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The rare earth element chemistry of estuarine surface sediments in the Chesapeake Bay

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ABSTRACT

Concentrations of rare earth elements (REE) were measured in the fine fraction of shallow surface sediments from the lower Chesapeake Bay as studies suggest that coagulation of colloids dominates the removal of REE from the dissolved load in low salinity regions of estuaries. REE in sediments showed spatial heterogeneity, both laterally and longitudinally. We observed the influence of salinity on the spatial and temporal variability in total REE content and on Eu-anomalies. Lower total REE was found in sediments deposited along the Eastern Shore. The chemistry of the mid-Bay Islands was distinct with higher overall REE content and slightly more positive Ce-anomaly values. Positive Ce/Ce* in the mid-Bay are attributed to Coriolis acceleration restricting freshwater flow towards the west away from the Islands leading to oxidative removal of Ce from the pore waters to the sediments. The presence of positive Eu/Eu* in sediments deposited along the Eastern Shore is linked to salinity. We suggest that unique local conditions along the Eastern Shore, possibly including submarine groundwater discharge of nutrient-rich reducing waters, combined with organic matter decay and the predominance of oceanic water flow toward this region leads to the development of a strong localized salinity gradient. This study demonstrates the utility of REE sediment chemistry in identifying and resolving local and estuarine-wide geochemical processes.

1. Introduction

Processes occurring in estuaries modify the abundance, species, and flux of trace elements, including the rare earth elements (REE; La to Lu), delivered by rivers to the ocean. Estuarine processes influencing the relative abundances of trace elements include coagulation of river-borne colloids across the salinity gradient, adsorption–desorption from particulate matter and sediments, and remobilization due to remineralization of sediments. REE are ideally suited to the study of estuarine processes as they form a coherent group of trace elements whose chemical properties change systematically across the series. For example, changes in the relative abundance of REE in the dissolved phase are attributable to coagulation of river colloids in estuaries (Sholkovitz, 1992, 1995; Sholkovitz and Szymczak, 2000).

The REE chemistry of estuarine sediments is largely controlled by both physical and chemical processes regulating the delivery of dissolved and particulate REE from river to ocean (Martin et al., 1976; Sholkovitz and Elderfield, 1988; Toyoda et al., 1990; Elderfield et al., 1990; Sholkovitz, 1995). As such, sediment chemistry results from a number of processes including sediment provenance (e.g., Taylor and McLennan, 1985; Murray and Leinen, 1993; Sholkovitz, 1993; Sholkovitz et al., 1999) as well as the chemistry of the water from which the particles settle (e.g., McLennan, 1989; Brookins, 1989; Sholkovitz, 1990; Sholkovitz et al., 1994; Sholkovitz et al., 1999). Although much is known about the large scale processes governing the behavior of REE in estuarine waters, comparatively little is known about the behavior of REE in estuarine sediments (Sholkovitz, 1990; Somayajulu et al., 1993; Nozaki et al., 2000; Chaillou et al., 2006; Lawrence and Kamber, 2006; Censi et al., 2007). Although REE chemistry of estuarine sediments is a product of exchange between surface waters, mineral surfaces, and pore waters, the processes leading to the resultant chemistry are often difficult to resolve. REE can be removed from the water column through adsorption, flocculation, and precipitation (Elderfield and Sholkovitz, 1987; Sholkovitz and Elderfield, 1988; Elderfield et al., 1990; Sholkovitz, 1992; Murray and Leinen, 1993; Bau, 1999; Lawrence and Kamber, 2006). Once deposited in the sediment the REE remain mobile with this mobility, both chemical and physical, leading to complexity in the distribution of REE in estuarine sediments.

