YREE scavenging in seawater:

A new look at an old model

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Abstract. In the ocean, yttrium and the rare earth elements (YREEs) show nutrient-like vertical profiles. Since the YREEs have no manifest biological function, their removal from solution (scavenging) is probably caused by sorption on particles rather than active microbial uptake, yet the exact nature of these particles is uncertain. An existing theoretical model describes scavenging as an equilibrium between complexation with dissolved inorganic ligands and with functional groups on particle surfaces. This model was able to predict input-normalized (i.e., shale-normalized) YREE abundance patterns in seawater without requiring poorly known parameters like particle concentrations or the site densities of functional groups. Employing well-established stabilities of inorganic YREE complexes, while assuming that the sorbent particles are organic with functional groups represented by a mixture of simple monocarboxylic acids, it reproduced some key features of seawater YREE patterns, specifically the characteristic increase of shale-normalized abundance with atomic number and distinctive anomalies of certain trivalent REEs (La and Gd). The familiar negative Ce anomaly of seawater, however, is due to redox reactions that were not explicitly accounted for.

In this study, we refined calculations of YREE solution speciation by adding complexation with desferrioxamine B to gauge the influence of strong organic ligands prevalent near the ocean surface. The scavenging model was then inverted by subtracting high-quality YREE abundance patterns, reported for the open ocean, from this solution speciation to yield an average pattern of relative YREE affinities for the sorbent particles. The resulting affinity pattern is compared with patterns of distribution coefficients, derived from laboratory experiments, for YREE sorption on relevant solid phases including hydrated Fe and Mn oxides (HFO/HMO), calcite, and the green macroalga *Ulva lactuca* as a substitute for marine organic matter. For deep seawater, the best agreement is observed with HMO, which may thus be the dominant carrier of YREEs to the sediment. Since Ce is catalytically oxidized on manganese oxide surfaces, this could have implications for the evolution of the Ce anomaly. Direct comparisons of distribution coefficient patterns with YREE analyses of suspended particles from the Atlantic Ocean also favor HMO, but this may be dictated in one case by the use of a selective leaching method. For shallow seawater, particularly in the Atlantic Ocean, the best agreement is observed with *U. lactuca* and calcite, although the latter is offset by the low YREE contents of this biogenic mineral. Matches with HFO are generally less convincing. The aforementioned mixture of simple monocarboxylic acids is not a good proxy for the sorptive properties of marine organic matter.

1. Introduction

Vertical profiles of the dissolved concentrations of many trace metals in seawater, including yttrium and the rare earth elements (YREEs), are called nutrient-like, referring to the behavior of nitrate, phosphate, and silicate (Bruland, 1983; Byrne, 2002). In the euphotic zone, nutrients are assimilated by phytoplankton, which subsequently sinks and is remineralized by bacteria who release them back into solution, resulting in concentrations that stay low near the ocean surface but increase rapidly with depth. The vertical profiles of some trace metals show remarkable correlations with specific nutrients, suggesting close associations with the microbial cycle of growth and decomposition. Correlations of Zn and the YREEs with silicate (Bruland et al., 1978; Elderfield, 1988) might be construed as evidence of incorporation into biogenic opal, however high-resolution synchrotron X-ray fluorescence (SXRF) elemental maps of individual diatom cells reveal that Zn and Si are not co-located (Nuester et al., 2012). The puzzling correlation of Cd, which is toxic to most living things, with phosphate (de Baar et al., 1994) became somewhat less so when Lee et al. (1995) demonstrated that it is capable of replacing Zn as a co-factor of the enzyme carbonic anhydrase under Zn-deficient conditions. The YREEs were recently found to replace Ca as a co-factor of the enzyme methanol dehydrogenase in unusual hyperacidophilic methanotrophic bacteria (Pol et al., 2014), but such a biological function has not been observed for any marine organism. Microbial uptake of Zn, Cd, and other micronutrient metals may hinge on extensive complexation with unidentified organic ligands (Jakuba et al., 2012; Baars et al., 2014), yet while the YREEs could be up to 30% organically complexed (Christenson and Schijf, 2011), similar levels have been observed for Pb (Capodaglio et al., 1990), a toxic metal that does *not* display nutrient-like distributions (Biller and Bruland, 2012). It appears that the YREEs, along with Sc, Ti, Zr, and Hf (Byrne, 2002), form a separate category of ostensibly non-essential (albeit non-toxic) metals whose vertical profiles are nevertheless distinctly nutrient-like (Fig. 1).

The emergent oceanic distributions of trace metals may have more to do with their reactivity, whereby highly reactive metals (e.g., Mn, Sn) are strongly scavenged and unreactive metals i.e., those that exist as large, single-charged cations (e.g., Cs, Tl), or oxyanions (e.g., Mo, Re), are conservative. The majority of metals is moderately reactive, leading to intermediate, nutrient-like behavior (Byrne, 2002). The sorption processes that underlie metal scavenging in seawater are fundamentally due to the formation of complexes with functional groups that are tightly bound to

particle surfaces. For mineral particles, like the oxides of silicon, iron, and manganese, these functional groups are hydroxyls, whereas for organic matter additional oxygen-bearing groups are involved, such as carboxyl and phosphoryl, although nitrogen- and sulfur-bearing groups may play a sizeable role as well (Gonzalez-Davila et al., 1995; Zoll and Schijf, 2012). At the pH of seawater, many of these groups are deprotonated and carry negative charge, imparting an electrostatic attraction to the positive metal ion. The primary interaction is with the free, hydrated metal cation and the sorption process is therefore in direct competition with metal complexation in solution. Solution complexation greatly diminishes the inherently high reactivity of the relatively small, trivalent YREE cations and it seems that marine microbes can similarly exert significant control over the reactivity of essential (or toxic) metals by producing strong chelators. Inorganic solution speciation in seawater is fairly easy to model, as most metals form complexes with a limited number of major anions, notably chloride, sulfate, and carbonate, whose stability constants have been carefully measured (Turner et al., 1981; Byrne et al., 1988). The identities of perhaps hundreds of organic ligands that dominate the solution speciation of various trace metals remain elusive, but voltammetric techniques allow at least their total concentrations and conditional stability constants to be determined (Pižeta et al., 2015). A much greater challenge is our scant knowledge of the sorbent particles, for example their bulk concentrations and surface areas, as well as intrinsic properties like the diversity, structures, and site densities of their functional groups.

The scavenging model of Byrne and Kim (1990) was built on an equilibrium between metal complexation with functional groups on particle surfaces (sorption) and with dissolved ligands (desorption). These authors realized that, unlike any single metal, the chemical coherence of the lanthanide series permits YREE scavenging to be modeled in a relative sense, eliminating several unknown parameters. Equally beneficial was an already advanced understanding of their solution speciation in seawater (Byrne and Sholkovitz, 1996). Byrne and Kim (1990) only needed an estimate of YREE affinity for the sorbent particles, which they assumed to be organic, based on a prolific microbial source and ubiquitous presence as reactive coatings on mineral surfaces. They consequently proposed that the main functional group can be represented by a mixture of fifteen randomly selected simple monocarboxylic acids. The model reproduced some key features of shale-normalized seawater YREE patterns, still measured at the time via Instrumental Neutron Activation Analysis (INAA), such as their positive slopes and minor anomalies of La and Gd, yet

without better information this exercise could be carried no further. In the present study, we utilize complete, high-quality seawater YREE patterns that have since become available through the development of inductively coupled plasma mass spectrometry (ICP-MS). Organic YREE complexation, which Christenson and Schijf (2011) inferred to be subsidiary but not negligible, is added to the solution speciation. While marine particulate matter continues to be inadequately characterized, we now have, from laboratory experiments, distribution coefficient patterns for YREE sorption on a few relevant solid phases: hydrated iron oxide (HFO), hydrated manganese oxide (HMO), calcite, and macroalgal tissue. Rather than guess the nature of marine particulate matter, we construct an average pattern of relative YREE affinities by inverting the scavenging model of Byrne and Kim (1990) in order to assess, by pairwise comparisons with the distribution coefficient data, which solid phases best match its sorptive properties.

