Initiation and Development of Wetlands in Southern Florida Karst Landscape Associated With Accumulation of Organic Matter and Vegetation Evolution

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Abstract Biological processes exert important controls on geomorphic evolution of karst landscapes because carbonate mineral dissolution can be augmented and spatially focused by production of CO₂ and biogenic acids from organic matter (OM) decomposition. In Big Cypress National Preserve in southwest Florida, depressional wetlands (called cypress domes) dissolved into surface-exposed carbonate rocks and exhibit regular patterning (size, depth, and spacing) within the pine upland mosaic. To understand when wetland basins began to form and the role of spatially varying OM decomposition on bedrock weathering, we constructed age profiles of sediment accretion using compound-specific radiocarbon analysis of long-chain fatty acids and measured bulk OM properties and biomarker proxies (fatty acids and lignin phenols) in different zones (center vs. edge) of the wetlands. Based on compound-specific radiocarbon analysis, landscape patterning likely began in the middle to late Holocene, with wetlands beginning to form earlier at higher elevations than at lower elevations within the regional landscape. Dominant vegetation appears to have shifted from graminoids to woody plants around 3,000 calendar years before the present, as reflected in downcore bulk carbon isotope data and lignin concentration, likely from increased precipitation and hydroperiods. OM is mostly accumulated in wetland centers, and wetland centers exhibit more carbonate dissolution due to inundation limiting atmospheric ventilation of CO₂. Landscape development and patterning thus arise from interactions between hydrology, ecology, and ecological community evolution that control carbonate mineral dissolution.

1. Introduction

Dissolution in landscapes underlain by carbonate minerals, which often leads to karst geomorphologies, is linked to organic carbon dynamics via the production and consumption of CO₂ and thus may be controlled by biological processes (De Montety et al., 2011; Gulley et al., 2015; Stallins, 2006). Settings where these biotic-geomorphic feedbacks are important are referred to as “biokarst” (Duane et al., 2003; Fiol et al., 1996; Watts et al., 2014) to indicate that production and respiration of organic matter (OM) strongly influences variation in carbonate mineral dissolution and precipitation (De Montety et al., 2011; Gulley & Florea, 2016; Gulley et al., 2016; Schneider & Torunski, 1983; Stallins, 2006). Biokarst feedbacks amplify carbonate dissolution and, through production of macroporosity, incrementally reinforce preferential hydrologic flow paths (Dreybrodt, 1990; Palmer, 1991; White, 2002). These feedbacks further imply that spatial variations in OM processes (fixation, mineralization etc.) are critical to landform development (e.g., karst and drainage features).

Warm, moist conditions in subtropical soils can result in high rates of microbial and OM turnover, augmenting dissolution of carbonate minerals and mobilization of mineral-bound inorganic carbon where bedrock consists predominantly of carbonate minerals (Davidson et al., 2000; Martin, 2017; Trumbore...
et al., 1996). Moreover, OM cycling rates are altered under inundated soils/sediments such as those in freshwater wetlands, leading to long-term OM storage where deposition rates exceed mineralization (Glaser et al., 2012; McDowell et al., 1969). Variation in OM storage can also reflect past changes in vegetation, hydrology, and depositional settings.

OM deposition and changes in composition have been widely employed to describe modern and past conditions in the Everglades in South Florida, USA (Hajje & Jaffé, 2006; Mead et al., 2005; Saunders et al., 2006). In contrast, very little work has been conducted in the adjacent forested wetland mosaic of Big Cypress National Preserve (BICY), which is the focus of this study. The BICY landscape pattern consists of regularly spaced and uniformly sized depressional wetlands, termed “cypress domes,” embedded within a mosaic of pine-dominated uplands (Figure 1). The origins of the observed self-organizing patterning are not well understood (Dong et al., 2018; Watts et al., 2014) but likely relate to interactions between OM burial, remineralization processes creating carbonic acid, and carbonate mineral dissolution and precipitation. Key uncertainties include the age of the extant landforms (e.g., Chamberlin et al., 2018) and the internal OM dynamics that are thought to control formation of the patterning.

While many studies have utilized bulk carbon measurements such as total organic carbon (TOC), stable carbon isotopes ($\delta^{13}C$), and bulk radiocarbon age (Craft & Richardson, 1993; Hodell et al., 1999) to characterize

