Iron monosulfide accumulation and pyrite formation in eutrophic estuarine sediments

Peter Kraal [*], Edward D. Burton, Richard T. Bush

Southern Cross GeoScience, Southern Cross University, PO Box 157, Lismore, 2480 NSW, Australia

Abstract

This study investigates iron (Fe) and sulfur (S) cycling in sediments from the eutrophic Peel–Harvey Estuary in Western Australia, which is subject to localized accumulation of strongly reducing, organic- and sulfide-rich sediments. Sedimentary iron was mostly present in highly reactive form (on average 73% of total Fe) and showed extensive sulfidization even in surface sediments, despite being overlain by a well-mixed oxygenated water column. This indicates that, under eutrophic marine conditions, Fe sulfidization may be driven by reductive processes in the sediment without requiring oxygen depletion in the overlying waters. Strong enrichments in iron monosulfide (FeS > 300 μmol g^{-1}) were observed in fine-grained sediment intervals up to 45 cm depth. This metastable Fe sulfide is commonly restricted to thin subsurface sediment intervals, below which pyrite (FeS$_2$) dominates. Our findings suggest inhibition of the dissolution–precipitation processes that replace FeS with FeS$_2$ in sediments. Rates of pyrite formation based on the FeS$_2$ profiles were much lower than those predicted by applying commonly used kinetic equations for pyrite formation. Dissolved H$_2$S was present at millimolar levels throughout the investigated sediment profiles. This may indicate that (i) pyrite formation via reaction between dissolved Fe (including Fe clusters) and H$_2$S was limited by low availability of dissolved Fe or (ii) reaction kinetics of pyrite formation via the H$_2$S pathway may be relatively slow in natural reducing sediments. We propose that rapid burial of the FeS under anoxic conditions in these organic-rich reducing sediments minimizes the potential for pyrite formation, possibly by preventing dissolution of FeS or by limiting the availability of oxidized sulfur species that are required for pyrite formation via the polysulfide pathway.
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1. INTRODUCTION

Formation and burial of iron sulfide minerals in sediments is the main pathway by which iron (Fe) and sulfur (S) are removed from the marine reservoir (Berner, 1970; Raiswell and Berner, 1985). Variations in iron sulfide burial have affected the bioavailability of the key elements Fe and S as well as the global coupled carbon–oxygen–sulfur biogeochemical cycles over geological timescales throughout Earth's history. In the first step of iron sulfide formation,

iron monosulfide (FeS) precipitates in the reducing sediment subsurface by reaction between dissolved ferrous Fe and sulfide. This FeS is ubiquitous in surficial marine sediments, but is generally rapidly replaced by the stable diagenetic end-member pyrite (FeS$_2$) by dissolution of FeS and subsequent reaction with dissolved H$_2$S or intermediate oxidation state sulfur species such as polysulfides (Rickard, 1975; Rickard and Luther, 1997). As a result, FeS$_2$ constitutes the principal long-term marine sink for Fe and S (Berner, 1970).

Both FeS and FeS$_2$ are important sinks for (toxic) trace elements during anoxic sediment diagenesis through adsorption and coprecipitation processes, thereby playing a crucial role in regulating the mobility and bioavailability of such elements in natural systems (Morse et al., 1987; Di Toro et al., 1990; Morse, 1994; Burton et al., 2006a). As

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* Corresponding author. Current address: Department of Earth Sciences – Geochemistry, Faculty of Geosciences, Utrecht University, Budapestlaan 4, 3584 CD Utrecht, The Netherlands. Tel.: +31 30 2535016.

E-mail address: pkraal1980@gmail.com (P. Kraal).

such, understanding sedimentary Fe–S dynamics under reducing conditions is not only of great environmental relevance, but also crucial for accurate interpretation of the links between sediment geochemistry and depositional conditions in ancient sediment records. Elevated ratios of highly reactive Fe – i.e. Fe that is not sequestered in refractory clay minerals, but is or has been involved in geochemical (redox) cycling – to total Fe (>0.38) and sulfidized Fe to highly reactive Fe (>0.7–0.8) have been linked to sediment deposition under anoxic or euxinic (i.e. containing free dissolved sulfide) waters, respectively (Raiswell et al., 1988; Raiswell and Canfield, 1998; Poulton and Raiswell, 2002; Anderson and Raiswell, 2004; Poulton and Canfield, 2011). Detailed characterization of Fe fractionation in modern sediments is important to increase our understanding of the links between oxygenation of overlying waters and sediment Fe redox chemistry.

