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Published in:
Geochimica et Cosmochimica Acta

DOI:
10.1016/0016-7037(95)00233-P

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1995

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Rare earth element exchange through the Bosporus: The Black Sea as a net source of REEs to the Mediterranean Sea

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(Received December 28, 1994; accepted in revised form May 28, 1995)

Abstract—The Bosporus is the only source of seawater to the Black Sea and helps to maintain the basin-wide salinity gradient that caused the Black Sea to become the largest permanently anoxic basin in the world, some 3000 years ago. Concentrations of dissolved rare earth elements (REEs) in each of the three layers of water that make up the Bosporus inflow/outflow system, substituted into a simple hydrographic model that evaluates the entrainment of outflowing Black Sea water in the inflowing Mediterranean Sea water, suggest that the Black Sea acts as a net source of REEs to the Mediterranean Sea. This holds true for Ce, which shows a considerable range of concentrations in the outflowing Black Sea water, even if the lower end of that range is taken to represent the Ce concentration of the Black Sea endmember.

1. INTRODUCTION

The Black Sea is an excellent site for studying almost any aspect of marine chemistry, mainly because of its hydrography. It receives freshwater from a great many rivers, the most important of which are the Danube, the Dniepr, the Dniestr, the Don, and the Kuban. This freshwater is partly transported out of the Black Sea through the Bosporus, which connects the Black Sea to the Sea of Marmara and ultimately to the Mediterranean Sea. At the same time, warm and highly saline Mediterranean Sea water is transported through the Bosporus into the Black Sea. The simultaneous input of freshwater from rivers and seawater from the Bosporus has given rise to a sharp halocline between the Black Sea surface water \((S \approx 18)\) and the Black Sea deep water \((S = 22.3)\). The resulting density gradient effectively reduces mixing between the surface water and the deep water and has caused the Black Sea to become the largest permanently anoxic basin in the world today, thereby providing a unique environment for studies of trace metal cycling (e.g., Spencer and Brewer, 1971; Haraldsson and Westerlund, 1988; German et al., 1991; Lewis and Landing, 1991; Schijf et al., 1991).

The complex hydrography of the Bosporus inflow/outflow system raises the question whether it leads to a net flux of trace metals into or out of the Black Sea. Similar questions have been addressed by others for a comparable system, the Strait of Gibraltar (e.g., Boyle et al., 1985; Sherrell and Boyle, 1988; van Geen et al., 1988; Greaves et al., 1991). As a first step towards a full-fledged REE mass balance for the Black Sea, we have tried to determine whether the Black Sea is a net source or a net sink of REEs to the Mediterranean Sea. To complete the REE mass balance, a study of major rivers draining into the Black Sea will be needed.

The Bosporus inflow/outflow system actually comprises three layers of water. Two of these, a warm surface layer and the Cold Intermediate Layer (CIL), flow out of the Black Sea, whilst the third, a warm and saline bottom layer, transports Mediterranean Sea water into the Black Sea. We present dissolved REE concentrations for water samples from each of these layers that were collected at a station near the north end of the Bosporus (Fig. 1). A simple hydrographic model, based on the balance of salinity or temperature, accounts for the entrainment of outflowing Black Sea water in the inflowing Mediterranean Sea water. Using this model and assuming (1) that dissolved REE concentrations are constant throughout each layer, (2) that particulate REE concentrations constitute a negligible fraction of total REE concentrations, and (3) that the REEs behave conservatively within the Bosporus inflow/outflow system, we show that the Black Sea apparently acts as a net source of REEs to the Mediterranean Sea.

Significantly higher concentrations of dissolved Ce, possibly due to atmospheric input, were found in the warm surface layer than in the CIL, in agreement with earlier observations at a station in the centre of the Black Sea basin (German et al., 1991; Schijf et al., 1991). This gives rise to some uncertainty as to what should be considered the correct Ce concentration of the Black Sea "endmember." Nevertheless, even if we minimize the estimated transport of Ce out of the Black Sea by assuming the Ce concentration of the Black Sea endmember to be equal to that of the CIL, the model presented here still predicts that the Black Sea should act as a net source to the Mediterranean Sea for all REEs.

