



YREE scavenging in seawater: A new look at an old model



Johan Schijf^{a,*}, Emily A. Christenson^a, Robert H. Byrne^b

^a University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory, P.O. Box 38, Solomons, MD 20688, USA

^b University of South Florida, College of Marine Science, 140 7th Avenue South, Saint Petersburg, FL 33701, USA

ARTICLE INFO

Article history:

Received 31 January 2015

Received in revised form 1 June 2015

Accepted 3 June 2015

Available online 14 June 2015

Keywords:

Rare earth elements

Yttrium

Scavenging

Model

Seawater

Particles

Sorption

Manganese oxide

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.

© 2015 Elsevier B.V. All rights reserved.

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

* Corresponding author.

E-mail address: schijf@cbl.umces.edu (J. Schijf).

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 (Billler 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:

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

with 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

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

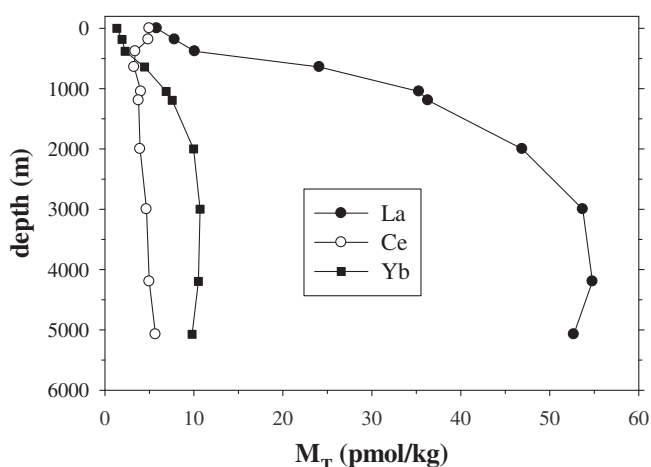


Fig. 1. Vertical profiles of total dissolved YREE concentrations, M_T , at station TPS 24 271-1 in the western Pacific Ocean (Piepgras and Jacobsen, 1992). Seawater was acidified but not filtered prior to ID-TIMS analysis. The anomalous behavior of cerium (Ce), caused by its unique redox chemistry, clearly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

Download English Version:

<https://daneshyari.com/en/article/1262714>

Download Persian Version:

<https://daneshyari.com/article/1262714>

[Daneshyari.com](https://daneshyari.com)