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Influence of dissolved organic matter on rare earth elements and yttrium distributions in coastal waters

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Data collected during this study indicate that dissolved Y and REE (rare earth element) behaviour can be monitored through shale-normalised ratios. Relationships occurring between these ratios suggest that leaching from lithogenic materials is the main source of REE in the studied area. This process involves riverine detrital matter in the inner area of the Gulf of Palermo. Features of shale-normalised patterns and the relationship recognised between dissolved Fe and Y/Ho suggest that REE are released from Fe-rich coatings of atmospheric dust. Observed similarities between dissolved Fe and chlorophyll- α content suggest that leaching of Fe-rich atmospheric particulates induces a fertilisation of shallow water layers influencing the dissolved organic content. In turn, the increasing chlorophyll- α content causes a progressive decrease in amplitude of the negative Ce anomaly in seawater that is also observed in water in the Central Mediterranean Sea, suggesting that organic matter generally plays a key role in REE behaviour at the solid–liquid interface. Shale-normalised REE features recognised in suspended particulate matter (SPM) indicate the occurrence of three different fractions from lithogenic matter, biogenic carbonates and authigenic components, respectively. The latter is formed during REE scavenging onto the surface of detrital biogenic particles and is mainly recognised in inner gulf waters.

Keywords: rare earth elements; chlorophyll- α ; Ce anomaly; Mediterranean Sea

1. Introduction

The geochemical processes controlling rare earth elements (REEs) and Y migration and deposition in the Earth's surface environment have been intensively investigated in recent years [1–5]. In marine systems, these processes mainly occur in shallow water layers, where atmospheric fallout represents the main source of trace elements, and in coastal waters, where the effects of trace element delivery from the surroundings can be observed. Along continental margins, the simultaneous

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presence of atmospheric fallout occurring in open water conditions is accompanied by the delivery of different materials from large rivers and local watersheds. Under these conditions, processes involving Y and REEs were investigated and an evaluation of their fate and dynamics was carried out [5–9]. The occurrence of anthropogenic pressure is a further complication when defining REE sources and processes that involve them. This is a very important topic in the study of epicontinental basins such as the Mediterranean Sea, where strong anthropogenic pressure occurs in coastal areas. Y and REE have only rarely been investigated in Mediterranean coastal systems [10,11] in order to identify their sources and the processes occurring along the water column.

Therefore, the aim of this research was to investigate Y and REE behaviour under natural seawater conditions in a coastal system in the Central Mediterranean Sea. The Y and REE investigation is associated with the evaluation of Fe and chlorophyll- α concentrations occurring in a dissolved pool in order to identify possible relationships. Moreover, features of shale-normalised REE patterns are used as proxy to recognise sources of these elements and processes involving them along the water column by means of an innovative graphical approach based on an evaluation of light, medium and heavy REE contents (LREE, MREE and HREE, respectively) expressed as a percentage of the whole REE content. The studied area was chosen as being a good example of a coastal system exposed to strong anthropogenic pressure, which causes the dissolved organic concentration to be higher than in the oligotrophic conditions usually occurring in the Mediterranean Sea.

2. REE in a seawater system

Shale-normalised concentrations are a classical method to present REE data and investigate processes involving these elements. The typical features of the distribution of shale-normalised REE concentrations, $[REE_i]_n$, calculated according to the expressions:

$$[REE_i]_n = \frac{[REE_i^{sample}]}{[REE_i^{PAAS}]}, \quad (1)$$

with respect to Post Archean Australian Shales (PAAS; [11]), consist of enrichment in HREE concentrations, compared to LREE and the occurrence of a negative Ce anomaly [12–15], defined as [16]:

$$\frac{Ce}{Ce^*} = \frac{2[Ce]_n}{[La]_n + [Pr]_n}. \quad (2)$$

This behaviour is justified by a progressive decrease of ionic radius with increasing atomic number observed along the lanthanide series. This phenomenon is responsible for slight differences in REE behaviour and enables fractionation processes among LREE, MREE and HREE mainly during interface processes occurring between the dissolved phase and suspended solids (for a detailed discussion see [17]). Therefore the progressive increase of shale-normalised REE concentrations with atomic number, except for Ce, is a consequence of the increasing stability of REE dissolved carbonate complexes from La to Lu [18–19]. In coastal systems, normalised REE patterns can exhibit different features due to particular environmental conditions and processes occurring therein [5, 20–24]. In general, shale-normalised REE patterns can show:

