

# Importance of microbial iron reduction in deep sediments of river-dominated continental-margins



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## ABSTRACT

Remineralization of organic carbon in deep-sea sediments is thought to proceed primarily via aerobic respiration and sulfate reduction because the supply of nitrate and metal oxides is not usually significant in deep-sea sediments. Dissimilatory metal reduction, on the other hand, may represent a dominant pathway in coastal and continental shelf sediments where delivery of terrigenous Fe(III) and Mn(IV/III) oxides is sufficiently high or where physical mixing processes near the sediment–water interface can result in the reoxidation of Fe<sup>2+</sup> or Mn<sup>2+</sup>. Passive continental margin sediments receiving outflow from large rivers are well-known deposition centers for organic carbon and may also be hotspots for metal-reducing microbial activity, considering the simultaneous rapid deposition of unconsolidated metal oxides of terrigenous origin. Despite its potential, only a few studies have examined the role of microbial metal reduction in C<sub>org</sub> remineralization in these environments. To investigate carbon remineralization processes in continental margin sediments, shallow cores across channels and levees in the Congo River fan (~5000 m) and Louisiana slope (<1800 m) were profiled for the main redox species involved in early diagenesis using a combination of voltammetric gold mercury (Au/Hg) microelectrodes and conventional analyses. Interestingly, metal reduction dominated carbon remineralization processes in the top ~20 cm of sediment subject to high deposition, while evidence for sulfate reduction was lacking. These findings suggest that dissimilatory Fe(III) reduction may be more significant than previously thought in continental slope sediments, which may have important implications on carbon cycling in marine environments. In addition, these findings may have geological implications in controlling atmospheric oxygen levels over geological time and the evolution of microbial life on Earth.

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## 1. Introduction

The magnitude and lability of organic carbon (C<sub>org</sub>) exported to marine sediments are generally inversely related with the depth of the overlying waters, due to increasing exposure time of marine and terrestrially derived C<sub>org</sub> to degradation processes and decreasing terrestrial inputs further from shore (Hedges et al., 1997; Honjo et al., 2008). In deep-sea sediments, where the flux and lability of organic carbon are usually low, C<sub>org</sub> oxidation is coupled almost entirely to the reduction of O<sub>2(aq)</sub> (the most thermodynamically favorable terminal electron acceptor; TEA), which may penetrate deeper than 1 m into sediments (Bowles et al., 2014; Cai and Reimers, 1995; Grundmanis and Murray, 1982; Rabouille and Gaillard, 1991), while anaerobic respiration processes such as dissimilatory NO<sub>3</sub><sup>-</sup>, Fe(III), Mn(IV/III), and SO<sub>4</sub><sup>2-</sup> reduction are relatively minimal or have little impact on

carbon transformation (Jorgensen, 1982; Bender and Heggie, 1984; Slomp et al., 1997). On the other hand, high C<sub>org</sub> remineralization rates in coastal sediments with higher deposition rates result in O<sub>2(aq)</sub> being consumed faster than it can diffuse into sediments. C<sub>org</sub> remineralization then proceeds primarily through SO<sub>4</sub><sup>2-</sup> reduction (Jorgensen, 1982) or through Fe(III) or Mn(IV) reduction (Meiggs and Taillefert, 2011; Thamdrup et al., 2000) if the areas receive significant terrigenous minerals (i.e. >30 μmol cm<sup>-3</sup> reactive Fe; Thamdrup et al., 2000) or their reduced products, H<sub>2</sub>S, Fe<sup>2+</sup> and Mn<sup>2+</sup>, are reoxidized by O<sub>2(aq)</sub> supplied by advection (Taillefert et al., 2007b) or macrofaunal bioturbation (Aller and Blair, 2006; Canfield et al., 1993; Jensen et al., 2003; Thamdrup et al., 2000). Relative to regions dominated by aerobic respiration, these regions may represent preservation centers (i.e. burial sites) for C<sub>org</sub> because deposition may be more rapid than processing by microorganisms (Canfield, 1994) and anaerobic respiratory processes are less efficient at processing the more refractory, terrestrially derived C<sub>org</sub> fraction (Hedges and Oades, 1997; Hartnett et al., 1998).

