Trace elements in coralline algae as a new proxy for seawater chemistry and metal pollution

Barrat Jean-Alix [2, 5, *], Chauvaud Laurent [1], Amice Erwan [1], Grall Jacques [5], Rouget Marie-Laure [3], Bayon Germain [4], Germain Yoan [4]

[1] Univ Brest, CNRS, Ifremer, IRD, LEMAR, Institut Universitaire Européen de la Mer (IUEM), Place Nicolas Copernic, 29280 Plouzané, France
[2] Institut Universitaire de France, Paris, France
[3] Univ Brest, CNRS UMS 3113, Institut Universitaire Européen de la Mer (IUEM), 29280 Plouzané, France
[4] Univ Brest, CNRS, Ifremer, Geo-Ocean, F-29280 Plouzané, France
[5] Univ Brest, CNRS, Ifremer, IRD, LEMAR, Institut Universitaire Européen de la Mer (IUEM), Place Nicolas Copernic, 29280 Plouzané, France

* Corresponding author : Jean-Alix Barrat, email address : barrat@univ-brest.fr

Abstract :

The abundances of some macronutrients, and trace elements (K, Al, P, V, Mn, Co, Ni, Cu, Zn, Rb, Sr, Mo, Cs, Ba, Pb, Th, U, Y and REE) were determined in a series of coralline algae (Lithothamnion corallioides) samples (n = 101) collected alive in the Bay of Brest and the Iroise Sea (Western Brittany, NW France), in order to assess the potential of these algae as archives of seawater chemistry and potential metal pollution. REY patterns are similar in shape to those of local seawater, exhibiting similar La, Ce and Y anomalies, but with abundances ranging between 4 and 5 orders of magnitude higher than seawater values. Variations in La anomalies (La/La* = 1.29–2.08), Y anomalies (Y/Ho = 38.6–55.8), and heavy rare earth enrichments (Prsn/Ersn = 0.22–0.52) are consistent with mixing of seawater with rivers flowing into the Bay of Brest. The behavior of other trace elements, such as Al and Cs, also reflects this mixing. Other parameters and processes can control the abundances of the other elements measured. For example, the presence of organic matter in studied samples controls the abundances of K and Rb. The abundances of base metals (e.g., Co, Ni, Cu) are highly sensitive to the various pollutants present in the Bay of Brest. In particular, the Pb content of coralline algae clearly reflects the pollution caused by mining of a nearby Pb deposit from the 18th to the early 20th century. Our results demonstrate the potential of coralline algae not only for tracing water masses, but also for studying metal pollution.

Graphical abstract
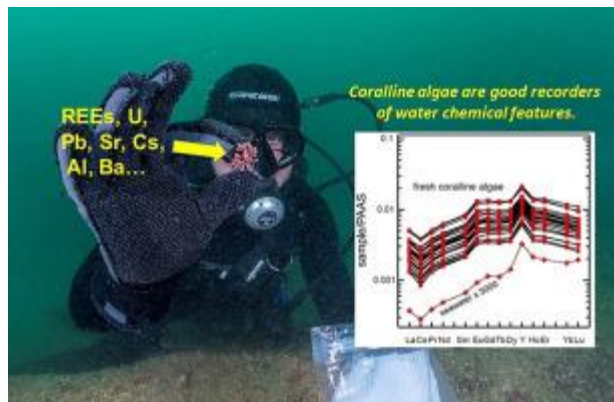
Highlights

► First detailed investigation of rare earth elements in coralline algae. ► Coralline algae bioaccumulate rare earths, yttrium and other trace elements (Sr, Ba, U, Pb…). ► REY distributions in coralline algae and seawater are similar. ► Coralline algae record base metal pollution and river water/seawater mixing.

Keywords : rare earth elements, trace elements, bioaccumulation, pollution, maerl, environmental proxy

1/ Introduction

For more than 50 years, geochemists and biogeochemists have recognized that biogenic carbonates offer a valuable window into the composition of seawater, and their study has been an extremely active research field. The composition of these minerals is largely controlled by the physico-chemical properties of the water from which they have precipitated. Corals and microbialites (i.e. microbially-mediated carbonates), for example, display rare earth element (REE) patterns parallel to those of seawater (e.g., Sholkovitz and Shen, 1995; Webb and Kamber, 2000). The chemical composition of these carbonates records the signature of ambient water masses, which can be used to address various issues related to e.g. pollution (Fallon et al., 2002) or environmental changes (e.g., Wyndham et al., 2004). Moreover, early work on corals, for example, has shown that seawater temperature can be inferred from Sr/Ca ratios (e.g. among many others, Smith et al., 1979; McCulloch et al., 1994; Reynaud et al., 2007). Therefore, biogenic carbonates are generally considered as excellent archives that record long-term environmental changes. Additionally, considerable effort has been made to investigate the suitability of other biogenic carbonates such as foraminifera, fish otoliths, and mollusk shells as archives of past seawater chemistry (e.g., Rosenthal et al., 1997; Bath et al., 2000; Eggins et al., 2003; Immenhauser et al., 2016). Other elements such as e.g. B, Ba, U, Co, Ni, Ti, Mn, have also been investigated as proxies for temperature, salinity, pH, phytoplankton dynamics, dissolved oxygen in seawater (Gillikin et al., 2006; Rollion-Bard et al., 2011; Frieder et al., 2014; Norrie et al., 2018; Poitevin et al., 2022; Schöne et al., 2022). Despite promising results, the ability of trace elements in biogenic carbonate as environmental proxies is not always simple. While it is certain that the incorporation of trace elements by shells or corals is partly controlled by environmental parameters, biological effects (called "vital effects") are of variable magnitude depending on the species involved. Meibom et al (2008) have shown that at the micrometric scale in corals,

trace element abundances display variability far beyond what can be attributed to variations in the marine environment. Furthermore, calibration attempts performed on several bivalve species (e.g., Poulain et al., 2015, Norrie et al., 2018, Wanaker and Gillikin, 2019) as well as systematic study of trace element distributions in shells (e.g., Schöne et al., 2011, 2023, Wang et al., 2020; Barrat et al., 2022a and b, among many others), have shown that physiological processes are determinant at least for some elements, including REEs. All the above-mentioned observations motivate further investigation of other biogenic seawater archives for which vital effects may be less pronounced.

Coralline algae (Corallinales, Sporolithales, Corallinophycidae, and Rhodophyta) also generate significant quantities of Mg-rich calcite (e.g., Kamenos et al., 2015). These algae are ubiquitously distributed worldwide, occurring in coastal waters from polar regions to subtropical environments (e.g., Johansen, 1981). They have been previously studied for their variability in Mg/Ca, Li/Ca, and Sr/Ca ratios as a seawater temperature proxy (Kamenos et al., 2008; Halfar et al., 2008), yielding time series spanning several decades (e.g., Halfar et al., 2013; Chan et al., 2017; Hetzinger et al., 2018). However, the chemistry of these algae has received far less attention compared to corals and bivalves, except for a handful of studies focused on particular trace elements such as U (Hetzinger et al., 2011), B (Cusack et al., 2015; Piazza et al., 2022) or Ni, the latter to trace pollution linked to metal production in New Caledonia (Darrenougue et al., 2018). Here we have conducted a detailed geochemical study of some macronutrients and trace element concentrations in coralline algae (maerl) from the Bay of Brest and the Iroise Sea (Brittany, France). Our aim was to assess the potential of these organisms to study the chemical characteristics of coastal seawater, with particular attention on their possible use for tracing water mass mixing using REEs and to detect metal pollution. We show here that these algae have great potential for studying marine biogeochemical processes, but also for tracing the composition of water masses.

2/ Sampling and procedures

2.1/ Study area

The Bay of Brest (Western Brittany, NW France) is a semi-enclosed macrotidal coastal system (180 km^2) connected to the Iroise Sea by a narrow and short 50-m deep strait (Fig. 1). The Bay is generally shallow, with 50 % of its surface less than 5 m deep. It collects freshwater inflows provided mainly by the local Aulne, the Elorn and the Daoulas rivers, with an average winter discharge of 54, 10 and 3 m^3/s respectively (Auffret, 1983). The Aulne River is by far the dominant source of freshwater with more than 60 % of the inflow. These river waters mix rapidly with the bay waters by a residual counterclockwise current (Le Pape et al., 1996). As a result, bottom water salinities vary between 32 and 35.3 g/l (Qui-Minet et al., 2018). Lower values are transitorily observed after heavy winter rainfall events, especially near the river mouths (Poppeschi et al., 2021). These freshwater inputs are however proportionally limited, since the total annual river discharge is equivalent to the volume exchanged with the Iroise Sea during a single tidal period (Le Pape et al., 1996). Water residence times in the Bay of Brest range from 7 to 25 days (Poppeschi et al., 2021).

The region around the Bay of Brest is economically very active, with various industrial activities that can generate significant metal pollution. First and foremost, Brest is one of France's leading ship repair centers, specializing in the maintenance of large vessels, particularly liquefied natural gas (LNG) carriers. Hull maintenance, for example, can generate antifouling paint particles containing base metals (e.g., Soroldoni et al., 2018). In addition to these industrial activities, the area is also home to intensive agricultural and farming practices. Pig and poultry farming is particularly noteworthy, accounting for about 500 and 240

industrial farms respectively in the areas drained by the Elorn and Aulne rivers. Copper and Zn are frequently added to pig and poultry diets (digestive flora regulators), and consequently are present in the manures spread as fertilizer on cultivated soils. These elements are further transported by run-off water and eventually discharge into coastal waters. This pollution is well known and has been studied both in Brittany and worldwide (e.g., Arzul and Maguer, 1990; Lopez-Alonso et al., 2002).

In addition to metal pollution from agricultural and farming activities, there are two other anthropogenic sources of dissolved trace metals to the Bay of Brest. Firstly, during the Second World War, the Brest area was bombed (more than 30,000 tons of bombs were dropped during this period), and the city was destroyed in 1944. The corresponding 'metal signature' of the WW2 is recorded in sediments from the Bay of Brest. Corroded ammunition and unexploded bombs from this period are still regularly found at sea and on land, and may locally explain the abundances of e.g., Co, Cu, Ni, Mn (e.g., Siano et al., 2021). Secondly, to this rapid inventory must be also added pollution linked to past mining activity. A deposit of argentiferous lead is known since antiquity in the Monts d'Arrée (SW of Brest). The Poullaouen and Huelgoat mines exploited it industrially between the 18th and 20th centuries, producing over 65,000 tons of Pb and 100 tons of Ag during this period. As the deposit is located in the Aulne watershed, this river was polluted by Pb from these mines, and still contributes to the metal pollution in the Bay of Brest (e.g., Lemière et al., 2000; Nasri et al., 2021) and associated marine fauna (e.g., Guillou et al., 2000; Cariou et al., 2017).

2.2/ Sampling stations

Several maerl beds are present in the Iroise Sea and the Bay of Brest, with coverage areas ranging from a few to several km^2 (Fig. 1). They are formed by the accumulation of free thalli of *Lithothamnion corallioides* (P & H Crouan) (Fig. 2) and sometimes of

Phymatholithon calcareum (Pallas), a less abundant species (Grall, 2002). Some of these beds were actively exploited in the 19th and 20th centuries for soil conditioning. These coralline algae have very slow growth rates, since their fine and brittle "branches" only grow less than 300 μm per year (Bosence and Wilson, 2003). Maerl beds are therefore particularly fragile ecosystems which takes a very long time (decades to centuries) to recover from anthropogenic effects (Grall and Hall-Spencer, 2003).

Three "purely" marine maerl stations (i.e. far from river mouths) were sampled in the Iroise Sea: Brenterc'h (48°23.7504' N, 004°46.7777' W; 10 m water depth), Camaret (48°17.598' N, 004°34.797' W; 18 m) and Molène (48°23.207'N, 004°51.279' W; 8 m). Five other stations were selected in the Bay of Brest: Le Dellec (48°21.4595' N, 4°33.0756' W; 13 m) and Lanvéoc (48°17.75716'N , 004°26.015'W; 10 m), both situated in areas without any direct river influence; Lomergat (48°17.4485' N, 004°21.0750' W; 6 m) and Rozegat (48°19.1921' N, 004°23.9357' W; 7 m), in areas whose surface waters are close to the mouth of the Aulne River; and Keraliou (48°21.8695' N, 004°26.5532' W; 6 m), in close proximity to the Elorn estuary (Fig. 1). Samples of *L. corallioides* were all collected by scuba divers on April and May 2023.

Finally, we collected two mud samples from the riverbeds of the Elorn (Chapelle Saint Jean) and the Aulne (cale de Tregarvan) in order to determine trace element concentrations in the sediments feeding the Bay of Brest.

