



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.

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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 μm 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 $2280 \text{ m}^3 \text{ s}^{-1}$ (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 $37^{\circ}00'$ to $38^{\circ}20'$ (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

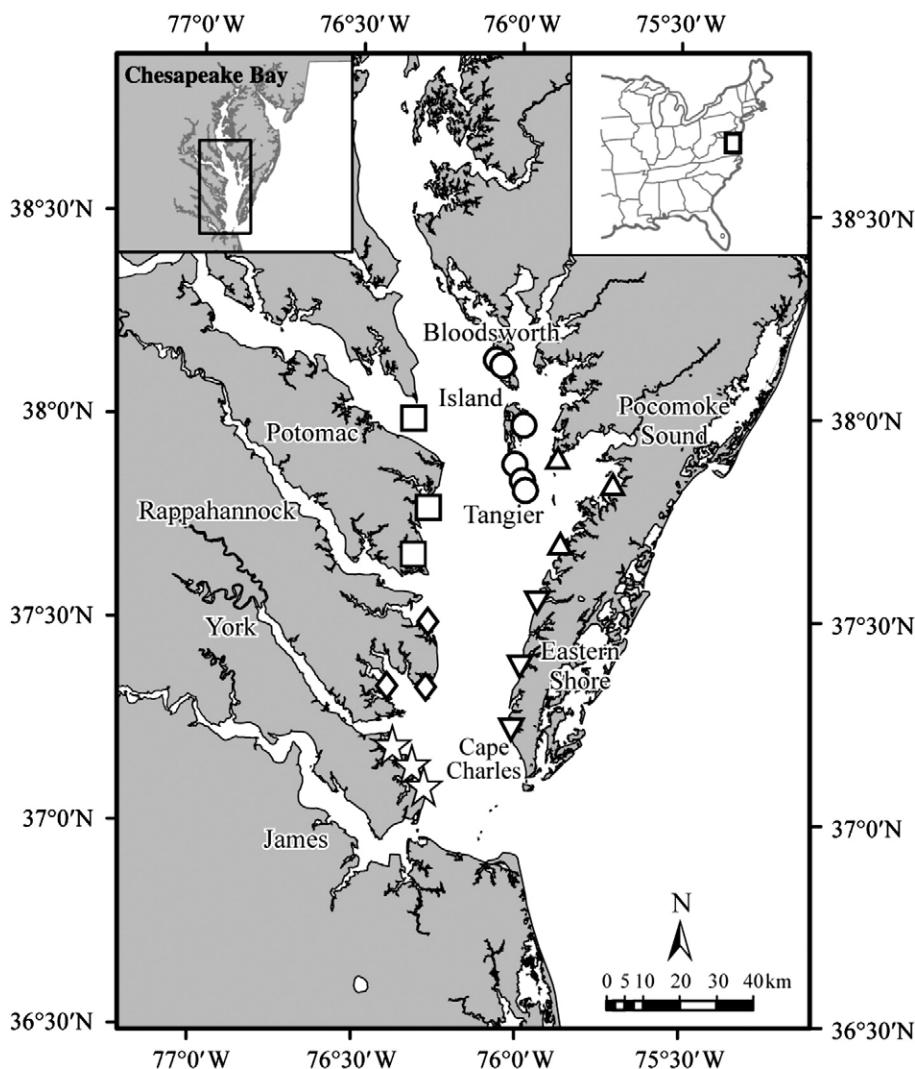


Fig. 1. Map of the Chesapeake Bay showing the locations of sampling areas and stations. Six seagrass habitats were sampled: Potomac (PORA, squares), Rappahannock (RAYO, diamonds), York (YOJA, stars), Islands (ISLE, circles), Pocomoke Sound (POSO, triangles), and lower Eastern Shore (LESH, inverted triangles).

- (3) YOJA (Western Shore; stars) — mouth of the York to the northern shore of the James River
- (4) POSO (Eastern Shore, triangles) — Pocomoke Sound
- (5) LESH (Eastern Shore, inverted triangles) — Lower Eastern Shore south of Pocomoke Sound to Cape Charles
- (6) ISLE (Islands, circles) — Tangier Island to Bloodsworth Island.

Within each sampling region we established stations along the salinity gradient. Stations were accessed using a 21-ft fiberglass boat with samples collected twice monthly during spring tide from July through September 2001. Mixing is maximized in the water column during spring tide (Valle-Levinson et al., 2000) and so we assume that surface water mixing was at maximum across the estuary. Under maximum mixing conditions, spatial differences in REE sediment chemistry among seagrass beds reflect minimal differences compared to neap tide conditions.

3.1. Sediment collection

Shallow (top 2–3 cm) sediment samples were collected using trace metal clean procedures. Samples were collected as grab samples from the top 2–3 cm using a fresh acid-washed Teflon scoop. Samples were transferred to acid-washed sterile whirlpaks and stored at 4 °C until prepared for analysis. In the laboratory, samples were air dried under laminar flow at room temperature and then at 110 °C in a drying

chamber. All samples were comprised of a minimum of 75% clay with the average clay-size (<63 μm) fraction accounting for an average of 90% of the bulk sample. After drying, samples were sieved using nylon mesh sieves and the fine fraction (<63 μm) was retained for analysis.

3.2. Sediment chemistry

Fifty mg of sample was completely dissolved by acid digestion (Murray and Leinen, 1993). Samples were digested under clean room conditions using Savillex digestion bombs and a digestion block with a combination of concentrated ultrapure HF and HNO₃ acids. Samples were repetitively dried down after digestion using aliquots of HNO₃ to remove any residual HF before analysis. Finally H₂O₂ (30%) was added to ensure complete oxidation of organic matter. Yttrium, quantified at ⁸⁹Y, was added as an internal spike to quantitatively monitor yield throughout digestion and analysis (>95%). Sub-samples (three splits per sample) were diluted within range of the calibration standards (1 ppb–200 ppb).

Concentrations were measured by external calibration with internal standardization (Indium). All trace metals were analyzed using a Perkin Elmer Sciex DRCII dynamic-reaction cell inductively coupled plasma mass spectrometer in peak jumping mode with reaction cell gas (NH₃) set to 0.8 mL min⁻¹. NH₃ reaction cell gas removed potential isobaric oxide–REE interferences, such as ¹³⁵Ba¹⁶O on ¹⁵¹Eu, from the sample stream (Feldman et al., 1999; Kishi et al., 2004). Most of the REE are free

Table 1
Mean water quality, Mn and rare earth element concentrations in parts-per-million for surface sediments from the lower Chesapeake Bay averaged across areas per sampling interval. Sample period 0 – July 10–16, 2001, Sample 1 – July 23–27, 2001, Sample 2 – August 6–9, 2001, Sample 3 – August 20–23, 2001, Sample 4 – September 4 – September 4–7, 2001.