To better constrain global C budgets, total C<sub>org</sub> remineralization rates and extents should be quantified in sediments from a variety of

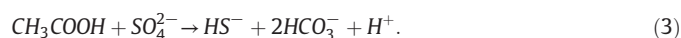
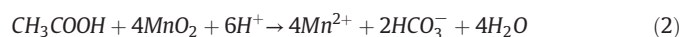
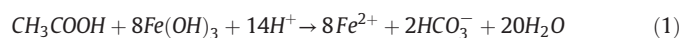
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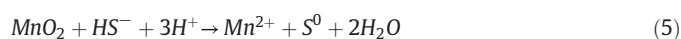
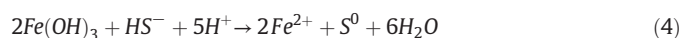
locations, depositional environments, and circulation regimes (Thullner et al., 2009). Interestingly, relatively high rates of  $C_{org}$  deposition have been observed in deep-sea sediments in specific regions at the base of continental slopes (Haese et al., 2000; Jahnke et al., 1990; Law et al., 2009; Rabouille et al., 2009; Schulz et al., 1994) and in sediments underlying waters where local circulation features may stimulate  $C_{org}$  deposition, including upwelling regions (Ferdelman et al., 1999; Haeckel et al., 2001; Thamdrup and Canfield, 1996), semi-enclosed basins (Lee et al., 2008), and even in the deepest trench on earth (Glud et al., 2013). These findings suggest anaerobic remineralization may be significant and that these areas could represent significant  $C_{org}$  burial sites (Canfield, 1994). Sulfate reduction is generally considered to be the primary pathway of anaerobic respiration in these sediments (e.g. Ferdelman et al., 1999; Grant et al., 1998; Lee et al., 2008; Lin et al., 2002; Lin and Morse, 1991), despite the fact that only a few studies have examined the role of Fe(III) reduction (Haese et al., 2000; Law et al., 2009; Nedelec et al., 2007; Thamdrup and Canfield, 1996; van der Zee et al., 2002).

In river-dominated ocean margins (RiOMars), suspended sediment and  $C_{org}$  may be discharged much farther than deltas and subsequently influence sediment biogeochemistry down continental slopes or even in deep-sea fans underlying slopes (McKee et al., 2004). These regions may also accumulate terrigenous minerals because of their close connection to land, allowing  $C_{org}$  remineralization to proceed via microbial Fe(III) and Mn(IV) reduction. For instance, the Louisiana slope (LAS) is subject to frequent mass slumping of spillover mud discharged from the Mississippi River (Bea et al., 1983; Bianchi et al., 2006) and produces unconsolidated clay and  $C_{org}$  rich deposits mid-slope at 1000 m depth (Coleman et al., 1998; Dixon and Weimer, 1998; Konyukhov, 2008). On the other hand, the Congo River Fan (CRF) is the only deep-sea fan in the world still directly connected to a large river through a submarine canyon (Babonneau et al., 2002). This unique geological feature generates frequent turbidite flows that deliver  $C_{org}$  rich mud and clay-sized particles to the abyssal plain at depths approaching 5000 m water depth (Babonneau et al., 2002; Rabouille et al., 2009).

As  $SO_4^{2-}$  reduction is able to remineralize two moles of carbon per mole of sulfate, assuming an average oxidation state of  $C^0$  in organic carbon (e.g. Eq. (3) with acetate as electron donor), whereas two moles of Mn(IV) and four moles of Fe(III) are required to remineralize one mole of carbon (Eqs. (1) and (2)), it is important to assess which of these anaerobic processes dominates in continental slope sediments:



Unfortunately, measurement of the reduced products of anaerobic respiration is not a definitive indicator for metal or  $SO_4^{2-}$  reduction activity, as metal oxides may also be reduced abiotically by  $\Sigma H_2S$  (Eqs. (4) and (5); Canfield et al., 1992), and  $\Sigma H_2S$  may also be removed from pore waters by precipitation with  $Fe^{2+}$  (Eq. (6); Pyzik and Sommer, 1981) and during the subsequent precipitation of pyrite (Eq. (7); Rickard and Luther, 1997):



In addition, changes in  $SO_4^{2-}$  concentrations may be too small to be detected in seawater. The detection of both  $\Sigma H_2S$  and aqueous

