The Organic Geochemistry of Blue Carbon Stores in a Changing Environment: A Contemporary and Paleo Perspective

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Introduction: Blue Carbon

Vegetated coastal ecosystems comprise the global carbon stock termed "blue carbon." Despite their relatively small aerial extent, these ecosystems store a similar amount of OC annually as do forested ecosystems worldwide, giving them an outsize importance in the global carbon cycle. Yet, despite their global importance in carbon cycling and storage, very little is known about the *mechanisms* of carbon storage in these ecosystems and how they might differ from other terrestrial environments, and especially how they may be affected by environmental change, including sea level rise, salinization, climate warming, and vegetation change. Here, we summarize the results of studies in the Schreiner lab aimed at elucidating how these environmental changes affect blue carbon storage in coastal marsh peats over both short and long timescales (Figure 1).

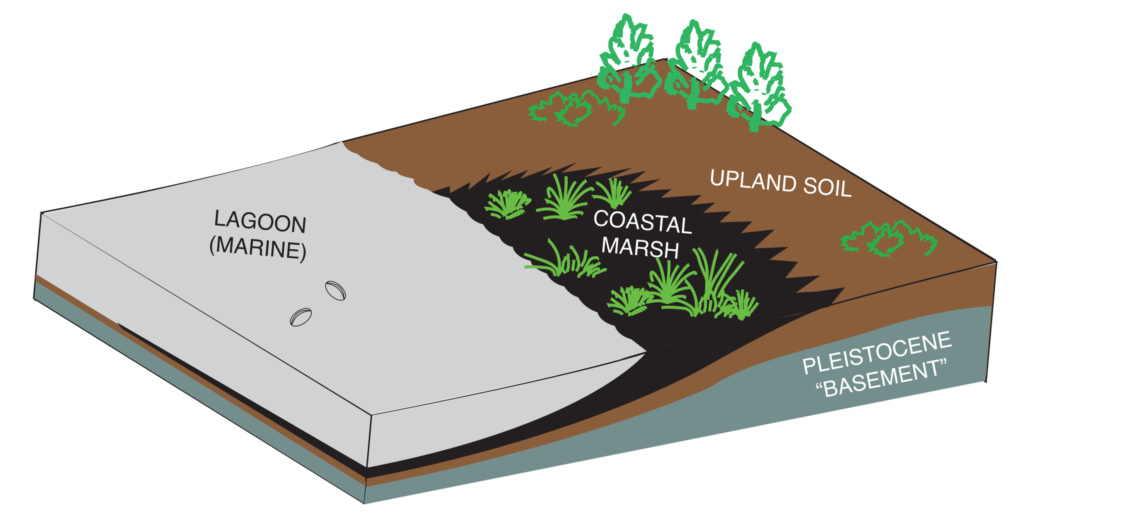

Figure 1: Model of sediment and soil deposits in a coastal marsh environment. As sea level rises, marshes can transgress upslope, encroaching on the upland (*research question 1*). The types of marsh vegetation present will affect the chemistry of the organic matter deposited in the marsh (*research question 2*). Long-term storage capacity and coincident chemistry changes in the stored carbon can be studied through coring of paleo marsh depsits (*research question 3*).

Research Questions

1. **How does sea level rise and subsequent vegetation change affect the chemistry of marsh soils?**
2. **What differences exist between marsh soils primarily formed in C3 vs C4 plant communi ties?**
3. **What is the long-term storage capacity of this carbon pool?**

