

# The Oceanic Chemistry of the Rare-Earth Elements [and Discussion]

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*Phil. Trans. R. Soc. Lond. A* 1988 **325**, 105-126

doi: 10.1098/rsta.1988.0046

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## The oceanic chemistry of the rare-earth elements

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Because of the unique chemical characteristics of the rare-earth elements (REES), they provide information as oceanic tracers of element source and reactivity. The absolute and relative concentrations of the REES in ocean waters reflect their input from rivers, by aeolian transport and from hydrothermal vents; their interaction with the biogeochemical cycle involving removal from surface waters by adsorption and oxidation at particle surfaces (probably with organic coatings) and deeper regeneration; and the effects of advective transport. Within the REE group, Ce anomalies occur in response to oceanic redox conditions; Eu anomalies in response to aeolian and hydrothermal input; and Nd isotopic variations reflect element sources. Both REE concentration patterns and Nd isotopic variations allow the effects of the vertical particle flux and of lateral advection to be separated.

### INTRODUCTION

One of the most fascinating but difficult areas of marine geochemistry is the interplay of ocean chemistry with biology and physics. Many trace elements added to seawater somehow become involved in the oceans' biogeochemical cycle. They are removed from surface seawater either directly or indirectly as a consequence of biological productivity. Some are regenerated in the deep sea when biogenic tissue is oxidised and their distributions are influenced by deep water circulation. The process of removal of elements from seawater can decouple the associations of elements found in input materials and, similarly, the coupling of elements found within ocean cycles can break down on ultimate burial in sediments.

It is necessary, therefore, to unravel the effects of advection and biogeochemical cycling in defining spatial distributions of the elements in the sea. It is necessary to provide a rigorous chemical treatment of the mechanisms encompassed by the term 'scavenging' (Goldberg 1954; Goldschmidt 1954; Krauskopf 1956; Turekian 1977) for describing the role of particles in controlling the chemical composition of seawater, in the upper water column where biologically formed particles predominate, in the deep oceans near the influence of sediments and at ocean margins where both influences are of importance.

Such work is enhanced by the study of those chemical elements whose properties as tracers of source and/or reactivity make them of particular importance for an understanding of oceanic processes. This paper provides an interpretation of the oceanic chemistry of the rare-earth elements (REES) based upon the recent data on REE concentrations in seawater (Elderfield & Greaves 1981, 1982, 1983; De Baar *et al.* 1983, 1985*a, b, c*, 1988; Greaves *et al.* 1985; Klinkhammer *et al.* 1983; Palmer 1983) and upon its Nd isotope composition (Piepgras & Wasserburg 1980, 1982, 1983, 1985, 1987; Piepgras *et al.* 1979; Stordal & Wasserburg 1986).

Studies of the concentrations and distributions of the rare-earth elements in seawater offer a unique insight to marine trace-element geochemistry. The REES are affected by nearly all the

important processes affecting marine trace-element behaviour (Bender 1982): river, atmospheric and hydrothermal input, adsorption and scavenging onto particles, coprecipitation, ion pairing, redox reactions. Moreover, studies of the REEs make it possible to judge how the behaviour of trace metals is determined by their fundamental chemical properties thus allowing the mechanisms that control their concentrations and distributions to be elucidated. This possibility exists because the fundamental chemical properties of all the REEs are generally rather similar but nevertheless show subtle but significant differences that vary in a predictable manner. It transpires that examining the response of the oceans to these small differences in physicochemical properties provides an extremely useful tool that is much more specific and sensitive than that gained from examination of more poorly related elements.

### FUNDAMENTAL CHEMICAL PROPERTIES

The chemical similarity of different members of the REE group occurs because of their electronic structure. There is a progressive filling of inner 4f electrons with increasing atomic number throughout the series and these electrons are sufficiently shielded by outer electrons not to lead to major differences in chemical reactivity. However, the natural abundances of elements resulting from nucleosynthesis show a rhythmic odd/even variation with atomic number because of the variations in the binding energy of the nucleus as a function of neutron and proton number. Nevertheless, it is easy to correct for this by normalization to a standard. In the example in figure 1, average shale is normalized to meteorite abundances giving a smooth pattern of relative abundance (often, as here, plotted on a logarithmic scale) against atomic number. This 'REE pattern' can be used to characterize different types of materials but,

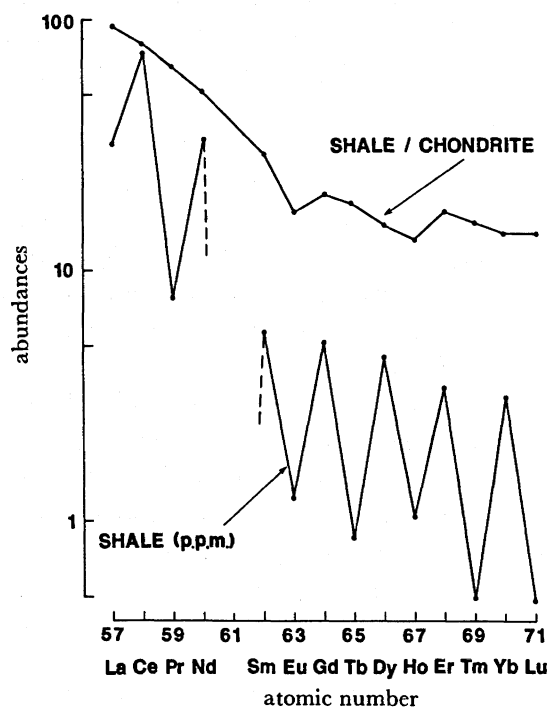


FIGURE 1. Abundances of the REEs in average shale (p.p.m.) and normalized to abundances in chondritic meteorite.

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more importantly, it makes it very simple to distinguish the minor mass fractionation between the various REES relative to a source material and the REES are unique in this respect.

The mass fractionation of the REES takes two forms. First, systematic changes in ionic radii (and hence complexation and surface-adsorption constants) occur with increasing atomic number. This may be recognized in the seawater speciation of the REES (table 1). Rare-earth

TABLE 1. REE SPECIATION IN SEAWATER

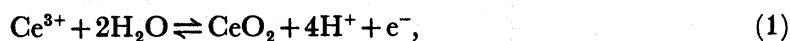
(Species as percentage of total dissolved metal ion<sup>a</sup>.)

REE	Z	REE <sup>3+</sup>	REE(OH) <sup>2+</sup>	REE(F) <sup>2+</sup>	REE(Cl) <sup>2+</sup>	REE(SO <sub>4</sub> ) <sup>+</sup>	REE(CO <sub>3</sub> ) <sup>+</sup>	REE(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup>
La	57	6.7	0.9	0.2	3.1	2.8	66.1	20.3
Ce	58	5.1	1.2	0.3	2.9	2.4	65.1	23.0
Pr	59	4.0	1.3	0.2	1.9	2.1	64.4	26.2
Nd	60	3.1	1.3	0.2	1.4	1.7	62.7	29.6
Pm	61	—	—	—	—	—	—	—
Sm	62	1.9	1.1	0.1	0.9	1.2	57.7	37.1
Eu	63	1.6	1.1	0.1	0.9	0.8	54.5	41.1
Gd	64	1.2	0.9	0.1	0.6	0.7	51.1	45.4
Tb	65	1.0	0.7	0.1	0.5	0.6	47.3	49.8
Dy	66	0.8	0.6	0.1	0.4	0.5	43.3	54.3
Ho	67	0.7	0.5	0.1	0.3	0.3	39.3	58.8
Er	68	0.6	0.8	0.1	0.3	0.3	35.1	62.9
Tm	69	0.5	0.9	0.0	0.2	0.3	31.1	67.1
Yb	70	0.4	0.7	0.1	0.2	0.2	27.2	71.2
Lu	71	0.3	1.3	0.1	0.1	0.1	23.5	74.7

<sup>a</sup> For seawater with [CO<sub>3</sub><sup>2-</sup>] = 1.39 × 10<sup>-4</sup> (TCO<sub>2</sub> = 2.3 × 10<sup>-3</sup>, pH = 7.90); from Cantrell & Byrne (1987) and R. H. Byrne personal communication (1987).

speciation in seawater is dominated by carbonate complexation (Cantrell & Byrne 1987) and the proportion of each REE complexed with seawater carbonate ligands increases with increasing atomic number. Hence, the proportion of the free ion decreases with increasing atomic number, which is important when the ability of the REES to adsorb onto particle surfaces is considered.

Second, although all the REES exist in the 3+ oxidation state, cerium and europium also exist in the 4+ and 2+ states, respectively;



Also, importantly, as shown by equation (1), the higher oxidation state of Ce is present as a solid phase and this is very insoluble in seawater. Therefore, it is possible to separate the role of oxidation in controlling the behaviour of Ce from all other processes affecting it by comparing its concentrations with those of adjacent REES. The Eu<sup>3+</sup>/Eu<sup>2+</sup> redox boundary is below the lower limit of the stability field of water at earth surface conditions but the redox chemistry of europium nevertheless is of significance in the oceans because of the preferential ability of Eu<sup>2+</sup> to substitute for Ca<sup>2+</sup> in certain silicate minerals, principally plagioclase, and because of the relevance to the marine geochemical budget of chemical fluxes associated with submarine hydrothermal activity. The formation of acidic, high-temperature fluids at sub-seafloor pressures leads to preferential mobility of Eu<sup>2+</sup>, relative to the other REES (Michard *et al.* 1983).

