Chemical Geology 308-309 (2012) 60–73

Contents lists available at SciVerse ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Enrichment and fractionation of rare earth elements in FeS- and organic-rich estuarine sediments receiving acid sulfate soil drainage

Bree Morgan [a,*], Andrew W. Rate [a], Edward D. Burton [b], Michael N. Smirk [a]

[a] School of Earth and Environment, The University of Western Australia, Crawley, WA 6009, Australia
[b] Southern Cross GeoScience, Southern Cross University, Lismore, NSW 2480, Australia

ARTICLE INFO

Article history:
Received 11 October 2011
Received in revised form 1 March 2012
Accepted 14 March 2012
Available online 23 March 2012

Editor: J.D. Blum

Keywords:
Rare earth elements
FeS
Organic-rich
Acid sulfate soil
Estuarine
Sediment

ABSTRACT

An understanding of processes controlling the behaviour of rare earth elements (REEs) within estuarine sediments is essential for the effective use of REEs as tracers of environmental conditions. This study investigates the enrichment and fractionation of REEs in sediments with abundant iron monosulfides (FeS, measured as acid-volatile sulfide, median = 156 μmol/g) and organic carbon (median = 3.2 mmol/g). We examined sediments collected from a eutrophic estuary in Western Australia, which comprised several sedimentary environments, including sites receiving drainage from acid sulfate soils (ASS). In general, sediment-bound REEs were highly soluble in HCl, with 1 mol/L HCl extractable REE concentrations amounting to >80% of corresponding total concentrations in approximately 70% of samples. A mid-REE (MREE) enrichment was consistently apparent in all sediment samples, with a median MREE enrichment value of 1.30 (range = 1.13–1.50) for the total REE concentrations and 1.26 (range = 1.17–1.44) in the 1 mol/L HCl extractions. Also, a Ce anomaly was consistently observed in the sediments examined here, with a median value of 1.11 (range = 0.79–1.58) for the total REE concentrations and 1.19 (range = 1.04–1.71) in the 1 mol/L HCl extracts. In general, a minor depletion of heavy-REEs (HREEs) relative to light-REEs (LREEs) was also apparent in many of the sediments (Yb/La<1). This fractionation trend, in addition to a strong positive correlation between the MREE enrichments and Yb/La ratios, is consistent with sediment organic matter acting as a REE host phase. Abundant sedimentary FeS was also hypothesised to have influenced REE behaviour in the field, based on the high proportion of total REEs extracted by 1 mol/L HCl, as well as strong correlations between total REE concentrations and both total Fe and total S in the sediments examined here. However, in our laboratory experiment we found that REEs exhibit little (or no) short-term sorptive affinity for FeS, implying that if any FeS–REE interactions were occurring, this must involve mechanisms other than rapid sorption to pre-existing FeS. Sites receiving ASS drainage were unique in displaying (1) a strong relative enrichment of total REE concentrations in comparison to non-impacted sites, and (2) a significant positive correlation between the magnitude of the positive Ce anomalies and the magnitude of MREE enrichment. This observation demonstrates the utility of REEs as tracers of anthropogenic influences (especially the influence of ASS drainage) in FeS- and organic-rich estuarine sediments.

1. Introduction

The rare earth elements (REEs) are a chemically similar group of elements that have been used extensively to trace geochemical processes and anthropogenic disturbances in natural systems (Elderfield and Sholkovitz, 1987; Wilde et al., 1996; Åström, 2001a; Haley et al., 2004; Davranche et al., 2005; Welch et al., 2009). While there are numerous studies that investigate rare earth element (REE) dynamics in surface waters and porewaters from a range of aquatic environments (Elderfield and Sholkovitz, 1987; Elderfield et al., 1990; Schijf et al., 1995; Åström, 2001a; Åström and Corin, 2003; Otsuka and Terakado, 2003; Haley et al., 2004; Johannesson et al., 2011), the cycling of REEs in estuarine sediments remains poorly understood.