Sea Level Rise and Marsh Transgression in Cheseapeake Bay

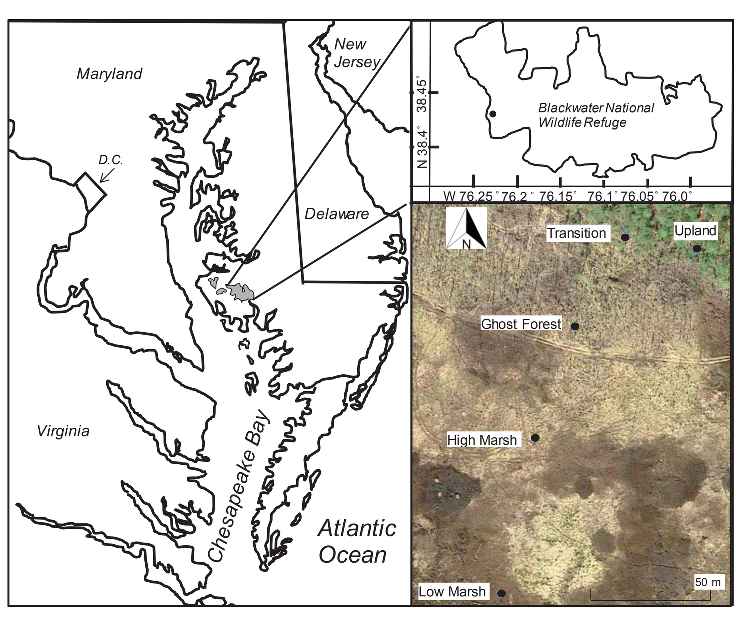

Figure 2: Map showing the location of the Blackwater Nationl Wildlife Refuge on the eastern shore of Chesapeake Bay. Five cores of approximately 20-25cm length were collected from each of the 4 marsh ecotones and the upland forest in summer 2015. Vegetation samples were collected summer 2016.

The Blackwater National Wildlife Refuge (Figure 2) is a location of active marsh transgression upslope where the marsh is encroaching upon an upland forested ecosystem (Figure 3). Core collection locations are shown in Figure 2. Cores were sampled at 1cm intervals, freeze-dried, and analyzed via EA-IRMS for %OC and $\delta^{13}C$. Lignin-phenols were extracted via cupric oxide method to determine source and stability of marsh organic matter (*research questions 1 & 2*). A summary of major vegetation types and corresponding $\delta^{13}C$ downcore profiles is shown in Figures 4&5. Figures 6, 7, and 8 summarize differences in total lignin phenols and lignin phenol degradation state.

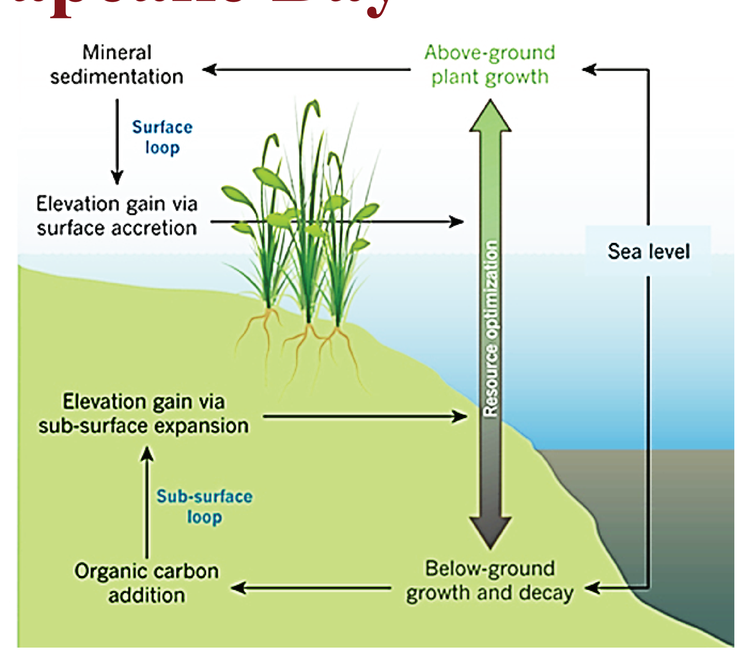

Figure 3: Conceptual model of interactions between sea level, plant growth, and elevation change in a coastal marsh. Adapted from Kirwan and Megonigal (2013).