Isotopic- as well as mass-fractionation of some REEs also occurs and although this does not take place within the oceans it is of significance to an understanding of oceanic processes. One of the isotopes of the rare-earth element samarium,  $^{147}\text{Sm}$ , is very weakly radioactive, with a half life of  $1.06 \times 10^{11}$  years, and decays to another REE isotope,  $^{143}\text{Nd}$ . Because of REE fractionation within the earth, different rocks have evolved with different Sm/Nd ratios and, hence, with different ratios of radiogenic  $^{143}\text{Nd}$  to non-radiogenic Nd, e.g.  $^{143}\text{Nd}/^{144}\text{Nd}$ . Figure 2 shows the separation of bulk earth into continental crust (lower  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio) and oceanic crust (higher  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio) and the temporal evolution of these geochemical reservoirs with distinctive  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios, expressed in terms of the symbol  $\epsilon_{\text{Nd}}(0)$  as parts per 10000 (by mass) deviations from the bulk-earth value today. As a result, the isotopic composition of Nd can serve as a 'fingerprint' to identify the sources of the element in seawater. The histogram in figure 3 shows a distinct range in Nd isotope values for sea water ranging from

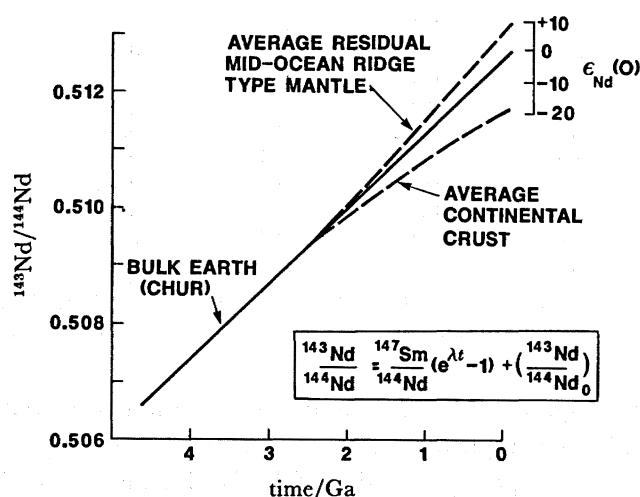
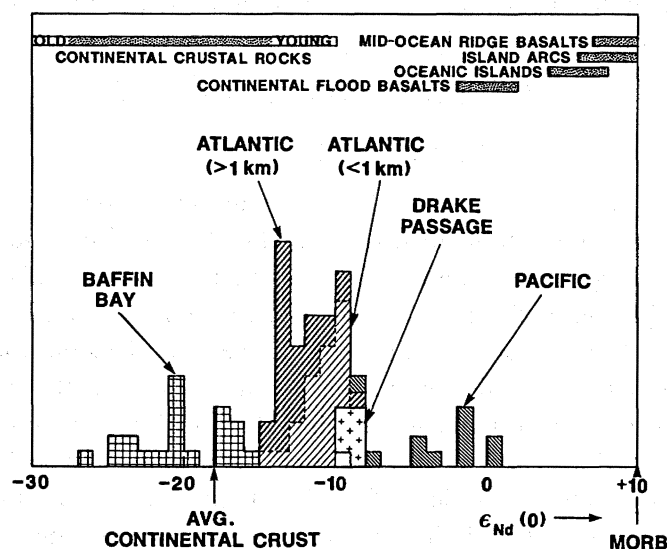


FIGURE 2. Neodymium isotope evolution diagram.

FIGURE 3. Histogram of neodymium isotopic composition of seawater. Data from Piepgras & Wasserburg (1980, 1982, 1983, 1987), Piepgras *et al.* (1979) and Stordal & Wasserburg (1986).

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low  $\epsilon_{\text{Nd}}(0)$  values in the North Atlantic Ocean reflecting drainage from old continental crust through to higher values in the Pacific Ocean. It is clear from figure 3 that neodymium is supplied to seawater predominantly from the continents (i.e. rivers and winds) rather than from oceanic crust (i.e. hydrothermal activity) although there is considerable uncertainty as to the exact proportions because of the unusual  $\epsilon_{\text{Nd}}(0)$  values reported for hydrothermal fluids (Piegras & Wasserburg 1985).

There are two further points of interest in the Nd isotope data. First, the differences in  $\epsilon_{\text{Nd}}(0)$  between the Atlantic and Pacific Oceans indicate a rather short oceanic residence time for neodymium. For example, strontium, which shows similar isotope systematics, has the same isotopic composition everywhere in the oceans because of its long (*ca.*  $10^6$  years) oceanic residence time. Second, a related point is that the contrast in  $\epsilon_{\text{Nd}}(0)$  between surface and deep waters in the Atlantic Ocean means that overall there must be significant vertical as well as lateral Nd isotope gradients in the oceans, showing a significant degree of preservation of the isotopic tracer of its sources.

## THE OCEANIC DISTRIBUTIONS OF THE REES

Although the available data set is only of moderate size, nevertheless it is now possible to describe the principal features of the vertical and lateral distributions of the REEs in ocean waters, the chief limitation being that results are not yet available for the Indian Ocean.

Examples of depth profiles of REE concentrations in seawater are shown in figure 4. With the

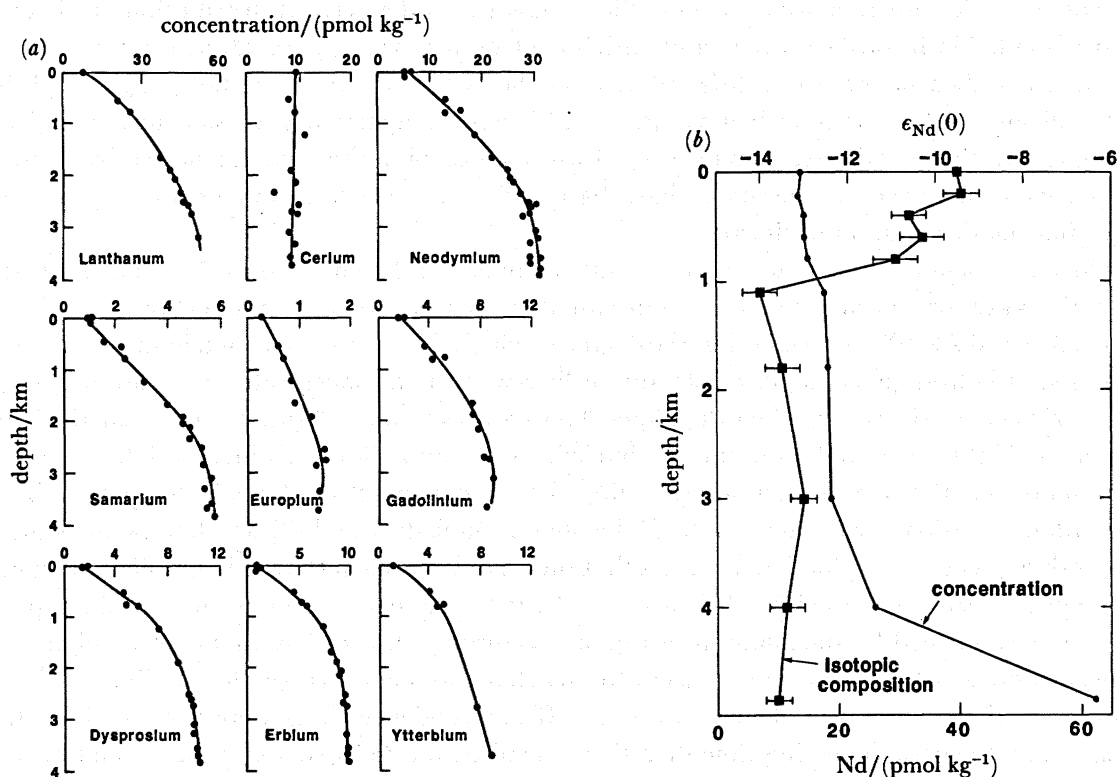


FIGURE 4. Depth profiles of REEs in seawater: (a) concentrations of La, Ce, Nd, Sm, Eu, Gd, Dy, Er and Yb (Klinkhammer *et al.* 1983); (b) Nd concentration and isotopic composition (modified from Piegras & Wasserburg 1987).



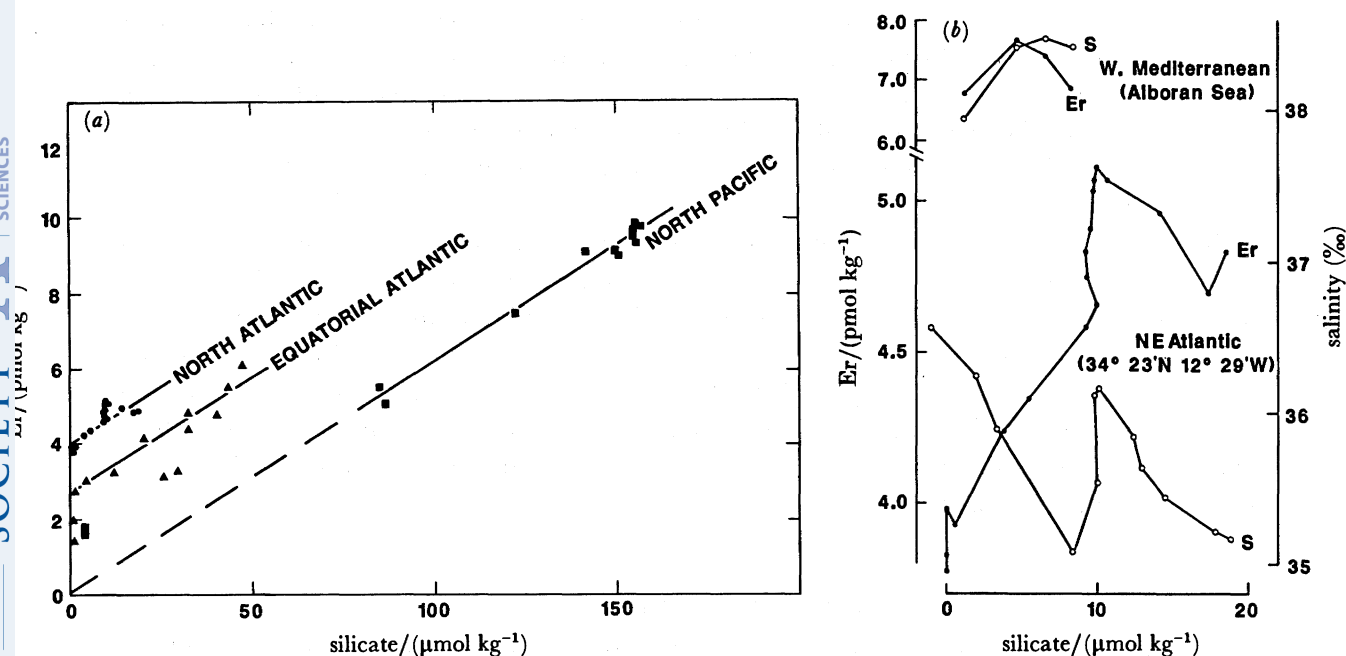


FIGURE 5. Erbium against silicate in seawater. (a) Comparison of three stations from N Atlantic, equatorial Atlantic and N Pacific. Data from De Baar *et al.* (1985a), Greaves *et al.* (1985) and Palmer (1983). (b) Comparison of stations from NE Atlantic and Alboran Sea, also showing salinity (S) against silicate. Data from Greaves *et al.* (1985).

exception of Ce, superficially they show the same form as the vertical distribution of silicate, that of depletion in surface waters and enrichment in deep waters. However, examination of results (described below) from different stations shows that the REEs are not coupled tightly with silicate in their oceanic behaviour. Nevertheless, comparison with silicate is useful in defining how the REEs depart from the cycle of assimilation in surface water, followed by settling of particles and deep regeneration that characterizes the vertical component of processes affecting the distribution of silicate.