Recent studies of permeable estuarine sediments suggest that the relative abundance of trace elements is controlled, in part, by the competitive influence of local conditions including advective transport and mixing of saline and freshwater such as under conditions of submarine groundwater discharge (Huettel et al., 1996, 1998; Moore, 1999; Jahnke et al., 2003; Charette and Buessler, 2004; Charette et al., 2005). In clay and organic matter rich estuarine sediments, like those in seagrass beds,

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colloidal material may serve as a repository for REE. In these sediments adsorption–desorption reactions occur in regions of high salinity as well as with seasonal changes in redox conditions (Aller, 1980; Sholkovitz and Elderfield, 1988; Charette et al., 2005). Discerning, from these sediments, changes in redox conditions can be accomplished using sediment Fe–Mn hydroxide abundances [e.g., (Froelich et al., 1979; Aller, 1980; Burdige, 1993) and the redox sensitive REE Cerium (Ce) and Europium (Eu).

The redox behavior of Ce is well understood. Depletions of dissolved Ce occur during oxidation of Ce(III) to insoluble particulate Ce(IV) leading to increased sediment Ce relative to neighboring La and Pr. Conversely, depletions in sediment Ce can be caused by reduction of Ce(IV) to soluble Ce(III). This leads to depletions in sediment Ce and enrichments in dissolved Ce. In addition to the redox sensitive Ce, Eu exhibits redox behavior. Enrichments in Eu in marine waters are associated with hydrothermal activity leading to the reduction of Eu(III) to Eu(II) (Erel and Stolper, 1993; Sholkovitz et al., 1994). Eu enrichments in estuarine sediments may also occur due to the slow dissociation rate of Eu-humate complexes at slightly alkaline pHs found in estuaries (Benes et al., 2003), by removal of Eu-organic complexes from the water under reducing conditions (Johannesson et al., 2004), and/or the presence of an adsorbed component formed under reducing conditions (McLennan, 1989; Erel and Stolper, 1993).

The shape and size of an estuary, as well as sediment type (sandy vs. clay-rich), influence sediment REE chemistry. In small narrow estuaries such as Waquoit Bay (MA) and the Fly/Gulf of Papua and Amazon estuaries, rapid cross-sectional mixing likely leads to little lateral variability in sediment REE chemistry. The variability observed in permeable sandy estuarine sediments can be attributed to localized phenomena such as advective transport of solutes and particles and submarine discharge of groundwaters along the coast (Huettel et al., 1996, 1998; Moore, 1999; Ataie-Ashtiani et al., 1999; Jahnke et al., 2003; Reimers et al., 2004; Charette et al., 2005). In large estuaries, such as the Chesapeake Bay where significant lateral variability in salinity exists, we hypothesize that REE sediment chemistry is laterally variable. Variation in sediment chemistry in this estuary may be related to large scale estuarine processes such as lateral mixing, changes in freshwater delivery of REE to the estuary, and tidal fluctuations. Superimposed on these processes is a record of local conditions including advective particle transport, variations in pore water chemistry due to submarine groundwater discharge, redox, and temperature and salinity dependent sediment–water solute exchange.

Here we present REE data from the fine fraction of shallow surface sediments collected from seagrass beds in the lower Chesapeake Bay. We chose to focus on the REE chemistry of the fine fraction as studies suggest that coagulation of colloids dominates the removal of REE from the dissolved load in low salinity regions of estuaries (Sholkovitz, 1995). Therefore, the fine fraction will record resuspension of REE due to adsorption–desorption related to changes in salinity, pH and redox. Examination of the fine fraction (<63 um which includes coarse silt to very fine clay; Lane et al., 1947) allowed us to explore the processes influencing estuarine sediment REE chemistry thereby providing unique insights that would be unavailable when studying permeable sediment or whole sediment chemistry. Given the dynamic physical structure and unique riverine–estuarine–ocean boundary conditions, Chesapeake Bay provides the ideal setting in which to elucidate potential processes controlling sediment REE.

