



## Short-term variability of dissolved rare earth elements and neodymium isotopes in the entire water column of the Panama Basin

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### ABSTRACT

The distribution of dissolved rare earth elements (REEs) and neodymium isotopes ( $\epsilon\text{Nd}$ ) in the open ocean traces water mass mixing and provides information on lithogenic inputs to the source regions of the water masses. However, the processes influencing the REE budget at the ocean margins, in particular source and sink mechanisms, are not yet well quantified. In this study the first dissolved REE concentrations and Nd isotope compositions of seawater from the Panama Basin (RV Meteor cruise M90) in the Eastern Equatorial Pacific (EEP) are presented. The EEP is characterized by one of the world's largest oxygen minimum zones (OMZs). It is dominated by high particle fluxes that are expected to enhance the removal of REEs from the water column by scavenging.

The measured REE concentrations peak at the surface indicating high lithogenic input, which is supported by shale-normalized REE patterns in surface waters and highly radiogenic  $\epsilon\text{Nd}$  signatures ranging between +1.4 and +4.3, the latter value constituting the most radiogenic value measured for seawater to date. In contrast, intermediate and deep water REE concentrations are low compared to other Pacific Basins and suggest enhanced removal via scavenging associated with high particle fluxes. The  $\epsilon\text{Nd}$  signatures of intermediate and deep waters are less radiogenic than surface waters ranging between -1.4 and +1.3 but significantly more radiogenic than source water masses in the EEP. The  $\epsilon\text{Nd}$  signatures consequently do not reflect mixing of intermediate and deep water masses entering the Panama Basin but can only be explained by lithogenic inputs originating from source rocks with highly radiogenic Nd isotope signatures such as the Central American Volcanic Arc ( $\epsilon\text{Nd} = +3$  to +10). Our data demonstrate significant surface input via continental particles, which are partially dissolved in the water column and thereby release REEs and particularly radiogenic Nd isotope signatures to the subsurface ocean. Data obtained from a re-occupied station in the southern Panama Basin for the first time shows that these processes can partially reset water mass Nd isotope and REE signatures of the entire water column proximal to continental sources on time scales of a few years.

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### 1. Introduction

Yttrium and the lanthanides form the rare earth element (REE) group. Their distributions in seawater have been recognized as tracers for water masses and of processes controlling the marine geochemical cycling of elements such as scavenging and desorption (e.g. Piepgras and Wasserburg, 1982; Zhang and Nozaki, 1996; Nozaki, 2001; Frank, 2002). Similar to depth profiles of nutrients, the dissolved REE concentrations generally increase with

water depth (Elderfield and Greaves, 1982; Zhang and Nozaki, 1998). A particularly strong relationship with dissolved silicate ( $\text{Si}(\text{OH})_4$ ) has been observed leading to suggestions that diatom opal carries REEs from the surface and releases them to deep waters when the opal dissolves (e.g. Alibo and Nozaki, 1999; Akagi, 2013; Garcia-Solsona et al., 2014). The behavior of cerium (Ce) is an exception as the oxidation of  $\text{Ce}^{3+}$  to poorly soluble  $\text{Ce}^{4+}$  results in Ce being more efficiently removed from seawater by scavenging (e.g. Moffet, 1990). This preferential removal leads to a lower shale-normalized Ce concentration in the dissolved phase compared to the neighboring REEs, the so-called Ce anomaly (Zhang and Nozaki, 1996; Alibo and Nozaki, 1999; Lacan and Jeandel, 2001).