2.3/ sample preparation and analytical procedures

2.3.1/ Algae

We selected only *live* thalli for this study. Samples were immediately rinsed with seawater to remove any possible adhering sediment or small animals (e.g., crabs) and dried in an oven (60°C) for about 12 hours. Cleaned fragments (branches) of about 100 to 250 mg weight (Fig. 2) were selected for analyses.

Each sample was spiked with a solution of pure Tm (Barrat et al., 1996) and attacked with 5 ml of 2.5 N HCl, at room temperature for one day. This procedure allows total digestion of the carbonates, leaving an organic residue representing only ≈4% of the sample mass, on a dry basis. An aliquot of the sample solution containing the equivalent of 5 mg of sample was dried and the residue was taken up in 5 ml of 2.5% HNO_3 before analysis.

Element concentrations (K, Al, P, V, Mn, Co, Ni, Cu, Zn, Rb, Sr, Y, Mo, Ba, REEs, Pb, Th and U) were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), using two separate Thermo Scientific ELEMENT XR™ spectrometers at the Pôle Spectrométrie Océan (Brest). Each solution was analyzed in triplicate using our routine procedure (the reader is referred to Charles et al., 2021 for interference corrections, and instrumental settings which were the same with both instruments), and the results were averaged. Results on two carbonate standards (CAL-S and BEAN) obtained during the sessions are compared with literature values in Table S1. Based on standards (carbonates and silicates), accuracies (RSD) for concentrations comparable to those measured here and elemental ratios are generally better than 3 % (e.g., Barrat et al., 2012, 2016, 2020).

For the normalization 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: $La_{sn}^* = Pr_{sn}^3/Nd_{sn}^2$, $Ce_{sn}^* = Pr_{sn}^2/Nd_{sn}$, $Gd_{sn}^* = Tb_{sn}^2/Dy_{sn}$. (e.g., Barrat et al., 2022a, 2023).

2.3.2/ Muds

About 2-3 g of mud were first dried overnight in a Teflon beaker on a hot plate at 120°C. 100 mg were precisely weighed, spiked with Tm using the same spike solution as above, dissolved and analyzed using a routine silicate protocol (e.g., Barrat et al., 2012, 2016). The accuracy is about 3 % for all the elements listed in Table-S1.

3/ Results

3.1/ Coralline algae

We analyzed 101 samples (9 to 15 samples per station), and the results are given in Table S1. Most of the elements analyzed show extremely variable abundances. Rare earth elements (REE) and yttrium (REY), for example, have low concentrations, and show variations of around an order of magnitude (e.g., La abundances range from 45 to 591 ng/g). REY patterns are light-REE depleted relative to PAAS (Pr_{sn}/Er_{sn} = 0.22-0.52) with positive La (La/La* = 1.29-2.08) and Y (Y/Ho = 38.6-55.8) anomalies (Fig. 3). They are strikingly similar to those of local coastal seawater (Freslon et al., 2011). No positive Gd anomaly (Gd/Gd*= 0.89-1.25) that could be ascribed to a pollution by contrast agents used in medical imaging is detected.

Like REY, many of the other elements we analyzed show variations of an order of magnitude or more: Al (1-254 µg/g), V (0.35-5 µg/g), Mn (16-248 µg/g), Co (52 ng/g-2.64

μg/g), Cu (0.21-1.68 μg/g), Zn (7.7-69 μg/g), Cs (3-58 ng/g), Pb (0.4-9.6 μg/g) and Th (0.6-43 ng/g). A few other elements, such as K (787-3026 μg/g), Rb (239-950 ng/g), Sr (1791-2559 μg/g and 1994-2559 μg/g only if we exclude two outliers), P (143-637 μg/g), Ni (0.32-1.39 μg/g), Mo (27-175 ng/g), Ba (5.1-6.8 μg/g) and U (252-663 ng/g), show more limited variations. All these variations will be discussed below.

3.2/ Muds

The results obtained on the two mud samples complement the data published by Bayon et al. (2015) on a similar sample from the Elorn River whose clay fraction is composed essentially of illite and chlorite in similar proportions. Both mud samples display typical geochemical compositions of detrital sediment, except for anomalously high Pb content measured in the Aulne River sediment (281 μg/g), illustrating the Pb pollution mentioned above for this river.

4/ Discussion

First, it should be emphasized that we analyzed fragments of fresh algal thalli (alive when sampled on the sea floor), clearly recognizable by their reddish color (Fig. 2). We can directly eliminate any post-mortem processes, including diagenesis, and the formation of authigenic minerals, which could alter the chemical composition of the thalli. Furthermore, our dissolution protocol, using only 2.5 N HCl at room temperature, has a limited effect on the organic matter, since cell residues representing ≈4 % of the mass of the samples (on a dry basis) resist this acid attack. The same applies to any possible detrital sediment particles adhered onto the thalli and not removed during sample preparation, which – if present - are

unlikely to have been fully dissolved upon acid digestion. Our analyses therefore essentially correspond to the biogenic mineral fraction of the thalli, with minor contributions from algal cells and eventually from terrigenous particles.

4.1/ Organic matter : K, Rb, P and U

Algae are enriched in alkali elements and in P. Phosphorus and K are major elements, with concentrations measured in red or black macroalgae of the order of 1 wt% or more (e.g., Tibbetts et al., 2016). Rubidium is present in macroalgae in concentrations of tens of µg/g, on a dry basis (e.g., Black and Mitchell, 1952; Hou and Yan, 1998). It is therefore not surprising that we measured sizeable amounts of these elements here, which probably derive from partial remineralization of the labile organic fraction associated with the thalli. We do not know whether the alkaline elements in coralline algae are contained mainly in the fluid of the cell vacuoles, or both in the vacuoles and elsewhere in the cell material. In any case, the K and Rb concentrations (K= 787-3026 µg/g, Rb=239-950 ng/g) we obtained are well above those of seawater, but below what would be expected if all the organic matter had been quantitatively dissolved.

Samples from the Iroise Sea and from the sites in the Bay of Brest where the fluvial influences are low show K/Rb ratios similar to those of seawater (Fig. 4). Some samples from sites closer to river mouths have lower K/Rb ratios, in between crustal values, and therefore suggesting the contribution of river waters.

Algae are well known for their ability to concentrate U (e.g., Mann and Fyfe, 1984), and concentrations between 230 and 4800 ng/g have been measured, for example, in brown and red macroalgae from Japan (Sakamoto et al., 2008). The U contents of the thalli we analyzed are in this range (U=252-663 ng/g), and correlate well with P abundances (r=0.80,

n=101, Fig. 5), suggesting that the labile fraction of organic matter dissolved during the preparation of the samples, could control U abundances in studied samples.

4.2/ The effect of terrigenous particles

Compared with the coralline algae, sediments are considerably enriched in terrigenous trace elements such as REY and Th, but also in Al. At first glance, we cannot rule out the possibility that some clay-size detrital particles may have been incorporated onto the surface of the thalli, or incorporated into them as they grew. While our sample dissolution protocol is unlikely to have resulted in total dissolution of clays, we cannot exclude partial detrital contamination in studied samples. Their possible contribution can be constrained using REEs, because their abundances in terrigenous sediments brought by rivers are well known, and the clays contained in the muds of the Elorn River were previously determined (Bayon et al., 2015). Contamination of thalli by minute amounts of terrigenous material would produce a strong enrichment in light REEs coupled with an increase in concentrations in all the REEs (Fig. 6). Such an effect is not observed. On the contrary, for each site, REE ratios and anomalies vary little and are independent of REE concentrations (e.g., at the Keraliou station, Sm concentrations in thalli vary from 19 to 127 ng/g, while Pr_{sn}/Sm_{sn} ratios only vary between 0.63 and 0.66). The mixing lines we have calculated imply that our samples contain much less than 0.05% clay particles. Very similar results are obtained with the two mud samples we analyzed (not shown). Thus, we are confident that the dissolution of terrigenous particles cannot account for the observed variability of trace element abundances in the thalli.

4.3/ Uptake of seawater REY by coralline algae

Two immediate observations emerge from the REY patterns (Fig. 3). Firstly, the REY patterns of coralline algae are extremely similar in shape to those of coastal seawater. The similarities between the patterns of coralline algae and seawater collected from the same station (Le Dellec; Freslon et al., 2011) are particularly striking (Fig. 3b and 3e). Secondly, REY abundances are extremely variable. For each of these elements, abundances vary by about an order of magnitude across all samples, and significant variations are observed within samples from the same station. For example, Yb concentrations range from 8 to 82 ng/g for all samples, and from 10.9 to 60.9 ng at Keraliou.

Coralline algae are considerably richer in REY than seawater. On average, algae are ~30,000 times richer in light REE and around 15,000 times richer in heavy REE than seawater (Fig. 7). The La, Ce and Y anomalies in the algae are also identical to those in seawater, confirming that the algae faithfully preserve the main REE characteristics of ambient seawater. They concentrate more REY (by an order of magnitude) than corals or mussel shells, without fractionating the light REE. Their ability to concentrate REY is similar to that of living foraminifera, but weaker than that of microbialites (Webb and Kamber, 2000; Terakado et al., 2010). Therefore, coralline algae appear to represent promising archives for studying the REY characteristics of coastal water masses.

4.4/ REY and the mixing of seawater and river waters

If coralline algae are able to record the chemical characteristics of ambient seawater, they should also provide suitable sedimentary archives for investigating coastal processes such as changes in riverine discharges near estuarine regions. The behavior of REY in estuarine waters is complex, since their abundances cannot be described by a conservative mixture between a seawater and river water (e.g., Elderfield et al., 1990, Andersson et al.,

1992). Despite evidence for limited freshwater discharge into the Bay of Brest and near constant bottom-water salinities near the mouths of the Aulne or Elorn rivers (Qui-Minet et al., 2018), the possibility that the compositions of coralline algae may record estuarine processes needs to be evaluated.

While REY abundances determined on algae from all the stations appear at first glance to display similar distribution patterns (Fig. 3), element ratios, such as those quantifying heavy REE enrichments (e.g., Pr/Er), Y anomalies (Y/Ho), and La anomalies (La/La*) show very significant variability. In fact, significant differences can be observed between samples collected at stations influenced by fluvial inputs and those from open ocean settings (Fig. 8). Thalli sampled in the Iroise Sea at Brenterc'h have the highest Y/Ho and La/La* ratios, and the lowest Pr/Er ratios. Those taken near the mouths of the Elorn and Aulne rivers show the lowest Y/Ho, La/La* and highest Pr/Er ratios. The other samples taken in the Iroise Sea (Camaret and Molène), as well as those taken in the Bay of Brest where river contributions are negligible (Le Dellec and Lanvéoc), have intermediate characteristics. They are likely to have recorded the chemical signature of regional seawater in this area. In the Y/Ho and Pr/Er vs. La/La* diagrams, the trends obtained are in agreement with the involvement of two endmembers: a marine component with La/La* ratios close to 2, and a river water component with a La/La* ratio closer to 1. The spread of the data in the Ce/Ce* vs. La/La* diagram, shown by both the Iroise Sea and the Bay of Brest samples, suggest that river waters and the seawater have Ce anomalies in the same ranges.

The correlation trends observed between some element ratios (Fig. 8c) are nevertheless surprising, given the limited salinity variations (35.3-32 ‰) recorded at stations near the mouths of the Elorn and Aulne rivers (Qui-Minet et al., 2018) and the limited volume of river water entering the Bay of Brest. They demonstrate the capability of coralline algae to record water chemical features and their potential for studying coastal processes.

4.5/ Other elements

As mentioned earlier, many of the elements we measured have concentration ranges that are proportionally as large as those of the REEs (i.e. variations of an order of magnitude). To describe the behavior of the elements, we have chosen to represent the data in diagrams with La abundances on the abscissa to illustrate possible decoupling from REE.

4.5.1/ Sr and Ba

These two elements are the least variable of those analyzed (Fig. 9a and 9b). The relative homogeneity of Sr concentrations is not surprising, since the budget for this element is certainly dominated by seawater, fluvial waters being relatively depleted in Sr compared to seawater. No difference is apparent between the purely marine samples and those from the Bay of Brest. For Ba, although variations are small, they seem to correlate with La abundances. Differences between stations are not marked, but samples from the Iroise Sea seem to be slightly less enriched in Ba than those from the Bay of Brest.

