



RESEARCH LETTER

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Key Points:

- Fifteen percent of the OC in the Wax Lake Delta sediments is bound to reactive iron
- The modeled decay rate of iron coprecipitated OC is 5 times less than the total OC
- Lignin-derived compounds and other phenolic acids are preferentially sorbed to iron (OC:Fe < 1)

Supporting Information:

- Supporting Information S1

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Enhanced terrestrial carbon preservation promoted by reactive iron in deltaic sediments

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Abstract We examined the role of reactive iron (Fe_R) in preserving organic carbon (OC) across a subaerial chronosequence of the Wax Lake Delta, a prograding delta within the Mississippi River Delta complex. We found that ~15.0% of the OC was bound to Fe_R, and the dominant binding mechanisms varied from adsorption in the youngest subaerial region to coprecipitation at the older, vegetated sites. The δ¹³C of the iron-associated OC was more negative than the total OC (mean = -2.6‰), indicating greater preference for terrestrial material and/or compounds with more negative δ¹³C values. However, only the adsorbed OC displayed preferential binding of lignin phenols. We estimate that ~8% of the OC initially deposited in deltaic systems is bound to Fe_R (equivalent to 6 × 10¹² gC yr⁻¹), and this percentage increases postdepositionally, as coprecipitation of Fe_R and OC allows for an even greater amount of OC to be bound to Fe_R.

1. Introduction

Understanding the mechanisms responsible for enhancing the stability and long-term storage of organic carbon (OC) in sediments and soils is important for predicting how the carbon cycle will respond to climate change [Schmidt *et al.*, 2011]. Carbon storage is considered a priority in systems that are currently acting as major carbon sinks such as the permafrost carbon in the Arctic [Schuur *et al.*, 2015], coastal and freshwater wetlands [Day *et al.*, 2008; Erwin, 2009], and continental margin sediments [Smith *et al.*, 2015]. Continental margin sediments are responsible for 87% of the approximate 169 × 10¹² g of OC that is buried in marine sediments each year [Smith *et al.*, 2015]. River deltas are responsible for much (41%) of this continental margin burial as a result of their high sediment loads [Burdige, 2005; Smith *et al.*, 2015]. This plays a major role in atmospheric CO₂ concentrations by providing a link between the short-term cycling of terrestrial and aquatic carbon and the long-term carbon cycle through burial and eventual incorporation into the rock cycle [Bernier, 1982; Hedges and Keil, 1995; Burdige, 2005].

The role of reactive iron (Fe_R) (nanoparticulate and amorphous phases of ferric oxides) in preserving OC has now been documented in both soils and marine sediments [Kaiser and Guggenberger, 2000; Lalonde *et al.*, 2012; Riedel *et al.*, 2013]. In an extensive study of several environments including the Southern Ocean, Mexican and Indian Margins, St. Lawrence estuary and gulf, and the Black Sea, Lalonde *et al.* [2012] reported that 21.5 ± 8.6% of the OC in marine sediments is bound to Fe_R phases. The association between OC and mineral particles has been the focus of several key studies in river-dominated continental margins [Mayer, 1994; Hedges and Keil, 1995; Ransom *et al.*, 1997; Blair and Aller, 2012]. However, except for a single surface sediment sample collected on the Mackenzie River Delta, the Fe_R mechanism for stabilizing OC has been largely overlooked in river deltas [Lalonde *et al.*, 2012]. Moreover, the dominant source of iron to ocean margins is in association with riverine and glacial particulates [Poulton and Raiswell, 2002, 2005], which further warrants the need for research on the potential role that Fe_R has on OC preservation in these deltaic systems.

Here we examine the role of Fe_R in preserving OC within the sediments of the Wax Lake Delta, Louisiana. The Wax Lake Delta is a prograding delta that formed as an unintentional consequence of dredging a navigational outlet off the Atchafalaya River in 1941 [Roberts *et al.*, 2003], and it was reported to have built ~100 km² of land from 1980 to 2009 [Kim *et al.*, 2009]. This delta provides an ideal system to study the role of iron in a rapidly evolving depositional system that receives sediments from both the Mississippi River and Red River drainage basins [Allison *et al.*, 2012]. Our objectives were to determine the following: (1) if

