# Temporal and Spatial Distribution of Iron Bound Organic Carbon in the Mississippi River Influenced Shelf Sediments

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## Abstract

Continental shelves are important land-ocean interfaces where natural and anthropogenic processes, as well as sediment geochemistry regulate the sequestration of organic matter (OM) in the sediment. In the Northern Gulf of Mexico, along the Louisiana shelf, the Mississippi River discharge asserts strong seasonal controls over primary production and sedimentary reserves of minerals. Recent studies have shown the importance of mineral-organic matter interactions in the sedimentary OM preservation, both of which are abundant in this region. Thus, the major objective of this work is to understand the spatial and temporal variability of the sediment organic carbon (OC) directly bound to the reactive iron (rFe) mineral phases such as goethite, ferrihydrite, lepidocrocite and hematite. Sediment samples were collected from five sites along the river plume during periods of low (August/September 2016) and high (May 2017) river discharge. Average rFe content in the top 20 cm of sediment was significantly higher at all sites in May (6.9 $\pm$1.5 mg gdw-1) compared to August (4.3$\pm$ 0.6 mg gdw-1), while particulate OC content in these sediments was higher in August (11.9 $\pm$ 3.7 mg gdw-1) compared to May (7.4$\pm$ 4.7 mg gdw-1). However, the bulk OC bound to rFe in these sediments did not vary significantly between the two seasons and ranged between 2.3 - 3.4 mg gdw-1. Molar OC: Fe ratios in the OC associated with rFe ranged between 0.9-6.2, with higher ratios in the deeper sediment sections (5-20 cm) than at the top (0-5 cm). Our results indicate that 27- 32% of the total OC in sediment is associated with rFe phase and preserved in these recent shelf sediments. A combination of X-ray diffractometry and Fe-K Edge X-ray absorption near edge structure spectroscopy analyses were carried out to identify the mineralogical composition of rFe bound to the organic carbon in the sediments. Preliminary findings indicate that most of the iron is found as non-reactive iron in clay mineral smectite, but the dominant form of rFe associated with OC is goethite.
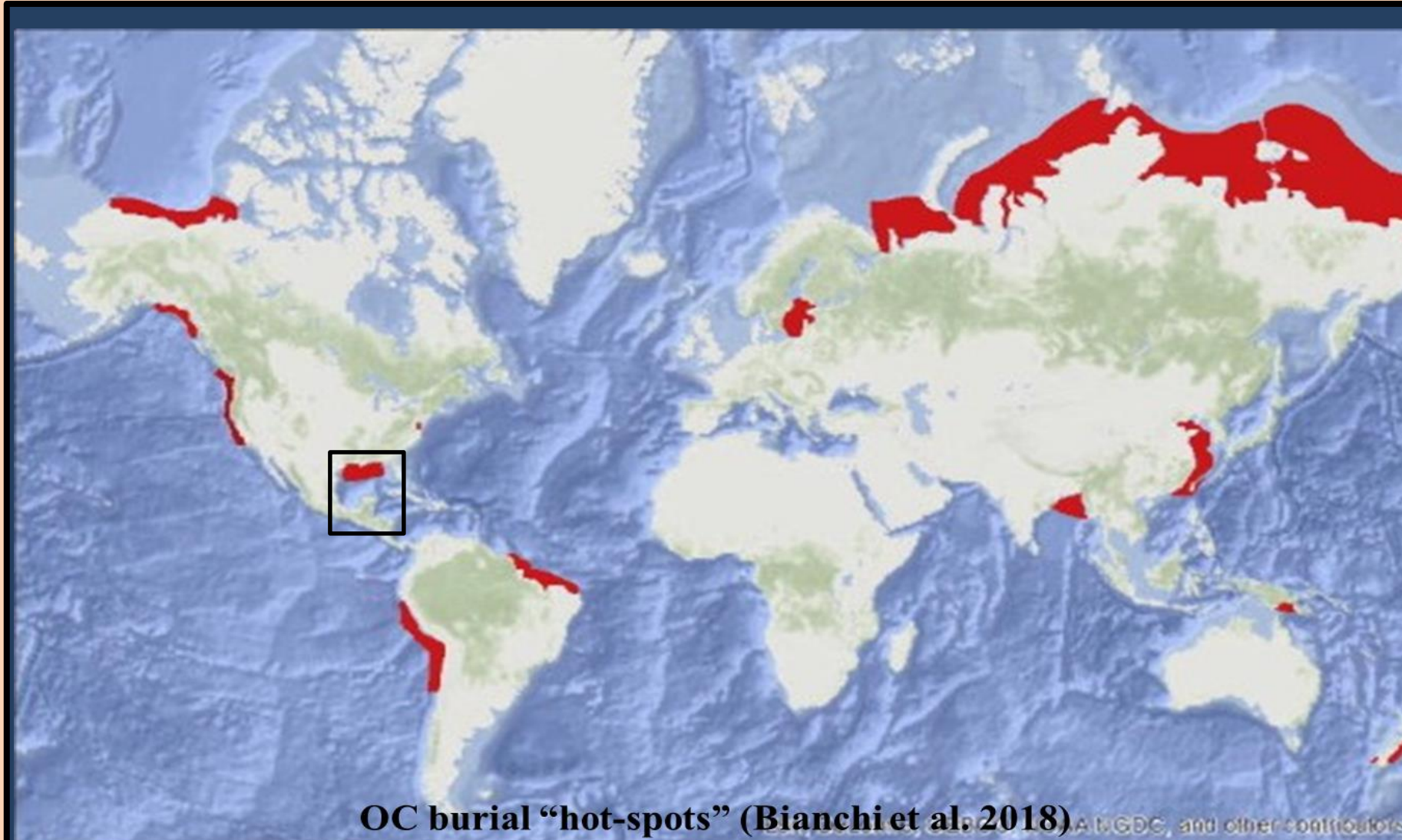
# Temporal and Spatial Distribution of Iron Bound Organic Carbon in the Mississippi River Influenced Shelf Sediments

