Balancing Rare Earth Element distributions in the Northwestern Mediterranean Sea

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Abstract

Elemental concentrations of Rare Earth Elements (REE) and isotopic compositions of Neodymium (ϵ_{Nd}) have been measured in three water column profiles in the North Western Mediterranean Sea. Clear enrichments of REE are observed when comparing to adjacent Atlantic waters suggesting REE inputs along the circulation in this area. For the first time, relative proportions of external sources including submarine groundwater discharges (SGD) have been quantified for the studied area. Atmospheric deposition is estimated to be the most important external source for all the REE with an average contribution of 44%, followed by diffusion from porewaters, which provide a 30%. Dissolved riverine fluxes account for 11%, SGD for 10% and dissolution of remobilized surface sediments the remaining 6%. Mass balances accounting for seawater transport and identified external sources have been delineated for the three main water masses (Modified Atlantic Waters, Levantine Intermediate Waters and Western Mediterranean Deep Waters). They show that the balances of REE in this area are dominated by seawater mass mixing. Superimposed on this hydrography, REE vertical profiles are affected by external sources and biogeochemical cycling. Dissolved REE are correctly balanced in deep waters whereas substantial missing fluxes are identified in the surface and intermediate water masses. Additional net LREE outputs and HREE inputs are required in the surface waters while net output fluxes for all the REE are missing at intermediate waters. The most likely process suggested here is an active reversible scavenging, consistent with a stronger adsorption of LREE compared to HREE. In the particular case of the redox-sensitive cerium, the most plausible mechanism to explain the net output missing fluxes is Ce^{+3} removal by particle scavenging via oxidation to insoluble Ce^{+4} . Estimated Ce oxidation rates of $0.33\% \cdot d^{-1}$ in surface waters agree well with previously published values. Exchange fluxes derived from the isotopic Nd mass balance indicate higher Nd scavenging in surface compared to intermediate waters.

Highlights

Significance of dissolved REE transport and external inputs in the NW Mediterranean Sea
Determination of REE fluxes associated with SGD and dissolution of reworked sediments
Importance of reversible scavenging for REE in seawater
Predominant conservative behavior of ϵ_{Nd} in deep waters

Keywords: Rare Earth Elements, Neodymium isotopes, North Western Mediterranean Sea, mass balance, external inputs, reversible scavenging

1. Introduction

The water balance in the Mediterranean Sea is dominated by the exchange with the Atlantic Ocean through the Strait of Gibraltar. The inflow of Atlantic Water (AW) surpasses the outflow

of Mediterranean Overflow Water (MOW) given that the mean evaporation exceeds precipitation (Hecht et al. 1988) and this has important implications for the circulation and biogeochemistry of the Mediterranean Sea (Tanhua et al. 2013). Water circulation is characterized by an anti-estuary pattern (Pinardi & Masetti 2000, and references therein). Atlantic surface water flows in the western Mediterranean Sea as Modified Atlantic Water (MAW; from 0 to 150 m water column depth) following a cyclonic path along the coasts of Italy, France and Spain (Millet, 1991). Some surface water passes through the Sicily strait and a saltier layer of Intermediate Levantine Water (LIW) is finally formed at the eastern Levantine Basin, normally occupying the 200 - 600 m depth range moving westwards (Bethoux & Gentili, 1996; Millet, 2013). The Western Mediterranean Deep Water (WMDW) constitutes the third distinct water mass layer encountered in the Western Mediterranean. This water body is formed during winter in the Gulf of Lion and in the Ligurian Sea where dense waters can reach the seafloor (Gasparini et al. 1999; Béthoux et al., 2002). It flows below the LIW, down to the seafloor and also following a cyclonic path.

Several processes play a role in controlling the composition of natural waters and their comprehension is of fundamental importance to marine geochemistry. In addition to Atlantic inputs, dissolved riverine fluxes and atmospheric deposition may significantly contribute to the chemical budgets in the Mediterranean Sea. However, some chemical imbalances have been detected giving clear proof that we have incompletely considered all the relevant mechanisms. This is the case for trace metals and nutrients such as copper, nickel, silicon and strontium (Spivack et al., 1983; Boyle et al., 1985; Jeandel and Oelkers, 2015; Rodellas et al., 2015), which are enriched in surface waters of the Mediterranean Sea in comparison with adjacent, Atlantic waters. It is thus required to better recognize and quantify the flow of chemical elements brought to the sea and especially to the Mediterranean basin, where trace metal distributions have not received much attention.

The Rare Earth Elements (REE) form a suite of 14 chemical elements with a coherent chemical behavior which have been investigated intensively as geochemical tracers in the marine environment (e.g., Piepgras and Jacobsen, 1992; Jeandel et al., 1998; Alibo and Nozaki, 2004) although the exact mechanisms that bring about their water mass patterns are not wholly understood (Crocket et al., 2018). They can be divided into light REE (LREE: La, Ce, Pr, Nd and Sm) and heavy REE (HREE: Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu). While HREE are strongly bound by stable carbonate complexes in seawater, the LREE are present with a greater proportion of free metal ions, conferring them a higher susceptibility to be removed from seawater by particle adsorption (Byrne and Kim, 1990; Sholkovitz et al., 1994). Among the REE, the isotopic composition of Nd (denoted as ϵ_{Nd} ; $\epsilon_{Nd} = ([(^{143}Nd/^{144}Nd)_{sample}/(^{143}Nd/^{144}Nd)_{CHUR}] - 1) * 10000$, where CHUR stands for the Chondritic Uniform Reservoir and represents a present-day average Earth value: $(^{143}Nd/^{144}Nd)_{CHUR} = 0.512638$; Jacobsen and Wasserburg, 1980) in seawater has been also recognized as tracer of water masses and of processes controlling the marine geochemical cycling of elements (e.g. Lacan et al., 2012; Siddall et al., 2008). Close to source regions and continental margins, they provide valuable information on lithogenic inputs (Jeandel et al., 2007). Far from the coasts, the particular use of ϵ_{Nd} as a water mass tracer in oceanographic and paleoceanographic studies is possible due to the quasi-conservative behavior of Nd at deep and intermediate water masses and the negligible biological fractionation affecting Nd isotopes (Goldstein and Hemming, 2003; Rickli et al., 2009; Elderfield et al., 2012; Martin et al., 2012; Stichel et al., 2012; Tachikawa et al., 2017).