Plots of Er against silicate for three separate stations are shown in figure 5a. They indicate that the REEs are regenerated very approximately in stoichiometric proportions to silicate ( $\Delta\text{Er}/\Delta\text{Si} = 6.2 \times 10^{-8} \text{ mol/mol}$ ) but the degree to which the REEs are depleted in surface waters differs greatly from place to place. Clearly, surface-water REE concentrations are not linked to those of silicate. Moreover, when the larger data set is examined (figure 6) it is clear that the coupling of the REEs and nutrients is, indeed, crude and shows distinct variability. This variability is real as can be seen in figure 5b, where a portion of the Er–silicate relation for a NE Atlantic station has been expanded. This shows coupled Er and silicate data points joined in depth sequence. The plot demonstrates that there is a very sharp change in gradient at about  $10 \mu\text{mol kg}^{-1}$  silicate caused by the injection of Mediterranean outflow water at mid-depths that, as is confirmed by the Alboran Sea data also displayed, contains anomalously high REE concentrations. Clearly the REE concentrations share to some degree the attributes of Nd isotopes in that they reflect elemental sources. If REE residence times were very significantly longer than the oceanic mixing time then their chemical and isotopic fingerprint would be less distinct and less useful. However, if REE residence times were extremely short, removal processes would significantly modify the size and pattern of the fingerprint and would also

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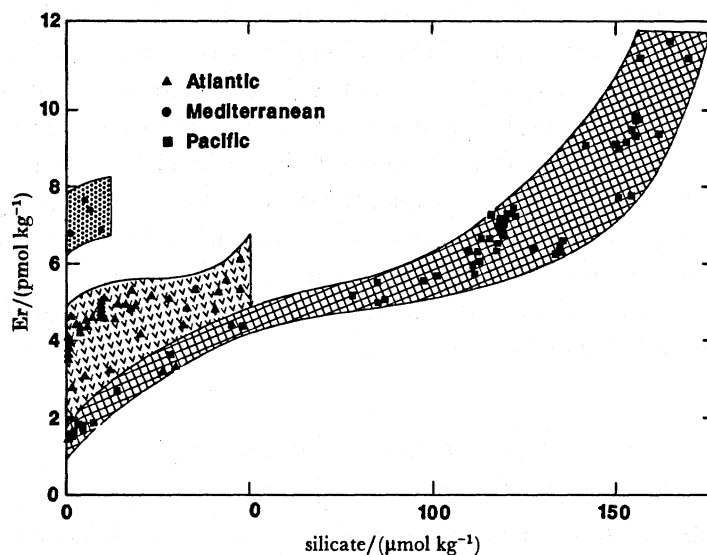


FIGURE 6. Erbium against silicate in seawater for the Atlantic and Pacific Oceans and the Mediterranean Sea. Data from Elderfield & Greaves (1981, 1982), De Baar *et al.* (1985*a, c*), Greaves *et al.* (1985), Klinkhammer *et al.* (1983) and Palmer (1983).

diminish its usefulness. From this example it would seem clear that vertical geochemical cycling does not dominate the processes controlling REE concentrations at depth; the effect of advective transport is readily recognizable from the REE concentrations and patterns.

As shown in figure 4, the depth profile of Ce in seawater is very different from those of the other REEs, Ce shows a gradual decline in concentration with increasing depth unlike the nutrient-like increases of the other REEs. This contrast is also seen in the REE–silicate plot for Ce (figure 7) as compared with those for the other REEs as exemplified by Er (figure 6). As has been seen from the Nd isotope data (figure 3) the principal source of REEs to the oceans is

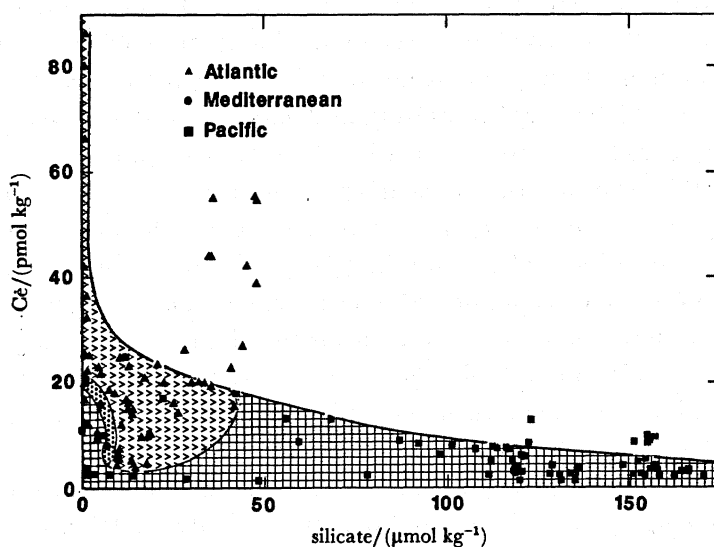


FIGURE 7. Cerium against silicate in seawater for the Atlantic and Pacific Oceans and the Mediterranean Sea. Data as for figure 6. Samples plotting above solid line are from deep waters with probable sediment input.



continental and, as for other trace elements, the dominant flux is likely to be into the Atlantic Ocean because of its larger river and aeolian input rates compared with the Pacific. The distribution of Er (figure 6) shows that the strictly trivalent REES increase in concentration with increasing silicate concentration, both as a function of depth and in the deep Pacific compared with the deep Atlantic, consistent with their mode of biogeochemical cycling coupled with the flow path of deep-water circulation. In contrast, the distribution of Ce (figure 7) shows that it decreases in concentration with increasing silicate concentration, both with depth and in the deep Pacific against the Atlantic. This difference must be because of removal of Ce from seawater by oxidation and it is clear that oxidative removal must be the dominant process by which the cerium content of seawater is defined.

#### MASS FRACTIONATION OF THE REES

Observations of interelement relations of the REES provide evidence of chemical fractionation within the oceans such that trace-element associations recorded in elemental sources become decoupled. It is obvious from the previous section that the behaviour of Ce differs very significantly from that of the strictly trivalent REES. The severe mass fractionation of Ce will be treated separately here, as will the behaviour of Eu.

First, bearing in mind that all the REES have similar fundamental chemical properties, it is useful to compare REES of very similar character. Figure 8*a* shows the relationship between the oceanic concentrations of Sm ( $Z = 62$ ) and Nd ( $Z = 60$ ), two atomic numbers apart in the REE series. The two elements exhibit no significant mass fractionation. The Sm/Nd ratio is very similar to that of average shale that has been used to typify continental input to the oceans (0.189 mol/mol) and is also similar to ratios measured in river waters (0.218 mol/mol) (Upstill-Goddard *et al.* 1987). Also, the Sm/Nd ratio is near constant in all sea waters and exhibits no interoceanic differences.

Next, figure 8*b* compares Er ( $Z = 68$ ) and Nd ( $Z = 60$ ), eight atomic numbers apart, and shows that there is significant mass fractionation between the heavy and light REES. All seawaters are enriched in Er relative to Nd ( $\text{Er/Nd} = 0.57\text{--}0.10$  mol/mol) when compared with shale (0.085 mol/mol) or riverwater (0.088 mol/mol; or 0.093–0.186 mol/mol after correction for fractionation during estuarine removal). Furthermore, Pacific seawaters (0.57–0.20 mol/mol) have higher Er/Nd ratios than Atlantic seawaters (0.33–0.10 mol/mol), i.e. they are even more enriched as compared with shale or riverwater.

Further features of this relation become clear when surface waters are distinguished from intermediate and deep waters. In the Atlantic, many surface samples have a shale-like Er/Nd ratio and high REE concentrations. These samples (figure 8*b*) come from a surface transect in the NE Atlantic from 55° N to the Equator and reflect a signal due to aeolian input of particles to surface waters, dissolution of REES from which leads to enhanced REE concentrations at the upper portion of depth profiles and a shale-like ratio directly reflecting element input. As will be shown later, aeolian input is often associated with anomalously low Eu concentrations that further characterize this source.