Area	Sampling period	Temp °C	diss. O ₂ (mg/L)	pH (std. units)	Salinity (‰)	Conductivity (mhos/cm)	Mn	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ce/Ce*	Eu/Eu*
ILES	0	28.43	7.74	8.41	16.80	29.26	54.11	115.53	251.50	26.40	100.51	17.42	3.08	14.29	2.01	10.53	1.86	5.93	0.83	5.35	0.86	1.01	−0.05
LESH	0	25.60	7.24	8.35	23.40	35.71	68.66	24.87	43.37	4.84	18.43	3.53	1.43	2.82	0.40	1.83	0.35	1.10	0.15	0.90	0.13	0.86	0.32
POSO	0	28.87	8.40	8.34	18.90	32.86	60.04	49.79	103.81	10.45	39.07	6.85	1.63	5.70	0.82	4.20	0.72	2.25	0.31	1.86	0.28	0.95	0.13
PORA	0	27.47	7.56	8.47	17.07	29.18	73.73	36.36	78.45	7.84	29.42	5.05	0.88	4.16	0.56	2.64	0.43	1.27	0.17	1.04	0.15	1.03	−0.06
RAYO	0	28.27	8.56	8.44	19.23	32.97	87.46	33.52	68.32	6.67	24.89	4.42	0.69	3.68	0.50	2.07	0.37	1.09	0.14	0.86	0.13	0.70	−0.09
YOJA	0	26.53	6.05	8.20	21.60	35.42	101.41	77.93	160.15	17.62	66.86	11.54	1.61	9.30	1.19	4.47	0.75	2.11	0.27	1.68	0.26	0.95	−0.14
ILES	1	26.30	7.76	8.11	17.18	28.67	53.02	119.75	239.58	22.25	83.90	14.84	2.70	12.69	1.90	8.86	1.73	5.38	0.75	5.83	0.96	1.03	−0.05
LESH	1	26.85	8.17	8.55	23.90	39.09	47.14	19.71	31.65	3.28	11.46	1.86	0.78	1.65	0.24	1.08	0.21	0.67	0.10	0.74	0.13	0.86	0.31
POSO	1	26.43	8.02	7.09	19.07	31.60	67.56	48.73	95.83	10.01	37.05	6.52	1.22	5.53	0.78	3.53	0.66	1.98	0.26	2.00	0.32	0.95	0.00
PORA	1	26.30	6.79	8.15	18.80	31.09	95.05	67.44	136.46	14.25	53.22	9.08	1.59	7.80	1.07	4.67	0.88	2.68	0.38	2.85	0.45	0.98	−0.08
RAYO	1	27.70	7.17	8.06	19.50	33.14	79.57	55.53	119.64	12.26	46.27	8.12	1.47	6.72	0.95	4.48	0.79	2.43	0.34	2.56	0.42	1.02	−0.04
YOJA	1	26.17	5.38	7.68	21.83	35.64	143.84	50.04	121.66	10.98	41.64	7.34	0.94	6.00	0.79	3.15	0.51	1.67	0.25	1.82	0.30	1.16	−0.17
ILES	2	30.27	6.99	8.05	17.82	31.94	101.19	87.39	191.93	20.16	76.74	13.56	2.44	11.14	1.57	7.80	1.32	3.96	0.56	3.95	0.63	1.02	−0.06
LESH	2	29.53	7.70	8.09	22.53	39.18	73.26	65.03	137.35	14.29	53.09	9.12	1.69	7.56	1.08	4.79	0.91	2.80	0.38	3.01	0.49	1.00	0.02
POSO	2	30.87	7.33	7.97	19.37	34.94	52.54	42.68	97.15	9.31	34.74	6.03	1.25	5.03	0.70	3.09	0.58	1.79	0.24	1.87	0.31	1.03	0.03
PORA	2	28.30	6.90	8.05	18.17	31.26	106.66	26.13	55.46	5.47	20.50	3.74	0.52	3.00	0.41	1.64	0.28	0.78	0.10	0.78	0.12	1.01	−0.13
RAYO	2	28.90	7.08	8.12	20.15	34.82	114.88	19.20	41.54	3.61	13.29	2.28	0.38	1.96	0.25	1.07	0.20	0.60	0.08	0.64	0.10	1.11	−0.09
YOJA	2	28.13	5.88	8.00	22.87	38.53	99.17	49.98	103.54	10.84	41.00	7.08	1.25	5.76	0.78	3.56	0.58	1.66	0.22	1.58	0.24	0.97	−0.06
ILES	3	27.76	7.32	8.09	17.03	29.27	42.06	51.38	115.09	11.54	43.74	7.66	1.32	6.15	0.83	3.57	0.68	2.15	0.30	2.38	0.40	1.05	−0.06
LESH	3	28.00	8.92	8.23	22.50	37.83	76.38	20.06	38.30	3.87	14.41	2.45	0.89	2.05	0.30	1.36	0.27	0.87	0.12	0.99	0.17	0.94	0.26
POSO	3	26.03	5.30	7.78	18.67	30.77	89.54	59.95	118.35	12.39	45.72	7.71	1.39	6.63	0.93	4.12	0.72	2.29	0.32	2.28	0.37	0.94	−0.06
PORA	3	27.37	6.73	8.25	17.67	30.03	86.30	34.21	74.69	7.54	28.81	5.07	0.77	4.10	0.56	2.29	0.42	1.24	0.17	1.28	0.21	1.01	−0.10
RAYO	3	28.60	8.22	8.28	20.90	35.91	42.74	15.02	29.66	3.01	11.01	1.87	0.32	1.61	0.23	1.05	0.20	0.65	0.09	0.72	0.12	0.94	−0.08
YOJA	3	27.77	8.32	8.25	22.30	37.37	101.38	51.73	104.49	11.11	41.93	7.39	1.27	6.29	0.89	3.94	0.73	2.20	0.30	2.29	0.37	0.97	−0.10
ILES	4	26.24	7.54	8.03	17.51	29.16	65.67	97.40	215.55	21.85	82.22	14.60	2.71	12.24	1.84	9.99	1.69	5.34	0.82	5.77	0.97	1.09	−0.05
LESH	4	26.50	8.69	8.20	22.45	36.67	92.11	55.55	110.19	12.41	47.28	8.51	1.94	7.21	1.09	5.10	0.99	3.06	0.43	3.30	0.54	0.90	0.23
POSO	4	25.13	6.49	7.85	19.27	31.11	65.08	56.57	120.46	12.57	47.69	8.45	1.79	7.11	1.03	5.22	0.88	2.73	0.38	2.96	0.49	0.97	0.10
PORA	4	26.03	6.53	8.11	18.37	30.31	87.79	80.25	174.29	18.41	69.82	12.25	2.16	10.17	1.41	7.40	1.18	3.71	0.52	4.01	0.66	0.98	−0.07
RAYO	4	27.05	8.26	8.16	19.60	32.77	118.49	69.89	145.63	15.50	59.14	10.69	1.97	9.26	1.42	7.76	1.27	3.89	0.53	4.02	0.65	0.97	−0.12
YOJA	4	26.30	7.90	8.00	22.00	35.94	54.94	32.87	68.73	7.05	26.46	4.75	0.86	4.04	0.58	2.57	0.48	1.44	0.19	1.47	0.24	0.98	−0.05
1NASC								32	73	7.9	33	5.7	1.2	5.2	0.85	5.8	1	3.4	0.5	3.1	0.48		

Eu/Eu* = $\log[2^{*}\text{Eu}_{\text{NASC}}/(\text{Sm}_{\text{NASC}} + \text{Gd}_{\text{NASC}})]$.