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## INTRODUCTION


OC burial "hot-spots" (Bianchi et al. 2018)

### Importance of Continental Margins in OC preservation

- Long term sink for organic carbon
- ~90% OC burial occurs in "hot spot" areas including river influenced shelves (~41% of burial ) (Walsh 1991)
- OC preservation via mineral matrix monolayers (0.5-1 mg OC m⁻²) (Mayer 1994), (Hedges et al 1995)
- Multiple regulating mechanisms control the ultimate stability of the structures in the coastal ocean, where changes in surface water conditions can strongly control the pathways of OC either towards remineralization of burial
- Avenues to probe deeper into the "unknown" molecular features of OC preservation continue to emerge by way of high resolution experimental methods that allow us to "observe" surface interactions

### Iron-Carbon Marine Sediment Cycle

- Fe kinetics are directly influenced by bottom water $O_2$
- In marine sediments, $21.5 \pm 8.6\%$ preserved OC is bound to rFe (Lalonde et al. 2012)
- Fe-mineralogical characterizations are limited by the rapid exchange between sediment and pore water

### Keywords

Reactive iron oxides (rFe), Organic Carbon (OC), Fe-K edge X-Ray absorption near edge spectroscopy (XANES), X-ray diffractometry (XRD),
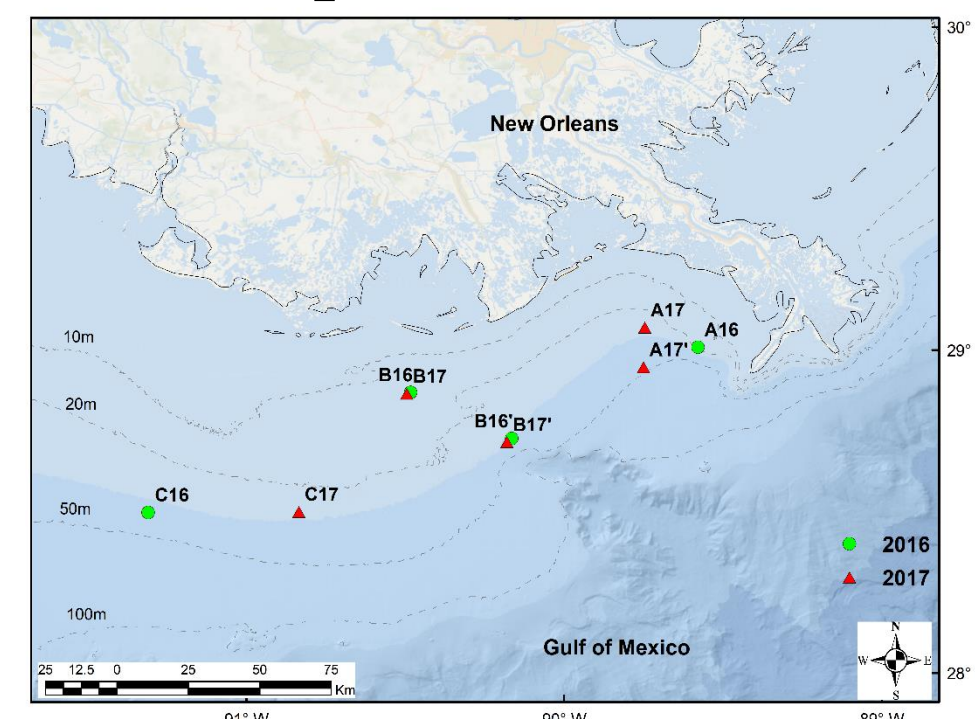
### Study Site: Mississippi River influenced Northern Gulf of Mexico

- Second largest river in the US, drains 41% continental US, enters Gulf of Mexico through Southwest Pass, spreads the plume within 30 km off shore (Milliman and Meade 1983, Walker et al. 2005), distinct seasonal patterns in river discharge associated supply of minerals and nutrients (Allison et al. 2007)
- Experiences one of the largest summer hypoxia in the world ( Dead Zone) (Rabalais et al. 2002)
- Average OC loading in the plume sediments after peak productivity ~0.32 mg OC m⁻² (Gordon et al. 2004, Goñi et al. 1998)

### Primary Goal

To ascertain the importance of rFe in directly protecting OC in the dynamic MR- NGoM sediments