Here we seek to describe the dissolved REE and ϵ_{Nd} distributions in the Northwestern (NW) Mediterranean Sea and disentangle the roles of different external sources such as the atmospheric input and those occurring at the land-ocean interface that can be considered as Boundary Exchange processes (Jeandel, 2016; Crocket et al., 2018): 1) Submarine Groundwater Discharge (SGD; Santos et al., 2012), 2) partial dissolution of reworked lithogenic sediments

and 3) dissolved REE release from porewaters. We here treat these processes separately although being aware that a clear differentiation among them (especially, the last two) is subject to discrepancies because of the nuanced (and not well-resolved) mechanisms involved (Haley et al., 2017). Our aim is to estimate the first and second processes with our own data and use literature values for the estimation of the third component. In addition, we attempt to assess the influence of physical transport (i.e., water mass mixing) relative to non-conservative biogeochemical processes (e.g., particle scavenging and remineralization). Very few data are available in the literature on the distribution of REE and Nd isotopes in the NW Mediterranean Sea. Only one profile of dissolved REE (Greaves et al., 1991) and one of neodymium isotopic composition (Henry et al., 1994; unfiltered samples) have been previously published in this region, measured in seawater collected in the 1980s. The other published data on dissolved REE and/or ϵ_{Nd} in the Mediterranean Sea are located close to the Alboran Sea or in the eastern basin (Tachikawa et al., 2004). Therefore, our set of data shall improve the understanding of distribution and biogeochemical cycles of these trace elements in the NW Mediterranean Sea.

2. Sampling and methods

The seawater sampling in the Northwestern Mediterranean Sea was conducted on May 2013 on board the Spanish vessel “Ángeles Alvariño” (MedSea-GA04 cruise; PI’s: Patrizia Ziveri and Jordi Garcia-Orellana, UAB) as part of the international GEOTRACES programme. We collected seawater samples for dissolved REE and ϵ_{Nd} analysis from three water column profiles (Figure 1): the Northern Algero-Balear (St. 20), the Central Algero-Balear (St. 21) and the Catalano-Balear (St. 22). Samples of 10 L for ϵ_{Nd} and 500 ml for REE were collected from Niskin bottles and filtered on board through 0.4 μ m pore size Supor membranes (142 mm, PTFE filter holders) within 4 h of sampling. All seawater samples were acidified to pH=2 with ultrapure concentrated HCl. Groundwater samples (120-250 ml for REE and 10L for ϵ_{Nd}) were collected from flowing coastal springs (*S. Centre*, *S. Peníscola*, *S. Ullals* and *S. Camping*) in areas where groundwater discharge has been previously estimated along the Spanish Mediterranean coast using these end-members (Mejías et al., 2008; Rodellas et al., 2012; Rodellas et al., 2017; Trezzi et al., 2016a). Also, fresh water (S=0.71) from the Ebro river was collected (40° 42.768' N; 0° 35.047' E; Oct 2014) for dissolved REE and ϵ_{Nd} in order to characterize the riverine influence. All these samples were filtered and treated as for the seawater samples. In addition, we conducted a batch experiment in the laboratory with 60L of filtered seawater and 55 g (dry weight) of typical coastal sandy sediments from the Eastern Spanish margin (40.358 °N, 0.402 °E) with c.a. 30% of carbonates and 70% of mineral phases dominated by quartz (López et al., 2016). The container was shaken daily to ensure sediment suspension. Dissolved silica (SiO₄) and pH measurements were made every day while aliquots for analyses of dissolved REE and Nd isotopes were collected at different time periods (t=0, 3, 7, 10, 13 and 17 days). Dissolved silica was analyzed at CMIMA/CSIC, Barcelona, Spain) by colorimetric determination (AA3/HR Autoanalyzer; Grasshoff et al., 1983).

Samples for dissolved REE analyses were spiked once in the laboratory with commercial ¹⁵⁰Nd (97.5600±0.01%) and ¹⁷²Yb (97.1500±0.05%) (Oak Ridge National Laboratory, US Department of Energy) and 0.65 mL of a Fe solution (3.7 g L⁻¹) were added. After equilibration, the pH was increased to 7–8 with ultrapur NH₄OH to induce REE co-precipitation with iron hydroxides. When the precipitate was well formed and settled, the bulk of the supernatant was discarded and the remaining precipitate was carefully rinsed with twice-distilled water and centrifuged several times, to eliminate as much salt as possible. The recovered REE-Fe(OH)₃ were fully dissolved in 3 ml of twice-distilled 1M HCl. After evaporation, the dry residue was dissolved in 1 ml 6 M HCl and loaded on an anion exchange column (AG1x8 resin, 100- 200 mesh) to isolate the REE fraction from Fe (Lacan and Jeandel, 2001). The Inductively Coupled Plasma Mass Spectrometer (ICP-MS) used for the REE concentration analyses was an Agilent 7500 CE. All REEs were determined by the external standard method, whereas Nd and Yb were additionally

determined by isotopic dilution, following Lacan and Jeandel (2001). The values obtained for Nd and Yb concentrations enable us to determine the analytical recovery (from 75% to 90% in both cases, except for MS_5 and MS_8 samples). Efficiencies of the chemical protocol for the other REE were calculated by linear interpolation with respect to their masses. Instrumental drift during the measurement session was monitored using an In/Re internal standard method. Procedural blank values ranged from 0-1% for all the REE and 1-3% for Ce. Sample to background signal ratios ranged from 50 to 6000. The percentages of oxide and hydroxide formations were previously determined by measurements of monoelemental REE standards and the calculated interferences were accurately subtracted from samples. They ranged from 0 to 2% for all the REE except for Gd and Eu, which were affected by interferences from 1 to 7%. Accuracy was assessed by comparison of measurements of the SLRS5 reference material (riverine water, NRC Canada, not certified for REE) with a compilation of analyses performed by 10 French laboratories (Yeghicheyan et al., 2013). The resulting accuracies ranged from 0.5% to 2.5 % for all the REE except for Eu (8%).

The particulate-derived REE concentrations were determined from the suspended particles trapped on the 0.4 μm pore size Supor membranes used for the collection of dissolved REE and ϵ_{Nd} . In the laboratory, the protocol consisted of a two-step digestion of the filters in a microwave oven (CEM Mars 5) equipped with TFM vessels. The filter was first digested with a mixture of 5 ml Plasma Pur HF and 5 ml of Plasma Pur HNO_3 . A volume of 17 ml of H_3PO_3 was then added for a second digestion to ensure complete removal of HF. After complete dissolution, the acid excess was removed up to incipient dryness using a PTFE Hot Plate in the clean lab and the final residue redissolved in diluted HNO_3 for spectrometric analysis. Particulate REE concentrations were determined with an Agilent 7500 CE ICP-MS using In/Re as an internal standard, as for the water samples. The proportion of oxide and hydroxide interferences were more important in these measurements due to the scarcity of the suspended material, ranging from 0-5% for all the REE except for Tb (5-15%), Gd (7-16%) and Eu (from 5 to 35% for the quantifiable samples). Europium was found to be below detection limit or too affected by interferences (>50% of oxides/hydroxides) in six samples. Total procedural blanks, including filter leaching, turned out to be 13 pg on average for the heavy REE and Sm, 60 pg for Pr; 270 pg for La, 415 pg for Nd and 500 pg for Ce.