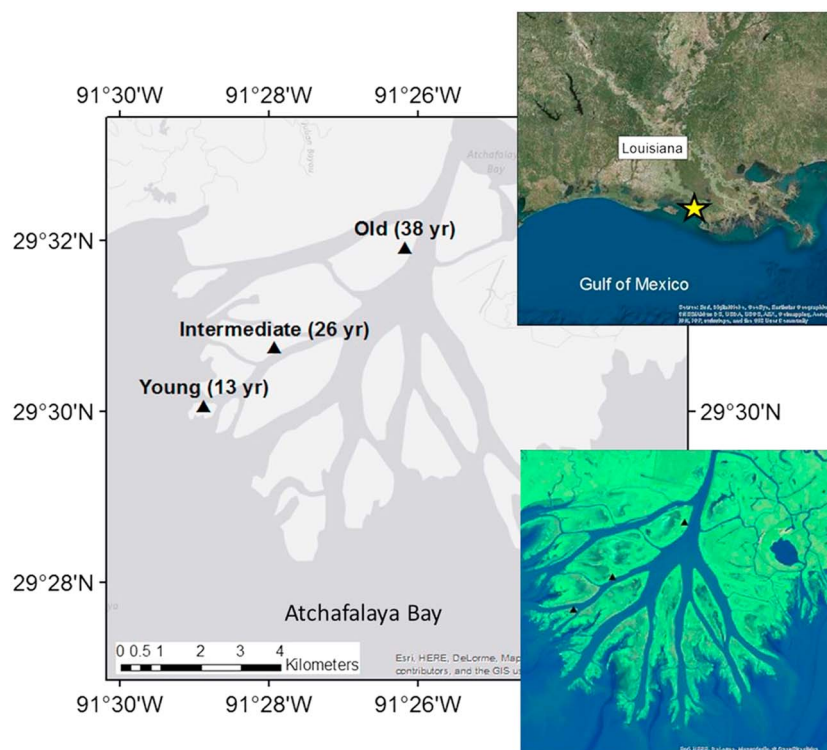


Figure 1. Sampling locations in the Wax Lake Delta, Louisiana. The satellite image of the delta was taken on 25 October 2014 (USGS). Values in parentheses represent the time since the area became subaerial.

Fe_R plays a significant role in binding OC in this young delta; (2) if there is a preference for either adsorption or coprecipitation during the different stages of subaerial development; (3) if Fe_R has a quantifiable impact on the decay rate of the OC in this system; and (4) if there is selective binding/preservation of lignin-derived organic matter and other phenolic organic compounds.

2. Materials and Methods

2.1. Site Description, Sample Collection, and Storage

The Wax Lake Delta, Louisiana, began prograding subaerially in 1973 after a major flooding event and has continued to advance into Atchafalaya Bay ever since (Figure 1) [Roberts *et al.*, 2003]. The sampling sites were chosen to represent a subaerial chronosequence that signify different ages since becoming subaerial. The “time since becoming subaerial” was determined via satellite imagery and is given in parentheses on Figure 1. The 0.5 m sediment cores were extracted on 1 February 2013 from each of the sites and were subsampled in the field (see Text S1 in the supporting information for more site details). These subsamples were transported to Texas A&M University on ice where they were stored frozen at $-20^{\circ}C$ and later freeze dried. Freeze-dried sediment was passed through a 2 mm mesh size sieve to remove larger roots and stems, homogenized, and stored in ashed ($450^{\circ}C$ for 4 h) scintillation vials.

2.2. Bulk Carbon Analyses

Total OC (TOC) and stable carbon isotope ratios ($^{13}C/^{12}C$) were measured at Concordia University, Montreal. Freeze-dried sediment samples were decarbonated by vaporization with concentrated HCl [Harris *et al.*, 2001] and analyzed using a Eurovector Elemental Analyzer coupled to an Isoprime stable isotope ratio mass spectrometer. Stable isotope data are reported in $\delta^{13}C$ (‰) notation as relative to the Vienna Pee Dee Belemnite standard.

2.3. Sediment Accumulation Rate

Geochronology of the Wax Lake cores were determined utilizing ^{210}Pb , a naturally occurring, particle-reactive radioisotope in the ^{238}U decay series ($t_{1/2} = 22.3$ y). Freeze-dried sediment aliquots were ground, packed, and

sealed vials and stored for ≥ 21 days to allow ^{210}Pb to reach secular equilibrium. Samples were counted for 1–2 days on a well geometry, Canberra low-energy germanium gamma spectrometer. See Text S1 for more details.

