co, Zn, V, Rb and Y) in shells of living mussels along the St. Lawrence River, Estuary and Gulf continuum. Our aim is to evaluate trace elements and REE specific signature in mussels' shells along a river to ocean continuum, and to detect specific pollution such as Gd or Pb pollution.

2. Material and Methods

Mussels were collected alive in the intertidal zone between June and October 2022 along the St. Lawrence system at 23 sampling sites. The sampling was partitioned into 7 river stations located between the upstream of Montreal and Québec city and 16 estuarine and marine stations. As the maximum turbidity zone (MTZ) occurring between Orleans Island and Coudres Island doesn't provide optimum ecological features/settings for mussel ecology, the other sampling sites were located in estuarine and seawater area, between the Saguenay fjord and Gaspé Bay, with one open water station located in the Prince Edward Island.

Different species of freshwater mussels were sampled, such as *Elliptio complanata*, *Elliptio crassidens*, *Lampsilis siliquoidea*, *Lampsilis ovata* and *Ligumia recta*. In seawater, *Mytilus edulis* or *Mytilus trossulus* were sampled but cannot be specifically recognized without genetic analyses. Therefore, seawater mussels in this study are referred as *Mytilus. spp*.

For each site, 2 or 3 mussels of the same size class (5± 0.5 cm) were sampled at the same place and stored on ice until the separation of the shell from the soft tissues. A total of 44 samples were finally selected for analysis.

Species were identified on the basis of shell morphology. Shells were cleaned out of impurities by polishing both the inner and outer sides. Only one shell fragment (up to 5 mm, 200-300 mg) located on the margin of the shell was collected, in order to select the most recent part of the shell.

Trace element concentrations were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using well-established procedures. Each sample was spiked with a solution of pure Tm (Barrat et al., 1996) and digested in a Teflon beaker by $2NHNO_3$. An aliquot of the sample solution containing the equivalent of 4 mg of sample was dried and the residue was taken up in 4 ml of 2.5% 2N HNO_3 before analysis (e.g., Wang et al., 2020; Barrat et al., 2023b). Concentrations of REE, V, Cr, Mn, Co, Cu, Zn, Sr, Y, Ba and Pb were determined using a Thermo Scientific ELEMENT XR™ spectrometer located at the "Pôle Spectrometrie Ocean", Institut Universitaire Européen de la Mer (IUEM), Plouzané. Each solution was analyzed in triplicate, and the results were averaged. Fresh water mussels are rich in Ba, and the interferences generated by this element were too large to be accurately corrected using this procedure. We thus used another aliquot of the sample solution, containing the equivalent of 100 mg of sample, and REEs and Y were separated from matrix elements and Ba, and concentrated before analysis using ion-exchange chromatographic columns loaded with about 1 ml DGA-Normal resin (DN-B50-S, 50-100 µm, produced by Triskem®) following the procedure developed by Barrat et al. (2020). Results on two carbonate standards (CAL-S and BEAN) obtained during the sessions are compared with literature values in Table S1. Based on standards and various replicates, the precisions (RSD) for concentrations and element ratios are better than 5 %.

For the normalisation of the concentrations, we use the Post Archean Australian Shale (PAAS) average obtained by Pourmand et al. (2012), adjusted to standard results obtained in our laboratory (Barrat et al., 2020). The La, Ce, and Gd anomalies are calculated using the La/La*, Ce/Ce*, Gd/Gd* ratios, where X* is the extrapolated concentrations for a smooth PAAS-normalised REE pattern and X_{SN} is the concentration of element X normalised to PAAS: $La_{SN}^* = Pr_{SN}^3/Nd_{SN}^2$, $Ce_{SN}^* = Pr_{SN}^2/Nd_{SN}$, $Gd_{SN}^* = Sm_{SN}^{1/3} \times Tb_{SN}^{2/3}$ (e.g., Le Goff et al., 2019; Barrat et al., 2023a). All the data obtained during the course of this study are given in Table S-1.

3. Results

The 44 analyzed shells composition in trace elements and REY patterns display significative differences between freshwater and seawater locations. Concentration of rare earth elements and trace elements are given in supplementary material.

The PAAS normalized REY in freshwater shells (Fig. 2) display a PAAS-like pattern, which is species independent. The highest concentration difference ranges between the two stations located upstream of Montreal, namely St. Lawrence River (station 2) and Ottawa

River (station 1). Abundances ranges from 10^{-4} to 3.10^{-3} the PAAS concentrations (Fig. 2a). The REY patterns are rather flat with no significant anomalies or specific partitioning of REY, either than a small heavy REE depletion (Tb_{SN}/Yb_{SN} = 1.08 – 1.65).

PAAS normalized REY patterns in estuarine and seawater shells from sites 8 to 22 (Fig. 2a,c) both display typical seawater signature, with positive La anomalies (La/La* = 1.58 – 2.96), positive Y anomalies (Y/Ho = 29.1 – 69.6), negative Ce anomalies (Ce/Ce* = 0.47 – 1.02) and with a marked but variable depletion in heavy REE (Tb_{SN}/Yb_{SN} = 1.86 – 5.53). Abundances are rather low, ranging from 10^{-4} to 10^{-2} the PAAS concentrations and span over a relatively narrow variation range. All shells present a small Gd anomaly (1.09 – 1.50), which slightly increases seaward. Similar REY patterns had been reported for marine mussels' shells (Ponnurangam et al., 2016; Wang et al., 2020; Castro et al., 2023). Shells from station 23 display a different REY pattern that clearly stands out from the others. The mussels' shells display less enriched REE content relative to PAAS (station 8 to 22: La = 0.066 – 0.339 µg/g, station 23: La = 0.01 µg/g) (Fig.2c) with more marked Ce and La anomalies, together with an enrichment in light REE (station 8 to 22: Pr_{SN}/Gd_{SN} = 0.65 – 1.2, station 23: Pr_{SN}/Gd_{SN} = 0.23 – 0.25).