### Research Objectives

- To understand the spatial and temporal patterns in rFe distribution in the recent ( upper 20 cm) sediments
- To quantify the OC directly associated with rFe
- To characterize the Fe-minerology and identify the dominant Fe-phases that protect OC
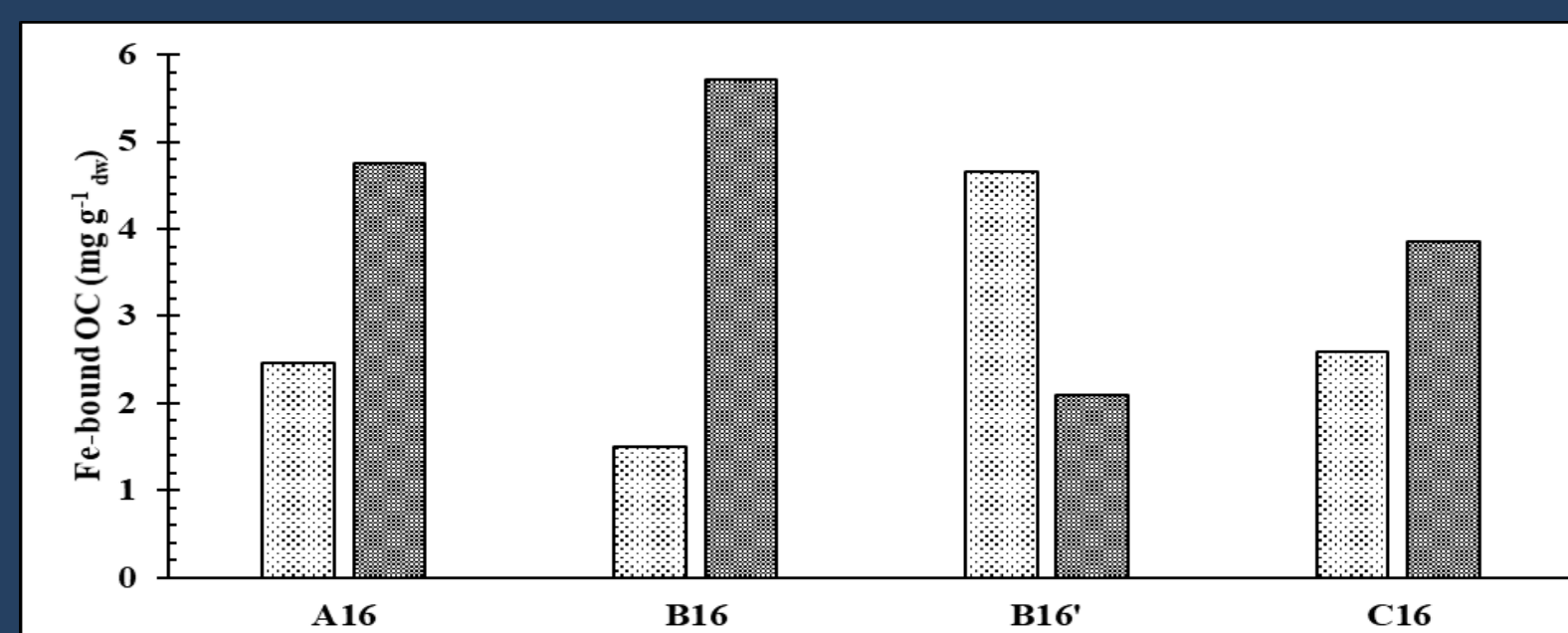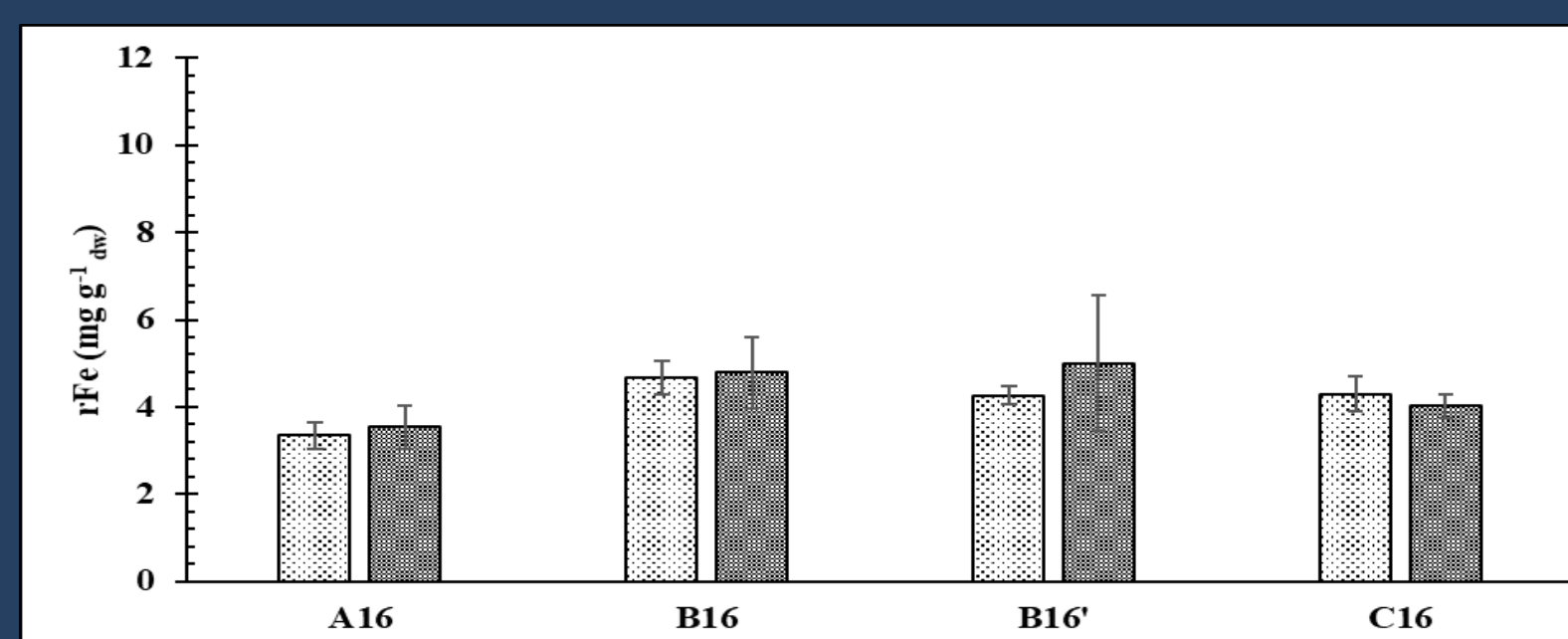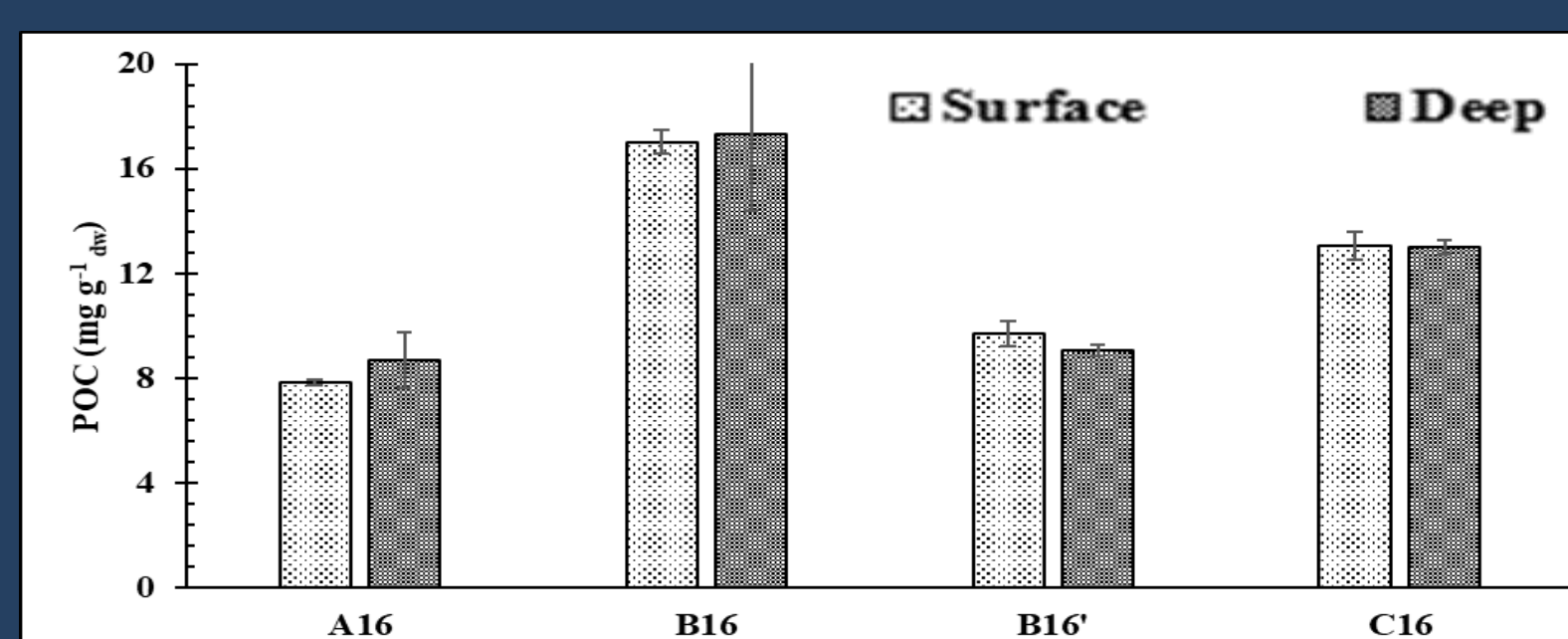
### Sample Collection