2. HYDROGRAPHY

The Black Sea is the largest permanently anoxic basin in the world (surface area 420,000 km²; volume 537,000 km³). Freshwater is supplied to the Black Sea by a large number of rivers. Total river input into the Black Sea amounts to about 350 km³/y, more than half of it (200 km³/y) coming from the Danube (Sorokin, 1983). The only source of seawater to the Black Sea is the Mediterranean Sea. The Dardanelles connect the Mediterranean Sea to the Sea of Marmara, which in turn is connected to the Black Sea by the Bosporus. The sill
FIG. 1. Map of the Turkish coastal waters of the Black Sea around the north end of the Bosporus, showing the locations of our HKS station (41°17'N, 29°10'E) and station 24 of Buesseler et al. (1991) (41°24.5'N, 29°19.2'E). Isobaths in meters. Solid line indicates the path followed by the Mediterranean Sea water after entering the Black Sea through the Bosporus (after Latif et al., 1991). Notice that station 24 is located well outside this path.

depths at the south and north ends of the Bosporus are approximately 35 m and 60 m, respectively (Latif et al., 1991).

A southerly flow of surface water from the Black Sea through the Bosporus is caused by the difference in sea level between the Black Sea and the Sea of Marmara (Gunnerson and Özturgut, 1974). This difference is largest during summer as a result of enhanced freshwater discharge to the Black Sea. The flow of surface water is occasionally blocked during periods of strong southerly winds.

Mediterranean Sea water is transported through the Bosporus as a strong northerly undercurrent. A large number of publications address the question whether the Mediterranean Sea water in fact reaches the Black Sea. Ullyott and Ilgaz (1946) assumed that the northern sill prevents the undercurrent from penetrating the Black Sea and that all Mediterranean Sea water is entrained in the southerly flow of surface water and returned to the Sea of Marmara. According to Pektaş (1958a) this situation occurs only during summer, when the difference in sea level between the Black Sea and the Sea of Marmara is largest, yet Mediterranean Sea water does flow into the Black Sea during winter, dispersing at a level of 150–200 m. Bogdanova (1963) demonstrated that Mediterranean Sea water flows into the Black Sea throughout the year, except during periods of strong northerly winds. Within the Bosporus, the Mediterranean Sea water entrains water from the CIL. Upon reaching the Black Sea the resulting mixture can sink to any depth depending on its density.

Profiles of salinity, potential temperature and $\sigma_\theta$ at the HKS station are shown in Fig. 2, where, as everywhere else in the text, salinity values are expressed according to the Practical Salinity Scale. Three water masses can be distinguished in the profile of $\sigma_\theta$, separated by distinct density gradients. The high salinity ($S = 35–36$) and temperature ($14.0–14.3^\circ C$) of the lowermost layer establish its Mediterranean origin. The salinity of the upper two layers is almost equal and the density gradient between them is caused by an abrupt decrease in temperature from 24.9 to 7.6°C. The middle layer is identified from its depth range and temperature as the Cold Intermediate Layer (CIL). This water mass, bounded by the 8°C isotherms, is formed in the northwestern part of the Black Sea whence it is transported throughout the entire basin (Tolmazin, 1985a; Murray and Izdar, 1989; Murray et al., 1989). The presence of CIL water at the HKS station seems to contradict the conclusions of Bogdanova (1963), who stated that only surface water flows out through the Bosporus during the pile up in the summer. Although the HKS station is located near the north end of the Bosporus and not within the Bosporus itself (Fig. 1), it is unlikely that the northern sill could prevent CIL water from flowing into the Bosporus, since the density gradient separating the upper two layers is situated well above the depth of that sill. Others have shown that the density gradient separating the Mediterranean Sea water and the Black Sea water occurs at a depth of about 20 m near the south end of the Bosporus (Tolmazin, 1985b; Ünlüata et al., 1990), hence the southern sill probably does not prevent CIL water from penetrating the Sea of Marmara either.