Trace elements abundances are consistent between shells located in the same zone and show different patterns along the continuum. Some elements, such as Co, Zn, V, Cr or Sc, do not show significant variation in concentration along the continuum (figure in supplement), contrary to Ba, Cu, Pb, Mn, P or Sr that display strong differences in concentration between freshwater and seawater mussels' shells (Fig. 3).

4. Discussion

4.1. Freshwater vs. seawater signatures recorded in shells

4.1.1. REE and Yttrium

a. Comparison with waters

Unlike many other rivers, the waters of the St. Lawrence River do not display noticeable REY fractionations (Dang et al., 2022b), but can show interannual variations of REE concentrations associated with hydrological events (Lafrenière et al., 2023). REEs were measured in the waters of the St. Lawrence by Dang and other Quebecers. Dang et al (2022b) obtained for some samples very pronounced positive Eu anomalies. These are very strongly correlated with the Ba/Sm ratios (not shown), indicating unambiguously that they should be considered as analytical artifacts related to isobaric BaO interferences, which are a well-known problem in ICP-MS for Ba-rich, REE-poor samples. Apart from these artifacts, the waters of the Saint-Lawrence River do not display large REY fractionations (Dang et al., 2022a; Lafrenière et al., 2023). Freshwater shells REY patterns are coherent with REY patterns in water, regardless of the mussels' species (Fig. 2a), but display rather unfractionated heavy REE abundances compared to seawater shells (freshwater shells: Tb_{SN}/Yb_{SN} =1.08 - 1.64, seawater shells: Tb_{SN}/Yb_{SN} = 1.85 - 5.3, Fig. 5a).

In EGSL water, REY display heavy REE enrichments relative to light REE and La and Ce anomalies (Dang et al., 2022a). REY patterns in shells are consistent with REY patterns in water (Fig. 4,6). The La, Ce and Y anomalies found in shells (Fig. 4) reflect the mixing behavior of water masses, as the water composition of the estuary itself is primarily controlled by the mixing of freshwater from the St. Lawrence River and seawater from the Gulf of St. Lawrence (Galbraith, 2006).

Shells from both estuary and gulf display similar REY patterns (Fig. 2b, c), that exhibit seawater features. Strong positive La and Y anomalies reflect a typical seawater signature, as well as negative Ce anomaly (Elderfield, 1988). Such anomalies are usual features for seawater bivalves' shells (e.g., Ponnurangam et al., 2016; Akagi and Edanami, 2017; Le Goff et al, 2019 ; Mouchi et al., 2020). Lanthanum anomalies in shells mirror those in water, increasing seaward with a sharp shift between freshwater and seawater shells (Fig. 6c). The origin of La anomalies in seawater are still not well understood but are probably related to the higher stability of La in solution compared to light REE (De Baar, 1985). Estuarine and gulf shells also display Y/Ho marine ratio between 44 and 74 (Fig.6c). These anomalies originate from active differential fractionation process between Y and the lanthanide series in low salinity region (Lawrence & Kamber, 2006), that had been observed in waters of the St. Lawrence Estuary (Dang et al., 2022a). Cerium anomalies display a linear evolution in shells with longitude, reflecting the Ce/Ce* in water (Fig. 6a). As a redox sensitive element, Ce can be oxidized in either Ce(III) or Ce(IV) (Sholkovitz & Schneider, 1991), displaying negative Ce anomaly in modern seawater (Elderfield et al., 1990), that can be used as geochemical proxy (German & Elderfield, 1990).

Mussels' shells from Prince Edward Island display different REY patterns (Fig.2c, 5b, 6b), reflecting a distinct water mass. They display enrichment in Sm, Eu, Gd and Tb, represented with a low Pr_{SN}/Sm_{SN} ratio of 0.49 (Fig. 4b), an overall less enriched REY abundances, lower by one order of magnitude (Fig. 2c, Fig. 5), as well as marked La and Ce anomalies (La/La*=2.78 –2.96, Ce/Ce*=0.47 – 0.55). Similar features were measured by Dang et al. (2022a) in some seawaters in the oriental part of the EGSL (station P23 in Dang et al. (2022a), La/La*=3.51, (Pr_{SN}/Sm_{SN}= 0.49). Surface water circulation and chemistry near Prince Edward Island are completely different from those occurring in the estuary and Gulf (Saucier, 2003), explaining radically different REY patterns in shells.

b. Vitals effects

REY patterns in freshwater mussels remain highly similar to each other, regardless of the species and along all the river section of the St. Lawrence. These similarities indicate that species-dependent vital effects play a lighter role than water chemistry for REY in these shells. However, this conclusion should not be extended to all mussel species, since REE are necessary elements for some abyssal mussels, whose enzymatic activities can significantly fractionate light REE (Wang et al., 2020; Barrat et al., 2022).