- A monotonous increasing behaviour along the REE series with a negative Ce anomaly, typical of oceanic environments (type 1).
- A stronger HREE enrichment than type 1, explained by the degradation of a particulate organic carbon (POC) or by increased HREE complexation [24].
- $[La/Sm]_n > [La/Lu]_n > [Tb/Lu]_n$ that involves LREE enrichment with respect to type 1 behaviour (type 3). These features are usually explained by the existence of an LREE enriched

source from the weathering of lithogenic materials that can be recognised in areas exposed to the effects of a large delivery of lithogenic particulate matter from atmospheric or riverine sources [25].

Similarly, shale-normalised REE distributions in SPM usually show some classical features:

- SPM with high REE content and a nearly flat shale-normalised REE pattern mirrored by $[La/Sm]_n \approx [Tb/Lu]_n \approx [La/Lu]_n$. According to the detrital source of these SPM, the Y/Ho molar ratio should be clustered around ‘crustal’ values (about 50 molar ratio).
- SPM with lower REE concentrations can present a higher authigenic fraction. In these materials positive Ce anomalies and LREE enrichment over HREE are often recognised due to preferential oxidative scavenging of Ce(IV) and LREE onto an authigenic fraction with respect to HREE that are more stable in the dissolved phase [25]. This material corresponds to surface coatings on detrital suspended particles, often related to the presence of organic particulates [26]. Detailed measurements of Y/Ho in SPM from oceanic seawater report ratio values intermediate between ‘crustal’ and ‘marine’ values, suggesting a similar behaviour for Y and Ho in SPM, mainly driven by similar valence and ionic radii [27].

3. Sampling strategies and analytical procedures

3.1. Sampling

Samples were collected in ten sampling stations along the Tyrrhenian coast of Sicily in the Gulf of Palermo, during the early summer of 2001 during the ANSIC 2001 cruise, aboard the R.V. ‘Urania’ (Figure 1). The sampling location was selected in order to gain knowledge on the delivery of terrestrial materials from the area surrounding the location, with sampling sites located close to the coastline named ‘inner stations’ (SS-01, 02, 03, 04, 05, 06), whereas sites located far from the coastal area, considered as reference sites with more classical marine conditions, were named ‘outer stations’ (SS-07, 08, 09, 10).

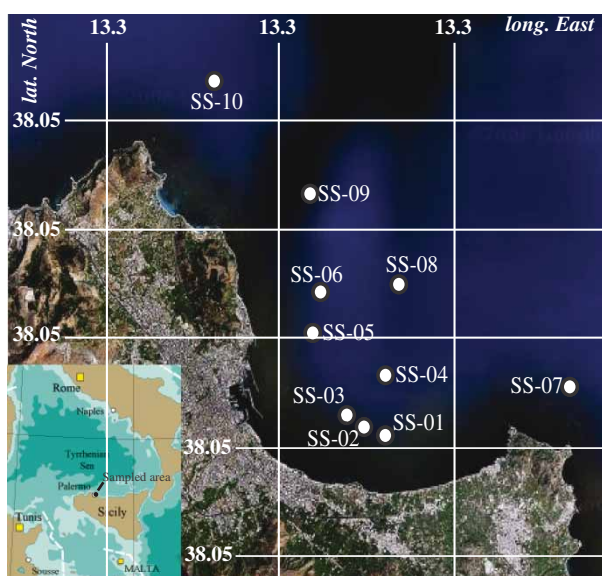


Figure 1. Location of the sampling sites. The satellite image showing the Gulf of Palermo was provided by http://visibleearth.nasa.gov/view_detail.php?id=1868.

The sampling system consisted of a Neil-Brown CTD rosette frame and a 24 × 12 L Teflon-lined GoFlo bottle. Upon recovery, water samples were immediately filtered through 0.2 μm Millipore® filters using a Teflon filtering manifold and acidified to pH 1–2 with HNO₃ (Merck ULTRAPUR®).

To minimise contamination, all material used for collecting and manipulating water samples was plastic-ware and previously cleaned using 1:10 hot high purity HNO₃ solutions (Merck ULTRAPUR®). Manipulations in the laboratory were carried out in a laminar flow clean bench.

