



Behavior of rare earth elements and yttrium during simulation of arctic estuarine mixing between glacial-fed river waters and seawater and the impact of inorganic (nano-)particles



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ABSTRACT

Rivers are the major source of many trace elements to the oceans. As a consequence of climate change, increasing volumes of glacial meltwater enter the oceans after being affected by estuarine processes. Although the behavior of high field strength elements such as the rare earth elements and yttrium (REY) has been intensively studied in tropical, temperate and boreal estuaries, little is known about arctic estuarine mixing of glacial-fed river waters that are poor in organic nanoparticles and colloids (NPCs), but rich in inorganic NPCs. Here we provide the first data set from estuarine mixing experiments with glacial-fed river waters and seawater. The glacial-fed river water endmembers originate from southern Iceland (sampled in 2010 and 2013) and from West Greenland (sampled in 2013); these endmembers are rich in NPCs and larger particles of (glassy) volcanic ash and of ultra-fine rock flour, respectively.

For the mixing experiments, 0.2 μm -filtered glacial-fed river water was mixed with seawater in different ratios to cover the full range of estuarine low- to high-salinity conditions. All 2010 freshwater endmembers show higher concentrations of individual REY (due to their high NPC load) than the respective seawater endmember, whereas the 2013 freshwater endmembers have higher light REY, but lower heavy REY concentrations (due to significantly less NPCs). Admixture of minute amounts of seawater (5% and 10% seawater (SW) admixture, i.e. salinities of ~ 1.7 psu and of ~ 3.4 psu, respectively) already has a strong impact on REY concentrations and REY signatures. In all experiments, a large amount of REY (e.g., up to 98.2% of Nd and 98.2% of Yb) is removed at very low salinities. At intermediate to high salinities, however, remobilization of REY from aggregated NPCs occurs if NPC-rich river waters are used in the experiments, whereas if the endmember is poor in NPCs, the REY mix almost conservatively. The REY removal is dependent on the amount of NPCs present in the glacial-fed river waters; NPC-rich river water shows larger REY removal than NPC-poorer river water. After the initial drop in REY concentrations under low-salinity conditions, the experiment with glacial-fed river water from Greenland reveals that heavy REY mix almost conservatively, but light REY are again remobilized from aggregated NPCs. Our results suggest that aggregated NPCs composed of rock flour (Greenland) and volcanic ash (Iceland) may cause different trace element behavior during estuarine processes. However, all experiments show similar Y-Ho fractionation during estuarine mixing, indicating that the actual type of particle is not a major constraint on Y-Ho behavior, but rather the availability of particle surfaces. Estuarine processes may cause the development of negative Ce anomalies during remobilization of REY at higher salinity if Ce(IV) compounds of low solubility are present in the (nano-)particle load. However, if only Ce(III) is present, such as in fresh mafic volcanic ash, no fractionation of Ce from its trivalent REY neighbors occurs.

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1. Introduction

Rivers are the major source of trace element input into the ocean. However, input of particle-reactive elements is limited by estuarine processes causing large-scale removal of particle-reactive elements at

low salinity (e.g., Elderfield et al., 1990; Goldstein and Jacobsen, 1988a; Lawrence and Kamber, 2006; Pokrovsky et al., 2014; Rousseau et al., 2015; Sholkovitz, 1993; Sholkovitz and Szymczak, 2000). The rare earth elements (REE; or REY if yttrium is included) are prime examples of particle-reactive elements and show very similar geochemical behavior. Only the decreasing ionic radius from La to Lu, also known as the lanthanide contraction, leads to gradual changes in their physical and chemical properties. Generally, all REY are trivalent except for Ce and Eu, which exhibit multiple valences (Ce^{3+} , Ce^{4+} , Eu^{2+} , and Eu^{3+})