REE sources as well as incorporation processes in shells are still debated. Phytoplankton represents a potential source of REE in shells, as mussels are water filter-feeders. REE abundances in phytoplankton from the St. Lawrence Estuary display surprising features such as marked negative Eu and Y anomalies (Eu/Eu*= 0.6-0.8, Y/Ho = 0.4 – 0.8), and no Ce nor La anomalies (Dang et al., 2023). These results are at odd with REE patterns in waters (Dang et al., 2022a). Additional works are necessary to confirm these results and are beyond the scope of this paper.

4.1.2. Other elements in shells

Trace element behavior and geochemistry in estuaries were extensively studied (e.g., Zhang 1995, Millward 1995, Smrzka et al., 2019 among many others), including in the St. Lawrence (Yeats & Loring, 1991). It is well known that seawater exhibit higher concentrations of Sr and V and lower concentrations of Cr, Co, Ba, Mn, Pb, Cu and Zn than river waters (Millot et al., 2003; Florence, 1980). Multiple trace elements, such as Co, Zn, V, and Rb, do not show abundances variation in shells along the St. Lawrence system (supplementary Table S-1). However, Ba, Rb, P, Mn, Pb or Sr display strong differences between freshwater and seawater shells (Fig. 3). Different composition patterns occur upstream and downstream of the maximum turbidity zone, which also corresponds to the sharp salinity shift zone. No shell can be found in the maximum turbidity zone, as environmental settings, such as suspended particulate matter or salinity shift, don't provide optimal conditions for bivalves settling. The estuarine turbidity maximum is known to play a crucial role in particulate and dissolved metal distributions (Cossa & Poulet, 1978; Gobeil et al., 1981). The brutal drop of Ba and Mn concentration in shells between freshwater and seawater (Fig. 3a, d) reflects the drop of Ba and Mn concentrations in water. Mn concentration in the St. Lawrence River is 100-150 times higher than those in seawater (Bewers & Yeats, 1978), and different mechanisms including sorption to particles and colloidal precipitation and destabilization remove dissolved Ba and Mn from in estuaries (Coffey at al., 1997; Sholkovitz E.R., 1978). Similar processes were observed elsewhere for *M. edulis* shells, which contain Ba in proportion to the water in which they grow (Gillikin et al., 2006). The Sr and P concentrations in shells seem to gradually increase seaward (Fig. 3e, f), reflecting usual trace elements variations in St. Lawrence Estuary (Lucotte 1989; Wadleigh et al., 1985). Naturally less concentrated trace elements in water, such as V, Cr, Co, Cu, or Zn (Martin and Meybeck, 1979), show little variations of concentration in mussels' shells along the continuum (supplementary Table S-1).

4.2. Pollution

4.2.1. REE

REY are emerging pollutants (Brewer et al., 2022), whose increasing use in diverse modern technologies raise the concern of their toxicity for aquatic environments and living compartment (Gonzalez et al., 2014). Among these elements, La, Sm pollution has already been described in the waters of major German rivers (Kulaksız & Bau, 2013). However, the data we have obtained show no anomalies in La and Sm that might suggest pollution for these elements.

More generally, a Gd pollution is observed in most industrialized and densely populated areas (Bau and Dulski 1996; Le Goff et al., 2019; Hatje et al., 2016; Castro et al., 2023). This Gd pollution is unquestionably linked to medical imaging. In MRI, patients who are injected with Gd-based contrast agents (GBCA), will quickly eliminate it (through urine) after the examination (Kümmerer & Helmers, 2000). These molecules (chelates) receive no efficient treatment from wastewater treatment plants (Möller et al., 2000), ending up in river water and then in coastal areas. Around 900 kg/year of Gd are used in our study area year (Dang, et al., 2022a). Positive Gd anomalies in the waters of Lake Erie, Lake Ontario or Niagara Falls (Bau et al., 2006) show that medical activities could be leaving an imprint in the waters of the EGSL. Surprisingly, this Gd pollution is not found in the St. Lawrence water

(Dang et al., 2022a) nor in mussels' shells (this study). This spatial distribution of the Gd positive anomaly is assumed to be essentially controlled by strong mixing of water-masses, and consequently by a dilution effect (Yeats & Loring, 1991). The small positive anomalies (Gd/Gd*=1.1-1.6) displayed by seawater mussels' shells probably reflect pristine abundances (Bau et al., 1999), rather than pollution.

4.2.2. Lead

Mussels are able to concentrate lead in their shells (Sturesson, 1976). Here, a few shells show Pb abundances higher than 0.2 µg/g (Fig. 3c). They were sampled at the mouth of the Saguenay Fjord (station 9), and near Rimouski (stations 12 and 14). Saguenay Fjord is known for its lead pollution (Cossa and Poulet, 1978; Cossa et al, 1990). For the Rimouski area, the pollution could be related to the past exploitation of a small Pb deposit located in Saint-Fabien (Beaudoin et al., 1989). In both cases, Pb concentrations in shells are not extremely high, and the impact of this pollution on mollusks should not be overemphasized. Our data illustrate the ability of bivalve shell chemistry to highlight local Pb anomalies, and thus to trace this type of pollution.