Figure 1. (a) Map of Florida with inlay of Big Cypress National Preserve and sampling sites. Yellow line defines the region of the Big Cypress National Preserve. (b) Aerial imagery of patterning near RP1. (c) Panorama photo of cypress dome at RP1. (d) LiDAR cross section of RP1 with sediment depth interpolation overlain.
OM dynamics, more detailed evaluations of sources and turnover rates can be ascertained using compound-specific isotopic and chemical biomarker measurements (Bianchi & Canuel, 2011; Yamamoto et al., 2005). For assessments of sediment age in carbonate landscapes, compound-specific radiocarbon analysis (CSRA) of long-chain fatty acids (LCFAs) is particularly relevant because it avoids the confounding “hard-water” effects. Likewise, in shallow sediments, root penetration may lead to modern carbon accumulation, a problem obviated by measuring the radioisotope composition of LCFAs. In this study, we used detailed organic geochemical measurements to understand the onset of pattern development, evaluate ecological composition shifts during development, and characterize OM preservation and decomposition effects on bedrock weathering across a dome. We sought to test hypotheses based on an assumption, evaluated in the project, that LCFAs provide better $^{14}$C age record of wetland development than other organic carbon (OC) sources. Assuming this assumption is correct, we test the hypotheses that (1) landscape patterning developed in the middle to late Holocene, as suggested by Dong et al. (2018) and Chamberlin et al. (2018); (2) vegetation changes in the historical landscape were driven by precipitation and local hydrological conditions; (3) soil OM in the center of the domes plays a more important role in bedrock weathering because prolonged inundation reduces CO$_2$ ventilation and increases carbonic acid production at the water-bedrock interface compared with the edges.

2. Materials and Methods

2.1. Site Description

Across South Florida, wetlands have been impacted by human-induced changes in fire frequency, hydrology, and nutrient enrichment from fertilizer applications (DeAngelis & White, 1994). Among the South Florida wetlands, BICY has experienced relatively minimal human impacts, though the regional canal system has likely altered hydroperiod locally. Limited anthropogenic impacts make BICY an ideal location to study links between carbonate mineral dissolution and hydrologic and biological processes in the natural development of wetland patterning.

Located in the western portion of South Florida (Figure 1), BICY exhibits a flat regional slope of ~3 cm/km. Bedrock consists mostly of the Late Miocene to Pliocene Tamiami Formation, a thin (~50 m) limestone unit mixed with sandstone, mud, and clay (McPherson, 1974), although a small region in eastern BICY is underlain by the Pleistocene Fort Thompson Formation. The BICY landscape consists of a thin layer of marl and sand sediments in shallow depressions that overlay carbonate bedrock that is exposed in the adjacent uplands. The wetland depressions are commonly referred to as cypress domes due to the dominance of bald cypress (Taxodium distichum) that stand tens of meters above the landscape. A diverse assemblage of wetland hydrophytes is also common in the wetlands (Duever et al., 1984). Sediment surfaces in wetland centers are 50–80 cm lower than that of surrounding uplands, with OM-rich sediment accumulations up to 300 cm thick. In contrast, the adjacent uplands have thin (<5–10 cm) OM-poor sediments, consisting of marl (calcitic clays) and sand (Watts et al., 2014). Variations in sediment thickness result in bedrock elevation differences of more than 300 cm, while surface elevations only differ slightly between wetlands and pine uplands. Consequently, local bedrock topography changes over 50–100 m of horizontal distances are orders of magnitude greater than the regional slope, and thus wetlands represent the primary topographic variation in BICY.

The contemporary climate in BICY is humid subtropical with distinct dry (October to April) and wet (April to October) seasons (Shoemaker et al., 2011). Annual precipitation averages 1,330 mm, but with ~1,100 mm of evapotranspiration, hydrological gains from precipitation are mostly lost to the atmosphere. The wetlands fill in the summer due to local rainfall excess but export excess water only when wetland stage exceeds a critical “spill” elevation (D. L. McLaughlin, personal communication, October, 2018). Low bedrock permeability and shallow regional relief allow for long hydroperiods in landscape depressions. Long hydroperiods were less likely before the mid-Holocene when climate became wetter and sea level reached its approximate elevation (Lambeck et al., 2014), which would have slowed drainage when precipitation increased. Because of the proximity of BICY to the coast, sea level likely controls the groundwater table in BICY, similar to many low-lying coast carbonate settings (Gulley & Florea, 2016; Gulley et al., 2016), suggesting the region may have been drier during the last glacial maximum through the mid-Holocene. Compared with karst landscapes characterized by greater topographic relief and higher-gradient streams (Kusumayudha et al., 2000; Siemers & Dreybrodt, 1998), BICY is more likely to be influenced by ecosystem processes (i.e., feedbacks
between hydrology and OM dynamics), resulting in landform patterns that reflect local and landscape-scale biological origins (Watts et al., 2014).

### 2.2. Sample Collection and Processing

Sediment samples were collected in the spring of 2015 from four wetlands in BICY, two of which were near Raccoon Point (RP1 and RP2) in the eastern half of the preserve and two near Turner River (TR1 and TR2) in the western half (Figure 1). Their sampling locations were selected based on access constraints, prior work (Watts et al., 2014), variation in lithology and hydrology, and visual differences in pattern geometry. The RP sites sit on the Pleistocene Fort Thompson Formation with shorter hydroperiods, and TR sites sit on the Miocene Tamiami formation with longer hydroperiods. TR sites also have greater water depth than RP sites. Based on LiDAR surveys, TR sites are higher in elevation than the RP sites. Uplands around TR1 and TR2 are around 4.0 and 3.8 m above sea level, while the RP1 and RP2 uplands are about 3.0 and 2.8 m above sea level (C. J. Quintero, personal communication, June 1, 2018).