For Nd isotope analyses, dissolved REEs from 10 L of filtered seawater/groundwater/river water were pre-concentrated in the laboratory by slowly (<20 ml/min) passing the water sample through SEP-PAK C18 cartridges (2 per sample), previously impregnated with 300 mg of HDEHP.H2.MEHP complexing agent (Shabani et al., 1992). Then, 5 ml of HCl 0.01 M were passed (20 ml/min) through the cartridge to eliminate the major fraction of barium and REE were next eluted from each cartridge with 35 ml of HCl 6M (same flow rate). The eluted sample was evaporated and 0.1 ml HNO_3 16 M was added to eliminate the organic matter by evaporation. Subsequently, a chromatographic extraction using cationic resin (Dowex AG 50WX8; 200-400 mesh size) was used to separate the REEs from major ions (such as Ca, Sr, Ba and Mg), and a final purification based on a reversed phase chromatography with anionic Ln resin was performed (Pin and Zalduegui, 1997).

Measurements of Nd isotopic compositions were carried out on a Finnigan MAT 261 thermal ionization mass spectrometer (TIMS) located at LEGOS in Toulouse; static mode and Nd measured as metal). The $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ to correct for instrumental-induced mass discrimination. An international standard (La Jolla, $^{143}\text{Nd}/^{144}\text{Nd} = 0.511858 \pm 0.000007$; Lugmair and Carlson, 1978; Lugmair et al. 1983) was routinely analyzed within the 7-days session to monitor instrument drift. The average value obtained was 0.511873 ± 0.000005 (2SE; n=40) and thus all the sample analyses were adjusted to the La Jolla value to take into account the average bias. The quoted uncertainties in isotopic values given here include the propagated uncertainties of these corrections. No measurable signal was detected in the three procedural blanks analyzed.

3. Results

Potential temperature *versus* salinity plots allow us to identify the water masses sampled (Figure 2). Modified Atlantic Waters (MAW) were partially mixed with Winter Intermediate Waters (WIW) at the first sampling depth of 100 m. Below, 250 m and 500 m depth samples correspond to Levantine Intermediate Waters (LIW), except for the 250 m sample of St. 21, which falls on the WIW layer (Castrillejo et al., 2017). All the other samples from 1000 m depth to the bottom were taken within the Western Mediterranean Deep Waters (WMDW).

Dissolved and particulate REE concentrations and dissolved ε_{Nd} are compiled in Tables 1 and 2. Dissolved REE show a rather narrow range of concentrations in the NW Mediterranean Sea (e.g. Nd = 19-23 pmol·kg⁻¹; Gd= 6.6-7.7 pmol·kg⁻¹ and Yb= 5.9- 6.6 pmol·kg⁻¹), without any significant trends at depth, especially for HREE (Figure 3). In the Northern Algero-Balear region (St. 20), some dissolved LREE (e.g. La) show higher concentrations in surface waters, relatively constant profiles in intermediate waters and increasing values at bottom depths (Figure 3). In the same region, HREE are quite homogeneous throughout the water column (Figure 3). The St. 21 in the Central Algero-Balear area shows higher concentrations in the upper 500 m with rather constant profiles below. The Catalano-Balear profile (St. 22) displays smooth profiles with perceptible minima in dissolved LREE at intermediate depths (250-500m). Dissolved cerium displays more variability (6.7-15.2 pmol·kg⁻¹). Pronounced enrichments are observed at the surface: they can reach 24 to 85% compared to the underlying waters at the three stations. They also show slightly increasing values towards the bottom at St. 20 and St. 21. Despite having been collected 30 years apart, it is worth comparing our dissolved REE concentrations with those documented in the nearby station 10708 of Greaves et al. (1991; Figure 3). These REE values are very similar for deep waters while differences are observed in the first 500 m or 1000 m, the concentrations reported by Greaves et al. (1991) being significantly higher (Figure 3). However, our data still show clear enrichments compared to adjacent Atlantic waters (St. 10404 from Greaves et al., 1991; 34°22'N, 12°29'W) that globally range from 60 to 100% in surface MAW/WIW, from 19 to 80% in the LIW layer and from 8 to 49% in WMDW. Such enrichment has been already indicated for several chemical elements (e.g. some metals and nutrients such as copper, nickel, cadmium and iron; Spivack et al. 1983; Boyle et al., 1985; Tovar-Sanchez et al., 2014).

In order to visualize elemental fractionation relative to the continental source and remove the even-odd variation in their natural abundances, dissolved REE concentrations are normalized to those in Post Archean Australian Shale ("PAAS", McLennan, 1989). The obtained PAAS-normalized REE concentrations show typical seawater patterns (Figure 4), with a heavy REE enrichment relative to the light REE that has commonly been attributed to preferential LREE scavenging by marine particles (Elderfield, 1988; Byrne and Kim, 1990; McLennan, 1994; Sholkovitz et al. 1994), although Akagi et al. (2011) suggested the dissolution of HREE-enriched diatom opal as the responsible. In addition, dissolved cerium (Ce³⁺) is typically depleted relative to its neighboring REEs, consistent with the low solubility of the oxidized form of this element (Ce⁴⁺; Elderfield, 1988; Byrne and Kim, 1990; Moffett, 1990; Bertram and Elderfield, 1993; Sholkovitz et al., 1994; German et al., 1995; Tachikawa et al., 1999; Figure 4). Slightly positive anomalies (i.e., an enrichment of a rare earth element relative to its neighbors) of La, Gd and Lu are also evident, but their causes are still under debate within the scientific community. The potential triggering factors are i) larger stability of these elements in the dissolved phase with respect to their neighbors and ii) seawater interaction with authigenic particles and barite crystal (Garcia-Solsona et al., 2014). In the case of Gd, these positive anomalies particularly high in surface waters are likely related to human contamination driven by the Gd extensive use as contrasting agent in radiography (Hatje et al., 2016).

Particulate REE concentration data are reported on a per-kg-of-filtered seawater basis because accurate weights of particles could not be determined. This allows us to compare dissolved and particulate concentrations, both expressed on pmol·kg⁻¹ of seawater, keeping in mind that the

REE particulate concentration value also comprises the particle abundance in the sample analyzed. Except for cerium, the REE concentrations in suspended particles represent between 1 and 10% of the total (dissolved + particulate) REE depending on the element, with three exceptions. The first one is surface waters of St. 20 (100 m depth), where particulate REE individually show high values compared to the remaining water column with enrichment factors (particulate REE at 100m divided by average particulate REE underneath) ranging from 6 (Lu) to 14 (Sm and Eu). Secondly, deep waters in St. 22 show relatively high particulate LREE, representing from 10 to 23% of the total LREE pool, depending on the element. The third case concerns the 1000 m depth at St 21, which presents 10-fold enhancements of particulate HREE compared to the rest of the water column (Figure 5, Table 2). The contributions of particulate Ce to the total pool of this particle reactive element peak at surface waters of St. 20 is of 80%, while intermediate to deep waters show particulate Ce proportions of 30-40%. The PAAS-normalized patterns of particulate REE point to a predominant lithogenic origin since they basically display a flat shape with some scattering of data in St. 21 (Figure 4).