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in natural environments. In low-temperature oxic environments, Ce^{3+} may be oxidized and form insoluble Ce(IV) compounds. Bau (1999) and Bau and Koschinsky (2009) describe that oxidative scavenging of dissolved Ce by Fe and Mn (oxyhydr-)oxide precipitates occurs in several steps: first, Ce^{3+} and other REY^{3+} are surface-complexed onto particles. The sorbed Ce^{3+} is partially oxidized to Ce^{4+} on the surface of the metal (oxyhydr-)oxide, and only the remaining Ce^{3+} is then desorbed back into the solution along with the other REY^{3+} , while Ce(IV) remains attached to the solid. Reduction of Eu^{3+} to Eu^{2+} is confined to high-temperature systems such as hydrothermal vents (Bau, 1991; Sverjensky, 1984). Yttrium is the geochemical twin of Ho (showing identical charge and very similar ionic radius) and its geochemical behavior is often discussed together with that of the rare earth elements (e.g., Bau, 1996). However, during estuarine mixing, Y may decouple from Ho (Bau et al., 1995; Lawrence and Kamber, 2006). The shale-normalized (subscript SN; shale is Post Archean Australian Shale, PAAS, from McLennan, 1989) REY patterns of seawater show large negative Ce_{SN} anomalies, large positive Y_{SN} anomalies, and enrichment of heavy REY (HREY) relative to the light REY (LREY) (e.g., Elderfield and Greaves, 1982). The REY_{SN} pattern of seawater represents the net effect of the interplay between surface-complexation on organic films and metal (oxyhydr-)oxides and solution-complexation (De Baar et al., 1985; Elderfield and Greaves, 1982; Elderfield, 1988; Klinkhammer et al., 1983). In contrast to that of seawater, the dissolved REY_{SN} patterns of rivers are rather variable. Most patterns are flat or slightly HREY-enriched with or without small negative Ce_{SN} anomalies (e.g. Goldstein and Jacobs, 1988 a, b), but some other rivers such as the Amazon River, Orinoco River or glacial-fed river waters from southern Iceland, show enrichment of middle REY (MREY) relative to the LREY and HREY (e.g. Deberdt et al., 2002; Tepe and Bau, 2014). Moreover, river waters from West Greenland show highly unusual REY_{SN} patterns with strong LREY enrichment relative to the HREY (Goldstein and Jacobsen, 1988b; Tepe and Bau, 2015).

The behavior of the REY during estuarine mixing has been studied intensively (Andersson et al., 1994; Elderfield et al., 1990; Goldstein and Jacobsen, 1988a; Hoyle et al., 1984; Kulaksiz and Bau, 2007; Lawrence and Kamber, 2006; Martin et al., 1976; Pokrovsky et al., 2014; Rousseau et al., 2015; Savenko et al., 2014; Sholkovitz, 1993, 1995; Sholkovitz and Elderfield, 1988; Sholkovitz and Szymczak, 2000) and it is commonly accepted that all REY are subject to large-scale removal in the low-salinity zone of estuaries (Goldstein and Jacobsen, 1988a; Lawrence and Kamber, 2006; Pokrovsky et al., 2014; Rousseau et al., 2015; Sholkovitz, 1993). As river water mixes with seawater, seawater cations modify the uniform negative surface-charge of REY-bearing nanoparticles and colloids (NPCs), causing these particles to aggregate and agglomerate and, upon reaching a certain size, to settle to the seafloor (e.g., Boyle et al., 1977). The only available data for estuarine mixing of polar river waters in the Arctic Ocean were published by Pokrovsky and Schott (2002) and Pokrovsky et al. (2014), who studied rivers rich in organic particles. Contrary to the common large-scale removal of REY in the low-salinity zone, they reported almost conservative REY behavior in the estuary (especially for HREY). However, there is no study regarding the estuarine mixing of waters of polar rivers which are rich in inorganic particles but very poor in organic ones.

Glacial-fed river waters in Iceland are usually poor in organic NPCs, but rich in inorganic NPCs derived from volcanic ash (Tepe and Bau, 2014). Comparison of the trace element distribution of river particulates ($>0.45 \mu\text{m}$ filter residues) and volcanic ash to that of the respective dissolved glacial-fed rivers ($<0.45 \mu\text{m}$ filtrates) reveals very close similarities, indicating that REY associated with NPCs control the dissolved particle-reactive element distribution in these glacial-fed rivers (Tepe and Bau, 2014). Glacial-fed rivers in Greenland are also poor in organic and rich in inorganic NPCs, but carry ultrafine rock flour and dust particles derived from the Archean basement rocks (Tepe and Bau, 2015).