4.5.2/ Al and Cs

Variations in these two elements in coralline algae are extremely similar, suggesting that they behave in the same way and are controlled by the same processes. Their abundances show a wide dispersion in the Al and Cs vs. La plots (Fig. 10), with samples from stations close to estuaries tending to have higher concentrations than those from marine stations. The concentrations of these two elements are remarkably correlated (Fig. 11, r=0.97, n=101). This correlation cannot be possibly explained by a contribution from Al- and Cs-rich terrigenous

sediments, since such a contribution would produce a mixing line significantly different from the observed trend (Fig. 11). More likely, the concentrations of these elements in coralline algae reflect those in water.

The behavior of these two particular elements in estuaries is quite complex, involving adsorption and desorption of terrigenous particles as well as flocculation of colloidal matter, which can cause a significant drop in dissolved Al in estuarine and coastal waters (e.g., Hydes and Liss, 1977; Mackin and Aller, 1984). Al and Cs abundances in coralline algae appear to be at least partially controlled by water mixing, since Al/Er (and Cs/Er, not shown) ratios are correlated with $(Pr/Er)_{sn}$ ratios, whose variations are produced by this mixing (Fig. 12). Note that the data are scattered and the trend obtained does not appear to be linear, indicating that the mixing is not perfectly conservative for these elements.

4.5.3/ Th, Mn, Mo, and base metals

The abundances of Th (Fig. 9c), Mn and Mo (Fig. 13 a and c) follow those of La. For these elements, no clear differences can be identified between samples from the Iroise Sea and the Bay of Brest. On the other hand, marked differences can be distinguished between samples from Bay of Brest and Iroise Sea for V (Fig. 13d), and especially for Ni, Co, Cu and particularly Pb (Fig. 13b and Fig. 14). For these latter elements, concentrations in coralline algae from the Bay of Brest are higher than those from the Iroise Sea for any given La abundance, clearly pointing towards an anthropogenic origin. The high Pb concentrations that control the Bay of Brest trend come from Lomergat (Fig 14a). This station is close to the mouth of the Aulne River, which is still polluted by former mining activities of the Huelgoat lead deposit. Excesses of Ni and Co are probably mainly linked to the port and industrial activities in Brest, but also to those located in the Aulne and Elorn catchment areas.

However, a residual contribution from rusty debris or ammunitions dating back to WW2 cannot be ruled out. Cu excesses can at first glance be attributed to pig and poultry farming. Cu pollution linked to these activities has been well documented (e.g., Arzul and Maguer, 1990), and it is therefore not surprising to observe an excess of Cu in the Bay of Brest, especially since this activity in the Finistère (the administrative department where Brest is located) account for about 20 % of the French national production of pigs.

The behavior of Zn is more difficult to explain. Admittedly, Zn concentrations in coralline algae from the Bay of Brest are higher than those observed in samples from certain stations located in the Iroise Sea, notably Camaret (Fig. 1). It is tempting to suggest that the high concentrations observed in the Bay of Brest could also result from anthropogenic pollution. They could indeed be explained by pig or poultry farming, but this interpretation is not unique, given the multiplicity of Zn uses (roofing, galvanizing, antifouling paints, sacrificial (galvanic) anodes for boat hulls...). However, high levels in excess of 50 µg/g Zn have also been observed in some samples from the Iroise Sea, for example, those collected at Brenterc'h, hence suggesting that other local, non-anthropogenic, parameters could possibly account for the observed high concentrations at this site. The wreck of an 82 m-long Panamanian cargo ship lies in the area. This ship, the Taboga, sank in 1953, and it seems unlikely that this wreck would still have an effect on the seawater Zn budget in the environment today, if it ever did. The origin of high Zn concentrations in coralline algae from the Iroise Sea and Bay of Brest is hence not fully understood and would require further investigation. The possibility that a significant proportion of Zn is also bound to organic matter, and thus participates in the biochemical cycles of these algae, could also be considered.

5/ Conclusions

Coralline algae are excellent archives of seawater chemistry for many trace elements, including REYs. Our study of algae from the Bay of Brest (Brittany, France) and the nearby Iroise Sea shows that their composition can be used to characterize water masses, but also to trace estuarine processes (freshwater/seawater mixing) and metal pollution. Given their worldwide distribution, they have enormous potential for studying marine processes, complementing what can be obtained with other archives commonly used today, such as corals and foraminifera.

In addition to studies on other regions or other species that can be immediately envisaged, it would be particularly interesting to complement this explorative work with further microscale observations, in order to better understand where and how trace elements are incorporated into these algae, but also how the recorded signatures resist aging in vivo, and post-mortem processes. These data, currently lacking, are essential for the validation of future time series based on chemical concentrations of trace elements such as REY or other metals.

Acknowledgements.

Appendix A. Supplementary material

Table S-1 contains all the trace element data obtained during the course of this study.

References

Alonso M., Benedito,J., Miranda M., Castillo C., Hernandez J., Shore R.F. (2002) Cattle as Biomonitors of Soil Arsenic, Copper, and Zinc Concentrations in Galicia (NW Spain). *Arch. Environ. Contam. Toxicol.* **43**, 103–108 (2002). https://doi.org/10.1007/s00244-002-1168-5

Andersson P.S., Wasserburg G.J., Ingri J. (1992) The sources and transport of Sr and Nd isotopes in the Baltic Sea. *Earth Planet. Sci. Lett.* **113**, 459-472.

Arzul G., Maguer J.F. (1990) Influence of pig farming on the copper content of estuarine sediments in Brittany, France. *Marine Poll. Bull.* **21**, 431-434.

Auffret, G. (1983) Dynamique sédimentaire de la Marge Continentale Celtique- Evolution Cénozoïïque-Spécificité du Pléistocène Supérieur et de l'Holocène. Ph.D. thesis. Université de Bordeaux I, 355 p.

Barrat J.A., Keller F., Amossé J., Taylor R.N., Nesbitt R.W., Hirata T. (1996) Determination of rare earth elements in sixteen silicate reference samples by ICP-MS after Tm addition and ion exchange separation. *Geostandards Newsletter* **20**, 1, 133-140.

Barrat J.A., Zanda B., Moynier F., Bollinger C., Liorzou C., and Bayon G. (2012) Geochemistry of CI chondrites: Major and trace elements, and Cu and Zn isotopes. *Geochim. Cosmochim. Acta* **83**, 79-92.

Barrat J.A., Dauphas N., Gillet P., Bollinger C., Etoubleau J., Bischoff A., Yamaguchi A. (2016) Evidence from Tm anomalies for non-CI refractory lithophile element proportions in terrestrial planets and achondrites. *Geochim. Cosmochim. Acta*, **176**, 1-17.

Barrat J.A., Bayon G., Wang X., Le Goff S., Rouget M.L., Gueguen B., Ben Salem B. (2020) A new chemical separation procedure for the determination of rare earth elements and yttrium abundances in carbonates by ICP-MS. *Talanta* **219**, 121244.

Barrat J.A., Bayon G., Carney R.S., Chauvaud L. (2022a) Rare earth elements as new biogeochemical proxies in deep-sea mussels. *Chem. Geol.*, https://doi.org/10.1016/j.chemgeo.2022.121102.

Barrat J.A., Chauvaud L., Olivier F., Poitevin P., Bayon G., Ben Salem D. (2022b) Rare earth elements and yttrium in suspension-feeding bivalves (dog cockle, *Glycymeris glycymeris* L.): accumulation, vital effects and pollution. *Geochim. Cosmochim. Acta* **339**, 12-21.

Barrat J.A., Bayon G., Lalonde S. (2023) Calculation of cerium and lanthanum anomalies in geological and environmental samples, *Chem. Geol* **615**, https://doi.org/10.1016/j.chemgeo.2022.121202.

Bath G.E., Thorrold S.R., Jones C.M., Campana S.E., McLaren J.W., Lam J.W.H. (2000) Strontium and barium uptake in aragonitic otoliths of marine fish. *Geochim. Cosmochim. Acta* **64**, 1705-1714.

Bayon G., Toucanne S., Skonieczny C., André L., Bermell S., Cheron S., Dennielou B., Etoubleau J., Freslon N., Gauchery T., Germain Y., Jorry S., Ménot G., Monin L., Ponzevera E., Rouget M.L., Tachikawa K., Barrat J.A. (2015) Rare earth elements and neodymium isotopes in World river sediments revisited. *Geochim. Cosmochim. Acta* **170**, 17-38.

Black W.A.P., Mitchell R.L. (1952) Trace elements in the common brown algae and in seawater. *J. Marine Biol. Assoc. of United Kingdom* **30**, 575-584.

Bosence D., Wilson J. (2003) Maerl growth, carbonate production rates and accumulation rates in the northeast Atlantic. *Aquatic Conserv: Mar. Freshw. Ecosyst.* **13**, S21–S31

Cariou E., Guivel C., La C., Lenta L., Elliot M. (2017) Lead accumulation in oyster shells, a potential tool for environmental monitoring. *Marine Pollution Bull.* **125**, 19-29.

Chan P., Halfar J., Adey W., Hetzinger S., Zack,T., Moore G.W.K., et al. (2017) Multicentennial record of Labrador Sea primary productivity and sea-ice variability archived in coralline algal barium. *Nat. Commun.* **8**, 15543. doi: 10.1038/ncomms15543

Charles C., Barrat J.A., Pelleter E. (2021) Trace element determinations in Fe–Mn oxides by high resolution ICP-MS after Tm addition. *Talanta* **233**, 122446.

Cusack M., Kamenos N.A., Rollion-Bard C., Tricot G. (2015) Red coralline algae assessed as marine pH proxies using ^{11}B MAS NMR. *Scientific Reports* **5**, 8175, DOI: 10.1038/srep08175

Darrenougue N., De Deckker P., Eggins S., Fallon S., Claude Payri C. (2018) A record of mining and industrial activities in New Caledonia based on trace elements in rhodolith-forming coralline red algae. *Chem. Geol.* **493**, 24-36.

Eggins S., De Deckker P., Marshall J. (2003) Mg/Ca variation in planktonic foraminifera tests : implications for reconstructing palaeo-seawater temperature and habitat migration. *Earth Planet. Sci. Lett.* **212**, 291-306.

Elderfield H., Upstill-Goddard R., Sholkovitz E.R. (1990) The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. *Geochim. Cosmochim. Acta* **54**, 971-991.

Fallon S.J., White J.C., and McCulloch M.T. (2002) Porites corals as recorders of mining and environmental impacts: Misima Island, Papua New Guinea. *Geochim. Cosmochim. Acta* **66,** 45-62.

Freslon N., Bayon G., Birot D., Bassoulet C., Barrat J.A. (2011) Determination of rare earth elements and other trace elements (Y, Mn, Co, Cr) in seawater using Tm addition and $Mg(OH)_2$ co-precipitation. *Talanta* **85**, 582–587.

Frieder, C.A., Gonzalez, J.P., Levin, L.A., 2014. Uranium in larval shells as a barometer of molluscan ocean acidification exposure. Environ. Sci. Technol. 48, 6401–6408.

Gillikin, D.P., Dehairs, F., Lorrain, A., Steenmans, D., Baeyens, W., Andr´e, L., 2006. Barium uptake into the shells of the common mussel (*Mytilus edulis*) and the potential for estuarine paleo-chemistry reconstruction. Geochim. Cosmochim. Acta 70, 395–407.

Grall J. (2002) Biodiversité spécifique et fonctionnelle du maerl: réponses à la variabilité de l'environnement côtier. PhD dissertation, Université de Bretagne Occidentale, Brest, 340 pp.

Grall J., Hall-Spencer J.M. (2003) Problems facing maerl conservation in Brittany. *Aquat. Conserv. Mar. Freshw. Ecosyst.* **13**, S55–S64.

Guillou M., Quiniou F., Huart B., Pagano G. (2000) Comparison of embryonic development and metal contamination in several populations of the sea urchin *Sphaerechinus granularis* (Lamarck) exposed to anthropogenic pollution. *Arch. Environ. Contam. Toxicol.* **39**, 337-344.

Halfar J., Steneck R.S., Joachimski M., Kronz A., and Wanamaker A.D.Jr (2008) Coralline red algae as high-resolution climate recorders. *Geology* **36** (6), 463–466. doi: 10.1130/G24635A.1

Halfar J., Adey W.H., Kronz A., Hetzinger S., Edinger E., and Fitzhugh W.W. (2013). Arctic Sea-ice decline archived by multicentury annual-resolution record from crustose coralline algal proxy. *Proc. Natl. Acad. Sci.* **110** (49), 19737–19741. doi: 10.1073/pnas.1313775110

Hetzinger S., Halfar J., Zack T., Gamboa G., Jacob D. E., Kunz B. E., et al. (2011) High-resolution analysis of trace elements in crustose coralline algae from the north Atlantic and north pacific by laser ablation ICP-MS. *Palaeogeography Palaeoclimatology Palaeoecol.* **302** (1-2), 81–94. doi: 10.1016/j.palaeo.2010.06.004

Hetzinger S., Halfar J., Kronz A., Simon K., Adey W. H., and Steneck R. S. (2018) Reproducibility of *Clathromorphum compactum* coralline algal Mg/Ca ratios and comparison to high-resolution sea surface temperature data. *Geochim. Cosmochim. Acta* **220**, 96-109.