Reduced sediments from eutrophic estuaries contain a heterogeneous mixture of organic matter, clays and carbonate minerals and can also be enriched in reactive iron sulfide species (Burton et al., 2006a,b,c; Morgan et al., 2012). In such systems, iron monosulfides generally consist of poorly crystalline FeS ('amorphous' Fes) and mackinawite (tetragonal FeS), with some more minor occurrences of greigite (Fe_3S_4) being possible (Rickard and Morse, 2005).

The reductive dissolution Fe (hydr)oxides in association with FeS formation in estuarine sediments has been recognised to release REEs in to overlying surface waters (Johannesson et al., 2011), emphasising geochemical interactions between the Fe and REE cycles. Furthermore,

* Corresponding author. Fax: +61 8 6488 1050.
E-mail address: morgab03@student.uwa.edu.au (B. Morgan).

0009-2541/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemgeo.2012.03.012

FeS is known to have a strong influence on contaminant behaviour, with trace metals from natural and anthropogenic sources adsorbing to, or coprecipitating with the solid phase (Arakaki and Morse, 1993; Simpson et al., 2000; Burton et al., 2006c). Despite this, to our knowledge there are currently no studies that specifically explore REE interactions with FeS as a mechanism for REE retention in sediments. The potential for sulfidic minerals to be a sink for REEs in marine sediments has been addressed briefly by a few field studies (Schijf et al., 1995; Chatillou et al., 2006). These studies suggest that sorption of REEs with iron sulfides may explain REE inclusion into benthic marine sediments. However, this has been proposed based on selective chemical extractions from field samples alone, and thus does not provide definite evidence for the importance of FeS–REE interactions.

Understanding sedimentary REE geochemistry is of particular importance in estuarine systems with increased REE loads from anthropogenic sources. For instance, the sub-aerial disposal of sediments dredged from estuarine systems is a common, but environmentally hazardous management strategy (Winger et al., 1999; Cappuyns et al., 2004; Clark and McConchie, 2004; Ohimain et al., 2004) that results in the oxidation of sulfides and the subsequent formation of acid sulfate soils (ASS) (Caille et al., 2003; Piou et al., 2009). Along with the production of acidic drainage rich in iron (Fe) and sulfate (SO_4^{2-}), ASS can also be a significant source of REEs feeding into receiving environments (Åström, 2001a; Åström and Corin, 2003; Welch et al., 2009; Åström et al., 2010; Gröger et al., 2011).

The objective of the current study was to examine REE retention and fractionation in FeS- and organic-rich estuarine sediments. For the first time, we specifically investigate the sorption of REEs to FeS as a possible mechanism for REE retention in FeS-rich estuarine sediments. We also compare sedimentary REE enrichment and fractionation in a variety of estuarine formation environments, including sites receiving ASS drainage.

2. Materials and methods

2.1. Study site description

The Peel–Harvey Estuarine System (PHES) is located on a coastal plain approximately 80 km south of Perth, Western Australia (Fig. 1). The PHES is a shallow system (generally <3 m water depth) and is surrounded by a variety of land uses, including urbanisation, agriculture, horticulture, and protected state forests (Brearley, 2005). This study site has a long history of issues associated with eutrophication, and more recently has been recognised to receive drainage from oxidising acid sulfate soils (Brearley, 2005; Degens, 2009). The sites, from which our sediment samples were collected, comprised a range of environments throughout the system. These formation environments were divided into the four categories of river, estuary, the South Yunderup main drain and the South Yunderup channel. Sites in the Serpentine and Murray Rivers are categorised as 'river', and the remainder of the sites that are not from either the South Yunderup main drain or South Yunderup channel are categorised as 'estuary'. The South Yunderup channel is a frequently dredged boating entrance to residential canals. The South Yunderup main drain is adjacent to an oxidising dredge spoil.