2.4. Iron Reduction and Extraction

Reactive iron and the associated OC were removed using the citrate-dithionite reduction method according to Mehra and Jackson [1958], as modified by Lalonde *et al.* [2012]. TOC, $\text{C}^{13}/\text{C}^{12}$, and cupric oxide (CuO) oxidation products were analyzed using the extracted sediment from which the Fe_R and associated OC were removed. Values for total Fe_R , Fe_R -associated OC, Fe_R -associated $\delta^{13}\text{C}$, and Fe_R -associated CuO oxidation products were determined by the difference between the bulk sediment and Fe_R -extracted sediment. See Text S1 for more details.

2.5. CuO Oxidation

Lignin-phenols and other CuO oxidation products were extracted and analyzed in each sample (pre- and post- Fe_R removal) according to the methods of Hedges and Ertel [1982], as modified by Goñi and Hedges [1995]. The eight major lignin oxidation products, vanillin, acetovanillone, vanillic acid (VAD), syringaldehyde, acetosyringone, syringic acid (SAD), *p*-hydroxycoumaric acid (CAD), and ferulic acid, were quantified and normalized to 100 mg-OC (VSC_{OC}). Additional CuO oxidation products include 3,5-dihydroxybenzoic acid (3,5 Bd), *p*-hydroxybenzaldehyde (PAL), *p*-hydroxybenzoic acid (PAD), and *p*-hydroxyacetophenol. See Text S1 for more details.

2.6. Statistical Analyses

Statistical analyses were conducted using the software program R [R Core Team, 2014]. A balanced bootstrap simulation was utilized for assessing statistical significance [Davison *et al.*, 1986]. Significance was determined using the 95% confidence intervals of the bootstrapped means of the raw data and difference data (Bulk minus Fe_R associated). Means with nonoverlapping confidence intervals and difference data with confidence intervals that do not include zero are considered significantly different. This significance is equivalent to a *p* value < 0.05 . Data are reported with the mean and confidence intervals in the following format: Mean [2.5% confidence interval (CI), 97.5% CI].

3. Results and Discussion

3.1. Organic Carbon Burial and Reactive Iron

TOC increased with time since becoming subaerial (Young to Intermediate to Old) (Figure 2). This increase was significant from the Young site to the Intermediate site, but not from the Intermediate site to the Old site and can be explained by the additional carbon sources from in situ vegetation (e.g., *Colocasia esculenta* and *Salix nigra*). This is also supported by the significant depletion of the $\delta^{13}\text{C}$ values observed at the Old and Intermediate sites when compared to the Young site (Figure 2).

The total Fe_R also increases from the Young site to the Intermediate and Old sites (Figure 2). The major source of Fe_R to these river-dominated systems is the riverine particles, with the finer fraction typically containing a greater proportion of highly reactive iron [Poulton and Raiswell, 2002, 2005]. This suggests that Fe_R is either produced over time in the sediment, as it becomes more densely vegetated or these regions are able to trap fine particles more efficiently [Nardin and Edmonds, 2014].

The average percentage of OC bound to Fe_R phases in these Wax Lake Delta sediments is 15.0% [12.3%, 17.9%] (Figure 2). Additionally, the amount of Fe_R -associated OC varies between the Young, Intermediate, and Old sites. The Young site contains the lowest fraction of iron-associated OC at 8.1% [4.9%, 11.2%], followed by the Old site at 15.0% [11.2%, 19.7%], while the Intermediate site contains the greatest fraction of Fe_R -associated OC at 20.2% [16.8%, 24.4%] (Figure 2). These percentages are less than but still comparable to that reported by Lalonde *et al.* [2012] for marine sediments globally at $21.8 \pm 8.6\%$, suggesting that binding of OC to reactive Fe_R is significant in the Wax Lake Delta.