2. The modified equilibrium model for YREE scavenging in seawater

In the original model (hereafter called the B&K model), scavenging is envisioned as an equilibrium partitioning of each YREE between the solution and filterable particles where, in the notation of Byrne and Kim (1990), the total YREE concentration in seawater, A_M , is equal to:

$$A_M = M_S + M_T, \quad (1)$$

M_S being the particulate YREE concentration and M_T the total dissolved YREE concentration (both in mol/L). Byrne and Kim (1990) named the concentration of particles ϕ_P (in g/L), so that the particulate YREE concentration in units of mol per g of particles is $M_P = M_S/\phi_P$. The YREE solid–solution distribution coefficient, D_M , was subsequently defined as:

$$D_M = \frac{M_P}{M_T} = \frac{M_S/\phi_P}{M_T}. \quad (2)$$

If we view YREE scavenging in the ocean in terms of a steady-state, single-box model (Schindler, 1975) then the flux of particles out of this box and into the sediment can be written as $F_P = \phi_P/\tau_P$, where τ_P is the particle residence time. This particle flux is the only means by which YREEs are removed from the box, with a concomitant metal flux

$$F_M = F_P \times M_P = F_P \times \frac{M_S}{\phi_P} = \frac{M_S}{\tau_P}. \quad (3)$$

The metal flux can also be written per definition as $F_M = A_M/\tau_M$, where τ_M is the YREE residence time with respect to scavenging. Using Eqs. 1–3, it follows that

$$\tau_M = \tau_P \times \frac{A_M}{M_S} = \tau_P \times \frac{M_S + M_T}{M_S} = \tau_P \times \left(1 + \frac{M_T}{M_S}\right) = \tau_P (1 + \phi_P^{-1} D_M^{-1}) \approx \tau_P \phi_P^{-1} D_M^{-1}, \quad (4)$$

since $\tau_M \gg \tau_P$ for the YREEs, which have oceanic residence times on the order of hundreds of years or longer (Nozaki and Alibo, 2003b). From the basic definition of residence time

$$\tau_M = \frac{A_M}{(dA_M/dt)}, \quad (5)$$

Byrne and Kim (1990) argued that τ_M (i.e., the term $\tau_P \phi_P^{-1} D_M^{-1}$), when plotted on a logarithmic scale, should resemble shale-normalized YREE abundance patterns in seawater, because relative steady-state YREE inputs into the global ocean are commonly assumed to have a shale-like source signature (Elderfield, 1988).

The YREE residence time can be quantified in terms of the stability of YREE complexes with dissolved ligands L_j and functional groups S_i :

$$\tau_M = \tau_P \phi_P^{-1} D_M^{-1} = \tau_P \times \frac{M_T}{M_S} = \tau_P \times \frac{M_T/[M]}{M_S/[M]} = \tau_P \times \frac{\sum_{j,n} (1 + {}_j\beta_n [L_j])}{\sum_i ({}_iK_S \times [\equiv S_i])}, \quad (6)$$

where $[M]$ is the free dissolved YREE concentration and the stability constant ${}_j\beta_n$ for the n^{th} YREE complex with dissolved ligand L_j is defined as:

$$M^{3+} + nL_j^{z-} \rightleftharpoons M(L_j)_n^{3-nz} \quad {}_j\beta_n = \frac{[M(L_j)_n]}{[M][L_j]^n} \quad (7a)$$

The stability constant ${}_iK_S$ for a YREE complex with functional group S_i is defined as:

$$M^{3+} + \equiv S_i^{z-} \rightleftharpoons \equiv S_i M^{3-z} \quad {}_iK_S = \frac{[\equiv S_i M]}{[M][\equiv S_i]} \quad (7b)$$

where $M_S = \sum_i [\equiv S_i M]$ and the triple-bond signs indicate that the functional group S_i and the complex $S_i M$ are tightly bound to a particle surface.

For the solution speciation, Byrne and Kim (1990) included YREE monocarbonato- and dicarbonato-complexes (with one and two carbonate anions), as well as chloride, fluoride, sulfate and hydroxide complexes, as reported by Stanley and Byrne (1990). For surface complexation, they assumed that marine particles are overwhelmingly organic, containing a single type of functional group whose stability constant, $\log \bar{K}_S$, was taken as the mean of fifteen randomly selected simple monocarboxylic acids. Combining Eqs. 5 and 6 in logarithmic form yields:

$$\log \frac{A_M}{(dA_M/dt)} = \log \left(\sum_{j,n} (1 + {}_j\beta_n [L_j]) \right) - \log \bar{K}_S + \log \left(\frac{\tau_p}{\sum_i [\equiv S_i]} \right) \quad (8)$$

In the following, we will refer to the term on the left as the abundance term, or A-term, and the first term on the right as the ligand term, or L-term. The third term on the right contains the ratio of the particle residence time, τ_p , and the sum concentration (total site density) of all functional groups, S_i . Both parameters are particle properties and independent of the sorbed metal, hence the third term is a constant that has the same value for all YREEs and does not affect their relative behavior. Byrne and Kim (1990) were thus able to calculate the A-term by ignoring this constant and to compare it with the best seawater YREE patterns available at the time. Here, we rearrange Eq. 8 as follows:

$$\log \bar{K}_S = \log \left(\sum_{j,n} (1 + \beta_n [L_j]) \right) - \log \frac{A_M}{(dA_M/dt)} (+ \text{constant}), \quad (9)$$

to calculate $\log \bar{K}_S$, which we compare with distribution coefficients for YREE sorption on relevant solid phases. For the L-term we do not consider YREE complexes with fluoride, which are negligible, but add complexation with strong organic ligands, represented by the siderophore desferrioxamine B (DFOB), which may constitute as much as 30% of total dissolved YREE concentrations near the ocean surface (Christenson and Schijf, 2011). Stability constants for YREE complexes with inorganic ligands are updated with the latest literature values. For the A-term we substitute complete, high-quality seawater YREE patterns from the Atlantic Ocean (Osborne et al., 2015) and the Pacific Ocean (Zhang and Nozaki, 1996), measured via ICP-MS.