Opportunistic cruises onboard R/V Pelican

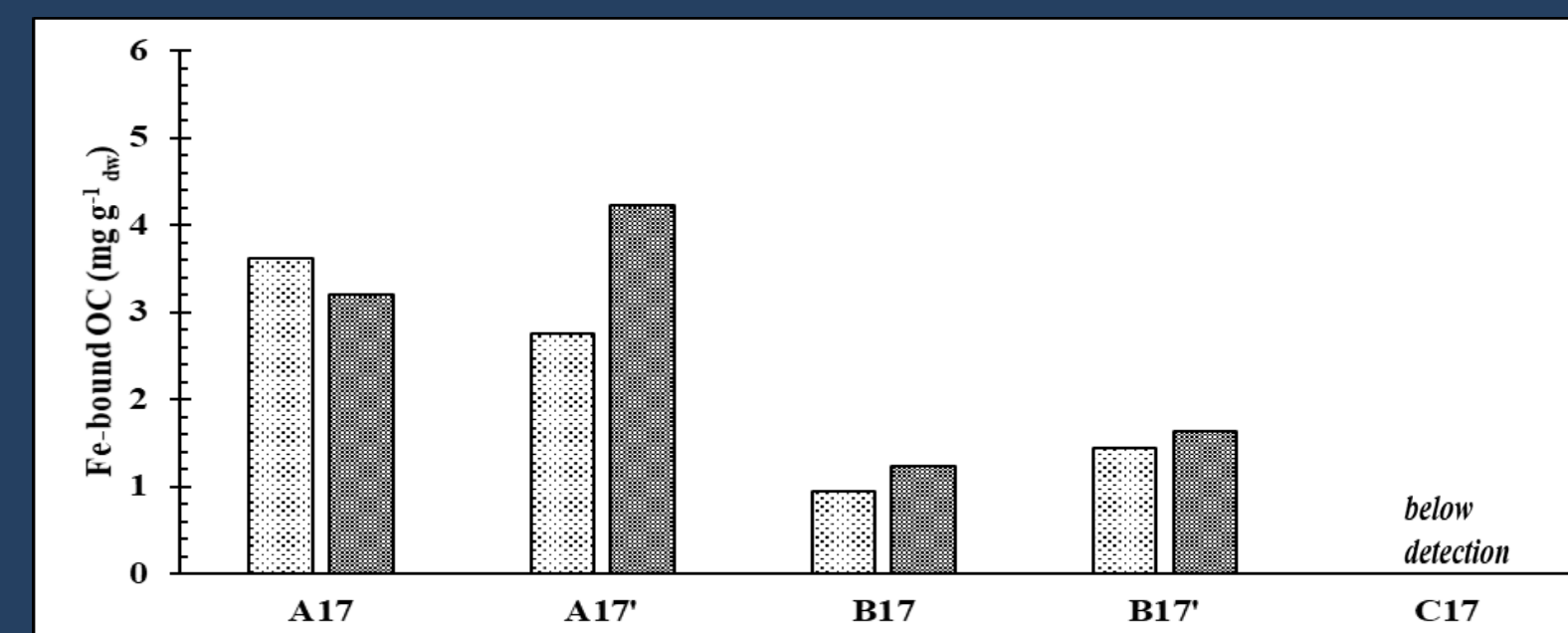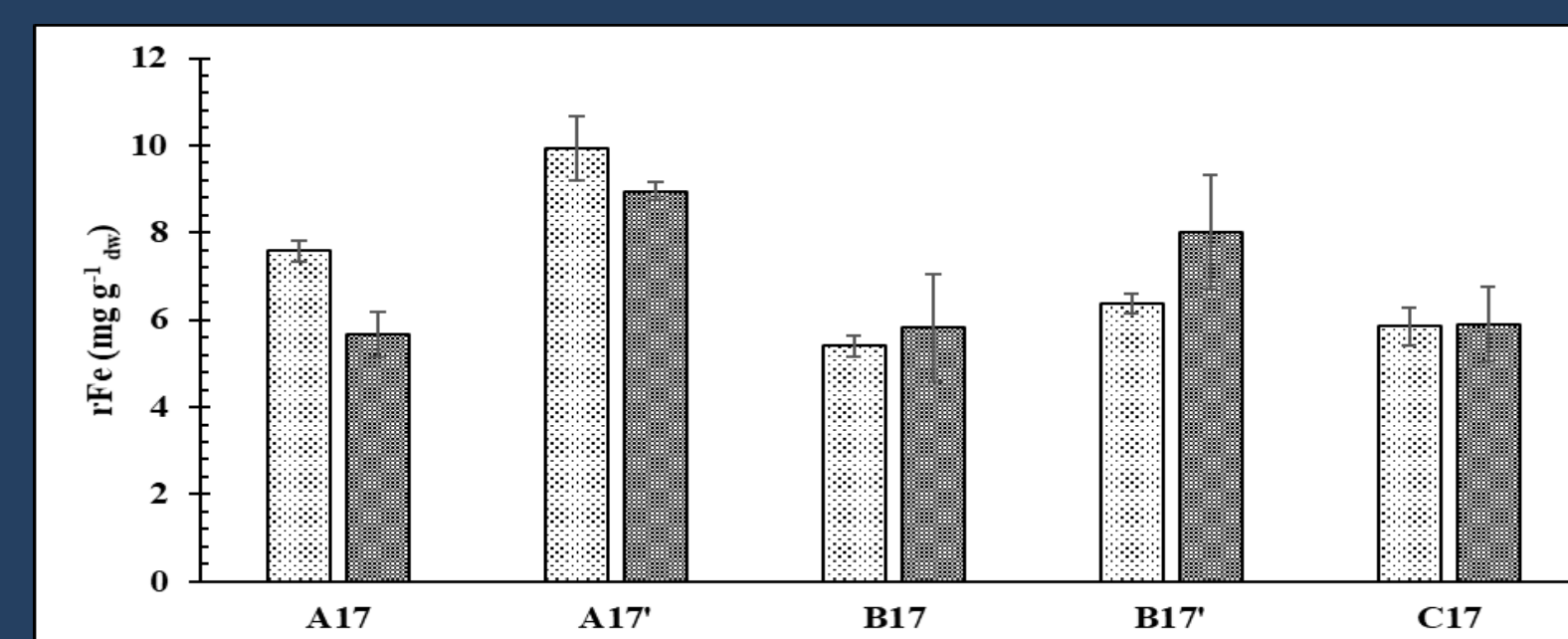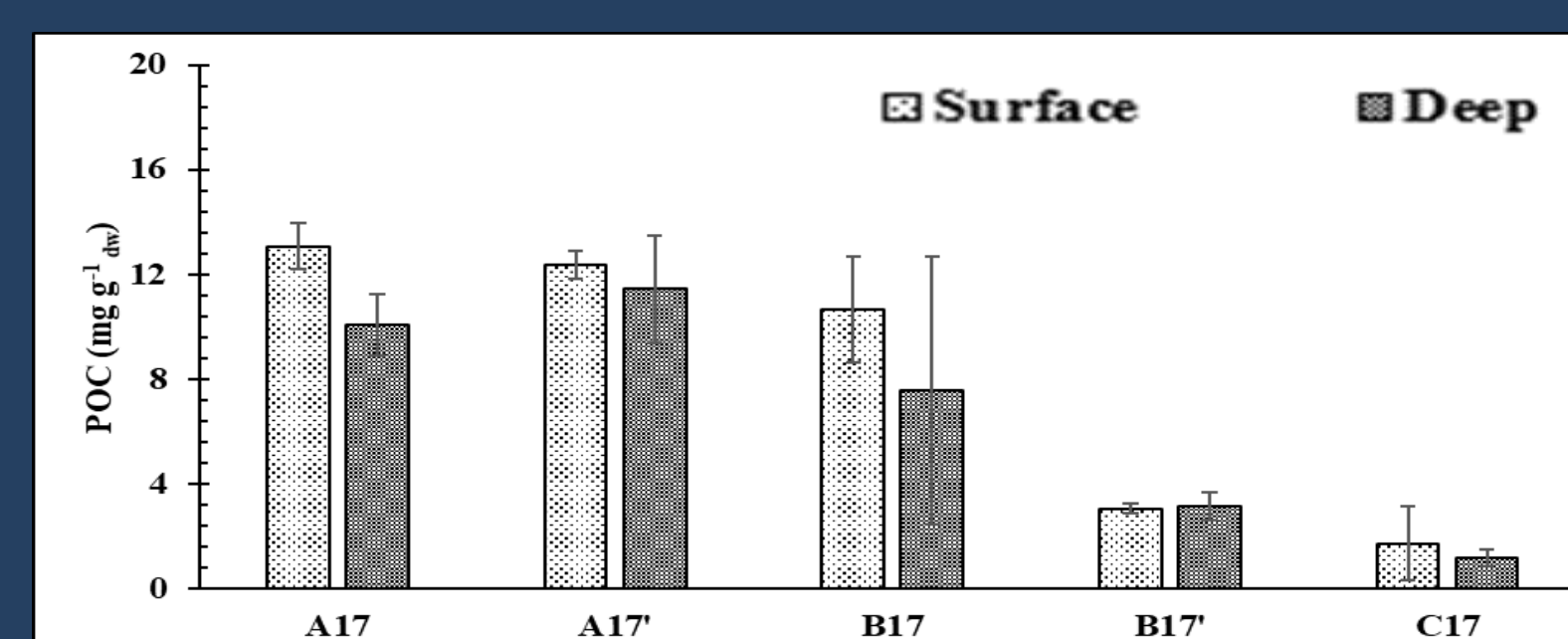During low discharge (August/September 2016) and high (May 2017) discharge conditions

