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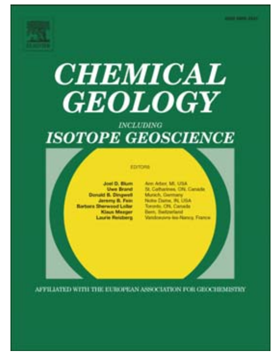

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Reconstructing Past Climates using Carbon Isotopes from Fulvic Acids in Cave Sediments

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Abstract

Little is known about the potential of organic substances found within cave sediments to provide useful reconstructions of past climatic changes. Here, we present a study of the carbon isotopes of fulvic acids extracted from sediments from a cave in west-central Florida. Fulvic acids are the most contemporaneous representation of soil humic substances derived from vegetation growing above the cave. Radiocarbon dating of these sediments constrains their depositional period to be late-Holocene. The range of the fulvic acid $\delta^{13}C$ record shows the dominance of C_3 vegetation during this period, but with changes in abundance and the shifting presence of C_4 plants. The $\delta^{13}C$ values record both the Little Ice Age and Medieval Climate Anomaly which produce drier and wetter conditions for Florida, respectively. Our conclusion that the stable carbon isotopic values of the cave sediment record as a proxy for vegetation change as driven by variability in precipitation is strongly supported by a comparison with the $\delta^{13}C$ and $\delta^{18}O$ values of two uranium-series dated speleothems from this part of Florida, with both being proxies for precipitation change.

Keywords: cave sediments; Florida; paleoclimate; fulvic acids; speleothems; precipitation; vegetation change

1. Introduction

Sedimentary records from lakes, wetlands, rivers and coastal environments are useful for reconstructing the paleoclimates of the regions from which they were collected. Information to be gained from these proxies relies on changing assemblages and quantities of pollen or diatoms, varve thicknesses, types of macro- and micro-fossils, varying types of sediment or elements, the narrow climatic tolerances of various types of insects, and charcoal concentrations, amongst others (Bradley, 1999). Climatic data provided by these proxies include changes in temperature and precipitation, and the occurrence of floods, droughts, fires, and hurricanes. From these reconstructions, conclusions have been made of shifts in the location and intensity of major atmospheric-oceanic circulations and their related teleconnections (Haug et al., 2001; Knudsen et al., 2011; Nigam et al., 2011), changing fire regimes (Higuera et al., 2009;

Marlon et al., 2009), and even the fall of human civilizations (Haug et al., 2003; Hodell et al., 2005; Polk et al., 2007; Holopainen and Helama, 2009). Some of the above paleoclimate proxies only record occasional weather events of sufficient magnitude to generate clear changes in their depositional layers. Sediments deposited in caves by aeolian or fluvial processes are examples of such records.

Speleothem-based climate reconstruction has come to prominence since the advent of high-precision uranium-series chronology using speleothem carbonate. The most commonly used proxy, the variability of $\delta^{18}O$ values in speleothem calcite, can result from multiple effects, including the local climate, moisture source variability, and changes in seasonal moisture. Cave sediments provide complementary information on local climate and other variables, such as changes vegetation type and amount, landscape evolution, hydrology, and geomorphology (Ellwood et al., 1997; Springer et al., 1997; Ford and Williams, 2007). Cave sedimentation typically results from the allogenic deposition of surface soils into caves (Brinkmann and Reeder, 1995; Polk et al., 2007). Surface soils, primarily comprised of detrital clay, sand, gravel, organic matter, and other regionally specific clastic components, are transported into caves by overland flow, streams, gravity, or other natural processes. Sediments enter the cave through entrances, small fissures and cracks in the bedrock, sinkhole piping, enlarged conduits, and groundwater (White, 1988; Palmer, 2007). These sediments can span hundreds to millions of years of deposition (Granger et al., 2001). The main benefit of using cave sediments for paleoenvironmental research is their protected environment that prevents pedogenesis and *in situ* alteration (Ellwood et al., 1997). Previous studies have focused on the physical analysis of clastic cave sediments, or using sediments to contextually constrain the timing of climate events or artifacts found within particular layers (Cordier, 1998; Foos et al., 2000; Courty and Vallverdu, 2001; Forbes and Bestland, 2007). Paleomagnetic dating of clastic sediments has been used to determine cave incision rates and providing chronologies for fossils found within caves (Sasowsky, 1995; Herries, 2006). Our study introduces a novel geochemical technique using a specific fraction of humic substances extracted from cave sediments, namely fulvic acids (FAs), to reconstruct changes in surface vegetation for the late Holocene in west-central Florida.

Fulvic acids are common organic materials found in surface soils (Yanagi et al., 2002; Ussiri and Johnson, 2003) and their high resistance to microbial decay makes them ideal for paleoclimate reconstruction (Calderoni and Schnitzer, 1984, Zech et al., 1997; Polk et al., 2007). They adsorb onto clays and other particles that allow their inclusion in cave sediments (Zech et al., 1997). In addition, they are the most contemporaneous fraction of soil organic matter, so their inclusion in the cave sediments allows for the reconstruction of vegetal change at the time of their deposition (Zech et al., 1997; Zalba and Quiroga, 1999; Webb et al., 2004; Dai et al., 2006; Polk et al., 2007).

Nissenbaum and Schallinger (1974) have shown that the carbon isotopes of soil FAs are the isotopic-equivalent of the vegetation contributing organic matter to the soil within which it is growing. Paleoecological information is derived from these isotopes because their isotopic composition is controlled by local plant matter that forms in equilibrium with the soil CO_2 (Quade et al., 1989). In addition, other studies have found that variations in the $\delta^{13}C$ recorded in cave sediments provide a record of vegetation change above the cave (Schwartz et al., 1986; Clapp et al., 1997; Panno et al., 2004). Shifts in vegetation between C_3 and C_4 plants are recorded in the $\delta^{13}C$ signal present in the organic matter trapped in the cave sediment layers (Clapp et al., 1997; Schwartz et al., 1986). Therefore, it is expected that the FAs $\delta^{13}C$ record of the cave sediments will be an accurate natural tracer of surface vegetal change over time, which is driven by precipitation.

Preliminary research we carried out on the carbon isotopes of FAs to reconstruct paleoenvironmental change in Belize led us to believe that this technique has merit, and that additional work was warranted. That investigation, using a low-resolution record of $\delta^{13}C$ of FAs extracted from cave sediments, determined that shifts in tropical vegetation were caused by the periodic occupation of the study area by the local Maya people (Polk et al., 2007). Available regional and local paleoclimate records used for the independent confirmation of our results were lacking in their chronological accuracy, however, thereby somewhat restricting the ability to test the robustness of our proxy against other existing records. Consequently, for this study we selected a cave close to an area with well-dated speleothem records, which are shown to record changes in precipitation over the last three millennia (van Beynen et al., 2007a, 2007b). Our period of investigation is the late Holocene, an interval known for two abrupt changes in climate, the Little Ice Age (LIA) and Medieval Climate Anomaly (MCA). These two events have the potential to drive changes in the local climate of the magnitude to cause a response in surface conditions that could then be recorded in the FAs isotopic signal. Our specific aim is to construct a record of changes in the $\delta^{13}C$ values of FAs over the last three millennia and compare this record to two speleothems from the local area in order to evaluate whether the FA carbon isotopes record known shifts in the regional paleoclimate.

2. Study Area

Our study was conducted in west-central Florida where the majority of Florida's air-filled caves are formed within the Brooksville Ridge and Ocala Uplift region (Florea et al., 2007a). Jennings Cave is located in Marion County, approximately 15 kilometers west of Ocala (Figure 1), and has an 8 m-deep, 2 m-wide vertical entrance that opens into several fracture-controlled vadose passages totaling ~200 m in length. The cave is ~30 meters above sea level and lies between the Ocala and Eocene limestones (Lane and Hoenstine, 1991; Florea, 2006). Some sediment enters the cave through thin fractures and conduits that extend upward several meters into the cave ceiling. However, as observed during rain events, the vast majority of sediment is washed in through the vertical entrance shaft. Sedimentation on the cave floor is widespread throughout the cave and is several meters in depth.

This region is characterized by notable karst features including a high density of sinkholes as well as dry valleys, caves, and interfluvial hills (Reeder and Brinkmann, 1998; Florea, 2007b). The geology consists of the fossiliferous, highly karstified Ocala Limestone and is intermittently covered (~8 to 10 m thick) by the Hawthorn Formation's undifferentiated clays and sands, which overlie most of the state's limestone (Florea et al., 2003; Lane and Hoenstine, 1991). Plio-Pleistocene quartz sands, clayey sands, and clays of varying depth overlie the Hawthorn in some locales (White, 1970).