5. Conclusion

The study of the chemical composition of mussel shells collected along the St. Lawrence and in the EGSL, over a transect of some 1200 km, has enabled us to compare the chemical characteristics of freshwater mussels with those from estuarine or marine environments. Several important results emerge from our study. Firstly, trace element abundances, including REY, largely reflect the features of the water masses present. We show that samples taken from Montreal to the estuary (over a distance of some 380 km) display the same characteristics, with variable but significant Ba and Mn concentrations, and rather flat PAAS-normalized REY patterns with no La, Ce or Y anomalies. These characteristics contrast sharply with those observed in EGSL mussel shells, which show marked La, Ce and Y anomalies. All EGSL mussels appear to belong to the same chemical group, with the exception of those collected from the easternmost station (Prince Edward Island), which show more pronounced anomalies, but above all a much sharper depletion in light REE compared to PAAS. None of the mussels analyzed, either in the river or in the EGSL, showed Gd anomalies, which could have mirror pollution by contrast agents used for medical imaging. This result contrasts with those of major European rivers (in water and mollusks), particularly in Germany, where large positive Gd anomalies have been reported for almost thirty years

(Bau and Dulski, 1996; Merschel and Bau, 2015). We conclude that this pollution in the St. Lawrence is still negligible, probably due to very significant dilution. On the other hand, occasionally higher Pb concentrations confirm the pollution of some segments of the system with this element, due to industrial (Saguenay Fjord) or extractive (Rimouski) activities. Our study illustrates the potential of bivalve shells for tracing the chemistry of water masses, and specific pollution such as Pb contamination.

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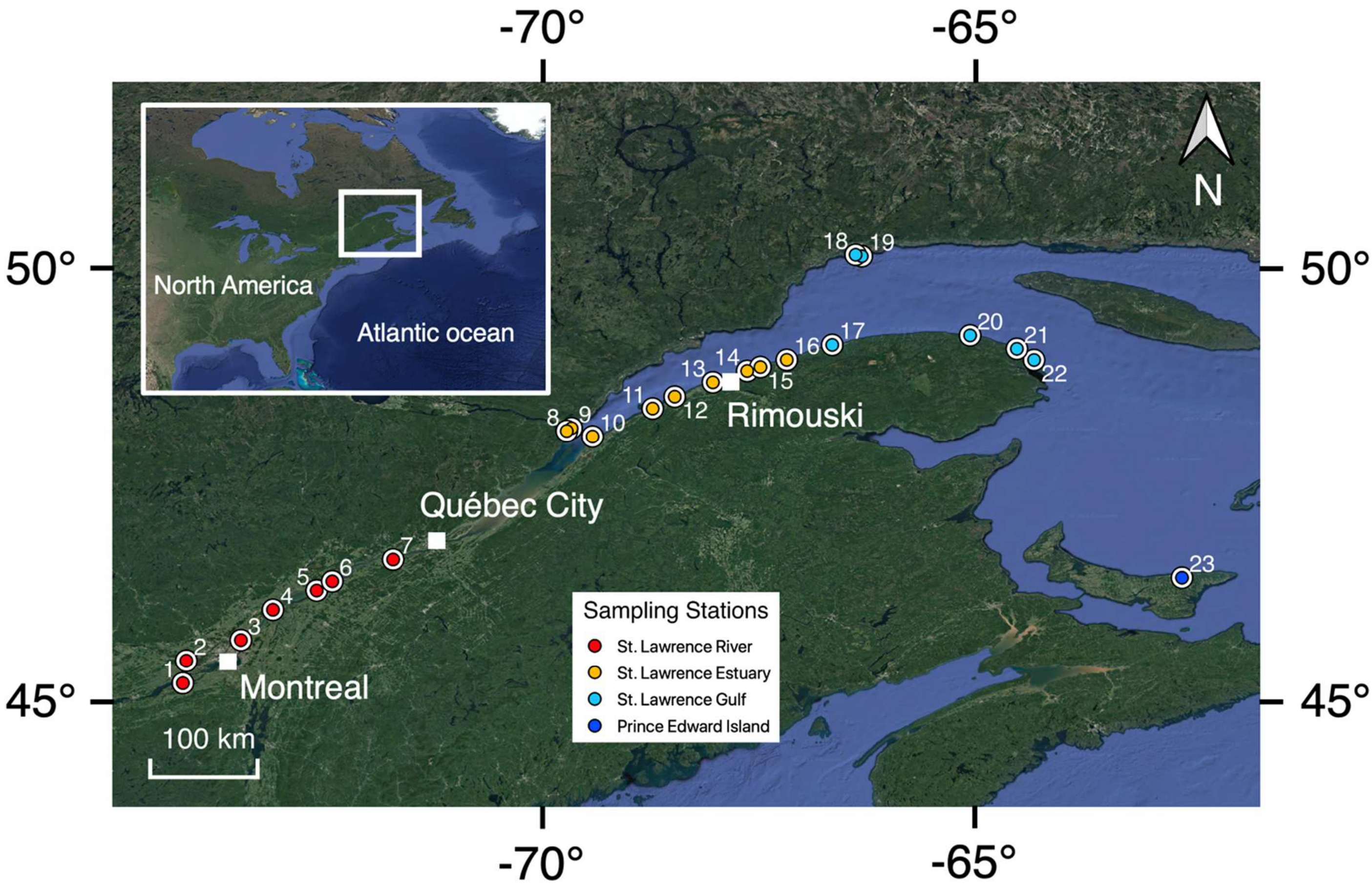