Sediments collected from stations (<60 m isobath)

## METHODS

### Reactive Iron (rFe) and Fe-bound Organic Carbon Extraction

- **rFe Extraction** (Adapted from Kostka et al (1994) and Poulton et al. (2005))

Single step dithionite extraction using a solution of 0.6M Sodium Dithionite, 0.35M Acetic Acid and 0.2M Sodium Citrate (pH 4.8) for 6 hours at 60ºC. Filtered supernatants were analyzed for total Fe/Mn on an ICP-OES

- **POC Extraction** (Modified from Hedges et al. (1984))

Pre and post dithionite extracted sediments, fumigated to remove inorganics. POC was determined using high T combustion on a Costech 1040 CHNOS Elemental Combustion System (EPA Method 440.0)

### Mineralogical Data Collection

#### XRD

- Measured on PANalytical Empyrean multipurpose diffractometer (copper anode: 40kV, 40mA.)
- Scan range: $4.0^\circ < 2\theta < 70.0^\circ$
- Treatments used: (1) air dried, (2) ethylene glycol vapor saturation, (3) 300ºC and (4) 550ºC for complete XRD
- Data was analyzed using Rietveld method (High Score Plus(PANalytical B.V) software package
- Information from clay minerology was used to identify the structural Fe for XANES analyses