The climate of the west-central Florida is humid-subtropical, with an average annual temperature of 22° C (yearly range of 22.4 C) and an average annual precipitation total of 1,300 mm (seasonal difference of ~140 mm) with clear seasonality in both (SE Regional Climate Center). Vegetation of this region is predominantly flatwood and mixed hardwood forests (Watts and Collins, 2008). This type of forest includes longleaf pine (*Pinus palustris)*, slash pine (*Pinus elliottii*), turkey oak (*Quercus laevis*), live oak (*Quercus virginiana)*, saw palmetto (S*erenoa repens*), wire grass (*Aristida* sp.), ericads, species of Holly (*Ilex*), forbs, and various scrub vegetation. The soil above the cave is the Candler fine sand series (Watts and Collins, 2008).

3. Materials and methods

3.1 Core extraction

In 2007 a trench was dug across the widest part of the main southwestern passage to ensure that the sediments were consistent in layering down-profile (Figure 2) thereby negating the need for multiple cores. Figure 2 illustrates the consistent and contiguous nature of the sediment across the passage. A 10 cm-diameter schedule 40 PVC core was taken at the end of the main southwestern passage in the cave floor next to the trench near the southern cave wall of the cave. The width of the core minimized sediment compaction and deformation and allowed for a sampling resolution of 1 cm, layer-averaged values for analyses and eliminated any minute intracore discrepancies in sediment deposition.

The core was cut lengthwise with one half sliced into 1 cm sections and classified for color, layer properties, grain type, texture, and any other discernible properties. The second half was refrigerated and kept intact for later inspection. Approximately 0.5 grams of charcoal, seeds, wood, and other organic matter was collected from layers with sufficient material to establish a chronological record of deposition. Radiocarbon analysis was carried out at BETA Analytic in Miami, Florida, using Accelerator Mass Spectrometry (AMS). Dates were calibrated to calendar ages using the CALIB 5.0.1 program and the INTCAL 04 radiocarbon database (Talma and Vogel, 1993; Stuiver et al., 1998; IntCal04, 2004).

3.2 FAs $\delta^{13}C$ Analysis

The FAs were extracted from the sediment for C isotope analysis according to a modified method of Hiradate et al. (2006). Initially, 5 g of each 1 cm increment of sediment was ground, and then mixed in a 1:10 soil to 0.1 M NaOH ratio in 55 mL polypropylene centrifuge tubes. The samples were shaken for 24 hours, after which they were centrifuged for 15 minutes at 10,000 rpm. Decantation into separate flasks followed and the process was repeated. The collected supernatants (mixed crude humic and fulvic acids) were acidified to a pH of 1.0 with 4 M HCl, stored overnight and then centrifuged at 10,000 rpm for 15 minutes to remove the precipitated humic acids. Samples were then filtered through a 0.2 micron pore-sized filter membrane and the supernatant was neutralized to a pH of 5.0 and left overnight. The precipitated FAs were collected by centrifuging at 6,000 rpm for 15 minutes, placed in a deep-freezer at -75° C and left overnight. Completion of the drying process was performed by placing the FA samples in a Labconco Lypholizer Vacuum Freeze-Dry System for 72 hours, until they became powdered and crystalline. The powdered FAs were placed in sealed containers and kept cool and dry until they were analyzed.

The $\delta^{13}C$ of the FA fractions were analyzed on a Carlo-Erba NA2500 Series II EA coupled to a ThermoFinnigan Delta+XL IRMS in continuous flow mode located at the USF College of Marine Science Paleoclimatology, Paleoceanography and Biogeochemistry Laboratory in St. Petersburg, Florida. Samples of ~30 μg were placed in tin boats and dropped from a Costech Zero-blank Autosampler into the EA combustion furnace thermostatically stabilized at 1000°C, where they were combusted with an excess of UHP O_2. Combustion products were entrained in a UHP He carrier stream and passed through a reduction furnace (to remove excess O_2 and reduce NO_x to N_2), a water trap and a GC column (3m, 0.25" dia. 5A mol sieve) before entering the IRMS via an open-split interface (ThermoFinnigan ConFlo II). Analyzed gases were measured against reference gases (UHP N_2 and UHP CO_2) and are expressed in per mil (‰) relative to their respective reference materials (VPDB for $\delta^{13}C$). Estimates of analytical precision were obtained by replicate measurements of internal lab reference materials and yield a precision of ± 0.3‰ for $\delta^{13}C$.

4. Results and Discussion

4.1 Sediment Core

The Jennings Cave sediment core J1-07 contains primarily allogenic inputs with no prominent autogenic contributions being detected. J1-07 is representative of the entire accumulation of sedimentary sequence in the main section of the cave as seen by the excavated trench dug across the passage exposing the consistent lateral sediment layers (Figure 2). Close examination of the core revealed an episodic pattern of deposition with recurring sand - organic layers. These are somewhat alternating and varved in nature, although not consistently throughout the entire depth of the core. The core consists of 64 fine sand layers, 69 organic matter layers (comprised of silty, clayey, organic-rich sand), 16 mixed sandy organic layers, and 2 orange iron-stained clayey-sand layers, all of varying thicknesses and fairly abrupt horizons. Quartz sand, based on qualitative HCl fizz testing, is the dominant sediment as it is present within every layer in varying amounts which is to be expected in west-central Florida where Quaternary quartz sand dominates the soil matrix (Watts and Collins, 2008).

4.2 Radiocarbon Dating

Nine radiocarbon dates of charcoal, wood, seeds, and organic matter, and a rabbit jawbone extracted from the core create the chronology for the age model of sediment deposition (Table 1). Fourth-order polynomial regression (r^2= 0.987, p<0.001) provides a robust record of deposition (Figure 3) with a tightly constrained chronology equivalent to similar lacustrine and marine sediment studies in its sedimentation rate and character (Curtis et al., 1998, 1999; Hodell et al., 2005).

The J1-07 FAs $\delta^{13}C$ values vary from -21.1 to -34.5‰, a range of ~13‰, which indicates notable changes in the surface vegetation for the past 3,000 years (Figure 4). This range of values falls within predominantly a C_3 vegetal assemblage, a result to be expected for a humid, subtropical environment (Webb et al., 2004). During the Holocene Neoglacial from 1,500 to 3,000 cal yr BP, the isotopic record averages ~24.5‰, albeit with brief excursions at ~1,600 cal yr BP (-21.1‰), 1,800 cal yr BP (-21.4‰), 1,950 cal yr BP (-28‰) and 2,150 cal yr BP (-28.8‰). From 1,200 to 800 cal yr BP the $\delta^{13}C$ values trend towards a maximum depletion value of -34.5‰, after which they rise sharply to enriched values of -21.1‰ by 500 cal yr BP. Finally, the carbon isotopes then trend towards more negative $\delta^{13}C$ values to the present day -24.5‰.

Changing climate is the most important controlling factor of vegetation type, with C_3 plants representative of wetter environments and C_4 plants indicating drier conditions (Panno et al., 2002; Dawson et al., 2002; Huang et al., 2006). The difference in $\delta^{13}C$ values occurs from the preferential discrimination or incorporation of ^{13}C during photosynthesis, with C_3 plants having more depleted $\delta^{13}C$ values (avg. -27‰) and C_4 plants being more enriched in ^{13}C, with $\delta^{13}C$ values averaging -13‰ (Martin et al., 1990; Boutton et al., 1998; Wynn et al., 2005; Huang et al., 2006). The isotopic signatures of vegetation translate relatively unaltered to the soil organic matter (SOM) during decomposition, providing an isotopic record of shifts in the relative abundance of C_3 to C_4 plants comprising the local vegetation (Boutton et al., 1998, Vagen et al., 2005) (Figure 5). Consequently, a possible interpretation of the variability of the J1-07 FA $\delta^{13}C$ values is that values depleted (enriched) in ^{13}C indicates a wetter (drier) C_3 (C_4) - dominated environment (Pessenda et al., 2001; Panno et al., 2004; Huang et al., 2006; Polk et al., 2007). Arising from this interpretation, the carbon isotopic records derived from the FAs analysis shows clear environmental changes during the depositional period of JC01-07. In particular, the FA $\delta^{13}C$ isotopic values appear to be most consistent with changing ratios of C_3-C_4 plants.