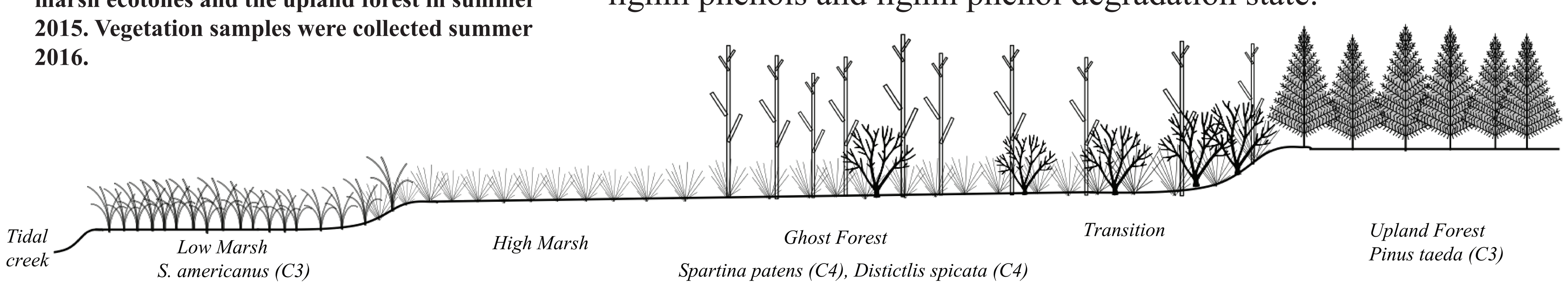

Figure 4: Model of major vegetation types in each ecotone in the BNWR study site.