The balance between the input of freshwater from rivers, evaporation, and the exchange of relatively freshwater and highly saline Mediterranean Sea water through the Bosporus maintains a substantial basin-wide halocline, separating the

![Fig. 1. Map of the Turkish coastal waters of the Black Sea around the north end of the Bosporus, showing the locations of our HKS station (41°17'N, 29°10'E) and station 24 of Buesseler et al. (1991) (41°24.5'N, 29°19.2'E). Isobaths in meters. Solid line indicates the path followed by the Mediterranean Sea water after entering the Black Sea through the Bosporus (after Latif et al., 1991). Notice that station 24 is located well outside this path.](image)

![Fig. 2. (a) Profiles of salinity (S) and potential temperature ($\Theta$) and (b) profile of $\sigma_\theta$ at the HKS station. Salinity values are expressed according to the Practical Salinity Scale. Data from White et al. (1989).](image)
behaviour from a vertical distribution of the Ce anomaly, such as
ations. Instead of a quantitative indication of possible anomalous Ce
any depth. It was therefore expected that the Ce anomaly would be
These blanks were not corrected for.

Lu) was caused to fail by isobaric interferences as well as small and
Yb and NdO, respectively. The analysis of some of the HREEs (Er-
sm and Eu, and <7% for Er-Lu. Gd (which is analyzed as GdO)
isotope dilution curve, were typically <2% for Ce and Nd, <5% for
errors, estimated by projecting the statistical errors in the
arrays. Errors, estimated by projecting the statistical errors in the
REE transfer from Black Sea to Mediterranean

<table>
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<th>Yb</th>
<th>Lu</th>
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</tr>
<tr>
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<td>0.078</td>
</tr>
</tbody>
</table>

Black Sea surface water ($S \approx 18$) from the Black Sea deep
water ($S \approx 22.3$). Restricted mixing across the ensuing den-
sity gradient has caused permanently anoxic conditions to de-
velop in the Black Sea deep water some 3000 years ago (Sor-
okin, 1983).

