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Geochimica et Cosmochimica Acta 197 (2017) 1–13

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Contrasting impact of organic and inorganic nanoparticles and colloids on the behavior of particle-reactive elements in tropical estuaries: An experimental study

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Received 25 May 2016; accepted in revised form 28 September 2016; Available online 4 October 2016

Abstract

Estuarine processes may affect the flux of dissolved organic carbon (DOC), iron and other particle-reactive elements such as the rare earth elements and yttrium (REY), into the ocean via salt-induced coagulation and subsequent removal of river-borne (nano-)particles and colloids. We experimentally assessed the impact of the admixture of seawater on DOC, Fe and REY associated with inorganic and organic nanoparticles and colloids (NPCs) present in tropical rivers, using Rio Solimões and Rio Negro, which are particularly rich in inorganic and organic NPCs, respectively, as river water endmembers. Similar to the conservative elements Sr, Rb and U, DOC behaves conservatively in *all* mixing experiments, whereas strong removal of Fe and REY (and preferential removal of light over heavy REY and of Ce relative to La and Pr) is confined to experiments with inorganic NPC-rich Rio Solimões water. This removal already occurs at very low salinity and is due to the aggregation of the inorganic NPCs. However, REY removal efficiency increases gradually with increasing salinity, which is in marked contrast to DOC-poor Arctic river waters from which REY removal at lowest salinity is significantly stronger. This suggests that the DOC concentrations in the water have a profound impact on the estuarine mixing behavior of particle-reactive elements. In marked contrast to the Rio Solimões mixing experiment, Fe and the REY in experiments with Rio Negro water behave similarly to DOC and mix conservatively with seawater, indicating that the organic NPCs, most of which are humic and fulvic acids, and their associated trace elements are much less susceptible to coagulation and estuarine removal than inorganic ones. Even at higher salinities, estuarine REY removal from inorganic NPC-rich Rio Solimões water significantly exceeds REY removal from organic NPC-rich Rio Negro water. Hence, the combination of higher element concentrations in and of less estuarine removal from organic NPC-rich rivers compared to inorganic NPC-rich rivers indicates that the former are a more important source of particle-reactive elements to the oceans than previously thought. This suggests that chemical complexation with organic ligands, such as humic and fulvic acids, may have a strong impact on the riverine flux and on the marine inventory of particle-reactive elements, and hence may play an important role for the isotopic composition of such elements in seawater.

Keywords: Rio Negro; Rio Solimões; Estuarine processes; Nanoparticles and colloids; Particle-reactive elements; Rare earth elements

1. INTRODUCTION

Rivers are a major source of trace elements to the ocean. Estuarine processes, however, have been shown to significantly influence the trace element input from rivers into

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http://dx.doi.org/10.1016/j.gca.2016.09.041
0016-7037/

seawater (e.g. Hoyle et al., 1984; Goldstein and Jacobsen, 1988a; Elderfield et al., 1990; Sholkovitz, 1993; Andersson et al., 1994; Lawrence and Kamber, 2006; Kulaksiz and Bau, 2007) and large-scale removal of particle-reactive elements is typical of most estuaries (Goldstein and Jacobsen, 1988b; Sholkovitz, 1993; Lawrence and Kamber, 2006; Rousseau et al., 2015). Hence, it is important to understand the physico-chemical processes governing the behavior of trace metals during estuarine mixing of river and seawater in order to estimate the impact of estuarine removal on the trace element budget of the world's oceans.