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The main source of dissolved REEs in seawater is lithogenic input while removal occurs via particle scavenging (Elderfield and Greaves, 1982; Bertram and Elderfield, 1993). For example, particles in plumes emanating from hydrothermal vents scavenge the REEs very effectively from seawater (Klinkhammer et al., 1983; German et al., 1990; Mills and Elderfield, 1995). When normalizing REE concentrations to continental input signatures (for example using Post Archean Australian Sedimentary rock (PAAS; Taylor and McLennan, 1985) to approximate the composition of the continental crust), REEs dissolved in seawater are characterized by a relative enrichment of the heavy (H)REEs compared to the light (L)REEs (e.g. Elderfield and Greaves, 1982; Bertram and Elderfield, 1993; Alibo and Nozaki, 1999; Nozaki, 2001). This is attributed to the lanthanide contraction (Zhang and Nozaki, 1996) and the HREEs building more stable carbonate complexes in seawater (Turner et al., 1981). As a result of having a higher free metal ion concentration in seawater the LREEs are more particle reactive and are preferentially removed by scavenging processes (e.g. Sholkovitz et al., 1994).

In addition to the REE distribution, the radiogenic isotope composition of the LREE neodymium (Nd) has been widely applied as a water mass tracer (e.g.; Jeandel et al., 1995; Grenier et al., 2013; Singh et al., 2012; Laukert et al., 2017). It is expressed as  $\epsilon\text{Nd}$  values:

$$\epsilon\text{Nd} = \left( \frac{{}^{143}\text{Nd}/{}^{144}\text{Nd}_{\text{sample}}}{{}^{143}\text{Nd}/{}^{144}\text{Nd}_{\text{CHUR}}} - 1 \right) \times 10,000$$

corresponding to the deviation of the measured  ${}^{143}\text{Nd}/{}^{144}\text{Nd}$  of the samples from the Chondritic Uniform Reservoir (CHUR:  ${}^{143}\text{Nd}/{}^{144}\text{Nd} = 0.512638$  according to Jacobsen and Wasserburg, 1980) in parts per 10,000. Old continental crust has more negative, unradiogenic  $\epsilon\text{Nd}$  values of  $-40$  to  $-10$  whereas rocks derived from the Earth's mantle, such as mid ocean ridge basalts and volcanic islands have more positive, radiogenic  $\epsilon\text{Nd}$  signatures of  $0$  to  $+10$  (e.g. Jeandel et al., 2007). Seawater is labeled with the Nd isotopic composition of the surrounding continents at the land–seawater interface. While partial dissolution of lithogenic particles releases REEs to seawater and thus modifies the Nd isotope composition of seawater (e.g. Goldstein and Jacobsen, 1987), there is also clear evidence for “boundary exchange” processes at the ocean margins during which the seawater Nd isotope composition can change without a corresponding change in Nd concentrations (Lacan and Jeandel, 2005; Arsouze et al., 2009; Rempfer et al., 2011; Grenier et al., 2013; Jeandel et al., 2013; Fröllje et al., 2016).

Consequently, water masses of different origin have different  $\epsilon\text{Nd}$  signatures. The Pacific Ocean that is surrounded by young mantle-derived rocks has average  $\epsilon\text{Nd}$  values near  $-3$  and is more radiogenic than the Atlantic Ocean with average  $\epsilon\text{Nd}$  values of  $-12$  (Goldstein and Jacobsen, 1987; Bertram and Elderfield, 1993). Given the average deep oceanic residence time of Nd between 300 and 1000 yr (Tachikawa et al., 2003; Arsouze et al., 2009; Rempfer et al., 2011), different water masses are characterized by distinct Nd isotope signatures. In the North Atlantic, North Atlantic Deep Water (NADW) is characterized by a highly unradiogenic  $\epsilon\text{Nd}$  of  $-13.5$  while Southern Ocean derived water masses such as Antarctic Intermediate Water (AAIW), Circumpolar Deep Water (CDW), and Antarctic Bottom Water (AABW) have  $\epsilon\text{Nd}$  values of  $-7$  to  $-9$  (Piepgras and Wasserburg, 1982; Jeandel, 1993; Stichel et al., 2012). In contrast, Pacific intermediate and surface waters ( $\epsilon\text{Nd} = -4$  to  $+3$ ) are much more radiogenic than Pacific deep and bottom waters ( $\epsilon\text{Nd} = -6$  to  $-3$ ) (e.g. Amakawa et al., 2000; Lacan and Jeandel, 2001; Grasse et al., 2012; Grenier et al., 2013). However, the oceanic mass balance of REEs and Nd isotope compositions and the exact source and sink processes, in particular at the continental margin–ocean interface are not

well characterized (e.g. Arsouze et al., 2009; Rempfer et al., 2011; Abbott et al., 2015a, 2015b; Rousseau et al., 2015).