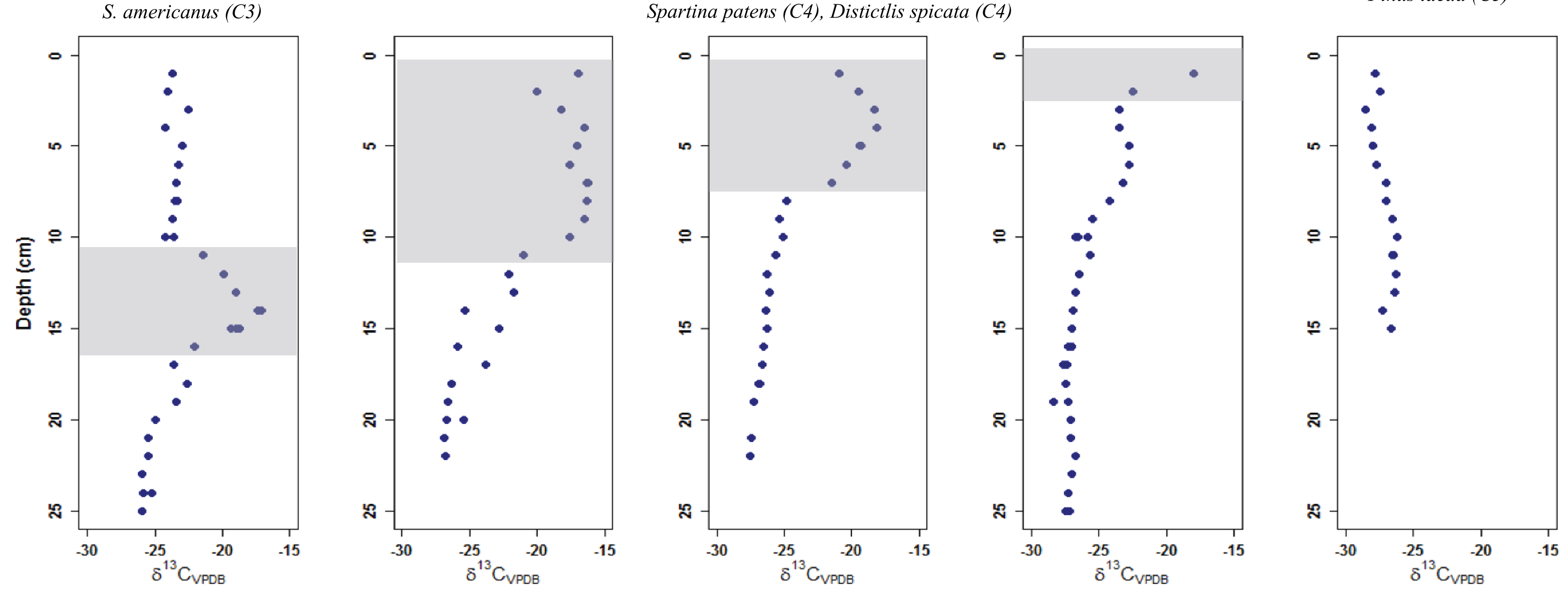

Figure 5: Downcore $\delta^{13}C$ profiles of the five ecotone regions in the BNWR site. Grey boxes highlight the C4 isotopic "pulse" as it enters the sediment in the Ghost Forest and High Marsh ecotones, and then is overlain by more C3 sediment in the Low Marsh. These five cores represent a chronosequence of marsh transgression into upland forest, with C3 marsh sediment (low marsh) overlaying C4 marsh sediment (high marsh) overlaying C3 upland dry soils.

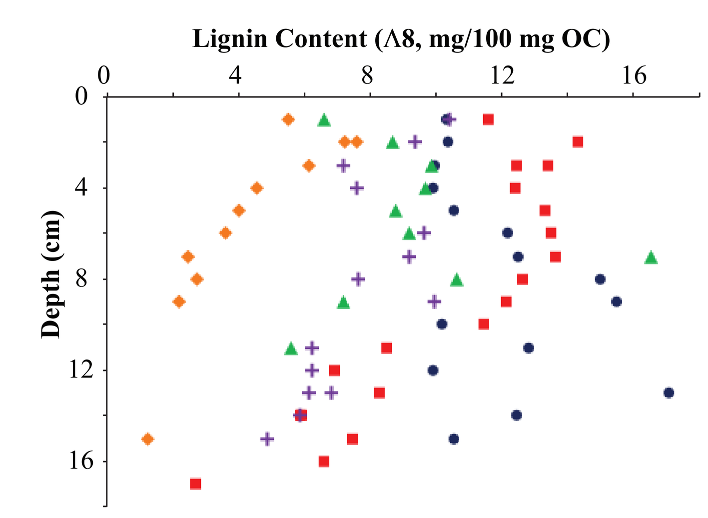

Figure 6: Total lignin content in each core, measured using cupric oxide oxidation technique (Hedges and Ertel 1982, Goni and Hedges 1995). Lignin content is significantly higher in marsh sediments than upland soils, with highest concentrations in waterlogged low marsh soils.

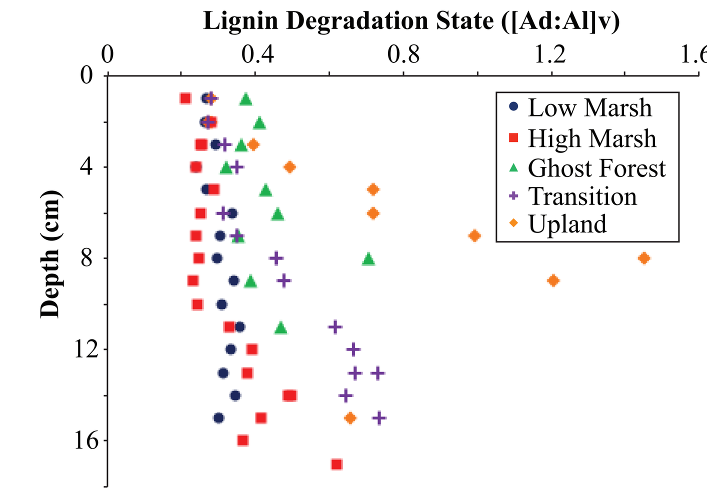

Figure 7: Degradation state of lignin-phenols measured by the ratio of vanillic acid to vanillin (carboxylic acid to aldehyde). Waterlogged soils -- both low and high marsh -- are significantly less degraded than upland soils where organic matter is exposed to oxygen.