Ce/Ce* = $\text{Ce}_{\text{NASC}}/(0.5^{*}(\text{La}_{\text{NASC}} + \text{Pr}_{\text{NASC}}))$.

¹Taylor and McLennan, 1985.

of isobaric interferences; however, we monitored multiple isotopes (^{55}Mn , ^{137}Ba , ^{138}Ba , ^{139}La , ^{140}Ce , ^{142}Ce , ^{141}Pr , ^{143}Nd , ^{146}Nd , ^{148}Sm , ^{149}Sm , ^{151}Eu , ^{153}Eu , ^{157}Gd , ^{158}Gd , ^{159}Tb , ^{161}Dy , ^{163}Dy , ^{164}Dy , ^{165}Ho , ^{166}Er , ^{167}Er , ^{169}Tm , ^{172}Yb , ^{173}Yb , ^{174}Yb , ^{175}Lu) as an additional check of isobaric interference (Hodge et al., 1998). REE³⁺/REE³⁺ ratios measured by the DRC II are consistently below 0.2%. Precision, as determined from triplicate analyses of the samples beginning with the original sample weighing, was generally <2% for the REEs. We used MAG-1 (U.S. Geological Survey marine sediment) to assess precision with this reference standard processed in the same way the samples were processed. Method detection limits (Hubaux and Vos, 1970) were below 2 parts-per-trillion for all elements. Least-square regression was applied with goodness of fit (r^2) greater than 0.999 for all analytes. Analysis of calibration standards and MAG-1 was performed every six samples.

Variations in REE composition between samples is assessed using the convention of normalization of concentrations to average shale (North American Shale Composite, NASC; Taylor and McLennan, 1985). Variations in redox conditions as well as differences in REE complexation and adsorption behavior are reflected by changes in the oxidation state of cerium Ce(III)–Ce(IV) and Eu(II)–Eu(III). These changes may result in differences in Ce and Eu abundances. Ce-anomaly (Ce/Ce*) and Eu-anomaly (Eu/Eu*) values are calculated by

$$\text{Ce/Ce}^* = \text{Ce}_{\text{NASC}} / (0.5 * (\text{La}_{\text{NASC}} + \text{Pr}_{\text{NASC}})) \quad (1)$$

and,

$$\text{Eu/Eu}^* = \log[2 * \text{Eu}_{\text{NASC}} / (\text{Sm}_{\text{NASC}} + \text{Gd}_{\text{NASC}})] \quad (2)$$

Ce/Ce* values less than 1.0, depletion in sediment Ce, suggest reductive dissolution of insoluble Ce(IV) to soluble Ce(III). Negative Eu/Eu* values (i.e., depletion in Eu) reflect oxidation of Eu(II) to Eu(III) and loss of Eu from the sediments.

Because water chemistry and physical properties influence sediment REE chemistry we measured water temperature, salinity, conductivity, pH (YSI 63), dissolved oxygen (DO; YSI 55) and depth at the time of sediment collection. The phase of the tide was also noted. The physical parameters (Dorval et al., 2005) and measured sediment analyte concentrations are reported in Table 1.

The first step in comparing REE abundances temporally and spatially was to determine that there was homogeneity of variance among areas over time. A modified Levene test (O'Brien, 1992; Hines and Hines, 2000) showed that there was homogeneity of variances among areas for all the variables measured in this study. Statistically significant differences in total REE between sampling periods within sites were noted in all sites except LES22, LES23, PORA 10 and YOJA 19 ($p < 0.05$). The differences in total REE between sampling periods are attributed to differences in salinity. Data for Yb from LESH samples and Ce/Ce* from POSO and YOJA were not normally distributed. Due to non-normality of some of our data we performed Principal Component Analysis (PCA), a multivariate technique that does not require the assumption of normality. We chose this test to evaluate the factors (spatial, temporal, and physical) that may influence REE abundances (e.g., Hannigan et al., 2001) as the REE abundances and relations to physical parameters were insufficient to describe the heterogeneity in REE chemistry we observed. Ce and Eu concentrations were not directly used in the PCA, as those measurements are reflected in the computation of their anomalies. No factor rotation was performed, and the PCA was run with a scale-invariant correlation matrix, thus the scale of measurements of the different variables had no effect on the outcome of the analysis. To further explore the processes governing REE sediment chemistry we used a proportional-odds model (e.g., Murphy et al., 1997; Agresti, 2002) to relate Eu/Eu* (as the response variable) to water salinity (explanatory variable). To apply this model to our data we transformed all Eu/Eu* estimated in Eq. (2) to a binary