Fig 1: Map of the St. Lawrence River, Golf and Estuary showing the mussels sampling stations (QGIS, Google Maps data view)

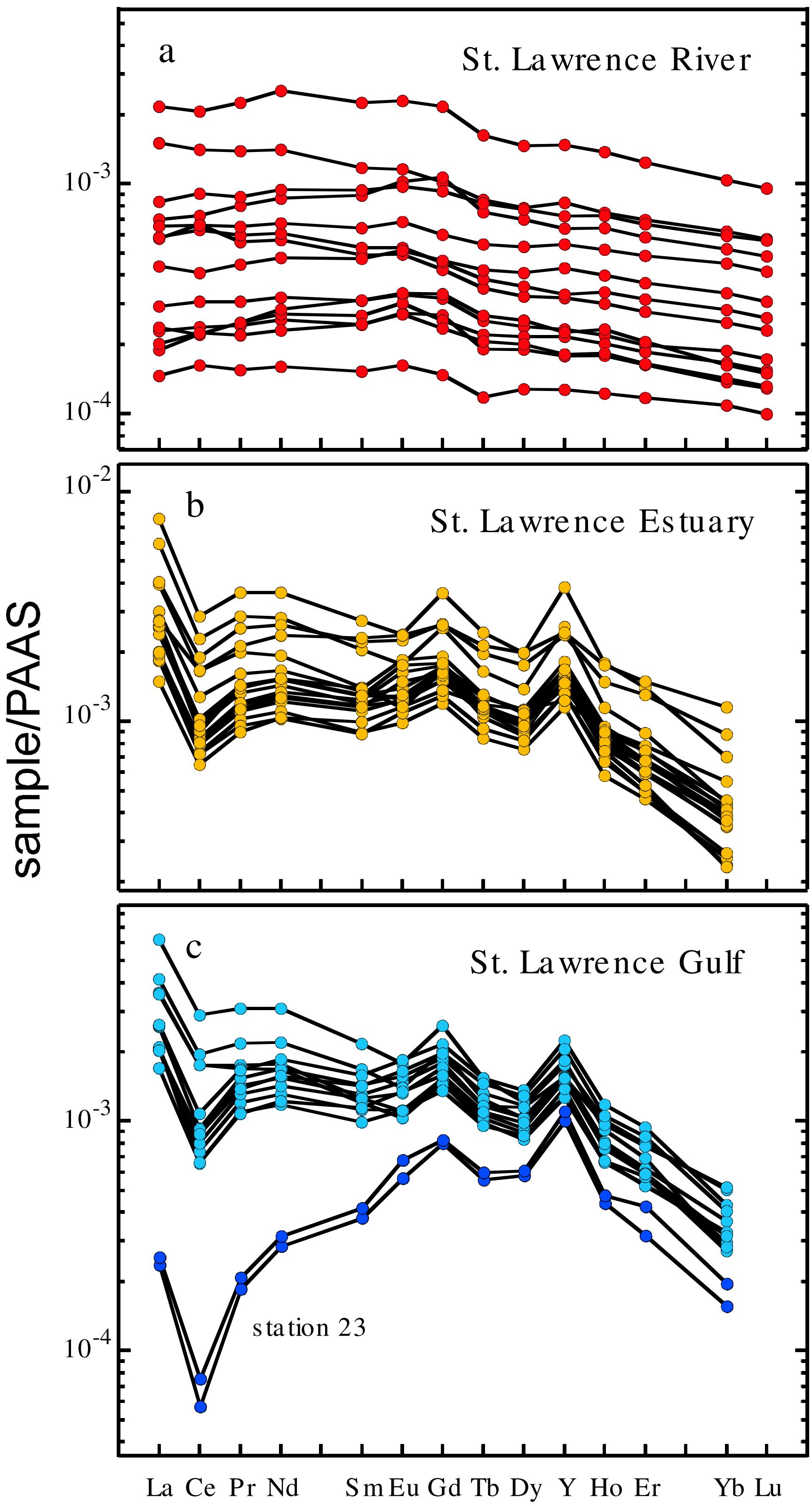


Fig 2: PAAS-normalized REY patterns of in mussels' shells in the St. Lawrence River, Estuary and Gulf.