Here we present the first data set of dissolved REE concentrations and Nd isotope compositions from the Panama Basin that is surrounded by volcanic source rocks on land. The water column in this area is characterized by high biological productivity, large biogenic particle abundances and organic matter fluxes, which are remineralized in the subsurface leading to a pronounced subsurface oxygen minimum zone (OMZ, Karstensen et al., 2008; Bishop et al., 1986). The goal of our study is to investigate if the dissolved REE and Nd isotope compositions in the intermediate and deep ocean near ocean margins with high biological productivity still reflect distinct water mass signatures and their mixing or if other processes dominate.

### 1.1. Hydrography of the Panama Basin

The Panama Basin is located in the Eastern Equatorial Pacific (EEP) and is bounded by the Central and South America in the north and east, the Cocos Ridge in the west, and the Carnegie Ridge in the South (Fig. 1a). The Intertropical Convergence Zone (ITCZ) mainly controls wind speed and direction and thus surface currents, as well as rainfall in this region. The large freshwater input caused by seasonally variable intense rainfall and river discharge linked to the position of the ITCZ in the Panama Basin and to ENSO (El Niño Southern Oscillation) results in the Eastern Tropical Pacific having some of the lowest mean surface water salinities (30 to 34) of the open oceans globally (Fiedler and Talley, 2006 and references therein). The mean location of the ITCZ at  $5^\circ\text{N}$  coincides with the position of the North Equatorial Countercurrent (NECC) and moves from approximately  $10^\circ\text{N}$  in August towards the Equator in March (e.g. Alory et al., 2012). In the Panama Basin surface waters mainly consist of Tropical Surface Water (TSW) (Fiedler and Talley, 2006). The flow of the surface currents fed by the Peru coastal upwelling and influenced by wind forcing, is generally anticlockwise along the Colombian Coast (Fig. 1a), whereas there are also southeastward directed near-surface currents in water depths of 20 m to 100 m as a continuation of the NECC (Kessler, 2006). In equatorial regions westward flowing surface currents including the South Equatorial Current (SEC) produce an eastward pressure gradient, which is the force driving the Equatorial Undercurrent (EUC) to flow eastward along the equator and to supply oxygen-rich waters to the Peruvian upwelling area (Toggweiler et al., 1991; Fiedler and Talley, 2006). At the Galapagos Islands the EUC separates into two branches. The main branch flows southeastward, feeding the Peru Undercurrent (PCUC) and reaches the Peruvian coast at approximately  $5^\circ\text{S}$  (Kessler, 2006; Montes et al., 2010). The surface counterpart to the PCUC is the Peru Coastal Current (PCC), which transports surface water masses from the upwelling region towards the north. Close to the Galapagos Islands the EUC flows at a depth of 50 m to 150 m (e.g. Czeschel et al., 2011; Grasse et al., 2012) and reaches our southernmost station (St. 1555; Fig. 1a). The EUC was also present at nearby Stations 159 and 160, which were sampled during Cruise M77-3 in February 2009 (Tables 1, 2; Fig. 1a; Grasse et al., 2012). For comparison with the data obtained in this study, only St. 160 is shown in the graphs given that only the upper 100 m were sampled at St. 159.

Surface waters at the sampling locations show a strong gradient towards lower salinities at St. 1552 closest to Panama, ranging from 29.62 to 32.63 PSU. The intermediate water masses in the Panama Basin show no distinct temperature or salinity differences between stations 1552, 1553, 1555, as well as St. 160 (Fig. 1b). Therefore intermediate water masses from the north and the south cannot be clearly distinguished by hydrographic properties and the intermediate water mass body is identified as

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