3. Results and discussion

3.1. YREE solution speciation in seawater

To derive the L-term of our modified scavenging model (Eq. 9), YREE solution speciation in seawater was calculated in two steps, using MINEQL2.0 (Westall et al., 1986). In the first step, solution speciation of the major cations and anions was calculated for a standard seawater sample of salinity $S = 35$. Major cations and anions considered were Na^+ , K^+ , Mg^{2+} , and Ca^{2+} , chloride (Cl^-), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), hydroxide (OH^-), and borate ($\text{B}(\text{OH})_4^-$). Although fluoride (F^-) forms ion pairs with Mg^{2+} , its concentration in seawater is low ($\sim 68 \mu\text{mol/kg}$; Byrne, 2002) and its contribution to YREE solution speciation negligible. It was therefore omitted from the calculations. Ion-pairing constants for these components were mostly taken from Millero and Schreiber (1982) and are listed in Table 1. Protonation constants for carbonate were taken from Luo and Byrne (2004) and converted to the free-ion concentration scale. The ionization constant of water was taken from Christenson and Schijf (2011). The protonation constant for borate was taken from Byrne and Kester (1974), as were constants for its ion pairs with the major cations, except K^+ .

Speciation calculations were executed at a fixed pH of 8.33 on the free-ion concentration scale, equivalent to 8.2 on the total scale. Before every iteration, MINEQL normally extrapolates the stability constants stored in its standard thermodynamic database (valid at $I = 0$) to the ionic

strength of the solution, using the Davies Equation. To ensure application of the most accurate values appropriate to seawater ($I = 0.7$), this extrapolation, which is less reliable for $I > 0.5$, was disabled by fixing the ionic strength at zero, after customizing the database with the constants from Table 1. Precipitation of solids and gas exchange with the atmosphere were also disabled. The results (not shown) are in good agreement with speciation calculations for standard seawater reported in the literature (e.g., Millero and Schreiber, 1982; Byrne, 2002).

In the second step, YREEs were added to the seawater speciation model. Only La and Ce are part of the MINEQL database, from which we eliminated their higher-order complexes with chloride and hydroxide. Others were added, such as the dicarbonato-complex. The database was supplemented with the latest literature values for YREE complexation in seawater (Table 2). Stability constants for chloride and sulfate complexes were taken from Luo and Byrne (2001) and Schijf and Byrne (2004), respectively, and first hydrolysis constants ($\log \beta_1^*$) from Klunness and Byrne (2000). Constants for mono- and dicarbonato-complexes and complexes with bicarbonate (HCO_3^-) were taken from Luo and Byrne (2004) and converted to the free-ion concentration scale. The limited number of slots available for extra cations or ligands forced a division of the YREEs into three groups: Y + LREEs (La, Ce, Pr, Nd); La + MREEs (Sm, Eu, Gd, Tb, Dy); and La + HREEs (Ho, Er, Tm, Yb, Lu). For convenience, total dissolved YREE concentrations, M_T , were fixed at 1 pmol/kg. Even in actual seawater, where M_T ranges from ~1 to <100 pmol/kg (Elderfield, 1988), most ligands (*viz.* the major anions) are too abundant to be affected by YREE complexation, or otherwise we held their free concentration constant (Section 3.2). This renders $\log M_T/[M]$, the ratio of the total dissolved and free YREE concentrations i.e., the L-term, which depends solely on free ligand concentrations (Eq. 6), insensitive to the value of M_T and it also justifies our involuntary calculation of the YREE speciation in three groups, as evidenced by identical results obtained for the shared element La.

The inorganic solution speciation of the YREEs in seawater at $S = 35$ and pH 8.2 is given in Table 3, where species contributions are expressed as a percentage of the total dissolved YREE concentration. Percentages are rounded to one decimal place, hence contributions smaller than 0.05% are not recorded. For all YREEs, a majority of the total dissolved concentration (>89%) consists of complexes with carbonate. For La, the monocarbonato-complex comprises about 52% and this contribution decreases with atomic number in favor of the dicarbonato-complex, which comprises about 88% for Lu. The two species are about equally abundant for Pr. Contributions

of complexes with the other major anions are minute, some as high as about 5% but typically less than 1%. The contribution of the free hydrated cation, which is most pertinent here, gradually declines with atomic number from 4.8% for La to less than 0.1% for Lu. Agreement with YREE speciations reported by Byrne et al. (1988) and Byrne and Sholkovitz (1996) is qualitatively good. Quantitative discrepancies are likely caused by slight variations in the major ion speciation or their use of marginally different conditions and stability constants that were modeled or not measured at the right ionic strength. Specifically, our calculations yield a larger contribution of the hydroxide complex, especially for HREEs, presumably reflecting more accurate stability constants for YREE complexes with hydroxide and carbonate (Table 2) that were not available to Byrne and Sholkovitz (1996). Comparison with an earlier YREE speciation reported by Turner et al. (1981) is hindered by the fact that they did not consider the important dicarbonato-complex.

Table 3 also lists values of the L-term (Eq. 9). The corresponding pattern is plotted in Figure 2, rising gradually with atomic number and displaying a pronounced negative Gd anomaly plus two faint ‘M-shaped tetrads’ (Monecke et al., 2002), for Gd–Ho and Er–Lu. The value for Y is approximately equal to that for Eu. Figure 2 moreover shows patterns for pH 7.8 and 7.4 (total scale), which may represent YREE speciations for deep seawater, or for seawater affected by progressive ocean acidification (e.g., Feely et al., 2004). Byrne et al. (1988) reported values of $\log M_T/[M]$ at pH 8.2 and pH 7.6 that are 0.1–0.2 units lower on average than ours, but 0.1–0.2 units higher for Y and La, leading to L-term patterns that have nearly the same slopes as those in Figure 2, but lack their subtle structure due to the use of interpolated stability constants.

3.2. The potential importance of YREE complexation with strong organic ligands

Turner et al. (1981) suggested that elements with a particular affinity for both carbonate and hydroxide may also have a strong tendency to form organic complexes. It is presently unclear what organic ligands might be involved in these complexes. Although stability constants have been measured for YREE complexes with numerous small organic ligands (Martell et al., 2004), many of these are relatively weak or not sufficiently abundant in seawater to alter YREE solution speciation. Christenson and Schijf (2011) recently showed that hexadentate YREE complexes with desferrioxamine B (DFOB), a model hydroxamate siderophore, are 3–4 orders of magnitude more stable than their dicarbonato-complexes and, under favorable conditions, may constitute a significant fraction of total HREE concentrations. Hydroxamate siderophores are probably not

the most abundant organic ligands in seawater (Vraspir and Butler, 2009), but they are common (Trick, 1989) and compounds in the desferrioxamine family have been detected at low-picomolar concentrations throughout the surface ocean (Mawji et al., 2008). While highly specific to Fe^{3+} , siderophores can form complexes with many metal cations and may well affect or even dominate their speciation and reactivity in seawater (Butler, 1998; Butler and Theisen, 2010). Another class of ligands likely to be important for YREE speciation are humic acids, however most investigations of YREE–humate complexation have focused on terrestrial systems (e.g., Davranche et al., 2004, 2008; Pourret et al., 2007; Pourret and Martinez, 2009), and their abundance and chemical behavior in the ocean are still largely unexplored.

In order to gauge the potential influence of organic complexation on YREE scavenging in seawater we expanded our MINEQL speciation model with DFOB to represent a strong organic ligand (Table 2). Since the exact concentrations and speciation of siderophores in seawater are not known, we controlled the extent of organic complexation by fixing the free concentration of the single-protonated ligand, HL^{2-} , the species that forms the most stable YREE complexes (where L^{3-} stands for fully deprotonated DFOB). Christenson and Schijf (2011) showed that DFOB complexes may contribute up to about 30% of the total Lu concentration in seawater. The free ligand concentration was thus adjusted to yield 30%, and also 10%, Lu complexation with DFOB at pH 8.2. The solution speciation of all other YREEs was then recalculated under those conditions, keeping the free ligand concentration fixed at the correct levels, which are $\sim 0.7 \times 10^{-13}$ and $\sim 2.8 \times 10^{-13}$ M, respectively. It should be noted that, due to competition with other trace metals and possibly with Mg^{2+} and Ca^{2+} (Wuttig et al., 2013), it would require an unrealistically high DFOB concentration to produce these conditions, yet we emphasize here as we have before (Christenson and Schijf, 2011; Schijf et al., 2015) that DFOB embodies a broader class of strong organic ligands that, in total, is much more abundant than hydroxamate siderophores alone.