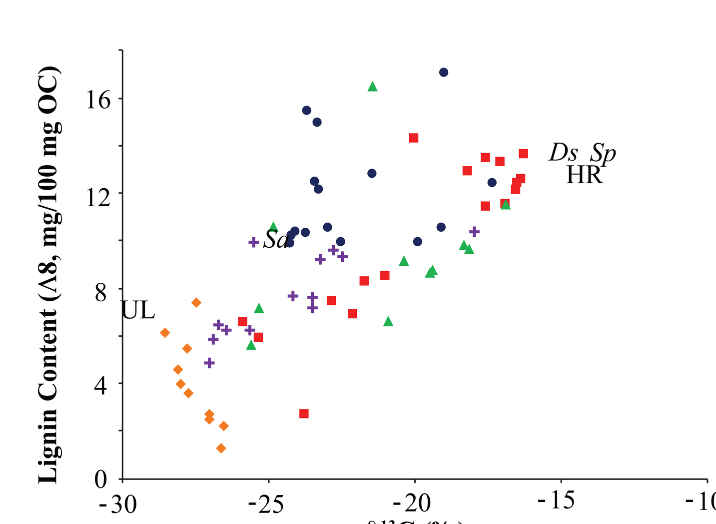

Figure 8: Lignin content vs $\delta^{13}C$ for all cores and endmember plant samples (see Figure 4 for acronyms). Higher lignin loading in the sediments corresponds to organic matter laid down during high marsh stands: high lignin corresponds (with low marsh exceptions) to C4 isotopic signatures.

Based on Pb-210 and Cs-137 dating of the Transition and Low Marsh cores, mass accumulation rates throughout the marsh are approximately 0.05 $g/cm^2/yr$, indicating the carbon accumulation rates are approximately 200 $gC/m^2/yr$, close to other published rates (*e.g.* 139 $gC/m^2/yr$, Duarte et al 2005).

Late Holocene Peat Deposits from Southern Louisiana

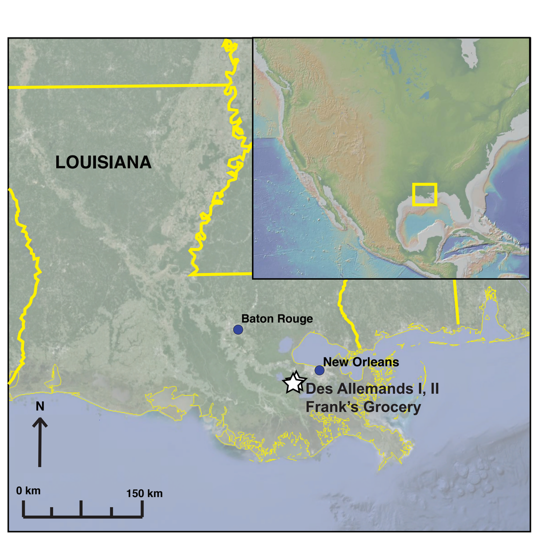

Figure 9: Map of coring locations in Southern Louisiana. All three cores (Des Allemands I & II and Frank's Grocery) are within 3km of each other. Only data from Des Allemands I & II are shown here.

In the sedimentary record, coastal marshes are preserved as basal peats, which can serve as a record of sea level change. Southern Louisiana peat deposits with ages of ~10k ybp are used here to investigate long-term storage of blue carbon, and coincident organic geochemical changes (*research question 3*). Peat cores (Figure 9) are separated by ~3km. Cores were subsampled and analyzed via EA-IRMS and cupric oxide extraction of lignin phenols (Figure 10).