Where this aeolian signal is less strong, as in other Atlantic surface waters and in the Pacific, there is significant Er enrichment relative to Nd that is readily explainable by preferential removal of light REES onto particles in surface seawater relative to heavy REES (which show a greater tendency to complex with seawater ligands in solution) with the result that seawater

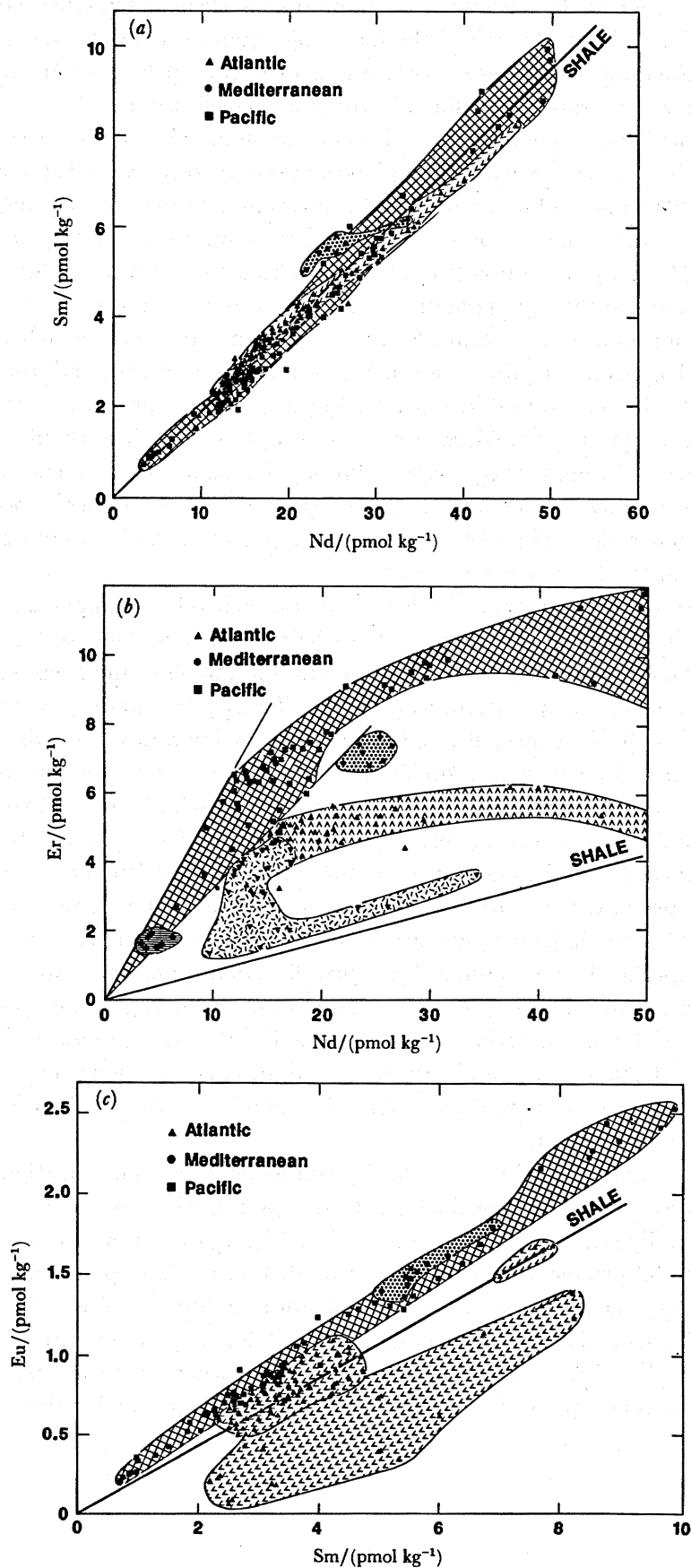


FIGURE 8. REE interelement plots. (a) Sm against Nd; (b) Er against Nd; (c) Eu against Sm. Lines with slopes having REE ratios for average shale are also shown. In (b), surface-water samples are distinguished by heavy shading and reversed symbols. In (c), surface waters showing evidence of aeolian input (significant negative Eu anomalies and shale-like Er/Nd ratios) are distinguished by heavy shading.

becomes heavy-REE enriched. The degree to which both REEs are depleted reflects the efficiency of this process relative to input fluxes and there is a suggestion in the data that this also may increase mass fractionation: the lower concentrations in Pacific surface waters are associated with slightly higher Er/Nd ratios than for the Atlantic or Mediterranean.

This pattern of heavy-REE enrichment is initially maintained with increasing REE concentration (i.e. depth) but in deep waters in both oceans the trend is reversed: the Er/Nd ratios tend towards shale-like values. One explanation for this is that vertical biogeochemical cycling returns the REEs to solution, i.e. dissolution of REEs from falling particles returns the preferentially removed light REEs to solution leading to decreased Er/Nd ratios. Although this can account for the patterns in the top kilometre or so of the water column there is evidence that this mechanism is not primarily responsible for the deep water ratios. This evidence comes from the persistence of advected REE features (figure 5*b*), as already discussed, and from Nd isotope data (figure 4*b*). If the REE ratios in deep waters reflect only downward transport and regeneration of REEs removed by particles from surface waters, then Nd isotopic compositions should be homogeneous throughout the water column. This is not the case. They appear to be roughly homogeneous only in the top *ca.* 800 m that defines an upper zone of element assimilation and regeneration. Therefore, an additional process or processes must be affecting REE concentrations in the lower zone, at depth.

There are two candidates and it is difficult to evaluate their relative importance at present. One requires very high concentrations of REEs to be carried in sinking surface waters, i.e. preformed REEs. Of course, advective transport is certain to influence the deep-water ratios to some extent, as is shown for the Mediterranean outflow (figure 5*b*), and the lower Er/Nd ratios in the deep Atlantic might be expected to influence deep Pacific ratios in the direction that is observed. The second is that there is significant REE input from the sediments as a result of diagenesis. The extremely low REE concentrations in seawater relative to sediment ( $K_{\text{Dseawater}}^{\text{sediment}} \approx 10^7$  mol/mol) would seem to favour this; the standing crop of REEs in the 4000 m oceanic water column is equivalent to the amount present in the uppermost 1 mm of ocean sediments. Indeed, very high concentrations of REEs have been measured in pore waters from reducing sediments (Elderfield & Sholkovitz 1987) but totally reliable data have not yet been reported for the deep sea. Superficial examination of the overall curvature of REE against silicate data (see, for example, figure 6) might imply scavenging of REEs, as for Cu, in the deep sea but the above examination of the mass-fractionation effect suggests that this cannot be the dominant process affecting REE behaviour at depth. Indeed, deep scavenging of REEs might be expected to produce heavy-REE enrichment in deep waters, the opposite to what is observed. The effect of mixing seems more important.

This point may be addressed, in principle, by considering Nd concentration against Nd isotope mixing relations in portions of the deep water column where  $\theta - S$  and  $\epsilon_{\text{Nd}}(0) - S$  (or  $\epsilon_{\text{Nd}}(0) - \text{Si}$ ) plots are linear. This approach is explored in figure 9 from data of Piepgras & Wasserburg (1987) and produces the unfortunate result that the high precision of the isotope data (*ca.* 10 p.p.m. (by mass)) is not enough to distinguish highly non-conservative behaviour from the conservative case. The mixing relations in figure 9 permit an interpretation of either *ca.* 15% Nd removal or *ca.* 15% Nd production, or neither removal nor production! Nevertheless, this approach is a crucial one and should eventually resolve this question.

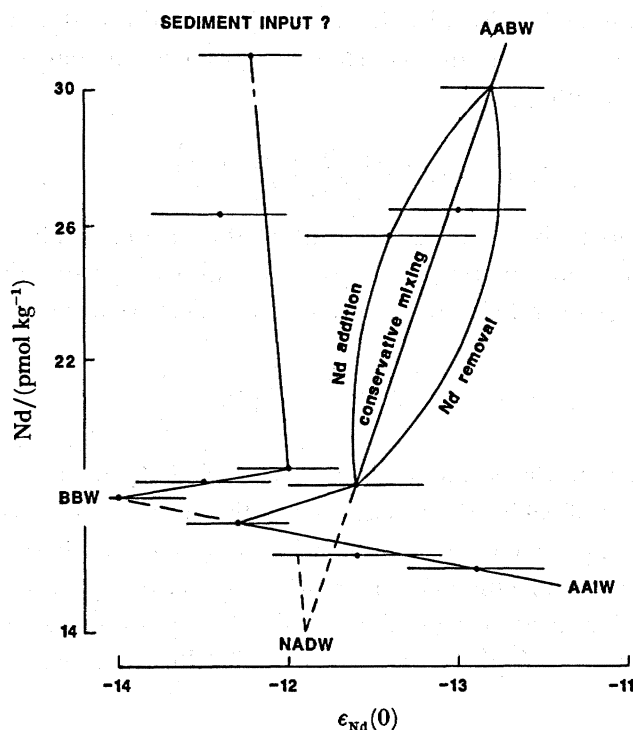


FIGURE 9. Neodymium concentration-isotopic composition diagram for the North Atlantic Ocean based upon data of Piepgras & Wasserburg (1987). The straight lines represent conservative mixing between samples which fall on linear  $\theta$ -salinity mixing lines. End-member compositions are indicated: NADW, North Atlantic Deep Water; AABW, Antarctic Bottom Water; AAIW, Antarctic Intermediate Water; BBW, Baffin Bay Water; and examples of non-conservative behaviour involving Nd addition and removal are shown for one mixing line.

### AN ADSORPTION-OXIDATION SCAVENGING MODEL FOR THE REES

#### *The trivalent REES*

The interpretation given above is that REE concentrations in seawater are controlled by adsorptive scavenging by particles, except that cerium behaves anomalously because its principal mode of removal is by oxidation to insoluble  $\text{Ce}^{\text{IV}}$ . This section attempts to treat these removal processes somewhat more rigorously by exploring whether published ideas about particle scavenging as controls on trace-metal concentrations in seawater can explain the mass fractionation of the REES outlined here.

The approach taken has been to apply a popular scavenging model developed by Schindler (1975) and Balistrieri *et al.* (1981) and used most recently by Whitfield & Turner (1987). The scavenging residence time of the REES is defined as

$$\tau_{\text{REE}}^{\text{SCAV}} = \frac{[\text{REE}^{\text{III}+}] + [\text{REE} - L] + [\text{REE}]_{\text{ADS}}}{\left(\frac{d[\text{REE}]}{dt}\right)_{\text{SCAV}}}, \quad (3)$$

which describes the competition between adsorption of the free metal ion onto particled surfaces (ADS) and complexation with ligands in solution ( $L$ ), which make less of the metal available for adsorption (see Balistrieri *et al.* (1981) for details and more general application).

Because REE speciation in seawater is dominated by carbonate complexation (table 1) the

competition referred to can be described by the ratios of the conditional REE stability constants for seawater ( $\beta_1$  and  $\beta_2$ ) to the formation constant ( $K_{Me}$ ) for a REE-particle surface complex (see also Cantrell & Byrne 1987)

$$\tau_{REE}^{SCAV} = \tau_P + A \left( \frac{\beta_1}{K_{Me}} + \frac{\beta_2}{K_{Me}} [L] \right), \quad (4)$$

where  $A$  is a constant and  $\tau_P$  is the residence time of the particles. This relation has been simplified further by establishing the relation between  $\beta$  and  $K_{Me}$  by using the term ' $m$ ', which is designated the 'binding constant': large values of  $m$  reflect a strong binding capacity of particles for REEs,

$$\tau_{REE}^{SCAV} = \tau_P + A \left( \beta_1^{1-m} + \frac{\beta_2}{\beta_1^m} [CO_3^{2-}] \right). \quad (5)$$

The REE scavenging residence times obtained by this method should be proportional to the ratios of the concentrations of each REE in seawater to that in input material.