The Ebro station, sampled at the freshest part of the estuary ($S = 0.71$) show low dissolved REE concentrations compared to other rivers in the literature (Sholkovitz, 1995; Rousseau et al., 2015), e.g. $Nd_{Ebro} = 20 \text{ pmol}\cdot\text{kg}^{-1}$ contrasting with $Nd = 700 \text{ pmol}\cdot\text{kg}^{-1}$ measured by Rousseau et al. (2015) at the fresh portion of the Amazon estuary. Our riverine sample presents the strongest HREE enrichment seen in our set of data and a positive Gd anomaly ($Gd/Gd^* = 1.7$; Figure 6), probably linked to anthropogenic contamination that is commonly observed in rivers in densely populated countries (Kulaksız and Bay, 2011). Such contamination reflects the impact of hospital wastes, stabilized Gd solution being often used as contrasting agent in radiography practices. Unfortunately, the particulate fraction could not be sampled at this station in the framework of the present study.

The dissolved REE content in the coastal springs' groundwater shows a positive linear correlation (except for Ce) with salinity ($R = 0.99$; $p \text{ value} < 0.01$; $n = 3$), suggesting progressive REE release from aquifer solids due to displacement from surface sites by more abundant competing cations (Sholkovitz, 1995; Sholkovitz and Szymczak, 2000; Johannesson et al., 2017). We do not observe removal of dissolved REE from groundwater due to salt-induced flocculation likely reflecting the very low organic carbon concentrations characterizing these waters (Johannesson et al., 2017). However, since we only have the salinity values of three coastal springs out of five groundwater samples (Table 1), we are aware of the weakness of the correlation and interpret these data with caution. The PAAS-normalized REE patterns in groundwater are enriched in HREE and also show positive Gd anomalies (Gd/Gd^* from 1.1 to 1.7), similar in magnitude or larger than in seawater (Gd/Gd^* from 1.13 to 1.18; Figure 6). A different pattern is obtained for well 6, with weak HREE enrichment and a large positive anomaly of europium of $Eu/Eu^* \approx 3$ (calculated following Grenier et al., 2018; Figure 6). Such feature may be explained by positive Eu anomalies in the volcanic massive sulfide deposit through which this groundwater is flowing (Trezzi et al., 2016b). Indeed, positive Eu anomalies (Eu/Eu^* from 2 to 5) are characteristic of massive sulfides in modern settings due to the redox conditions of ore-forming hydrothermal fluids (Leybourne and Cousens, 2005).

The seawater column profiles of Nd isotopic compositions are plotted in Figure 7. The most radiogenic value of $\epsilon_{Nd} = -7.6$ is found at 500 m depth of St. 20, corresponding to Levantine Intermediate Waters coming from the eastern basin. Upper MAW and intermediate LIW at St. 22 are also relatively radiogenic (-8.0 at 100 m and -7.9 at 250 m) while St. 21 shows unradiogenic surface waters with $\epsilon_{Nd} = -9.2$ coinciding with the core of the MAW recorded at this station (Figure 2). Rather constant values are observed for WMDW with average $\epsilon_{Nd} = -8.9 \pm 0.4$, excluding bottom waters of St. 22. These latter waters display a substantial increase in ϵ_{Nd} to a more radiogenic value (from -9.6 at 1800 m to -8.0 at bottom 2200 m depth) potentially reflecting the influence of lithogenic material, as indicated by increased particulate REE concentrations (Figure 5). Overall, our data are less radiogenic than the seawater from the eastern Mediterranean Sea (Levantine Basin ϵ_{Nd} values from -4.8 to -7.8 ; Tachikawa et al.,

2004) but more radiogenic than westernmost seawaters (Alboran Sea and Strait of Gibraltar ϵ_{Nd} values from -8.9 to -10.8; Tachikawa et al., 2004), consolidating the previous findings that Nd values become more radiogenic during the eastward circulation in the Mediterranean Sea and unradiogenic again when they come back to the western basin and Gibraltar exit (Tachikawa et al., 2004).

4. Discussion

4.1. SGD-related fluxes of Rare Earth Elements into the NW Mediterranean Sea

Submarine groundwater discharge to the coastal zone could be a relevant contributor to the dissolved REE budget in the study area as it has been demonstrated for other elements (Garcia-Solsona et al., 2010; Rodellas et al., 2015; Trezzi et al., 2016a) and in other oceanic regions (Johannesson et al., 2011; Kim and Kim, 2014; Johannesson et al., 2017). A first approximation of the SGD-associated input of REE is estimated by multiplying the groundwater REE concentration ($\text{pmol}\cdot\text{kg}^{-1}$ of water) by the SGD water flux ($\text{m}^3\cdot\text{y}^{-1}\cdot\text{km}^{-1}$ of coastline). The *S. Centre* brackish spring is taken as the groundwater end-member for dissolved REE concentrations. The water flux is estimated by averaging the SGD fluxes in the studied region from published literature (i.e., $130,000\text{ m}^3\cdot\text{d}^{-1}$ from Mejías et al., 2008; $53,000\text{ m}^3\cdot\text{d}^{-1}$ from Rodellas et al., 2012; $175,000\text{ m}^3\cdot\text{d}^{-1}$ from Rodellas et al., 2017 and $39,000\text{ m}^3\cdot\text{d}^{-1}$ from Trezzi et al., 2016a) after normalization for their particular coastlines (0.4 km, 0.5 km, 15 km and 0.7 km, respectively). The obtained shore-normalized SGD flux for the NW Mediterranean Sea is of $46\cdot 10^6 \pm 30\cdot 10^6\text{ m}^3\cdot\text{km}^{-1}\cdot\text{yr}^{-1}$, which falls in the range of total SGD calculated for the Mediterranean Sea ($6\cdot 10^6$ to $100\cdot 10^6\text{ m}^3\cdot\text{km}^{-1}\cdot\text{yr}^{-1}$; Rodellas et al., 2015). The large uncertainties derive from the natural spatial and temporal variability of the SGD fluxes.

The resulting SGD-derived REE fluxes to the NW Mediterranean Sea range from 0.07 ± 0.04 (Lu) to 3.0 ± 1.9 (La) $\text{mol}\cdot\text{yr}^{-1}\cdot\text{km}^{-1}$ and are 5 to 200 times lower than other available estimates for several sites in southern Korea (Kim and Kim, 2011; 2014) and the Indian River Lagoon in Florida (Johannesson et al., 2011; Table 3). The divergence is driven by both higher SGD fluxes and dissolved REE-SGD concentrations in the first case and by higher REE concentrations in the second one. Here we hypothesize that rapid SGD flow systems like the carbonated/karstified aquifers in the NW Mediterranean Sea do not favor groundwater enrichments in REE compared to other slower-flowing systems. Our estimated REE fluxes are comparable to those calculated for the Pettaquamscutt Estuary (Rhode Island, USA; Table 3), underlain by fractured Proterozoic and Paleozoic crystalline bedrock (Chevis et al., 2015). On a global scale, Johannesson and Burdige (2007) estimated the SGD Nd fluxes to the Atlantic, Indian, Pacific and Arctic oceans assuming the SGD to represent 6 % of the riverine discharge in each case. These global Nd fluxes ranged from 50 to $350\text{ mol}\cdot\text{yr}^{-1}\cdot\text{km}^{-1}$ depending on the ocean (coastline data from Central Intelligence Agency, 2016), i.e., one to two orders of magnitude higher than our estimated Nd flux. We therefore emphasize the need of further studies devoted to quantify REE-SGD fluxes to obtain representative coverage of the different structures, compositions and potential reactions occurring in subterranean estuaries.