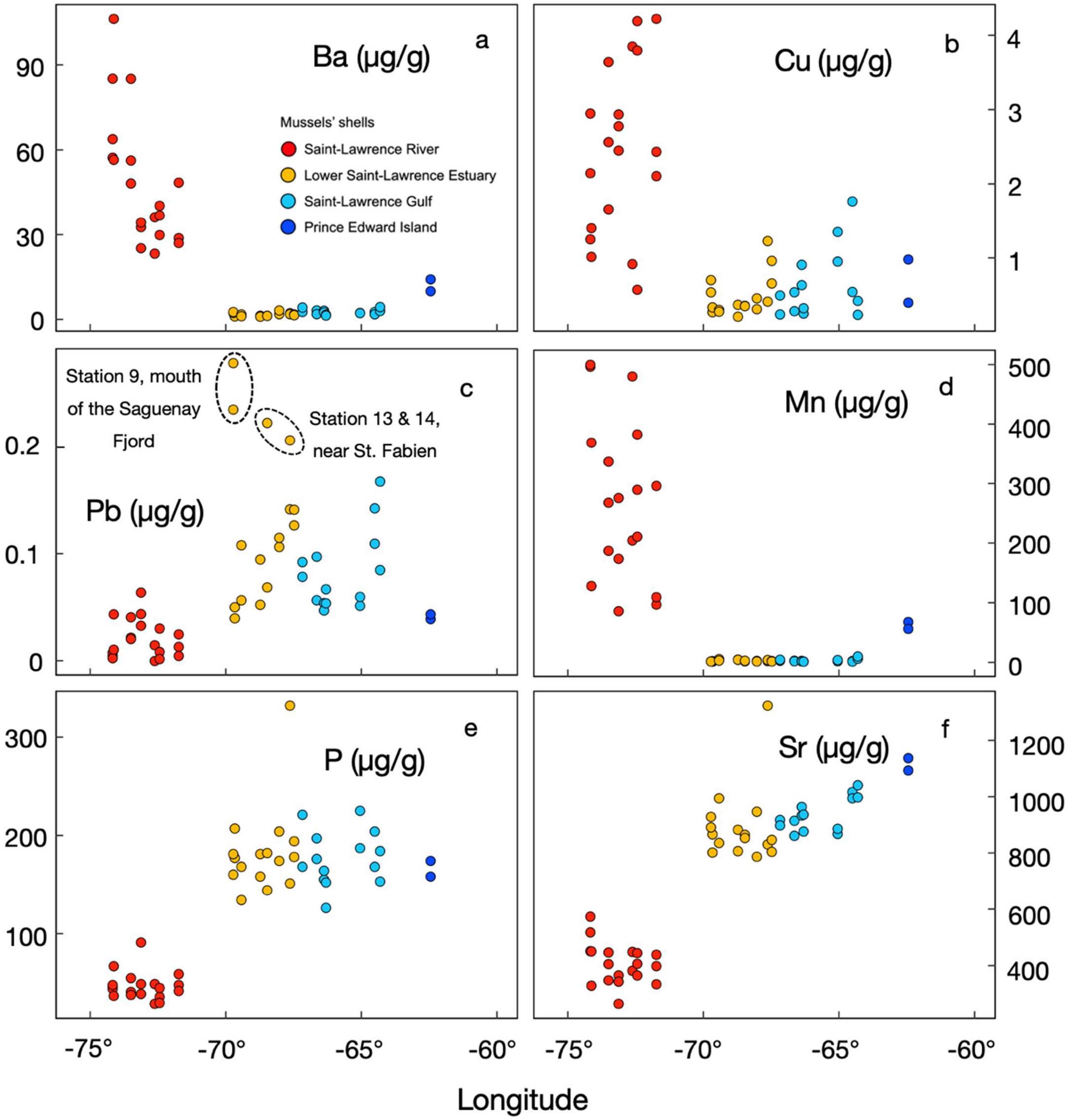


Fig 3. Ba, Cu, Pb, Mn, P and Sr concentrations (in µg/g) in mussels' shells of the St. Lawrence River, Estuary, Gulf and Prince Edward Island.