3.2. Seawater analysis

In situ chlorophyll- α measurements were carried out by means of a SBE 911 CTD profiler and a SeaTech fluorometer enclosed in the G.O. rosette manifold. The SeaTech (Corvallis, OR) chlorophyll- α fluorometer was equipped with filters optimised for chlorophyll- α in seawater ($\lambda_{\text{ex}} = 330$ nm; $\lambda_{\text{em}} = 450$ nm; bandwidth = 60 and 65 nm, respectively). Oceanographic data were acquired at the maximum frequency of 24 Hz using a PC running Windows XP and Sea-Bird's Seasave Version 5.33 for Windows software. During collection of these data, the sequence of recognised salinity values allowed two main water layers to be identified: a shallow layer above 70 m with salinity of 37.8, and a bottom layer from 70 m to about 300 m with a higher salinity.

Water samples were collected using a 24-position SBE 32 Carousel sampler with 12 litre water sample bottles at different depths. Lanthanide analyses in the dissolved phase were carried out on filtered seawater samples. The optimisation of the seawater REE analysis was performed by pre-concentrating 2000 mL seawater samples with CHELEX 100® (200–400 mesh) chelating resin. pH, measured according to the methods of Butler et al. [28], Dickson [29,30] and Millero et al. [31], was adjusted to 6.0 with CH₃COONH₄ and the sample was loaded into an 8 cm long column filled with CHELEX-100 cleaned and conditioned previously [32,33]. REEs were eluted by 5 mL of HNO₃ 3.5 M yielding a 400-fold enrichment factor. Accuracy and precision of chemical analyses have been assessed according to the following procedure [34]: ten litres of a seawater batch solution were passed twice onto CHELEX-100 resin to remove originally contained Y and REE. Five one-litre aliquots of this solution were used for seawater samples in order to assess the effects of chemicals used during seawater manipulation as procedural blanks (PB) to evaluate the critical values (L_C), the detection limits (L_D) and the limits of quantification (L_Q) for the investigated trace elements, according to the Water Research Centre Procedure for the Determination of L_C , L_D (and ISO/IUPAC determination of L_Q) (see <http://www.epa.gov/waterscience/methods/det/faca/techworkgroup/WRCP.pdf>). Their analyses are reported in Supplementary Table S1 (online only) and represent the contribution to analytical error larger than that due to instrumental sources. Furthermore, 500 μL of standard solution of known REE concentration was added to 5 L of REE-free seawater batch solution and other five 1 L aliquots were obtained (EL 1–5) to measure the recovery of each REE and Y, estimated from the analysis of the five replicate samples. The result of the estimated recovery for each REE is reported in Supplementary Table S1 and range from 88% for Er to 96% for Ce.

3.3. Suspended particulate matter (SPM)

SPM (about 0.015 g) was collected on a 0.2 μm filter from approximately 6 L of seawater. After weighing (± 0.01 mg accuracy), SPM was digested to collect the labile fraction containing trace elements in the exchangeable phases, bounded to carbonates and Fe, Mn oxyhydroxides [35,36]. Extraction was carried out using a microwave oven (CEM Mars 5) equipped with TFM™ fluorurated polymer vessels, adding 25 mL of HNO₃ 0.01 M ULTRAPUR®. Solutions were analysed directly by a ThermoFinnigan ELEMENT 2 ICP-SFMS after the addition of Rh as the internal standard (0.97 nmol L⁻¹), without any further dilution.

All the measurements reported in this paper were carried out in a high resolution mode allowing the signal from the elements to be separated from those of most isobaric interferences, such as BaO^+ .

4. Results

Sampling depth, temperature, salinity, chlorophyll- α , iron, yttrium and REE contents measured in seawater collected at sampling sites are reported in Supplementary Table S2 (online only). Sampling depth, weight of collected particulates, Y and REE contents in SPM are reported in Supplementary Table S3 (online only). Salinity in seawater from the Gulf of Palermo ranges from 37.8–38.6 in the first 300 m of depth, whereas the potential temperature ranges from 14–26 °C. Both in shallow and bottom waters, the distribution of chlorophyll- α is similar over the whole gulf area. Chlorophyll- α is widely scattered, with values from about 0.5–1.1 $\mu\text{g L}^{-1}$ in shallow water, reaching values close to 2 $\mu\text{g L}^{-1}$ at about 80 m and decreasing to 0.4 $\mu\text{g L}^{-1}$ in the deeper part of the water column. These values are higher than those reported in other coastal waters of the Central Mediterranean Sea.