2.2. Field sample collection

2.2.1. Sediment and porewater

Intact sediment cores were collected from each site with the use of a polypropylene coring device. At Sites 2 and 9, three replicate cores were collected within a 1 m×1 m area to investigate field variability. At all other sites only a single core was collected, resulting in field replicates being collected for 20% of all samples. The length of cores varied between 4 cm and 25 cm, depending on our ability to penetrate the sediment with the coring device. The sediment from Site 11 was too fluid to be sectioned accurately, and accordingly the sediment at this site was collected from the upper 25 cm and homogenised as a bulk sample.

Following sediment retrieval, surface water was siphoned off and each core was extruded and rapidly (<2 min) sectioned into 2 cm (for the 0–10 cm depth) or 5 cm (for the 10–25 cm depth) segments. The segments were placed into thick, plastic zip-sealed bags with all air excluded. Immediately following, the sample was homogenised by manual manipulation of the bag for approximately 1 min. One corner of the bag was then cut away and the sediment samples were squeezed into 50 mL centrifuge tubes and sealed with no bubbles or headspace by a gas tight screw cap. Centrifuge tubes were transported on ice to the laboratory, and kept at 1–4 °C prior to being processed for analysis (within 12–24 h). Porewater was extracted from sediment samples by centrifuging at 4000 rpm and removing the resulting supernatant.

2.2.2. Surface water

The pH and redox potential (E_h) of the surface water overlying the sediment was recorded with calibrated electrodes. Depending on the surface water depth and visibility, these measurements were taken from the middle to bottom of the water column. Water was pumped from the same depth and filtered through a 0.45 μm syringe driven filter (Pall, Acrodisc supor membrane). Immediately following filtering, an aliquot of the sample was added to a sulfide preservation solution (20% zinc acetate in 2 mol/L NaOH) to precipitate dissolved sulfide ($\sum S^{2-}$, which includes H_2S, S^{2-}, HS^- and aqueous sulfide complexes) as ZnS. Another portion of the filtered water was immediately acidified to pH<2 with 50% (v/v) HNO_3 for subsequent analysis of total Fe (Fe^{2+}, Fe^{3+} and colloidal Fe species) and analysis of REEs. Samples were frozen prior to analysis.

2.3. Analyses

2.3.1. General preparation

All laboratory glassware was soaked in 10% (v/v) HCl for at least 24 h, and then rinsed a minimum of three times with Milli-Q water (18.2 MΩ.cm) prior to use. All chemicals used were of analytical grade and all reagents and standards were prepared in Milli-Q water. The sediment water content was determined by weight loss over 24 h at 105 °C, with sediment parameters reported herein on a dry weight basis. For total element determinations, sediment samples were dried in polypropylene tubes, and then finely ground into a powder. Dried ground samples were used for aqua regia digestion, as well as analysis of solid phase S and C. For all analysis, triplicate blank samples (Milli-Q water) were also analysed for quality control.

2.3.2. Porewater

Calibrated electrodes for pH (Cyberscan) and E_h (TPS) were inserted into an aliquot of the extracted porewater within a nitrogen filled glove-bag. The pH/E_h reading was recorded when a steady state was obtained. The E_h probe was calibrated against Zobell's solution and cleaned regularly with 0.1 mol/L HCl and micro-abrasive paper. E_h readings are reported in mV relative to the standard hydrogen electrode, SHE.

Additional porewater was passed through a syringe driven 0.45 μm filter (Pall, Acrodisc supor membrane); and this 'dissolved' fraction was divided into aliquots for analysis. One aliquot was preserved in a $\sum S^{2-}$ preservation solution prior to analysis of $\sum S^{2-}$ by the methylene blue method (Cline, 1969). A second porewater aliquot was acidified with HCl to pH<2 for analysis of DOC on a TOC 5000a analyser (Shimadzu, Kyoto, Japan). For these analyses, limited porewater resulted in a lack of laboratory replication; however median variability between replicate samples collected from individual site locations was 9% for $\sum S^{2-}$ and 11% for DOC.