3. METHODS

Water samples for the analysis of dissolved REE concentrations
were collected on July 27 during Leg 5 of the 1988 Black Sea Ex-
pedition at a station near the north end of the Bosporus (Fig. 1). From a CTD profile that was recorded during the downcast (Fig. 2a),
the presence of three distinct layers of water was established, bounded
by a strong temperature gradient at about 16 m and a strong salinity
gradient at about 60 m. During the upcast a sample was taken
roughly from the core of each of these three layers. The samples were
collected with 30 L GoFlo bottles mounted on a CTD/Rosette frame. Upon recovery of the GoFlo bottles their contents were immediately
pressure-filtered inside the shipboard class 100 clean air laboratory
through 0.22 $\mu$m polycarbonate membrane filters (Nuclepore, Ø142
mm) into hot-acid-cleaned 5 L LDPE narrow-mouth bottles. Each
sample was then acidified to pH 2 with triple-quartz-distilled 6.5 N
HCl in order to preserve it until analysis in the shore laboratory.
In the class 100 clean air laboratory of the Laboratory for Isotope
Geology (Free University, Amsterdam) 2 L subsamples were spiked
with 0.2–0.3 g of an isotopically enriched spike solution containing
all REEs. After an equilibration period of one week, the REEs were
preconcentrated with Chelex 100 resin and then separated from re-
maining seasalt cations and Ba, and divided into two fractions (one
containing La and some of the Ce and one containing Ce-Lu) with
AG 50W-X8 cation-exchange resin, using the methods of de Baar et
al. (1988), modified after Schijf (1992). Clean techniques were used
throughout the procedure and all reagents were cleaned by multiple
subboiling quartz-distillation or by subboiling quartz-distillation
and further cleaning over a Chelex 100 column.
The Ce-Lu fraction was analyzed by IDMS on a Finnigan MAT
261 thermal ionization mass spectrometer, using double Re-filament
arrays. Errors, estimated by projecting the statistical errors in the
isotopic ratios ($\delta$) on the calculated REE concentrations via the
isotope dilution curve, were typically <2% for Ce and Nd, <5% for
Sm and Eu, and <7% for Er-Lu. Gd (which is analyzed as GdO)
and Dy could not be analyzed due to severe isobaric interference by
Yb and NdO, respectively. The analysis of some of the HREEs (Er-
Lu) was caused to fail by isobaric interferences as well as small and
unstable ion beams. Based on a 2 L sample, procedural blanks were
0.2 pmol/kg for Ce, 0.04 pmol/kg for Nd, 0.01 pmol/kg for Sm, and
below the detection limit of our IDMS method for all other REEs.
These blanks were not corrected for.
The water column at the HKS station is not anoxic or suboxic at
any depth. It was therefore expected that the Ce anomaly would be
negative throughout the water column and not show significant vari-
ations. Instead of a quantitative indication of possible anomalous Ce
behaviour from a vertical distribution of the Ce anomaly, such as
often required in studies of the aqueous geochemistry of the REEs in
anoxic basins (e.g., de Baar et al., 1988; German et al., 1991; Schijf
et al., 1991), a more qualitative indication from a vertical distribution
of the Ce/Nd ratio was deemed sufficient. Consequently, the tedious
and extremely time-consuming analysis of La, generally taking
longer than that of all other REEs together, was not carried out.

4. RESULTS

Dissolved REE concentrations, Ce/Nd ratios, and Yb/Nd
ratios are presented in Table 1. Dissolved Ce, Nd, and Yb
concentrations, and Ce/Nd ratios are also presented in Fig. 3.
In our model calculations we will assume that dissolved REE
concentrations are constant within each of the three layers of
water that make up the Bosporus inflow/outflow system. Each
of the data points in Fig. 3 therefore represents a layer of water
whose thickness is depicted by the vertical “error bars”.
For the strictly trivalent REEs there is a minor but signifi-
cant difference between water originating in the Black Sea
(the upper two layers), which has somewhat higher concen-
trations, and water originating in the Mediterranean Sea (the
lowermost layer). The ratio of Ce concentrations in the CIL
and in the lowermost layer is comparable to that of the strictly
trivalent REEs, yet the behaviour of Ce in the warm surface
layer is clearly different, its concentration being almost twice
that in the CIL, whereas the concentrations of the strictly tri-
valent REEs are only slightly higher.
Elevated concentrations of dissolved REEs in the warm
surface layer were also observed at a station in the centre of
the Black Sea basin (German et al., 1991; Schijf et al., 1991).
Indeed, dissolved REE concentrations at that station and at
the HKS station are nearly equal for depths corresponding to
the same isopycnal, in the upper 30 m of the water column.
While these elevated concentrations may be due to atmo-
spheric input, both for Ce and for the strictly trivalent REEs,
Ce may be more readily solubilized by photo-reduction of
Ce(IV) and by photo-inhibition of microbially mediated ox-
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The anomalous behaviour of Ce in the warm surface layer is
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Table 1. Dissolved REE concentrations (pmol/kg), Ce/Nd ratios and Yb/Nd
ratios in three water samples collected at the HKS station. La was not
analyzed for these samples. Analysis of Gd and Dy failed due to severe
isobaric interferences. REE abundances in mean shale (µmol/kg) from PIPER
(1974).

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The Yb/Nd ratios are equal in all three layers within the un-
certainty of the measurement (Table 1) and indicate signifi-
cant HREE enrichment. These characteristics, a negative Ce anomaly and a distinct HREE enrichment, are typical of all open ocean waters.