Hou X., Yan X. (1998) Study on the concentration and seasonal variation of inorganic elements in 35 species of marine algae. *Sci. Total. Env.* **222**, 141-156.

Hydes D.J., Liss P.S. (1977) The behaviour of dissolved aluminium in estuarine and coastal waters. *Estuarine and Coastal Marine Sci.* **5**, 755-769.

Immenhauser A., Schöne B.R., Hoffmann R., Niedermayr A. (2016) Mollusc and brachiopod skeletal hard parts: intricate archives of their marine environment. *Sedimentology* **63**, 1-59.

Johansen H.W. (1981) Coralline Algae, A first synthesis. CRC Press, Boca Raton, Florida, USA, 239 p; https://doi.org/10.1201/9781351070928

Kamenos N.A., Cusack M., Moore P.G. (2008) Coralline algae are global palaeothermometers with bi-weekly resolution. *Geochim. Cosmochim. Acta* **72**, 771-779.

Kamenos N.A., Cusack M., Huthwelker T., Lagarde P., Scheibling R.E. (2009) Mg-lattice associations in red coralline algae. *Geochim Cosmochim Acta* **73**,1901-1907.

Le Goff S., Barrat J.A., Chauvaud L., Paulet Y.M., Gueguen B., Ben Salem D. (2019) Compound-specific recording of gadolinium pollution in coastal waters by great scallops. *Scientific Reports* **9**, 8015.

Lemiere B., Clozel B., Martel-Jantin C., Trautmann F., Cam A. (2000) Etude de l'origine des pollutions métalliques naturelles du bassin versant de la rade de Brest - Etat des données disponibles pour l'interprétation géochimique des eaux de surface du bassin versant de la rade de Brest. Rapport BRGM/RP - 50227 - FR, 29 fig., *5* tab. 61 p.

Le Pape O., Del Amo Y., Menesguen A., Aminot A., Quequiner B., Treguer P. (1996) Resistance of a coastal ecosystem to increasing eutrophic conditions: the Bay of Brest (France), a semi-enclosed zone of Western Europe. *Continental shelf res.* **16**, 1885-1907.

Mackin J.E., Aller R.C. (1984) Processes affecting the behavior of dissolved aluminum in estuarine waters. *Marine Chemistry* **14**, 213-232.

Mann H., Fyfe W.S. (1984) An experimental study of algal uptake of U, Ba, V, Co, and Ni from dilute solutions. *Chem. Geol.* **44**, 385-398.

McCulloch M.T., Gagan M.K., Mortimer G.E., Chivas A.R., Isdale P.J. (1994) A high-resolution Sr/Ca and $\delta^{18}O$ coral record from the Great Barrier Reef, Australia, and the 1982-1983 El Niñio. *Geochim. Cosmochim. Acta* **58**, 2747-2754.

Meibom A., Cuif J.P., Houlbreque F., Mostefaoui S., Dauphin Y., Karin L. Meibom K.L., Dunbar R. (2008) Compositional variations at ultra-structure length scales in coral skeleton. *Geochim. Cosmochim. Acta* **72**, 1555-1569.

Nasri K., Gregoire G., Murat A., Fiallo M. (2021) Unlikely lead-bearing phases in river and estuary sediments near an ancient mine (Huelgoat, Brittany, France). *Environ. Sci. Pollut. Res.* **28**, 8128-8139.

Norrie C.R., Dunphy B.J., Ragg N.L.C., Lundquist C.J. (2018) Ocean acidification can interact with ontogeny to determine the trace element composition of bivalve shell. *Limnology and Oceanography Letters* **3**, 393-400.

Piazza G., Bracchi V.A., Langone A., Meroni A.N., Basso D. (2022) Growth rate rather than temperature affects the B/Ca ratio in the calcareous red alga Lithothamnion corallioides. *Biogeosciences* **19**, 1047-1065.

Ponnurangam, A., Bau, M., Brenner, M., Kochinsky, A. (2016) Mussel shells of Mytilus edulis as bioarchives of the distribution of rare earth elements and yttrium in seawater and the potential impact of pH and temperature on their partitioning behavior. *Biogeosciences* **13**, 751–760.

Poitevin, P., Roy, V., Galbraith, P.S., Chaillou, G., 2022. Insights into coastal phytoplankton variations from 1979 to 2018 derived from Ba/Ca records in scallop shells (*Chlamys islandica*) from a fishing ground in the northern Gulf of St Lawrence. *Marine Env. Res.* **181**, 105734.

Poppeschi C., Charria G., Goberville E., Rimmelin-Maury P., Barrier N., Petton S., Unterberger M., Grossteffan E., Repecaud M., Quéméner L., Theetten S., Le Roux J.F. and Tréguer P. (2021) Unraveling salinity extreme events in coastal environments: a winter focus on the Bay of Brest. *Front. Mar. Sci.* **8**,705403. doi: 10.3389/fmars.2021.705403

Poulain C., Gillikin D.P., Thébault J., Munaron J.M., Bohn M., Robert R., Paulet Y.M., Lorrain A. (2015) An evaluation of Mg/Ca, Sr/Ca, and Ba/Ca ratios as environmental proxies in aragonite bivalve shells. *Chem. Geol.* **396**, 42–50.

Pourmand, A., Dauphas, N., Ireland, T.J. (2012) A novel extraction chromatography and MC-ICP-MS technique for rapid analysis of REE, Sc and Y: Revising CI-chondrite and Post-Archean Australian Shale (PAAS) abundances. *Chem. Geol.* **291**, 38-54.

Qui-Minet Z.N., Delaunay C., Grall J., Sixa C., Cariou C., Bohner O., Legrand E., Davoult D.,Martin S. (2018) The role of local environmental changes on maerl and its associated non-calcareous epiphytic flora in the Bay of Brest. *Estuarine, coastal, shelf Sci.* **208**, 140-152.

Quinby-Hunt M.S., Turekian K.K. (1983) Distribution of elements in seawater. *Eos Trans. AGU* 64, 130-131

Reynaud S., Ferrier-Pagès C., Meibom A., Mostefaoui S., Mortlock R., Fairbanks R., Allemand D. (2007) Light and temperature effects on Sr/Ca and Mg/Ca ratios in the scleractinian coral *Acropora* sp. *Geochim. Cosmochim. Acta* **71**, 354-362.

Rollion-Bard C., Blamart D., Trebosc J., Tricot G., Mussi A., Cuif J.P. (2011) Boron isotopes as pH proxy: A new look at boron speciation in deep-sea corals using 11B MAS NMR and EELS. *Geochim. Cosmochim. Acta* **75**, 1003-1012.

Rosenthal Y., Boyle E.A., Slowey N. (1997) Temperature control on the incorporation of magnesium, strontium, fluorine, and cadmium into benthic foraminiferal shells from Little Bahama Bank: Prospects for thermocline paleoceanography. *Geochim. Cosmochim. Acta* **61**, 3633-3643.

Sakamoto N., Kano N., Imaizumi H. (2008) Determination of rare earth elements, thorium and uranium in seaweed samples on the coast in Niigata Prefecture by inductively coupled plasma mass spectrometry. *Applied Geochem.* **23**, 2955-2960.

Schöne B.R., Zhang Z., Radermacher P., Thebault J., Jacob D.E., Nunn E.V., Maurer A.-F. (2011) Sr/Ca and Mg/Ca ratios of ontogenetically old, long-lived bivalve shells (*Arctica islandica*) and their function as paleotemperature proxies. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **302**, 52–64.

Schöne, B.R., Huang, X., Jantschke, A., Mertz-Kraus, R., Zettler, M.L., 2022. High-resolution reconstruction of dissolved oxygen levels in the Baltic Sea with bivalves – a multi-species comparison (*Arctica islandica*, *Astarte borealis*, *Astarte elliptica*). Front. Mar. Sci. 9, 820731.

Schöne B.R., Marali S., Jantschke A., Mertz-Kraus R., Butler P.G., Fröhlich F. (2023) Can element chemical impurities in aragonitic shells of marine bivalves serve as proxies for environmental variability? Chem. Geol., https://doi.org/10.1016/j.chemgeo.2022.121215

Siano R., Lassudrie M., Cuzin P., Briant N., Loizeau V., Schmidt S., Ehrhold A., Mertens K.N., Lambert C., Quintric L., Noël C., Latimier M., Quéré J., Durand P., Penaud A. (2021) Sediment archives reveal irreversible shifts in plankton communities after World War II and agricultural pollution. *Current Biology* **31**, 1-8, https://doi.org/10.1016/j.cub.2021.03.079

Smith S.V., Buddemeier R.W., Redalje R.C., Houck J.E. (1979) Strontium-calcium thermometry in coral skeletons. *Science* **204**, 404-407.

Sholkovitz E. and Shen G. T. (1995) The incorporation of rare earth elements in modern coral. *Geochim. Cosmochim. Acta* **59,** 2749-2756.

Soroldoni S., Castro I.B., Abreu F., Duarte F.A., Choueri R.B., Möller O.O. jr., Fillmann G., Pinho G.L.L. (2018) Antifouling paint particles: sources, occurrence, composition and dynamics. *Water Res.* **137**, 47-56.

Terakado Y., Ofuka Y., Tada N. (2010) Rare earth elements, Sr, Ba, Fe, and major cation concentrations in some living foraminiferal tests collected from Iriomote Island, Japan: an exploration for trace element behavior during biogenic calcium formation. *Geochem. J.* **44**, 315-322.

Tibbetts S.M., Milley J.E., Lall S.P. (2016) Nutritional quality of some wild and cultivated seaweeds: Nutrient composition, total phenolic content and in vitro digestibility. *J. Appl. Phycol.* **28**, 3575-3585.

van der Heijden and Kamenos N.A. (2015) Reviews and syntheses: Calculating the global contribution of coralline algae to total carbon burial, *Biogeosciences* **12**, 6429–6441, https://doi.org/10.5194/bg-12-6429-2015.

Wanamaker A.D., Gillikin D.P. (2019) Strontium, magnesium, and barium incorporation in aragonitic shells of juvenile *Arctica islandica*: insights from temperature controlled experiments. *Chem. Geol.* **526**, 117–129.

Wang X., Barrat J.A., Bayon G., Chauvaud L., Feng D. (2020) Lanthanum anomalies as fingerprints of methanotrophy. *Geochem. Persp. Let.* **14**, 26–30.

Webb G.E., Kamber B.S. (2000) Rare earth elements in Holocene reefal microbialites: a new shallow seawater proxy. *Geochim. Cosmochim. Acta* **64**, 1557-1565.