Greater details of this approach and results will be given elsewhere and only a brief application is given here. Figure 10 shows the model-derived pattern of relative REE scavenging residence times as a function of atomic number obtained by plotting values of the  $\beta$  term in parentheses in (5) normalized to  $La = 1$ . The two examples illustrated were obtained by using

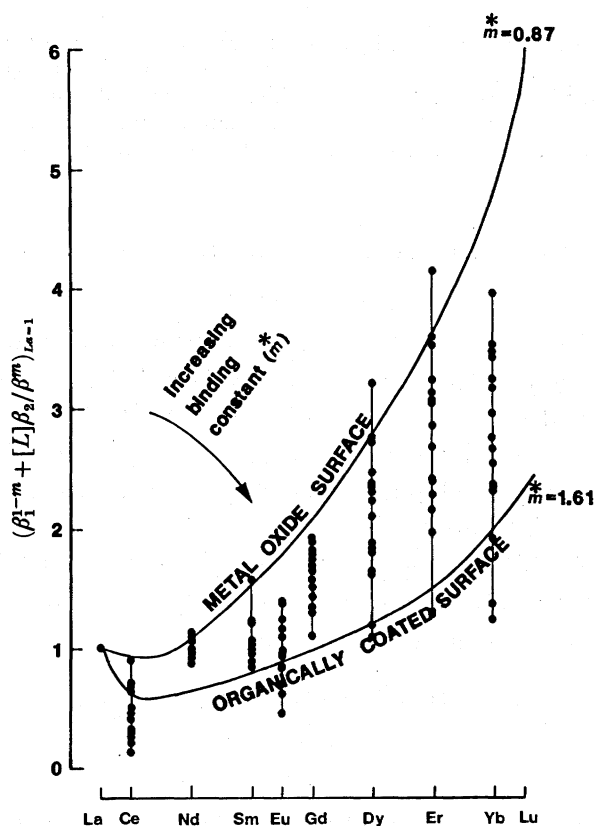


FIGURE 10. Adsorption scavenging model for the REEs. Plot of  $\beta$  term (normalized to  $La = 1$ ) in (5) of text against REE atomic number showing model-derived patterns for metal oxide surface and organically coated surface together with patterns for REEs in northeast Atlantic seawaters (Elderfield & Greaves 1982) normalized to average shale and  $La = 1$ .



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values of binding constant equivalent to those used in the Balistrieri model: a lower value for an inorganic surface and a higher value for an organically coated surface.

The model makes a number of predictions. First, the heavy REEs have longer scavenging residence times than the light REEs. Second, the contrast in residence times depends on the strength of the surface adsorption complex. Organically coated surfaces have stronger binding characteristics than oxide surfaces and therefore allow less mass fractionation in solution. Third, it is interesting that the model predicts that the REE with the lowest residence time is not the lightest REE (La).

Figure 10 also compares the model with one example of REE concentrations from a station in the northeast Atlantic Ocean, normalized to average shale. Clearly, Ce fits the model prediction poorly but the other REEs fit the model with some degree of success mostly falling between the two curves and La does not have the lowest normalized abundance, in agreement with the model prediction. Perhaps a better alternative to normalizing the seawater data to shale is to normalize to average river input. Although there is yet no generally agreed REE pattern for average riverwater it now seems clear that rivers are to some degree heavy-REE enriched relative to shale (Upstill-Goddard *et al.* 1987). Therefore, agreement between river normalized data and model prediction requires adsorption by surfaces with strong binding capacity. Adsorption by inorganic oxide surfaces would predict much more REE fractionation than is observed in nature.

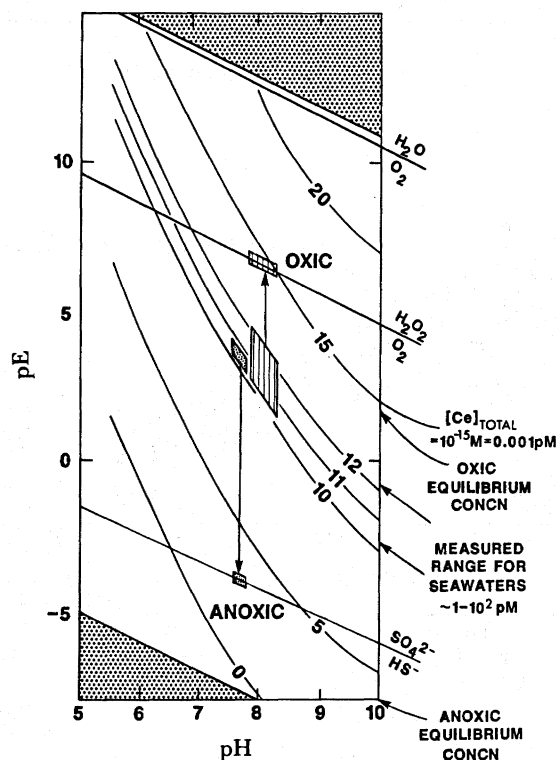


FIGURE 11. A pE-pH diagram showing the predicted isopleths of total dissolved  $\text{Ce}^{\text{III}}$  concentrations (as  $p\text{Ce}_{\text{TOTAL}}$ ) in equilibrium with solid  $\text{CeO}_2$ . Also shown are upper and lower stability boundaries for water, pE-pH relations for  $\text{H}_2\text{O}/\text{O}_2$  and  $\text{H}_2\text{O}_2/\text{O}_2$  in equilibrium with atmospheric oxygen and for  $\text{SO}_4^{2-}/\text{HS}^-$ . The shaded areas show the actual and predicted Ce concentrations for oxic and anoxic seawaters. Modified from De Baar *et al.* (1988). (In this paper,  $pE = -\lg a_e$ , where  $a$  is activity.)



*The behaviour of cerium*

The adsorptive scavenging model outlined above describes the behaviour of Ce poorly. Cerium concentrations are much lower than predicted (figure 10). Nevertheless pE–pH relations (figure 11) show that  $\text{Ce}^{3+}$  is supersaturated in seawater and equilibrium concentrations are even lower than those observed. Therefore, the scavenging model that is an equilibrium model cannot apply. Ce is under kinetic control and is removed from seawater by oxidation.

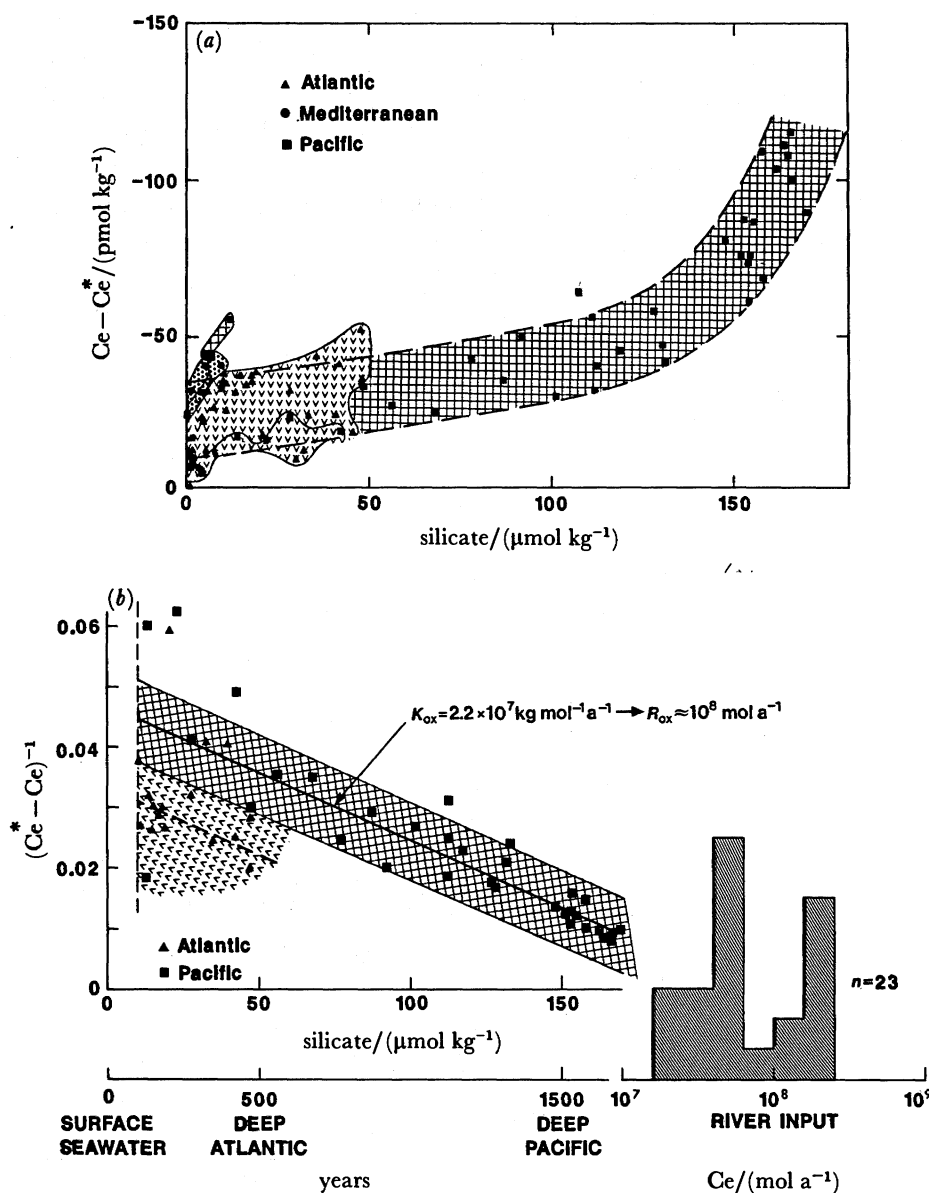


FIGURE 12. Ce removal from seawater by oxidation. (a) Plot of oxidative Ce removal against silicate.  $\text{Ce}^*$  is the Ce concentration expected if Ce behaves like the trivalent REEs and obtained by linear interpolation between La and Nd. (b) Plot of reciprocal of Ce removal term against silicate. Also shown is crude timescale for deep-water flow leading to quoted second-order oxidation rate constant ( $K_{\text{ox}}$ ) and removal rate ( $R_{\text{ox}}$ ). The histogram shows the estimated river input flux of Ce based upon Ce concentrations in 23 rivers (Upstill-Goddard *et al.* 1987) and the total annual river discharge rate. Estuarine removal would decrease the flux to ca. 60% of these values.