$FeS_{(aq)}$  clusters as a function of depth in sediments using gold/mercury (Au/Hg) voltammetric microelectrodes (Brendel and Luther, 1995; Luther et al., 2008; Taillefert et al., 2000b), however, may provide indirect evidence for  $SO_4^{2-}$  reduction.  $FeS_{(aq)}$  clusters are in equilibrium with an amorphous  $FeS_{am}$  solid that eventually converts to mackinawite ( $FeS_s$ ; Rickard and Morse, 2005; Theberge and Luther, 1997) and are also expected to be precursors to pyrite mineral formation (Rickard and Luther, 1997). These  $FeS_{(aq)}$  complexes have been detected in a variety of sediments at the transition between metal- and sulfate-reducing conditions (Rickard et al., 1999; Taillefert et al., 2002a,b; Carey and Taillefert, 2005), suggesting they could be used in addition to  $\Sigma H_2S$  to locate the sulfate reduction zone. In addition, Au/Hg voltammetric microelectrodes are able to detect organic complexes of Fe(III) (Taillefert et al., 2000a), which are pervasive in coastal sediments dominated by metal reduction (e.g. Jones et al., 2011; Meiggs and Taillefert, 2011; Taillefert et al., 2002a,b, 2007b). As the reactivity of these complexes with  $\Sigma H_2S$  is extremely fast (Taillefert et al., 2000a), their presence in pore waters may provide evidence that  $SO_4^{2-}$  reduction is not ongoing.

In this study, we present new evidence for the importance of microbial metal reduction in deep continental margin sediments based on voltammetric microelectrode depth profiles combined with conventional measurements in both the dissolved and solid phases. These data were collected in two river-dominated regions near the Mississippi and the Congo Rivers currently receiving massive terrigenous deposits. The dataset is used to discuss the relative importance of  $SO_4^{2-}$  reduction and dissimilatory metal reduction in deep RiOMar sediments receiving significant  $C_{org}$  and reactive terrigenous inputs.

## 2. Study sites

Sediment cores (9.6 cm ID × 70 cm) from the LAS were obtained using a multicorer (MC-800, Ocean Instruments) during a cruise on the R/V *Cape Hatteras* (University System of North Carolina, NC) in July 2012. Sediments were collected across a depth transect from the continental shelf (stations GOM2, 65 m and GOM3, 128 m) to the middle of the continental slope (GOM12, 980 m), and finally at the base of the slope (GOM10, 1777 m) (Fig. 1a). Station GOM2 experiences recurring bottom water hypoxia (<2 mg  $O_2$   $L^{-1}$ , ~63  $\mu M$ ) associated with summertime eutrophication (Rabouille et al., 2008; Obenour et al., 2013). Bottom waters at station GOM3 are only rarely hypoxic, whereas GOM10 and GOM12 are outside the hypoxic zone. These stations were selected to represent areas where  $SO_4^{2-}$  reduction is active (hypoxic zone) in addition to slope sediments where metal reduction may dominate. However, at the time of sampling, water column hypoxia was not observed at any of the LAS stations. Sediment cores (9.6 cm ID × 70 cm) from the Congo River fan (CRF) were obtained using a multicorer from 3 stations approaching 5000 m depth and up to 800 km offshore (Fig. 1b) during a cruise on the N/O *Pourquoi Pas?* (Ifremer, Brest, France) from December 2011 to January 2012. CRF stations (Rabouille and Congolobe-group, submitted for publication) are located along a transect from an extinct channel no longer receiving turbidite flows (CoLE, 4750 m), to a station ~10 km north from the active channel (CoLB, 4823 m), and to a station directly on the present channel levee (CoLA, 4759 m) which shows high OC content (Stetten et al., 2015).

## 3. Methods

### 3.1. Analyses

Depth profiles of dissolved  $O_{2(aq)}$ ,  $Fe^{2+}$ , organic-Fe(III) complexes,  $\Sigma H_2S$  ( $=H_2S + HS^- + S(0) + S_x^{2-}$ ), aqueous FeS clusters ( $FeS_{(aq)}$ ), and pH were obtained using solid-state Au/Hg voltammetric microelectrodes (Luther et al., 2008; Taillefert et al., 2000b) and needle combination pH microelectrodes immediately after retrieval of intact cores (Meiggs and Taillefert, 2011). Both measurements were conducted

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