



Research article

Oxidative transformation of iron monosulfides and pyrite in estuarine sediments: Implications for trace metals mobilisation



Girish Choppala^{a,*}, Richard Bush^a, Ellen Moon^a, Nicholas Ward^a, Zhaohui Wang^a,
Nanthi Bolan^b, Leigh Sullivan^a

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

^b Global Centre for Environmental Remediation (GCER), University of Newcastle, Callaghan Campus, 2308, NSW, Australia

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ABSTRACT

Iron monosulfides are the initial iron sulfide minerals that form under reducing conditions in organic-rich sediments. Frequently referred as monosulfidic black ooze (MBO), these sediments exist in a range of anoxic systems including estuaries, coastal wetlands and permeable reactive barriers. The objective of this study was to investigate the transformation of solid phase sulfur, iron fractions and trace metals mobilisation in organic-rich hypersulfidic sediments during dredging. Two sediments from geographically contrasting sites in the Peel-Harvey Estuary were collected and subjected to oxidation through resuspension over 14 days. During oxidation, redox potential rapidly and continuously increased, although minimal change in pH was observed in both sediments. The majority of FeS was oxidised within 48 h. Although not as dynamic as FeS, unusually high rates of FeS₂ oxidation were measured in both sediments at circumneutral pH, with between 39 and 58% of FeS₂ oxidised over 14 days. The rapid oxidation of FeS₂ may be attributed to the presence of nano-size FeS₂ crystals (≈ 550 – 860 nm) with a high surface area. Before resuspension, solid bound Fe(total) was most abundant as measured by HCl-extractable Fe(II), followed by organic bound Fe(total) and oxide bound Fe(total). There was a marked decrease in these three fractions in both sediments during resuspension, with an increase in Fe(III) fraction. No significant release of trace metals was observed during resuspension of sulfidic sediments. However, disturbance to these estuarine sediments increases Fe(III) formation and further deteriorates the environment through smothering biological surfaces, deteriorating food sources and the quality of benthic habitats.

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1. Introduction

Iron sulfides form in diverse anoxic and sub-oxic environments as a result of the metabolic activity of sulfate reducing bacteria (Berner, 1984). Iron monosulfides (FeS) including mackinawite, pyrrhotite and greigite vary in form, occur in organic rich anoxic sediments and are highly reactive (Bush et al., 2004a; Rickard and Luther, 2007). The first FeS phases formed in sedimentary systems are metastable, nano-particulate mackinawite with a Fe/S ratio of 1:1 (Wolthers et al., 2005). In addition to the presence of iron and sulfur, the formation of FeS in sediments requires sufficient amounts of reducing agents such as organic carbon. Sulfide, produced through the oxidation of organic matter by sulfate reducing

bacteria, reacts with Fe(II) to form insoluble FeS (Berner, 1984; Rickard, 1995).

Mackinawite and greigite can be converted to pyrite under anoxic conditions (Hurtgen et al., 1999), however, the formation and existence of greigite in aqueous systems has not been recognized (Rickard and Luther, 2007). Amorphous FeS is largely responsible for the black colour of the anoxic sediments, and monosulfidic black oozes (MBOs) (organic matter also contributes to this colour). Thick layers (0–45 cm) of MBO accumulate in estuaries, wetlands and waterways associated with eutrophication, acid sulfate soils and salinisation (Bush et al., 2004b; Sullivan et al., 2002).

Hyper-accumulation of monosulfides is attributed to a number of factors, particularly depletion of H₂S by rapid FeS formation in Fe rich sediments (Burton et al., 2006a, b) and the slow reaction between FeS and H₂S in anoxic environments (Benning et al.,

* Corresponding author.

E-mail address: girish.choppala@scu.edu.au (G. Choppala).

2000). These sediments are important sinks for toxic trace metals such as cadmium and lead during sediment diagenesis through sorption and co-precipitation reactions (Smith and Melville, 2004).

The availability and speciation of iron in estuary sediments has major control on synergetic and diagenetic pyrite formation in modern depositional settings (Poulton and Canfield, 2005). The formation of different Fe phases are influenced by redox conditions, quantity and quality of organic matter and sedimentation rate (Raiswell and Canfield, 2012). Furthermore, the reactivities of solid phase Fe in marine sediments influence the mineral heterogeneity and crystallinity and have a major impact on the speciation of trace elements. For example, reactive Fe(III) oxides act as an important sink for the phosphate and metal pollutants in oxic marine sediments (Zhu et al., 2012). Therefore, understanding the speciation and transformation of Fe and their influence on aquatic environments is an important domain of research (Raiswell and Canfield, 2012).

The rapid development in boat traffic in the Peel-Harvey Estuary has demanded channel excavation for safe navigation. Earlier studies have confirmed a substantial accumulation of MBOs in Peel-Harvey Estuary channels (Morgan et al., 2012a; Kraal et al., 2013). These channels contain fine silty materials enriched with organic matter and are known hotspots for MBO formation. Contaminated metals often accumulate in the sediments and extracted back into the water column through dredging induced resuspension and bioturbation (Kim et al., 2016).

Previous studies have focused on total iron content and spatial variability and distribution in sediments. Burton et al. (2006b) and Morgan et al. (2012b) demonstrated the negative impacts from the resuspension of FeS. However, to date, no systematic study has been carried out on speciation of solid state Fe, mineralogical transformation, and dissolved trace metals in water column during the resuspension of hypersulfidic sediments.