Iron, ranging from 664–920 pmol L^{-1} , is an essential micronutrient for phytoplankton growth and plays a limiting role for primary productivity [37–39]. The values found in the studied area are in agreement with those reported by Bonnet and Guieu [40], showing Fe concentrations from 200–1200 pmol L^{-1} , respectively, in lower spring and summer. Figure 2 shows that both iron and chlorophyll- α concentration have similar profiles, suggesting a large Fe bioavailability in the dissolved phase. According to Visser et al. [41], this may indicate that more soluble poorly crystalline materials provide dissolved Fe in seawater. Unexpectedly, no significant statistical relationships occur in the studied area between dissolved Fe and chlorophyll- α concentrations, suggesting the existence of several iron sources.

4.1. Dissolved fraction

The distribution of shale-normalised REE concentrations are shown in Figure 3, where the composition of the oligotrophic Levantine Intermediate Water (LIW; [42]), is reported as a reference. In

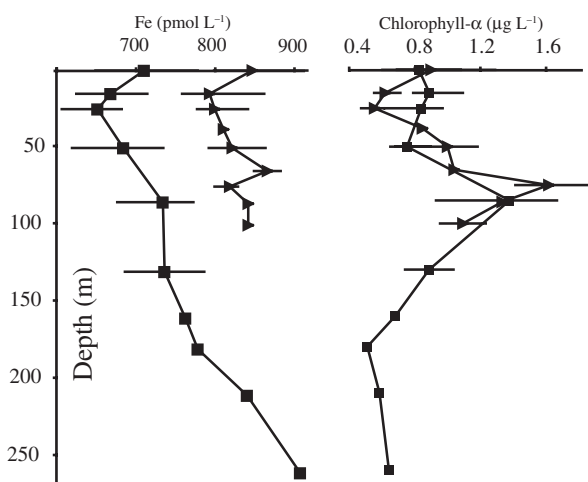


Figure 2. Distribution of Fe and chlorophyll- α concentration along the studied water columns. \blacktriangle : Inner gulf waters. \blacksquare : Outer gulf waters.