Wyndham T., McCulloch M., Fallon S., Alibert C. (2004) High-resolution coral records of rare earth elements in coastal seawater: biogeochemical cycling and a new environmental proxy. *Geochim. Cosmochim. Acta* **68**, 2067-2080.
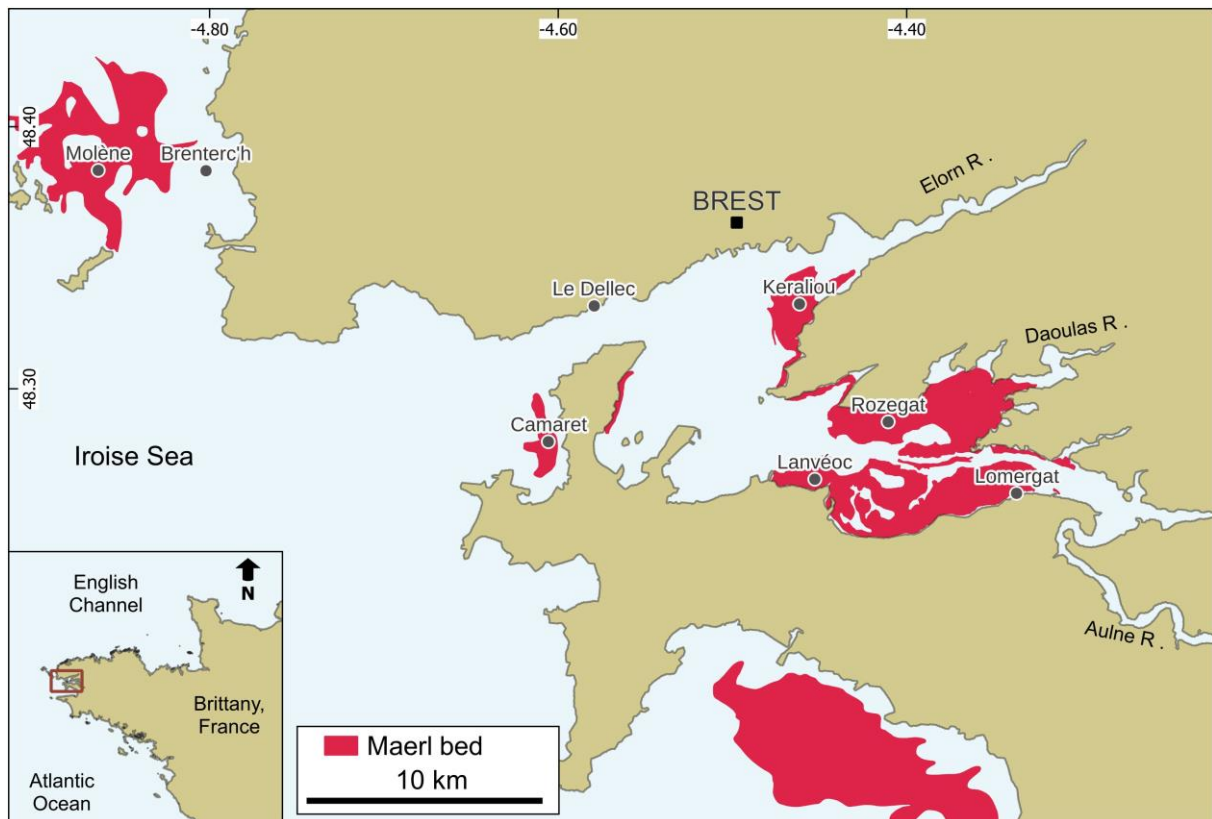
Figure 1. Location of the Bay of Brest and its main maerl beds.