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The role of oxidation can be defined by subtracting the observed Ce concentrations in seawater from the concentrations that would be expected if Ce behaved like its REE neighbours. This treatment shows increasing Ce removal from seawater in the direction of deep-water flow (figure 12*a*). Furthermore, by placing a crude timescale upon this pattern it is possible to estimate the rate of Ce removal. The pattern best fits removal by second-order kinetics (implying that Ce oxidation is autocatalytic, like that of Mn in seawater) and shows (figure 12*b*) that Ce is removed from seawater by oxidation at approximately the same rate as the rate

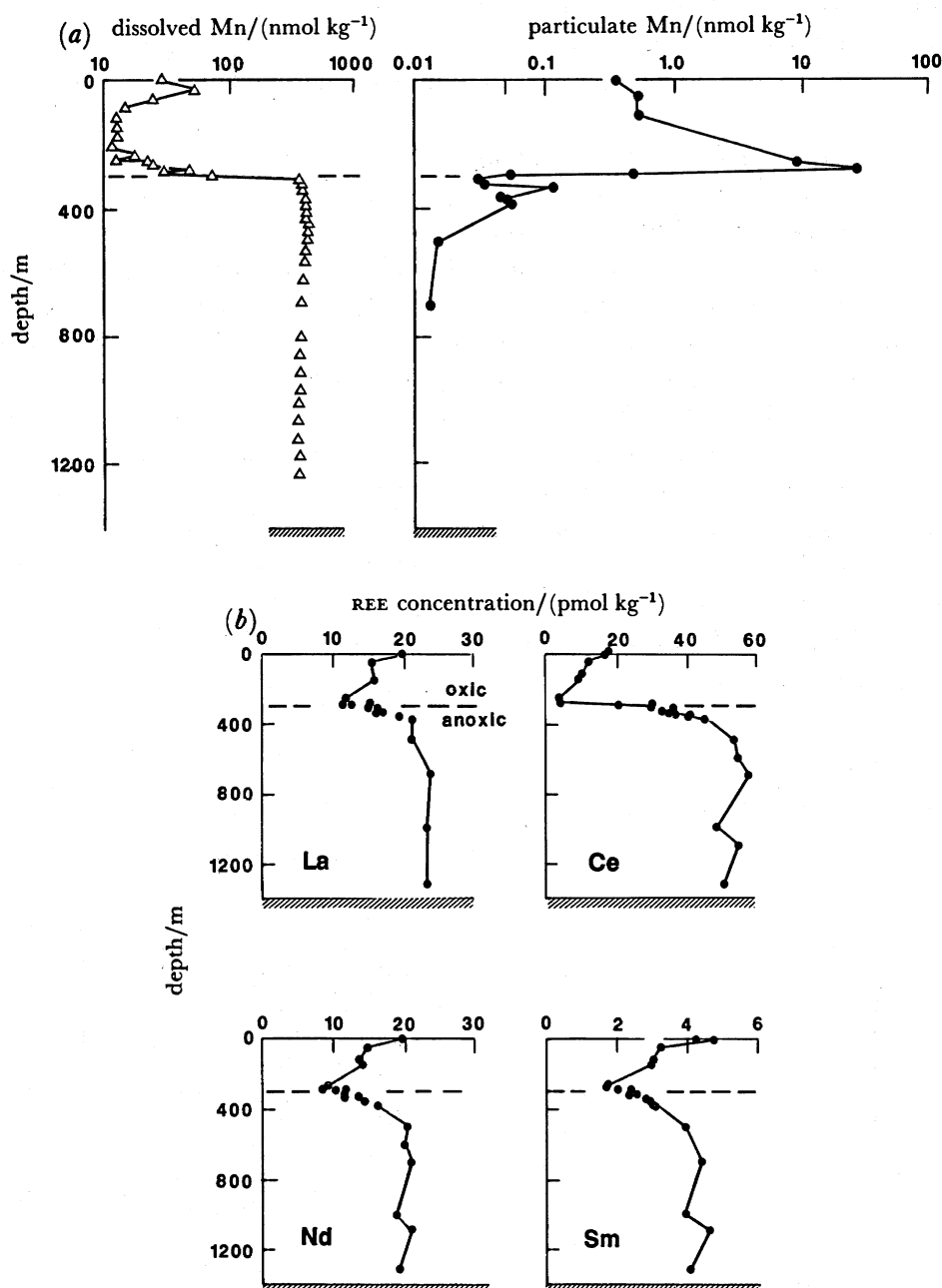


FIGURE 13. Concentration profiles in the Cariaco Trench. (a) Dissolved and particulate Mn. (b) Examples of REE concentrations. Data from De Baar *et al.* (1988).

of Ce input to the oceans from rivers (*ca.*  $10^8 \text{ mol a}^{-1}$ ). Because the negative Ce normally in the normalized REE pattern for seawater is roughly an order of magnitude in scale, Ce must be removed from seawater by oxidation about an order of magnitude more rapidly than by the other processes affecting REE removal. Therefore, the oxidation-removal rate term must be the dominant one for cerium.

### *Evidence from anoxic basins*

The concentrations of the REEs in ocean waters, and their variabilities, are consistent, therefore, with adsorption and autocatalytic oxidation by particles and both the equilibrium scavenging model and the oxidation-rate calculation for cerium offer support for this concept. Some key supporting evidence comes from an unusual environment, that of the anoxic basin.

Figure 13 shows the seawater concentrations of Mn and the REEs across the  $\text{O}_2$ - $\text{H}_2\text{S}$  boundary in the Cariaco Trench. Because of its redox chemistry, Mn is recycled across the boundary, being reduced and dissolved in the lower anoxic water and oxidised and precipitated just above the oxic-anoxic interface to produce a standing crop of reactive particles (figure 13*a*). The REEs are incorporated into this cycle (figure 13*b*). The behaviour of dissolved Ce is identical to that of dissolved Mn; this is not surprising because of their similar oxidation-reduction characteristics. However, the strictly trivalent REEs also are recycled across the  $\text{O}_2$ - $\text{H}_2\text{S}$  interface and this must be because of a similar particle-scavenging process to that described for the open ocean but, unlike the situation in the open ocean, the particles bearing the scavenged REEs settle into the lower waters of the anoxic basin where they dissolve. Therefore, one would predict that the REEs in the deeper anoxic waters should (unlike deeper oxic ocean waters) be heavy-REE depleted because of the preferential enrichment of the light REEs, which are transported downwards in particles and dissolve. This is exactly what is observed (figure 14*a*); the Er/Nd ratio is significantly lower below the  $\text{O}_2$ - $\text{H}_2\text{S}$  interface than in the overlying oxic seawater.

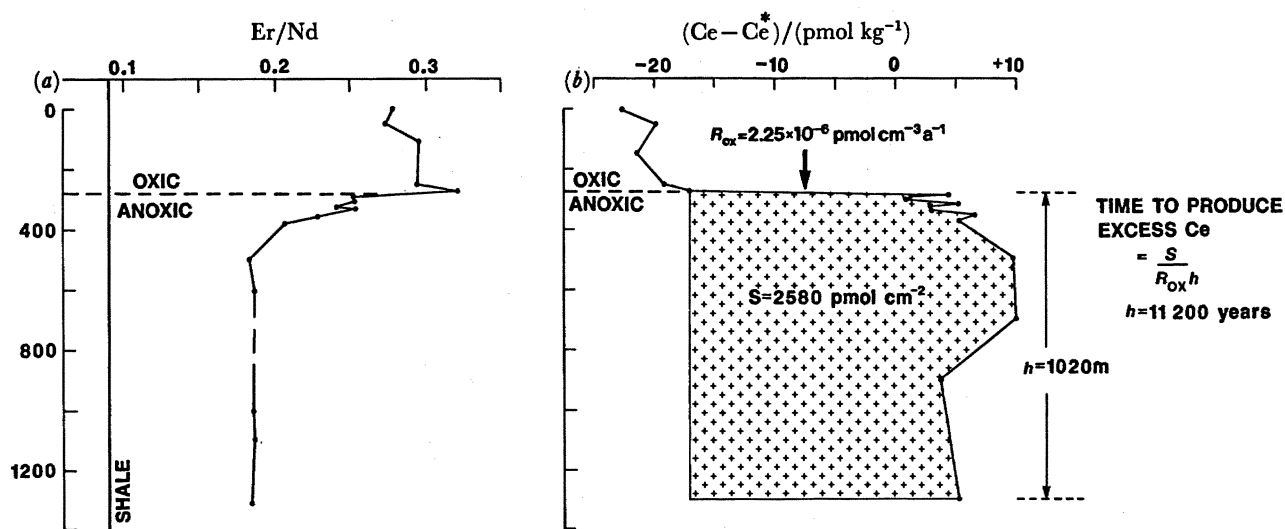


FIGURE 14. (a) Er against Nd in the Cariaco Trench. Modified from De Baar *et al.* (1988). (b) Plot of excess Ce against depth in the Cariaco Trench (symbols as for figure 12).  $R_{\text{ox}}$  is based on  $K_{\text{ox}}$  given in figure 12;  $S$  is the standing crop of Ce below the  $\text{O}_2/\text{H}_2\text{S}$  boundary.

