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# Rare earth element distribution in Caribbean seawater: Continental inputs versus lateral transport of distinct REE compositions in subsurface water masses

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ABSTRACT

The rare earth element (REE) concentrations of full water column profiles from ten stations in the Caribbean, the Gulf of Mexico, and the Florida Straits, as well as of surface waters close to the mouth of the Orinoco River have been analyzed. The results show a high concentration of REEs in surface waters, in particular close to the mouth of the Orinoco, and a middle-REE-enrichment that is strongest in the south and east of the study area suggesting that fluvial inputs are the main sources rather than REEs supplied by Saharan dust. The surface waters close to the Orinoco are heavy REE enriched compared to the potential fluvial sources, emphasizing the importance of processes in the estuaries and the surface ocean that preferentially remove light- and middle-REEs. Relatively small heavy-REE enrichments in near-bottom water samples at the mouth of the Orinoco may be the result of preferential release of light REEs from river-transported sediments. The REE patterns of distinct subsurface water masses are largely coherent across the Caribbean basin, suggesting that the lateral transport of preformed compositions is not significantly influenced by vertical processes of scavenging and release. In particular, low Dy/Er molar ratios are associated with Antarctic Intermediate Water and have most likely been advected into the Caribbean from the Southern Ocean. In contrast, deep waters in the Caribbean are enriched in light and middle REEs compared to incoming Upper North Atlantic Deep Water suggesting that release from sinking particles or from sediments is an important source of these REEs in the deep ocean, in particular when deep water residence times are long.



## 1. Introduction

The rare earth elements (REEs) are a closely related group with similar chemical behavior (Elderfield, 1988). Dissolved REEs in seawater are supplied to the oceans from the continents but typically show a heavy-REE (HREE) enriched pattern compared to the average continental crust (De Baar et al, 1985; Elderfield and Greaves, 1982; Elderfield, 1988; Klinkhammer et al., 1983; Taylor and McLennan, 1985). As REEs are not considered to be biologically important, the seawater pattern has instead been attributed to differing solid/solution partition coefficients (Byrne and Kim, 1990). With the exception of Ce(IV) and Eu(II), the REEs are trivalent and show an increasing tendency for complexation as atomic number rises (Cantrell and Byrne, 1987; De Baar et al, 1991). Affinities can be predicted from experiments and show that light-REEs (LREEs) are adsorbed to most surfaces, whereas HREEs are more strongly complexed by ligands and thus preferentially stay in solution (Byrne and Kim, 1990; Cantrell and Byrne, 1987). Much of the preferential removal of LREEs from river water entering the ocean occurs at low salinities and may be driven by salt induced coagulation of river-borne colloids (Elderfield et al, 1990; Goldstein and Jacobsen, 1988; Sholkovitz, 1976, 1992, 1993, 1995; Sholkovitz and Elderfield, 1988). There is also evidence for preferential release of HREEs at higher salinities in estuaries, which would further increase the HREE enrichment in seawater relative to the average composition of continental rocks (Sholkovitz and Szymczak, 2000). Vertical processes in the water column under full marine conditions, such as particle scavenging and release, are also important in modifying the concentrations of REEs relative to one another (Byrne and Kim, 1990; Elderfield and Greaves, 1982; Sholkovitz et al., 1994). Consistent with the residence time of the light trivalent REEs on the order of several 100 years (e.g. Rempfer et al., 2011) and a most likely even longer residence time of the heavy REEs, a further important factor influencing the distribution of REE compositions in seawater is lateral advection of pre-formed compositions, which has led to the suggestion that REE patterns can be used as water mass tracers (German et al., 1995; Haley et al., 2014; Molina-Kescher et al., 2014; Piepgras and Wasserburg, 1982; Zhang and Nozaki, 1996).

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The Caribbean and the Gulf of Mexico (GOM) provide a unique setting to examine the relative importance of vertical and horizontal processes on the REE composition of seawater. The surface ocean in the Caribbean is likely to have been strongly affected by inputs from the Amazon, Orinoco and Magdalena Rivers, which together comprise approximately 20% of the global fluvial discharge (Hu et al., 2004; Müller-Karger et al., 1989). Further inputs of REEs are expected from the Mississippi River as well as from Saharan dust (Prospero and Mayol-Bracero, 2013), similar to observations in the Southeast Atlantic (Bayon et al., 2004). Vigorous circulation channels large volumes of Atlantic water through surface and intermediate depths in the Caribbean (28 Sv, Johns et al., 2002), whereas turnover in the deep Caribbean is limited by a maximum sill depth of ~1800 m and is very slow (0.2 Sv, Fratantoni et al., 1997; Joyce et al., 1999; MacCready et al., 1999; Stalcup et al., 1975; Sturges, 1975; Worthington, 1955). A companion paper has shown that all of these factors, in particular additions and/or exchange with the sediments, significantly alter the radiogenic isotope composition of the REE Nd in deep waters of the Caribbean (Osborne et al., 2014). Here we examine if and how the dissolved REEs in seawater are transformed during passage through the Caribbean and the GOM.