At each site, sediments at the center and edge of the wetland were collected from the surface to the bedrock contact. Samples at TR sites were collected using a vibracore, and samples at RP site were collected using a piston corer. Cores were split lengthwise, and half the core was stored as archival material in a cold room at University of Florida. The other half was sectioned at 1-cm intervals from which we analyzed subsamples at 5-cm increments. Rock fragments and woody material were removed from the subsamples, which were freeze dried and hand ground with mortar and pestle to homogenize the sediment for chemical processing and analyses. An additional short core was taken at RP1 center location using a piston corer for $^{210}$Pb dating. This core was sampled in 3- or 4-cm intervals, and dry bulk density was measured on each sediment section.

### 2.3. Age Dating

The RP1 short center core (RP1C, 42 cm) was dated using the naturally occurring radioisotope $^{210}$Pb (half-life of 22.3 years). Homogenized dry sediment samples were packed and sealed in vials for 21 days to reach secular equilibrium. Radiometric measurements ($^{210}$Pb, $^{226}$Ra and $^{137}$Cs) were made using low-background gamma counting with well-type intrinsic germanium detectors (Schelske et al., 1994). Sediment ages were calculated using the constant rate of supply model (Oldfield & Appleby, 1984). A disequilibrium of $^{226}$Ra and $^{210}$Pb (i.e., $^{226}$Ra > $^{210}$Pb) was found in deeper samples (36–42 cm). We adjusted for the disequilibrium by increasing the total $^{210}$Pb in all samples to account for self-attenuation of supported $^{210}$Pb. The adjustment factor ($A_P$) was calculated from the mean of the ratios of $^{226}$Ra to $^{210}$Pb in the deeper samples showing disequilibrium (36–42 cm).

$^{14}$C measurements were made on bulk OM, plant debris, and LCFAs at depths below 40 cm where $^{210}$Pb was in secular equilibrium with $^{226}$Ra at RP1C. Bulk OM was measured on homogenized carbonate mineral-free sediment samples. Plant debris (i.e., woody stems) were picked from original sediments and cleaned by an acid-base-acid wash of 1 N HCl solution and 0.5 N KOH solution, both at 70 °C (Oswald et al., 2005). This sequence was repeated several times until the solution was clear. Then woody stems were cleaned again in 1 N HCl, washed three times using Milli-Q water, and oven dried at 60 °C. Fatty acids were extracted and methylated following the process mentioned later (without standards) with one additional purification on a silica gel column by elution with hexane and hexane:dichloromethane (1:1 v/v). The hexane:dichloromethane elution was used for collecting individual long-chain (C24, C26, C28, C30, and C32) fatty acid methyl esters (FAMEs) on a preparative capillary gas chromatography (PC-GC; Eglinton et al., 1996). A combination of those five FAMEs was used to determine the radiocarbon age of sediments as they have been shown to have similar $^{14}$C ages (Feng et al., 2015). $^{14}$C results were corrected for PC-GC procedural blanks (Cui et al., 2017) and derivative carbon.

The material extracted from each of these three sample types was sealed under vacuum into quartz tubes with CuO pellets and combusted at 900 °C for 3 hr to convert OC to CO$_2$. The generated CO$_2$ gas was purified cryogenically, sealed in Pyrex reactor tubes using the Zn reduction method (Xu et al., 2007), and converted to graphite by combustion at 500 °C for 3 hr and 550 °C for 4 hr. Graphite samples were analyzed for radiocarbon content using accelerator mass spectrometry at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility at the Woods Hole Oceanographic Institution. All radiocarbon dates obtained in radiocarbon years before the present ($^{14}$C years BP) were calibrated into calendar years before the present (cal. BP) using IntCal13 Curve (Reimer et al., 2013). Sediment accretion rate in the dated core (RP1C) was determined by linear regression analysis of selected $^{14}$C ages.
2.4. Total Organic Carbon and Stable Carbon Isotope Analyses

Organic carbon and its carbon isotope ratios were measured on carbonate mineral-free aliquots of the sediments. Carbonate minerals were removed from homogenized sediment samples using concentrated HCl vapor for 8 hr and dried at 60 °C for 24 hr. The carbonate-free samples were analyzed for TOC and δ¹³C in the Light Stable Isotope Mass Spectrometry Laboratory, University of Florida. Collected plants from our study sites, used as isotopic end-members, were freeze dried and analyzed for bulk δ¹³C.

