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 Fe²⁺ or Mn²⁺. 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_{org} remineralization in these environments. To investigate carbon remineralization processes in continental margin sediments, shallow cores across channels and levees in the Congo River fan (~5,000 m) and Louisiana slope (<1,800 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.

1. INTRODUCTION

The magnitude and lability of organic carbon (C_{org}) exported to marine sediments is generally inversely related with the depth of the overlying waters, due to increasing exposure time of marine and terrestrially derived C_{org} 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_{org} oxidation is coupled almost entirely to the reduction of $O_{2(aq)}$ (the most thermodynamically favorable terminal electron acceptor; TEA), which may penetrate deeper than 1 meter 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_3^- , Fe(III), Mn(IV/III), and SO_4^{2-} 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_{org} remineralization rates in coastal sediments with higher deposition rates result in $O_{2(aq)}$ being consumed faster than it can diffuse into sediments. C_{org} remineralization then proceeds primarily through SO_4^{2-} 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. $> 30 \mu mol cm^{-3}$ reactive Fe; Thamdrup et al., 2000) or their reduced products, H_2S , Fe^{2+} and Mn^{2+} , are reoxidized by $O_{2(aq)}$ 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_{org} 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_{org} fraction (Hedges and Oades, 1997; Harnett et al., 1998).

1 To better constrain global C budgets, total C_{org} remineralization rates and extents should
2 be quantified in sediments from a variety of locations, depositional environments, and circulation
3 regimes (Thullner et al., 2009). Interestingly, relatively high rates of C_{org} deposition have been
4 observed in deep-sea sediments in specific regions at the base of continental slopes (Haese et al.,
5 2000; Jahnke et al., 1990; Law et al., 2009; Rabouille et al., 2009; Schulz et al., 1994) and in
6 sediments underlying waters where local circulation features may stimulate C_{org} deposition,
7 including upwelling regions (Ferdelman et al., 1999; Haeckel et al., 2001; Thamdrup and
8 Canfield, 1996), semi-enclosed basins (Lee et al., 2008), and even in the deepest trench on earth
9 (Glud et al., 2013). These findings suggest anaerobic remineralization may be significant and
10 that these areas could represent significant C_{org} burial sites (Canfield, 1994). Sulfate reduction is
11 generally considered to be the primary pathway of anaerobic respiration in these sediments (e.g.
12 Ferdelmen et al. 1999; Grant et al., 1998; Lee et. al 2008; Lin et. al, 2002; Lin and Morse 1991),
13 despite the fact that only a few studies have examined the role of Fe(III) reduction (Haese et al.,
14 2000; Law et al., 2009; Nedelec et al., 2007; Thamdrup and Canfield, 1996; van der Zee et al.,
15 2002).

16 In river-dominated ocean margins (RiOMars), suspended sediment and C_{org} may be
17 discharged much farther than deltas and subsequently influence sediment biogeochemistry down
18 continental slopes or even in deep-sea fans underlying slopes (McKee et al., 2004). These
19 regions may also accumulate terrigenous minerals because of their close connection to land,
20 allowing C_{org} remineralization to proceed via microbial Fe(III) and Mn(IV) reduction. For
21 instance, the Louisiana slope (LAS) is subject to frequent mass slumping of spillover mud
22 discharged from the Mississippi River (Bea et al., 1983; Bianchi et al., 2006) and produces
23 unconsolidated clay and C_{org} rich deposits mid-slope at 1,000 m depth (Coleman et al., 1998;

1 Dixon and Weimer, 1998; Konyukhov, 2008). On the other hand, the Congo River Fan (CRF) is
 2 the only deep-sea fan in the world still directly connected to a large river through a submarine
 3 canyon (Babonneau et al. 2002). This unique geological feature generates frequent turbidite
 4 flows that deliver C_{org} rich mud and clay-sized particles to the abyssal plain at depths
 5 approaching 5,000 m water depth (Babonneau et al., 2002; Rabouille et al., 2009).

6 As SO₄²⁻ reduction is able to remineralize two moles of carbon per mole of sulfate,
 7 assuming an average oxidation state of C⁰ in organic carbon (e.g. Eq. 3 with acetate as electron
 8 donor), whereas two moles of Mn(IV) and four moles of Fe(III) are required to remineralize one
 9 mole of carbon (Eq. 1 and 2), it is important to assess which of these anaerobic processes
 10 dominates in continental slope sediments:

14 Unfortunately, measurement of the reduced products of anaerobic respiration is not a definitive
 15 indicator for metal or SO₄²⁻ reduction activity, as metal oxides may also be reduced abiotically
 16 by ΣH₂S (Eq. 4 and 5; Canfield et al., 1992), and ΣH₂S may also be removed from pore waters
 17 by precipitation with Fe²⁺ (Eq. 6; Pyzik and Sommer, 1981) and during the subsequent
 18 precipitation of pyrite (Eq. 7; Rickard and Luther, 1997):

1 In addition, changes in SO_4^{2-} concentrations may be too small to be detected in seawater. The
2 detection of both $\Sigma\text{H}_2\text{S}$ and aqueous $\text{FeS}_{(\text{aq})}$ clusters as a function of depth in sediments using
3 gold/mercury (Au/Hg) voltammetric microelectrodes (Brendel and Luther, 1995; Luther et al.,
4 2008; Taillefert et al., 2000b), however, may provide indirect evidence for SO_4^{2-} reduction.
5 $\text{FeS}_{(\text{aq})}$ clusters are in equilibrium with an amorphous FeS_{am} solid that eventually converts to
6 mackinawite (FeS_s ; Rickard and Morse, 2005; Theberge and Luther, 1997) and are also expected
7 to be precursors to pyrite mineral formation (Rickard, 1997). These $\text{FeS}_{(\text{aq})}$ complexes have been
8 detected in a variety of sediments at the transition between metal- and sulfate-reducing
9 conditions (Rickard et al., 1999; Taillefert et al., 2002a and b; Carey and Taillefert, 2005),
10 suggesting they could be used in addition to $\Sigma\text{H}_2\text{S}$ to locate the sulfate reduction zone. In
11 addition, Au/Hg voltammetric microelectrodes are able to detect organic complexes of Fe(III)
12 (Taillefert et al., 2000a), which are pervasive in coastal sediments dominated by metal reduction
13 (e.g. Jones et al., 2011; Meiggs and Taillefert, 2011; Taillefert et al., 2002a and b; Taillefert et
14 al., 2007b). As the reactivity of these complexes with $\Sigma\text{H}_2\text{S}$ is extremely fast (Taillefert et al.,
15 2000a), their presence in pore waters may provide evidence that SO_4^{2-} reduction is not ongoing.

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

2. STUDY SITES

Sediment cores (9.6 cm ID x 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) (Figure 1a). Station GOM2 experiences recurring bottom water hypoxia ($<2 \text{ mg O}_2 \text{ L}^{-1}$, $\sim 63 \text{ } \mu\text{M}$) 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 x 70 cm) from the Congo River fan (CRF) were obtained using a multicorer from 3 stations approaching 5,000 m depth and up to 800 km offshore (Figure 1b) during a cruise on the N/O *Pourquoi Pas?* (Ifremer, Brest, France) from December 2011 to January 2012. CRF stations (Rabouille et al., submitted) 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, ΣH_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 with an Analytical Instrument Systems, Inc. (AIS, Inc.) DLK-100 potentiostat. The pH microelectrode purchased for this application included a 10 cm long needle of 1.6 mm diameter beveled at the end to protect the bulb of the electrode (Microelectrodes, Inc.). The pH microelectrode was calibrated before each profile using TRIS buffer in synthetic seawater (Dickson, 1993). Voltammetry was conducted in a three-electrode configuration with an Ag/AgCl reference electrode and a Pt counter electrode. Working microelectrodes made of 100 μm gold wire (GoodFellow Corp.) soldered to the copper wire of a coaxial cable with BNC connector were encased in pyrex glass with a tip of 5 cm long and ≤ 1 mm diameter and sealed with marine epoxy (West Marine) as previously reported (Brendel and Luther, 1995; Luther et al., 1999). Reference and counter electrodes were made similarly by encasing 1 mm diameter Ag wire and 0.5 mm Pt wire in 3 mm diameter PEEK tubing sealed with marine epoxy, letting the wire protrude from the casing by about 1 cm. The AgCl coating was formed on the Ag reference electrode by applying +9V between the Ag wire and the Pt electrode in a KCl saturated solution, and the AgCl coated wire was encased in a KCl solution with a porous glass frit (BioAnalytical Systems, Inc.) for contact with the outside solution (Brendel and Luther, 1995). The working voltammetric microelectrodes were plated with Hg by maintaining the electrode at -0.2 V for 4 minutes in a 0.1 M $Hg(NO_3)_2$ solution in 2%