Grimm et al. (2006) and Huang et al. (2006) have both proposed that Florida was dominated by a mixed C_3 - C_4 environment during the Holocene, which agrees with our interpretation. However, with Florida's subtropical climate, a complete shift in dominance to either C_3 or C_4 vegetation is unlikely during the Late Holocene, but certain areas may have undergone periods of low tree abundance for long durations, such as open oak-grass savannas (Huang et al., 2006). The modern vegetation of west-central Florida is dominated by C_3 plants, but with distinct concentrations of C_4 vegetation in certain local environment (Watts and Collins, 2008).

Another possible explanation is a temporal shift in dominance between oak (*Quercus)* and pine (*Pinus)* species (Grimm et al., 2006; Huang et al., 2006), as both vary slightly in their $\delta^{13}C$ values, approximately 1-3‰. Shifts in the relative abundances of pine and oak have occurred over the last 50,000 cal yr BP in Florida based on pollen assemblages from lake sediments (Watts et al., 1992; Grimm et al., 2006). However, these records extend into the last glacial period, whereas the J1-07 record spans the relatively stable Late Holocene climate, thus, it is unlikely that complete shifts in species dominance occurred in the study area during this time. The pollen record from the J1-07 sediment core shows that both species were present at the site but did vary in their relative abundances throughout most of the record (Figure S1.). Consequently, the shifting abundance of these two species is caused by changing climate appears to be the driving force behind in the sedimentary $\delta^{13}C$ values.

4.3 Paleoclimatic interpretation of the JC01-07 FAs $\delta^{13}C$ record

The Little Ice Age (LIA, ~250 to 650 cal yr BP) and Medieval Climate Anomaly (MCA, ~800 to 1,200 cal yr BP) (Broecker, 2001) are intervals of pronounced climate shifts during the Late Holocene. Prolonged excursions in the J1-07 FA carbon isotopes correspond with these two events (Figure 4) with more negative (positive) $\delta^{13}C$ values during the MCA (LIA) indicating a wetter (drier) climate and a possible increase in the abundance (decline) of C_3 vegetation. The timing of both events as recorded in the cave sediments closely agree with other climate studies (Haug et al., 2001; Broecker, 2001; van Beynen et al., 2007a, 2007b).

A speleothem isotopic record from Briar Cave, ~15 km southeast of the Jennings Cave (van Beynen et al., 2007a), allows a local comparison with the J1-07 FA $\delta^{13}C$ record of vegetation and precipitation changes over the last 3,000 cal yr BP. The speleothem carbon isotopes (BRIARS04-02) are a record of the carbon signal derived changes in soil productivity above the cave reflecting variable amounts of precipitation. The J1-07 and BRIARS04-02 $\delta^{13}C$ records show close agreement (Figure 6) illustrating a regional shift in the vegetation driven by changing precipitation for both the MMP and the LIA. Although the BRIARS04-02 $\delta^{13}C$ values deviate less (-8.5‰ to -11‰) than the Jennings Cave sediment values, this is a result of the interaction of percolating water through the soil with bedrock before it enters the cave, thereby dampening the range in the speleothem $\delta^{13}C$ values (Fairchild et al., 2006). The close temporal coherency of the J1-07 and BRIARS04-02 $\delta^{13}C$ records also is indicative of the fulvic acids being a contemporaneous proxy for vegetation change. There is little discernable lag between the timing of variations in the two records, with the dating of the speleothem $\delta^{13}C$ values providing an absolute chronology of the changing climatic conditions influencing both proxy records.

The correspondence between both records relies on the mechanism of enrichment (depletion) in ^{13}C by C_3 plants in response to drier (wetter) periods due to changes in their photosynthetic process during these variable climatic conditions (Boutton, 1996; Turney et al., 2001; Dawson et al., 2002). The $\delta^{18}O$ records from two speleothems from different caves, BRIARS04-02 and BRC03-02, are established records of precipitation variability: the more (less) negative values are indicative of wetter (drier) periods. Their common signals show the changes in precipitation are regional (van Beynen et al., 2007a , 2007b). To confirm that the J1-07 FA $\delta^{13}C$ record is driven by changing precipitation, there must be close agreement between the speleothem $\delta^{18}O$ and sediment $\delta^{13}C$ records (Figure 7). The match of the J1-07 sediment FA $\delta^{13}C$ to the BRIARS04-02 stalagmite $\delta^{18}O$ curve is stronger than for the BRC03-02 stalagmite $\delta^{18}O$ curve because of the close proximity of Jennings and Briar Caves. BRC is located ~65 km southwest of Jennings Cave. In addition, discrepancies between the records are likely attributable to both a lag in the vegetation's response to shifting climate and the respective records age models. However, the correspondence of all three records supports our initial conclusion that the J1-07 FA $\delta^{13}C$ record does indicate long-term changes in regional climate for the Late Holocene in west-central Florida.

5. Conclusions

Agreement between the J1-07 FA $\delta^{13}C$ and the BRIARS04-02 and BRC03-02 $\delta^{18}O$ records demonstrates the influence of changing amounts of precipitation on vegetation in west-central Florida. With the subtropical climate of the region, a wholesale shift of C_3 to C_4 vegetation is unlikely. It is more probable, based on the range of the J1-07 $\delta^{13}C$ values, that there was a change in the ratio of pine/oak with both falling within the C_3 grouping, and varying contributions of C_4 plants during drier phases. This finding concurs with the pollen record for the sediments. Returning to the main objective of this paper, we conclude that the J1-07 $\delta^{13}C$ values of fulvic acids from cave sediments are a record of changing climatic conditions and are worthy of further study. Research of this nature at higher resolutions and with accepted major shifts between C_3/C_4 vegetation would cement this novel technique as a viable proxy record. When speleothems and surface paleoclimate records are not available, the carbon isotopic record extracted from cave sediment FAs may provide the only attainable paleoclimatic information for a region. This work demonstrates the strength of the combined cave sediment-speleothem isotope proxy approach to climate reconstruction.

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References

Boutton, T.W., Archer, S.R., Midwood, A.J., Zitzer, S.F., and Bol, R., 1998. $\delta^{13}C$ values of soil organic carbon and their use in documenting vegetation change in a subtropical savanna ecosystem. Geoderma 82, 5-41.

Bradley, R.S., 1999. Paleoclimatology: Reconstructing Climates of the Quaternary. Academic Press, San Diego.

Calderoni, G., and Schnitzer, M. 1984. Effects of age on the chemical structure of paleosol humic acids and fulvic acids Geochimica et Comsochimica Acta 48(10), 2045-2051.

Clapp, C.E., Layese, M.F., Hayes, M.H.B., Huggins, D.R., and Alimaras, R.R., 1997. Natural Abundances of ^{13}C in Soils and Water. **In**: Humic Substances in Soils, Peats, and Waters: Health and Environmental Aspects, M.H.B. Hayes and W.S. Wilson, (eds.). The Royal Society of Chemistry, Cambridge.

Cordier, D.J., 1998. Sequence stratigraphy of siliciclastic cave sediments: depositional response to a paleohydrologic cycle, Western Alachua County, Florida. University of Florida, Thesis.

Courty, M.A. and Vallverdu, J., 2001. The microstratigraphic record of abrupt climate changes in cave sediments of the Western Mediterranean. Geoarchaeology. Special Issue: Rockshelter Sediment Records and Environmental Change in the Mediterranean Region: Part II, 16(5), 467–499.

Curtis, J.H., Brenner, M., Hodell, D.A., Balser, R.A., Islebe, G.A., and Hoogheimstra, H., 1998. A multi-proxy study of Holocene environmental change in the Maya Lowlands of Peten, Guatemala. Journal of Paleolimnology 19, 139-159.

Curtis, J.H., Brenner, M., Hoddell, D.A., 1999. Climate change in the Lake Valencia Basin, Venezuela, ~12,600 yr BP to present. The Holocene 9(5), 609-619.

Dai, J., Ran, W., Xing, B., Gu, M., and Wang, L., 2006. Characterization of fulvic acid fractions obtained by sequential extractions with pH buffers, water, and ethanol from paddy soil. Geoderma 135, 284-295.

Dawson, A.G., Hickey, K., Holt, T., Elliott, L., Dawson, S., Foster, I.D.L., Wadhams, P., Jonsdottir, I., Wilkinson, J., McKenna, J., Davis, N.R., and Smith, D.E., 2002. Complex North Atlantic Oscillation (NAO) Index signal of historic North Atlantic storm-track changes. The Holocene 12(3), 363-369.