2.5. Fatty Acids

Fatty acids were extracted via accelerated solvent extraction with dichloromethane:methanol (9:1 v/v) and then saponified with 0.5 M KOH in methanol for 2 hr (70 °C). Neutral lipids were removed from the extracts using hexane. The remaining aqueous solution was acidified by concentrated HCl and fatty acids were extracted with hexane:dichloromethane (4:1 v/v). Fatty acids were then dried under nitrogen gas and derivatized with boron trifluoride (BF₃) in methanol to FAMEs. After purification on a silica gel column, FAMEs were analyzed by gas chromatography-mass spectrometry (GC-MS). Peak areas were quantified relative to internal standards added before Accelerated Solvent Extraction (C₁₉₀ fatty acid) and GC-MS analysis (ethyl oleate). A calibration curve was developed based on a standard mixture containing 23 short-chain fatty acids (SCFAs) and LCFAs. Fatty acids, diagnostic of different OM sources, have been effective biomarkers for separating complex mixtures of OM in soils and sediments (e.g., Bianchi & Canuel, 2011). For example, the sum of the even-numbered LCFAs (≥C₂₄) can be used as tracers of terrestrial vascular plants (Harwood, 2012; Rielley et al., 1991), while even-numbered SCFAs (C₁₂ + C₁₄) are generally associated with algal/marine sources (Bianchi & Canuel, 2011; Waterson & Canuel, 2008).

2.6. Lignin Phenols

Lignin phenols were extracted by the alkaline CuO oxidation method (Gotli & Hedges, 1992). Homogenized sediments were oxidized by CuO in 2 N NaOH solution under oxygen-free condition for 3 hr (150 °C). The aqueous solution was then acidified with HCl and extracted with ethyl acetate. Extracts were blown down to dryness and redissolved in pyridine. Then, samples were derivatized using bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) and quantified using a Thermo Scientific Trace 1310 Gas Chromatograph interfaced to a Thermo Scientific TSQ8000 Triple Quadrupole Mass Spectrometer (GC-MS/MS). Quantification of individual lignin phenol was based on an internal standard (ethyl vanillin) added after oxidation and a standard (methyl 3,4-dimethoxybenzoate) added before injecting on the GC-MS/MS. A mixed lignin-derived phenol standard was used for the external calibration curve. The sum of eight lignin phenols (Λ₈), syringaldehyde (SAL), acetylsyringone (SON), syringic acid (SAD), vanillin (VAL), acetovalone (VON), vanillic acid (VAD), p-coumaric acid (CAD), and ferulic acid (FAD) normalized to 100 mg OC, is a commonly used index for terrestrial vascular plants (Hedges & Mann, 1979; Spencer et al., 2009). The ratio of VAD to VAL (Ad/Al) can be used as an index of lignin degradation in soils and sediments (Gotli et al., 2000; Opsahl & Benner, 1995). It should be noted that lignin phenols were only measured at the TR sites to better understand the large shifts in δ¹³C.

3. Results

3.1. Age Profile of Sediment Cores: Bulk Versus LCFAs

Among the three types of organic materials dated, woody stems showed younger ¹⁴C ages than bulk OM and LCFAs, with little change in age with depth (Figure 2a and Table 2). The intermediate ages determined from the bulk OM showed reversals with sediment depth. Only LCFAs had increasing ages with depth as well as the oldest ¹⁴C ages for dated materials. Linear regression of the ages of LCFAs with depth at RP1C suggested a sediment accretion rate, from 1,600 to 3,500 cal. BP, to be 0.03 cm/year ($r^2 = 0.89$). In contrast, the estimated mean sediment accretion rate in RP1C, based on ²¹⁰Pb dating, was 0.45 cm/year for sediments <30 cm deep (Figure 2b and supporting information Table S4).

Although we have only single values at other watersheds, those sample ages were similar to the age of the deepest samples at RP1C of 3,545 cal. BP at 105–106 cm. The age of the near-bottom layer from RP2C was 3,733 cal. BP at 75–76 cm (Table 1). The deepest sediment layer from TR2C with sufficient LCFAs was 50–51 cm which showed an age of 2,541 cal. BP.
3.2. Organic Bulk Parameters

TOC contents showed an exponential decline at shallow depths of the center (labeled “C”) and edge (labeled “E”) of the wetlands (Figure 3 and Table S1), though edge cores had lower TOC contents and more rapid decline with depth than center cores. TOC contents in deep sediments (below 30 cm) were greater at RP than TR wetlands. Average values were 5.1 ± 1.8% at RP1C, 5.2 ± 1.0% at RP2C, 0.9 ± 0.5% at TR1C, and 2.4 ± 2.0% at TR2C (Figure 3). Surface sediments in wetland centers contained more than 37% TOC compared to lower values at edge locations in both RP (< 33%) and TR (<15%) sites (Table 2 and Figure 3). At edge locations, TOC contents are greater in RP surface samples (32.0 ± 0.8 %) than TR surface samples (12.0 ± 3.3 %).