1 HNO₃. Au/Hg microelectrodes were then polarized at -9V for 90 seconds to ensure a better
2 penetration of the mercury into the gold (Brendel and Luther 1995). They were then calibrated in
3 a MnCl₂ solution (0 to 400 μM), and the pilot ion method was used to calculate concentrations of
4 Fe²⁺ and ΣH₂S in the pore waters (Luther et al., 2008). Dissolved oxygen was calibrated *in situ*
5 with the salinity and temperature of the overlying waters, assuming they were at saturation. As
6 the exact chemical composition of organic-Fe(III) and FeS_(aq) complexes is unknown, the
7 voltammetric responses of these complexes cannot be quantified and are instead directly reported
8 in peak current intensities (Taillefert et al., 2000b). To compare the signal intensities of these
9 species measured with different electrodes, each electrode's response to Mn²⁺ was normalized to
10 a typical Mn²⁺ response, and this ratio was used to adjust the current response of the
11 unquantifiable analytes.

12 Sediment cores were kept on ice while profiling to maintain *in situ* temperatures. The pH
13 and Au/Hg voltammetric microelectrodes were affixed to a micromanipulator capable of sub-
14 millimeter increments (AIS, Inc.), while Ag/AgCl reference and Pt counter electrodes were kept
15 in the overlying waters. At each depth, O_{2(aq)} was measured by linear sweep voltammetry (LSV)
16 between -0.1 and -1.85 V with a conditioning period of 10 s at -0.1 V. All other species were
17 measured by CSW voltammetry using a 200 mV/s scan rate and a preconditioning time of 10 s at
18 -0.1 V. If dissolved sulfides or soluble organic-Fe(III) signals were detected, an additional
19 cleaning step at -0.9V for 10 s was added to clean the electrode surface between each
20 measurement (Luther et al., 2008; Taillefert et al., 2000b). At the end of each profile, the
21 electrodes were returned to the overlying waters to ensure they provided the same O_{2(aq)} and pH
22 signals as before deployment. Peak heights and surface area were determined using a semi-
23 automated VOLTINT software package (Bristow and Taillefert, 2008). A few sediment samples

from the surface (upper ~20 cm) of LAS cores were frozen in ziplock bags (-80 °C) and shipped on dry ice to Georgia Tech for solid-phase Fe speciation. Sediment cores from the CRF were sectioned onboard into slices of approximately 7 mm under N₂ atmosphere and at 4 °C, and each section was centrifuged under N₂ atmosphere for about 20 minutes at 3,000 RPM to extract pore waters. Pore waters were then immediately filtered onto 0.2 µm Whatman Puradisc syringe filters under N₂ atmosphere at 4 °C, and analyzed or preserved within 30 minutes. The leftover sediment was frozen (-20 °C) in 50 mL tubes and shipped on dry ice to Georgia Tech. Soluble orthophosphates (ΣPO_4^{3-}) were measured spectrophotometrically using the molybdate-blue technique (Murphy and Riley, 1962). Dissolved inorganic carbon (DIC) was measured by flow-injection analysis (Hall and Aller, 1992). Finally, sediments were extracted using ascorbate and dithionite to partition solid-phase Fe concentrations between a highly reactive and total Fe(III) (oxy)hydroxide fraction, with a pool of more crystalline Fe being inferred by difference between the ascorbate and dithionite fractions (Kostka and Luther, 1994). Preliminary analyses demonstrated that Fe in FeS minerals represented an insignificant portion of Fe extracted by dithionite (data not shown).

3.2. Thermodynamic calculations and modeling

The saturation state of FeS_(aq) clusters was determined to provide insight into the relative roles of Fe and SO₄²⁻ reduction in the sediments. The solubility of FeS_(aq) is related to Fe²⁺ and HS⁻ concentrations by:

$$K_{sp} = \frac{\{Fe^{2+}\} \{HS^{-}\}}{\{H^{+}\}} \quad (\text{Eq. 8})$$

Assuming measurements with Au/Hg voltammetry provide concentrations of H₂S and HS⁻ mainly, the fraction of $\Sigma\text{H}_2\text{S}$ in the form of HS⁻ as a function of pH can be calculated with the Henderson-Hasselbalch approximation equation:

$$\alpha_{HS^-} = \frac{[HS^-]}{[\Sigma H_2S]} \quad (\text{Eq. 9})$$

$$\alpha_{HS^-} = \frac{\{H^+\}K_1}{\{H^+\}^2 + \{H^+\}K_1 + K_1K_2} \quad (\text{Eq. 10})$$

where K_1 and K_2 are the first and second acid dissociation constant for H_2S . Combining Eq. 8, Eq. 9, and Eq. 10, the equilibrium concentration of total dissolved sulfides can be calculated from the concentration of Fe^{2+} and the pH of the pore waters:

$$[\Sigma H_2S] = \frac{K_{sp} \{H^+\}}{\gamma_{Fe^{2+}} [Fe^{2+}] \cdot \gamma_{HS^-} \alpha_{HS^-}} \quad (\text{Eq. 11})$$

Acid-base equilibrium constants (pK_{a1} and pK_{a2}) of 6.8 and 17.0 (Davison, 1991) and a dissociation constant ($\log K_{sp}$) of -2.2 (Rickard, 2006) were used for these calculations. Values of the activities of the free HS^- and Fe^{2+} ions, γ_{HS^-} and $\gamma_{Fe^{2+}}$, were calculated using Pitzer parameters for Fe^{2+} (Millero and Schreiber, 1982) and HS^- (Millero, 1983).

The freely available program SUPCRT92 (Johnson et al., 1992) was used to compare reaction favorabilities by calculating the ΔG^0_{rxn} at various pressures and temperatures using an updated thermodynamic database (slop07.dat) and amended with the ΔG^0 (-705.2 kJ mol⁻¹), ΔH^0 (-827.1 kJ mol⁻¹), and ΔS^0 (122.2 J K⁻¹ mol⁻¹) for hydrated 2-line ferrihydrite ($Fe(OH)_3$; Snow et al., 2013). A ΔV^0 of 42.96 cm³ mol⁻¹ was calculated using a unit cell volume of 71.33 Å³ (from www.mindat.org), and Maier-Kelley heat capacity coefficients of $a = 0$, $b = 0.016$ cal K⁻² mol⁻¹, and $c = 0$ were obtained by reproducing C_p data from Snow et al., 2013, and solving for the slope of the line of best fit through the region of temperatures between 270 and 302 K, i.e. those temperatures relevant in the ocean. All energies were converted to calorie units as required by SUPCRT92. Deviations of the Gibbs free energy from non-standard state conditions at each of the new references states obtained from the SUPCRT92 output were then calculated using the

reaction quotient determined from the activities of the reactants and products obtained with seawater activity coefficients from the literature (Millero and Schreiber, 1982) or calculated using Pitzer parameters for Fe^{2+} (Millero and Schreiber, 1982) and HS^- (Millero, 1983).