3.2. Adsorption Versus Coprecipitation

The association between OC and Fe_R occurs through simple sorption onto discrete iron oxide particles or the iron oxide surfaces of aluminosilicate minerals, or OC can bind to Fe_R through the coprecipitation of OC and

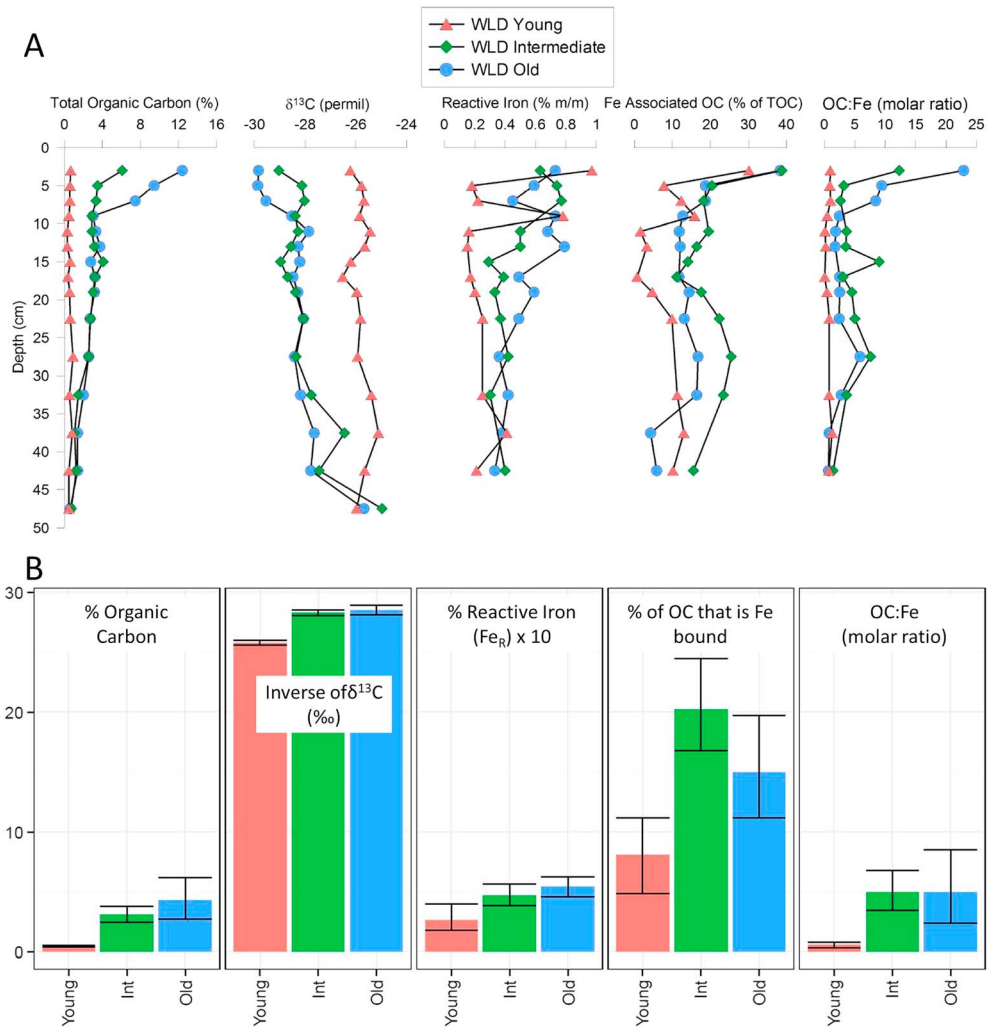


Figure 2. (a) Downcore profiles of the total organic carbon (TOC; % of sediment), $\delta^{13}\text{C}$ (‰), reactive iron (Fe_R ; % m/m), Fe_R -associated organic carbon (% of TOC), and molar OC:Fe ratios for the Young, Intermediate (Int) and Old sites. (b) The average TOC, $\delta^{13}\text{C}$, Fe_R , Fe_R -associated OC, and OC:Fe molar ratios. The values for $\delta^{13}\text{C}$ have been multiplied by -1 , and the values for Fe_R have been multiplied by 10 in order to make the values visible on the same y axis. The 95% confidence intervals of the bootstrapped means are shown by the error bars.