Figure 2. Detail of the surface of a maerl bed (Camaret, depth= 18 m), showing between pieces of bivalve shells, live (pink-purple) and dead (white) *L. corallioides* thalli.
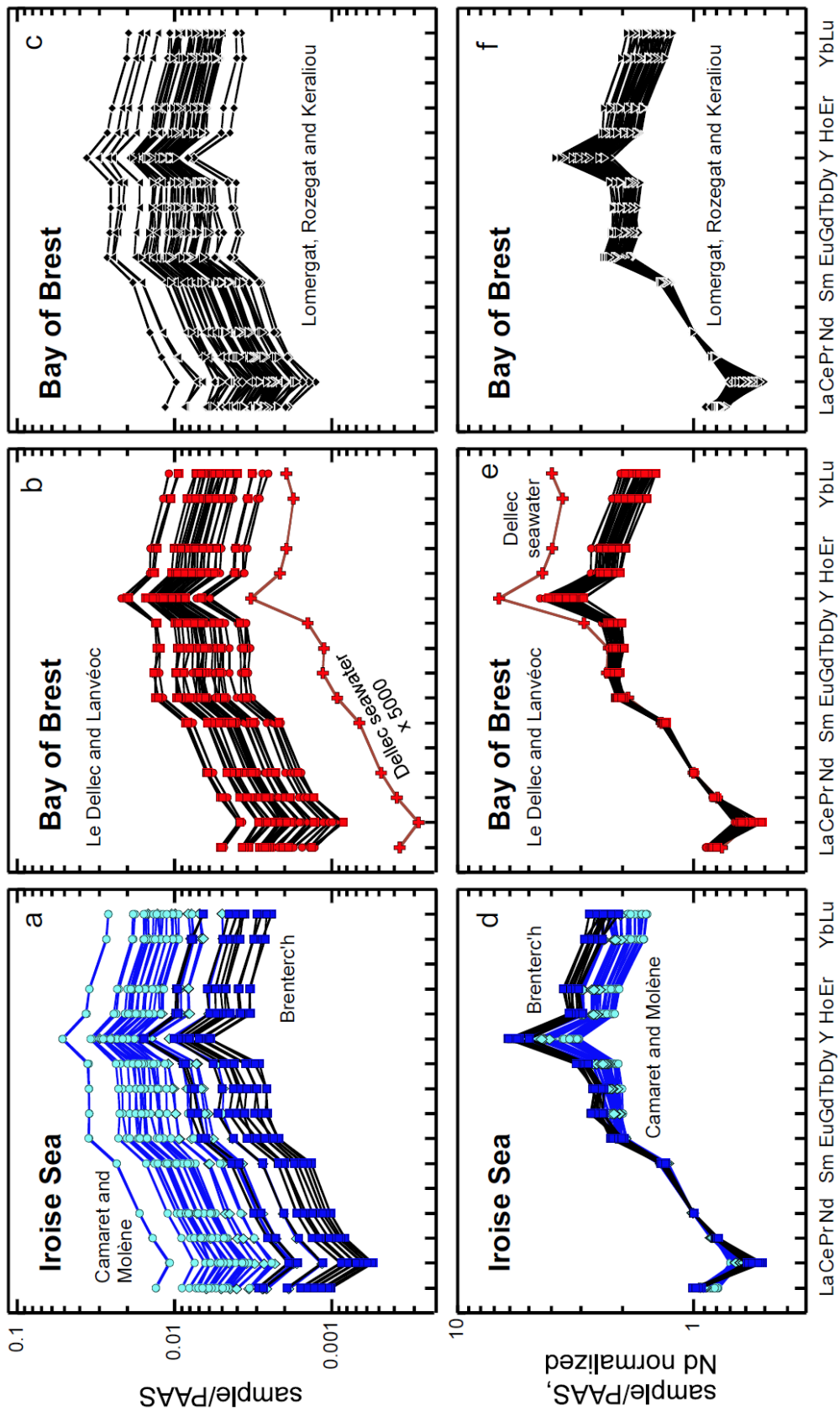
Figure 3. PAAS-normalized REY patterns and Nd-normalized REY patterns for coralline algae from Bay of Brest and Iroise Sea. Pattern of local seawater is shown for comparison (Freslon et al., 2011).
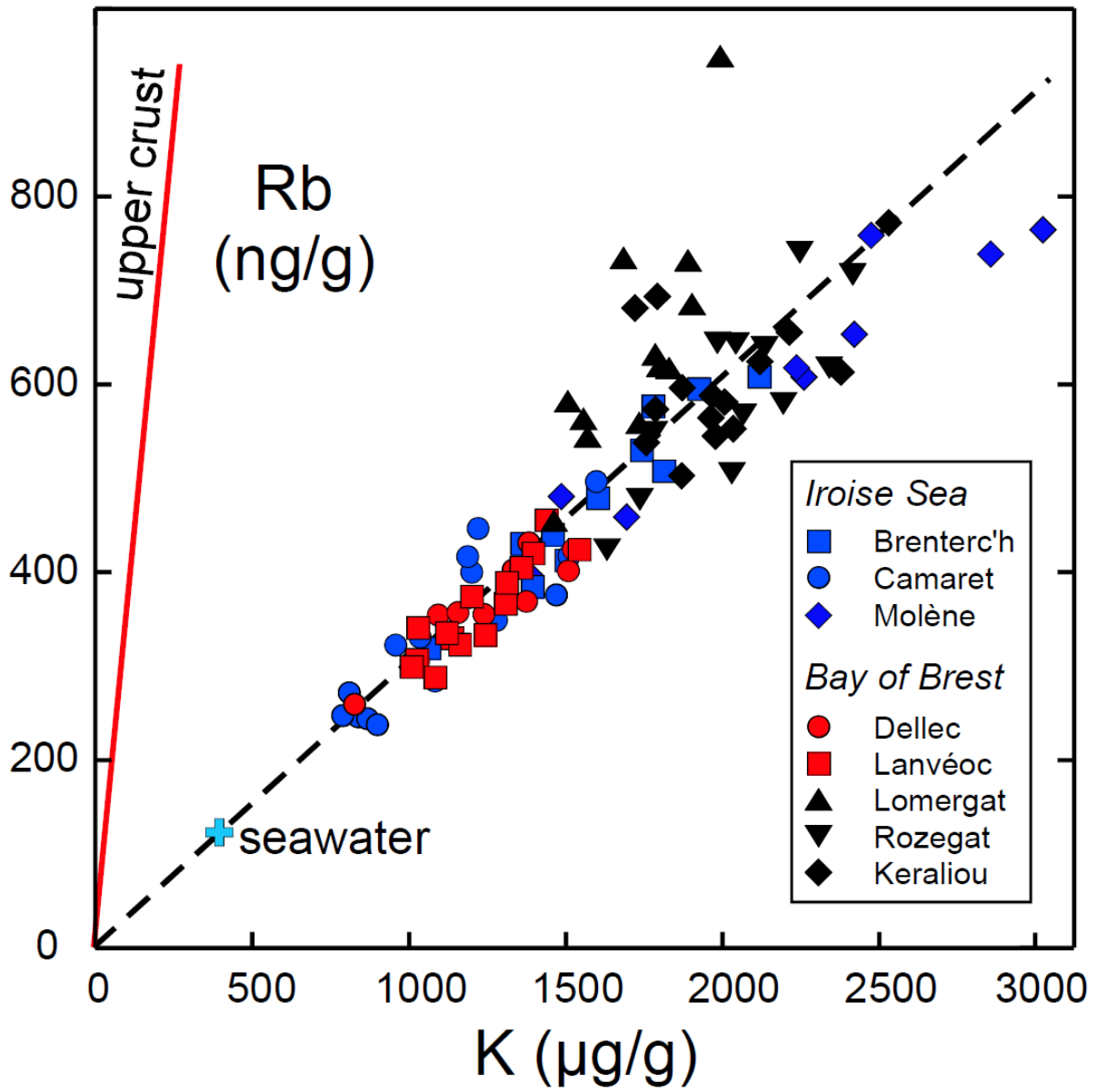
Figure 4. Rb vs. K plot for coralline algae from Bay of Brest and Iroise Sea. Seawater composition from Quinby-Hunt and Turekian (1983).
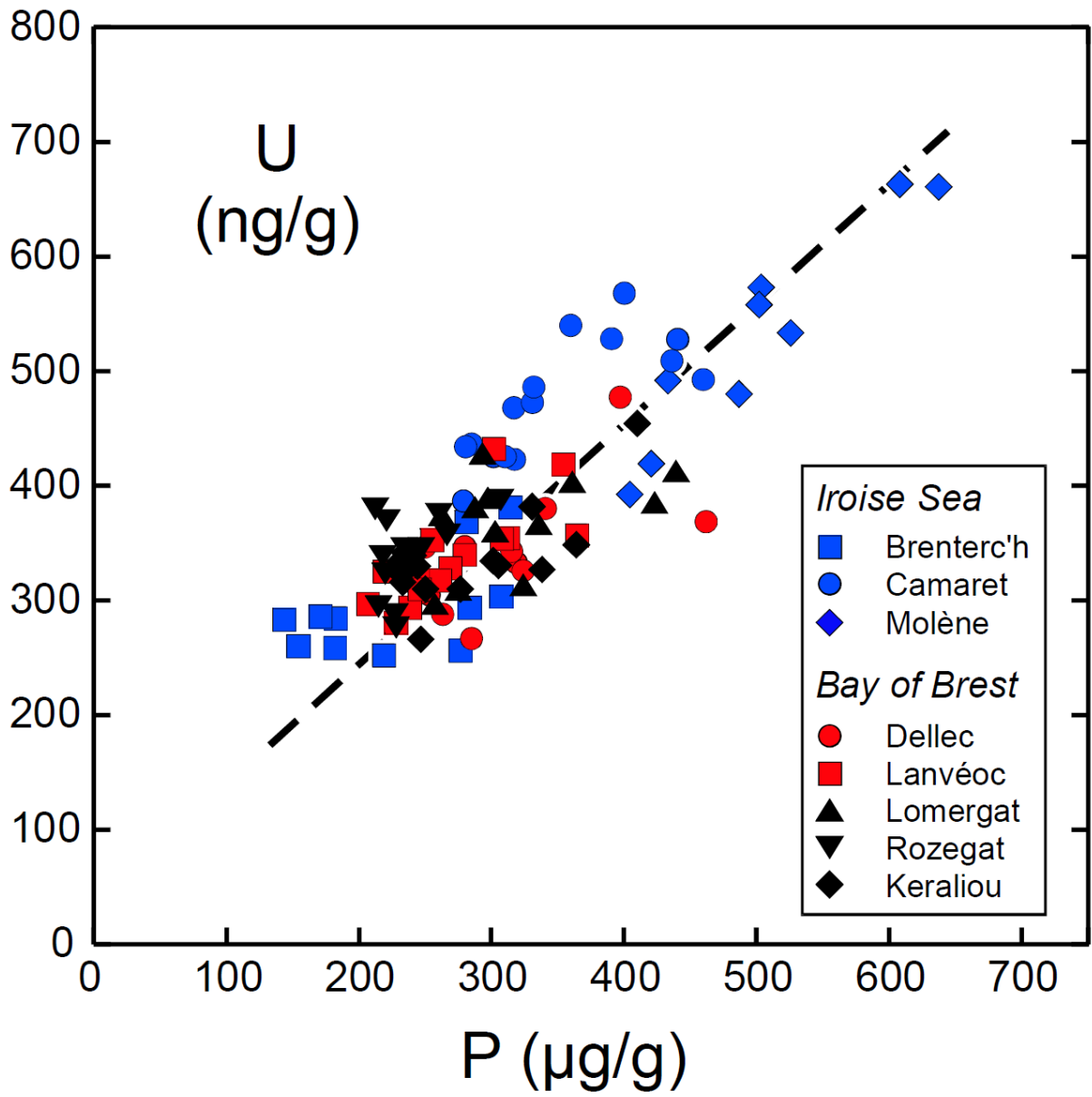
Figure 5. U vs. P plot for coralline algae from Bay of Brest and Iroise Sea.
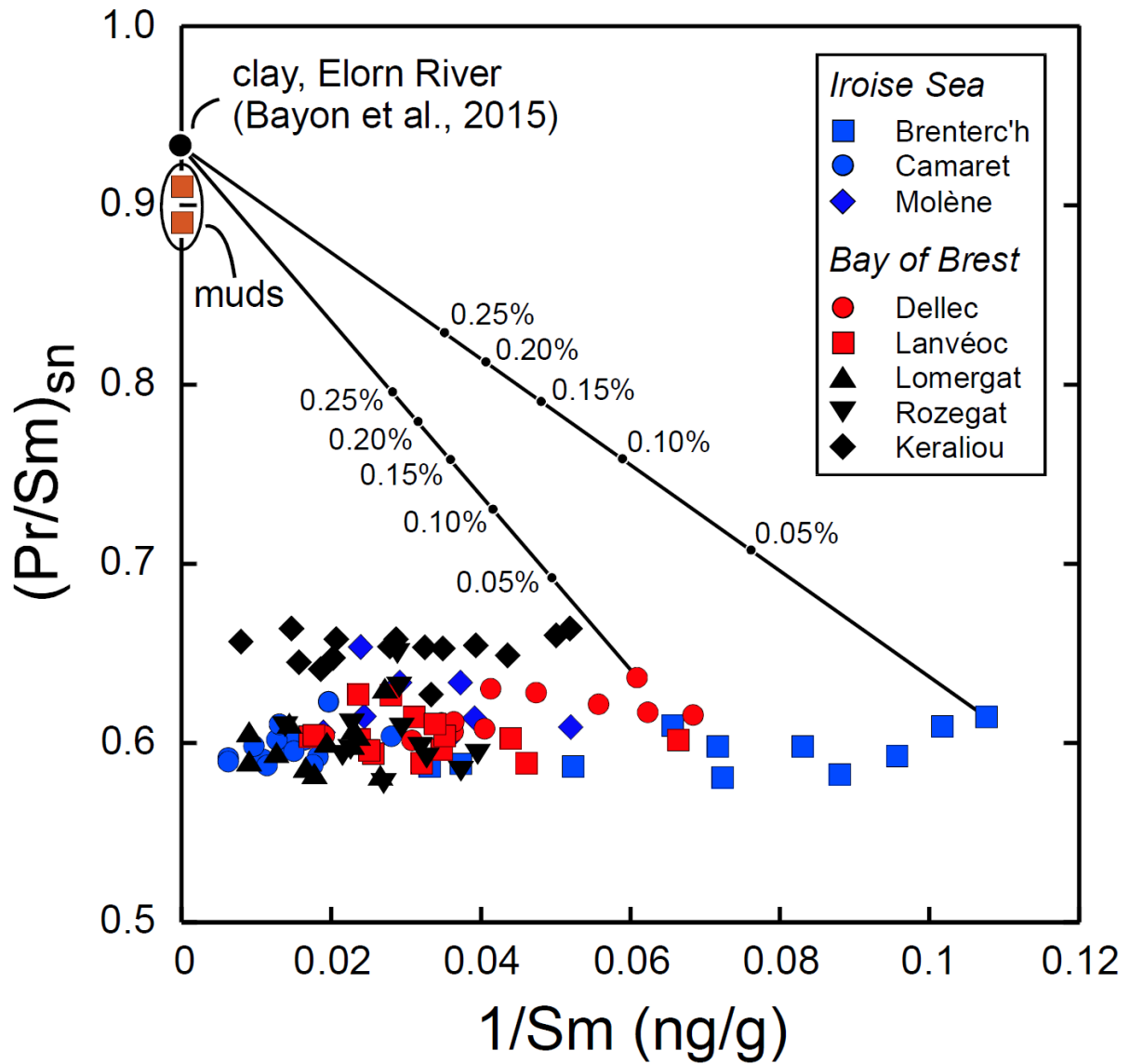
Figure 6. (Pr/Sm)sn vs. 1/Sm plot for the Bay of Brest and Iroise Sea coralline algae. Mixing lines are calculated between two algae and the clay from Elorn River (Bayon et al., 2015). They show that contamination by a terrigeneous component cannot explain the range of REE abundances displayed by the algae. The two muds analysed during the course of the study are shown for comparison, and same conclusions would be obtained by using them as terrigeneous endmembers.
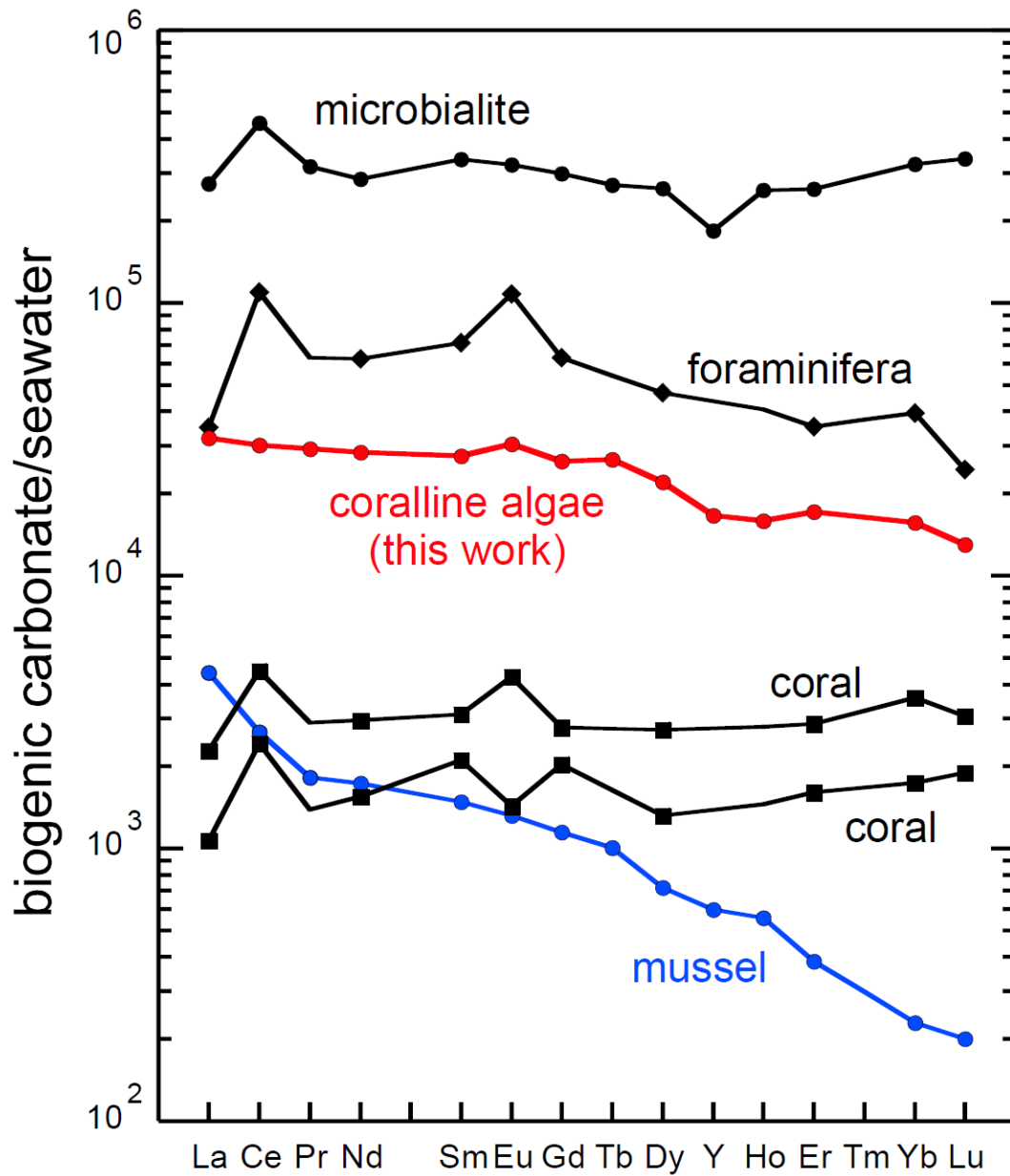