3.3. Flux Calculations

The maximum diffusive fluxes of O_2 , Fe^{2+} , Mn^{2+} , HS^- , and HCO_3^- (as a proxy for DIC) in each sediment core were determined from the slope of the maximum gradient in concentrations of both species and the following relationship (Boudreau, 1997):

$$F_x = -\phi \frac{D_x}{\theta^2} \frac{dC_x}{dz} \quad (\text{Eq. 12})$$

where F_x is the diffusive flux of species x, ϕ is the sediment porosity, D_x is the ionic or molecular diffusion coefficient of species x corrected for temperature (Boudreau, 1997), θ is the tortuosity estimated from Archie's law ($\theta^2 = \phi^{1-m}$ with $m = 2.5-3$ for fine grained sediments (Ullman and Aller, 1992)), C_x is the concentration of species x, and z the depth of the sediment column. The molecular diffusion coefficient of dissolved oxygen was calculated at the salinity, temperature, and pressure of the sites according to:

$$D_{\text{O}_2} = 4.72 * 10^{-9} \frac{T}{\mu V_b^{0.6}} \quad (\text{Eq. 13})$$

where D^0 is the molecular coefficient of $\text{O}_{2(\text{aq})}$ [$\text{cm}^2 \text{s}^{-1}$], T is the absolute temperature [K], μ is the dynamic viscosity of seawater at the temperature, pressure, salinity of the site [poise], and V_b is the molar volume of molecular oxygen [$\text{cm}^3 \text{l}^{-1}$] (Boudreau, 1997). The ionic diffusion coefficient of Fe^{2+} , Mn^{2+} , HS^- , and HCO_3^- were calculated from an empirical relationship that is function of the temperature (Boudreau, 1997).

4. RESULTS

4.1. Louisiana slope transect sediment biogeochemistry

Oxygen penetration depths across the LAS shelf and slope increased with the overlying water column depth, from < 1 mm at GOM2 (65 m), to ~3 mm at GOM3 (128 m), ~6 mm at GOM12 (980 m) and 10 cm in the sediments of GOM10 (1778 m) (Figure 2a, c, e, and g). Simultaneously, diffusive oxygen uptake (DOU) fluxes decreased across the LAS shelf (Table 1). Interestingly, the pH of the overlying waters ranged between 7.5 and 7.7 at GOM2 and GOM3 but much higher (>8.3) at the offshore stations GOM12 and GOM10, suggesting that respiration processes in the hypoxic zone were responsible for the decrease in pH of the overlying waters (Figure 2b and d). Accordingly, bottom water $O_{2(aq)}$ saturation ratios ~1 m above the sediment-water interface (SWI), as measured by a CTD-mounted SBE 43 oxygen sensor, were low (55% and 52% at GOM2 and GOM3) but not hypoxic by definition (< ~30%). The CTD, however, is not capable of measuring $O_{2(aq)}$ directly above the sediment, and $O_{2(aq)}$ concentrations could drop rapidly with depth just above the SWI (Figure 2). Indeed, pH profiles always decreased more drastically in the zone of aerobic respiration, and then gradually decreased throughout the sediment column, reaching ~ 7.0 at GOM2 and GOM3 (Figure 2a and c) and between 7.5 and 8 at GOM12 and GOM10 (Figure 2e and g). Although ΣH_2S was never detected in any of the cores (MDL < 0.2 μM), a voltammetric current for molecular clusters of FeS ($FeS_{(aq)}$) was detected below 6 cm at GOM2 and throughout the sediment column at GOM3 (Figure 2b and d) but not at the deeper stations (Figure 2f and h). Simultaneously, dissolved Mn^{2+} was detected immediately below the SWI at GOM2 (Figure 2a) and at 4.5 cm at GOM3 (Figure 2c) and reached relatively constant concentrations (250 - 300 μM) at depth. In turn, dissolved Fe^{2+} remained below detection limit (~20 μM) at GOM2 (Figure 2a) and formed a

small peak between 12.5 and 15.5 cm ($< 100 \mu\text{M}$) at GOM3 (Figure 2c). Similarly, voltammetric signals for soluble organic-Fe(III) complexes were just above detection limit ($\sim 1 \text{ nA}$) throughout the sediment at GOM2 (Figure 2b) and increased with depth below 12 cm to reach current intensities of 55 nA (Figure 2d). In contrast to the shelf stations, $\text{FeS}_{(\text{aq})}$ was not detected at both slope stations (GOM12 and GOM10) (Figure 2f and h). Instead, dissolved Mn^{2+} was produced 3 cm below the SWI at GOM12 (Figure 2e), eventually increasing to maximum concentrations of 1.9 mM at 20 cm depth. In these sediments, dissolved Fe^{2+} and soluble organic-Fe(III) complexes were produced below 6 cm and reached concentrations of $\sim 1 \text{ mM}$ and current intensities of $\sim 300 \text{ nA}$ within the first 20 cm depth (Figure 2e and f). Interestingly, dissolved Mn^{2+} and Fe^{2+} were below detection limit (~ 15 and $20 \mu\text{M}$) at GOM10, the deepest station of the LAS (Figure 2g), and only small current intensities for organic-Fe(III) complexes were detected (Figure 2h). Except for GOM10 where their fluxes were negligible, the diffusive fluxes of Mn^{2+} and Fe^{2+} across the LAS were contrastingly different. Although the flux of Mn^{2+} remained relatively constant across the transect, the flux of Fe^{2+} increased from the shelf to the slope (Table 1). Reactive Fe hydroxide (Fe_{reac}) concentrations (ascorbate-extractable Fe) of 13.3 ± 3.8 , 24.2 ± 4.0 , and $11.5 \pm 1.3 \mu\text{mol/gdw}$ (grams of dry weight sediment) were measured in the top 10 cm at GOM2, GOM12, and GOM10 (no data for GOM3), while crystalline Fe(III) oxides (Fe_{crys}) concentrations, as determined by the difference between dithionite-extractable and ascorbate-extractable Fe, of 16.4 ± 9.8 , 20.0 ± 14.1 , $31.1 \pm 7.1 \mu\text{mol/gdw}$ were found at the same stations.

4.2. Congo River fan sediments

Depth profiles of the main redox species, pH, DIC, and orthophosphate obtained at CoLA, CoLB, and CoLE in the CRF demonstrate the influence of channel proximity on sediment

1 biogeochemistry. CoLE is located in an extinct submarine channel that no longer receives
 2 turbidite deposits, whereas CoLA, located at the entrance of the lobe complex on the levee
 3 adjacent to the present day channel, or CoLB, located between the two stations (Figure 1) are
 4 exposed to frequent slumping events. Although $O_{2(aq)}$ concentrations in the overlying waters
 5 were similar at each station ($247 \pm 12 \mu\text{M}$ at CoLE, $259 \pm 7 \mu\text{M}$ at CoLB, and $261 \pm 19 \mu\text{M}$ at
 6 CoLA), $O_{2(aq)}$ gradients were progressively sharper from CoLE, where the $O_{2(aq)}$ penetration
 7 depth was 7 cm (Figure 3a), to CoLB with a penetration depth of 1.2 cm (Figure 3d), and finally
 8 to CoLA with a penetration depth of 8 mm (Figure 3g). Simultaneously, DOU fluxes increased
 9 from CoLE to CoLA according to the same pattern (Table 1). At all stations, NO_x ($NO_3^- + NO_2^-$)
 10 concentrations were as high as $30 \mu\text{M}$ at the SWI and decreased across the redoxcline (Figure 3a,
 11 d, and g). Interestingly, a subsurface peak of NO_x was found between 2 and 8 cm at CoLB and
 12 CoLA that reached 6 and $100 \mu\text{M}$ (Figure 3d and g). This NO_x peak overlapped with dissolved
 13 Fe^{2+} and organic-Fe(III) complexes, which were pervasive at CoLA and CoLB (Figure 3e and h)
 14 but not at the extinct canyon (CoLE), where they were below detection limit throughout the
 15 profile (Figure 3b). Dissolved Fe^{2+} was produced just below the first NO_x^- minimum at CoLB
 16 (up to $116 \mu\text{M}$ at 1.8 cm), then slowly decreased down to below detection limit between 6 and 9
 17 cm, before increasing progressively to concentrations as high as $240 \mu\text{M}$ at a depth of 14 cm
 18 (Figure 3e). In the same pore waters, currents for organic-Fe(III) complexes were not observed
 19 until the zone of maximum Fe^{2+} concentration, where they were concomitantly produced in
 20 current intensities ranging between 126 and 186 nA (Figure 3e). As at CoLB, organic-Fe(III)
 21 complexes at CoLA were also formed in the zone of Fe(III) reduction but about 1 cm below the
 22 onset of Fe^{2+} production only (~ 4 cm). Current intensities for these complexes mirrored Fe^{2+}
 23 concentrations below that depth, and oscillated between 50 and 125 nA (Figure 3h). Mn^{2+} was