Fe_R in the sediments [Eusterhues et al., 2011; Lalonde et al., 2012; Chen et al., 2014]. Coprecipitation occurs when reduced iron migrating through anoxic pore waters is oxidized in the presence of dissolved OC at the oxic/anoxic interface [Riedel et al., 2013]. Previously, these binding mechanisms have been distinguished by the molar ratio of OC to iron (OC:Fe) [Lalonde et al., 2012]. An OC:Fe of 1.0 or less indicates that the dominant form of the OC- Fe_R species is through sorption, while coprecipitation yields OC:Fe ratios between 6 and 10 [Wagai and Mayer, 2007]. However, recent results suggest that iron monosulfides can bias the ratio toward lower values due to the oxidation of FeS to FeOOH (or $\text{Fe}(\text{OH})_3$) upon freeze drying (Y. G. Yves Gélinas, personal communication, 2015). Pore water measurements of salinity and hydrogen sulfide (H_2S) concentrations at the current sampling locations in 2010/2011 indicated low salinity (0.2 to 1.2 ‰) and H_2S concentrations (overall mean: 0.01 mM) [Henry and Twilley, 2014]. Therefore, we believe that a FeS bias was not important in affecting our data.

The OC:Fe ratio at the Young site is 0.55 [0.33, 0.77] (Figure 2), which indicates that sorption of OC is the dominant method of OC- Fe_R association at this site. This suggests, along with the lignin phenol data presented below, that the OC bound to Fe_R in these sediments was formed predepositionally in association to the riverine sediments. It is likely that these particles initially supply the delta with an already Fe_R bound OC fraction until additional iron associations occur postdepositionally. This is not unique to the Wax Lake Delta as

the Mackenzie River Delta sediments measured by *Lalonde et al.* [2012] also exhibited a low OC:Fe ratio of 0.20. Furthermore, it has been shown that TOC is significantly correlated to the amount of Fe_R in the suspended and bed sediments of four climatologically and lithologically diverse river systems (Amazon, Isere, Glomma, and the Huanghe) and four glacial systems [Poulton and Raiswell, 2005]. Therefore, we expect that the type of association occurring at the Wax Lake Delta Young site is the dominant mechanism for other locations with high clastic sedimentation rates.

The shift in the dominant mechanism for binding OC and Fe_R is evident at the Intermediate and Old sites where the average OC:Fe ratio is 4.95 [3.42, 6.82] and 4.94 [2.38, 8.55], respectively (Figure 2). The highest OC:Fe ratio occurs in the top 5 to 10 cm of the sediment cores, which includes ratios of 22.9, 14.9, 12.3, 9.4, and 8.4. This is indicative of the surface redox boundary where coprecipitation occurs. Below this depth interval, the average OC:Fe ratio is 4.59 [3.27, 6.13] and 2.35 [1.61, 3.27] at the Intermediate and Old sites, respectively. The OC:Fe molar ratio decreases around 40 cm depth at the Old and Intermediate sites that indicate more sorption or partial oxidation of the Fe_R -associated OC.

3.3. Impact of Reactive Iron on the Modeled Degradation Rate of Organic Carbon

Diagenetic models were developed to study the apparent degradation rate of organic matter in sediments [Berner, 1964; Westrich and Berner, 1984; Canfield, 1994; Arndt et al., 2013], and the most basic model, the One-G model, assumes two pools of organic matter, a metabolizable and nonmetabolizable pool. This metabolizable pool is assumed to be remineralized at a constant rate (k), such that

$$G_m = G_{m0}e^{-kt} + G_\infty \quad (1)$$

where G_{m0} is the concentration of metabolizable OC at the sediment surface, G_∞ is the nonmetabolizable OC where the modeled OC approaches an asymptote, and t is time.

We used this model to calculate the apparent decay rate for both the bulk OC and Fe_R -associated OC pools for the Intermediate and Old sites (Figure 3). In order to strengthen the diagenetic model, we combined the Old and Intermediate sites due to the evidence that the Old site and Intermediate Site are evolving conservatively over time corresponding to a true chronosequence (See Text S2 and Figures S1–S4). The downcore ages of the Intermediate site were adjusted to match the year since becoming subaerial for the Old site. Furthermore, the goal of these diagenetic models is to compare the overall reactivity of the Fe_R -associated OC to the TOC, and this age adjustment only strengthens the fit of the model without altering the differences between the two carbon pools.

Interestingly, the One-G-modeled decay constant for the Fe_R -associated OC is larger ($k = 0.159 \text{ yr}^{-1}$) than the bulk OC ($k = 0.104 \text{ yr}^{-1}$) (Figure 3). However, both decay constants are skewed by the initial decrease in concentration within the surface sediments. The Fe_R -associated OC appears to consist of only an initial highly reactive component and a nonreactive (G_∞) pool at 4.05 mg-OC/g-sediment. With the OC:Fe ratios plotted as point-size in the diagenetic model, it becomes readily apparent that the highly reactive OC- Fe_R pool corresponds to the greatest OC:Fe molar ratios (OC:Fe > 8). As discussed previously, we hypothesize that these high OC:Fe ratios are indicative of the surface redox boundary where coprecipitation is occurring. The sediment below this active cycling corresponds to more stable OC:Fe molar ratios that are still indicative of coprecipitation, but with the outermost loosely bound OC removed. This coprecipitated Fe_R -associated OC lies along the G_∞ asymptote and provides further empirical evidence that these interactions are acting to stabilize the OC in this delta.