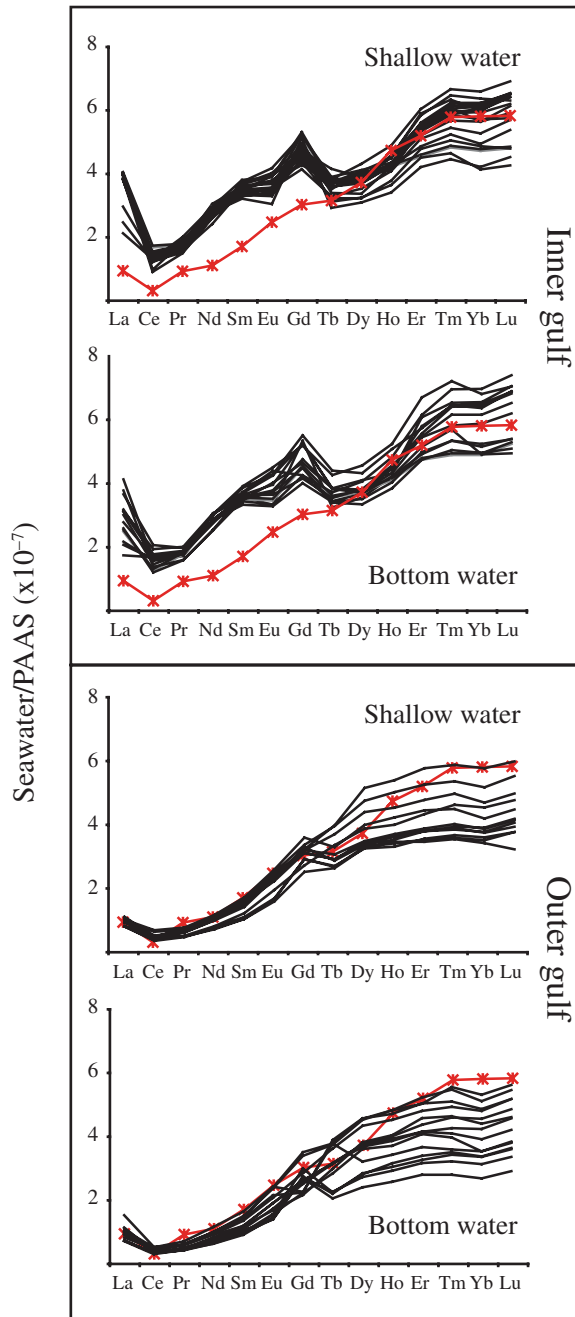


Figure 3. Shale-normalised (PAAS) REE patterns of the analysed seawater samples at different depths [11]. Red path represents REE concentrations measured in LIW [41].

the investigated area, all the samples show LREE depletion, a negative Ce anomaly and Gd enrichment, especially in inner waters. We also found that outer gulf waters have a lower REE than inner waters that are relatively enriched in LREE compared to the LIW. This evidence implies that the shape of shale-normalised REE patterns from inner gulf waters span between type 1 (Figure 4a) and type 3 (Figure 4c) distributions, as evidenced by trend (II) in Figure 4d. On the contrary, low LREE

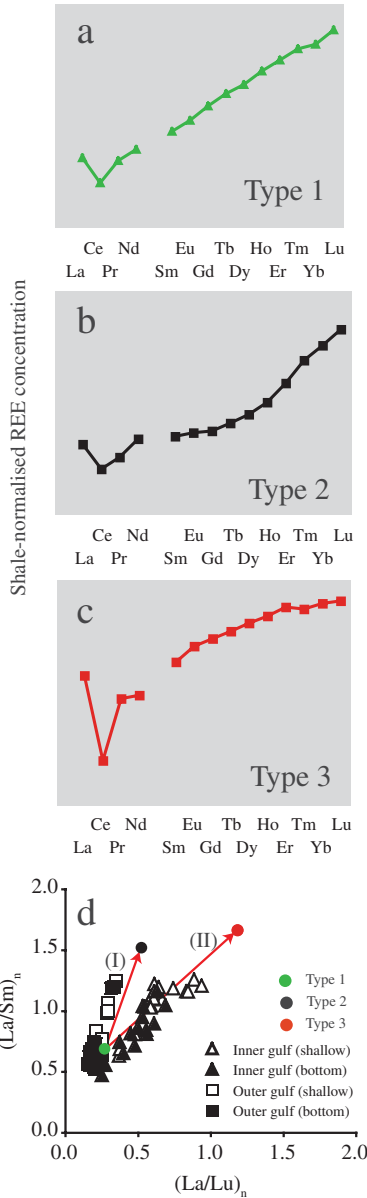


Figure 4. REE patterns usually recognised in seawater. a: type 1, b: type 2, c: type 3. d: distribution of investigated seawater samples in terms of $(La/Sm)_n$ vs. $(La/Lu)_n$ shale-normalised ratios. Trend (I) and trend (II) in diagram (d) indicate evolution of features of shale-normalised behaviour from type 1 to type 2 and from type 1 to type 3, respectively.

content and different features of shale-normalised patterns of the outer-gulf waters with respect to the sample collected in the inner gulf area are evidenced in terms of $(La/Sm)_n$ and $(La/Lu)_n$ ratios that range from type 1 (Figure 4a) to type 2 (Figure 4b) along the water column (Figure 4d). These trends suggest that in inner gulf waters there exists a LREE-enriched source, whereas in outer gulf waters, LREE-depleted materials are dissolved, probably represented by an Fe-rich coating of atmospheric dust, the dominant external input of iron to seawater [43]. This process, corresponding to an evolution along trend (III) from type 1 to type 3, agrees with the observed relationship between Y/Ho ratio and Fe concentration in outer gulf waters. The increase of Fe concentration