The DA II (C3-influenced) core has lower lignin content and lower 3,5-Bd in the peat layers, vs the DA I (C4-influenced) core with higher lignin content and higher 3,5-Bd in the peat layers. Peats in both cores have similar %OC content. These trends are also reflected in the modern data from Chesapeake Bay, with higher lignin content in C4-influenced depths in each core.

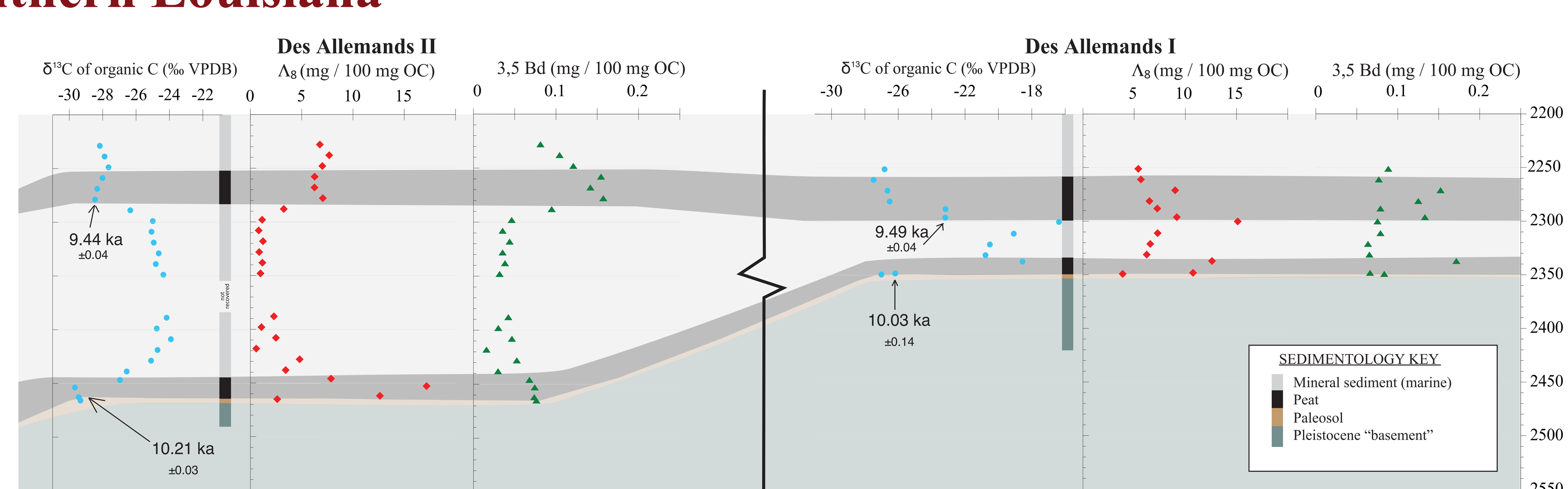

Figure 10: Downcore profiles of $\delta^{13}C$, total lignin, and the biomarker 3,5-Bd for Des Allemands I & II. 3,5-Bd is a biomarker for highly degraded soil organic matter and is an indicator of soil forming processes (Goni et al 1995). DA I shows significantly more enriched carbon isotopes than DA II, indicating a primarily C4 input to the former and primarily C3 input to the latter. Lignin content of DA I is also higher on average than DA II, with higher values of 3,5-Bd as well. This supports what was seen in the modern Chesapeake Bay system above: higher lignin-phenol concentrations in C4 peats.

Figure 11: $\delta^{13}C$ vs log (%OC) for all cores. Marine sediments with low %OC focus close to -24‰ with higher %OC values following a mixing line to more enriched (C4, DA II) or more depleted (C3, DA I) carbon inputs basal and upper peat deposits. The two paleosol samples fall off the C3 mixing line, with more depleted isotope values but lower %OC, supporting the hypothesis that coastal marsh blue carbon deposits can store more carbon by mass than dryland soils over long time periods.