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Acidic drainage drives anomalous rare earth element signatures in intertidal mangrove sediments

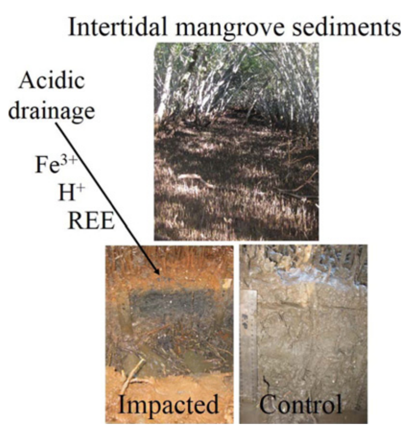
Bree Morgan [a,b,*], Scott G. Johnston [b], Edward D. Burton [b], Roslyn E. Hagan [b]

[a] School of Earth, Atmosphere & Environment, Monash University, Clayton, VIC 3800, Australia
[b] Southern Cross GeoScience, Southern Cross University, Lismore, NSW 2480, Australia

HIGHLIGHTS

- REE examined in intertidal sediments exposed to long-term (~20 y) acidic drainage
- Acidic drainage drives REE enrichment in reactive sediment fraction.
- Distinctive REE fractionation observed in sediments closest to acidic source
- REE signature reflects sediments rich in reactive Fe(III) due to acidic influence.
- Site uninfluenced by CASS has REE fractionation typical of coastal sediments.

GRAPHICAL ABSTRACT



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ABSTRACT

Sedimentary rare earth element (REE) signatures can provide powerful insights into nearshore biogeochemical processes and anthropogenic influences. Despite this, there is limited research investigating REE behaviour in sediments influenced by coastal acid sulfate soils (CASS). Here, we explore REE abundance and fractionation in intertidal mangrove sediments that received CASS drainage for ~15–20 y within the Hastings Catchment in NSW, Australia. Sediments close to the CASS discharge point (<200 m) were compared with those further downstream (1300–1600 m), and at a nearby control site. Average ΣREE concentrations were highest near the CASS discharge point (148–186 mg/kg), and decreased with distance downstream (111–146 mg/kg) and in control sediments (70 mg/kg). Reactive Fe concentrations (defined by 1 M HCl extractability) were also significantly higher in surface sediments (0–6 cm) near the CASS discharge point. Middle-REE (MREE) enrichments dominated fractionation patterns at all sites (>1.5), with a high proportion (63–100%) of REEs residing in the reactive (1 M HCl extractable) sediment fraction. Interestingly, the degree of MREE enrichment was significantly correlated with Ce anomalies ($r^2 = 0.72$, $P < 0.001$) and the heavy-REE (HREE) to light-REE (LREE) ratios (HREE/LREE, $r^2 = 0.74$, $P < 0.001$) in the reactive sediment fraction, only in those sites situated closest to the CASS drainage. The observed high MREE enrichments, positive Ce anomalies (>1) and HREE/LREE ratios (>1) are consistent with reactive Fe(III) oxides/oxyhydroxides driving REE retention in these sediments. This study indicates that CASS drainage alters REE signatures in receiving sediments by (1) providing a source of REEs, thereby enhancing sedimentary REE concentrations, and (2) causing accumulation of reactive Fe(III) phases with a high affinity for

* Corresponding author at: School of Earth, Atmosphere & Environment, Monash University, Clayton, VIC 3800, Australia.
E-mail address: bree.morgan@monash.edu (B. Morgan).

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REEs. Together, these two factors drive the development of distinctive REE signatures in CASS-impacted sediments. The recognition of such signatures may provide a promising tool for identifying coastal sediments receiving anthropogenic CASS drainage inputs.

1. Introduction

Rare earth element (REE) signatures can act as tracers of anthropogenic influences and provide powerful insights into sedimentary biogeochemical processes (Elderfield and Sholkovitz, 1987; Piper, 1974). Despite this, relatively few studies consider REE behaviour in estuarine and coastal sediments (Willis and Johannesson, 2011; Morgan et al., 2012; Chevis et al., 2015), which often act as sinks for inland-derived contamination. For example, mangrove sediments buffer coastal waters from terrestrially derived contaminants and promote accumulation of fine-grained, organic-rich sediments that act as physical and chemical traps for trace elements (Harbison, 1986; Clark et al., 1998; Tam and Wong, 2000; Bayen, 2012; Sappal et al., 2014). Although trace metal stores in mangrove sediments have been investigated extensively (Lacerda et al., 1993; Clark et al., 1998; Tam and Wong, 2000; Burton et al., 2005; Burton et al., 2006d; Burton et al., 2006b; Janaki-Raman et al., 2007; Marchand et al., 2011; Qiu et al., 2011; Banerjee et al., 2012; Bayen, 2012; Johnston et al., 2016), comparatively few studies consider REE behaviour in these dynamic, intertidal sedimentary environments (Prasad and Ramanathan, 2008; Silva-Filho et al., 2011; Zhang et al., 2013; Sappal et al., 2014). This is particularly true for mangrove sediments influenced by anthropogenic drainage from coastal acid sulfate soils (CASS).