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Furthermore, the Ce data supports the description of the open ocean process too. Examination of the cerium concentrations for the anoxic waters on the pE–pH diagram (figure 11) shows that whereas oxic seawater is supersaturated with Ce, anoxic seawater is considerably undersaturated. Therefore, the concentration of Ce attained in the deep waters of the Cariaco Trench should record the progressive enrichment of reduced Ce in the anoxic seawater. Figure 14*b* shows that the water column standing crop of excess Ce would have taken 11 200 years to accumulate at the Ce oxidation rate obtained previously (figure 12*b*) and assuming instantaneous reduction of Ce<sup>IV</sup> within the anoxic water column. Observations of water-column stability of the Cariaco Trench suggest that it could overturn within less than 200 years (Scranton *et al.* 1987). However, the bottom sediment record reveals that the Trench has been anoxic for the past 11 000 years (Heezen *et al.* 1959). The more rapid flushing time would require a 50 times faster production rate of reduced Ce, presumably through dissolution of detrital Ce and/or enhanced uptake of Ce from oxic seawater in association with the recycling across the O<sub>2</sub>–H<sub>2</sub>S interface.

## EUROPIUM ANOMALIES IN SEAWATER

Figure 8*c* shows the relation between the concentrations in oceanic waters of Eu and Sm, elements of adjacent atomic numbers. Figure 8*a* shows, as was discussed earlier, that Nd and Sm, two atomic numbers apart, behave extremely coherently with no significant mass fractionation.

What then is the reason for the range of Eu/Sm ratios? Some surface waters have anomalously low Eu/Sm ratios because they record the pattern of aeolian input that in the Atlantic appears to contain a negative Eu anomaly and these plot below the shale-ratio line in figure 8*c*. However, many sea waters have high Eu/Sm ratios, especially those in the Pacific Ocean that are higher than the generally shale-like values for Atlantic samples not affected by aeolian input. A river-input ratio significantly different from shale is one possible explanation although the similarity between the shale ratio (0.212 mol/mol) and the non-aeolian Atlantic values (0.21 mol/mol) and the currently available river-water data (0.229 mol/mol) would argue against this. Another explanation is that the concept of comparing REE behaviour in terms of linear mass fractionation is too simplistic, as the scavenging model indeed implies.

Nevertheless there remains a likelihood that the anomalously high Eu/Sm ratios in seawater are not a consequence of the river-input ratio or of mass fractionation with the oceans. If so, it is inescapable that the Eu/Sm ratio records hydrothermal input to seawater and there is evidence to support this explanation. Figure 15*a* shows the seawater-normalized REE pattern of a typical high-temperature vent fluid. This contains more than 3000 times more Eu than normal seawater but only 100 times more Sm. In addition, this high ratio is preserved during mixing with ambient seawater as illustrated in figure 15*b*. The samples shown contain less than 0.15% of hydrothermal end member yet show very elevated Eu/Sm ratios that extrapolate to high end-member ratios such as those recorded in vent fluids. If this interpretation is supported by future work, the Eu/Sm ratio could prove to be useful as a hydrothermal tracer because it is evident from figure 15*b* that this mass ratio behaves somewhat as an isotope ratio and is not affected by removal processes. It may help in addressing the importance of ridge-crest hydrothermal processes to the geochemical mass balance of the oceans.

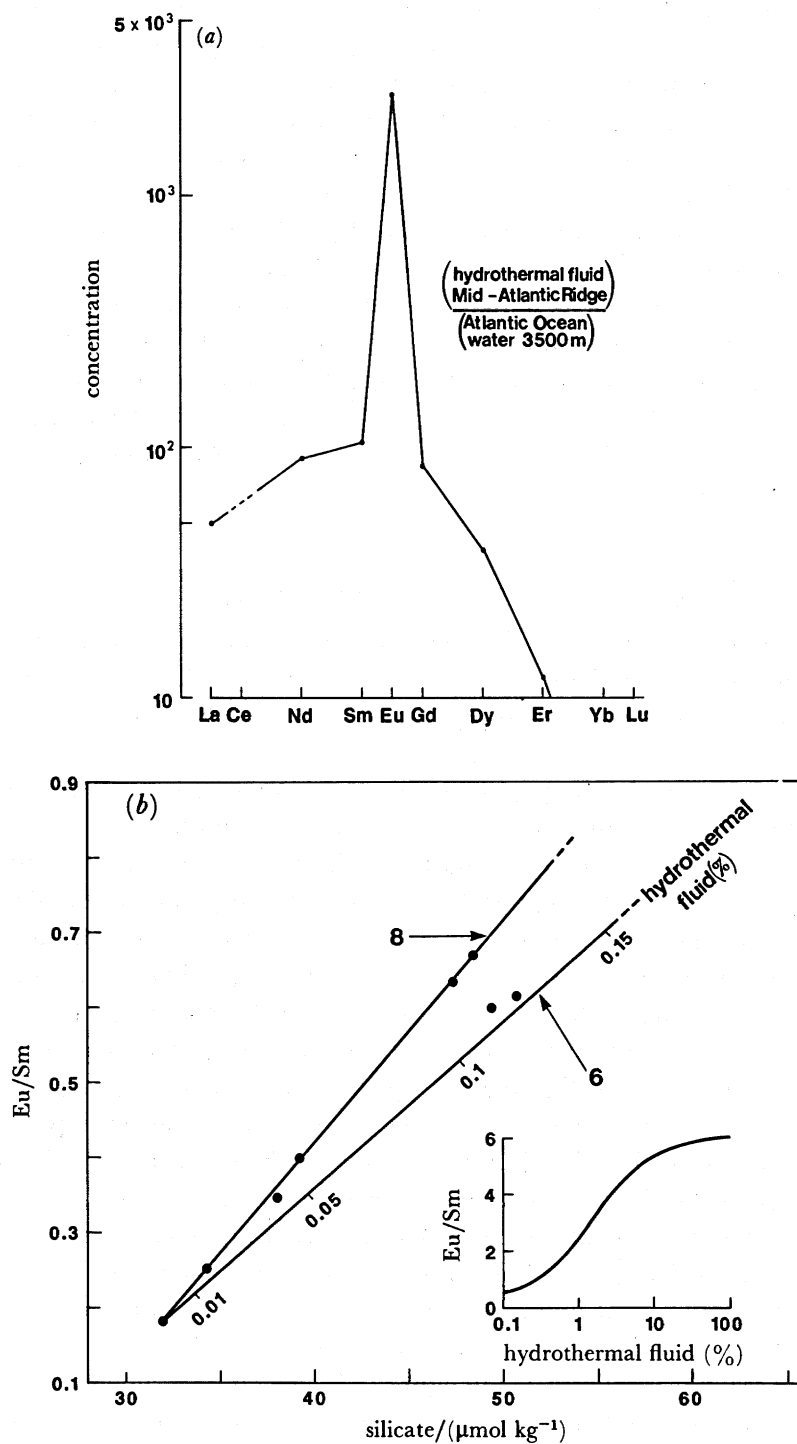


FIGURE 15. (a) REE concentrations in hydrothermal fluid from Mid-Atlantic Ridge normalized to concentrations in Atlantic ocean water. (b) Eu/Sm ratio against silicate for samples of hydrothermal plume in Mid-Atlantic Ridge median valley. Data from Elderfield *et al.* (1987). The values indicated by the arrows are for  $(\text{Eu}/\text{Sm})_{\text{HF}}$ .

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## CONCLUDING COMMENT

Work on the REE chemistry of seawater has occupied only a very recent period in the history of rare-earth element research. The first concentration measurements were reported almost 25 years ago (Goldberg *et al.* 1963) but it is only in the last 5 years that there has been a concerted effort to try and understand what controls their oceanic chemistry. Nevertheless, this year is a most appropriate one in which to present this review because 1987 is the 200th anniversary of the discovery of the rare earths by Lieutenant Carl Axel Arrhenius who found a black mineral in a quarry in the village of Ytterby near Stockholm in 1787. However, it took a further 120 years' work to complete the separation of the individual REE, a process that, as shown above, the oceans perform with consummate ease.

Finally, it is worth reporting a further historical event that occurred 100 years ago, almost exactly at the half-way point of REE research. On the Friday evening of 18 February 1887, William Crookes, F.R.S., delivered a lecture at the Royal Institution that was published one week later in the *Chemical News* (Crookes 1887). The lecture concerned the genesis of the elements and Crookes was particularly intrigued by the metals of the rare earths, which he discussed as part of a category 'of elements associated with other elements more or less closely allied to themselves', no doubt impressed by their chemical coherence. Earlier in his article, Crookes writes 'These elements perplex us in our researches, baffle us in our speculations, and haunt us in our very dreams. They stretch like an unknown sea before us – mocking, mystifying and murmuring strange revelations and possibilities'. This seems a most apt summary of the state of understanding of marine trace-element chemistry from which we are now emerging. It is hoped that this review will be of use in describing some of the 'strange revelations and possibilities' obtained from studying rare-earth elements in the sea.

I acknowledge the contributions of the past and present members of the Marine Geochemistry Group at Cambridge who have worked with me on oceanic REE chemistry, and the Natural Environment Research Council for supporting this work. I am grateful to Carma Schilpp for tracing the quotation by Sir William Crookes. This is Cambridge Earth Sciences Series Contribution no. 1010.

## REFERENCES

- Balistrieri, L., Brewer, P. G. & Murray, J. W. 1981 Scavenging residence times of trace metals and surface chemistry of sinking particles in the deep ocean. *Deep Sea Res.* **28A**, 101–121.
- Bender, M. L. 1982 Trace elements and ocean chemistry. *Nature, Lond.* **296**, 203, 204.
- Cantrell, K. J. & Byrne, R. H. 1987 Rare earth element complexation by carbonate and oxalate ions. *Geochim. cosmochim. Acta* **51**, 597–605.
- Crookes, W. 1887 Genesis of the elements. *Chem. News, Lond.* **55**, 83–99.
- De Baar, H. J. W., Bacon, M. P. & Brewer, P. G. 1983 Rare-earth distributions with a positive Ce anomaly in the Western North Atlantic Ocean. *Nature, Lond.* **301**, 324–327.
- De Baar, H. J. W., Bacon, M. P., Brewer, P. G. & Bruland, K. W. 1985a Rare earth elements in the Atlantic and Pacific Oceans. *Geochim. cosmochim. Acta* **49**, 1943–1959.
- De Baar, H. J. W., Brewer, P. G. & Bacon, M. P. 1985b Anomalies in rare earth distributions in Seawater: Gd and Tb. *Geochim. cosmochim. Acta* **49**, 1961–1969.
- De Baar, H. J. W., Elderfield, H. & Bruland, K. W. 1985c Rare earth elements at VERTEX IV in the Central North Pacific gyre. *Trans. Am. geophys. Un.* **66**, 1291.
- De Baar, H. J. W., German, C. R., Elderfield, H. & Van Gaans, P. 1988 Rare earth element distributions in anoxic waters of the Cariaco Trench. *Geochim. cosmochim. Acta*. (In the press.)
- Elderfield, H. & Greaves, M. J. 1981 Negative cerium anomalies in the rare earth element patterns of oceanic ferromanganese nodules. *Earth planet. Sci. Lett.* **55**, 163–170.