Ellwood, B.B., Petruso, K.M., and Harrold, F.B., 1997. High-resolution paleoclimatic trends for the Holocene identified using magnetic susceptibility data from archaeological excavations in caves. Journal of Archaeological Science 24, 569-573.

Fairchild, I.J., Smith, C.L., Baker, A., Fuller, L., Spotl, C., Mattey, D., and McDermott, F., 2009, Modification and preservation of environmental signals in speleothems. Earth-Science Reviews, 75, 105–153

Florea, L.J., Kelley, K., Hashimoto, T., Miller, D., and Mrykalo, R., 2003. Karst geomorphology and relation to the phreatic surface: Briar Cave, Marion County, Florida. **In**: Florea, L.J., Vacher, H.L., and Oches, E.A., eds.,Karst Studies in west-central Florida. University of South Florida/Southwest Florida Water Management District, pp. 9-19.

Florea, L.J., 2006. Architecture of air-filled caves within the karst of the Brooksville Ridge, west-central Florida. Journal of Cave and Karst Studies 68(2), 64-75.

Florea, L.J., Vacher, H.L., Donahue, B., and Naar, D., 2007a. Quaternary cave levels in peninsular Florida. Quaternary Science Reviews 26, 1344-1361.

Florea, L.J. and Vacher, H.L., 2007b. Eogenetic Karst Hydrology: Insights from the2004 Hurricanes, Peninsular Florida. Groundwater 45(4), 439-446.

Foos, A.M., Sasowsky, I.D., LaRock, E.J., and Kambesis, P.N., 2000. Detrital origin of a sedimentary fill, Lechuguilla Cave, Guadalupe Mountains, New Mexico. Clay and Clay Minerals 48(6), 693-698.

Forbes, M.S., and Bestland, E.A., 2007. Origin of the sedimentary deposits of the Naracoorte Caves, South Australia. Geomorphology 86, 369-392.

Ford, D.C. and Williams, P.W., 2007. Karst Geomorphology and Hydrology, second ed. Wiley, West Sussex, England.

Granger, D. E., Fabel, D., and Palmer, A. N., 2001. Pliocene-Pleistocene incision of the Green River, Kentucky, determined from radioactive decay of cosmogenic ^{26}Al and ^{10}Be in Mammoth Cave sediments. Geological Society of America Bulletin 113(7), 825-836.

Grimm, E.C., Watts, W.A., Jacobsen Jr., G.L., Hansen, B.C.S., Almquist, H.R., Dieffenbacher-Krall, A.C., 2006. Evidence for warm wet Heinrich events in Florida. Quaternary Science Reviews 25, 2197-2211.

Haug, G.H., Hughen, K.A., Sigman, D.M., Peterson, L.C. and Röhl, U., 2001, Southward migration of the Intertropical Convergence Zone through the Holocene. Science 17(293), 1304–1308.

Haug, G.H., Günther, D., Peterson, L.C., Sigman, D.M., Hughen, K.A. and Aeschlimann, B., 2003. Climate and the Collapse of Maya Civilization. Science 299, 1731–1735.

Herries, A.I.R., Reed, K.E., Kuykendall, K.L., and Latham, A.G., 2006. Speleology and magnetobiostratigraphic chronology of the Buffalo Cave fossil site, Makapansgat, South Africa. Quaternary Research 66, 233–245

Higuera, P.E., Brubaker, L.B., Anderson, P.M., Hu, F.S. and Brown, T.A., 2009. Vegetation mediated the impacts of postglacial climate change on fire regimes in the south-central Brooks Range, Alaska. Ecological Monographs 79, 201–219.

Hodell, D.A., Brenner, M., and Curtis, J.H., and Guilderson, T., 2001. Solar Forcing of Drought Frequency in the Maya Lowlands. Science 292, 1367-1370.

Hodell, D.A., Brenner, M., and Curtis, J.H., 2005. Terminal classic drought in the northern Maya lowlands inferred from multiple sediment cores in Lake Chichancanab (Mexico). Quaternary Science Reviews 24, 1413-1427.

Hiradate, S., Yonezawa, T., and Takesako, H., 2006. Isolation and purification of hydrophilic fulvic acids by precipitation. Geoderma 132, 196-205.

Holopainen, J. and Helama, S., 2009. Little Ice Age farming in Finland: Preindustrial agriculture on the edge of the Grim Reaper's scythe. Human Ecology 37, 213-225.

Huang, Y., Shuman, B., Wang, Y., Webb, T., Grimm, E.C., and Jacobson, G.L., 2006. Climatic and environmental controls on the variation of C_3 and C_4 plant abundance in central Florida for the past 62,000 years. Palaeogeography, Palaeoclimatology, Palaeoecology 237, 428-435.

IntCal04., 2004. Calibration Issue. Radiocarbon 46(3).

Knudsen, M.F., Seidenkrantz, M.-S., Jacobsen, B.H., Kuijpers, A., 2011. Tracking the Atlantic Multidecadal Oscillation through the last 8,000 years. Nature Communications 2, 178.

Lane, E., and Hoenstine, R.W., 1991. Environmental geology and hydrogeology of the Ocala area, Florida. Florida Geological Survey Special Publication 31.

Marlon, J.R., Bartlein, P.J., and Walsh, M.K., 2009. Wildfire responses to abrupt climate change in North America. PNAS 106(8), 2519-2524

Nigam, S., Guan, B. and Ruiz-Barradas, A., 2011. Key role of the Atlantic Multidecadal Oscillation in 20th century drought and wet periods over the Great Plains. Geophysical Research Letters, 38, L16713, doi:10.1029/2011GL048650

Nissenbaum, A., and Schallinger, K.M., 1974. The distribution of the stable carbon isotope ($^{13}C/^{12}C$) in fractions of soil organic matter. Geoderma 11, 137-145.

Palmer, A.N., 2007. Cave Geology. Cave Books: Dayton.

Panno, S.V., Curry, B.B., Wang, H., Hackley, K.C., Liu, C.L., Lundstrom, C., and Zhou, J., 2004. Climate change in southern Illinois, USA, based on the age and $\delta^{13}C$ of organic matter in cave sediments. Quaternary Research 61, 301-313.

Pessenda, L.C.R., Boulet, R., Aravena, R., Rosolen, V., Gouveia, S.E.M., Ribeiro, A.S., and Lamotte, M., 2001. Origin and dynamics of soil organic matter and vegetation changes during the Holocene in a forest-savanna transition zone, Brazilian Amazon region. The Holocene 11(2), 250-254.

Polk, J.S., van Beynen, P., and Reeder, P., 2007. Late Holocene environmental reconstruction using cave sediments from Belize. Quaternary Research 70, 53-63.

Polk, J.S., 2009. Proxy records of climate change in subtropical and tropical karst environments. PhD dissertation, University of South Florida, Tampa.

Quade, J., Cerling, T.E., and Bowman, J.R., 1989. Development of Asian monsoon revealed by marked ecological shift during the latest Miocene in northern Pakistan. Letters to Nature 342, 163-166.

Reeder, P. and Brinkmann, R., 1998. Paleoenvironmental Reconstruction of an Oligocene-Aged Island Remnant in Florida, USA. Cave and Karst Science 25, 7-13.

Sasowsky, I.D., White, W.B., and Schmidt, V.A., 1995. Determination of stream-incision rate in the Appalachian plateaus by using cave-sediment magnetostratigraphy. Geology 23, 415-418.

Schwartz, D., Mariotti, R., Lanfranchi, R., and Guillet, B., 1986. $^{13}C/^{12}C$ ratios in soil organic matter as indicators of vegetation changes in the Congo. Geoderma 39, 97-103.

Springer, G.S., Kite, J.S., and Schmidt, V.A., 1997. Cave sedimentation, genesis, and erosional history in the Cheat River Canyon, West Virginia. GSA Bulletin 109(5), 524-532.

Stewart, G.R., Turnbull, M.H., Schmidt, S., and Erskine, P.D., 1995. ^{13}C natural abundance in plant communities along a rainfall gradient: a biological integrator of water availability. Australian Journal of Plant Physiology 22, 51-55.