4.2. Contributions of dissolved REE from sediments

Dissolved REE distributions in seawater are affected by variable contributions from sediments, including partial dissolution of remobilized particles (Grenier et al., 2013; Pearce et al., 2013) and diffusion of REE from porewaters (Abbott et al., 2015; Haley et al., 2017). Although conscious that the discrimination between these processes might be ambiguous and subject to discrepancies (Haley et al., 2017), we will here treat them separately.

Submarine weathering of deposited sediments along the margins may substantially contribute to the geochemical budgets in the ocean (Jeandel, 2016). The relatively high particulate concentrations of LREE measured in deep waters of St. 22 may actually indicate recent re-suspension of LREE-enriched deposited material. We propose here to estimate the flux of REE released into solution from partial dissolution of remobilized sediments using results of our batch experiment. The seawater dissolved silica increases by 8% during the experiment, confirming the release of chemical species from the particulate phase to the dissolved one (Figure S1). Concomitantly, the seawater ϵ_{Nd} changes progressively from unradiogenic values to more radiogenic ϵ_{Nd} , probably evolving towards the signal of the reacting particulate material (Figure S1). Unfortunately, we could not measure the particle isotopic signature to corroborate this hypothesis although Ayache et al. (2016) simulation of ϵ_{Nd} in margins attributes a value of approx. -9 to our region. Similar outcomes have been derived from other particulate weathering studies (Jones et al., 2012a, 2012b, Pearce et al., 2013). Pearce et al. (2013) showed that dissolved REE concentrations (with the exception of La) decrease during the first 3 days of the experiment and increase afterwards, clearly overcoming the initial levels, until day 13, from whereon they remain constant (Figure 8). Dissolved La increases from the beginning of the experiment, whereas Ce decreases by 80% until day 7 and then remains quite constant until the end of the experiment. The initial decrease in dissolved REE concentrations likely results from the precipitation of secondary phases (e.g. REE phosphate mineral rhabdophane, which is rapidly super-saturated in seawater; Oelkers et al., 2008; Roncal-Herrero et al., 2011) leading the scavenging of a large fraction of these elements from the reacting water (Pearce et al., 2013).

Using these experimental data, we have calculated the dissolved REE fluxes from partial dissolution of reworked sediments (F_{in}^{res}) as follows. The obtained total increase in REE ($\text{pmol}\cdot\text{kg}^{-1}$ of seawater) throughout the batch experiment is converted to $\text{pmol}\cdot\text{kg}^{-1}$ of sediment by the sediment-to-seawater ratio of the experiment (0.00145). This value is multiplied by the average sediment delivery estimated for the northwestern Mediterranean basin ($283\pm 76 \text{ t}\cdot\text{km}^{-2}\cdot\text{yr}^{-1}$; UNEP/MAP, 2003) and considering our study area (225000 km^2). The obtained values (F_{in}^{res} , Table 4) suggest that dissolution of reworked sediments represents a relevant source of dissolved LREE (except for cerium, for which they are a sink) with minimal influence in net HREE addition to the water column (e.g., $8860 \text{ mol}\cdot\text{yr}^{-1}$ of La, $2169 \text{ mol}\cdot\text{yr}^{-1}$ of Nd, $54 \text{ mol}\cdot\text{yr}^{-1}$ of Ho and $8 \text{ mol}\cdot\text{yr}^{-1}$ of Yb; Table 4).

In absence of an incubation experiment with sediment cores, diffusion of REE from porewaters to the overlying water column (F_{in}^{diff}) has been estimated from the literature. Among the several studies reporting REE fluxes from porewaters (summarized by Soyol-Erdene and Huh, 2013) we have considered the values derived from coastal oxic sediments of the Californian margin (St. 10 from Haley et al., 2004) to better represent the environment we have in the northwestern Mediterranean Sea. These sediments are typical of nearshore margins having high terrigenous and organic content. Although the most suitable approximation, we are probably overestimating the porewater REE fluxes given the major volcanic influence on California sediments compared to the northwestern Mediterranean Sea and therefore, we need to interpret these data cautiously as a first approximation. The F_{in}^{diff} fluxes range from $180 \text{ mol}\cdot\text{y}^{-1}$ for Tm to $12,000 \text{ mol}\cdot\text{y}^{-1}$ for Ce (Table 4). Contrarily to the dissolved REE flux from reworked sediments, porewaters are a net source of dissolved Ce to overlying waters.

4.3. Mass balance for dissolved REE in the NW Med sea and determination of net missing fluxes

The distribution of REE in the ocean is determined by sources and sinks as well as the physical ocean transport. A mass balance calculation will allow us to estimate the role of the different fluxes (F_{xx}^{xx}) of external inputs versus water mass mixing in the budgets of dissolved REE in the NW Mediterranean Sea water column (equations 1, 2 and 3; F_{xx}^{xx} in $\text{pmol}\cdot\text{d}^{-1}$). We divided the

study area in three boxes (A, B and C), according to the main water masses: A) MAW/WIW are represented by the 100 m depth samples from the three stations plus the 250 m depth sample of St. 21; B) LIW are denoted by the samples from 500 m depth and the 250 m depth samples from St. 20 and St. 22; and C) WMDW sampled from 1000 m depth to the bottom of each station. The identified input and output fluxes for dissolved REE are indicated in Figure 9. The abbreviations “sAlb”, “sTS”, “iTS”, “sIS” and “dAlb” indicate surface Alboran, surface Tyrrhenian, intermediate Tyrrhenian, surface Ionian and deep Alboran seas, respectively.

$$(1) \quad 0 = \frac{dREE^A}{dt} = F_{in}^{SGD} + F_{in}^R + F_{in}^{atm} + F_{in}^{sAlb} + F_{in}^{sTS} - F_{out,sIS}^A - F_{out,sTS}^A - F_{out,C}^A + F_{miss}^A$$

$$(2) \quad 0 = \frac{dREE^B}{dt} = F_{in}^{iTS} - F_{out,dAlb}^B - F_{out,C}^B + F_{miss}^B$$

$$(3) \quad 0 = \frac{dREE^C}{dt} = F_{in}^A + F_{in}^B + F_{in}^{diff} + F_{in}^{res} + F_{out,dAlb}^C + F_{miss}^C$$

The final term (F_{miss}) in all the equations represents the unidentified (missing) net addition or removal of dissolved REEs that can be calculated at steady state. Negative values of F_{miss} indicate the system requires a net input to be balanced, and the contrary applies when F_{miss} is a positive value. Equations 1, 2 and 3 may be broken down as follows, taking Nd as an example for REE (equations 4, 5 and 6).