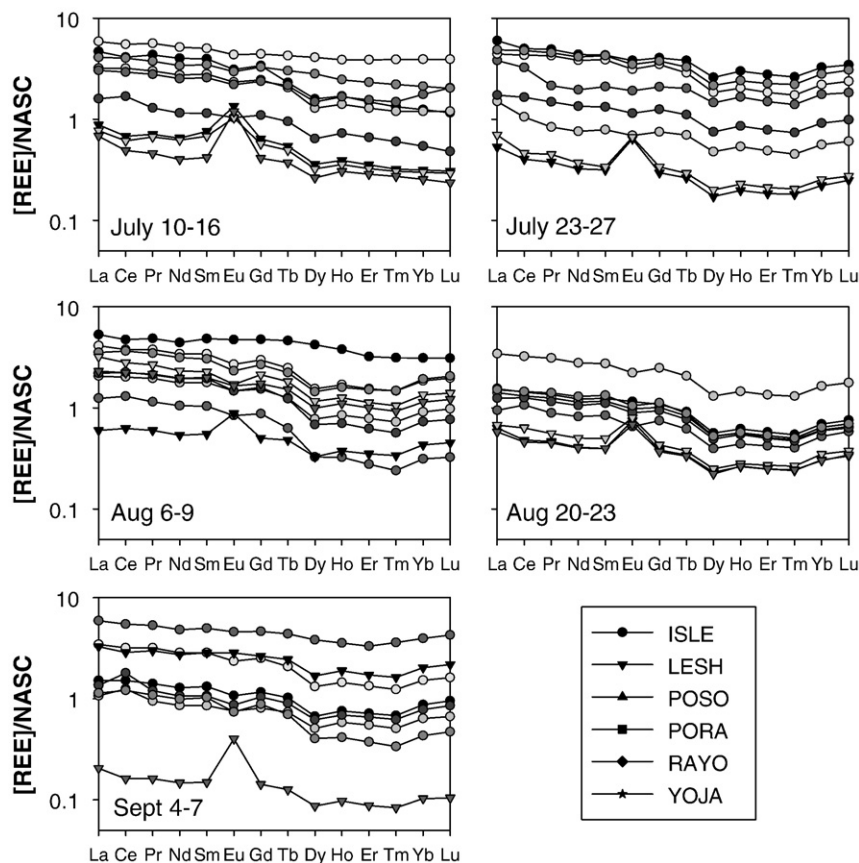


Fig. 2. Shale-normalized REE abundance patterns of Chesapeake Bay sediment samples averaged within areas. Shaded symbols represent different sampling sites within the area. Spatial variation between areas is seen. Temporal variation was found, within areas, to be insignificant. Note the spatial variation in Ce and Eu abundances, particularly in the LESH samples.

dataset by assigning a value of 1 to any positive estimate and a value of 0 to any negative estimate. This transformation allowed us to use the Logit regression model (Eq. (3)) as a statistical method (Agresti, 2002) to determine the probability (p) that a sediment sample collected in an area with known salinity will exhibit a negative Eu/Eu*.

$$\text{Logit}(p) = \log[p/(1-p)]. \quad (3)$$

4. Results and analyses

4.1. Environmental (physical and chemical) variables

Variations in water temperature, salinity, dissolved oxygen (DO), and pH are described in Dorval et al. (2005). Those results showed that there were no significant differences in dissolved oxygen (DO) between sampling intervals and that these shallow environments had consistently high DO values. Similarly, salinity within zone over time was consistent and no statistical differences were found. Differences in salinity between zones were significant. Temperature was spatially similar within a sampling period across all zones but temporally variable (Dorval et al., 2005).

4.2. Sediment chemistry

Shale-normalized (North American Shale Composite, NASC) REE abundance patterns were slightly enriched in (Fig. 2; LREE; La to Nd; $(\text{La/Yb})_{\text{NASC}} > 1.0$). REE sediment chemistry was spatially consistent within a given area across time; no significant differences were found between sample sites within areas or between sampling periods within zones. The only significant differences in REE chemistry were seen between areas and are associated with salinity (Fig. 3). LESH

showed consistently distinct Eu abundances (Fig. 2) and lower ΣREE towards the end of the sampling period.

Overall, total REE concentrations were highest in the Islands (Fig. 4) with patterns that were flat or slightly heavy REE depleted (Fig. 2, Ho to Lu; $(\text{Tb/Yb})_{\text{NASC}} > 1.0$). No significant difference was observed in total REE between Eastern Shore LESH sediments and those collected from the Western Shore at PORA, RAYO, and YOJA. Thus, we saw consistent REE chemistry between the Eastern Shore and Western Shore sediments with the exception of the higher concentrations of Eu in Eastern Shore samples (Fig. 2). For both mean Ce- and Eu-anomalies, the LESH sediments were significantly different from those collected from the Islands and Western Shore. The mean Ce-anomaly of samples collected in the Islands and Western Shore was close to 1.0, indicative of oxygenated pore waters and/or sediment/water interface. In contrast, mean Ce-anomaly in Eastern Shore samples was slightly below 1, but significantly different from the Ce-anomaly values of sediments from the Islands and Western Shore. Similarly, mean Eu-anomaly was not significantly different between samples from the Islands and Western Shore, while Eastern Shore mean sediment Eu-anomaly was significantly different from those of Island and Western Shore. Relations between the anomalies (Fig. 5) show the distinctiveness of the LESH sediments which are consistently different throughout the sampling period. Variability in Eu concentration between sites (e.g., Fig. 2) within the LESH is not significant.

No relation was found between Ce/Ce* and Eu/Eu* with dissolved oxygen. Similarly, comparison between the anomaly values and Mn concentration, which might indicate redox behavior for Ce and Eu, also revealed no relation. It is expected that increases in sediment Mn due to reduction of Mn(IV) to particulate Mn(II) may result in a loss of Ce from the sediment due to reduction of Ce(IV) to Ce(III). If this occurred it is not evident in our samples. We also found no significant relation between Eu/Eu* and Mn at any of the sites.

Evaluation of complex relations among variables requires a multivariate approach to identify processes which may be responsible for the variance in composition of the sediments across sample sites. Use of Principal Components Analysis (PCA) allows us to reduce the variance in the data to unique “components” thereby allowing us to assess the overarching processes governing the chemistry of the sediments. PCA revealed that the first two principal components (PC1–PC2) accounted for 90% of the variability (i.e., in terms of cumulative proportion of total variance) in the data; therefore, only those two principal components were used in further analyses (c.f. Khattree and Naik, 2000). PC1 contrasted the behavior of the REEs and Ce/Ce* (positive score coefficients) against Mn and Eu/Eu* (negative score coefficients, PC1, Fig. 6) separating ISLE samples from Eastern Shore samples, POSO and LESH. PC2 contrasted the behavior of the LREEs (La to Nd), Mn and Ce/Ce* to that of the HREEs and Eu/Eu*, and separated Western Shore samples PORA and YOJA from Island and Eastern Shore samples ISLE, POSO and LESH.

Our PCA results indicate that Eu/Eu* responds to condition(s) unique to the Eastern Shore. To further elucidate the potential causes of the unique Eu-anomaly chemistry in this area, we used a logit regression to test the hypothesis that Eu/Eu* is responding to salinity. The Chi-square distribution-based probability for this model was highly significant, indicating that salinity predicted Eu/Eu* (Eq. (4), Fig. 7)

$$\text{Logit}(p) = \log[p/(1-p)] = 10.9557 - 0.4679 \cdot \text{Salinity} \quad (4)$$

In contrast to the Eu/Eu* results, Logit Regression using Ce/Ce* as the response variable was not significant ($p = 0.1453$), demonstrating that salinity had no predicative power for Ce/Ce*.