#### Fe-K edge XANES

- Spectra were collected in fluorescence at the HEXAS beam line of Center for Advanced Microstructures and Devices (CAMD), LSU, using a seven-element Ketek™ silicon drift detector. A Fe-foil was kept in between the 2nd and 3rd chambers for all runs
- Duplicate spectra for each sample were merged, normalized and calibrated (Fe foil: 7112eV) using Athena software package ( Ravel et al. 2005)
- Samples were selected to represent variability in river influence as well as depths ( to observe change in mineralogy due to redox activity)
- Standards were run along with the samples to include the following: Fe-bearing phyllosilicates (SWY-2 Smectite), rFe oxides ( goethite, ferrihydrite), hematite, and magnetite (Fe(II)/Fe(III) mixture compound)
- Linear combination fitting (LCF) was performed in the XANES region (-20 to 30eV norm (μ (E)) to obtain relative distributions of different Fe phases
- Selection for four standards to represent the dominant Fe-phases was based on lowest chi-square value and improvement in R by iterative addition of each standard ( Chen et al. 2017)
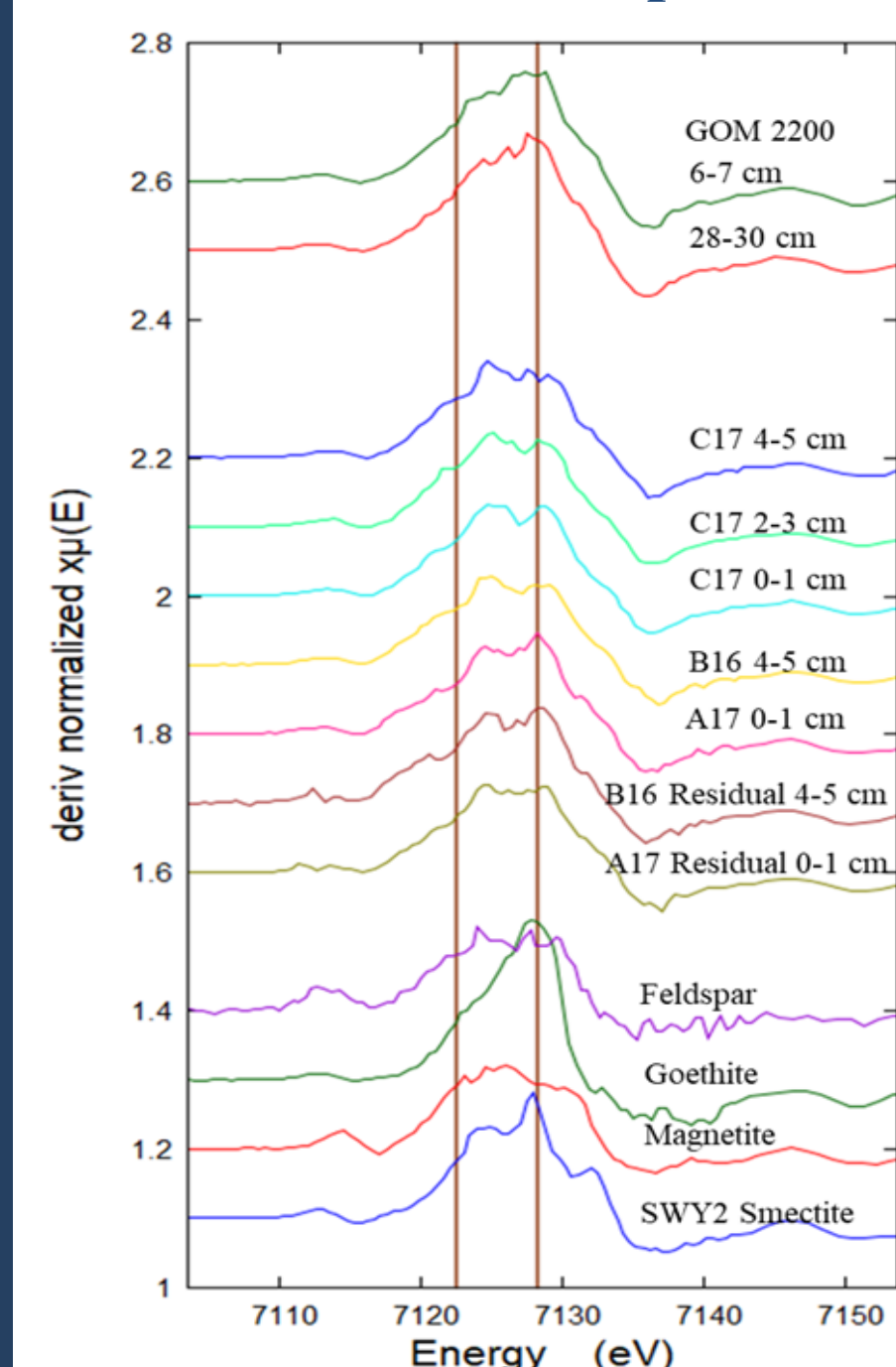
## RESULTS AND DISCUSSION

### September 2016



### May 2017



Distributions of rFe, POC , Fe-bound OC in the surface (0-5 cm) and deep (5-20 cm) sediments



Distribution of dissolved $Fe^{2+}$ and total Fe in the surface (0-5 cm) and deep (5-10 cm) pore water

### Mineralogical Observations

#### XANES Spectra- samples and standards



- Little variability between sediments from different sites
- Observable peaks ~4eV apart suggest a mixture of Fe(II) and Fe(III) phases
- Sharper features coincident with Fe(III) in the surface (0-1 cm ) spectra
- Relative shift towards lower energy apparent in the sub-oxic depth (4-5 cm) spectra indicative of redox driven changes