1 never detected in CRF sediments, suggesting that its involvement in early diagenesis is not
 2 significant. No evidence of SO_4^{2-} reduction was observed in CRF sediments, as neither $\Sigma\text{H}_2\text{S}$,
 3 nor $\text{FeS}_{(\text{aq})}$ were observed at CoLE (Figure 3b), CoLB (Figure 3e), and CoLA (Figure 3h).
 4 Overall, the flux of Fe^{2+} along with that of DIC increased from CoLE to CoLB, and to CoLA,
 5 reflecting the increase in respiration in these sediments (Table 1),

6 The pH followed the expected behavior as a result of the intensity of aerobic respiration,
 7 NO_3^- reduction, and Fe(III) reduction in CRF sediments. The pH decreased less pronouncedly at
 8 CoLE from 8.26 in the overlying waters to ~ 7.92 at the bottom of the zone of aerobic and NO_3^-
 9 respiration, and then decreased more slowly deeper, finally reaching a value of 7.83 at a depth of
 10 18 cm (Figure 3a). At CoLB, the pH was much lower in the overlying waters (~ 7.9), suggesting
 11 that respiration processes were more intense. It decreased more rapidly below the SWI to 7.3 by
 12 the bottom of the zone of NO_3^- reduction, and remained stable at 7.3 for the rest of the profile
 13 (Figure 3d). The pH profile of CoLA was particularly interesting, with three distinct regions
 14 (Figure 2c). It first decreased drastically from ~ 8.14 in the overlying waters to ~ 7.6 at 7 mm
 15 below the SWI, followed by a less rapid decrease to 7.3 at 5.6 cm in the zone of NO_x production,
 16 and an increase back to 7.44 in the zone of intense Fe(III) reduction at 15 cm (Figure 3g). DIC
 17 generally increased steadily as a function of depth from 2.5 mM at the SWI to 5.4 mM at 13 cm
 18 at CoLE, the deepest depth where it was measured (Figure 3b), 11.5 mM at 11.5 cm in CoLB
 19 sediments (Figure 3e), and 8.2 mM at 11 cm at CoLA (Figure 3h).

20 Reactive Fe hydroxide (Fe_{reac}) concentrations extracted from the solid phase averaged
 21 $211 (\pm 23) \mu\text{mol/gdw}$ in the top 8 cm of the sediment of CoLE but increased to $366 (\pm 48)$
 22 $\mu\text{mol/gdw}$ deeper in the sediment column (Figure 3c). In the same sediments, Fe_{crys}
 23 concentrations were generally lower than Fe_{reac} in the top 6 cm ($38 (\pm 60)$) but reached as high as

259 $\mu\text{mol/gdw}$ below that depth (Figure 3c). Fe_{reac} concentrations were higher at CoLB than at CoLE but quite variable (between 90 and 611 $\mu\text{mol/gdw}$) and with the highest concentrations in the top 2 cm (Figure 3f). Little Fe_{cryst} was observed at CoLB until below 6 cm, where concentrations reached 484 $\mu\text{mol/gdw}$; Figure 3f). Similar to CoLB, Fe_{reac} concentrations were highest in the top 2 cm of CoLA (672 $\mu\text{mol/gdw}$ maximum) but were less variable, remaining above 225 $\mu\text{mol/gdw}$ throughout the profile (Figure 3i). Fe_{crys} was observed throughout the profile at CoLA, albeit at low concentrations between 42 and 167 $\mu\text{mol/gdw}$ (Figure 3i). Finally, ΣPO_4^{3-} adsorbed onto reactive Fe hydroxides (P_s) was low at CoLE, at concentrations of only 11 $\mu\text{mol/gdw}$ in the surface of sediment, and decreased to as low as 2 $\mu\text{mol/gdw}$ deeper in the core (Figure 3c). Interestingly, solid phase ΣPO_4 (P_s) concentrations were much higher at CoLB (max concentration 103 $\mu\text{mol/gdw}$) and especially CoLA (between 92 and 214 $\mu\text{mol/gdw}$), and both profiles mirrored that of Fe_{reac} (Figure 3f and i).

5. DISCUSSION

5.1. Absence of dissolved sulfides and dominance of dissimilatory metal reduction

Both the LAS and CRF sediments are enriched in C_{org} relative to other deep areas of the ocean, suggesting SO_4^{2-} reduction may be an important respiration process in these sediments. In LAS sediments, the C_{org} content was reported to be 1.3% 25 km to the west of the slope station GOM12 at 574 m water depth compared to 0.8 - 1.0% near the shelf and shelf-break stations GOM2 and GOM3 (Lin and Morse, 1991; Morse and Rowe, 1999). In CRF sediments, C_{org} content is $>3\%$ compared to Congo slope concentrations that are $\leq 2\%$ (Rabouille et al., 2009; Stetten et al., 2015). Interestingly, dissolved sulfides were not observed in any of the LAS or CRF sediment pore waters (Figure 2 and 3), indicating either that SO_4^{2-} reduction was not

1 significant or that sufficient reactive Mn and Fe minerals titrated $\Sigma\text{H}_2\text{S}$ in these sediments.
 2 Voltammetric signals for $\text{FeS}_{(\text{aq})}$, however, were consistently detected deeper than 6 cm at
 3 GOM2 (65 m water depth; Figure 2a) and immediately below the SWI at GOM3 (128 m water
 4 depth; Figure 2c), indicating that SO_4^{2-} reduction was ongoing in these shelf sediments. In
 5 contrast, the absence of $\Sigma\text{H}_2\text{S}$ and $\text{FeS}_{(\text{aq})}$ at GOM12 (Figure 2e and f), GOM10 (Figure 2g and
 6 h), and at all the CRF stations (Figure 3) indicate that SO_4^{2-} reduction was not significant in these
 7 continental slope sediments.

8 Thermodynamic analysis can provide insight into the relative roles of microbial Fe(III)
 9 reduction and SO_4^{2-} reduction in these sediments, assuming that the production and consumption
 10 of $\text{FeS}_{(\text{s})}$ are near steady-state. The concentration of $\Sigma\text{H}_2\text{S}$ that should be in equilibrium with
 11 $\text{FeS}_{(\text{aq})}$ at a particular pH can be determined using Eq. 11 as a function of pore water Fe^{2+}
 12 concentrations (Figure 4). Interestingly, Fe^{2+} (MDL < 20 μM) and $\Sigma\text{H}_2\text{S}$ (MDL < 0.2 μM)
 13 remained below detection limits in GOM2 and most of GOM3 sediments, even though any
 14 theoretical equilibrium concentration of Fe^{2+} or $\Sigma\text{H}_2\text{S}$ at pore water pH reflecting those of the
 15 pore waters of GOM2 and GOM3 (between 7.1 and 7.6) should be well above the detection limit
 16 of the Au/Hg microelectrodes (Figure 4). As the concentrations of Fe^{2+} and $\Sigma\text{H}_2\text{S}$ were below
 17 saturation, the existence of the $\text{FeS}_{(\text{aq})}$ clusters in solution may be due either to their resilience to
 18 dissociation or the continuous solubilization of FeS solid phases. Accordingly, high
 19 concentrations of sediment total reducible sulfides (TRS, $\text{FeS}_{\text{am}} + \text{FeS}_{\text{s}} + \text{pyrite}$; 158 $\mu\text{mol/g}$)
 20 were previously observed in sediments near GOM2 (Morse and Rowe, 1999), suggesting these
 21 sediments could provide a constant source of $\text{FeS}_{(\text{aq})}$ clusters. These findings are consistent with
 22 previous work that suggests that these shelf sediments are not at steady-state and that SO_4^{2-}
 23 reduction is controlled by a dynamic cycling between oxic and hypoxic conditions in the