Figure 7. Apparent partition coefficients between biogenic carbonates and seawater, for mussel shells (Ponnurangam et al., 2016), corals (Sholkovitz and Shen, 1995, Terakado et al., 2010), microbialite (Webb and Kamber, 2000), foraminifera (Terakado et al., 2010) and coralline algae (this work, calculated using the Dellec samples and the Dellec seawater measured by Freslon et al, 2011). The marked anomalies in Ce or Y are explained by the highly variable Ce or Y abundances in seawater.
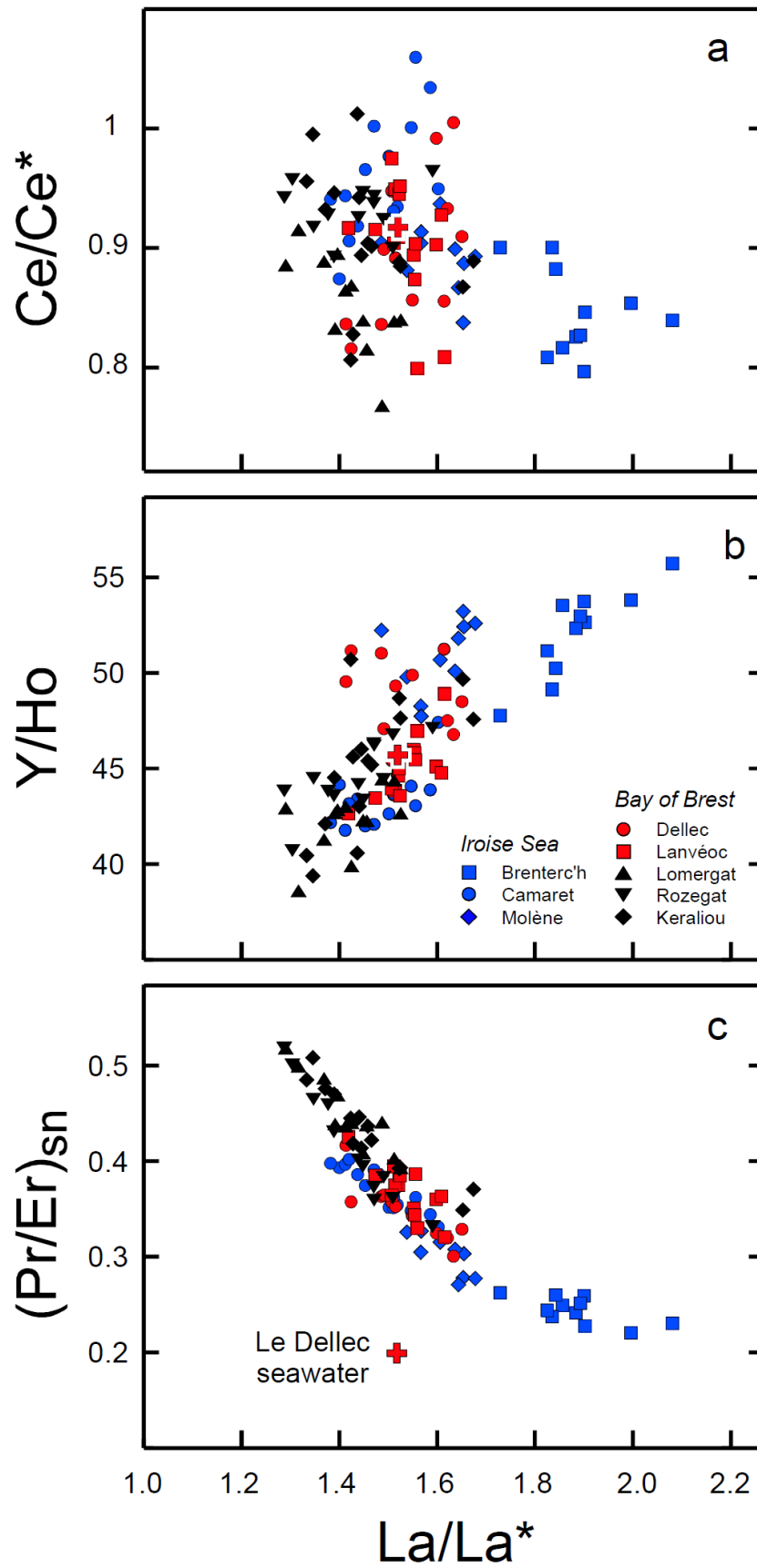
Figure 8. Ce/Ce* (a), Y/Ho (b) and (Pr/Er)$_{sn}$ (c) vs. La/La* plots for coralline algae from Bay of Brest and Iroise Sea.
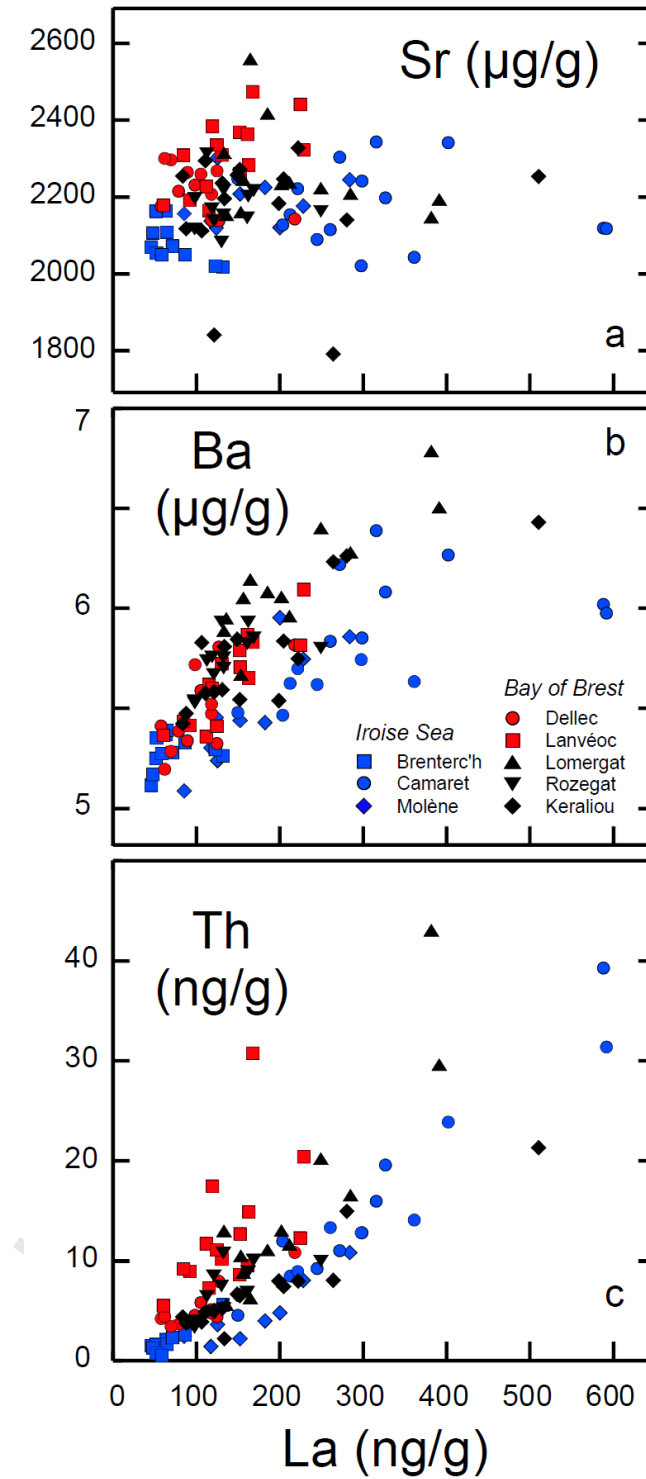
Figure 9. Sr (a), Ba (b) and Th (c) vs. La plots for coralline algae from Bay of Brest and Iroise Sea.
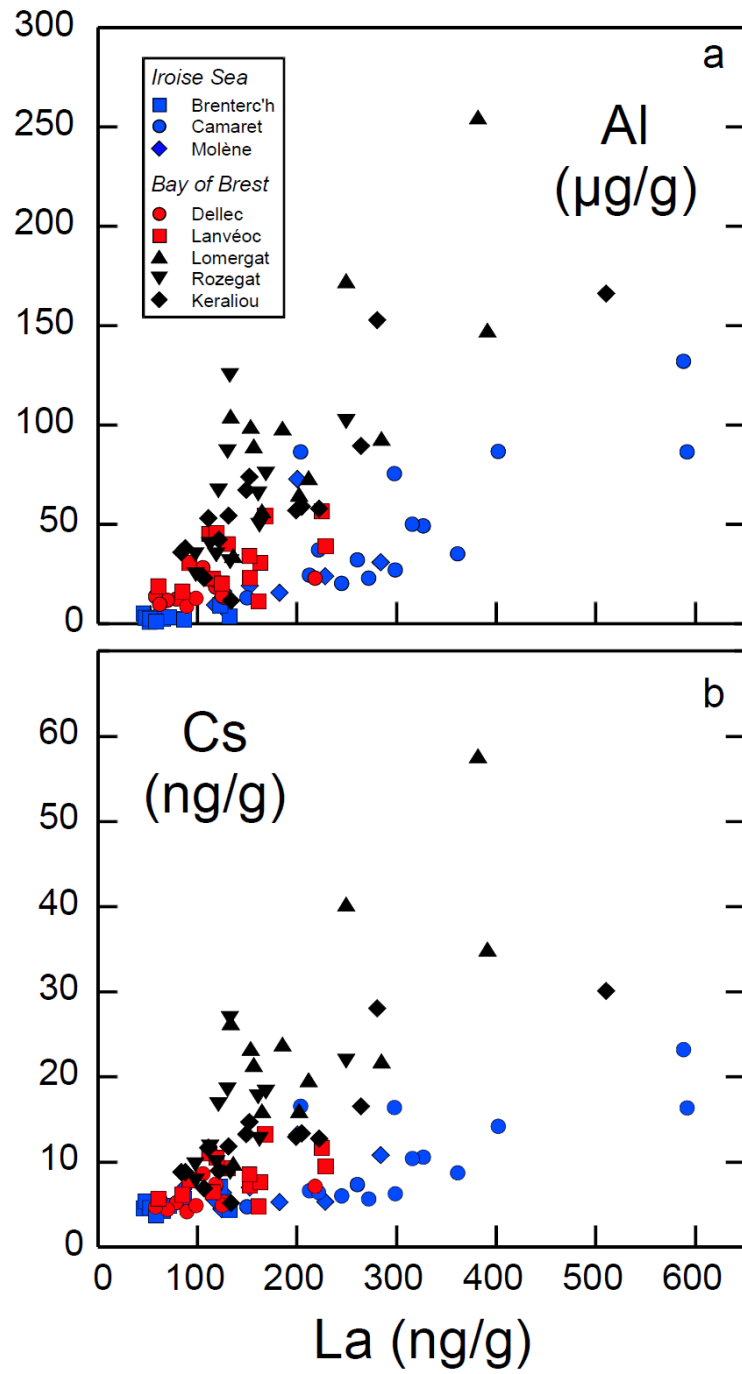
Figure 10. Al (a), and Cs (b) vs. La plots for coralline algae from Bay of Brest and Iroise Sea.
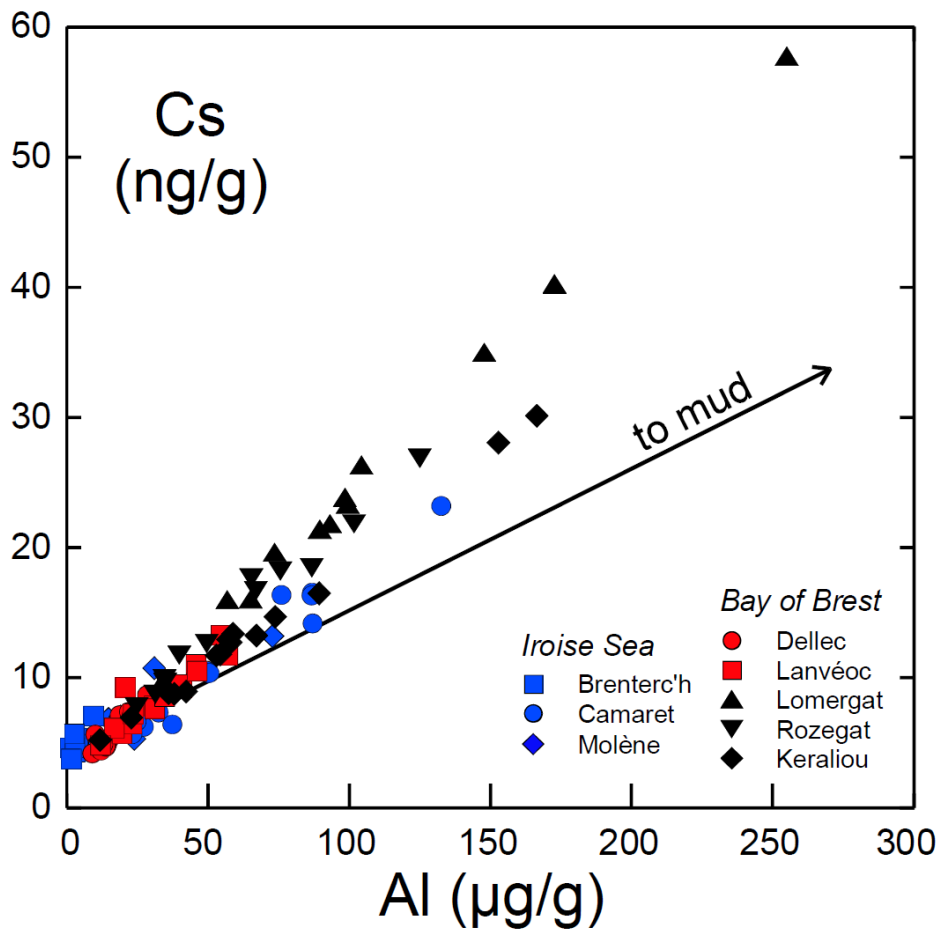
Figure 11. Cs vs. Al plot for coralline algae from Bay of Brest and Iroise Sea.
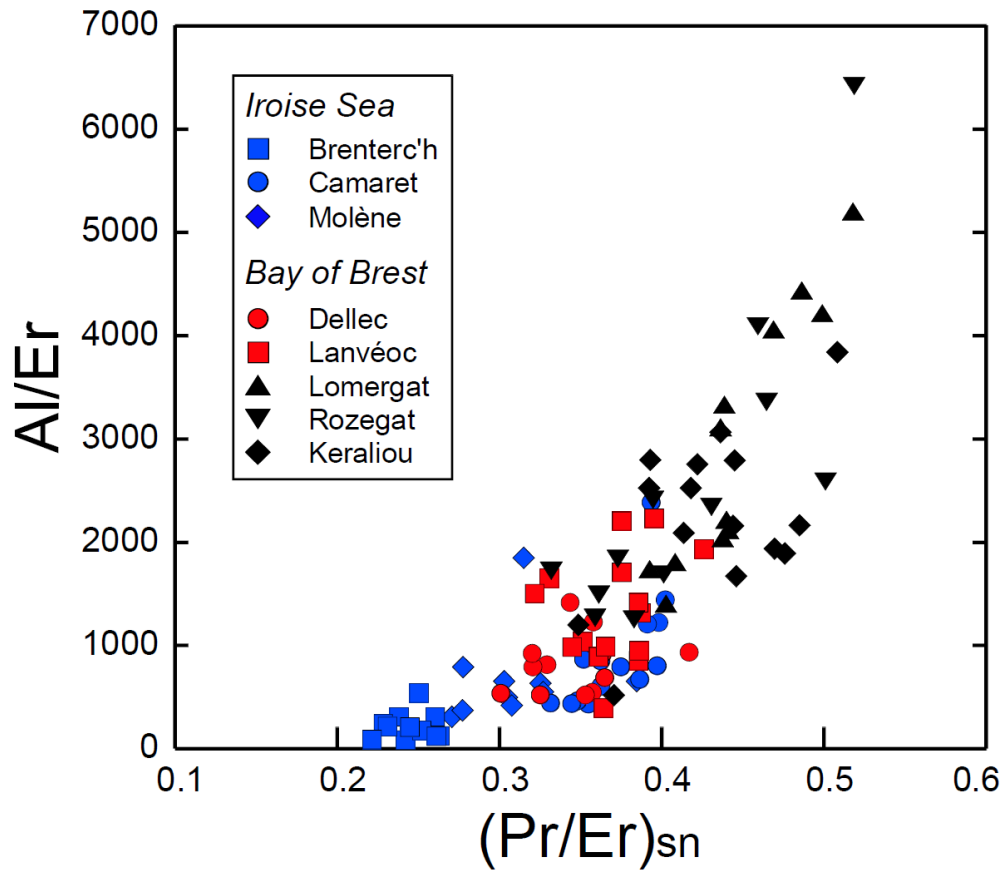
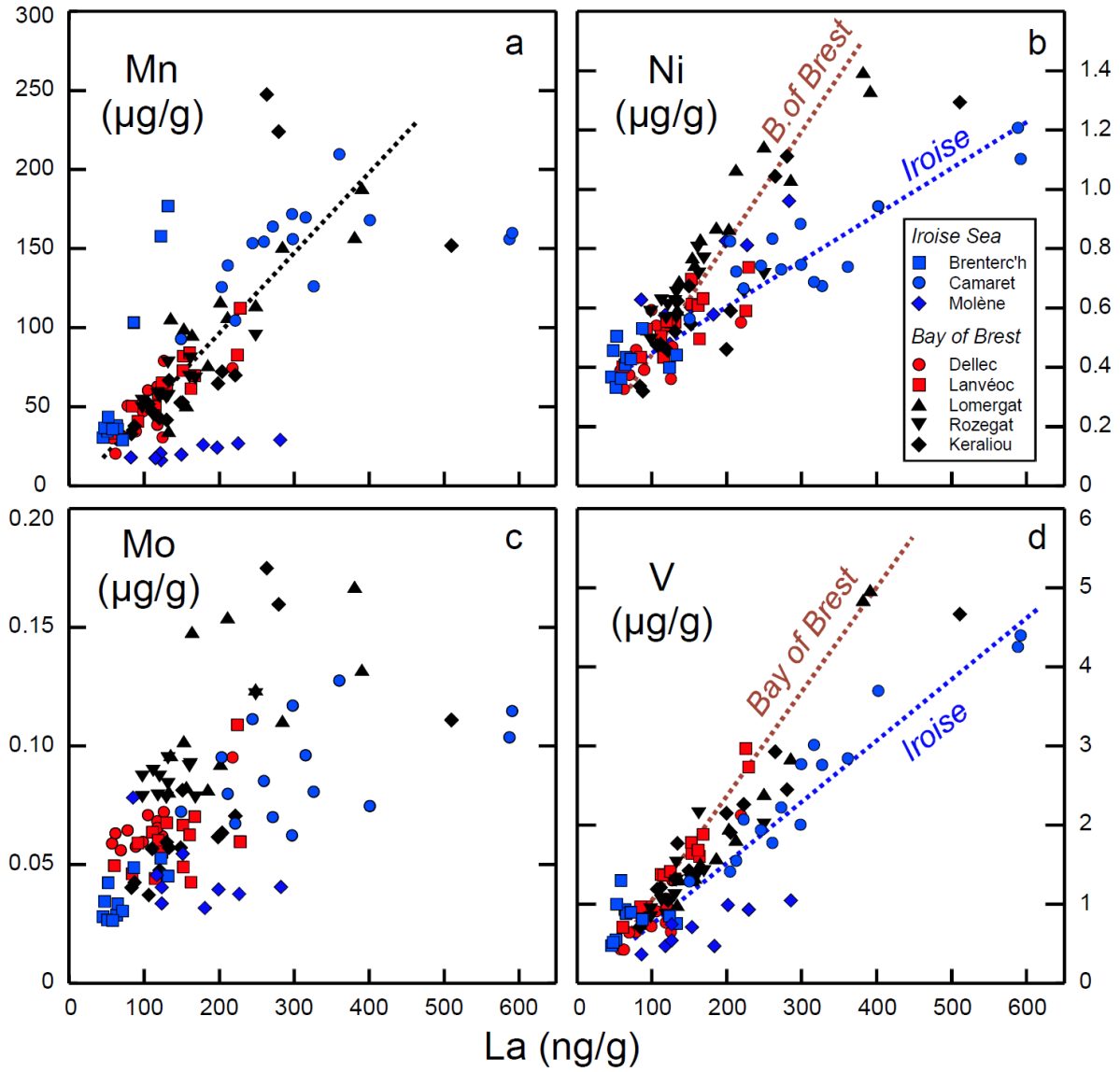Figure 12. Al/Er (both elements in μg/g) vs $(Pr/Er)_{sn}$ for coralline algae from Bay of Brest and Iroise Sea.