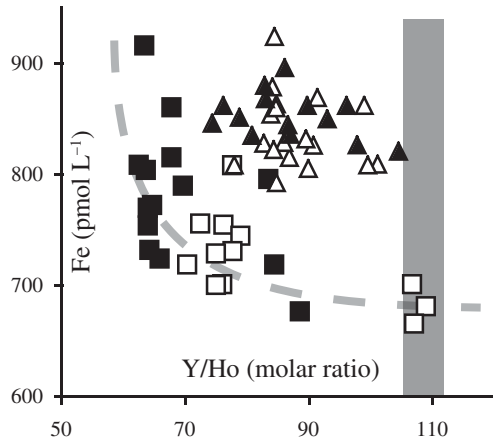


Figure 5. Dissolved Fe concentration and Y/Ho ratio measured in studied seawater. The dashed area represents typical Y/Ho values measured in other areas of the Mediterranean Sea [10,41,43]. Symbols as in Figure 4d. The dashed curve represents a hypothetical mixing array.

from typical values recorded in Mediterranean seawater [10, 44] to higher values is associated to a progressive decrease of Y/Ho values in outer gulf waters only (Figure 5). This evidence suggests a progressive dissolution of Fe-rich materials that are usually characterised by low Y/Ho ratios [45].

4.2. Suspended particulate matter (SPM)

Shale-normalised SPM patterns, displayed in Figure 6, show two different features: a ‘flatter’ pattern, often associated with higher REE contents that can be recognised in materials collected closest to Palermo (SS-01, SS-02 and SS-03 in Figure 6a), and a LREE-enriched pattern, characterised by lower REE concentrations that occur in other collected materials (Figure 6a, b). Both types of pattern show positive Ce anomalies. These two patterns can also be recognised in La/Lu_n–La/Sm_n space, where the studied SPM show two different linear trends (Figure 6c). SPM from the outer gulf area mainly have lower La/Lu_n and La/Sm_n values falling on the left side of both trends, whereas SPM from the inner gulf area show higher values of both ratios. This evidence suggests that La enrichment, previously recognised in the dissolved phase from inner gulf waters, also occurs in suspended materials. Therefore, trends suggest that the observed features in shale-normalised SPM patterns can be explained in terms of reciprocal differences in LREE, MREE and HREE in suspended materials. Therefore, we calculated the fractions relative to LREE, MREE and HREE as percentages of the whole shale-normalised concentration of each SPM sample and plotted them in Figure 7. This figure shows that SPM spans between the MREE–HREE enriched area, where biogenic marine carbonates are deposited as corals [46] and planktonic foraminifera [47], and the LREE corner. Outer gulf SPM are mainly clustered close to biogenic carbonate compositions, whereas inner gulf SPM samples evidence variable LREE enrichments. These shale-normalised SPM features indicate that, in the suspended matter in the studied area, there occurs a lithogenic and biogenic carbonatic contribution, whereas progressive LREE enrichments are suggestive of an authigenic component produced by LREE scavenging as a coating on detrital-biogenic particles [48]. According to this viewpoint, the most LREE-enriched SPM are those collected in the inner gulf area, falling along trends A and B for higher [La/Sm]_n and [La/Lu]_n ratios. On the contrary, suspended matter collected along the water column of outer gulf is less affected by LREE enrichment, falling closer to the origin in Figure 6c.