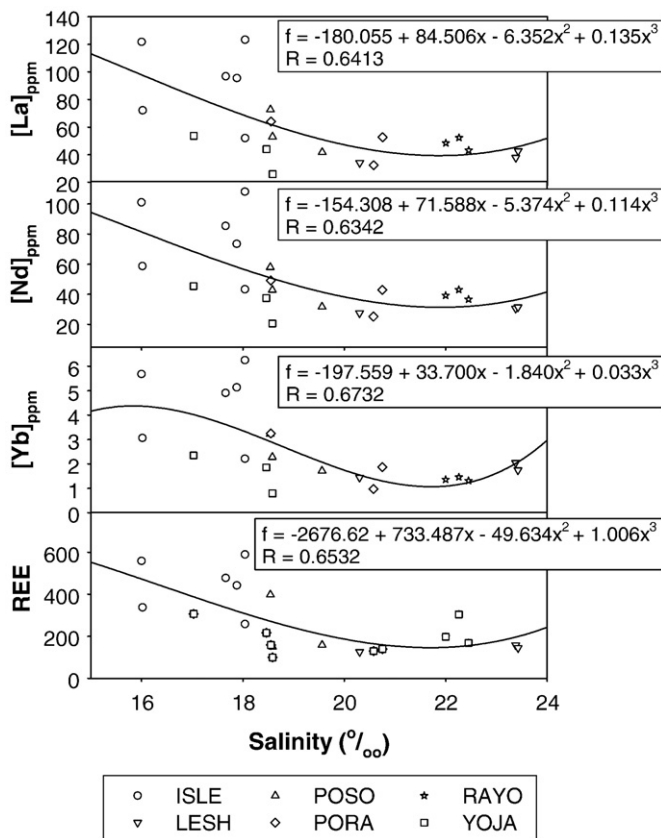


Fig. 3. Within area mean La, Nd, Yb and ΣREE compared to salinity showing lateral and longitudinal variation in REE abundances. ISLE samples are consistently higher in REE than other regions. The relation between REE abundance and salinity is evident with the mean REE falling along the salinity gradient (non-linear regression, solid line).

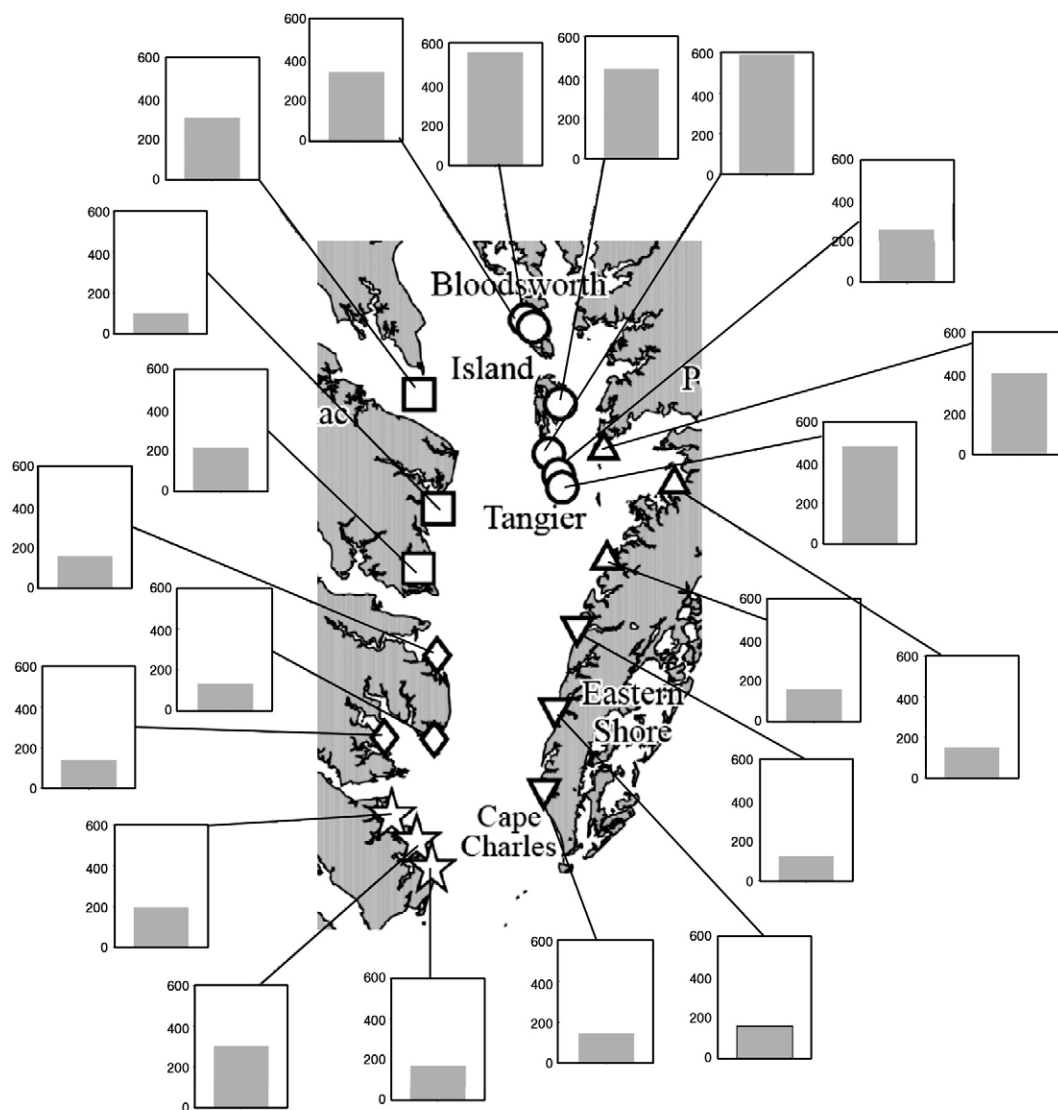


Fig. 4. Map showing mean ΣREE at each site. Though temporal differences were significant for most sites the mean relations are consistent with ISLE samples having the highest overall REE abundances.