The δ¹³C values were gradually enriched in ¹³C with depth at both RP wetlands. The centers were enriched by 2.1‰ at RP1C and 2.2‰ at RP2C, and the edges were enriched by 2.8‰ at RP1E and 3.3‰ at RP2E between surface and bottom layers (Figure 3). The TR wetlands exhibited greater downcore variation of δ¹³C value, with a step shift of 6.4‰ between 35 and 45 cm at TR1C and a step shift of 6.0‰ between 50 and 60 cm at TR2C (Figure 3). The edge of the TR wetlands showed no obvious trend, with average values of −22.9 ± 1.2‰ for TR1E and −23.6 ± 1‰ for TR2E. δ¹³C values of surface samples were similar from all wetland centers, averaging at −28.7 ± 0.2‰, but were isotopically more enriched by 1.8‰ to 4.4‰ than at the wetland edges.

3.3. Biomarkers

Downcore LCFAs concentrations at wetland centers were greater at the RP than the TR (Figure 4 and Table S2) with average LCFAs concentrations of 1.4 ± 0.5 mg/g OC at RP1C, 1.4 ± 0.4 mg/g OC at RP2C, 0.9 ± 0.2 mg/g OC at TR1C, and 0.7 ± 0.3 mg/g OC at TR2C. LCFAs concentrations in surface samples were similar in all center locations (0.9 ± 0.2 mg/g OC). SCFAs concentrations showed a general decrease with depth at all sites, consistent with TOC decreases with depth. SCFAs concentrations in TR surface samples were higher (0.8 ± 0.1 mg/g OC) than RP surface samples (0.4 ± 0.1 mg/g OC; Figure 4).

A₈ in TR1C decreased from surface (5.1 mg/100 mg OC) to 30 cm (1.1 mg/100 mg OC) and then stabilized from 30 to 80 cm (1.0 ± 0.2 mg/100 mg OC) with only minor variations with depth (Figure 5). A₈ concentrations at 85 and 90 cm (1.9 mg/100 mg OC) were higher than those from 30 to 80 cm. At TR1C, the [Ad/Al]r ratio, an index for lignin decay, displayed a maximum of 0.7 at a depth of 30 cm, decreasing to ~0.4 at the surface and deepest layer. At TR2C, A₈ concentration was greater in the upper 50 cm (3.5 ± 1.1 mg/100 mg OC) than deeper layers (1.0 ± 0.6 mg/g OC).

Table 1

| Site | Depth  | Type     | ¹⁴C years BP | Median-calibrated BP | 95.4% (2σ) calibrated age range |
|------|--------|----------|--------------|----------------------|---------------------------------|
| RP1  | 45–46  | Sediment | 922 ± 20     | 851                  | 790–912                         |
|      | 61–62  | Sediment | 1,252 ± 15   | 1,220                | 1,175–1,265                     |
|      | 85–86  | Sediment | 570 ± 15     | 585                  | 536–633                         |
|      | 45–46  | Woody Stems | 187 ± 15   | 144                  | 0–287²                         |
|      | 61–62  | Woody Stems | 155 ± 15   | 144                  | 5–28²                          |
|      | 45–46  | LCFAs    | 1,752 ± 20   | 1,661                | 1,605–1,716                     |
|      | 61–62  | LCFAs    | 2,123 ± 15   | 2,097                | 2,041–2,152                     |
|      | 85–86  | LCFAs    | 2,336 ± 15   | 2,348                | 2,338–2,358                     |
|      | 105–106| LCFAs    | 3,321 ± 20   | 3,545                | 3,480–3,610                     |
| RP2  | 75–76  | LCFAs    | 3,445 ± 25   | 3,733                | 3,637–3,828                     |
| TR2  | 50–51  | LCFAs    | 2,456 ± 20   | 2,541                | 2,379–2,703                     |

Note. RP = Raccoon Point; TR = Turner River; BP = before the present; LCFAs = long-chain fatty acids.

²Large uncertainty because of proximity to 1950.
Figure 3. Downcore profile of TOC and $\delta^{13}$C values of center and edge locations in four different sites. (a, b) TOC content and $\delta^{13}$C values of sediment cores at RP1. (c, d) TOC content and $\delta^{13}$C values of sediment cores at RP2. (e, f) TOC content and $\delta^{13}$C values of sediment cores at TR1. (g, h) TOC content and $\delta^{13}$C values of sediment cores at TR2. TOC = total organic carbon; RP = Raccoon Point; TR = Turner River.
Table 2

| Location | Site | TOC (%) | δ¹³C (‰) | Total FA | LCFAs (≥C₁₂₄₄) | SCFAs (C₁₂ + C₁₄) |
|----------|------|---------|----------|----------|----------------|------------------|
| Center   | RP1  | 44.98   | −28.49   | 15.76    | 0.69           | 0.35             |
|          | RP2  | 44.08   | −28.71   | 11.39    | 1.12           | 0.64             |
|          | TR1  | 38.65   | −28.97   | 14.63    | 1.06           | 0.97             |
|          | TR2  | 37.26   | −28.48   | 9.20     | 0.83           | 1.11             |
| Edge     | RP1  | 32.59   | −25.88   | —        | —              | —                |
|          | RP2  | 31.40   | −26.88   | —        | —              | —                |
|          | TR1  | 9.65    | −24.93   | —        | —              | —                |
|          | TR2  | 14.38   | −25.74   | —        | —              | —                |