The rather modest effect of the siderophore is shown in Figure 2 and mainly restricted to the HREEs. Even at 30% Lu–DFOB complexation, the speciation of Y and La–Gd remains largely unchanged. Values of the L-term, $\log M_T/[M]$, are raised for elements heavier than Gd and deviations increase gradually with atomic number. The net effect is more HREE fractionation relative to the LREEs. The effect on Ce could not be determined because rapid oxidation of Ce(III) by the ligand prevented Christenson and Schijf (2011) from measuring the stabilities of its DFOB complexes. However, in accordance with the behavior of neighboring elements La and

Pr, it should be negligible. At 10% Lu–DFOB complexation, the effect is the same but less pronounced. As the three lowest acid dissociation constants of DFOB are in the pH range 8.5–9.7 (Christenson and Schijf, 2011), the ligand quickly protonates below pH 8.2 and its influence on YREE solution speciation wanes. These calculations were therefore not repeated at lower pH.

We stated in Section 1 that the identities of strong organic ligands in seawater are largely unknown. Nonetheless, the effect in Figure 2 is arguably typical for a variety of conceivable candidates. Figure 3 compares the dicarbonato-complexes, which dominate inorganic YREE speciation in seawater, with hexadentate DFOB-complexes, hexadentate EDTA-complexes, and complexes with the phenolic sites of terrestrial humic acid. Despite stability constants that span 8 orders of magnitude, the four patterns are resemblant, with values increasing from La to Lu, a negative Gd anomaly, and Y falling among the MREEs. Their slope seems to be higher for the stronger ligands, but does not increase in a consistent way. Different organic ligands should consequently have a similar effect on the shape of the L-term pattern, although the degree of change will depend on ligand type, strength, and abundance. In summary, we are confident that the pattern for 30% Lu–DFOB complexation at pH 8.2 (Fig. 2), while perhaps an upperbound scenario, is a reliable estimate of YREE solution speciation near the ocean surface, regardless of the true nature of marine organic ligands.

3.3. Comparisons of the refined B&K model with modern shale-normalized YREE patterns

For their original scavenging model, Byrne and Kim (1990) calculated the A-term on the left-hand side of Eq. 8 and qualitatively compared it with shale-normalized REE patterns from the Pacific Ocean reported by de Baar et al. (1985). These patterns, generated with INAA and missing only the elements Y, Dy, and Er, were the best then available, but their irregular shapes evince the inherently lower accuracy and precision of that technique. The virtually synchronous development of Isotope Dilution–Thermal Ionization Mass Spectrometry (ID–TIMS) (Greaves et al., 1989) and ICP-MS combined with improved extraction methods (Shabani et al., 1992) has enabled superior analyses of the YREEs in seawater. Patterns measured via ID–TIMS, which is all but independent of the extraction efficiency, are highly accurate yet incomplete since the mono-isotopic elements (Y, Pr, Tb, Ho, Tm) cannot be determined (e.g., Piegras and Jacobsen, 1992). For the present study we preferred patterns measured via ICP-MS which, when combined with a quantitative extraction method, gives excellent data for 14 REEs (except Pm) and Y. For

almost a decade, such patterns were published predominantly by the group of the late Dr. Nozaki (Nozaki et al., 1997, 1999; Alibo and Nozaki, 1999, 2000; Nozaki and Alibo, 2003a,b; Hongo et al., 2006). The launch of the international GEOTRACES program circa 2010 has resulted in the unification and intercalibration of analytical protocols (Pahnke et al., 2012; van de Flierdt et al., 2012), plus a revived interest in YREE marine geochemistry. A spate of new studies has appeared (e.g., Garcia-Solsona et al., 2014; Haley et al., 2014; Molina-Kescher et al., 2014; Osborne et al., 2014, 2015; Hathorne et al., 2015), but several unfortunately either do not report Y concentrations, or focus entirely on the upper or lower water column.

Because a detailed geographic investigation of YREE scavenging is beyond the scope of this work, we somewhat arbitrarily selected one shallow and one deep sample each from the Atlantic Ocean (Osborne et al., 2015) and the Pacific Ocean (Zhang and Nozaki, 1996). Their YREE patterns, normalized to Post-Archaeon Australian Shale (PAAS) (McLennan, 1989), are shown in Figure 4. Being on opposite ends of the Global Conveyor Belt and spanning a large depth range, we contend that these four samples encompass much of the natural variation in seawater pattern shapes (Bertram and Elderfield, 1993). Apart from an order-of-magnitude difference in concentrations, the shallow and deep patterns are similar, albeit the latter have more negative Ce anomalies, de-emphasized here as these cannot be reproduced by the equilibrium scavenging model, and smaller Y enrichments. All display the characteristic increase of shale-normalized abundance with atomic number, however the Atlantic patterns are less fractionated than the corresponding Pacific patterns. A distinct maximum around Er is seen in both shallow patterns and therefore probably real, yet invoking a detailed explanation would be too speculative.

Our initial approach is to refine the B&K model (Eq. 8) and compare it more directly with these high-quality seawater patterns. For the L-term, we substituted our YREE solution speciations (Fig. 2), which differ from the ones employed by Byrne and Kim (1990) as described in Section 3.1. For the $\log \bar{K}_s$ term, Byrne and Kim (1990) made some sweeping assumptions. Since the exact nature of marine particles is uncertain, their relative affinity for the YREEs had to be estimated. Particulate organic matter is plentiful near the ocean surface, whereas the sorptive properties of mineral particles are governed by organic coatings (Loder and Liss, 1985; Stanley and Byrne, 1990), hence Byrne and Kim (1990) surmized that most marine particles are essentially organic. It was further assumed that the main functional groups are carboxylic acids, important mediators of YREE sorption on organic matter (Ngwenya et al., 2009; Zoll and Schijf,

2012), and that YREE complexation with carboxylic acid functional groups is much like solution complexation with carboxylate ligands. They thus selected fifteen monocarboxylic acids from the volumes of *Critical Stability Constants* (Martell and Smith, 1977, 1982; Smith and Martell, 1989) and calculated average values of $\log \beta_1$ (Eq. 7a) for every REE, largely at $I = 0.1$ and $T = 25^\circ\text{C}$, to represent $\log \bar{K}_s$. We recalculated $\log \bar{K}_s$ from the original data (Byrne and Li, 1995), corrected with revisions from the NIST database (Martell et al., 2004), and added values for Y.