- Elderfield, H. & Greaves, M. J. 1982 The rare earth elements in seawater. *Nature, Lond.* **296**, 214–219.
- Elderfield, H. & Greaves, M. J. 1983 Determination of the rare earth elements in seawater. In *Trace metals in seawater* (ed. C. S. Wong, E. Boyle, K. W. Bruland, J. D. Burton & E. D. Goldberg), pp. 427–445. New York & London: Plenum Press.
- Elderfield, H. & Sholkovitz, E. R. 1987 Rare earth elements in the pore waters of reducing nearshore sediments. *Earth planet. Sci. Lett.* **82**, 280–288.
- Elderfield, H., Greaves, M. J., Klinkhammer, G. P. & Edmond, J. M. 1987 Rare earth elements in hydrothermal fluids and plumes: influence on geochemical mass balance. Abstract, IUGG Symposium, Vancouver 1987.
- Goldberg, E. D. 1954 Marine geochemistry 1. Chemical scavengers of the sea. *J. Geol.* **62**, 49–265.
- Goldberg, E. D., Koide, M., Schmitt, R. A. & Smith, R. H. 1963 Rare-earth distribution in the marine environment. *J. geophys. Res.* **68**, 4209–4217.
- Goldschmidt, V. M. 1954 *Geochemistry* (730 pages.) Oxford: Clarendon Press.
- Greaves, M., Klinkhammer, G., Elderfield, H., Lambert, C. & Risler, N. 1985 Rare earth geochemistry in the Alboran Sea. *Terra cogn.* **5**, 190.
- Heezen, B. C., Menzies, R. J., Broecker, W. S. & Ewing, M. 1959 Stagnation of the Cariaco Trench. In *Preprints International Oceanographic Congress* (ed. M. Sears), pp. 99–102. Washington D.C.: Am Assoc. Adv. Science.
- Klinkhammer, G., Elderfield, H. & Hudson, A. 1983 Rare earth elements in sea water near hydrothermal vents. *Nature, Lond.* **297**, 185–188.
- Krauskopf, K. B. 1956 Factors controlling the concentration of thirteen rare metals in sea water. *Geochim. cosmochim. Acta* **9**, 1–32.
- Michard, A., Albarede, F., Michard, G., Minster, G. F. & Charlou, J. L. 1983 Rare-earth elements and uranium in high temperature solutions from East Pacific Rise hydrothermal vent field (13° N). *Nature, Lond.* **303**, 795–797.
- Palmer, M. 1983 Rare earth elements and Nd and Sr isotopes in the Atlantic Ocean. Ph.D. thesis, University of Leeds. (284 pages.)
- Piepgas, D. J. & Wasserburg, G. J. 1980 Neodymium isotopic variations in sea water. *Earth planet. Sci. Lett.* **50**, 128–138.
- Piepgas, D. J. & Wasserburg, G. J. 1982 Isotopic composition of neodymium in waters from the Drake Passage. *Science, Wash.* **217**, 207–214.
- Piepgas, D. J. & Wasserburg, G. J. 1983 Influence of the Mediterranean outflow on the isotopic composition of neodymium in waters of the North Atlantic. *J. geophys. Res.* **88**, 5997–6006.
- Piepgas, D. J. & Wasserburg, G. J. 1985 Strontium and neodymium isotopes in hot springs on the East Pacific Rise and Guaymas Basin. *Earth planet. Sci. Lett.* **72**, 341–356.
- Piepgas, D. J. & Wasserburg, G. J. 1987 Rare Earth element transport in the western North Atlantic inferred from Nd isotopic observations. *Geochim. cosmochim. Acta* **51**, 1257–1271.
- Piepgas, D. J., Wasserburg, G. J. & Dasch, E. J. 1979 The isotopic composition of Nd in different ocean masses. *Earth planet. Sci. Lett.* **45**, 223–236.
- Schindler, P. W. 1975 Removal of trace metals from the oceans: a zero order model. *Thalassia jugosl.* **11**, 101–111.
- Scranton, M. I., Sayles, F. L., Bacon, M. P. & Brewer, P. G. 1987 Temporal changes in the hydrography and chemistry of the Cariaco Trench. *Deep Sea Res.* **34**, 945–963.
- Stordal, M. C. & Wasserburg, G. J. 1986 Neodymium isotopic study of Baffin Bay water: Sources of REE from very old terranes. *Earth planet. Sci. Lett.* **77**, 259–272.
- Turekian, K. K. 1977 The fate of metals in the oceans. *Geochim. cosmochim. Acta* **41**, 1139–1144.
- Upstill-Goddard, R., Elderfield, H. & Sholkovitz, E. R. 1987 Rare earth elements in rivers and estuaries. (In preparation.)
- Whitfield, M. & Turner, D. R. 1987 The role of particles in regulating the composition of sea water. In *Aquatic surface chemistry* (ed. W. Stumm), pp. 457–493. New York: Wiley.

### Discussion

M. WHITFIELD (*Marine Biological Association, Plymouth, U.K.*). Most stability constants for REE complexation in seawater are obtained by analogy rather than by experiment. Therefore, arguments that depend on the magnitude of carbonate complexation rather than the relative trends must be treated with caution. Is Dr Elderfield sure that the model he presents can distinguish between ‘inorganic’ and ‘organic’ interactions?

H. ELDERFIELD. Yes. The model I presented used experimentally determined data by Cantrell & Byrne (1987) rather than the earlier data of Turner *et al.* (1981), which were obtained by analogy.

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*Reference*

Turner, D. R., Whitfield, M. & Dickson, A. G. 1981 The equilibrium speciation of dissolved components in fresh water and sea water at 25 °C and 1 atm pressure. *Geochim. cosmochim. Acta* **45**, 855–881.

M. WHITFIELD. Dr Elderfield's data show a similarity between the REE chemistry of Mediterranean and Pacific waters. How does he explain this?

H. ELDERFIELD. They are similar in the sense that both Mediterranean and Pacific surface waters show similar REE mass fractionation as shown by their Er/Nd ratios. This is a consequence of the removal of REEs from surface seawater by adsorption at particle surfaces, which is a ubiquitous process. However, surface-water concentrations in the Mediterranean are much higher than in the Pacific. This has been recognized for other trace metals (see, for example, Boyle *et al.* 1985) and has been explained by the anti-estuarine circulation of the Mediterranean that permits less vertical recycling of nutrients and hence less removal of metals from surface waters relative to deep waters.

*Reference*

Boyle, E. A., Chapnick, S. D., Bai, X. X. & Spivack, A. 1985 Trace metal enrichments in the Mediterranean Sea. *Earth planet. Sci. Lett.* **74**, 405–419.

J. D. BURTON (*Department of Oceanography, University of Southampton, U.K.*). The possible importance of transport of rare earths in colloidal forms in rivers was mentioned. Would Dr Elderfield like to comment on the importance of destabilization and aggregation of colloids in estuaries in relation to the fluxes from continental weathering processes?

H. ELDERFIELD. This is a process that we have been considering recently (Hoyle *et al.* 1984; Upstill-Goddard *et al.* 1987). It is striking that the variations of REE concentrations in six estuaries now examined invariably are similar to those in iron. The highest REE concentrations we have measured in rivers are from rivers containing iron-rich colloidal materials and it seems very likely that the REEs are associated with such phases.

*Reference*

Hoyle, J., Elderfield, H., Gledhill, A. & Greaves, M. 1984 The behaviour of the rare earth elements during mixing of river and sea waters. *Geochim. cosmochim. Acta* **48**, 143–149.

M. P. BACON (*Woods Hole Oceanographic Institution, Woods Hole, U.S.A.*). Dr Elderfield has tended to use REE ratios in average shale for comparison with the seawater data. To what extent does he consider that shale typifies the pattern of REE input to the oceans from the continents?

H. ELDERFIELD. Although I tended to display shale REE ratios for comparative purposes, I mentioned that the conclusions reached also apply were REE ratios for riverwaters used. Recently we have measured REE concentrations in 23 rivers (Upstill-Goddard *et al.* 1987) and have found that their patterns do not always resemble that of average shale. After correction for REE fractionation during estuarine removal the pattern of river input is heavy-REE enriched but not to the degree found in ocean waters. Therefore, *some* of the REE fractionation implied

to have occurred in seawater by normalizing patterns to average shale may be an artefact of the normalization procedure but it cannot explain the major effects such as differences between different ocean basins. There are four problems in the choice of an average riverwater pattern for normalization. There is a variability in pattern between different rivers. Temporal variations in pattern occur in individual rivers. The effect of estuarine removal on the REE input pattern has not yet been evaluated thoroughly. Other sources of REE to seawater are important locally, principally aeolian input.

P. S. LISS (*School of Environmental Sciences, University of East Anglia, U.K.*). In view of the similar redox chemistry of cerium and manganese, is there any evidence either from the field or the laboratory for photochemical reduction of  $\text{Ce}^{\text{IV}}$  to  $\text{Ce}^{\text{III}}$  in the presence of dissolved organic matter, as appears to occur for manganese ( $\text{Mn}^{\text{IV}} \rightarrow \text{Mn}^{\text{II}}$ )?

H. ELDERFIELD. This is an interesting suggestion, in particular because the free-energy changes for  $\text{Ce}^{\text{IV}}$  and  $\text{Mn}^{\text{IV}}$  reduction are very similar. Surface-water enrichments of Ce have been observed at some stations but these are invariably associated with enrichments of other REEs too, and may be attributed to aeolian input. However, a positive Ce anomaly in western North Atlantic surface waters has been recorded (De Baar *et al.* 1983) and although it was attributed to advective input from reducing marginal sediments, photochemical reduction is an equally plausible explanation.