5. DISCUSSION

The hydrography of the Bosporus is described in great detail in a large number of publications (e.g., Bogdanova, 1963; Gunnerson and Özturgut, 1974; Sorokin, 1983; Tolmazin, 1985b; Ünlüata et al., 1990; Yüce, 1990; Latif et al., 1991; Oğuz et al., 1991). The magnitudes of the inflow of Mediterranean Sea water and the outflow of Black Sea water through the Bosporus are well known. It is also well known that these magnitudes vary both seasonally and as a result of certain weather patterns. Specifically, inflow and outflow depend on the difference in surface level between the Black Sea and the Sea of Marmara (Ünlüata et al., 1990) and can even be cut off completely during periods of adverse winds (Latif et al., 1991). Nevertheless, we were not able to find direct estimates of these variations in the literature. We therefore decided to circumvent the problem altogether by using annual averages. Part of the Black Sea water flowing out through the Bosporus is entrained in the Mediterranean Sea water flowing in the opposite direction and returned to the Black Sea (Bogdanova, 1963; Boudreau and Leblond, 1989). Table 1 of Ünlüata et al. (1990) contains an extensive list of estimates of the average annual inflow and outflow, not including the entrainment flow, compiled from a host of publications.

The magnitude of the entrainment flow may be calculated from the balance of salinity or temperature. In the terminology of Buesseler et al. (1991):

\[ P_\alpha = P_0 + (1 - P_0)P_c, \]

where \( P_\alpha \) is some conservative property in the outflow (CIL), \( P_0 \) in the initial inflow (the Mediterranean "endmember"), and \( P_c \) in the inflow that is modified by entraining a fraction \( F_0 \) of CIL water. We assume that the entrained water originates in the CIL, because the CIL directly overlies the inflow. The same conclusion was drawn by Buesseler et al. (1991) from a \( \Theta-S \) diagram. In accordance with the data of Ünlüata et al. (1990) and the ranges reported by Buesseler et al. (1991), we adopt \( P_0 = 38.5 \) and \( 14.8°C \) for the salinity and temperature of the Mediterranean endmember, respectively. Based on salinity, substituting \( P_0 = 18.2 \) and \( P_\alpha = 35.8 \) (Fig. 2a), we calculate \( F_0 = 0.13 \). A calculation based on temperature, substituting \( P_0 = 7.6°C \) and \( P_\alpha = 14.2°C \) (Fig. 2a), although much more sensitive to the choice of parameters, leads to almost the same result: \( F_0 = 0.09 \). In our model calculations we will use the average (\( F_0 = 0.11 \)).

Boudreau and Leblond (1989), using a sophisticated time-dependent variable-size box model of the balances of water and salinity in the Black Sea, also calculated the magnitude of the entrainment flow and found \( F_0 = 0.20 \). Buesseler et al. (1991) calculated \( F_0 \) from the balance of salinity and arrived at \( F_0 = 0.88-0.92 \), in sharp contrast with these results. For salinity they used \( P_\alpha = 20.8 \), obtained from a salinity profile recorded at their station 24, near the north end of the Bosporus, yet further offshore than our HKS station (Fig. 1). Upon entering the Black Sea, the outflow from the Bosporus, while retaining a strong Mediterranean signature, follows a narrow path that extends onto the shelf in the direction of the main Bosporus channel and then curves sharply to the northwest several kilometers from the mouth (Yüce, 1990; Latif et
that dissolved REE concentrations in the Mediterranean end member, $P_i$, may be calculated from Eqn. 1. We also implicitly assume that dissolved REE concentrations are constant throughout each layer, $P_o$, and $P_i$ were taken from Table 1 and $F_0 = 0.11$ was used for the calculation of the $P_i$. Results are presented in Table 2 for those REEs for which dissolved REE concentrations could be determined in all three layers. These values of $P_i$ may be compared with measurements of dissolved REE concentrations in the Eastern Mediterranean Deep Water: approximately 11 pmol/kg Ce, 22 pmol/kg Nd, 5.0 pmol/kg Sm, 1.4 pmol/kg Eu, and 7.0 pmol/kg Yb (Schijf, 1992; Schijf and de Baar, 1995). The comparison is surprisingly favourable, considering that the Mediterranean endmember probably derives from shallower water in the Aegean (rather than the Ionian) Basin that may well have been altered by nonconservative processes during its transport through the Sea of Marmara.