1 overlying waters (Morse and Eldridge, 2007). Simultaneously, the presence of Mn^{2+} but not Fe^{2+}
 2 in the pore waters at these two stations suggest several possible scenarios: (i) microbial
 3 Mn(IV/III) but not Fe(III) reduction was ongoing at GOM2 and GOM3; (ii) precipitation of
 4 carbonate minerals selectively removed Fe^{2+} from pore waters; (iii) Fe^{2+} was oxidized to Fe(III)
 5 during mixing with oxygenated overlying water, or (iv) both Mn^{2+} and Fe^{2+} were produced by
 6 reduction of Mn(IV/III) and Fe(III) oxides by $\Sigma\text{H}_2\text{S}$, but only Fe^{2+} was sequestered into sulfur
 7 minerals as a result of the high solubility of MnS minerals. Microbial Mn(IV/III) reduction,
 8 however, is likely not much more prevalent than microbial Fe(III) reduction given the generally
 9 higher concentrations of Fe(III) oxides compared to Mn(IV/III) oxides in marine sediments
 10 (Canfield et. al, 1993). In addition, both siderite and rhodochrosite (Fe and Mn carbonates,
 11 respectively) display similar solubilities, and the kinetics of precipitation of rhodochrosite,
 12 though generally slow, is faster than that of siderite (Jensen et al., 2002), suggesting that Mn^{2+}
 13 should have been removed preferentially by carbonate precipitation. Finally, detection of
 14 dissolved $\text{O}_{2(\text{aq})}$ as deep as 20 cm is highly unusual, especially in carbon-rich fine-grained
 15 sediments, such that the Fe^{2+} oxidation scenario is unlikely. Overall, these considerations suggest
 16 that Fe^{2+} was selectively removed from the pore waters at GOM2 and GOM3 during FeS
 17 precipitation and that sulfate reduction was therefore significant at these stations. In the vicinity
 18 of GOM2 and GOM3, respectively, pyrite concentrations were generally high ($73 \mu\text{mol/g}$ in
 19 sediments from 75 m water depth) but decreased when transitioning to sediments of 135 m water
 20 depth ($11 \mu\text{mol/g}$), demonstrating the decreasing influence of SO_4^{2-} reduction from the shelf to
 21 the slope (Lin and Morse, 1991).

22 At GOM12, midway down the slope (980 m water depth), neither $\Sigma\text{H}_2\text{S}$ nor $\text{FeS}_{(\text{aq})}$ were
 23 observed in the pore waters, while Fe^{2+} and Mn^{2+} diffusive fluxes were the most significant of

the LAS sediments (Table 1) and their pore water concentrations reached more than 1 mM deeper than 6 cm in the sediments (Figure 2c). Thermodynamic considerations indicate that in the presence of such high Fe^{2+} concentrations, only $\sim 0.1 \mu\text{M}$ of $\Sigma\text{H}_2\text{S}$ should be required to form $\text{FeS}_{(\text{aq})}$ at pH 7.6 (Figure 4). The lack of $\Sigma\text{H}_2\text{S}$ and $\text{FeS}_{(\text{aq})}$ in the pore waters therefore suggests that SO_4^{2-} reduction is negligible in these sediments. The occurrence of soluble organic-Fe(III) complexes at the onset of Fe(III) reduction represents another piece of evidence that dissolved sulfides are not formed in these sediments. These complexes, produced as intermediates in the reduction of Fe(III) oxides by model iron-reducing bacteria (Jones et al., 2010; Taillefert et al., 2007a) and as a result of the oxidation of Fe^{2+} by Fe(III) oxides in the presence of DOM (Beckler et al., 2015), are expected to react rapidly with dissolved sulfides (Taillefert et al., 2000a). Supporting this notion, SO_4^{2-} is not depleted to any great extent in the pore waters of sediments obtained 25 km to the west of GOM12 at 574 m water depth, and sediment pyrite never exceeds $5 \mu\text{mol/g}$ (Lin and Morse, 1991). These findings suggest that SO_4^{2-} reduction rates are low in these sediments and microbial metal reduction dominates anaerobic respiration processes. Although denitrification was not quantified and data is not available in the literature for the LAS sites, the gap between $\text{O}_{2(\text{aq})}$ penetration and Mn^{2+} production depths is only $\sim 2.5 \text{ cm}$ (Figure 2a, c, and e), thus limiting the importance of the denitrification zone in LAS sediments to less than $\sim 4 \text{ cm}$ as the maximum rates of denitrification should occur above the zone of Mn^{2+} accumulation.

Similarly, several lines of evidence suggest that the extremely high concentrations of Fe^{2+} at CoLA and CoLB are a product of dissimilatory metal reduction and not due to the abiotic reaction of Fe(III) oxides with $\Sigma\text{H}_2\text{S}$ produced during SO_4^{2-} reduction. First, $\Sigma\text{H}_2\text{S}$ and $\text{FeS}_{(\text{aq})}$ are not observed in the pore waters (Figure 3e and h). Although it is possible that $\Sigma\text{H}_2\text{S}$ could escape detection by immediate reaction with labile Fe(III) hydroxides, relatively high

1 voltammetric signals for organic-Fe(III) complexes, extremely high aqueous Fe^{2+} concentrations
 2 (Figure 3e and h), as well as high Fe^{2+} fluxes (Table 1) would not be expected if SO_4^{2-} reduction
 3 was ongoing, as any excess $\Sigma\text{H}_2\text{S}$ should more readily react with organic-Fe(III) complexes or
 4 aqueous Fe^{2+} instead of Fe(III) minerals (Rickard and Luther, 1997; Rickard et al., 1999;
 5 Taillefert et al., 2000a). Second, a good correlation ($R^2 = 0.70$) exists between organic-Fe(III)
 6 current intensities and Fe^{2+} concentrations when considering all the stations (Figure 5),
 7 suggesting organic-Fe(III) complexes at CoLA and CoLB are intermediates produced mainly
 8 during Fe(III) reduction but not Fe^{2+} oxygenation. Indeed, examination of the individual profiles
 9 reveal that organic-Fe(III) complexes are produced much deeper than $\text{O}_{2(\text{aq})}$ penetration depths in
 10 these sediments (Figure 3e and h). Third, ΣPO_4^{3-} associated with the solid phase mirrors Fe_{reac} at
 11 CoLB and CoLA (Figure 3f and i). If $\Sigma\text{H}_2\text{S}$ was responsible for Fe(III) mineral dissolution,
 12 adsorbed ΣPO_4^{3-} should be released and produce pore water ΣPO_4^{3-} concentrations greater than
 13 the relatively low maxima ($\leq 10 \mu\text{M}$) observed at these two stations (Figure 3e and h) because
 14 secondary minerals formed as a product of $\Sigma\text{H}_2\text{S}$ reacting with Fe(III) oxides have a low
 15 adsorption capacity for ΣPO_4^{3-} (Anschutz et al., 1998; Rozan et al., 2002). Finally, considering
 16 that denitrification or dissimilatory nitrate reduction to ammonium (DNRA) should have a
 17 negligible impact on DIC production given the NO_x concentrations in the pore waters, then a
 18 $\Sigma\text{H}_2\text{S}$ flux ranging between 1 and 2 $\text{mmol m}^{-2} \text{day}^{-1}$ (estimated by subtracting the DOU flux from
 19 the DIC flux in Table 1 and accounting that one mole of sulfate oxidizes two moles of carbon
 20 equivalent) would have had to be produced at CoLB and CoLA if SO_4^{2-} reduction dominated
 21 respiration processes and Fe(III) was reduced by $\Sigma\text{H}_2\text{S}$ in order to account for the proportion of
 22 the DIC flux generated by anaerobic processes. These fluxes would correspond to pore water
 23 concentrations between 1.5 and 4 mM of $\Sigma\text{H}_2\text{S}$ to generate the 3 to 8 mM DIC concentrations

produced above background seawater concentrations in these sediments (Figure 3b, e, and h). Alternately, the formation of a subsurface peak in NO_x at CoLA and CoLB (Figure 3) that could tentatively result from the coupling between Fe(III) reduction and the anaerobic oxidation of ammonium (Yang et al. 2012) and fuel denitrification may have poised the redox potential of the sediment to higher values, thus preventing sulfate reduction in these sediments. Taken together, these data indicate the high concentrations (Figure 2 and 3) and fluxes (Table 1) of Fe^{2+} are produced by dissimilatory Fe(III) reduction. In turn, the absence of dissolved organic-Fe(III), Fe^{2+} , Mn^{2+} , and $\text{FeS}_{(\text{aq})}$, and $\Sigma\text{H}_2\text{S}$ at CoLE is not surprising given the depth of penetration of dissolved $\text{O}_{2(\text{aq})}$ (~ 6 cm) and the low fluxes (Table 1) at this station, indicating respiration is slowed in this extinct canyon no longer receiving high concentrations of C_{org} during turbidite flows.