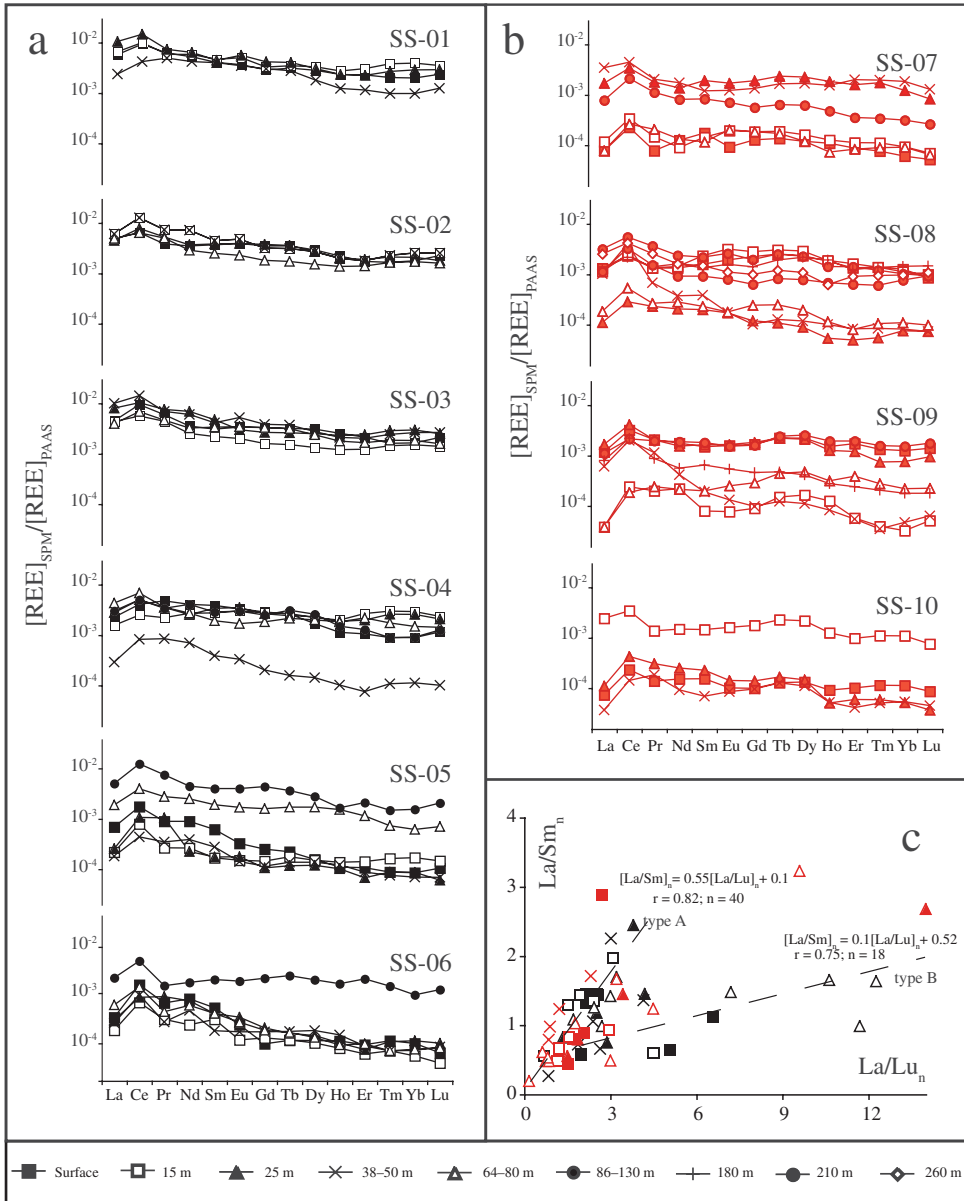


Figure 6. Shale-normalised REE patterns of the SPM samples at different depths. a: Inner gulf area (black symbols); b: outer gulf area (red symbols); c: distribution of investigated SPM in terms of La/Sm vs. La/Lu shale-normalised ratios. The observed evolutions on the latter ratios along two calculated linear trends are reported (colour online).

5. Discussion

The evaluation of amplitudes of LREE, MREE and HREE shale-normalised concentrations, both in the dissolved phase and in suspended materials, is based on the identification of two main sources for released REE in seawater and three different contributions to the SPM budget in the studied area. In particular, shale-normalised REE distributions, Fe concentrations and Y/Ho ratios in the dissolved phase suggest that shallow outer gulf waters receive Fe-rich products and their dissolution influences both the Fe concentration and REE fractionations along the water

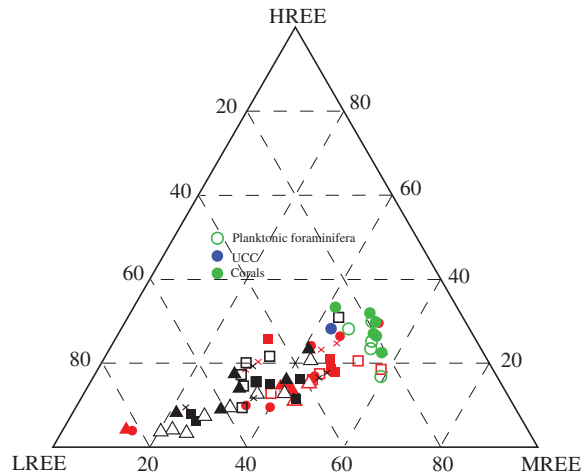


Figure 7. Percent LREE, MREE and HREE contents calculated in SPM. Symbols as in Figure 6. Point representative of mean concentration of Upper Continental Crust (UCC) from [11] (colour online).

column. On the contrary, this process is not evidenced in inner gulf waters, where shale-normalised dissolved REE distributions show a progressive increase of LREE enrichment from deeper to shallower waters, suggesting an additional source of trace elements probably of riverine nature.