One-G models are often oversimplifications of heterogeneous systems [Arndt et al., 2013]. Multi-G models have been developed to account for this heterogeneity and changing decay rates throughout burial [Jørgensen, 1978]. A multi-G model that is commonly utilized is the 2G Model [Westrich and Berner, 1984]. This model adds one additional pool of metabolizable carbon such that there is a highly reactive component, less reactive component, and nonreactive component on the timescale of interest. It is modeled to devolve two reaction rates, k_1 and k_2 , for the highly reactive and less reactive pools, respectively. This equation is written as

$$G_T(t) = G_{01}e^{-k_1t} + G_{02}e^{-k_2t} + G_\infty \quad (2)$$

where, G_T is the concentration of the total OC at the sediment surface, G_{01} is the initial concentration of the highly reactive fraction, G_{02} is the initial concentration of the less reactive fraction, G_∞ is the concentration of the nonreactive component, and t is time [Westrich and Berner, 1984]. See Text S3 for a detailed description of how G_T , G_{01} , G_{02} , and G_∞ were determined.

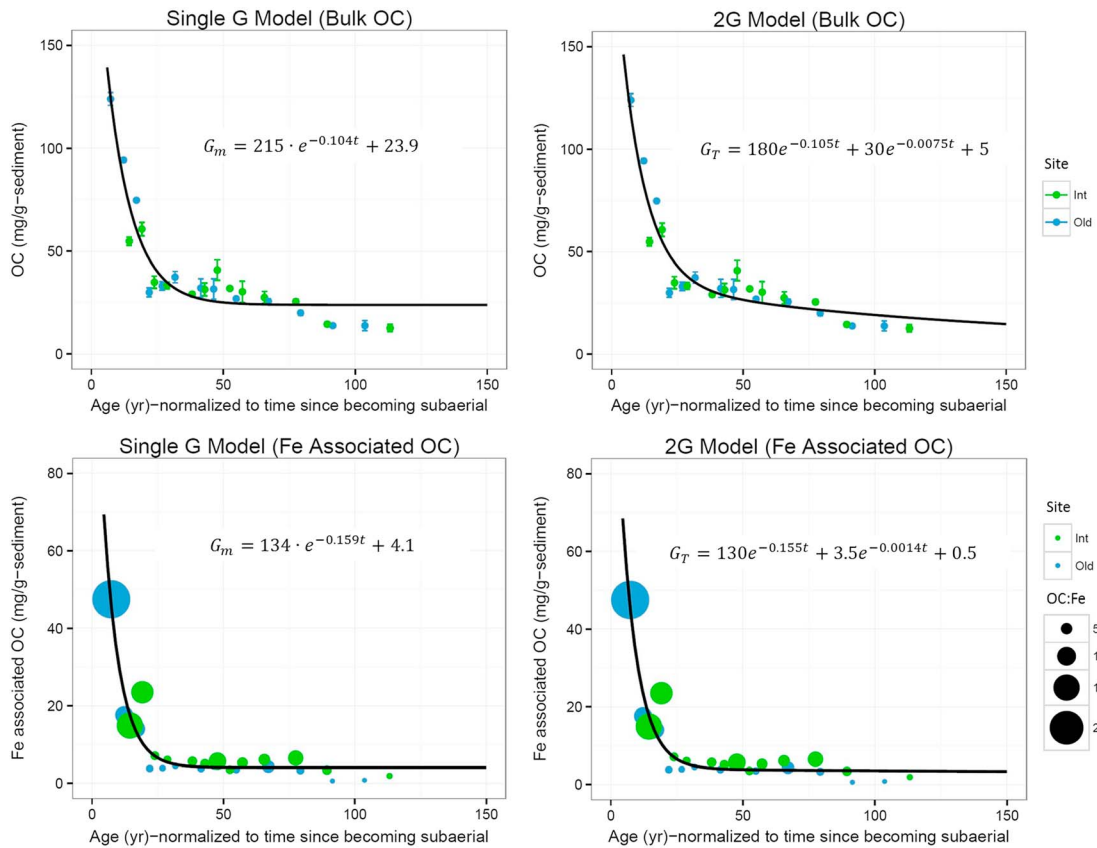


Figure 3. TOC concentration (mg-OC/g-sediment) versus time (corrected to match time since becoming subaerial) for the Intermediate and Old sites are fit with Single G models and 2G models for both the bulk organic carbon and the organic carbon associated to Fe_R . The OC:Fe molar ratio is plotted as point size for the Fe-associated OC. Fe-associated OC with high organic carbon to iron ratios (OC:Fe > 8) decays rapidly, while the region below lies along the G_∞ asymptote. The 2G model decay constant of the less reactive pools (G_{02}) suggests that the coprecipitated OC decays at a slower rate than the corresponding bulk OC once the OC:Fe molar ratio is less than 8 ($k = 0.0014 \text{ yr}^{-1}$ versus $k = 0.0075 \text{ yr}^{-1}$, respectively).