In this study we examined the oxidative transformation of iron species in MBO materials from Peel-Harvey Estuary, Western Australia. Sediments from two contrasting sites in the Peel-Harvey Estuary were collected and resuspended in the laboratory over a 14 day period. Water quality parameters (pH and redox potential) and detailed sulfur speciation (acid volatile sulfide, elemental sulfur and chromium reducible sulfur) and solid phase changes of iron (acid soluble, reactive-organic bound, crystalline and pyritic) were measured Table 1.

Table 1
Physico-chemical properties of sediments used in oxidation experiment.

Properties	Site 1	Site 2
pH	7.21	7.37
Redox potential (mV)	−9	37
Moisture content (% wt wt ^{−1})	54	50
Total organic carbon (%C)	2.9	2.5
Total inorganic carbon (%C)	2.6	1.9
Acid volatile sulfur (μmol g ^{−1})	121.8	21.7
Elemental sulfur (μmol g ^{−1})	43.2	38.1
Chromium reducible sulfur (μmol g ^{−1})	115.7	157.1
Iron (total) (μmol g ^{−1})	333	403
Nickel (μg g ^{−1})	5.9	6.4
Manganese (μg g ^{−1})	77.8	43.8
Lead (μg g ^{−1})	11.9	9.7
Zinc (μg g ^{−1})	20.7	17.8
Cadmium (μg g ^{−1})	0.1	0.0
Copper (μg g ^{−1})	8.7	7.1
Arsenic (μg g ^{−1})	0.8	0.3
Chromium (μg g ^{−1})	5.7	6.2

2. Materials and methods

2.1. Estuarine sediment sampling

The Peel-Harvey Estuary is located at Mandurah, 70 km south-west of Perth, Western Australia (Fig. 1a). This estuary covers an area of approximately 136 km² with an average depth of 1.2–2.0 m and is fed by three river systems including the Murray, the Harvey and the Serpentine. The estuary is surrounded by agricultural, farming lands, urban areas that discharge large quantities of nutrients, eventually leading to eutrophication and algal blooms (Brearley, 2005). The sediments of this estuary are often enriched with organic matter (3–6%) and iron monosulfides (acid volatile sulfide (AVS) content $\geq 300 \mu\text{mol g}^{-1}$) (Morgan et al., 2012a). Site 1 (32°34'54.3S, 115°45'37.2E) is located within the navigational channel, and has both MBO and non-MBO sediments. Site 2 (32°35'50.5S, 115°42'79.2E) is located away from the navigation channel, and is representative of the estuary, with lower MBO concentrations (AVS $< 20 \mu\text{mol g}^{-1}$) (Fig. 1b). The Peel-Harvey Estuary surface sediment samples (3 subsamples at each site) were collected with a grab sampler. The pH and redox potential (Eh) of fresh sediments were measured immediately after sampling using HACH HQd portable meters (USA) with freshly calibrated probes. Immediately after collection the surface sediment samples were stored in glass containers with no headspace to maintain anoxic conditions, then transferred to the laboratory and frozen until use.

2.2. Experimental setup

Sediment pH and Eh were determined using calibrated probes. The Eh measurements are reported relative to the standard hydrogen electrode (SHE). Moisture content was measured after drying the sediments at 105 °C until no change in weight was observed. Particle size distribution was analysed by laser diffraction (Malvern Mastersizer Hydro 2000MU, UK) using the protocol described in Kraal et al. (2013). Sediment preparation for the laboratory experiment was performed under N₂ in an anaerobic chamber to minimise oxidation artefacts.

2.3. Oxidation of hypersulfidic sediments

Frozen sediments from both sites were thawed and homogenised in an anaerobic chamber. Wet sediment (5 g) was transferred into 50 mL Falcon tubes in the anaerobic chamber and mixed with 25 mL of artificial sea water (ASW) (L^{−1}: 25.0 g NaCl; 1.0 g MgCl₂·6H₂O; 5.0 g MgSO₄·7H₂O; 0.7 g KCl; 0.15 g CaCl₂·2H₂O; 0.5 g NH₄Cl; 0.1 g KBr; 0.27 g KH₂PO₄; 0.04 g SrCl₂·6H₂O; 0.025 g H₃BO₃) (ASTM, 2003). Subsequently, for abiotic oxidation experiments, sodium azide (6.5 g L^{−1}) treated ASW was used. The tubes were left opened under regular atmospheric pressure and placed on a shaking table (130 rpm). Sub-samples were removed periodically (1, 8, 12, 24, 48, 120, 168 and 336 h), centrifuged at 1472 g for 20 min, and filtered (0.45 μm). The liquid phase was immediately analysed for pH and Eh. Immediately after filtering, aliquot of the water samples were acidified with reagent grade HCl and stored in refrigeration until further analyses. Concentrations of Ni, Mn, Pb, Zn, Cd, Cu, As and Cr were analysed by ICP-OES (Perkin Elmer 4300DV, USA). The solid phase was frozen for further analysis. A control sample containing 5 g of wet sediment and 25 mL of N₂ purged ASW was sealed and kept in an anaerobic chamber.

2.4. Solid phase analyses

Reduced inorganic sulfur (RIS) species (including AVS, elemental sulfur (ES) and chromium reducible sulfur (CRS)) were quantified

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