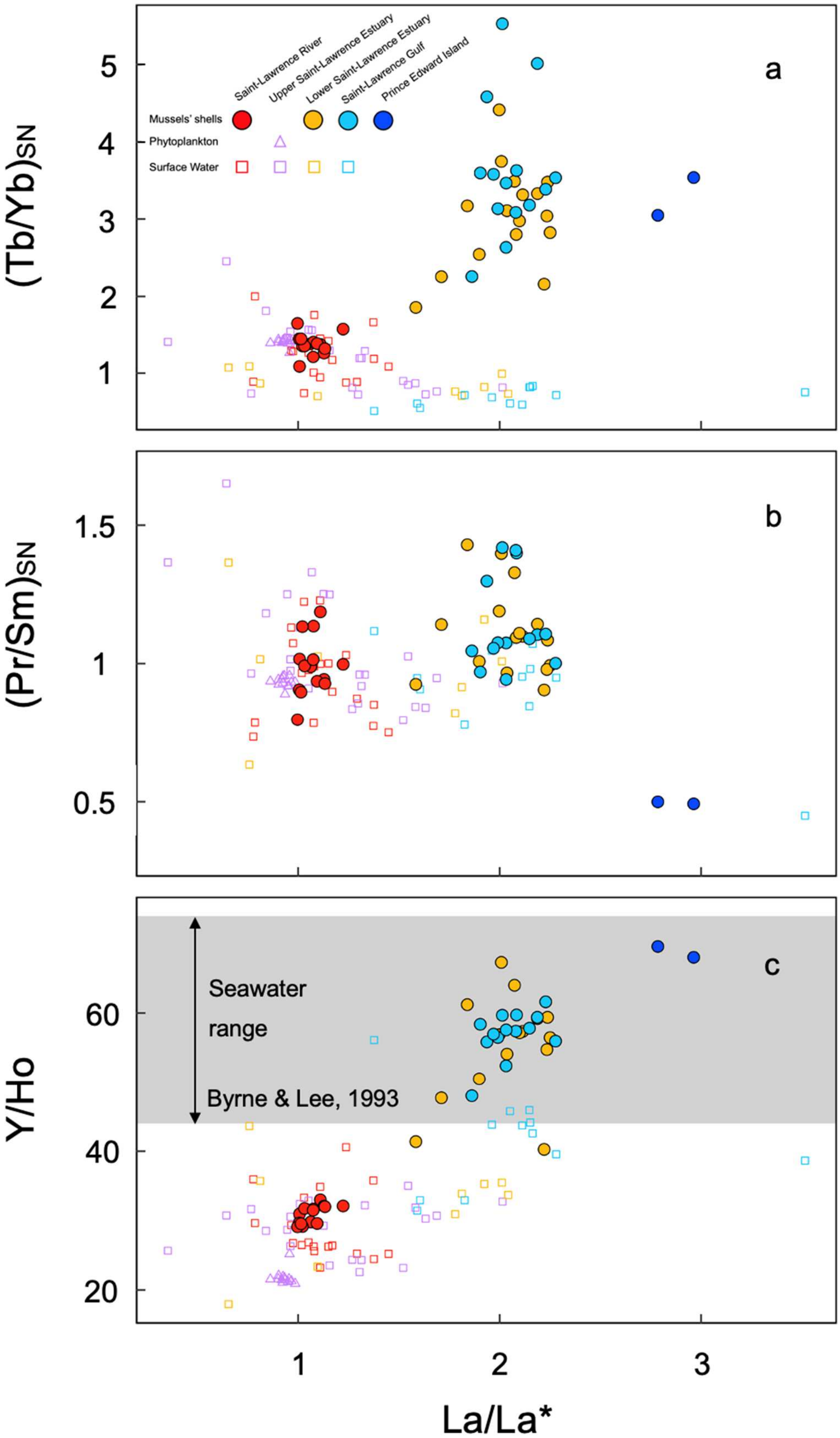
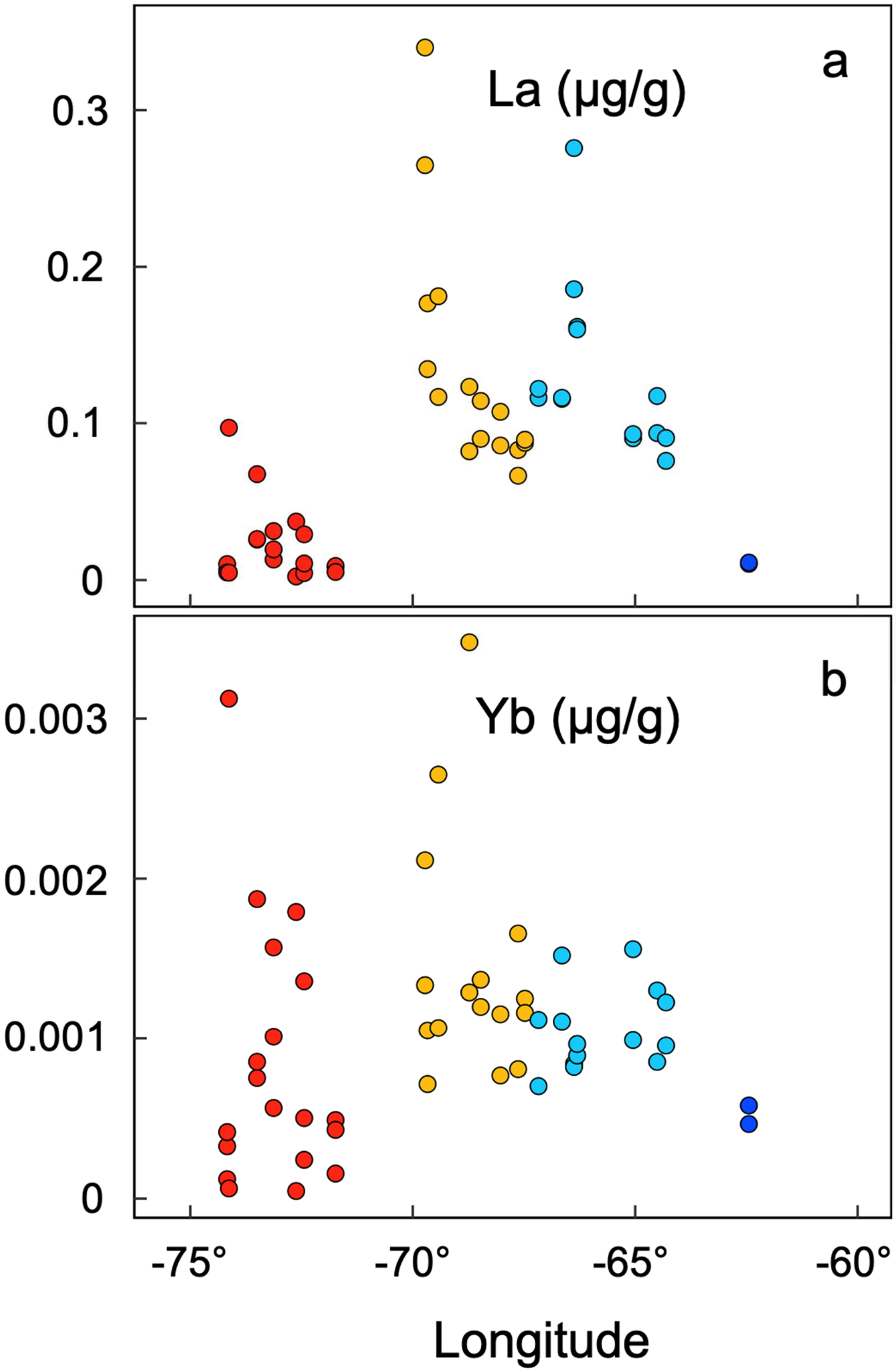