Figure 13. Mn (a), Ni (b), Mo (c) and V (d) vs. La plots for coralline algae from Bay of Brest and Iroise Sea.
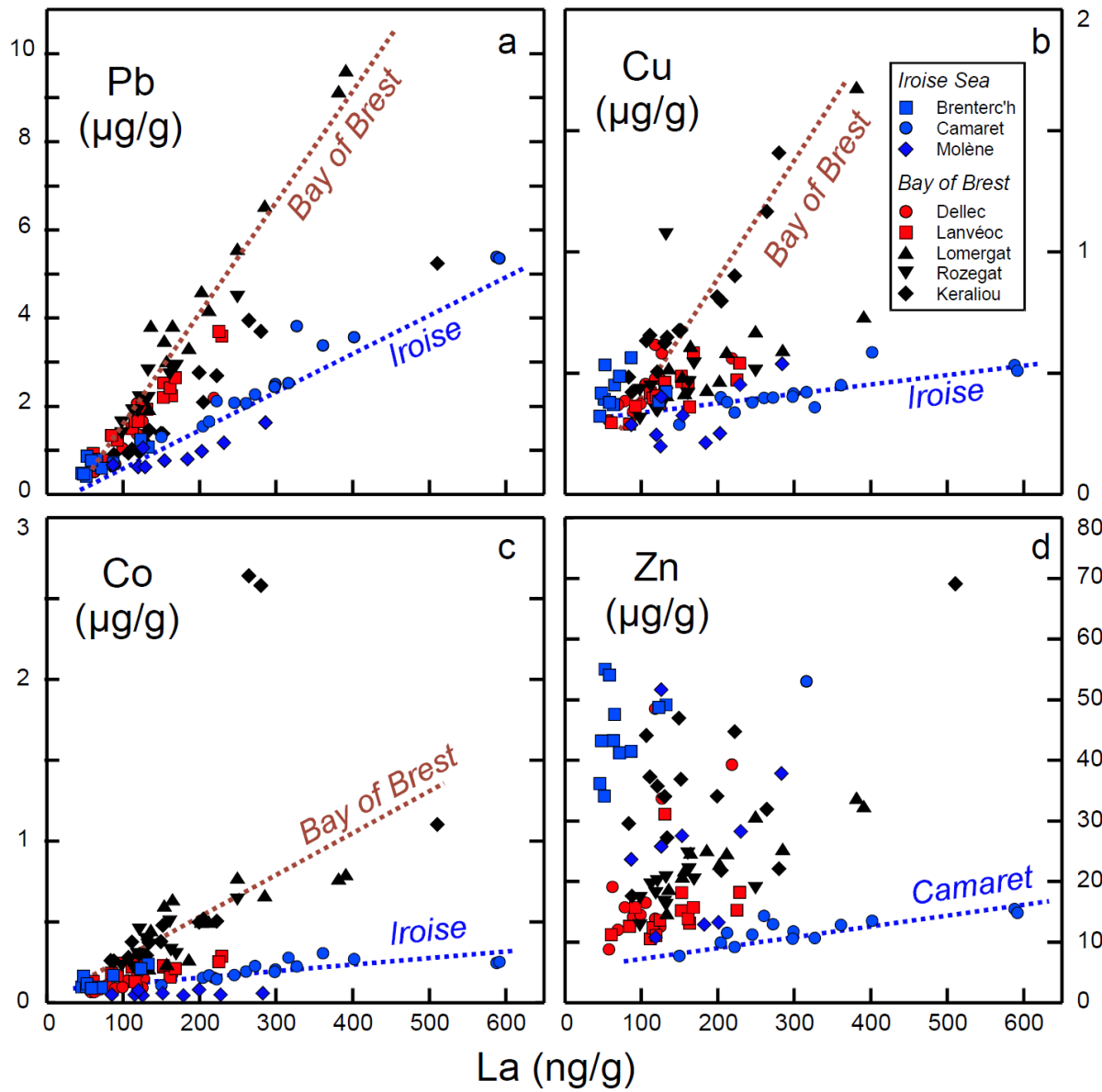
Figure 14. Pb (a), Cu (b), Co (c) and Zn (d) vs. La plots for coralline algae from Bay of Brest and Iroise Sea.
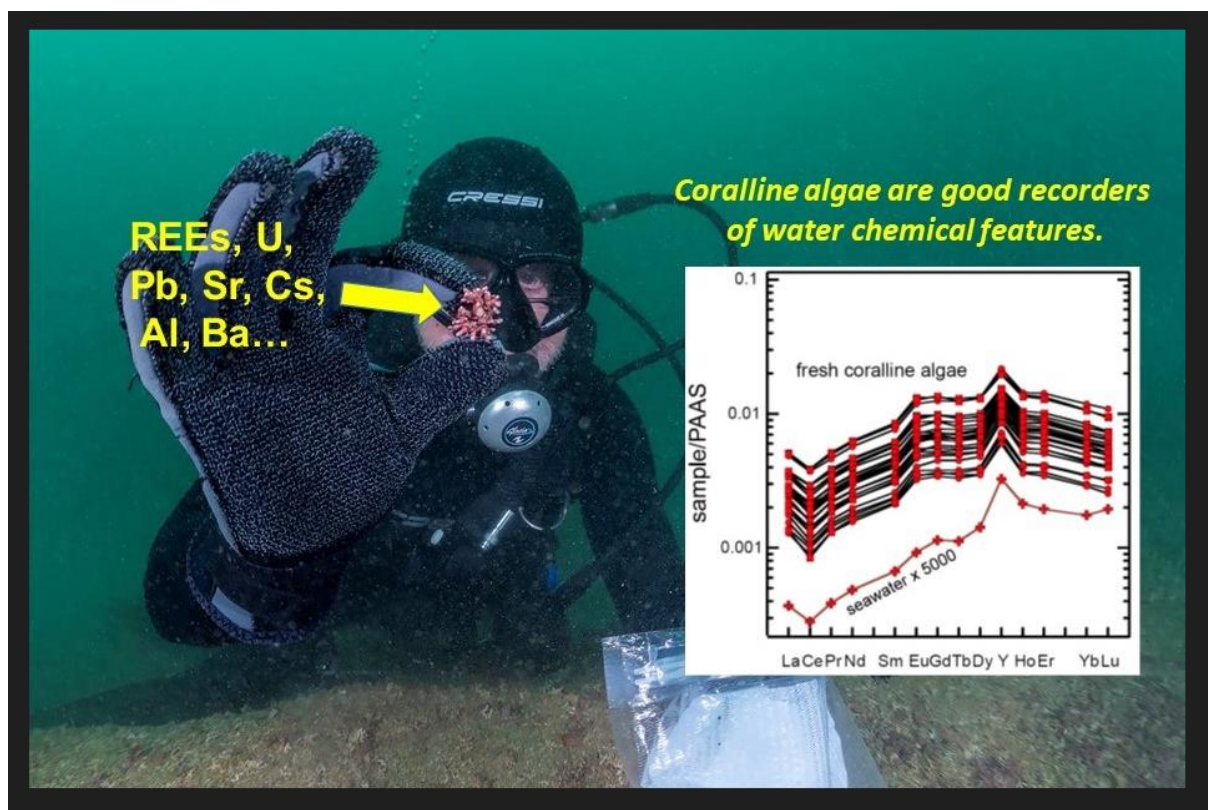
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical abstract

Highlights

- First detailed investigation of rare earth elements in coralline algae.

-Coralline algae bioaccumulate rare earths, yttrium and other trace elements (Sr, Ba, U, Pb…).

-REY distributions in coralline algae and seawater are similar.

-Coralline algae record base metal pollution and river water/seawater mixing.