Stuiver, M., Reimer, P.J., Bard, E., Beck, J.W., Burr, G.S., Hughen, K.A., Kromer, B., McCormac, G., van der Plicht, J. and Spurk, M., 1998. IntCal98 radiocarbon age calibration, 24,000–0 cal BP. Radiocarbon 40(3), 1041–83.

Talma, A.S., and Vogel, J. C. 1993. A Simplified Approach to Calibrating C14 Dates. Radiocarbon 35(2), 317-322.

Turney, C.S.M., 1999. Lacustrine bulk organic $\delta^{13}C$ in the British Isles during the last glacial-Holocene transition. Antarctic and Alpine Research 31(1), 71-81.

Ussiri, D.A.N., and Johnson, C.E., 2003. Characterization of organic matter in a northern hardwood forest soil by ^{13}C NMR spectroscopy and chemical methods. Geoderma 111, 123-149.

van Beynen, P.E., Ford, D., and Schwarcz, H., 2000. Seasonal variability in organic substance in surface cave waters at Marengo Cave, Indiana. Hydrological Processes 14, 1177-1197.

van Beynen. P.E., Soto, L., Pace-Graczyk, K., 2007a. Paleoclimate reconstruction derived from speleothem strontium and $\delta^{13}C$ in Central Florida. Quaternary International doi:10:1016/j.quaint.2007.03.019.

van Beynen, P.E., Asmerom, Y., Polyak, V., Soto, L., Polk, J.S., 2007b. Variable intensity of teleconnections during the Late Holocene in Subtropical North America from an isotopic study of speleothem from Florida. Geophysical Research Letters 34, L18703, doi:10:1029/2007GL031046.

Watts, W.A., Hansen, B.C.S, and Grimm, E.C., 1992. Camel Lake: a 40,000-yr record of vegetational and forest history from Northwest Florida. Ecology 73(3), 1056-1066.

Watts, F.C., and Collins, M.E., 2008. Soils of Florida. Soil Science Society of America Inc.: Madison, WI.

Webb, E.A., Schwarcz, H.P., and Healy, P.F., 2004. Detection of ancient maize in lowland Maya soils using stable carbon isotopes: evidence from Caracol, Belize. Journal of Archaeological Science 31, 1039-1052.

White, W.A., 1970. The Geomorphology of the Florida Peninsula. Florida Bureau of Geology, Bulletin No. 51.

White, W.B., 1988. Geomorphology and Hydrology of Karst Terrains. Oxford University Press: New York.

Yanagi, Y., Tamaki, H., Otsuka, H., and Fujitake, N., 2002. Comparison of decolorization by microorganisms of humic acids with different ^{13}C NMR properties. Soil Biology and Biochemistry 34, 729-731.

Zalba, P. and Quiroga, A.R., 1999. Fulvic acid carbon as a diagnostic feature for agricultural soil evaluation. Soil Science 164, 57-61.

Zech, W., Senesi, N., Guggenberger, G., Kaiser, K., Lehmann, J., Miano, T.M., Miltner, A., and Schroth, G., 1997. Factors controlling humification and mineralization of soil organic matter in the tropics. Geoderma 79, 117-161.

Figure Captions

Figure 1. Study area map. Location of Jennings Cave, Marion County, Florida.

Figure 2. J1-07 core and in-cave trench. On the left is a photo of the J1-07 core with 10 cm intervals marked along its length. The photo on the right is the trench dug across the cave passage prior to coring demonstrating continuous layering.

Figure 3. The J1-07 age model. The age model is based on nine radiocarbon dates using 4th order polynomial regression.

Figure 4. Sediment core δ^{13}C data. Fulvic acid δ^{13}C data from the J1-07 sediment core, indicating periods of variability between wetter and drier conditions through the Late Holocene. The Medieval Warm Period and Little Ice Age are denoted as excursions in the isotopic record, where more negative δ^{13}C values indicate wetter conditions, and less negative δ^{13}C values occur during drier periods.

Figure 5. Theoretical model of sediment deposition under changing climatic conditions, wherein carbon isotope values are controlled by the influence of C_3 or C_4 plants.

Figure 6. Cave sediment and speleothems comparison. A comparison between the J1-07 and BRIARS04-02 speleothem δ^{13}C records.

Figure 7. J1-07 proxy comparisons. A comparison between the J1-07 sediment core, BRIARS04-02 and BRC03-02 (low-resolution) δ^{18}O shows close agreement.

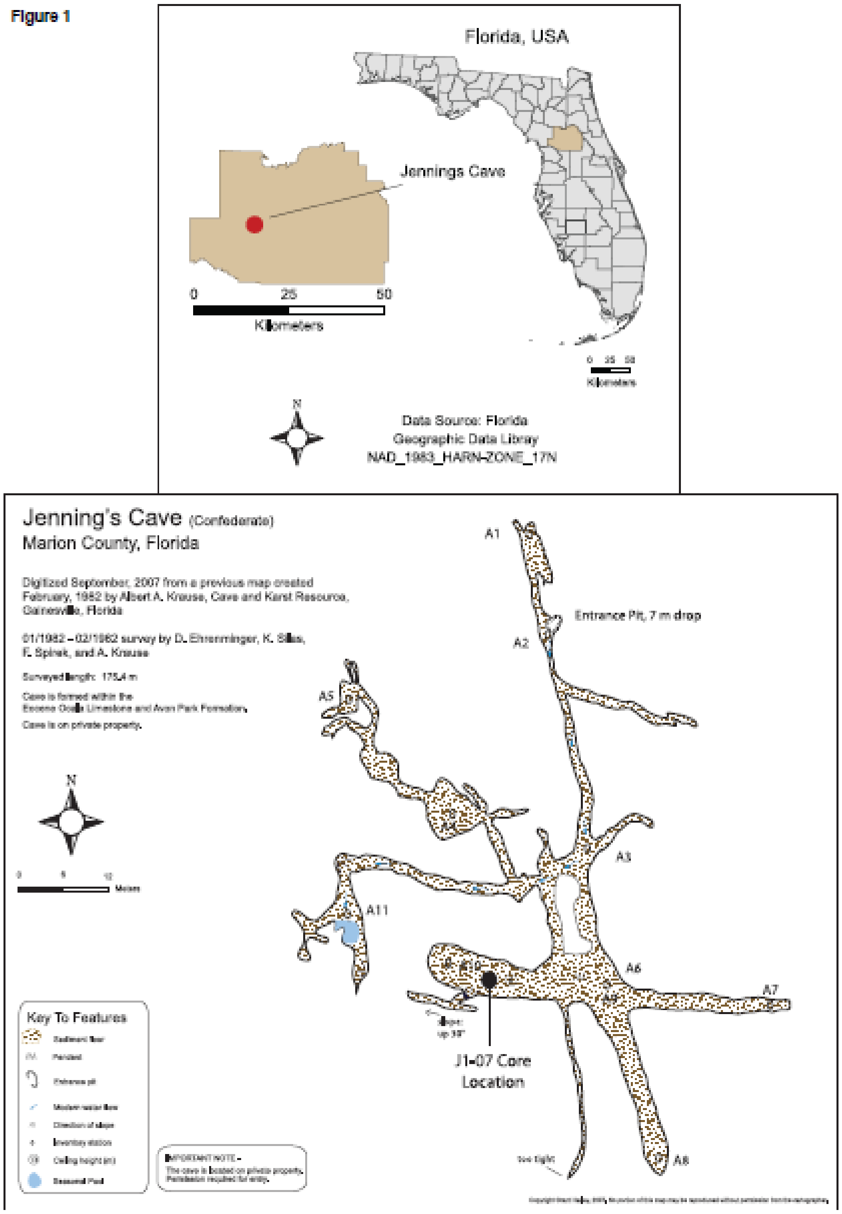
Figure S1. J1-07 pollen data. Percent abundance of pollen of major taxa vs. depth for J1-07 core from Jennings Cave (age in cal yr BP plotted next to depth). Boundaries of pollen zones are visible based on CONISS results. No pollen was available for analysis where the gray line crosses the chart.

Table 1. Radiocarbon ages for core J1-07 Core from Jennings Cave. Calibrations are based on the CALIB 5.0.1 program and the INTCAL 04 radiocarbon database (Talma and Vogel 1993; Stuiver et al. 1998; IntCal04 2004).