5. Discussion and conclusions

The REE chemistry of the shallow sediments along and across the lower Chesapeake Bay varied significantly. Variation cannot be solely attributed to estuarine mixing and differences in salinity, although salinity clearly sediment REE chemistry. Other factors such as physical mixing, sediment provenance, groundwater discharge, and seasonal anoxia may also contribute to differences in REE abundances. Teasing out the impact of each process on sediment REE in our data is difficult. However, it is possible to interpret the relation between Ce/Ce^* and Eu/Eu^* as evidence of competitive processes whereby Eu/Eu^* is responding to salinity and Ce/Ce^* is responding to slight changes in oxidation as well as physical mixing and particle settling. The relation between the two anomalies approaches that of binary mixing; however, we lack the data to accurately assess the influence of specific conditions, aside from salinity, that lead to this relation. The Islands and Eastern Shore (ISLE, POSO, and LESH) samples have distinct REE chemistries from one another and from the Western Shore samples, with spatial variations fully resolvable across all seagrass habitats in the lower Bay. Variation in sediment REE chemistry is expected given that during estuarine circulation progressive mixing of fresh and oceanic water leads to removal of these elements from the dissolved load along the salinity

gradient (Goldstein and Jacobsen, 1988; Sholkovitz and Elderfield, 1988; Sholkovitz, 1992, 1993, 1995; Guieu et al., 1998; Bau, 1999; Lawrence and Kamber, 2006; Chaillou et al., 2006). Austin (2004) showed that the salinity gradient in the lower Chesapeake Bay has a gentle but uniform gradient. This gradient is preserved in the shallower seagrass habitats of our study area and plays a fundamental role in controlling the chemistry of the dissolved load (Dorval et al., 2005) and sediment. In a wide estuary, such as Chesapeake Bay, Coriolis acceleration modifies estuarine circulation restricting the outflow of freshwater from rivers such as the Potomac, Rappahannock, York and James. Coriolis acceleration restricts outflow to the western shore and inflow of oceanic water toward the Eastern Shore (Pritchard, 1952; Austin, 2004). The resulting density gradients are likely responsible for the spatial differences in REE abundance patterns from the Western to the Eastern Shore. Superimposed on the development of lateral density gradients are localized phenomena including submarine discharge of freshwater along the Eastern and Western Shores (Simmons, 1989, 1992; Reay et al., 1992; Reay and Simmons, 1992; Moore, 1999) and summer season hypoxia within the Bay (Officer et al., 1984; Breitburg, 1990; Adelson et al., 2001). Competing effects of the salinity gradient, Coriolis acceleration, associated complexation reactions, and redox cycles lead to spatial heterogeneities in the redox sensitive REE such as Ce and Eu and in the

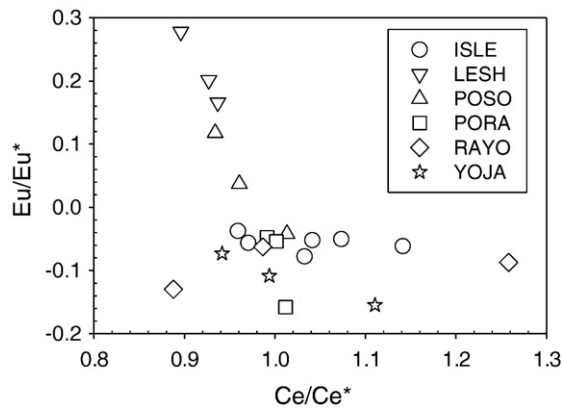


Fig. 5. Variation in Ce/Ce^* and Eu/Eu^* in surface sediments of the Chesapeake Bay. ISLE and LESH samples are distinct with the bulk of the LESH sediments having positive Eu/Eu^* values across sampling periods.

degree of HREE depletion (Ho to Lu ; $(Tb/Yb)_{NASC} > 1.0$) and LREE enrichment (La to Nd ; $(La/Yb)_{NASC} > 1.0$).

Variation in relative abundances of REE occurs, for the most part, along the salinity gradient where progressive mixing of freshwater and ocean water leads to colloidal removal of REE from the dissolved load and sequestration in the sediments (Sholkovitz, 1995). Sediment REE chemistry in the lower Bay is consistent with the observations of Sholkovitz and Elderfield (1988). Our data show that the colloidal material deposited in the seagrass beds is enriched in LREE and depleted in HREE. The degree of LREE enrichment ($(La/Yb)_{NASC}$) is more pronounced in regions significantly influenced by estuarine mixing such as along the Western Shore. Studies of estuarine REE chemistry point to the fact that not only does estuarine mixing reduce the flux of dissolved REE to estuaries but that chemical and physical processes associated with mixing modify the relative abundances of REE reaching the oceans. We infer that these processes similarly alter the material deposited in estuaries. This inference is supported by the spatial variability in REE concentrations and abundance patterns in the Chesapeake Bay sediments which are attributed primarily to salinity differences.

5.1. Anomalies of Ce

Both positive and negative Ce/Ce^* values occur in marine pelagic sediments. The relation between oxidation of the overlying water column and pore waters to sediment Ce/Ce^* is straightforward (e.g.,

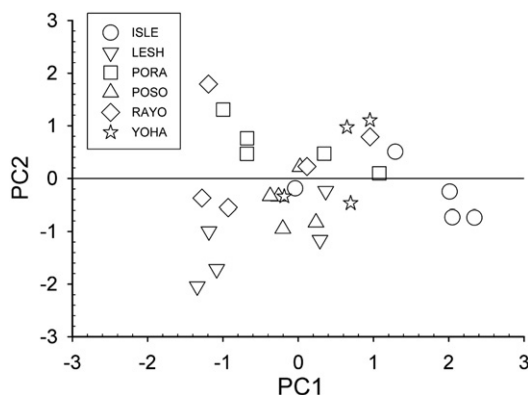
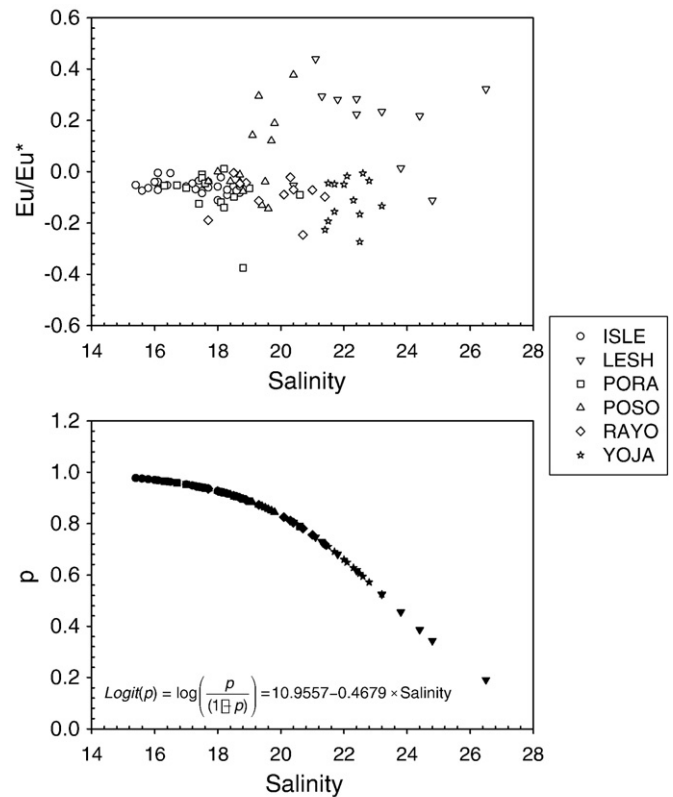


Fig. 6. Principal component loadings of samples on PC1 and PC2. PC1 contrasts the REE and Ce/Ce^* against Mn and Eu/Eu^* separating ISLE samples from eastern shore samples POSO and LESH. PC2 contrasts the light REE (La to Nd), Mn and Ce/Ce^* against the HREE (Tb to Lu) and Eu/Eu^* separating western shore samples PORA and YOJA from island and eastern shore samples ISLE, POSO, and LESH.