5.2. The importance of riverine delivery

The sediment profiles across the LAS transect demonstrate a transition from SO_4^{2-} reduction on the shelf to a system dominated by Fe(III) and Mn(IV) reduction on the slope. In the CRF, an intensification of $\text{O}_{2(\text{aq})}$ and Fe(III) respiration is observed near the active channel relative to the extinct channel. The existing paradigm suggests that to maintain significant concentrations of Fe_{reac} in deep sea sediments, reoxidation of Fe^{2+} via faunal or bottom current-induced irrigation is necessary (Thamdrup and Canfield, 1996; Wollast, 2003; Jensen et al. 2003). Although burrows were not observed in any of the fine-grained sediments of GOM12 or GOM10, bioirrigation cannot be ruled out given the limited number of observations in the LAS. Similarly, although the concentration of iron oxides is enhanced in the oxygenated zone of the sediments of the main channel of the CRF (Figure 3f and i), few macroscopic organisms were observed in levee sediments during several weeks of visual observation, and ^{210}Pb profiles

1 decreased conservatively with depth (Rabouille et al., 2009), further evidence that mixing
2 processes were minimal. Although these two environments are quite different from one another,
3 these considerations suggest that the internal redox cycling of iron may only affect the surface
4 sediments and that the delivery of terrestrial C_{org} and oxidized Fe(III) and Mn(IV) minerals sets
5 the stage for metal reduction-driven biogeochemistry in these sediments. Major river-derived
6 sediments may be deposited in delta regions (Type I system; e.g. Mississippi-Atchafalaya) or
7 transported laterally alongshore on the shelf (Type II system; e.g. Amazon; McKee et al., 2004).
8 In such systems, C_{org} remineralization generally proceeds via anaerobic pathways, particularly in
9 more tropical climates (Aller and Blair, 2006). The Mississippi RiOMar is a Type IIIa system
10 (McKee et al., 2004) because a significant proportion ($> 10\%$) of the river plume is transported
11 down-slope indirectly. Particles from the Mississippi, including C_{org} synthesized within the
12 Mississippi River plume (Bianchi et al., 2006; Sampere et al., 2011), accumulate on a prograding
13 delta near the shelf-break (Coleman, 1988) and may spill-over in storms (Bea et al., 1983), or
14 more infrequently, during large-scale mass-slumping of rapidly deposited, over pressurized muds
15 (Coleman et al., 1998; Dugan and Stigall, 2010). The net effect is an accumulation of
16 terrigenous material much farther downslope than normal mixing processes would allow
17 (Konyukhov, 2008), as has been demonstrated in the Ursa basin to the east of GOM12 (Long et
18 al., 2011; Reece et al., 2012). Interestingly, Fe_{reac} concentrations in GOM12 sediments are close
19 to the $\sim 30 \mu\text{mol cm gdw}^{-1}$ threshold (converted from $30 \mu\text{mol cm}^{-3}$ assuming a 60% porosity and
20 solid phase density of 2.6) at which the rate of microbial Fe(III) reduction is not limited by the
21 concentration of Fe_{reac} (Thamdrup, 2000). However, a smectite-rich tongue, likely derived from
22 the great-plain soils in the Missouri River drainage basin (Sionneau et al., 2008), extends from
23 the Mississippi River delta to the Mississippi deep-sea fan (Balsam and Beeson, 2003), and

1 Mississippi River delta sediments consist of 90% clays, mostly smectite and illite (Jaisi et al.,
2 2008). Although Fe silicate minerals should not be extracted significantly by the ascorbate and
3 dithionite methods used in this study (Kostka and Luther, 1994), some may serve as terminal
4 electron acceptors (TEA) for microbial Fe(III) reduction (Bishop et al., 2010; Jaisi et al., 2005;
5 Kostka et al., 1999; O'Reilly et al., 2006) and thus provide a significant source of Fe²⁺ in these
6 sediments.

7 In turn, most canyon systems were last active during the glacial period, when lower sea
8 levels allowed rivers to be directly connected to their canyons and to deliver sediment directly
9 across the continental shelf to the slope (Babonneau et al., 2002). Today, most deep-sea fans
10 (e.g. Amazon and Indus) no longer directly receive fluvial deposits and are covered in pelagic
11 calcareous ooze instead of mud (Damuth and Kumar, 1975; Prins et al., 2000; Weimer, 1990).
12 The Congo RiOMar is a Type IIIb system (McKee et al., 2004) because the river is still directly
13 connected to its submarine canyon. Due to the low suspended sediment load in the Congo River,
14 the active channel remains unfilled and thus extends 30 km up the estuary, such that river
15 particles accumulate in the canyon head in large-scale terrigenous deposits which are funneled
16 through the canyon to the abyssal plain by turbidity currents (Babonneau et al., 2002). Flows
17 remain confined in the deeply entrenched channel and are capable of traveling 800 km offshore.
18 These processes explain how the Congo River, with such a low suspended sediment load, can
19 produce such a large deep-sea fan (Babonneau et al., 2002). Accordingly, C/N ratios and $\delta^{13}\text{C}$ of
20 organic matter in the CRF demonstrate the organic matter is largely terrestrially derived (Stetten
21 et al., 2015). The CRF consists of a series of lobes formed during the overflow of the finest-clay
22 sized particles from these turbidite flows (Babonneau et al., 2002). The particles are rich in
23 labile Fe(III) hydroxides extractable by ascorbate, and concentrations reach 600 $\mu\text{mol gdw}^{-1}$

(Figure 3f and i), much greater than poorly crystalline Fe concentrations even in coastal sediments dominated by Fe(III) reduction (e.g. Jensen et al., 2004, Koretsky et al., 2003, Taillefert et al., 2007b; Beckler et al., 2014). The extinct channel levee, on the other hand, harbors 65% less ascorbate-extractable iron in the top 2 cm of sediments than the active channel (Figure 3c), and Fe(III) reduction is barely detectable (Figure 3a). Although these Fe_{reac} concentrations are still relatively high compared to most sediments dominated by Fe(III) reduction (Thamdrup, 2000), both dissolved ΣPO_4^{3-} (Figure 3b) and P_s (Figure 3c) remain low throughout the sediment, suggesting labile organic carbon limitations may prevent significant Fe(III) reduction.

The relative intensities of dissimilatory Fe(III) and Mn(IV/III) reduction between the LAS and CRF (Table 1) and the resulting lack of dissolved Mn^{2+} in CRF fan sediments may be controlled by the mineral composition of the input material. Elemental composition of the suspended loads indicates almost equivalent concentrations of Mn in either river (24 and 26 $\mu\text{mol Mn gdw}^{-1}$ for the Mississippi and Congo, respectively) but 33% higher Fe in the Congo River (846 and 1268 $\mu\text{mol Fe gdw}^{-1}$; Martin and Meybeck, 1979). Further, the maximum concentrations of Fe_{reac} measured (24 and 672 $\mu\text{mol Fe gdw}^{-1}$) indicate that up to 2.9% and 53% of the solid phase Fe may be in the form of Fe_{reac} in the Mississippi and Congo sediments, assuming a similar composition between the riverine suspended material and offshore sediment. Thus, the ratios of total Mn in the suspended load to the maximum measured Fe_{reac} content in the sediments are 26 times greater for the Mississippi than the Congo Rivers on a per mole basis (0.98 and 0.038), suggesting that Mn(IV/III) reduction is more likely to occur in LAS sediments than CRF sediments. Additionally, as hypothesized for other systems (Thamdrup et al., 2000),

bacteria may be specialized for Fe(III) reduction in the CRF given the significantly higher concentration of Fe(III) oxides than Mn(IV/III) oxides.