$$(4) \quad F_{miss,Nd}^A = C_{Nd}^{SGD} \cdot \psi_{SGD} + C_{Nd}^R \cdot \psi_R + F_{Nd}^{atm} + Q_{in}^{sAlb} \cdot C_{Nd}^{sAlb} + Q_{in}^{sTS} \cdot C_{Nd}^{sTS} - Q_{out,sIS}^A \cdot C_{Nd}^A - Q_{out,sTS}^A \cdot C_{Nd}^A - Q_{out,C}^A \cdot C_{Nd}^A$$

$$(5) \quad F_{miss,Nd}^B = Q_{in}^{iTS} \cdot C_{Nd}^{iTS} - Q_{out,dAlb}^B \cdot C_{Nd}^B - Q_{out,C}^B \cdot C_{Nd}^B + F_{miss,Nd}^B$$

$$(6) \quad F_{miss,Nd}^C = Q_{in}^A \cdot C_{Nd}^A + Q_{in}^B \cdot C_{Nd}^B + F_{in,Nd}^{diff} + F_{in,Nd}^{res} + Q_{out,dAlb}^C \cdot C_{Nd}^C$$

The water fluxes entering and leaving the boxes (Q_{in}^X, Q_{out}^X) are based on Bethoux and Gentili (1999) for the Algero-Provençal Basin (Table S1 in the Appendix). The terms C_{Nd}^A, C_{Nd}^B and C_{Nd}^C are the average REE concentrations (in this example, Nd) in boxes A, B and C respectively (Table S1 in the Appendix). The term C_{Nd}^{SGD} is the Nd concentration in the groundwater end-member (*S. Centre*) and ψ_{SGD} is the average submarine groundwater discharge (SGD) calculated for the NW Mediterranean Sea ($4.6 \cdot 10^{13} \text{ kg} \cdot \text{yr}^{-1}$); C_{Nd}^R is the Nd concentration in river water end-member, taking the Ebro river as representative (Table 1) and ψ_R is the average freshwater discharge to the NW Mediterranean Sea ($9.8 \cdot 10^{13} \text{ kg} \cdot \text{yr}^{-1}$; Ludwig et al., 2009), dominated by the Rhone and Ebro rivers (Arnau et al., 2004). Dissolved REE (especially LREE) loads in rivers may be substantially removed by salt-induced coagulation in estuaries (Rousseau et al., 2015). However, the globally low REE concentrations and the pronounced enrichment in HREE with respect to LREE (e.g. (La/Yb)_n = 0.12) measured in Ebro waters seems to indicate that the potential LREE estuarine removal has already taken place and therefore the sampled Ebro waters can be considered a representative upper estuarine end-member (Goldstein and Jacobsen, 1988).

Atmospheric inputs (F_{in}^{atm}) have been estimated considering the total atmospheric mass deposition of the previous month to the sampling at the NW Mediterranean Sea (Frioul station-Moose Network; $37 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ in May 2013, ca. the mean of the annual range $26\text{-}57 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$), the REE composition of Western Saharan desert mineral particulates (Moreno et al., 2006) and the % of REE mobilization estimated by Greaves et al. (1994) from a marine aerosol of

Saharan origin. The terms C_{Nd}^{sAlb} , C_{Nd}^{sTS} and C_{Nd}^{iTS} stand for the water mass end-members of surface Alboran and surface and intermediate Tyrrhenian Sea waters, respectively (Table S1 in the Appendix). We have used average dissolved REE concentrations in surface waters of the Alboran Sea from Tachikawa et al. (2004; stations B and C), except for Eu (not reported in that study) that is taken from Greaves et al. (1991; St. 10707, 25 m depth). In absence of suitable published data, average REE concentrations in the Sicily Strait have been considered as representative of the Tyrrhenian Sea end-member (surface and intermediate waters from Censi et al., 2004). Diffusion of REE from porewaters (F_{in}^{diff}) and the flux of dissolved REE during sediment resuspension (F_{in}^{res}) are estimated as mentioned above. Table 4 summarizes the REE fluxes calculated from Eq. 1, 2 and 3.

The proportion of dissolved REE supplied by external sources compared to those associated to water mass advection range from 0.5% to 2.2% at surface waters and from 0.4 to 2.2 % at deep waters. Thus, the dissolved REE budgets are dominated by the circulation and mixing of ocean water masses (Table 4). However, superimposed on this hydrography, vertical profiles of REE are indeed affected by external sources and ocean biogeochemical cycling. Taking into account the five identified external sources of dissolved REE in the whole water column, atmospheric fluxes are the most important for all the REE (average contribution of 44%), especially for the LREE and in particular for Ce; Figure 10). Surface waters of St. 20 show a substantial particulate REE peak probably associated to lithogenic input. Diffusive REE fluxes from porewaters account for 30% of the total external inputs. Rivers and SGD represent 11% and 10% respectively of the REE external sources in the studied region, on average. Lastly, dissolution of reworked lithogenic sediments supply an average of 6% of the total external sources (particularly La; Figure 10) although acts as a sink for Cerium, the most particle reactive REE.

Missing fluxes for dissolved REE (Figure 11; Table 4) are significant in surface MAW (Box A) and intermediate LIW (Box B) waters, where the imbalances between inputs and outputs range from 3 to 30% for all REE except for Ce (see discussion below for the latter). More specifically, additional net LREE (La to Sm) outputs and HREE (Eu to Lu) inputs are required in surface waters while additional net output fluxes are required for all the REE in intermediate waters, with the exception of Sm and Lu, pretty much balanced. Considering the uncertainties, dissolved REE are correctly balanced in deep waters, as shown by the insignificant imbalances (F_{miss}^C) quantified for all the REE, excluding Ce (Figure 11; Table 4).

The most likely process explaining the missing dissolved REE fluxes in surface MAW and intermediate LIW waters is likely an active reversible scavenging, here understood as adsorption onto particles with subsequent release due to dissolution or remineralization of the carrier particles (Haley et al., 2017). Reversible scavenging could indeed be responsible for both positive and negative missing fluxes, depending on the net result of the exchange. Our results are in agreement with a stronger adsorption of LREE onto particles compared to HREE (Sholkovitz et al., 1994, Oka et al., 2009), consistent with the stronger complexation of the HREE than of the LREE with carbonates. Actually, enrichments in HREE solution concentrations relative to the LREEs are attributable to much larger increases in solution complexation with increasing REE atomic number than is observed for changes surface complexation with increasing atomic number (Byrne and Kim, 1990). The reversible scavenging process could therefore explain the positive $F_{missing}$ of LREE (requirement of net LREE outputs) and the negative $F_{missing}$ of HREE (requirement of net HREE inputs) calculated for surface MAW. If reversible scavenging was the responsible for the positive $F_{missing}$ (requirement of net REE outputs) at intermediate LIW, adsorption onto suspended particles would dominate above remineralization. As observed in the batch experiment, dissolved REE may also precipitate as secondary mineral phases (e.g. rhabdophane, which is super-saturated in seawater).