	Estimate	Standard Error	Chi-square p
Intercept	10.9557	2.8150	< 0.0001
Salinity (slope)	-0.4679	0.135	0.0006

Fig. 7. Relation between Eu/Eu^* and salinity. A. Eu/Eu^* vs. salinity showing the distinct nature of the eastern shore samples LESH and POSO compared to the other areas of the Bay. B. Probability that Eu/Eu^* will be negative for a given salinity, derived from Logit regression analysis, vs. salinity (Eq. (3)) showing the strong relation between salinity and Eu/Eu^* . Chi-square probability is significant showing that salinity can predict sediment Eu/Eu^* . Logit regression of Ce/Ce^* on salinity was not significant.

Murray and Leinen, 1993). Preferential oxidation of $Ce(III)$ to $Ce(IV)$ and scavenging of $Ce(IV)$ from seawater to sediment leads to positive Ce-anomalies in equatorial Pacific red clays (Toyoda et al., 1990). Sholkovitz (1995) showed that removal of dissolved Ce in the Amazon Estuary is enhanced in the low salinity zone as well as in the zone of high biological productivity (salinity 18–26; Sholkovitz, 1993).

Similar linkages between biological productivity and the development of redox fronts within the sediment or at the sediment–water interface have been documented in a number of estuarine settings (e.g., Toyoda et al., 1990; Riedel et al., 1999). When comparing our data to water quality parameters such as PO_4^{3-} (Dorval, 2004), Ce/Ce^* positively correlates only in the mid-Eastern Shore (Pocomoke Sound) suggesting that the slightly negative Ce/Ce^* could be associated with biological productivity. This is a possibility but cannot be substantiated without further investigation. Our data showed no direct influence of salinity on Ce/Ce^* . Given the redox behavior of Ce, the intermittent positive Ce-anomalies could be attributable to oxidative removal of $Ce(IV)$ from the water column and accumulation of Ce in the sediments.

Though intermittent positive Ce-anomalies were found, we did not find a statistically significant relation between dissolved oxygen of the overlying waters and sediment Ce-anomaly. The absence of a direct linkage between dissolved oxygen and Ce/Ce^* does not preclude that positive Ce/Ce^* values in these samples are attributable to changes in redox conditions. Direct inquiry into the influence of oxidative accumulation of Ce in the sediments resulting in Ce/Ce^* values greater than 1.0 in some samples requires measurement of pore water REE

chemistry. The vast majority of samples had Ce/Ce^* values below 1.0 indicative of Ce depletion in the sediments due to reduction of $Ce(IV)$ to $Ce(III)$ and resuspension of $Ce(III)$ to the water column. The majority of positive Ce/Ce^* values were found in samples collected in the Islands suggesting oxidative removal of Ce and accumulation of Ce in the sediments in this region.

If redox is playing a role in the resuspension of $Ce(III)$ to the water column we would expect to see a relation between Ce and redox sensitive trace metals such as Mn. As mentioned above the presence of reducing conditions in the Bay could be due to microbial degradation of organic matter (Froelich et al., 1979; Aller, 1980; Kristensen et al., 2002). Under reducing conditions $Mn(IV)$ will be reduced to $Mn(II)$ which is released to the dissolved phase depleting the sediment of Mn. The reduction of $Mn(IV)$ and transfer of $Mn(II)$ occurs in the Bay when suboxic and anoxic conditions develop in spring and summer (Taft et al., 1980; Seliger et al., 1985). Remobilization of Mn from reducing sediments controls most of the supply of Mn into surface waters of the Bay (Eaton, 1979). This supply of $Mn(II)$ may originate from the reduction and dissolution of oxidized manganese particles formed in deep anoxic water of the Bay (Gavis and Grant, 1986). As the PCA results indicated, PC1 contrasted the behavior of Ce/Ce^* to Mn suggesting that the two variables are, to some extent, decoupled. The relation between Ce/Ce^* and Mn in the sediments indicates resuspension of REE and Mn under reducing conditions. The fact that this relation is not strong may be attributable to the fact that Ce is less mobile than Mn as well as leading to a moderate inverse relation between the two variables.

Variations in sediment Ce in the Loire Estuary (Negrel, 1997) were related, at least in part, to the *in situ* formation of particles within the turbidity maximum. Our samples were collected south of the turbidity maximum such that large scale production of particles is unlikely. Localized turbidity zones may develop where submarine groundwater discharge occurs with a resulting steep salinity gradient leading to the development of negative Ce/Ce^* values. Though this may be occurring we do not have sufficient data to support the formation of these localized turbidity maxima beyond circumstantial data provided by Ce/Ce^* . We expect that Ce concentrations would be elevated in the pore waters of the upper 2 cm of the sediments studied here as was observed by Sholkovitz and Elderfield (1988) in samples north of our study area. Sholkovitz and Elderfield (1988) suggest that benthic flux of anoxic REE-rich fluids is required to explain the high concentrations of Ce observed in some pore water samples from Chesapeake Bay. Benthic flux of REE-rich anoxic fluids can be provided via submarine groundwater discharge, particularly along the Eastern and Western Shore (Reay and Simmons, 1992; Reay et al., 1992; Moore, 1999; Charette and Buessler, 2004). Discharge of anoxic freshwater at depth combined with Coriolis acceleration restricting inflow of oxygenated seawater to the east could lead to localized intermittent sediment hypoxia and development of negative Ce-anomalies. The spatial variation in Ce/Ce^* we found in the sediments is commensurate with the water column redox conditions described by Dorval et al. (2005).

5.2. Anomalies of Eu

Our data reveal that anomalies of Ce and Eu are decoupled. Decoupling of these anomalies can be related to the slow dissolution rate of Eu-humate complexes (Benes et al., 2003), differences in the complexation behavior of Eu relative to the other REE (Moermond et al., 2001), and the presence of allochthonous adsorbed Eu (Erel and Stolper, 1993).