Sample ID	Depth (cm)	Description	Age (^{14}C yr BP)	± (1σ)	Age (cal yr BP)	± (2σ)
BETA-228643	1.5	Charcoal	Post-bomb	0.4 pMC	50	-
BETA-228644	2.5	Charcoal	370	40	340	40
BETA-228645	15.5	Wood	610	40	600	40
BETA-228656	36.5	Charcoal	1560	40	1560	40
BETA-28647	51.5	Organics	1610	40	1580	40
BETA-228648	63	Charcoal	1930	40	1820	40
BETA-228649	82.5	Charcoal	2210	40	2210	40
BETA-228650	100.5	Organics	2680	40	2670	40
BETA-228651	104	Jaw Bone	2650	40	2710	40

AMS radiocarbon dates from J1-07, given in cal yr BP.

Figure 1


Florida, USA
Jennings Cave
0
25
50
Kilometers
N
Data Source: Florida
Geographic Data Libray
NAD_1983_HARN-ZONE_17N
Jenning's Cave (Confederate)
Marion County, Florida
Digitized September, 2007 from a previous map created
February, 1982 by Albert A. Krause, Cave and Karst Resource,
Gainesville, Florida
01/1982 – 02/1982 survey by D. Ehrenminger, K. Sillas,
F. Spinek, and A. Krause
Surveyed length: 175.4 m
Cave is formed within the
Eocene Ocala Limestone and Avon Park Formation.
Cave is on private property.
A1
Entrance Pit, 7 m drop
A2
A3
A5
A6
A7
A8
A11
J1-07 Core
Location
Key To Features
IMPORTANT NOTE -

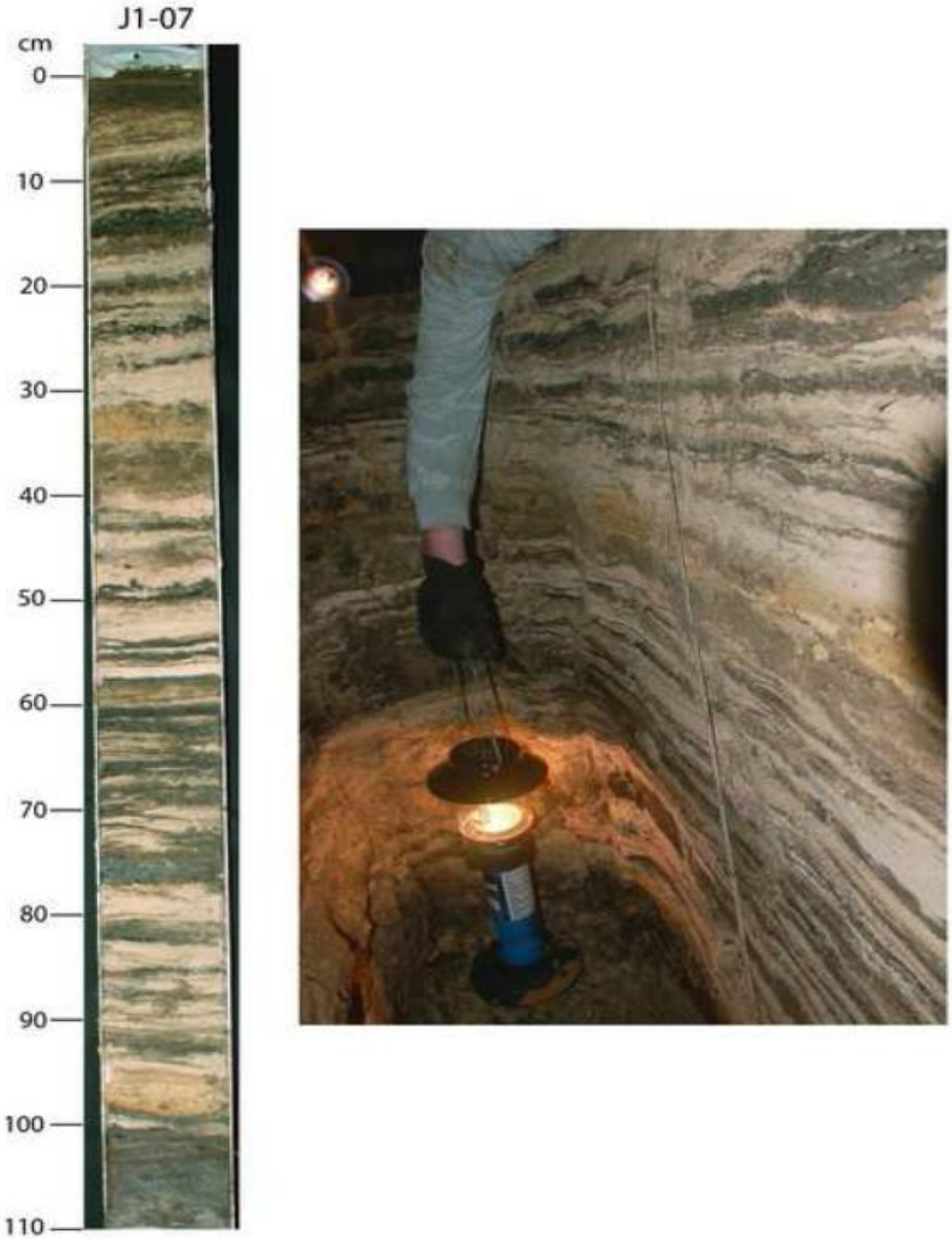
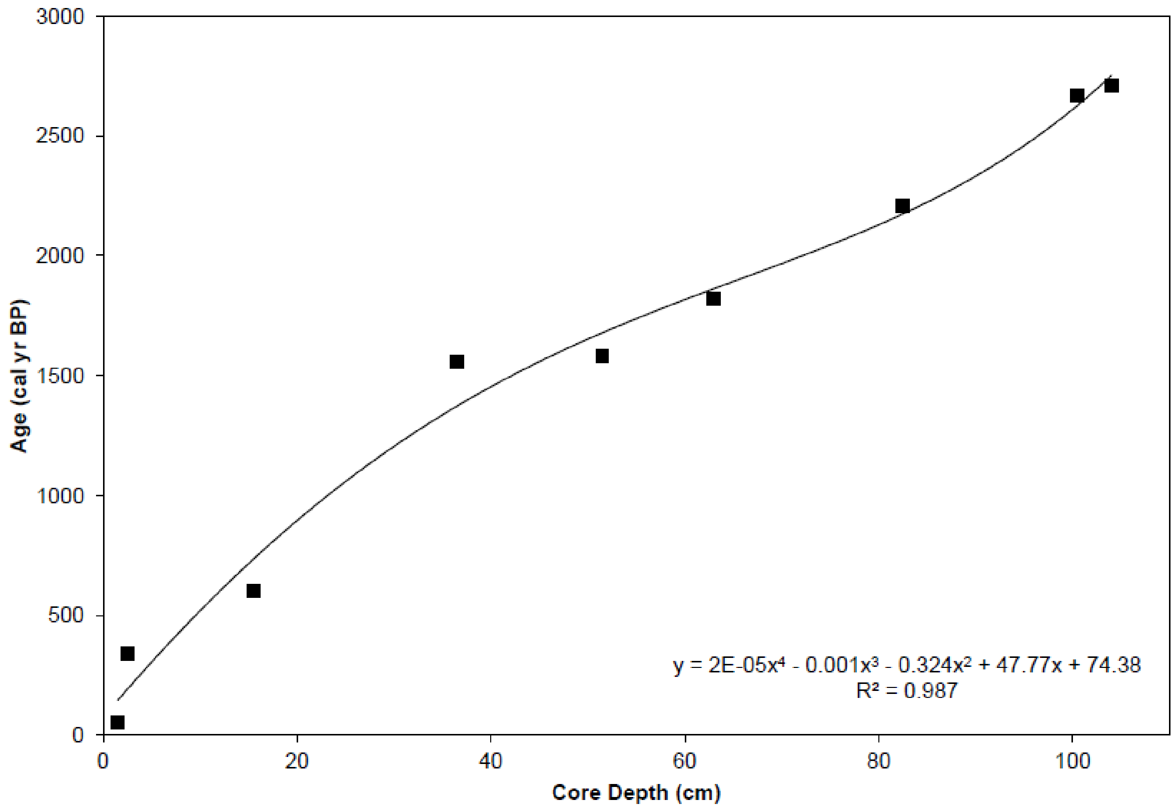


Figure 2



3000
2500
2000
1500
1000
500
0
Age (cal yr BP)
0
20
40
60
80
100
Core Depth (cm)
y = 2E-05x⁴ - 0.001x³ - 0.324x² + 47.77x + 74.38
R² = 0.987