To construct model curves of shale-normalized YREE abundances in shallow and deep seawater, the recalculated $\log \bar{K}_s$ values were subtracted from our $\log M_T/[M]$ values at pH 8.2 (without organic complexation) and pH 7.6, respectively (Fig. 4). The B&K model (Eq. 8) is only accurate within a constant identical for all YREEs (*cf.* Eq. 9), so the curves were vertically shifted to maximize overlap with the average shallow or deep seawater pattern, and yield a more quantitative metric of their comparative agreement. This was accomplished by minimizing the sum-of-squares difference for each pair, obtained from the logarithmic A-term values of all shared YREEs, excluding Y and Ce whose unique chemistries induce behavior not well correlated with that of the other lanthanides. Average shallow and deep seawater was calculated after matching the Atlantic to the corresponding Pacific patterns in the same manner.

Our model curves have a lot more structure than those reported by Byrne and Kim (1990). They show negative La and Gd anomalies (Fig. 4), deviating markedly from the seawater patterns, as well as insufficient Y fractionation. Contrary to observations, HREE enrichment of the model curves decreases at depth, where the pH is lower, which is a fundamental flaw. The Ce anomaly is not reproduced for reasons already mentioned. When supplied with the latest stability constants, the scavenging model of Byrne and Kim (1990) is actually less skilled at predicting key features of high-quality seawater YREE patterns from widespread locations and depths, invalidating the premise that carboxylate ligands can emulate the sorptive properties of marine particulate matter. In order to avoid any such conjecture, we constructed model curves of $\log \bar{K}_s$ by inverting the B&K model through a straightforward rearrangement of terms (Eq. 9).

3.4. Comparisons of the inverted model with distribution coefficients for relevant solid phases

In recent years, careful laboratory experiments have been conducted to determine distribution coefficients, $\log \beta_1 K_s$, for YREE sorption on various pure solid phases, in seawater-like solutions (e.g., 0.5 M NaCl). These include hydrated Fe and Mn oxides (Ohta and Kawabe, 2001; Quinn et

al., 2006b; Schijf and Marshall, 2011; K.S. Marshall, unpubl. data), calcite (Toyama and Terakado, 2014), and the green macroalga *Ulva lactuca* L. (Zoll and Schijf, 2012), taken as a substitute for marine organic matter. We compare distribution coefficient patterns for each solid phase, chosen at the highest available solution pH (7.4–8.2), with model curves of $\log \bar{K}_S$, which again were vertically shifted to maximize overlap. Section 4 presents an evaluation of all pairwise comparisons, but here only the best matches in shallow and deep seawater are discussed (Fig. 5). For the blue model curves, shallow Atlantic and Pacific seawater patterns (Fig. 4) were subtracted from the L-term at pH 8.2 with 30% Lu–DFOB complexation (Fig. 2). For the red model curves, deep seawater patterns (Fig. 4) were subtracted from an L-term at pH 7.6 without organic complexation (not shown), more typical of seawater below 3000 m.

Figures 5A and B reveal that the distribution coefficient patterns for *U. lactuca* and HFO are similar in shape, especially for Gd–Lu, and match model curves for shallow seawater much better than for deep seawater. The main reason is the steeper slope of the shallow model curves, which is due to the higher pH and particularly to YREE complexation with organic ligands (Fig. 2). On the other hand, even the best match, between *U. lactuca* and shallow Atlantic seawater, shows discrepancies for the MREEs and a pronounced mismatch at Pr–Nd. Figure 5A also confirms that the $\log \bar{K}_S$ pattern used in the B&K model (Section 3.3) is not a good match for *U. lactuca*, in other words for marine organic matter. While it does simulate Y enrichment, the slope is too low and it is too straight, lacking the structure of both our model curves and the distribution coefficient patterns. Whereas the stability constants employed in the calculation of $\log \bar{K}_S$ mostly apply to $I = 0.1$ (Byrne and Li, 1995), this should not greatly affect its pattern. More likely the functional groups of marine organic matter are not well represented by a mixture of simple monocarboxylic acids, or the ones chosen are not the most suitable, given that individual ligands in the mixture show a wide range of behaviors (Byrne and Kim, 1990).

Figure 5C shows that the distribution coefficient pattern for HMO is in excellent agreement with the model curve for deep Pacific seawater, suggesting it to be the primary YREE scavenger in the abyssal ocean. The better match than for shallow seawater in this case results mainly from the smaller slope between Er and Lu, caused by the absence of organic complexation. A minor mismatch occurs at La, but the Pacific model curves do reproduce its enrichment relative to Y, not observed for *U. lactuca* and HFO (Figs. 5A and B). The large positive Ce anomaly in the distribution coefficient pattern reflects the fact that Ce is catalytically oxidized on manganese

oxide surfaces (Ohta and Kawabe, 2001; Davranche et al., 2005, 2008; K.S. Marshal, unpubl. data), which could partly explain the large negative Ce anomalies of deep seawater (Fig. 1).

A number of experimental studies have addressed YREE partitioning from seawater into calcite, but oceanic conditions were approximated most closely (0.68 M NaCl, ~2 mM Ca, 20–30 pM REE, pH 8.4–8.5) in the novel study of Toyama and Terakado (2014). Unfortunately, REE concentrations were measured via ID–TIMS so the partition coefficient patterns are incomplete. Terakado and Masuda (1988) conducted their experiments at lower ionic strength. They also used YREE concentrations that were 3–4 orders of magnitude higher, as did Zhong and Mucci (1995), Tanaka et al. (2004), and Tanaka and Kawabe (2006). The latter two papers contain complete patterns measured via ICP-MS at pH 6.6 and YREE concentrations of 60–120 nM in solutions of near-seawater ionic strength, yet different composition (0.2 M CaCl₂, 0.05 M NaCl).

In all five studies, the partition coefficients were defined in terms of total dissolved YREE concentrations. We converted these to distribution coefficients for comparison with our model curves, using $\log M_T/[M]$ values derived from MINEQL calculations of YREE speciation for the exact solution compositions given by Tanaka and Kawabe (2006) and Toyama and Terakado (2014). The distribution coefficients include normalization to Ca and are therefore assigned the symbol D_{Ca} and not ${}_iK_{Ca}$ (Fig. 5D). It should be noted that Toyama and Terakado (2014) also recalculated the YREE solution speciation of Tanaka and Kawabe (2006) and found it to be dominated by the free cation and not the monocarbonato-complex as the authors had proposed. Our own recalculation is somewhere in between, with the free cation dominating for La–Nd and the monocarbonato-complex for the others REEs. The ICP-MS analyses of YREE sorption on calcite in artificial seawater by Zhong and Mucci (1995) could not be so converted, because the fixed but variable pH of their solutions was not reported. Haley et al. (2005) calculated partition coefficients for biogenic calcite by normalizing their ID–TIMS analyses of the REE contents of a planktic foraminifer (*Neogloboquadrina dutertrei*), collected from sediment core tops, to REE concentrations in shallow seawater reported for nearby stations. We converted these to distribution coefficients using our YREE solution speciation at pH 8.2 (Fig. 2). The resulting pattern is remarkably similar to that of Toyama and Terakado (2014) and model curves are compared with the average of the two.