Since our suspended particulate material was totally digested, we cannot discern between lithogenic and authigenic (scavenged from the water column) particulate REE. The PAAS-normalization indicates rather flat patterns probably because the lithogenic REE component is remarkably more abundant than the authigenic REE concentrations (as it has been observed in Alboran Sea suspended particles; Tachikawa et al., 2004). Future studies on suspended particle sampling would require sequential leaching steps to elucidate between lithogenic and authigenic REE patterns.

4.4 The behavior of Cerium in the water column

The estimated external sources of dissolved REE in the present study show that atmospheric fluxes are especially important for Ce, consistent with the large enrichment in particulate Ce measured in the surface waters of the Northern Algero-Balear site (St. 20). In the Central Algero-Balear (St. 21) and the Catalano-Balear (St. 22) regions, the particulate Ce concentrations are higher at 250 m depth coinciding with a decrease in dissolved Ce that probably points to a direct interaction between phases (further discussed below). On the other hand, if the calculated Ce flux from sediment remobilization is representative, it suggests acting as a significant net sink for dissolved Ce of around $5000 \text{ mol} \cdot \text{yr}^{-1}$ in the northwestern Mediterranean Sea.

The imbalance calculated for dissolved cerium (Table 4) implies that we are missing an output flux corresponding to the 77% (surface waters) and 96% (intermediate waters) of the cerium flux leaving the box due to water mass advection. The most plausible mechanism is Ce^{+3} removal by particle scavenging via oxidation to insoluble Ce^{+4} , the thermodynamically stable form. Iron and manganese oxyhydroxides are strongly enriched in Ce (Byrne and Sholkovitz, 1996; Bau and Koschinsky, 2009), indicating that oxidation on Fe/Mn oxides may be the relevant mechanism. Such a reaction is congruent to the measured significant contributions of particulate Ce to the total Ce pool that vary from 30-40% in intermediate and deep waters and rise up to 80 % in surface waters. Assuming that the missing Ce-flux leaving surface and intermediate waters is due to oxidation (either microbiologically mediated – Moffett, 1990- or not –Bau, 1999), we have calculated the Ce oxidation rates with respect to average Ce concentrations in the respective box. The obtained values are $0.33\% \cdot \text{d}^{-1}$ and $0.08\% \cdot \text{d}^{-1}$ for box A and B, respectively. The former is in good agreement with previous results by Moffett (1990; from 0.3 to 0.8 % approx. in the first 200 m depth). Cerium oxidation obtained for intermediate waters is remarkably weaker, likely because of remineralization taking place at these depths. The results of the balance in deep waters denote that there is a slight net output flux still required. Potential explanations would rely on either an underestimation in the sediment sink or an overestimation of the cerium fluxes coming from the surface and intermediate waters.

4.5. Balancing the isotopic composition of Nd: exchange fluxes

Nd is the REE for which an isotopic mass balance may also be arranged by incorporating the pertinent ϵ_{Nd} in each term of the equations (e.g., equation 7, for the deep box). Balancing the isotopic composition is interesting regarding what is called the “Nd Paradox issue”, i.e. that there is a discrepancy between the Nd concentration and isotope oceanic budgets (Tachikawa et al, 2003; Goldstein and Hemming, 2003). While concentrations allow estimating the net input-output flux balance for any given natural reservoir, the isotopic compositions allow tracing if any exchange occurred between the different terms at play in the reservoir. Fitting the models with both tracers adds an interesting constraint to disentangle involved processes, as illustrated with the “Boundary Exchange” hypothesis, that aim to solve the “paradox” on a global scale for example (Lacan and Jeandel, 2005).

$$\begin{aligned}
(7) \quad & \varepsilon_{Nd,miss}^C \cdot F_{miss,Nd}^C \\
& = \varepsilon_{Nd}^A \cdot C_{Nd}^A \cdot Q_{in}^A + \varepsilon_{Nd}^B \cdot C_{Nd}^B \cdot Q_{in}^B + \varepsilon_{Nd}^{diff} \cdot F_{Nd}^{diff} + \varepsilon_{Nd}^{res} \\
& \cdot F_{Nd}^{res} + \varepsilon_{Nd}^C \cdot C_{Nd}^C \cdot Q_{out,dAlb}^C
\end{aligned}$$

The ε_{Nd} value for SGD and riverine inputs were measured at -9.4 ± 0.3 and -7.8 ± 0.4 , respectively. The atmospheric dust input has been estimated from the average composition of Saharan dust ($\varepsilon_{Nd} = -13.2 \pm 0.5$; Aarons et al., 2013). The MAW incoming from the Alboran Sea displays average ε_{Nd} values of -9.3 ± 0.2 (Dubois-Dauphin et al., 2017). The ε_{Nd} of Tyrrhenian surface and intermediate waters are of about -8.9 and -8.0 , respectively (*P. Montagna pers. comm*). Regarding the input by dissolution of reworked sediments, we estimated a ε_{Nd} value of -8.3 ± 0.2 from the average composition of outcropping sediments in the region (Ayache et al., 2016). In absence of porewater data and given that bottom seawater isotopic composition differs substantially from that in porewaters (Haley et al., 2004), we assume that diffusive fluxes from porewater have the same isotopic Nd than surrounding sediments (i.e., -8.3 ± 0.2).

If scavenging is the process responsible for the missing flux, it should not induce any change in seawater ε_{Nd} , i.e. $\varepsilon_{Nd,miss}$ equals the average seawater ε_{Nd} in each box (Table S1) and we can solve equation 7 for $F_{miss,Nd}$ in each box. Thereby, the ε_{Nd} balances result in higher $F_{miss,Nd}$ for surface waters ($270,000 \pm 54,000 \text{ molNd} \cdot \text{yr}^{-1}$) and lower $F_{miss,Nd}$ for intermediate waters ($86,000 \pm 30,000 \text{ molNd} \cdot \text{yr}^{-1}$) compared to the $F_{miss,Nd}$ derived from the dissolved REE mass balances ($167,000 \pm 32,000$ and $120,000 \pm 33,000 \text{ molNd} \cdot \text{yr}^{-1}$, respectively). The larger Nd scavenging estimated in the surface layers with the isotopes than with the concentrations reflects that part of the scavenged flux is exchanged between the dissolved and particulate phases. Contrastingly, it seems that isotopes underestimate the flux released from the particles, likely reflecting that part of the solid phase has the same isotopic composition as the water. Concerning deep waters, the isotopic mass balance provides insignificant $F_{missing}$ fluxes for Nd ($-38,000 \pm 50,000 \text{ molNd} \cdot \text{yr}^{-1}$) in agreement with the REE mass balance results ($-11,000 \pm 22,000 \text{ molNd} \cdot \text{yr}^{-1}$).

We must keep in mind that the isotopic model is very sensitive to the average ε_{Nd} in the water bodies under study and the water mass end-members. Additional studies with increased sampling resolution in water column profiles are thus compulsory in order to achieve more accurate isotopic mass balance approaches.