Figure 3

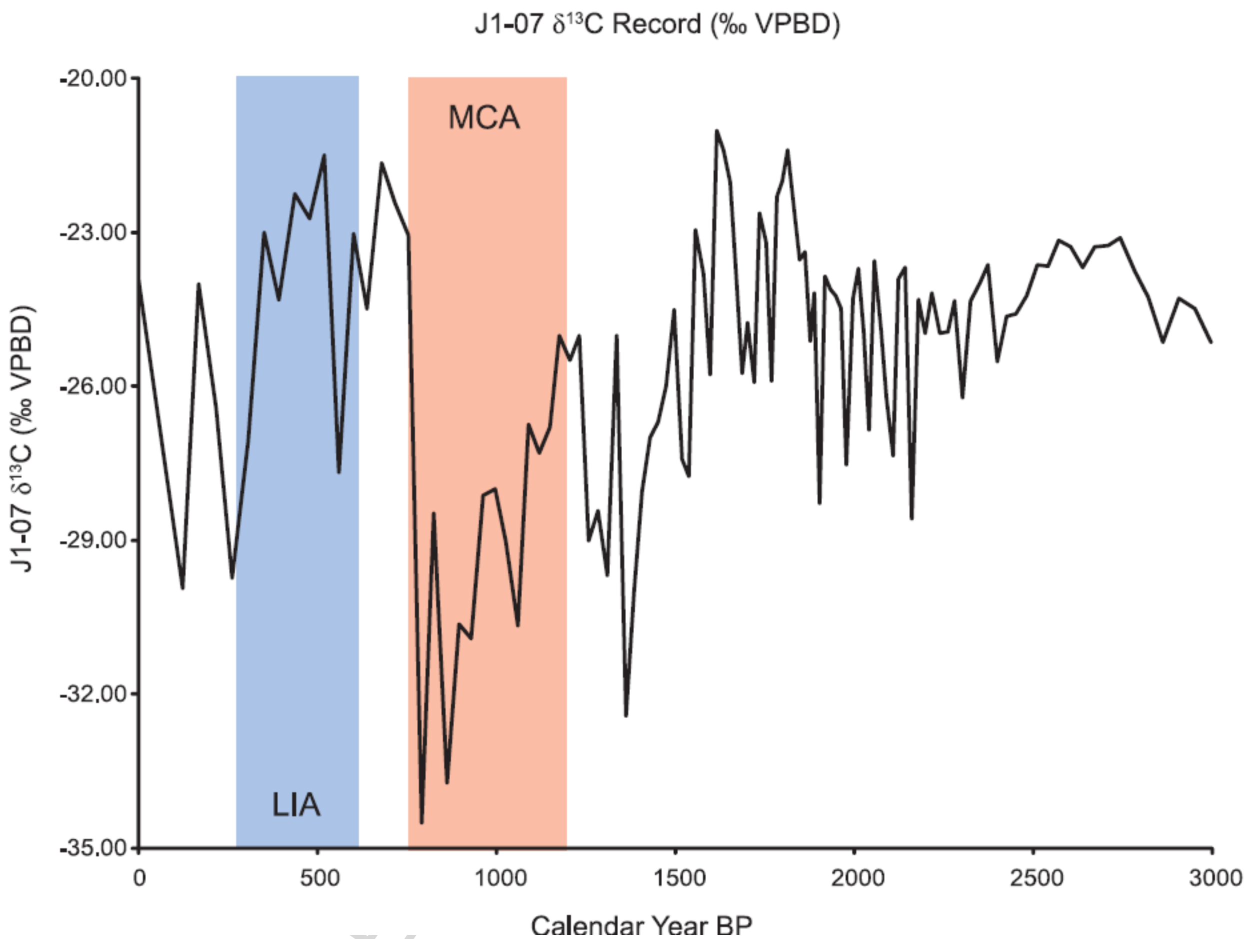

J1-07 δ13C Record (‰ VPBD)
J1-07 δ13C (‰ VPBD)
-20.00
-23.00
-26.00
-29.00
-32.00
-35.00
MCA
LIA
0
500
1000
1500
2000
2500
3000
Calendar Year BP

Figure 4

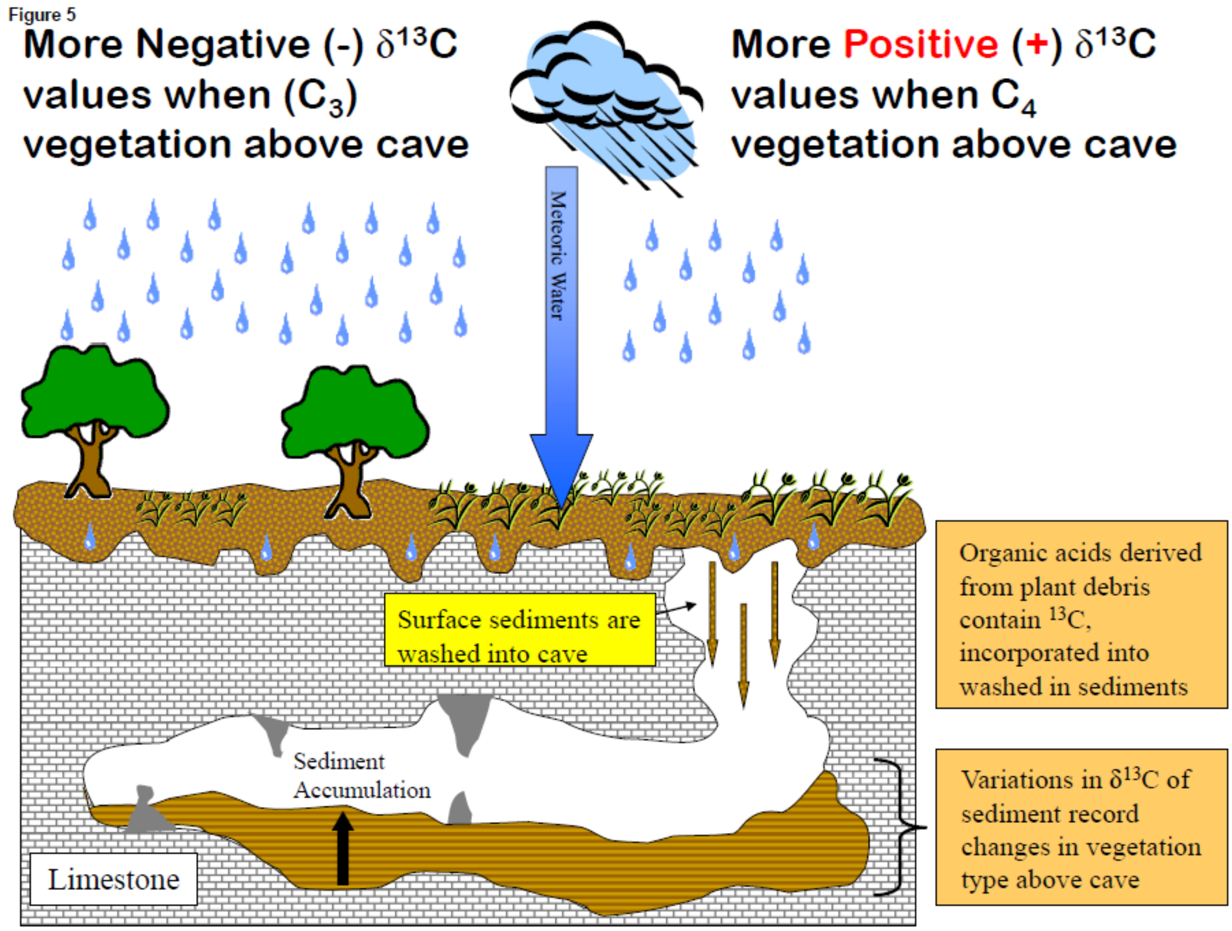
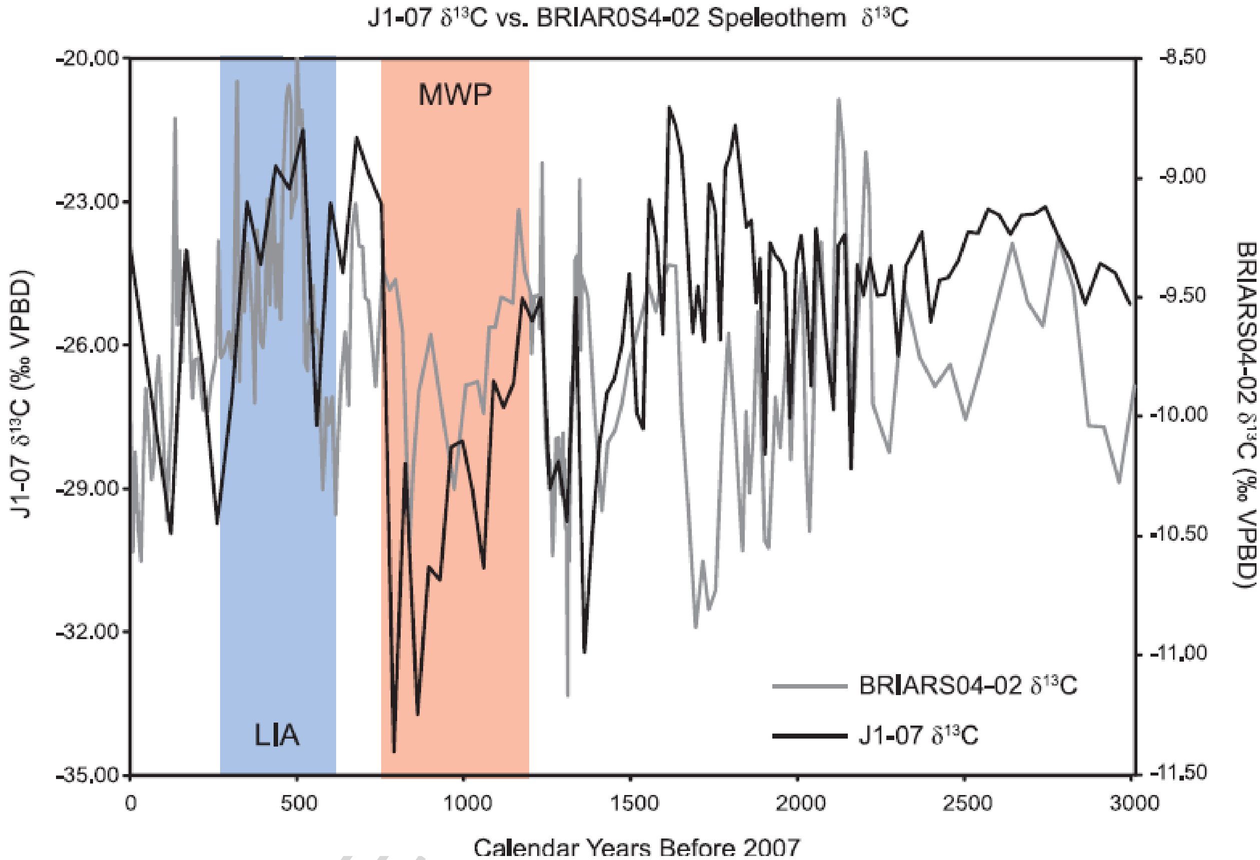