It is more difficult to assign a value to $P_{BS}$. For the strictly trivalent REEs, dissolved concentrations in the upper two layers are nearly equal, yet for Ce the dissolved concentration in the uppermost layer is higher by a factor of about 2 (Fig. 3). Although possibly due to (local) atmospheric input, it cannot be ruled out that this is a basin-wide phenomenon in the Black Sea and that the elevated concentrations in the uppermost layer should be taken into account in our model calculations. The best choice therefore seems to be a weighted average of the concentrations in the uppermost layer and in the intermediate layer (Table 1), weighting each concentration with the thickness of the corresponding layer, which from Fig. 2b were estimated to be about 16 m and 44 m, respectively (Table 2).

Table 1 of Ünlüata et al. (1990) shows substantial variation in the estimates of the average annual inflow and outflow, with $Q_i$ ranging from 176 to 312 km$^3$/y and $Q_o$ from 340 to 612 km$^3$/y. Ünlüata et al. (1990) pointed out however that $Q_o \approx 2Q_i$ for each pair of estimates, a condition

Table 2. Net dissolved REE fluxes through the Bosporus, calculated from equation (2) for those REE for which dissolved concentrations could be determined in all three layers of the Bosporus inflow/outflow system. Positive values of $F_{REE}$ correspond to net dissolved REE fluxes out of the Black Sea. $P_i$ are dissolved REE concentrations in the Mediterranean Sea water before, and $P_{BS}$ after entrainment of CIL water, which itself has dissolved REE concentrations $P_0$. $F_{REE}$ are dissolved REE concentrations in the Black Sea endmember. $F_{REE}(min)$ and $F_{REE}(max)$ were calculated from the lowest and highest reported estimates of the average annual inflow and outflow, respectively (see text). $^1$Assuming that $P_{BS} = P_0$. Dissolved REE concentrations in pmol/kg (mol/km$^3$); net dissolved REE fluxes in mol/yr.

<table>
<thead>
<tr>
<th>REE</th>
<th>$P_{ss}$</th>
<th>$P_0$</th>
<th>$P_i$</th>
<th>$P_{BS}$</th>
<th>$F_{REE}(min)$</th>
<th>$F_{REE}(max)$</th>
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<td>Ce</td>
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<td>15.4</td>
<td>21</td>
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<td>$6.7 \times 10^3$</td>
</tr>
<tr>
<td>Nd</td>
<td>20.2</td>
<td>23.5</td>
<td>19.8</td>
<td>24</td>
<td>$4.7 \times 10^3$</td>
<td>$5.5 \times 10^3$</td>
</tr>
<tr>
<td>Sm</td>
<td>4.40</td>
<td>5.47</td>
<td>4.27</td>
<td>5.5</td>
<td>$1.1 \times 10^3$</td>
<td>$2.0 \times 10^3$</td>
</tr>
<tr>
<td>Eu</td>
<td>1.31</td>
<td>1.56</td>
<td>1.28</td>
<td>1.6</td>
<td>$0.3 \times 10^3$</td>
<td>$0.6 \times 10^3$</td>
</tr>
<tr>
<td>Yb</td>
<td>8.13</td>
<td>9.37</td>
<td>7.98</td>
<td>9.6</td>
<td>$1.9 \times 10^3$</td>
<td>$3.4 \times 10^3$</td>
</tr>
</tbody>
</table>

where $Q_i$ and $Q_o$ are the average annual inflow and outflow, not including the entrainment flow, respectively, $P_{BS}$ are dissolved REE concentrations in the Black Sea endmember, and $P_i$ now represents dissolved REE concentrations in the Mediterranean endmember. Note that positive values of $F_{REE}$ correspond to net dissolved REE fluxes out of the Black Sea.