5.3. Thermodynamic considerations

Although the high Fe(III) oxide concentrations in continental slope sediments may sustain microbial Fe(III) reduction, SO_4^{2-} concentrations are also high and SO_4^{2-} reduction should be expected in such a C_{org} -rich environment (Thamdrup, 2000). Deep ocean sediments may offer additional competitive advantages to metal-reducing bacteria, including increases in the thermodynamic energy yields of respiration reactions and enhanced viabilities relative to other types of microbes at higher hydrostatic pressures and lower temperatures (Fang and Bazylinski, 2008). Several lines of experimental and theoretical evidence indicate that Fe(III)-reducing organisms may have an advantage in seawater at high pressures. *Shewanella* sp. are some of the most common and widely distributed bacteria isolated from the deep sea (Kato and Nogi, 2001), and many *Shewanella* sp. are piezophilic and psychrophilic (i.e. pressure- and cold-tolerant; Fang et al., 2010). For example, the freshwater strain *S. oneidensis* MR-1 reduces Fe(III) oxides faster at high pressures than at surface pressures (Picard et al., 2012).

Thermodynamically, Fe(III) reduction becomes more favorable than SO_4^{2-} reduction in seawater at higher pressures because Fe(III) reduction involves the dissolution of a solid phase (Fang and Bazylinski, 2008). Further, ion-pairing with seawater ions decreases the availability of SO_4^{2-} as TEA while the activity of Fe(III) oxides remain unchanged. Lastly, lower temperatures further decrease the potential energy of SO_4^{2-} reduction. Thermodynamic calculations for the anaerobic respiration of different Fe(III) oxides and SO_4^{2-} with acetate as electron donor (Eq. 1 and 3) in shallow freshwater, shallow coastal, and deep-sea sediments show that 2-line ferrihydrite reduction coupled to acetic acid oxidation is always favored relative to SO_4^{2-}

reduction at any realistic Fe^{2+} concentrations (i.e. $< 10 \text{ mM}$) even in the presence of low dissolved sulfide concentrations (Figure 6). With more crystalline Fe (oxy)hydroxides, however, significant energy differences are observed, and the accumulation of reduced substrate must be considered. For example, at an assumed equilibrium pore water HS^- concentration of $1 \text{ }\mu\text{M}$ prior to the onset of intensive SO_4^{2-} reduction coupled to $100 \text{ }\mu\text{M}$ acetic acid, goethite reduction is still thermodynamically more favorable than SO_4^{2-} reduction in seawater in the presence of Fe^{2+} concentrations as high as $17 \text{ }\mu\text{M}$ at 10 m depth and $25 \text{ }^\circ\text{C}$, but at $5,000 \text{ m}$ and at 2°C , this upper limit is more than doubled to $43 \text{ }\mu\text{M}$ Fe^{2+} . These calculations suggest that the supply of freshly formed Fe(III) oxides should allow Fe(III) reduction to dominate SO_4^{2-} reduction in most marine environments provided sufficient electron donors are available. In environments dominated by more crystallized Fe(III) oxides, however, microbial Fe(III) reduction should only dominate if Fe^{2+} is removed from pore waters via adsorption onto the solid phase, precipitation of siderite, or any other Fe^{2+} minerals.

5.4. Biogeochemical Implications

The fact that C_{org} oxidation proceeds through dissimilatory metal reduction in river-dominated continental margin sediments such as the LAS and CRF has important implications for the cycling of carbon in marine environments. Although benthic $\text{O}_{2(\text{aq})}$ fluxes into CRF sediments are much higher than typical abyssal sediments (Rabouille et al., 2009), *in situ* C_{org} remineralization rates inferred from these measurements represented only $1/3$ of total C_{org} deposition rates, suggesting that the CRF could be a C_{org} megaburial center. As dissimilatory Fe(III) reduction is the primary anaerobic respiratory process in CRF sediments, however, C_{org} remineralization rates inferred from $\text{O}_{2(\text{aq})}$ fluxes may be underestimated due to the formation of secondary minerals such as siderite or vivianite which prevent reoxidation of Fe^{2+} by dissolved

1 $O_{2(aq)}$ (Glud, 2008). More importantly, the concentration of Fe(III) oxides available to
2 remineralize C_{org} in these sediments is about 5.4 times higher on a per mole C basis (corrected
3 from C/TEA stoichiometry) than SO_4^{2-} (181 mmol eq L^{-1} compared to 33.6 mmol eq L^{-1} , using
4 an Fe_{reac} content of 684 $\mu\text{mol gdw}^{-1}$, a porosity of 0.6, and solid phase density of 2.65 g cm^{-3}),
5 suggesting that dissimilatory Fe(III) reduction may be more important than SO_4^{2-} reduction for
6 organic matter remineralization in such environments. This is a conservative estimate, as much
7 of the Fe^{2+} produced can also be oxidized near the sediment water interface to recycle Fe(III)
8 oxides. Additional evidence for the increased remineralization of carbon in iron-rich sediments
9 includes that the dissolution of Fe(III) oxides releases otherwise protected natural organic matter
10 that could promote microbial respiration (Lalonde et al., 2012). In a similar manner, Fe(III)
11 oxides may catalyze hydrolytic reactions through both oxidative and non-oxidative pathways,
12 forming smaller organic carbon compounds that may be more labile for microbial respiration
13 (Mayer, 1995; Sunda and Kieber, 1994; Torrents and Stone, 1994). Finally, the production of O_2
14 radicals by Fe^{2+} oxidation near the SWI may generate peroxide (Burns et al. 2010), which
15 abiotically oxidizes a fraction of C_{org} (Burdige, 2007). On the other hand, SO_4^{2-} -reducing
16 conditions may actually promote C_{org} preservation, as vulcanization reactions between lignin and
17 alkyl-rich substances in the presence of sulfide may produce polymers more resistant to
18 fermentation (Hedges and Oades, 1997). Whether iron reduction dominates other RioMar
19 systems remains to be evaluated. Several large rivers in Asia or Oceania (e.g. the
20 Ganges, Yellow, and Irrawady) discharge high concentrations of iron-rich suspended sediment
21 beyond their shelves, and even arctic rivers may transport terrigenous material off-shelf via pack
22 ice (McKee et al. 2004; Martin and Meybeck 1979). To our knowlegde, however, iron

1 biogeochemistry in deep continental margin sediments adjacent to these rivers has yet to be
2 investigated.

3 Over geologic timescales, atmospheric O₂ levels are controlled by pyrite weathering
4 (Berner, 2001; Berner and Canfield, 1988; Berner and Petsch, 1998). If erosion processes supply
5 enough freshly formed Fe(III) oxides in RiOMar sediments, the findings of the present study
6 suggest that SO₄²⁻ reduction, and thus pyritization, can be controlled by the discharge of Fe(III)
7 oxides. Although the implications of such findings on atmospheric O₂ levels on a geological
8 timescale are difficult to evaluate, increases in temperature (Barnett et al., 2005; Levitus et al.,
9 2001; Lyman et al., 2010), seawater levels (Wigley, 2005), and the frequency of ENSO events
10 (Khan et al., 2006) associated with climate change affect precipitation intensity and frequency
11 and, thus, riverine discharge (Goudie, 2006; Hamilton, 2010). As the supply of Fe(III) oxide
12 minerals to the oceans may be increased as a result of increasing riverine discharge, this process
13 may have an even larger negative impact on the potential for pyritization in these environments.
14 Finally, these findings may have important implications for the changes in redox conditions on
15 the Early Earth. If increases in riverine discharge associated with increases in temperatures
16 provided enough freshly formed Fe(III) oxides to RiOMar sediments around the globe, dissolved
17 sulfides present in the deep euxinic water column of the oceans during the Proterozoic may have
18 been titrated during oxidation by Fe(III) oxides and precipitation of FeS_(s) (Arnold et al., 2004;
19 Canfield et al., 2008; Lyons et al., 2009), which could have facilitated a shift in microbial
20 processes from less energetically favorable SO₄²⁻ reduction to more energetically favored Fe(III)
21 reduction in deep-sea sediments and favored the onset of oxygenic conditions on Earth.