#### Linear Combination Fitting using different Fe-phases
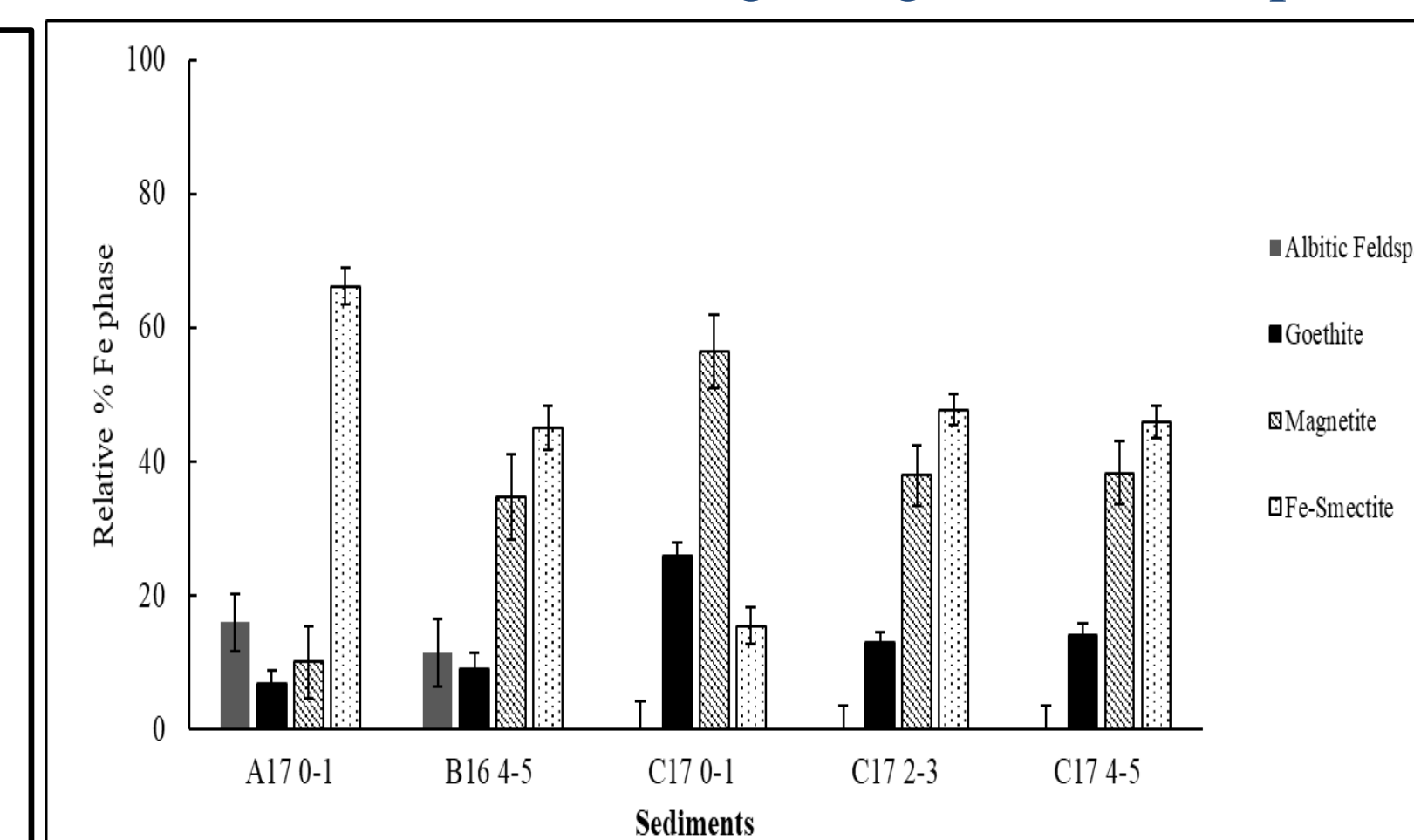


- Montmorillonite is the dominant clay mineral (75.4 ± 4.3%) identified by XRD analyses
- Majority of Fe present ( possibly as Fe³⁺) within structural montmorillonite (smectite) in all the sediments
- Goethite was the rFe phase that produced the best fit in the 4-component iterative LCF fit.
- Magnetite, although not categorized as "rFe" (for this study), was detected as a major component during all the LCF combinations. This was supported by sequential extractions of selected sediments (1.32 mg g⁻¹) from this region.

- LCF fit (reduced χ²: 1.1E-04) using dithionite residual spectra and goethite for the corresponding natural sediment
- A similar 2 member fit was inconclusive for Fe phases – ferrihydrite, lepidocrocite, hematite
- The rFe extracted appears to be goethite



- Average POC in September was 1.7 times that of May, inversely, rFe was 1.6 times higher in May 2017.
- Bulk POC and rFe do not vary between the surface (0-5) and deep (5-20) sediments
- Fe associated with OC constitutes 32 ± 3.03 % (September 2016) and 27 ± 0.90% (May 2017) of the total POC.
- Molar OC:Fe in the Fe-bound OC were higher in September 2016 (1.5- 6.3), compared to May 2017 (0.8- 2.6) and increased with depth.



Global relation between Fe-bound OC and POC in diverse oceanographic settings from multiple sources

## CONCLUSIONS

- Study demonstrates MS river and associated primary productivity can impact the rFe bound OC in the shelf
- Fe-exchange is strongly coupled with the overlying bottom water conditions (temperature, dissolved $O_2$, primary productivity)
- The average Fe-bound OC of NGoM sediments is ~32% of the total POC stored in the upper 20 cm, which is higher than the global average (21%)
- Redox transformations appear to regulate the Fe-mineralogy, in addition to driving the sediment-pore water Fe exchange.

### Future Work

- Include the total Fe data for a relative rFe: Total Fe for these samples (*pending analyses*)
- Obtain rFe estimates from other diverse oceanographic environments within the Gulf of Mexico
- Extend the mineralogical study to the EXAFS region to understand the Fe-C complexes that participate in OC protection (*pending analyses*)