Removal of dissolved REEs upon mixing of relatively fresh Black Sea water with highly saline Mediterranean water is unlikely, since it has been shown that in estuaries such removal is already largely completed at salinities $< 5$ (Eldredge et al., 1990). We therefore assume that the REEs behave conservatively within the Bosporus inflow/outflow system and that dissolved REE concentrations in the Mediterranean endmember, $P_i$, may be calculated from Eqn. 1. We also implicitly assume that dissolved REE concentrations are constant throughout each layer, $P_o$, and $P_i$ were taken from Table 1 and $F_0 = 0.11$ was used for the calculation of the $P_i$. Results are presented in Table 2 for those REEs for which dissolved REE concentrations could be determined in all three layers. These values of $P_i$ may be compared with measurements of dissolved REE concentrations in the Eastern Mediterranean Deep Water: approximately 11 pmol/kg Ce, 22 pmol/kg Nd, 5.0 pmol/kg Sm, 1.4 pmol/kg Eu, and 7.0 pmol/kg Yb (Schijf, 1992; Schijf and de Baar, 1995). The comparison is surprisingly favourable, considering that the Mediterranean endmember probably derives from shallower water in the Aegean (rather than the Ionian) Basin that may well have been altered by nonconservative processes during its transport through the Sea of Marmara.

It is more difficult to assign a value to $P_{BS}$. For the strictly trivalent REEs, dissolved concentrations in the upper two layers are nearly equal, yet for Ce the dissolved concentration in the uppermost layer is higher by a factor of about 2 (Fig. 3). Although possibly due to (local) atmospheric input, it cannot be ruled out that this is a basin-wide phenomenon in the Black Sea and that the elevated concentrations in the uppermost layer should be taken into account in our model calculations. The best choice therefore seems to be a weighted average of the concentrations in the uppermost layer and in the intermediate layer (Table 1), weighting each concentration with the thickness of the corresponding layer, which from Fig. 2b were estimated to be about 16 m and 44 m, respectively (Table 2).

Table 1 of Ünlüata et al. (1990) shows substantial variation in the estimates of the average annual inflow and outflow, with $Q_i$ ranging from 176 to 312 km$^3$/y and $Q_o$ from 340 to 612 km$^3$/y. Ünlüata et al. (1990) pointed out however that $Q_o \approx 2Q_i$ for each pair of estimates, a condition

Table 2. Net dissolved REE fluxes through the Bosporus, calculated from equation (2) for those REE for which dissolved concentrations could be determined in all three layers of the Bosporus inflow/outflow system. Positive values of $F_{REE}$ correspond to net dissolved REE fluxes out of the Black Sea. $P_i$ are dissolved REE concentrations in the Mediterranean Sea water before, and $P_{BS}$ after entrainment of CIL water, which itself has dissolved REE concentrations $P_0$. $F_{REE}$ are dissolved REE concentrations in the Black Sea endmember. $F_{REE}(min)$ and $F_{REE}(max)$ were calculated from the lowest and highest reported estimates of the average annual inflow and outflow, respectively (see text). $^1$Assuming that $P_{BS} = P_0$. Dissolved REE concentrations in pmol/kg (mol/km$^3$); net dissolved REE fluxes in mol/yr.