Note: TOC = total organic carbon; FA = fatty acids; LCFAs = long-chain fatty acids; SCFAs = short-chain fatty acid; RP = Raccoon Point; TR = Turner River.

4. Discussion

4.1. Comparison of Different ¹⁴C Dating Materials

We used the radiocarbon ages of LCFAs to obtain a reliable accretion rate for the sediment core RP1C. Our study is, as far as we know, the first application of CSRA of LCFAs in South Florida, where dating wetland sediments is often challenging. Charcoals, terrestrial plant macrofossils (plant debris), and bulk OM are commonly used for radiocarbon dating in wetlands, while shells are commonly dated for inorganic carbon. Each material has limitations. Charcoal is often scarce because its deposition depends largely on the frequency of fires and material that is burned. For example, large woody charcoal fragments are likely to be better preserved than grass or soft tissues. Apart from its scarcity, blackened plant detritus may be mistakenly picked as charcoal because of similar appearance, as stated in Glaser et al. (2012), which showed hard-water affected charcoal dates. Terrestrial plant macrofossils are also rare. Besides, some root pieces may be picked as woody stems as their appearance can be confusing. Thus, estimated depositional age will appear younger as roots can penetrate to deeper sediments. This may explain the modern radiocarbon age of woody stem material (actually root pieces) as deep as 62 cm in RP1C (Figure 2a). Even though bulk OM is the most commonly used ¹⁴C dating material in South Florida (Donders et al., 2005; Glaser et al., 2012; McDowell et al., 1969), its interpretation requires caution because it is a mixture of different components. The two major issues for bulk OM are translocation of younger carbon into deeper and older layers through root systems and hard-water effects in algae and aquatic plants, which can assimilate “old” carbon from carbonate minerals.

In our study, the ¹³C ages of bulk OM were younger than CSRA of LCFAs and older than woody stems in the same layers, showing numerous reversals in ¹⁴C age with depth, which clearly demonstrated the unreliability of bulk radiocarbon ages.

Even though hard-water effects are almost inevitable for shells found in wetland system, it can be corrected in some systems to provide reliable ages (Glaser et al., 2012). Corrections require shells near the top of sediments and scattered throughout the core to assess whether the effect is constant through the time, conditions that are not possible in our cores.

Compared with other dating materials, LCFAs have many advantages. LCFAs originate largely from terrestrial vascular plants as leaf wax lipids (Bianchi & Canuel, 2011), and thus the primary source of ¹⁴C for LCFAs should be atmospheric CO₂, avoiding hard-water effects. Because LCFAs originate from leaves, they are unlikely translocated through root systems. In addition, LCFAs are relatively more recalcitrant than other organic compounds such as proteins, amino acids, and sugars, resulting in slower decay rates (Feng et al., 2015; Matsumoto et al., 2001; Uchida et al., 2001). With advances in accelerator mass spectrometry techniques, as little as 10 μg C can be dated, which is easily achieved for chemical extractions of LCFAs from most wetland samples. The reliability of obtaining ages of wetland sediments is supported by the linear increase of ages of LCFAs at RP1C (Figure 2a). This method could potentially be widely applied to other wetland systems for more reliable radiocarbon dating results.