Observed similarities between Fe and chlorophyll- α concentrations suggest that leaching of Fe-rich atmospheric particulates induces a fertilisation of shallow water layers under oligotrophic conditions [43,49–52]. The increase of dissolved organic content, in terms of chlorophyll- α , is related to this process and can play an important role in determining REE dissolved behaviour in less oligotrophic coastal systems. This suggestion comes from the observed relationship between the amplitude of the Ce anomaly and chlorophyll- α concentration (Figure 8) in the studied waters, indicating that the dissolved organic carbon can influence the fate of Ce during scavenging processes, as proposed by experimental studies on the effects of dissolved organic contents and the amplitude of the Ce anomaly in water [53–56]. Also, samples collected in the Strait of Sicily between the surface and a 300 m depth [10,57] fall on the same trend reported in Figure 8. This evidence suggests that the Ce/Ce* vs. chlorophyll- α relationship can have general significance, at least for oligotrophic systems such as the Mediterranean Sea. This evidence could indicate that Ce oxidation is avoided in the presence of higher chlorophyll- α concentrations, or that CeO₂ which

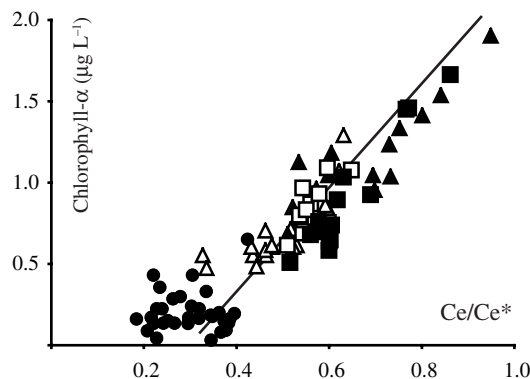


Figure 8. Relationship between chlorophyll- α and Ce anomaly in seawater. Symbols are reported in Figure 2. Full circles (●) represent seawater samples collected in the Strait of Sicily [10]. The linear trend is calculated on all the samples of this study.

is formed is progressively scavenged onto a colloidal organic fraction and cannot be recognised with the usual filtration procedures [58].

The occurrence of an authigenic LREE-enriched SPM fraction mainly occurring in inner gulf areas, where the largest REE and Fe concentrations are measured, both in dissolved and suspended fractions, explains the observed lack of correlation between Fe and Y/Ho values in inner gulf waters (Figure 5). This additional source of REE is probably related to riverine input of organic stabilised Fe-rich colloids that coagulate under high salinity conditions [23]. After colloidal coagulation, LREE are enriched in SPM due to their high particle reactivity, whereas MREE and HREE are enriched in the dissolved phase. In this phase the recognition of positive Gd anomaly values suggests an anthropogenic signature, Gd organic compounds, being widely used as contrast medium in magnetic resonance imaging [9, 59–61]. Moreover, LREE enrichment observed in shale-normalised SPM patterns represents a further effect of anthropogenic pressure [62] and agrees with the organic-rich nature of the authigenic SPM fraction [63].

6. Conclusions

This study shows that REEs in the investigated coastal area are influenced by the delivery of lithogenic materials both from atmospheric and riverine sources. Due to the strong anthropogenic pressure in surrounding coastal areas, the studied site is a less oligotrophic system compared to the usual conditions occurring in the Mediterranean basin. In the studied area, water masses from the inner Gulf are more influenced by the effects of the delivery of terrestrial anthropogenic input, which is recognised especially by positive Gd anomalies in the dissolved phase. On the contrary, the effect of the dissolution of Fe-rich atmospheric dust is evidenced by the relationship between the dissolved Fe concentration and Y/Ho molar ratio. As monitored in terms of chlorophyll- α concentration, iron dissolution fertilises the shallow water masses in the external gulf area and influences the phytoplankton production. This process enables a modification of Ce behaviour during oxidative scavenging that is reflected by the limited amplitude of the recognised Ce anomaly values in seawater. This work highlights the role played by chlorophyll- α concentration on REE distribution in coastal water systems.

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