<table>
<thead>
<tr>
<th>REE</th>
<th>$P_{ss}$</th>
<th>$P_0$</th>
<th>$P_i$</th>
<th>$P_{BS}$</th>
<th>$F_{REE}(min)$</th>
<th>$F_{REE}(max)$</th>
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<tr>
<td>Ce</td>
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<td>16.9</td>
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<td>$6.7 \times 10^3$</td>
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<tr>
<td>Nd</td>
<td>20.2</td>
<td>23.5</td>
<td>19.8</td>
<td>24</td>
<td>$4.7 \times 10^3$</td>
<td>$5.5 \times 10^3$</td>
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</tr>
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</table>
that is imposed by the salinity balance. It appears from careful investigation of Eqn. 2 that under this condition higher values of \( Q_e \) (and thus of \( Q_0 \)) always lead to higher values of \( F_{\text{REE}} \). In Table 2, \( F_{\text{REE}}(\text{min}) \) was calculated from the lowest \( (Q_e = 176 \text{ km}^3/\text{y}; Q_0 = 340 \text{ km}^3/\text{y}) \), and \( F_{\text{REE}}(\text{max}) \) from the highest \( (Q_e = 312 \text{ km}^3/\text{y}; Q_0 = 612 \text{ km}^3/\text{y}) \) reported estimates of \( Q_e \) and \( Q_0 \) (Unluata et al., 1990). While the difference between the net flux of dissolved Eu and that of dissolved Ce and Nd is more than an order of magnitude, all the \( F_{\text{REE}} \) are positive, suggesting that the Bosphorus inflow/outflow system causes a net flux out of the Black Sea for all REEs.

Dissolved REE concentrations of the Black Sea end-member must fall somewhere between those of the warm surface layer and of the CIL, yet a weighted average as calculated above may not be a good approximation of the correct values of \( P_{\text{REE}} \). For the strictly trivalent REEs this will not lead to large errors, since their dissolved concentrations in the upper two layers are nearly equal. However, this is not true for Ce, whose dissolved concentration ranges from 16.9 pmol/kg in the CIL to 31.7 pmol/kg in the warm surface layer. A recalculation of \( F_{\text{REE}}(\text{min}) \), replacing the weighted average (21 pmol/kg) with the concentration in the CIL in order to make sure that minimizing the dissolved Ce concentration of the Black Sea end-member will not cause a reversal of the net Ce flux, still results in a net flux out of the Black Sea (Table 2). Consequently, even if the estimated transport of Ce out of the Black Sea is at its lowest, it can be maintained that the Black Sea is a net source to the Mediterranean Sea for all REEs.

6. CONCLUSIONS

Profiles of salinity and temperature, recorded at a station near the north end of the Bosphorus, confirm that the Bosphorus inflow/outflow system comprises three layers of water, the upper two layers transporting relatively freshwater out of the Black Sea and the lowermost layer transporting highly saline Mediterranean Sea water into the Black Sea. From a simple hydrographic model based on the balance of salinity or temperature, it is estimated that ~11% of the incoming water consists of CIL water that is entrained in the Mediterranean Sea water and returned to the Black Sea. Substituting measurements of dissolved REE concentrations in each of the three layers into this model, it follows that the Black Sea is a net source to the Mediterranean Sea for all REEs, including Ce, notwithstanding some uncertainty in the dissolved Ce concentration of the Black Sea end-member.

Acknowledgments—The authors sincerely thank James W. Murray and Erol Izdar for their efforts towards realizing the 1988 Black Sea Expedition, as well as the National Science Foundation for letting us participate. We especially want to acknowledge the courageous cooperation of master Michael Palmieri of R/V Knorr who allowed Hein de Baar to do a CTD-cast in the middle of one of the world’s busiest shipping corridors, at what became popularly known as Hein’s Kamikaze Station (HKS). Johan Schijf is grateful to the University of Utrecht and to the Laboratory for Isotope Geology (Free University, Amsterdam) for funding and accommodating his Ph.D. research, of which this study formed a part. Critical remarks by Chris German, Catherine Jeandel, and one anonymous reviewer led to important improvements in the manuscript.

Editorial handling: C. R. German

REFERENCES


REE transfer from Black Sea to Mediterranean