### 1.1. Hydrographic setting

The hydrography of the study area and sampling stations has been presented in detail in Osborne et al. (2014). In brief, seawater channeled through the Caribbean is an important part of the Western Boundary Current, which forms the upper, northward-flowing limb of the Atlantic Meridional Overturning Circulation (Schmitz and McCartney, 1993; Schmitz and Richardson, 1991). The Caribbean, Loop and Florida Currents transport thermocline waters through the Caribbean and the GOM into the Western North Atlantic (Fig. 1). Caribbean Water (CW, 0–80 m) is a mixture of Atlantic and Orinoco water, with seasonally varying amounts of Amazon River water delivered via the Guyana Current (Müller-Karger et al., 1989). Subtropical Under Water (SUW) originates in the tropical and subtropical Atlantic gyres and is transported into the Caribbean via the Northern Equatorial Current (Johns et al., 2002; Wüst, 1964). Eighteen Degree Water (EDW) (Worthington, 1959, 1976) is present in the northern part of the Caribbean basin, having formed in the western North Atlantic subtropical gyre (Forget et al., 2011), otherwise the water mass directly below SUW is North Atlantic Central Water (NCW). Low salinity Antarctic Intermediate Water (AAIW) is found between ~400 and 1000 m and is more prominent in the southern and eastern parts of Caribbean (Wüst, 1964). The deepest water entering the Caribbean is restricted by the maximum depth of the sill connecting it to the Atlantic and thus the deep Caribbean is filled with Upper North Atlantic Deep Water (UNADW) to a depth of ~1800 m (Wüst, 1964).

## 2. Methods

Samples were taken during Meteor Cruise 78, Leg 1 in February and March 2009 (Fig. 1). Surface water samples at Sites 226-3 and 249-1 were collected using an acid cleaned 20 L polycarbonate cylindrical plastic vessel, deployed in the upper meters using a clean nylon/polymer recovery tether. All other samples were collected in Niskin bottles attached to the shipboard CTD-rosette. Approximately 20 L of seawater was recovered at each sampling depth and was filtered through 0.45 μm Millipore® cellulose acetate filters and acidified to pH ~ 2 with double distilled concentrated HCl within a few hours of collection. The samples

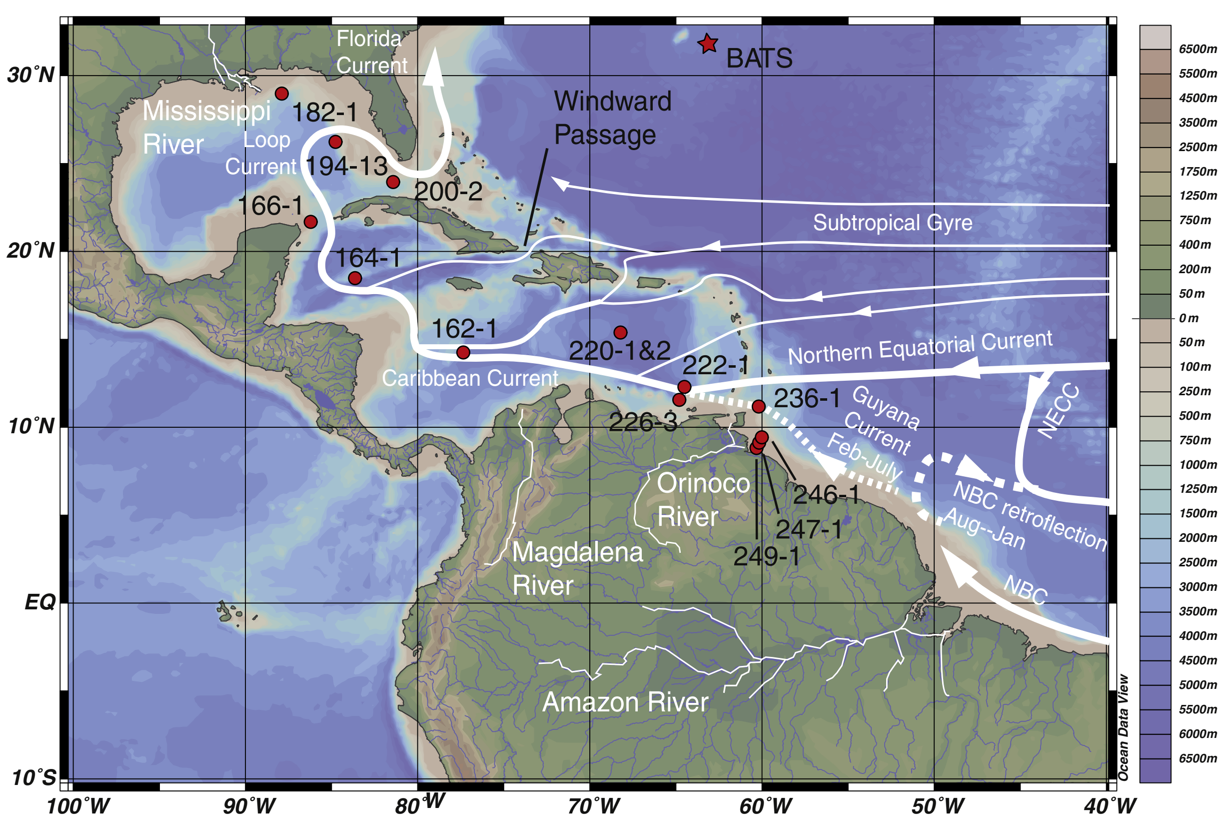


**Fig. 1.** Location map. Sampling stations occupied during RV Meteor cruise M78/1 (red circles) and the BATS site (red star, Van de Flierdt et al., 2012). Also shown are major rivers and surface ocean currents, modified from Osborne et al. (2014) following Hellweger and Gordon (2002), Jouanno et al. (2008), Lumpkin and Garzoli (2005), Schott et al. (2002) and Steph et al. (2006). NBC, North Brazil Coastal Current; NECC, Northern Equatorial Counter Current. The figure was produced using Ocean Data View (Schlitzer, 2011). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)