Conclusions

We have described the distribution of dissolved REE and Nd isotopes in the Northwestern Mediterranean seawater column. Clear dissolved REE excess have been measured compared to adjacent Atlantic waters indicating that there is a substantial enrichment in REE along the circulation in the Mediterranean basin. Although physical seawater transport typically governs the distribution of dissolved REE on global terms, surface and bottom waters are also influenced by external sources. The implemented REE mass balances revealed that the atmospheric flux is the most important external source (44%), followed by diffusion from porewaters, which provide the 30% of the external inputs on average. Riverine fluxes contribute with 11%, more significant for HREE. Submarine groundwater discharge contributes between 3 and 20% of the external REE inputs and dissolution of reworked sediments are estimated to supply between 0.3 and 32% of the REE external inputs. Missing fluxes for dissolved REE are important for surface and intermediate waters, where the percentage of imbalances –with respect to inputs or outputs– range between 2 and 30% for all the REE, except for Ce. More specifically, we are lacking net LREE (La to Sm) outputs and HREE (Eu to Lu) inputs in surface waters while we miss output fluxes for basically all the REE at intermediate waters. We ascribe these missing fluxes to an active reversible scavenging, the net result of which could certainly explain both positive and negative missing fluxes. This is in accordance with a

stronger adsorption of LREE –more particle reactive- compared to HREE -more easily desorbed and kept in solution by inorganic complexation-. When assuming missing fluxes have the same ϵ_{Nd} than seawater, the mass balance for the $\square\square\square\square\square\square\square$ composition of Nd indicates even higher Nd scavenging in the upper seawater layer compared to intermediate waters, which is in accordance with greater particle concentrations in surface waters. However, lowering the uncertainties associated with averaged ϵ_{Nd} in the three water boxes considered is strictly required to ascertain this. Finally, the most plausible mechanism that explains the net output missing fluxes for cerium is Ce^{+3} removal by particle scavenging via oxidation to insoluble Ce^{+4} . Estimated Ce oxidation rates of $0.33\% \cdot d^{-1}$ in surface waters are indeed in accordance with previously published values.

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Appendix A. Supplementary material

Figure captions

Figure 1. Locations of seawater stations (St. 20, St. 21 and St. 22) and groundwater (coastal springs) samples in the present study. The region considered for the REE and ϵ_{Nd} mass balances is delineated by a black square. The existing previous profiles of REE (Greaves et al., 1991) or isotopic neodymium (Henry et al., 1994) in the region are also indicated.

Figure 2. Potential temperature versus salinity diagram for the three stations in the NW Med Sea. We can distinguish the main seawater masses: Modified Atlantic Waters (MAW), Levantine Intermediate Waters (LIW) and Western Mediterranean Deep Waters (WMDW). Enlarged circles indicate sampled waters.

Figure 3. Water column profiles of representative dissolved REE (La, Ce, Nd, Sm, Dy and Yb) in the three stations of the present study and those measured by Greaves et al., (1991) in the same region (station 10708).

Figure 4. PAAS-normalized dissolved and particulate REE (dREE and pREE, respectively; $pmol \cdot \square mol^{-1}$) patterns for the NW Mediterranean Sea stations. The dREE patterns display typical seawater features such as HREE enrichments, Ce depletions (negative anomalies) and slight La, Gd and Lu positive anomalies. As for the particulate phase, flat patterns are indicative of a predominant lithogenic fraction in the particulate material. Some scattering is observed in St. 21, with 1000 m deep waters having a pattern closer to that of seawater.

Figure 5. Water column profiles of representative pREE (La, Ce, Nd, Sm, Dy and Yb) in the three stations of the present study (in $pmol \cdot k^{-1}$ of seawater). Low concentrations are present in the whole profiles although remarkable peaks, particularly for LREE, have been measured for surface waters of St. 20.

Figure 6. PAAS-normalized dREE patterns in groundwater samples from the east and southeast Spanish Mediterranean coast (coastal springs and well 6) and in the Ebro River. Differing from all the other samples, Well 6's groundwater shows a prominent positive Europium anomaly probably linked to the volcanic massive sulfide deposit through which it flows. Coastal springs show an enrichment in HREE and a positive Gd anomaly, features that are particularly marked in surface waters from the Ebro River.

Figure 7. Dissolved ε_{Nd} profiles at depth in stations 20, 21 and 22. The most radiogenic value of $\varepsilon_{Nd} = -7.6$ was found at 500 m depth of St. 20, corresponding to LIW from the eastern basin. St. 21 shows unradiogenic surface waters with $\varepsilon_{Nd} = -9.2$ coinciding with the less modified MAW sampled. Bottom waters of St. 22 show an excursion towards a more radiogenic value (from -9.6 at 1800 m to -8.0 at bottom 2200 m depth) likely indicating the influence of lithogenic material.

Figure 8. Dissolved REE evolution in seawater throughout the batch experiment. A general decrease is observed during the first three days of the experiment while dREE increase afterwards because of suspended sediment dissolution, as supported by the increase in dissolved silica.

Figure 9. Mass balance model indicating the input and output fluxes of dissolved REE in the NW Med Sea, divided in three boxes according to the water mass structure: A for surface Modified Atlantic Waters, B for Levantine Intermediate Waters and C for Western Mediterranean Deep Waters. External contributors to dREE in box A comprise submarine groundwater discharge (F_{SGD}^{in}), rivers (F_R^{in}) and atmospheric wet and dry depositions (F_{atm}^{in}). In addition, water mass advection through this box includes seawater inputs from the Alboran (F_{sAlb}^{in}) and the Tyrrhenian Seas (F_{sTS}^{in}) and seawater outputs to the Ionian Sea (F_{sIS}^{out}), to the Tyrrhenian Sea (F_{sTS}^{out}) and to deep waters of box C ($F_C^{out,A}$). Seawater fluxes into the Intermediate box (B) come from the Tyrrhenian Sea (F_{ITS}^{in}) while the output fluxes go to deep waters ($F_C^{out,B}$) and the Alboran Sea ($F_{dAlb}^{out,B}$). As for the deep box (C), the inputs considered include seawater from boxes A (F_A^{in}) and B (F_B^{in}), the REE diffusion from sediments/porewater (F_{diff}^{in}) and the dissolved REE input from resuspended lithogenic sediments (F_{res}^{in}). Water fluxes leaving box C go to the deep Alboran Sea ($F_{dAlb}^{out,C}$).

Figure 10. Relative contributions of the dREE external sources in the NW Mediterranean Sea. Atmospheric fluxes of dREE from dust are the most important and they are predominantly enriched in LREE. Dissolved riverine loads and SGD represent similar fluxes, with the latter providing more HREE into the system. According to our estimations, sediments constitute the last contributor in absolute terms of dREE inputs.

Figure 11. Missing fluxes of dREE ($\text{mol}\cdot\text{y}^{-1}$) derived from the mass balances. They are relevant in surface MAW and intermediate LIW waters, where they vary from 3 to 30% of the calculated inputs/outputs (except for Ce). These figures indicate that our MAW budget requires additional net LREE outputs ($F_{missing} > 0$) and HREE inputs ($F_{missing} < 0$), while additional net output fluxes are needed for all the REE in intermediate waters. Insignificant missing fluxes are obtained for WMDW denoting we have correctly balanced the dREE with the considered terms.

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