Due to their high charge and small ionic radius, the rare earth elements (REE) are prime examples of particle-reactive trace elements. They behave coherently in the natural system; only the gradual decrease in ionic radius with increasing atomic number and the increase in covalence due to the gradual filling of the 4f-orbital cause systematic changes across the group. Small anomalies of La, Gd and maybe Lu may occur in natural waters due to small differences between the stabilities of their chemical complexes, while larger anomalies of Ce and Eu ultimately result from variable redox-conditions, as both of these elements are redox-sensitive. In oxic low-temperature environments, Ce^{3+} may be oxidized to Ce^{4+}, while at elevated temperature Eu^{3+} may be reduced to Eu^{2+} (e.g., Brookins, 1989). In estuaries, the REE, like other particle-reactive elements, undergo large-scale removal in the low-salinity zone (e.g. Hoyle et al., 1984; Elderfield et al., 1990; Sholkovitz, 1993; Sholkovitz and Szymczak, 2000; Lawrence and Kamber, 2006; Pokrovsky et al., 2014; Savenko et al., 2014). Yttrium is typically associated with the REE (then termed REY), as it is the geochemical twin to Ho. In tropical river waters, most of the particle-reactive elements (e.g. >95% of REY in the Rio Solimões; Gerard et al., 2003) are bound to particles. This particulate pool is defined to comprise all particles >0.2 μm, while everything that passes a 0.2 μm filter membrane is considered to be dissolved (Elderfield et al., 1990). However, <0.2 μm-sized nanoparticles and colloids (NPCs) pass this filter membrane and carry their associated particle-reactive element load with them. As river water mixes with seawater, the seawater cations modify the negative surface-charge of these NPCs, inducing flocculation (Boyle et al., 1977) in the low-salinity zone of an estuary. As these aggregates grow larger, they effectively remove the associated elements from solution, limiting their input into seawater. Removal rates of up to 97% have been observed in the low-salinity zone of the Amazon River (Sholkovitz, 1993). However, exceptions to this large-scale removal have been reported for small, organic-rich rivers, draining polar permafrost regions, which exhibit almost conservative behavior of particle-reactive elements upon mixing with Arctic seawater (Pokrovsky and Schott, 2002).

Here we present results of mixing experiments with freshwater from tropical rivers rich in organic and in inorganic (colloids/nano-)particles, respectively, and seawater. These laboratory experiments were performed with the aim to investigate how the presence and type of NPCs affects the estuarine mixing behavior of the REY and other trace elements. We use river water from the Rio Solimões and from the Rio Negro as representatives of tropical river waters which are rich in either inorganic or organic NPCs, respectively. The geochemistry of both rivers has been studied extensively, making them ideal river water endmembers for such an experimental study (e.g., Konhauser et al., 1994; Gerard et al., 2003; Seyler and Boaventura, 2003). Complementing existing data from the Amazon Estuary, mixing experiments in the laboratory allow for a better evaluation of the geochemical processes at work, as environmental and hydrological parameters such as discharge, flow velocity, suspended matter content, tidal waves or spatial and temporal variations of the freshwater-saltwater interface, do not influence mixing as they do in natural estuaries.

Our results reveal significant differences between organic and inorganic NPC-rich river water with regard to the behavior of particle-reactive elements such as the REY, during estuarine mixing, which may have profound implications for riverine trace element fluxes into the ocean.

2. CHARACTERIZATION OF RIVER WATER AND SEAWATER ENDMEMBERS

The Amazon River is the world's largest river in terms of discharge, as it provides approximately 20% of all freshwater that enters the world's oceans. The Amazon River officially begins at the confluence of the Rio Solimões and the Rio Negro at the city of Manaus, Amazonia, Brazil. Both rivers were sampled in July 2014, at high water level, some kilometers upstream from their confluence at a water depth of ca 0.50 m below the surface.

The sample collected from the Rio Solimões that was used in the mixing experiments, had an *in-situ* temperature of 28 °C and a pH of 6.56. The water sample taken from the Rio Negro had an *in-situ* temperature of 29 °C and a pH of 4.67. The seawater sample was collected during RV Sonne cruise SO229 in the Pacific Ocean at 18°S and 169°E, at a depth of 1800 m. Its potential temperature was 2.75 °C, its pH 7.81 and its salinity 34.7 psu.

The Rio Solimões drains the Andes. It is rich in inorganic mineral particles and colloids (e.g., Konhauser et al., 1994) and carries a mean concentration of suspended particulate matter of 128.9 g/m^3 (Martinez et al., 2015). This suspended load is dominated by clay minerals which are mainly comprised of smectite, illite and small amounts of kaolinite (Martinelli et al., 1993; Martinez et al., 2015). Similar to the suspended load, the colloid fraction in Rio Solimões waters is also dominated by (ultrafine) clay particles. In contrast, humic acids and fulvic acids only occur at very low concentrations. Filtration and ultrafiltration studies revealed that >95% of particle-reactive elements (e.g., Fe and REY) are associated with the suspended load (>0.2 μm). In the dissolved fraction (<0.2 μm), 35–60% of these particle-reactive elements are truly dissolved (<10 kDa), while the remaining 40–65% are bound to colloids (Deberdt et al., 2002; Gerard et al., 2003).

In marked contrast to the Rio Solimões, the Rio Negro drains the heavily weathered podzolic soils (called *Terra firme*) of the Guyana shield. As these soils are heavily weathered and hence poor in leachable ions, almost only