Here we present results of two-component batch mixing experiments performed to simulate arctic estuarine mixing between glacial-

fed river water and seawater. Such experiments have the advantage that they eliminate the complicating impact of temporarily and spatially variable hydrological conditions that characterize natural estuaries. $0.2 \mu\text{m}$ -filtered glacial-fed river waters from Iceland and Greenland were mixed with seawater in different ratios to represent different low- to high-salinity environments. Using $0.2 \mu\text{m}$ -filtered endmembers provides information on the behavior of dissolved REY during estuarine mixing without the presence of larger particles that may mediate the coagulation of NPCs.

2. Sampling and methods

2.1. Sampling

Rivers from Greenland and Iceland can be divided into four different categories commonly referred to as “glacial-fed”, “spring-fed”, “lake-fed” and “direct runoff” (Louvat et al., 2008). For our laboratory mixing experiment we decided to focus on organic-poor glacial-fed rivers in Iceland and Greenland to investigate the roles of fine volcanic ash particles and of rock flour and dust particles, respectively, during estuarine mixing.

Seven mixing experiments between glacial-fed river waters and seawater were performed. Four different glacial-fed river water endmembers from southern Iceland were sampled in September 2010. One glacial-fed river from southern Iceland was sampled in May 2013 and one from the Kangerlussuaq area, West Greenland, was sampled in August 2013. The river water endmembers from 2010 originate from the Markarfljót River ($\text{N}63^{\circ}37'0.984''$; $\text{W}20^{\circ}0'59.94''$), Jökulsá í Sólheima River ($\text{N}64^{\circ}14'44.066''$; $\text{W}14^{\circ}31'33.254''$), Gígjukvísl River ($\text{N}63^{\circ}56'25.044''$; $\text{W}17^{\circ}22'11.424''$) and Hornafjarðarfljót River ($\text{N}64^{\circ}21'15.732''$; $\text{W}15^{\circ}22'13.26''$). The endmember sample from 2013 was again taken from the Markarfljót River and the sample from the Kangerlussuaq area, West Greenland, originates from the Watson River ($\text{N}67^{\circ}00'20.33''$; $\text{W}50^{\circ}41'04.91''$).

The seawater samples used as endmembers were sampled at different locations. The tropical Atlantic seawater endmember, which was used for all 2010 mixing experiments, was sampled during the RV Meteor cruise M81/1. For the mixing experiment between glacial-fed river water from Iceland and seawater from 2013, the seawater endmember was directly sampled from the beach close to Jökulsarlón lagoon in Iceland and will further be referred to as “North Atlantic coastal seawater”. The Pacific seawater endmember for the experiment with the sample from Greenland was taken during RV Sonne cruise SO229.

2.2. Analytical methods

For 2010 and 2013, all freshwater endmembers were sampled in acid-cleaned 3 L polyethylene (PE) bottles in Iceland and Greenland and transported to Germany. Within two weeks after the initial sampling of the freshwater endmembers, the mixing experiments were performed in the Geochemistry Laboratory of Jacobs University Bremen. For all individual laboratory steps acid-cleaned PE bottles were used. The endmembers were filtered through $0.2 \mu\text{m}$ cellulose acetate filters, and then mixed at ratios that covered the full range of low- to high-salinity conditions. These mixing solutions were then shaken for 24 h and again filtered through $0.2 \mu\text{m}$ cellulose acetate filters to remove NPCs aggregated during the mixing experiments. After acidification with suprapure 6M HCl to a pH between 1.8 and 2.0, a Tm spike was added as an internal standard. A 30 mL aliquot was used for the determination of trace element concentrations by inductively coupled plasma-mass spectrometry (ICP-MS; Perkin Elmer, Elan DRC-e). The remaining sample volume was used for REY separation and preconcentration following a method routinely applied in the determination of REY concentrations of natural waters (for details see, e.g. Bau and Dulski, 1996; Kulaksiz and Bau, 2007). Each sample was passed through a C_{18} cartridge (Waters, Sep-Pak® Classic C_{18} , single use),

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