Figure 5D shows that the model curve for shallow Atlantic seawater is in reasonable agreement with the average of the patterns of Haley et al. (2005) and Toyama and Terakado

(2014), although its slope is too small between La and Gd. Conversely, the model curve for deep Pacific seawater is a surprisingly good match for the pattern of Tanaka and Kawabe (2006), on par with HMO (Fig. 5C). This is probably fortuitous and certainly counterintuitive, because their experimental conditions (pH 6.6, 0.2 M CaCl₂, 60–120 nM YREEs) are much less seawater-like and calcite does not persist in the deep ocean, especially in the Pacific where the lysocline occurs higher in the water column. The agreement of calcite with shallow Atlantic seawater appears comparable to that of *U. lactuca* and HFO (Figs. 5A and B), yet the importance of biogenic calcite as a YREE scavenger is offset by its low contents (Roberts et al., 2012). Martínez-Botí et al. (2009) found that the elevated YREE (Nd) contents of planktic foraminifera are associated with occluded organic tissue that is resistant to chemical cleaning and not with the calcite test or Fe-Mn oxide coatings. They argued that the strong correlation between foraminiferal YREE and Mn contents reflects a similar association of Mn with the occluded organic tissue.

Two important solid phases not considered here are biogenic silica (opal) and authigenic clay minerals. Whereas there seem to be few laboratory studies of YREE sorption on hydrated silica (Byrne and Kim, 1990; Takahashi et al., 1998; Marmier et al., 1999), opal is commonly believed to be an insignificant YREE scavenger in marine systems or large lakes (Murray and Leinen, 1993; Sholkovitz et al., 1994; Kuss et al., 2001; Tanaka et al., 2007; Xiong et al., 2012). This is in sharp contrast to recent claims by Akagi et al. (2011) and Akagi (2013), who founded their conclusions on analyses of opal corrected for a detrital signal that actually constitutes most of the vertical YREE flux in the diatom-dominated Bering Sea, as well as on an erroneous speciation model. There are many laboratory studies of YREE sorption on clay minerals (Aagaard, 1974; Bruque et al., 1980; Takahashi et al., 2004; Tertre et al., 2005; Wan and Liu, 2005) yet most involve just one element (Kowal-Fouchard et al., 2004; Bradbury et al., 2005; Rabung et al., 2005; Tertre et al., 2006) and, as far as we know, none were done in seawater. González López et al. (2005) reported MREE-enriched patterns (when normalized against Upper Continental Crust) for siltstones and claystones from kaolinite-rich rocks of marine origin that underwent only early diagenesis. However, these contain many potentially YREE-rich accessory minerals and being of Lower Cretaceous age it is difficult to know what seawater YREE composition or speciation should be used to calculate distribution coefficients. The authors conclude that clay minerals are not “the main phase in the REE control” of these marine sedimentary rocks.

3.5. Comparisons of the best-matching solid phases with marine particulate matter

Marine geochemists have tried to shed light on YREE scavenging in seawater by directly analyzing either small suspended particles collected by filtration, or larger sinking particles collected with sediment traps. The interpretation of such data can be challenging because the residence time of particles is typically much shorter than that of the water from which the particles are obtained (Fowler et al., 1992) hence they may not present an instantaneous signal of scavenging but rather one that is integrated across the overlying water column. It is furthermore difficult to measure the size, surface area, and even the composition of natural particles. A few strategies exist to circumvent these problems. In many studies, selective leaching techniques (Sholkovitz et al., 1994; Lerche and Nozaki, 1998; Akagi et al., 2011) or some version of Principal Components Analysis (Murphy and Dymond, 1984; Kuss et al., 2001; Takebe, 2005) were used to separate various empirically defined fractions of bulk particulate matter. In others, the contribution of detrital YREEs is subtracted by employing known ratios of the YREEs and an element unique to that fraction, like Al or Ti (Murray and Leinen, 1993; Tachikawa et al., 1999b). Analysis of the $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratio has been a powerful tool for quantifying rapid YREE exchange at the particle–water interface without net removal (Bertram and Elderfield, 1993; Tachikawa et al., 1997, 1999a). Arraes-Mescoff et al. (2001) investigated YREE release during the decomposition of large marine particles in laboratory incubations. Several groups have stressed the importance of manganese oxides as YREE carriers (Masuzawa and Koyama, 1989; Sholkovitz et al., 1994; Takebe, 2005), although there are dissenting views (Kuss et al., 2001). It may therefore be instructive to compare the distribution coefficient patterns for HMO and *U. lactuca* with the YREE contents of marine particles.

In Figure 6, HMO and *U. lactuca* are compared with two datasets for YREE concentrations in marine particles. Here, the distribution coefficient patterns were vertically shifted to maximize overlap with the particle patterns and the number of shared elements is smaller. Figure 6A shows the 25% acetic acid leach, which releases YREE cations that are weakly bound or contained in the calcite and manganese oxide fractions, for particles from 200 m and 2000 m depth in the Sargasso Sea, normalized to YREE concentrations in the surrounding seawater (Sholkovitz et al., 1994). The authors showed that their patterns are very similar in shape to patterns calculated for particles from the Indian Ocean, analyzed by Bertram and Elderfield (1993). Particles were obtained by 0.4- μm filtration of 28-L samples collected with GoFlo bottles. We converted

reported distribution coefficients, $\log K_D$, from total to free concentrations, using our YREE solution speciations at pH 7.8 for the 200-m and at pH 7.4 for the 2000-m sample (Fig. 2). The YREE concentrations were measured via ID-TIMS and are thus lacking the mono-isotopic elements. Figure 6B shows data for suspended particles from 100 m and 2500 m depth at a mesotrophic station in the eastern Atlantic Ocean that were collected with an in-situ 0.65- μm filtration system and corrected for detrital YREE contributions by using the YREE/Al ratio (Tachikawa et al., 1999b). Due to an analytical artifact, ICP-MS data for Y, Eu, Tb, Ho, Tm, and Lu were not reported. We converted partition coefficients to $\log K_D$ values using ancillary data provided by Tachikawa et al. (1999b) and our YREE solution speciations at pH 8.2 and 7.4 (Fig. 2) for the 100-m and 2500-m sample, respectively.

Despite the missing elements, particles from the Atlantic Ocean are in better agreement with *U. lactuca* in shallow seawater and with HMO in deep seawater, as expected (Section 3.4). The only exception is the shallow sample from the Sargasso Sea, which better matches the distribution coefficient pattern for HMO (Fig. 6A). It may be that the sequential leaching method of Sholkovitz et al. (1994) biased the outcome for both the shallow and deep Sargasso Sea samples. Note however that all four particle samples have a positive Ce anomaly, a feature that is unique to HMO and not acquired by any of the other solids phases (Fig. 5).

4. Summary and implications

No uncertainties are indicated in Figures 5 and 6 for the distribution coefficients or any of the model curves. If distribution coefficients or stability constants are measured simultaneously for all YREEs, their analytical errors are highly correlated across the lanthanide series (e.g., Quinn et al., 2006a) and have no effect on the slope or shape of the pattern. Errors that could affect the slope or shape are those associated with the A-term and the L-term (Eq. 9). The slope of the L-term appears to be foremost a function of seawater pH and the degree of YREE organic complexation (Fig. 3). The L-term results from an iterative calculation involving numerous ion-pairing and stability constants, and component concentrations (Section 3.1). Estimating its uncertainty by propagating the known errors of these parameters is consequently not feasible, and would in reality require a sophisticated sensitivity analysis that is beyond the scope of this work. Analytical errors in the A-term, usually on the order of 1–2% (Shabani et al., 1992), are not a good indicator of the natural variability of seawater pattern slopes and shapes, which is

more suitably illustrated by a selection of patterns from widespread locations and depths (Fig. 4).