2. Area descriptions, methods and material studied

2.1. Study area

We studied the REE composition of 92 shallow surface sediment samples from seagrass beds within the lower portion of the Chesapeake Bay (Fig. 1). Freshwater input to the Bay is provided by five major tributaries: Susquehanna, Potomac, Rappahannock, York and James. Mean freshwater discharge to the Bay is approximately 2280 $m^3 s^{-1}$ (Austin, 2004) with the Susquehanna, Potomac and James contributing 80% of the total freshwater input (Valle-Levinson and Lwiza, 1995; Valle-Levinson et al., 2000). Besides the Susquehanna, freshwater input along the Western Shore is provided mainly by the Potomac, York, James and Rappahannock Rivers. Dissolved REE chemistry of the tributaries is governed, to a large extent, by the geology of the drainage basins. The geology of the Potomac, Rappahannock, York, and James drainage basins falls across four physiographic provinces which are, from West to East, the Valley and Ridge Province (Paleozoic sedimentary rocks), the Blue Ridge Province (Mesoproterozoic crystalline basement and Late Neoproterozoic to Early Paleozoic units), the Piedmont Province (Proterozoic and Paleozoic units including sedimentary units, metamorphic sequences and intrusive igneous rocks) and the Coastal Plain Province (Tertiary and Quaternary sand, silt, and clay). The Potomac and James initiate in the Blue Ridge Province. The York initiates in the Piedmont Province, the most geologically complex region, and the James initiates in the Valley and Ridge Province. The James River drains the largest area of the Piedmont. Although there are local variations in bedrock within these regions, these rivers drain predominantly identical geological terrain. Along the Eastern Shore minor tributaries drain Quaternary coastal plain sediments and provide minimal seasonal freshwater input into the Bay. Samples collected along the lower Eastern Shore from the Cape Charles region are located within the zone of the Chesapeake impact crater (Poag, 1997; Johnson et al., 1998). Despite the location of the samples, no evidence of mineralogic influence was found. The coarse fraction contained no plagioclase or clinopyroxene. We found no mineralogical indication of granodiorite basement in any of the samples and expect REE signatures attributable to granodiorite to be absent and therefore assume that any observed enrichment in Eu in the fine fraction of the samples to be attributable to estuarine processes.

Submarine groundwater discharge has been recorded along both the Eastern and Western Shores of the Bay (Hussain et al., 1999; Charette and Buessler, 2004) and is a potential influence on sediment chemistry. Recent studies of permeable estuarine sediment chemistry have shown development of redox fronts associated with the formation of a salt wedge caused by a plume of flowing fresh groundwater and recirculated seawater (e.g., Li et al., 1999; Ataie-Ashtiani et al., 1999; Charette et al., 2005). The mixing of these two waters leads to changes in redox conditions within the pore waters, altering the Fe and Mn redox chemistry and transport of Fe–Mn hydroxides) (Charette et al., 2005). Such phenomena may be recorded by the redox sensitive REE, Ce and Eu. Although near-shore shallow waters of the Bay periodically experience hypoxia/anoxia (Officer et al., 1984; Breitburg, 1990; Adelson et al., 2001; Hagy et al., 2004), dissolved oxygen values at the sample sites (mean dissolved oxygen within sea grass beds, mg/L: Islands = 7.47 ± 0.32, Pocomoke Sound (Eastern Shore) = 7.11 ± 1.24, Lower Eastern Shore = 8.14 ± 0.69, Potomac–Rappahannock = 6.90 ± 0.39, Rappahannock–York = 7.86 ± 0.69, York–James = 6.71 ± 1.31) indicate well oxygenated water column conditions (Dorval et al., 2005). The influence of variations in dissolved oxygen in the pore water and at the sediment–water interface cannot be discounted.

3. Methods

Briefly, samples were collected from 37°00′ to 38°20′ (N) latitude from regions historically dominated by seagrass beds (Moore et al., 2000; Dorval et al., 2005). These beds are located close to the confluence of tributaries on the Western Shore and represent shallows where desorption of REE from sediments is likely to occur. Based on the physical characteristics of these seagrass beds and their spatial distribution, we divided our sampling scheme into six areas (Fig. 1).

(1) PORA (Western Shore, squares) — mouth of the Potomac to the northern shore of the Rappahannock River
(2) RAYO (Western Shore, diamonds) — mouth of the Rappahannock to the northern shore of the York River