4.2. Age of Wetland Formation and Sediment Accretion Rates

The correspondence of radiocarbon-age profiles of LCFAs with changes in sea level is consistent with several independent estimates of the initiation of depressions. These observations suggest that early bedrock dissolution may be linked to stable sea level over the past several thousand years. Ages of the deepest sediment samples in RP1C and RP2C were ~3,500 and ~3,700 cal. BP, respectively (Table 1). Although low concentrations of LCFAs at the TR site limited age determination of the deep sediment samples, assuming a constant sediment accretion rate throughout TR2C core, sediment deposition would have occurred at the bedrock contact around 6,000 cal. BP (Table 1). Similar mid-Holocene ages for initiation of the formation of depressions were found based on calcium and phosphorus mass balance estimates in BICY (Chamberlin et al.,
Figure 4. Downcore concentrations of LCFAs and SCFAs at center locations of four sampling sites. (a, b) Concentrations of LCFAs and SCFAs in RP1C. (c, d) Concentrations of LCFAs and SCFAs in RP2C. (e, f) Concentrations of LCFAs and SCFAs in TR1C. (g, h) Concentrations of LCFAs and SCFAs in TR2C. Dash lines indicate mean concentration in each core. LCFAs = long-chain fatty acids; SCFAs = short-chain fatty acid; RP = Raccoon Point; TR = Turner River.
2018) and theoretical estimates of the time necessary to dissolve bedrock under wetlands to a depth of 2 m (Dong et al., 2018). McDowell et al. (1969) reported that peats were deposited right above the limestone in the northern Everglades at ~4,280 BP. Dekker et al. (2015) reported peatland initiation in the middle Holocene in the Greater Everglades, with around 2,000–4,500 years for BICY. These bulk sediment measurements have greater uncertainty, but still likely suggest an early development of wetland conditions in southern Florida in middle/late Holocene. We suggest that correspondence between an early deposition date and the stabilization of global sea level around 6,000 years ago (Church et al., 2013; Dutton et al., 2015; Lambeck et al., 2014; Scholl et al., 1969; Wanless et al., 1994) allowed for persistent feedbacks between shallow basin morphology and the dissolution control processes (i.e., aqueous OM respiration) and led to the early development of BICY wetlands.

Recent sediment accretion rate estimated from $^{210}$Pb dating for RP1C have a mean value of 0.45 cm/year for sediments above 30 cm, while long-term sediment accretion rate for sediments below 30 cm is ~ 0.03 cm/year, based on $^{14}$C dating of LCFAs. Sediment accretion rates estimated from these two techniques commonly vary because of compaction, dissolution, OM remineralization, and increased sedimentary gaps resulting in lower long-term sediment accretion rates (e.g., Baskaran et al., 2017; Craft & Richardson, 1998; Glaser et al., 2012; Piotrowska et al., 2010; Suckow et al., 2001). Nevertheless, the fifteenfold higher rate of recent sediment accretion in BICY still indicates high deposition of organic rich soil in recent decades and/or excessive decomposition of OM in deep sediments. OM of the deep sediments (Figure 3) may have been oxidized by respiration especially during warm dry periods (Davidson et al., 2000) and fires (Watts & Kobziar, 2013). The $^{14}$C sediment accretion rate of RP1C is similar to sediment accretion rates previously...
measured for sediments deposited in the central Everglades (0.02 cm/year) over the past 4,600 years (Glaser et al., 2012), and Fakahatchee Strand Preserve State Park (0.01 cm/year) in BICY from 1,000 to 3,500 cal. BP (Donders et al., 2005).

4.3. Difference in Carbon Source and OM Accumulation Between Center and Edge

Surface TOC content was greatest in the cypress dome centers and decreased to the upland edge (Figures 3), suggesting higher biomass inputs and/or less time for respiration of OM at the cypress dome centers. Trees in these wetlands are usually taller and older in the center, producing more litter fall than trees and graminoids at the edges (C. J. Quintero, personal communication, October 23, 2018). Wetland edges are inundated by shallower water for shorter periods than the center and are often exposed to air. This exposure to atmospheric oxygen would enhance remineralization of OM at the edges relative to anaerobic processes in the center - that would use less energy efficient electron acceptors such as metal oxides (Neue, 1985). Moreover, specific respiration rates (mass flux per mass) were higher at the edges than at the centers (C. J. Quintero, personal communication, October 23, 2018). Exposure at the edge sites would also enhance ventilation of CO2 produced through remineralization processes. Conversely, much of the CO2 produced in the centers would be retained and enhance dissolution of the bedrock (Dong et al., 2018).

Retained CO2 gas plays an important role in local land patterning by carbonate dissolution and the formation of biokarst landscapes (Phillips, 2016; Watts et al., 2014). This dissolution results from OM decomposition (biogenic CO2 and organic acids), which contributes about 80% of weathering in subtropical karst and about 93% in tropical karst, as a result of higher respiration rates and air temperature in the warm climate (Phillips, 2016). Thus, wetland development in BICY is likely a result of extensive vegetation growth in the wetlands, especially in the center, that lead to accumulation and respiration of OM in sediments. The greater accumulation of OM resulting from development of accommodation space for the sediments results in greater soil thickness and is also supported by the longer accumulation time of OM in the center compared to the edge (Figure 1).

Greater enrichment of δ13C at the edge compared with the center may be related to the difference of vegetation type at the two locations. Even though cypress trees are the dominant woody plants in BICY, other woody species (e.g., willow, slash pine) and graminoid plants (e.g., muhly grass, sawgrass) also occur. The abundance of graminoid plants increased from the center to the edge, while tree size decreased (Figure 1). The δ13C values of the two most abundant graminoid species at the wetland edge, Muhly grass (Muhlenbergia capillaris, −25%; Burke et al., 1988) and sawgrass (Cladium jamaicense, −18%; this study), were more enriched than dominant plant species in the center (e.g., cypress trees, −28%; this study). Thus, the lower δ13C value in the center of the domes probably reflects greater deposition of OM from woody plants (e.g., cypress trees) than graminoids.