Figure 7 contains minimized sum-of-squares differences for all pairwise comparisons between distribution coefficient patterns and model curves of $\log \bar{K}_s$ (left panel) or particle patterns (right panel). Each bar in the graph represents a pair of patterns, one member indicated by the shading of the bar and the other by the x-axis label. Without knowing true uncertainties, it allows a quantitative evaluation of the spectrum of agreement across different locations, depths, and solid phases, whereby smaller values indicate a better match. Sum-of-squares differences should not be compared between the two panels, since the number of shared elements is not the same. The graph shows at a glance that *U. lactuca*, calcite (disregarding the pattern of Tanaka and Kawabe, 2006), and HFO are all a better match in shallow than in deep seawater, and better in the Atlantic than in the Pacific. In contrast, HMO is a better match in deep seawater and in the Pacific. The agreement for *U. lactuca* in shallow Atlantic seawater is better than for calcite and HFO, in that order, but it is worse than for HMO in deep Pacific seawater. The match between the $\log \bar{K}_s$ pattern of the B&K model and *U. lactuca* (i.e., organic matter) is substantially worse than the best ones generated by our inverted scavenging model. Suspended particles are in excellent agreement with *U. lactuca* in the shallow Atlantic and with HMO in the deep Atlantic, except in the Sargasso Sea where both shallow and deep particles resemble HMO, possibly due to the use of a selective leaching method (Sholkovitz et al., 1994).

Our inverted scavenging model, a modification and refinement of the model devised by Byrne and Kim (1990), subtracts high-quality shale-normalized YREE patterns for shallow and deep open ocean waters from the L-term, calculated from YREE solution speciation, to derive $\log \bar{K}_s$ (Eq. 9), which theoretically represents average relative YREE affinities for marine particles. The nature of these particles is then investigated by comparing our model curves with patterns of distribution coefficients for YREE sorption on relevant solid phases, measured in laboratory experiments at seawater conditions. Figure 7 suggests that model curves for shallow seawater, calculated at pH 8.2 and including YREE complexation with strong organic ligands, have some features in common with distribution coefficient patterns for the green macroalga *Ulva lactuca*, a substitute for organic matter, and for calcite and HFO, but do not match any of them exactly. Especially good agreement is found between model curves for deep seawater and distribution coefficient patterns for HMO. Marine particles near the ocean surface are likely to be a complex assemblage of different biogenic (organic matter, calcite, opal) and authigenic (Fe-Mn

oxides, clays) phases. It is possible that our model curves for shallow seawater would overlap more closely with a linear combination of the various distribution coefficient patterns, but we did not attempt this. Other quasi-equilibrium processes, such as the slow dissolution of atmospheric dust particles (Sholkovitz et al., 1993; Greaves et al., 1994), and non-equilibrium processes, such as active microbial uptake and photochemistry (Moffett, 1994), may play a role in YREE scavenging. In addition, marine particles themselves are subject to highly dynamic cycles of aggregation and disaggregation, so that a more sophisticated, kinetic scavenging model may well be required (Jannasch et al., 1988). Finally, scavenging in the upper ocean is dominated by ubiquitous organic and Fe-Mn oxide coatings that obscure the surface of most particles (Byrne and Kim, 1990; Sholkovitz et al., 1994). The superior match of the model curves for deep seawater with the distribution coefficient pattern for HMO (Fig. 5C) may thus indicate that particles in the abyssal ocean are more homogeneous and less subject to dynamic cycling, and that YREE scavenging is mediated by manganese oxides lacking an organic surface coating, probably because it has been stripped off by bacterial decomposition.

In conclusion, manganese oxides may be the dominant scavenger of YREEs throughout the abyssal ocean, and perhaps even in the upper water column. Near the ocean surface, where marine particulate matter comprises a complex assemblage of biogenic and authigenic phases, altered by reactive coatings and subject to many non-equilibrium mechanical and chemical processes, more sophisticated kinetic models of YREE scavenging may be needed, particularly for the redox-driven scavenging of Ce(III). The influence of complexation with strong organic ligands on YREE scavenging also merits further study.

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Table 1. Ion-pairing constants, K_{MX}^* , for major cations and anions in seawater ($I = 0.7$) taken from Millero and Schreiber (1982). Protonation constants for (bi)carbonate (Luo and Byrne, 2004), measured in $0.7\ m\ NaClO_4$, were converted to the free-ion concentration scale using ion-pairing constants for Na^+ and $pK_0 = 1.52$. The ionization constant of water ($0.7\ M\ NaClO_4$) is from Christenson and Schijf (2011). Constants for borate are from Byrne and Kester (1974).

		M				
		H^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
X	Cl^-	—	—	—	—	—
	SO_4^{2-}	30.9	2.0	1.8	10.2	10.8
	HCO_3^-	$10^{6.13}$	0.30	—	1.9	2.1
	CO_3^{2-}	$10^{9.92}$	2.6	—	87	126
	OH^-	$10^{13.74}$	—	—	50	—
	$B(OH)_4^-$	$10^{9.00}$	0.57	—	8.03	13.0

Table 2. Stability constants ($I = 0.7$) for YREE complexes with the major seawater anions and with desferrioxamine B (DFOB), which is taken to represent a strong organic ligand. Data for (bi)carbonate are from Luo and Byrne (2004), for chloride from Luo and Byrne (2001), for sulfate from Schijf and Byrne (2004), for hydroxide ($\log \beta_1^*$) from Klungness and Byrne (2000), and for DFOB from Christenson and Schijf (2011). Values for DFOB are from direct measurements; all others were calculated from extended Debye-Hückel relations given in the corresponding papers. Values for (bi)carbonate, measured in 0.7 m NaClO_4 , were converted to the free-ion concentration scale using ion-pairing constants for Na^+ (Table 1). Stability constants for the Ce–DFOB complexes could not be determined due to rapid oxidation of Ce(III) by the ligand (see Christenson and Schijf, 2011).

M	$\log \text{CO}_3 \beta_1$	$\log \text{CO}_3 \beta_2$	$\log \text{HCO}_3 \beta_1$	$\log \text{Cl} \beta_1$	$\log \text{SO}_4 \beta_1$	$\log \beta_1^*$	$\log \text{DFOB} \beta_1$	$\log \text{DFOB} \beta_2$	$\log \text{DFOB} \beta_3$
Y	6.18	10.99	1.37	−0.40	1.82	−8.11	6.16	10.51	13.98
La	5.43	9.66	1.39	−0.40	1.93	−9.12	4.88	7.70	10.09
Ce	5.76	10.12	1.36	−0.40	1.93	−8.65	—	—	—
Pr	5.93	10.44	1.30	−0.40	1.94	−8.63	5.45	8.96	11.96
Nd	5.98	10.53	1.33	−0.40	1.92	−8.49	5.54	9.24	12.33
Pm	—	—	—	—	—	—	—	—	—
Sm	6.16	10.89	1.39	−0.40	1.95	−8.15	5.93	10.09	13.38
Eu	6.18	10.99	1.52	−0.40	1.96	−8.07	6.07	10.32	13.67
Gd	6.09	10.84	1.41	−0.40	1.93	−8.14	6.04	10.31	13.67
Tb	6.16	11.14	1.51	−0.40	1.91	−7.95	6.24	10.67	14.15
Dy	6.26	11.27	1.55	−0.40	1.89	−7.90	6.35	10.83	14.40
Ho	6.25	11.36	1.51	−0.40	1.86	−7.87	6.32	10.89	14.53
Er	6.31	11.48	1.54	−0.40	1.83	−7.83	6.38	10.99	14.66
Tm	6.38	11.63	1.57	−0.40	1.80	−7.70	6.44	11.13	14.90
Yb	6.51	11.66	1.58	−0.40	1.78	−7.55	6.53	11.27	15.17
Lu	6.45	11.73	1.54	−0.40	1.76	−7.58	6.48	11.25	15.19

Table 3. Inorganic speciation of the YREEs in seawater at $S = 35$ and $pH = 8.2$ (total scale), calculated with MINEQL2.0 using the ion-pairing and stability constants in Tables 1 and 2. Fluoride complexation of the YREEs is negligible and was omitted. Species contributions are expressed as a percentage of the total dissolved YREE concentration, rounded to one decimal place. Due to rounding, which does not reflect statistical uncertainties, the contributions of all species may not add to exactly 100%. The last column contains the first term on the right-hand side of Eq. 9 (the L-term).