Fig 4. REY ratios relative to La anomalie in mussels' shells, phytoplancton and surface water of the St. Lawrence River, Estuary and Gulf. Data according to Dang et al., (2022a) using surface data only, Dang et al., (2023) using phytoplankton data only and Byrne and Lee (1993).



a
La (µg/g)
0.3
0.2
0.1
0
b
Yb (µg/g)
0.003
0.002
0.001
0
-75°
-70°
-65°
-60°
Longitude

Fig. 5. La and Yb abundances (in µg/g) in mussels' shell of the St. Lawrence River, Estuary, Gulf and Prince Edward Island. Same caption as figure 3.

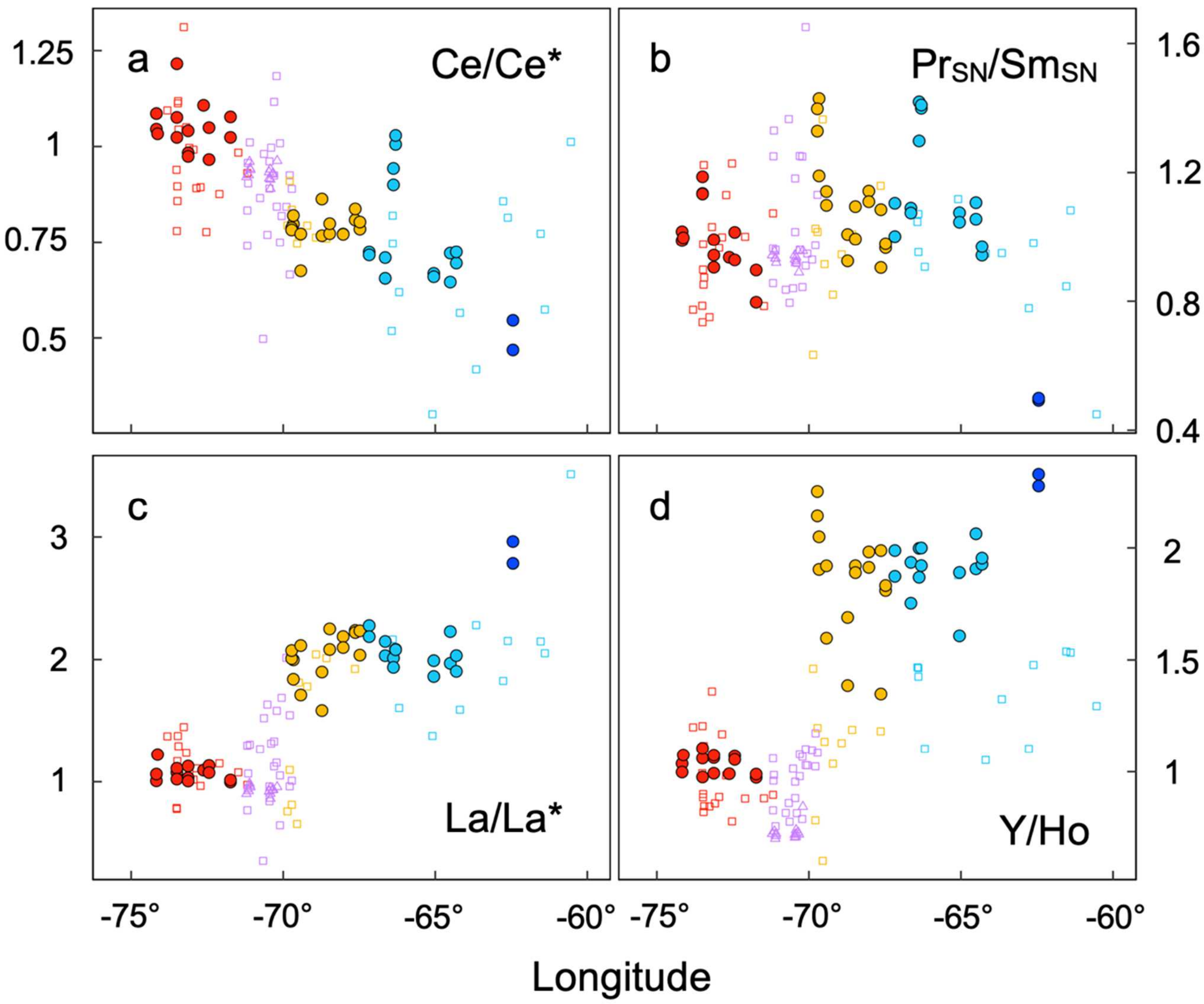


Fig 6. Anomalies in La, Ce and Y, and Pr_{SN}/Sm_{SN} ratio in mussels shells relative to longitude in mussels' shells, phytoplankton and surface water. Data according to Dang et al., (2022a) using surface data only, Dang et al., (2023)using phytoplankton data only and Byrne and Lee (1993). Same caption as figure 4.