22

23

6. CONCLUSIONS

Sediments of river-dominated ocean margins (RiOMars) represent accumulation centers for C_{org} and terrigenous minerals, but relatively few studies have examined the pathways of anaerobic respiration in these sediments. In this study, two transects of the Congo River fan and Mississippi shelf and slope sediments were conducted using a combination of Au/Hg voltammetry and traditional wet chemistry techniques. In Mississippi slope and Congo fan sediments, Au/Hg voltammetry revealed C_{org} mineralization in the top ~20 cm was dominated by dissimilatory Fe(III) and Mn(IV/III) reduction, as no evidence for SO_4^{2-} reduction was detected. The Congo fan provides evidence demonstrating that continuous discharge of freshly-weathered Fe minerals results in Fe(III)-reducing conditions in sediments and that shifts in turbidite flows may alter the intensity of Fe(III) reduction. An intensification of aerobic and Fe(III) respiration is observed near the active channel because of increased delivery of C_{org} and Fe(III) oxides, demonstrating the reliance of benthic microorganisms on the continuous delivery of fresh terrigenous material. The Mississippi slope, on the other hand, demonstrates a transition from SO_4^{2-} reduction on shelf sediments to metal reduction in slope sediments subject to mass slumping or shelf-spillover of unconsolidated oxidized minerals. Whether these processes occur in other large RiOMars with significant sediment shelf export or are even more universal to passive continental margins subject to submarine landslides (i.e. those without river input) remain to be evaluated. Climate-change induced effects in Fe depositional patterns may alter the pathways, rates, and extent of C_{org} remineralization in Fe-rich sediments, ultimately affecting global carbon inventories. Simultaneously, pyrite precipitation may be prevented in such environments, with important implications on the evolution of atmospheric oxygen over

1 geological timescales. Finally, delivery of Fe(III) oxides to RiOMar sediments may have titrated
2 sulfides from the ocean, perhaps promoting the onset of oxygenic conditions on the early earth.

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Table 1 – Maximum diffusive fluxes of dissolved $O_{2(aq)}$, Fe^{2+} , Mn^{2+} , and DIC calculated from the vertical pore water profiles using equation 12. As ΣH_2S concentrations were below detection limit in all the cores investigated, their fluxes were omitted in this table. DIC was not quantified in GOM sediments but, when measured, the flux of DIC is larger than that of $O_{2(aq)}$, demonstrating the importance of anaerobic mineralization in these sediments.

	flux rate ($mmol\ m^{-2}\ day^{-1}$)						
	GOM2	GOM3	GOM12	GOM10	ColA	ColB	ColE
O_2	3.57 ± 0.58	1.44 ± 0.23	0.71 ± 0.13	0.61 ± 0.07	2.66 ± 0.52	2.35 ± 0.42	1.26 ± 0.3
Fe^{2+}	0	0.12 ± 0.02	0.85 ± 0.17	0	0.57 ± 0.03	0.22 ± 0.00	0
Mn^{2+}	0.25 ± 0.01	0.18 ± 0.03	0.24 ± 0.06	0	0	0	0
DIC	-	-	-	-	4.39 ± 2.69	6.99 ± 0.65	3.16 ± 0.08

FIGURE CAPTIONS

Figure 1 – Maps of sediment core locations on a) the Louisiana slope (courtesy of J. Moriarty and C. Harris, Virginia Institute of Marine Science), and b) the Congo River Fan including the high resolution bathymetry obtained at the site during the same cruise (courtesy of Laurence Droz, ©Ifremer, Congolobe cruise).

Figure 2 - Depth profiles of dissolved redox chemical species ($O_{2(aq)}$, organic-Fe(III), Mn^{2+} , Fe^{2+} , $FeS_{(aq)}$, and $\sum H_2S$) and pH in sediments collected during a transect from the shelf to the slope of the northern Gulf of Mexico from a - b) GOM2 (65 m); c - d) GOM3 (123 m); e - f) GOM12 (980 m); and g - h) GOM10 (1800 m). Error bars represent the standard deviations of triplicate voltammetric scans obtained from a single core. The transect reveals a transition from predominantly SO_4^{2-} reduction on the shelf (a - d), to metal reduction on the mid-slope (e - f), and finally to aerobic respiration at the base of the slope (g - h). Dissolved $\sum PO_4^{3-}$ and DIC were not measured because the pore waters were not extracted from these sediments.

Figure 3 - Depth profiles of dissolved redox chemical species ($O_{2(aq)}$, organic-Fe(III), Mn^{2+} , Fe^{2+} , $FeS_{(aq)}$, and $\sum H_2S$), as well as DIC, $\sum PO_4^{3-}$, pH, reactive Fe(III) (oxy)hydroxides (Fe_{reac}), more crystalline (oxy)hydroxides (Fe_{crys}), and solid phase $\sum PO_4^{3-}$ in Congo River fan sediments at the extinct channel, CoLE (a - c), a station intermediate to the extinct and active channels, CoLB (d - f), and from the active channel levee, CoLA (g - i). Error bars represent the standard deviations of triplicate voltammetric scans, the standard error from calibration curves of DIC and $\sum PO_4^{3-}$, or the

standard deviations of duplicate solid phase analyses obtained from a single core. Both aerobic and anaerobic respiration processes are more intense closer to the active channel currently subject to turbidite flows.

Figure 4 - Relationship between expected dissolved $\Sigma\text{H}_2\text{S}$ and Fe^{2+} concentrations in equilibrium with $\text{FeS}_{(\text{aq})}$ at several pH values. Detection limits for $\Sigma\text{H}_2\text{S}$ and Fe^{2+} are indicated by dashed lines. LAS shelf and shelf-break stations GOM2 and GOM3 display $\text{FeS}_{(\text{aq})}$ in pore waters in the absence of $\Sigma\text{H}_2\text{S}$ and Fe^{2+} , suggesting the system is not at steady-state. The LAS slope station GOM12 and the CRF stations show high-concentrations of Fe^{2+} but no $\Sigma\text{H}_2\text{S}$, suggesting SO_4^{2-} reduction is not important in these sediments.

Figure 5 - Current intensities of organic-Fe(III) complexes as a function of Fe^{2+} concentrations measured at each depth in the pore waters of the LAS and CRF continental slope stations. Although correlations are not necessarily evident when examining individual sites due to the variety of reactions that are responsible for the production and consumption of these two species, a positive correlation ($R^2 = 0.70$) between organic-Fe(III) complexes and Fe^{2+} exists for the entire dataset, suggesting that in general sulfate reduction is minimal in these sediments and that dissimilatory Fe(III) reduction instead dominates anaerobic respiration.

Figure 6 - ΔG_{rxn} for 2-line ferrihydrite, goethite, and SO_4^{2-} reduction coupled to the oxidation of $100\ \mu\text{M}\ \text{CH}_3\text{COOH}$ (Thurman, 1985) as a function of the reduced product (either Fe^{2+} or $\Sigma\text{H}_2\text{S}$) for a freshwater (25°C , 1 bar, $I = 0$), coastal marine (25°C , 1 bar, $I = 0.7$), and deep-sea (2°C , 500 bar, $I = 0.7$) sediment. All calculations were conducted with SUPCRT92 (Johnson et al.,

1992) using HCO_3^- concentration of 1.93 mM (Millero, 2005) and at a pH of 7.4 (typical pH of CRF sediment). Fe(III) reduction becomes thermodynamically more favorable as depth increases, whereas SO_4^{2-} reduction becomes less favorable.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6