While FeS is generally regarded as a transient iron sulfide species, anomalous enrichments have been observed in various reducing freshwater and marine systems. Such enrichments have been attributed to the retardation of pyrite formation by numerous physicochemical factors, particularly depletion of H_2S by rapid FeS formation in Fe-rich systems (Boesen and Postma, 1988; Gagnon et al., 1995; Burton et al., 2006b) and slow reaction between FeS and H_2S under strictly anoxic conditions (Schoonen and Barnes, 1991; Hurtgen et al., 1999; Benning et al., 2000). Other factors, such as competition for reactants by organic compounds and conversion of H_2S to HS^- at high pH, may also affect the rate and extent of pyrite formation (Morse and Wang, 1997; Morse, 1999; Luther, 2005; Rickard and Morse, 2005).

Eutrophic estuaries offer great potential for sedimentary iron sulfide formation; abundant reactive Fe is delivered in riverine input, and high organic matter loading drives benthic oxygen depletion. Accumulation of FeS is of great environmental importance in shallow coastal systems, as sediments are relatively easily disturbed and oxidation of the highly reactive FeS can have severe negative impacts due to the potential for deoxygenation, acidification and metal release (Burton et al., 2009; Morgan et al., 2012b). Iron monosulfide enrichments have been observed in eutrophic estuaries, and have been linked to inhibition of pyritization by high sedimentation rates (Machado et al., 2004) and high concentrations of dissolved organic compounds that complex dissolved FeS (Morgan et al., 2012a). However, detailed studies linking physicochemical sediment properties to FeS accumulation remain scarce. As such, the accumulation of FeS in coastal marine systems remains incompletely understood.

In this study, we investigate Fe and S cycling in sediments from the shallow eutrophic Peel–Harvey Estuary in Western Australia. Detailed geochemical porewater and solid-phase analyses are combined with particle size analyses to elucidate the relative importance of and interaction between physical and chemical sediment properties in controlling the sedimentary biogeochemical cycles of Fe and S. Our results reveal tight coupling between physical factors

such as grain size distribution and the chemical forms and abundance of sedimentary Fe and S.

2. MATERIALS AND METHODS

2.1. Site description and field sampling

The Peel–Harvey Estuary is a semi-restricted estuarine water body in southwest Western Australia (Fig. 1). The estuary is shallow with an average depth of $\sim$2 m and is eutrophic due to anthropogenic nutrient inputs from the surrounding developed land (Lenanton et al., 1985; Lukatelich and McComb, 1986; McComb and Lukatelich, 1995). In March 2011, the water column and sediment were investigated at several sites (Fig. 1). Sites 2 and 3 were located in navigation channels in the Peel Inlet near the mouths of the Serpentine River and Murray River. Site 6 was situated in a navigation channel in the Harvey Estuary. Site 8 was a control site, located away from navigation channels, representative of the 'normal' estuary bottom. The water depth at all sites was between 1.5 and 2 m. Water column properties such as dissolved oxygen (DO) were measured at various intervals throughout the water column using a Hydrolab DataSonde 5. At each site, sediment cores between 40 and 70 cm length were collected with overlying water using a 1-m stainless steel coring device (5 cm diameter). The sediment cores were immediately capped, put on ice and transported back to the laboratory for further processing.

2.2. Porewater and solid-phase analyses

Within 6 h of collection, sediment cores were sectioned at 3-cm intervals into 50 mL polypropylene centrifuge tubes. Porewater was extracted by centrifugation at 4000 rpm for 20 min and filtered over 0.45 μm. Small aliquots of filtered porewater were immediately dispensed into cuvettes with trapping solutions for the colorimetric determination of alkalinity (bromophenol blue method: Sarazin et al., 1999), dissolved Fe^{2+} (1,10-phenanthroline method: APHA, 2005), dissolved inorganic phosphate, DIP (molybdenum blue method: Strickland and Parsons, 1972), and dissolved total sulfide, ΣS^{2-} (methylene blue method: APHA, 2005). The pH and E_h (reported against standard hydrogen electrode) in the centrifuged sediment were determined concurrently, after which the tubes with sediment were purged with N_2 and frozen at $-20\,°C$ prior to further processing. An aliquot of the remaining filtered porewater was frozen and later used for determination of NH_4^+ ($NH_3 + NH_4^+$), NO_3^- and NO_2^- with a flow-injection nutrient analyzer (APHA, 2005). A second aliquot was acidified to pH < 1 with 32% HCl and frozen, and later used for SO_4^{2-} determination by ion chromatography. A third aliquot of filtered porewater was acidified to pH 2 with 5 M HCl and stored at $4\,°C$ prior to DOC analysis using a Shimadzu TOC 5050. Separate wet samples were taken with 5 mL syringes to determine dry and wet bulk density.

Later, the frozen sediment residues were allowed to thaw in an oxygen-free chamber with an atmosphere of 95% N_2