4.4. Differences in Carbon Sources and Vegetation Trajectory Between TR and RP Sites

TOC concentration and fatty acid components reflect differences in carbon sources in TR and RP sites. Deep sediments (>30 cm) at the RP sites had TOC concentrations nearly 5 times higher than those in the TR sites (Figure 3). The RP sites also had higher LCFAs concentrations, suggesting more terrestrial woody plants supply than at the TR sites (Figure 4). This woody plant sourced OM includes many recalcitrant components (e.g., lignin, cutins, and tannins) that are less prone to decomposition and production of CO2 (Crawford & Crawford, 1980; Neue, 1985). The SCFAs concentrations in surface sediments of the TR sites were approximately twofold greater than those of the RP sites (Figure 4). Together, they suggest the TR sites have a greater source of algal OM than the RP sites. The greater abundance of algal versus terrestrial woody OM at TR sites compared with RP sites, is consistent with wetter conditions, longer hydroperiods (up to a whole year), and greater water depths at TR sites.

Diagenetic alteration of organic carbon can cause up to 4‰ shifts in its C isotopic values (Meyers, 1994; Spiker & Hatcher, 1984), and thus small downcore shifts (≤2.2‰) of δ13C in RP sites could be explained by remineralization fractionations. However, the large downcore shifts (>6‰) of δ13C in the TR center cores require another explanation, such as changes in vegetation type through time (Figure 3). This shift occurred at TR2C around 50- to 55-cm depth, which our CSRA data indicate occurred around 2,500–2,800 cal. BP. This timing corresponded with the transition of BICY from wet prairie to swamp forest environment between 3,500 and 2,000 cal. BP, caused by increasing precipitation and wetness around 3,000 cal. BP.
A shift from wet prairie with relatively more graminoids to swamp forest with dominant woody plants was also supported by the increase of $\Lambda_8$ (Figure 5) in the upper 50 cm at TR2C, along with more depleted $\delta^{13}C$ (Figure 3). Considering the proximity of TR1 and TR2, they are very likely to have the same transition. However, the increase of $\Lambda_8$ in the upper 45 cm of TR1C was not as apparent as TR2C because of high degradation of lignin, as indicated by higher $[\text{Ad}/\text{Al}]_v$.

The different vegetation trajectories of the TR and RP sites, as indicated by $\delta^{13}C$, may reflect the differences in the timing of initial depression establishment relative to climate variability and also may be shaped by differences in elevation and thus inundation dynamics. The early development of RP and TR wetlands estimated from CSRA results were ~3,500–3,700 and ~6,000 cal. BP, respectively. Since RP sites were likely formed around or shortly before the time of increasing precipitation, RP may not have experienced wet prairie conditions, or perhaps just for a short time. This is in agreement with lower elevation at RP sites which can provide longer inundation for the possible growth of swamp forest. While the BICY wetlands were formed as a result of bio-hydro interactions driving dissolution, environmental (specifically rainfall) and preexisting geomorphic conditions could control plant community succession.

5. Conclusions

We present the first use of CSRA of LCFAs for dating wetland sediments from South Florida. Our results indicate this approach is more reliable for age dating compared with using other dating materials because of the myriad confounding factors that can impact shallow sediments in this warm carbonate-dominated environment. Our LCFAs age dates from wetlands in BICY indicate development of the modern patterned landscape in the middle to late Holocene, in agreement with estimates from mass balance modeling (Chamberlin et al., 2018). During early development, RP sites were likely dominated by woody plants (e.g., cypress trees), while TR sites exhibited a dominance of graminoids, a contrast that likely arose from differences in elevation and hydroperiods. As domes developed, vegetation at TR sites shifted toward woody plant dominance around 2,500–2,800 cal. BP, likely due to increase of precipitation and attendant changes in wetland hydroperiod. The absence of a similar shift at the RP sites may reflect more recent basin development and long hydroperiods after basin formation because of lower elevation. More recently, TR sites are wetter than RP sites, with longer hydroperiods leading to greater abundance of algal versus terrestrial woody OM at TR sites. Higher terrestrial woody plant inputs at the RP sites may lead to better preservation of OM in soil, as woody plant litters are more recalcitrant than algal materials. Within a cypress dome, higher biomass inputs and longer hydroperiods in the wetland centers increased OM accumulation compared to the edges. Although the rate of OM decomposition is lower in the dome center, it plays a more important role in biokarst bedrock weathering because CO$_2$ produced from OM decomposition is retained in water to interact with the bedrock, in contrast to rapid ventilation at the edges. Our results reflect the complex interactions between ecosystem processes (succession, OM cycling), hydrology, and carbonate mineral dissolution for karst landscape development.

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