This model captured the trend in the bulk OC better than the One-G model by allowing for the slower decay rates of the low reactive pools. The decay constants for the bulk OC were $k_1 = 0.105 \text{ yr}^{-1}$ and $k_2 = 0.0075 \text{ yr}^{-1}$, while the decay constants for the Fe_R -associated OC were $k_1 = 0.155 \text{ yr}^{-1}$ and $k_2 = 0.0014 \text{ yr}^{-1}$. These Two-G models separate out the initially high decay rates in the surface sediments and also suggest that the coprecipitated Fe_R -associated OC decays at a rate approximately 5 times slower than the bulk OC once the OC:Fe ratio is less than ~8 in the subsurface.

3.4. Preferential Sorption of Terrestrial Material

In the Wax Lake Delta sediments, the $\delta^{13}C$ value of the Fe_R -associated OC was normally more negative than the bulk OC ($\delta^{13}C$ difference of -2.6‰ [-7.2‰ , 0.5‰]). This is in contrast to that found in marine sediments where the Fe_R -associated OC was typically more enriched in carbon-13 relative to the bulk ($\delta^{13}C$ increased by $1.7 \pm 2.8\text{‰}$) [Lalonde et al., 2012]. However, the Mackenzie River Delta sediment sample from Lalonde et al. [2012] was an outlier exhibiting a much more negative $\delta^{13}C$ for the Fe_R -associated OC (-36.31‰) relative to the bulk (-26.70‰). Although more work is needed on other river deltas, this suggests that the Fe_R in deltaic sediments is preferentially binding more ^{13}C depleted organic matter.

There are several biomolecules and biomolecular classes that tend to be more depleted or more enriched in carbon-13 relative to the bulk organic matter [Meyers, 1997]. One aromatic/phenolic macromolecule that is known to be more depleted than the bulk organic matter is lignin [Benner et al., 1987]. In our study, the VSC_{OC} indicates that lignin was preferentially associated to Fe_R at the Young site (Figure 4). Moreover, this adsorbed OC was enriched in the more acidic oxidation products (vanillic acid, syringic acid, cinnamic acid, and