Figure 5
More Negative (-) δ13C values when (C3) vegetation above cave
More Positive (+) δ13C values when C4 vegetation above cave
Meteoric Water
Surface sediments are washed into cave
Organic acids derived from plant debris contain 13C, incorporated into washed in sediments
Sediment Accumulation
Variations in δ13C of sediment record changes in vegetation type above cave
Limestone

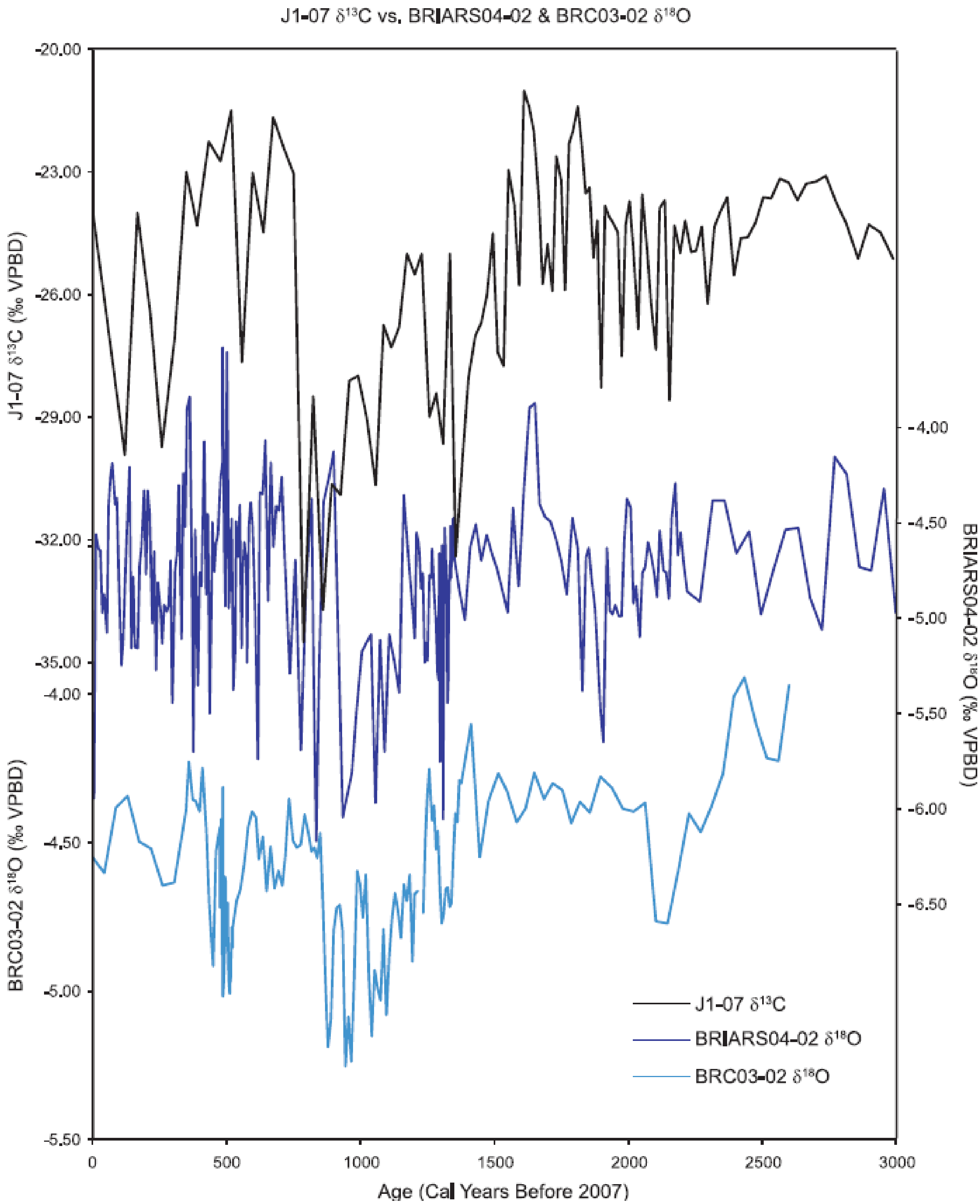
Figure 5



J1-07 δ13C vs. BRIAR0S4-02 Speleothem δ13C
-20.00
-23.00
-26.00
-29.00
-32.00
-35.00
J1-07 δ13C (‰ VPBD)
-8.50
-9.00
-9.50
-10.00
-10.50
-11.00
-11.50
BRIARS04-02 δ13C (‰ VPBD)
MWP
LIA
BRIARS04-02 δ13C
J1-07 δ13C
0
500
1000
1500
2000
2500
3000
Calendar Years Before 2007

Figure 6

Figure 7


J1-07 δ13C vs. BRIARS04-02 & BRC03-02 δ18O
-20.00
-23.00
-26.00
-29.00
-32.00
-35.00
J1-07 δ13C (‰ VPBD)
-4.00
-4.50
-5.00
-5.50
BRC03-02 δ18O (‰ VPBD)
-4.00
-4.50
-5.00
-5.50
-6.00
-6.50
BRIARS04-02 δ18O (‰ VPBD)
0
500
1000
1500
2000
2500
3000
Age (Cal Years Before 2007)
J1-07 δ13C
BRIARS04-02 δ18O
BRC03-02 δ18O

Polk- Chem Gly Highlights

- We test the use of cave sediments for paleoclimate reconstruction.
- We compared the results to stalagmite isotopes in Florida.
- Carbon isotopes of fulvic acids in cave sediments records changes in vegetation.
- This method is a novel approach proven to work well in this region.