M	MCO_3^+	$M(CO_3)_2^-$	M^{3+}	MCl^{2+}	MSO_4^+	MOH^{2+}	$MHCO_3^{2+}$	$\log M_T/[M]$
Y	27.0	71.4	0.4	0.1	0.3	0.7	< 0.05	2.36
La	52.3	36.4	4.8	1.0	4.5	0.8	0.2	1.32
Ce	48.7	45.7	2.1	0.5	2.0	1.0	0.1	1.68
Pr	41.6	55.1	1.2	0.3	1.2	0.6	< 0.05	1.92
Nd	39.6	57.5	1.0	0.2	0.9	0.7	< 0.05	1.99
Pm	—	—	—	—	—	—	—	—
Sm	30.7	67.4	0.5	0.1	0.5	0.8	< 0.05	2.28
Eu	27.0	71.2	0.4	0.1	0.4	0.8	< 0.05	2.36
Gd	29.6	68.2	0.6	0.1	0.6	0.9	< 0.05	2.23
Tb	20.1	78.4	0.3	0.1	0.3	0.8	< 0.05	2.47
Dy	19.0	79.7	0.3	0.1	0.2	0.7	< 0.05	2.59
Ho	15.8	83.2	0.2	< 0.05	0.2	0.6	< 0.05	2.66
Er	14.1	85.1	0.2	< 0.05	0.1	0.5	< 0.05	2.77
Tm	12.0	87.2	0.1	< 0.05	0.1	0.5	< 0.05	2.91
Yb	14.6	84.5	0.1	< 0.05	0.1	0.7	< 0.05	2.96
Lu	11.3	88.0	0.1	< 0.05	0.1	0.6	< 0.05	3.01

Figure 1. Vertical profiles of total dissolved YREE concentrations, M_T , at station TPS 24 271-1 in the western Pacific Ocean (Piepgras and Jacobsen, 1992). Seawater was acidified but not filtered prior to ID-TIMS analysis. The anomalous behavior of cerium (Ce), caused by its unique redox chemistry, clearly contrasts with that of the strictly trivalent YREEs, represented by the light element lanthanum (La) and the heavy element ytterbium (Yb).

Figure 2. Ratio of total and free dissolved YREE concentrations in seawater ($\log M_T/[M]$), the first term on the right-hand side of Eq. 9, derived from MINEQL calculations of YREE solution speciation in the presence of inorganic ligands only, at different pH (total scale). Results for pH 8.2 are listed in Table 3. Bold curves illustrate the effect of YREE complexation with strong organic ligands, represented by the model siderophore DFOB. The free concentration of the HL^{2-} species was fixed at levels that yield 10% and 30% contributions of the organic complex for Lu (see text). Below pH 8.2 DFOB quickly protonates, diminishing its influence.

Figure 3. Stability constants ($I = 0.7$) for YREE complexes with two carbonate anions, the strongest inorganic ligand in seawater, and for hexadentate DFOB complexes (Table 2). Stability constants for Ce–DFOB complexes could not be measured (Christenson and Schijf, 2011). Also shown are stability constants ($I = 0.5$) for hexadentate EDTA complexes (Martell et al., 2004) and intrinsic constants for YREE binding to strong (type B = phenolic) sites of terrestrial humic acids (HA), converted as indicated by Sonke (2006) from his recommended values of pK_{MHA} .

Figure 4. Patterns of shale-normalized total dissolved YREE concentrations, $(M_T)_N$, for shallow and deep seawater samples from the Atlantic Ocean (station 162-1, 70 and 4033 m; Osborne et al., 2015) and the Pacific Ocean (station SA-12, 74 and 3936 m; Zhang and Nozaki, 1996). normalized to Post-Archaean Australian Shale (PAAS) (McLennan, 1989). See the references for station locations and other details. Bold curves are input-normalized abundance patterns for seawater predicted by the refined B&K model, expanded to include Y and using $\log \bar{K}_S$ values recalculated with stability constants from the NIST database (Martell et al., 2004). Model curves for the shallow and deep samples, based on YREE solution speciations at pH 8.2 and 7.6, respectively (Fig. 2), were vertically shifted to maximize overlap with the average shallow and deep seawater patterns, as described in the text.

Figure 5. Comparison of the inverted scavenging model with distribution coefficients for YREE sorption on (A) *Ulva lactuca* (Zoll and Schijf, 2012); (B) hydrous ferric oxide (HFO) (Schijf and Marshall, 2011); (C) hydrous manganese oxide (HMO) (K.S. Marshall, unpubl. data); and (D) synthetic calcite and planktic foraminiferal calcite (*N. dutertrei*). Panel A also shows $\log \bar{K}_s$ as defined by Byrne and Kim (1990). Colored model curves (legends in B and C) are the same in all four panels, except for vertical shifts to maximize overlap with the distribution coefficient patterns. Only the best-matching model curves for shallow and deep seawater are shown in each panel.

Figure 6. Comparisons of $\log iK_{Mn}$ and $\log iK_S$, the distribution coefficients for YREE sorption on HMO (K.S. Marshall, unpubl. data) and *Ulva lactuca* (Zoll and Schijf, 2012), respectively, with measured distribution coefficients for suspended particles from (A) the Sargasso Sea, leached with 25% acetic acid (Sholkovitz et al., 1994); and (B) a mesotrophic station in the eastern Atlantic Ocean (Tachikawa et al., 1999b), corrected for detrital contributions by means of REE/Al ratios. Particulate concentrations were normalized to ambient seawater. The $\log iK_{Mn}$ and $\log iK_S$ curves were vertically shifted to maximize overlap with the particle patterns.

Figure 7. Sum-of-squares difference for pairwise comparisons of distribution coefficients for relevant solid phases with all Atlantic and Pacific model curves, some of which are shown in Figure 5 (left panel), and for all comparisons shown in Figure 6 (right panel). Lower values signify better agreement. Bar color and shading (see legend) correspond to one member of each pair and x-axis labels to the other. Summation was performed over a total of n elements shared by all pairs (excluding Y and Ce). Values in the left panel should not be compared with those in the right panel, because they were summed over different elements. CAL8 is the average of data from Toyama and Terakado (2014) at pH ~ 8.45 and from Haley et al. (2005), while CAL6 are data from Tanaka and Kawabe (2006) at pH 6.6 (Fig. 5D). SS and EA are suspended particles from the Sargasso Sea (Sholkovitz et al., 1994) and the eastern Atlantic Ocean (Tachikawa et al., 1999b), respectively, at the indicated depths (Fig. 6).