Generally little variation in Eu/Eu^* is observed in marine sediments with the majority of marine sediments having negative Eu/Eu^* except under hydrothermal conditions (McLennan, 1989; Erel and Stolper, 1993). One would anticipate that conditions within the sediment or at the sediment–water interface are insufficient to change the oxidation state of Eu. Eu-anomalies in estuarine sediments

tend to be negative as is the case in the majority of the Bay samples. Negative Eu-anomalies are explained by the reductive remobilization of $Eu(II)$ from the sediments to the surface waters leading to negative Eu-anomalies in the sediment (Elderfield and Sholkovitz, 1987). Positive Eu/Eu^* have been observed in marine sediments (e.g., Prego et al., 2009) where these positive values are attributed to sediment parent material. The distinct positive Eu/Eu^* values of the LESH samples suggest unique conditions in this region of the Bay. We discount the influence of mineralogy as no plagioclase was found in these sediments and the positive Eu/Eu^* were found in the fine sediment fraction representative of relatively fresh colloidal material.

One possible explanation for the positive Eu-anomalies is that extreme reducing conditions are developed in the lower Eastern Shore sediments. Erel and Stolper (1993) and McLennan (1989) found that model water–sediment distribution coefficients predict small positive Eu-anomalies ($Eu/Eu^* \sim 0.1–0.2$) due to the elevated first hydroxide binding constant of Eu being higher than that of Gd and Sm (Brookins, 1989). Erel and Stolper (1993) hypothesize that positive Eu-anomalies in sediments form as a consequence of the adsorption chemistry of Eu rather than being an inherited signature from solution. Because coatings of organic matter and Mn–Fe oxides play a major role in the binding of REE to particle surfaces (Sholkovitz et al., 1994) it is no surprise that, in the fine fraction of these sediments, we find a unique record of sediment deposition conditions. However, statistical examination of the data did not reveal the influence of redox on the development of positive Eu/Eu^* in these sediments and pointed, instead, to salinity as the primary variable influencing Eu chemistry.

Diagenetic reactions occurring under reducing conditions have been invoked to explain the positive Eu/Eu^* values found in phosphate rich sedimentary rocks (Kidder et al., 2003; Murthy et al., 2004). While diagenesis can lead to the formation of positive Eu-anomalies under extreme reducing conditions (Ogihara, 1999) such explanations cannot be invoked for the Bay's positive Eu-anomalies. These shallow surface sediments contain relatively fresh colloidal material as the samples were collected from the top 2–3 cm of the sediment column at each seagrass bed and so have not undergone significant diagenetic alteration. To explain the positive Eu/Eu^* values we need to identify conditions unique to the Eastern Shore where samples consistently showed positive Eu/Eu^* values. We hypothesize that decay of organic matter and the development of very localized reducing conditions combined with submarine discharge of reducing groundwaters and restricted inflow of oxygenated saline waters could lead to the development of unique conditions within these sediments. Organic matter decay rates in this area have not been directly measured at our study sites. Zimmerman and Canuel (2001) found, at sites in the center of the Bay due west of our LESH sites, lower total organic carbon concentrations in the southern Chesapeake Bay. These authors found the organic matter in this region to be primarily autochthonous and suggested that this material undergoes less degradation prior to deposition. Being more labile this material degrades in summer and fall (Zimmerman and Canuel, 2001). This degradation may lead to localized seasonal reducing conditions which are maintained by a persistent off-shore convergent residual eddy (Hood et al., 1999) resulting in down welling and further restriction of flow along the Eastern Shore. The combination of organic matter degradation, down welling and strong tidal circulation in the south Bay may lead to reducing conditions at the sediment surface as well as a steep salinity gradient.

The decoupling of Ce/Ce^* and Eu/Eu^* requires an explanation for positive Eu/Eu^* to be developed that is unique to the lower Eastern Shore. As discussed above, unique conditions do exist in this region. In addition to the above we propose that submarine groundwater discharge of anoxic groundwaters occurring along the Eastern Shore enhances the development of redox and salinity conditions unique to this area of the Bay. Support for submarine groundwater discharge

occurring along the Eastern Shore includes the observation that brackish water moves into shallow, near-shore marine environments under positive hydraulic head (Simmons, 1992). Submarine groundwaters in this region are enriched in ammonium with little to no nitrate (Reay et al., 1992) indicative of reducing conditions. The submarine groundwater discharge rate for the entire Chesapeake Bay system is estimated to be $17 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ (Hussain et al., 1999). The ^{222}Rn estimated groundwater discharge in the Elizabeth River estuary on the southern Western Shore is $8.5 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ (Charette and Buessler, 2004). Submarine groundwater discharge at a site close to our LESH samples has been measured at a rate of $23.2 \text{ m}^3 \text{ d}^{-1}$ (Simmons, 1989). A recent study of the shallow groundwater chemistry along the Eastern Shore revealed decreases in groundwater levels and decreased chlorinity (Sanford et al., 2009). Submarine groundwater discharge along the Western Shore is significantly higher than the discharge along the Eastern Shore. Along the Western Shore the influence of these fluids on sediment REE chemistry is overwhelmed by the freshwater discharge of the rivers and less dramatic salinity changes from Bay mouth to river mouth. Conditions along the Eastern Shore are distinct from the Western Shore and are such that the surface sediments in this area are more likely to record local conditions, including submarine groundwater discharge, due to the limited inflow of oxygenated seawater and little, if any, surface water input. The combination of reducing fresh water from submarine groundwater discharge, Coriolis acceleration restricting ocean water inflow to the east, and local downwelling leads to conditions under which the groundwater fluids are not well-mixed. These fluids, we propose, would cross a strong localized salinity gradient leading to reduced coagulation of clays, poor efficiency of REE removal, reduction of Eu(III) to Eu(II) leading to the development of positive Eu/Eu* and negative Ce/Ce*. This hypothesis cannot be confirmed by our data and requires a focused study relating submarine groundwater discharge, pore water chemistry, and sediment chemistry in this region of the Bay.

6. Conclusions

We show spatial heterogeneity, both laterally and longitudinally, in the REE chemistry of shallow fine-grained estuarine sediments. The chemistry of the Islands is distinct with higher overall REE content and more positive Ce-anomaly values. Positive Ce/Ce* are attributed to the Coriolis acceleration restricting freshwater flow towards the west away from the Islands, thus leading to oxidative removal of Ce from the pore waters to the sediments. Our data reveal positive Eu/Eu* in sediments deposited along the Eastern Shore. We propose that unique conditions along the Eastern Shore, submarine groundwater discharge of reducing freshwaters combined with organic matter decay and restricted saline oceanic water flow toward this region, leads to the development of a strong localized salinity gradient. These unique conditions reduce the efficiency of sediment removal leading to lower total REE concentrations in the sediments as well as reduction of Eu(III) to Eu(II) and consequent development of positive Eu/Eu* and negative Ce/Ce*. Whether these anomalies persist throughout the year and are the result of groundwater interactions with the pore waters and/or surface waters remains to be determined.

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