CASS form due to oxidation of sediments containing natural sulfidic minerals, such as mackinawite (tetragonal FeS) and pyrite (cubic FeS_2). This produces sulfuric soils and acidic drainage rich in iron (Fe), sulfate (SO_4^{2-}), and trace metals (Åström, 1998; Johnston et al., 2004; Burton et al., 2006c; Burton et al., 2006a; Macdonald et al., 2007; Nordmyr et al., 2008), resulting in degradation of both on-site and off-site ecosystems (Astrom, 2001; Preda and Cox, 2001; Powell and Martens, 2005). Additionally, REEs can be mobilised under acidic conditions, with enrichments widely-documented in surface waters (Åström, 2001; Astrom, 2001; Åström and Corin, 2003; Cao et al., 2001; Gammons et al., 2005; Fernández-Caliani et al., 2009), and to a lesser-extent in submerged surface sediments of CASS influenced coastal systems (Morgan et al., 2012).

However, REE behaviour and abundance is poorly constrained in intertidal mangrove sediments receiving CASS drainage and this represents a significant gap in our understanding of REE cycling in coastal sedimentary systems. Mangrove sediments are influenced by a complex combination of physical (tides) and biological factors (microbial, bioturbation, root activity e.g. (Otero et al., 2009)). These factors have the potential to influence physiochemical conditions (i.e. pH, Eh) and subsequent transport, immobilisation, remobilisation and fractionation of REEs - both on-site and in downstream receiving environments.

In addition, significant shifts in sedimentary Fe and S cycling have recently been reported in intertidal mangrove sediments receiving long-term (~15–20 y) CASS drainage (Johnston et al., 2016). This is important given the known influence of sedimentary Fe speciation on REE cycling (Elderfield et al., 1981; Quinn et al., 2006; Willis and Johannesson, 2011), and the limited understanding of S-REE interactions (Morgan et al., 2012). Hence, mangrove sediments influenced by CASS drainage offer a unique opportunity to explore REE signatures in the dynamic setting of intertidal sediments. In this study, we investigate REE abundance and fractionation patterns in sediments with altered Fe and S biogeochemistry as a result of a prolonged CASS drainage influence. We hypothesised that sedimentary REE signatures in coastal mangrove systems would provide an indicator of sites receiving acute contamination from an inland source, such as a CASS wetland.

2. Materials and methods

2.1. Study site description

The study site is located on the Hastings River, ~5 km west of Port Macquarie in NSW, Australia (Fig. 1), where the climate is sub-tropical and average annual rainfall is ~1400 mm. The estuarine floodplain has a history of extensive drain manipulation dating back to the early 1900s. Exposure of previously saturated soils to the atmosphere has caused widespread (542 ha) oxidation of natural sulfidic minerals and production of acid sulfate drainage, resulting in the classification of Partridge Creek wetland as a CASS hotspot.

Partridge Creek wetland is connected to Fernbank Creek via an artificial drain, from which there is a seasonal discharge of surface water into the Hastings River (Fig. 1). It has been estimated that ~860–1100 t of acid has been discharged annually into the Hastings River (via Fernbank Creek), from the Partridge Creek CASS hotspot. Prior to remediation there were regular occurrences of acidic (pH < 4) discharge, with Al and Fe concentrations (>5 mg/L) exceeding regulatory ecological guidelines (ANZECC and ARMCANZ, 2000). Remediation efforts, including the application of lime ($CaCO_3$), infilling of artificial drains and the installation of a weir to decrease groundwater discharge, commenced in 2001 and were complete in December 2003. It has been estimated that since 2004 there has been a 67–79% decrease in acidic

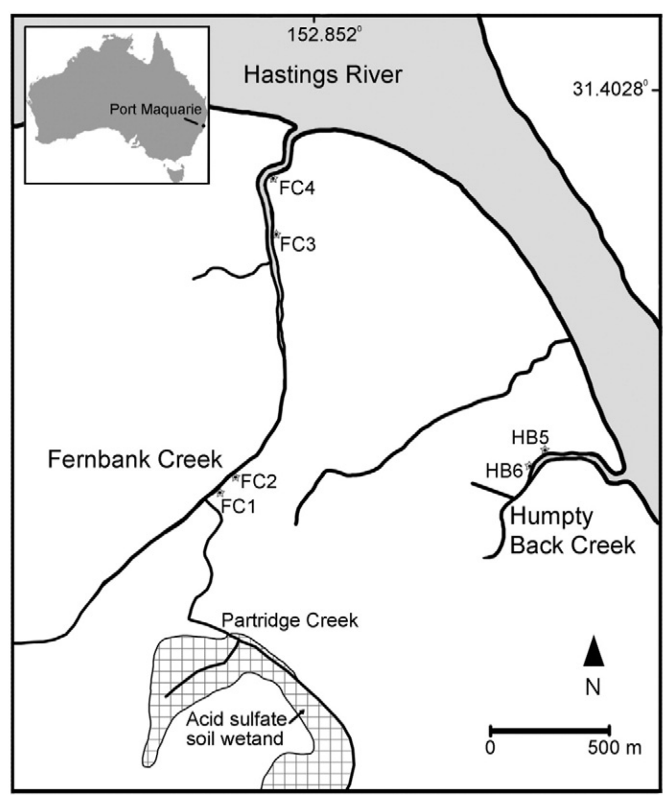

Fig. 1. Map of the study site with sediment collection points marked for CASS influenced Sites FC1–FC4 and reference sites HB5–HB6. The acid sulfate soil wetland influencing Partridge Creek is also visible.