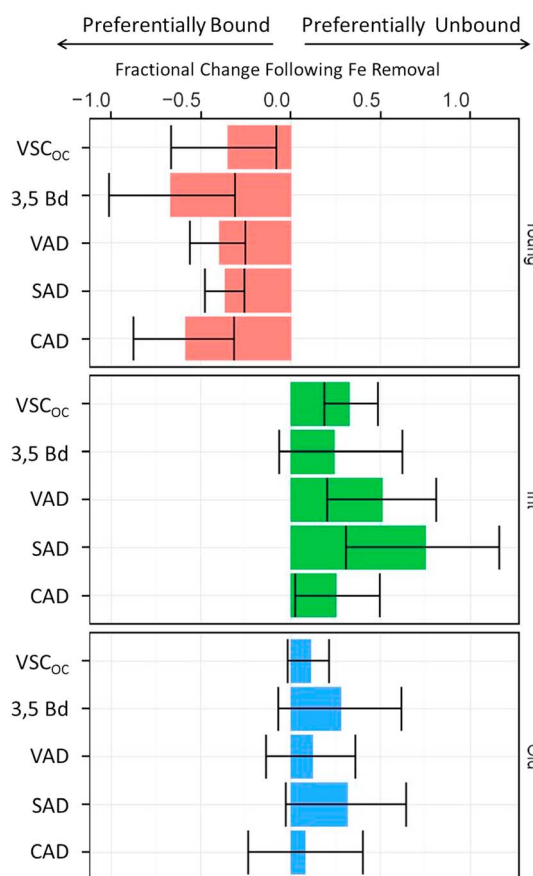


Figure 4. The proportional change in organic carbon normalized concentrations of total lignin oxidation products (VSC_{OC}) and acidic oxidation products including 3,5-dihydroxybenzoic acid (3,5 Bd), vanillic acid (VAD), syringic acid (SAD), and *p*-hydroxycoumaric acid (CAD). This proportional change is determined as the bootstrapped differences divided by the mean of the bulk data. Lignin phenols and aromatic acids are preferentially sorbed to Fe_R (OC:Fe < 1) at the Young site but are not preferentially bound during coprecipitation at the Intermediate and Old sites. The 95% confidence intervals of the scaled bootstrapped differences are shown by the error bars.

3,5-dihydroxybenzoic acid) (Figure 4). However, we did not find any preferential binding of lignin-derived organic matter from coprecipitation at the Intermediate and Old sites.

The composition of Fe_R-associated organic matter has been studied in laboratory experiments [Kaiser and Guggenberger, 2000; Eusterhues et al., 2011], in soils [Kramer et al., 2012], and both [Riedel et al., 2013], and each of these studies reports an enrichment of aromatic compounds in the Fe_R-associated pool. A recent study on the properties of OM adsorbed and coprecipitated to iron at varying OC:Fe molar ratios indicated that there is ligand exchange between COO⁻ functional groups and Fe_R during both coprecipitation and adsorption [Chen et al., 2014]. Furthermore, the OC associated to Fe_R is enriched in aromatic/phenolic compounds at lower OC:Fe ratios, but not at high OC:Fe ratios. Our results support the notion that there is preferential retention of dissolved aromatic acids and lignin-derived dissolved organic matter with reactive minerals at low OC:Fe ratios [Kaiser and Guggenberger, 2000; Kramer et al., 2012; Chen et al., 2014], and the lack of preferential binding of lignin-derived organic matter at higher OC to Fe_R ratios is in agreement with the study by Chen et al. [2014].

4. Conclusions and Possible Implications

Large delta-front estuaries are utilized as recorders of global environmental change [Bianchi and Allison, 2009]. Several of these tools used for reconstruction include the use of biomarkers such as lignin oxidation products. Our findings warrant that continued caution must be used when utilizing these proxies to track changes in the degradation or sources of organic matter. Although these lignin phenols are removed from Fe_R during the CuO oxidation process [Hernes et al., 2013], the selective preservation of acidic phenols in sediments could lead to a misinterpretation of the degradation indices.

The results of our study suggest that the role of Fe_R in deltaic sediments needs to be considered when discussing carbon burial in these depositional systems. An average of 15.0% [12.3%, 17.9%] of the OC in the Wax Lake Delta was directly bound to Fe_R. The Young site, representing a potential riverine sediment end-member, shows that an average of 8.1% of the OC in these sediments is directly sorbed (OC:Fe < 1) to Fe_R. This is similar to the 7.6% of OC sorbed to Fe_R in Mackenzie River Delta (OC:Fe = 0.20). Moreover, it has been shown that the proportion of Fe_R is comparable in several riverine and glacial sediments, regardless of differences in catchment and bedrock lithology [Poulton and Raiswell, 2002]. If we assume that the flux of Fe_R-associated OC behaves similarly to the total Fe_R, then it is reasonable to expect that approximately 8% of the carbon deposited in deltaic systems

is directly sorbed to Fe_R (equivalent to $6 \times 10^{12} \text{ gC yr}^{-1}$) [Hedges and Keil, 1995; Smith et al., 2015]. This estimate is conservative, as it does not include the coprecipitation of OC that occurs postdepositionally and allows for an even greater percentage of OC to be preserved by Fe_R [Lalonde et al., 2012; Chen et al., 2014]. Because this interaction has been shown to increase the residence time of carbon in the organic form, Fe_R must be an important component of long-term atmospheric carbon sequestration in these systems.

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