δ^{13}C OF CAVE SPELEOTHEMS LOCATED IN KENTUCKY AND OHIO, U.S.A.: IMPLICATION FOR PALEOVEGETATION AND PALEOCLIMATE STUDIES

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ABSTRACT

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Calcium carbonate $\delta^{13}C$ values of actively growing/actively dripping speleothems have been evaluated for comparison to the range predicted for modern vegetation. Some geochemical models suggest that speleothem calcium carbonate $\delta^{13}C$ values from caves under C_3 surface vegetation should exhibit $\delta^{13}C$ values predicted for C_3 vegetation; however, several field studies have shown that this relationship is unreliable. In this research, $\delta^{13}C$ values were measured on speleothem, soil and bedrock samples in various caves in Ohio and Kentucky. These caves include: Crooked Creek Ice Cave, Floyd Mullins Cave, Great Salt Peter Cave, Hard Baker Cave, and Pine Hill Cave located in Rockcastle Co., KY; Seneca Caverns and Perry's Cave in Seneca and Erie Counties, Ohio respectively. Soil organic matter $\delta^{13}C$ values closely matched the range for C_3 vegetation with three samples demonstrating slight enrichment. Speleothem $\delta^{13}C$ values were not consistent with the published predicted values. The modern speleothems collected at the various caves indicate a large $\delta^{13}C$ variability ranging from $^{-}11.34$‰ to $^{-}2.96$‰ VPDB. The percentage of measured speleothem $\delta^{13}C$ values not agreeing with published predictions ranges from 20% to 80% depending on which predicted values are used. The process most responsible for the differences between measured and predicted $\delta^{13}C$ values remains unclear. At one sample location, enriched values relative to that predicted for C_3 vegetation can be attributed to C_4 vegetation. Enrichment due to kinetic fractionation during calcium carbonate precipitation, and prior degassing are possible sources at the other locations. In this study, speleothem calcium carbonate $\delta^{13}C$ analysis alone does not reliably reflect the modern surface vegetation because of the other processes affecting the ^{13}C.

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INTRODUCTION

The correlation between the photosynthetic pathway utilized by surface vegetation and the δ^{13} C values of speleothem calcium carbonate has the potential to reveal paleovegetation and ultimately paleoclimate. A relationship between actively growing speleothem calcium carbonate δ^{13}C values and modern vegetation δ^{13}C values needs to be more clearly defined. Most research to date involving ancient speleothem carbonate δ^{13}C values have focused on interpreting paleovegetation, particularly changes in C_3 versus C_4 dominance within the landscapes over caves. The focus of this research is to determine if modern, actively growing speleothem calcium carbonate δ^{13}C values can indicate a present day, temperate, C_3 dominant vegetation source above various caves located in Kentucky and Ohio (Figure 1). Specifically, this research will: 1.) determine if soil organic matter δ^{13}C values reflect the C_3 vegetation above the caves, and 2.) determine if the δ^{13}C value of actively growing speleothem calcium carbonate reflects the predicted values for C_3 vegetation.

Speleothem calcium carbonate precipitating seepage waters derive carbon dioxide (CO_2) primarily from the soil atmosphere (Dorale et al., 1992; White and White, 1989; Hendy, 1971). In the soil horizon, the decomposition of soil organic matter and plant root respiration are the dominate sources of soil CO_2 in temperate climates (Biedenbender et al., 2004; Smith and White, 2004; Kelly et al., 1993 and 1998). The decomposition of the parent vegetation leads to slightly enriched soil organic matter δ^{13}C values that closely reflect the parent vegetation (Salomons and Mook, 1986). Works by Park and Epstein (1960) and Smith and Epstein (1971) helped to establish: 1.) the mechanisms of carbon fractionation associated with terrestrial photosynthesis and 2.) the two main photosynthetic pathways resulting in two distinct carbon isotopic signatures: C_3 ($^{-}$34‰ to $^{-}$24‰ Pee Dee Belemnite (PDB)) and C_4 ($^{-}$19‰ to $^{-}$6‰ PDB). The mechanisms are based on the pathway by which atmospheric carbon dioxide (≈ $^{-}8$‰ PDB) is converted to carbohydrates through uptake (Farquhar et al., 1989).

The photosynthetic pathway most relevant to this research is the "C_3" (Calvin/Benson) cycle which is dominant in moist, colder environments (most hardwood trees and some grasses). In these environments, ribulose-1,5-bisphosphate (RuBP) reacts by the use of the enzyme RuBP carboxylase with carbon dioxide to form the three carbon molecule 3-phosphoglycerate (PGA), hence the name C_3 (Mauseth, 1998; O'Leary, 1981). The C_3 plants are highly discriminatory against ^{13}C, mostly due to the carboxylation of RuBP (roughly $^{-}30$‰). Both internal partial pressure carbon dioxide (pCO_2) and the diffusion of CO_2 through stomata openings affect δ^{13}C values by roughly $^{-}4.4$‰. These C_3 plants exhibit δ^{13}C values between $^{-}35$‰ to $^{-}22$‰ PDB (Ambrose and Sikes, 1991; Dorale et al., 1992; Park and Epstein, 1960; Smith and Epstein, 1971).

The photosynthetic pathway for the "C_4" (Hatch-Slack) cycle may also influence speleothem δ^{13}C composition. This photosynthetic pathway is best suited for hot environments with low moisture (most grasses, some agricultural plants). The C_4 process involves binding carbon dioxide to phosphenolpyruvate (PEP) by the enzyme PEP carboxylase to form oxaloacetate (Mauseth, 1998). C_4 plants show a more enriched δ^{13}C values, compared to C_3 plants, which range between $^{-}19$‰ and $^{-}6$‰ PDB (Ambrose and Sikes, 1991; Dorale et al., 1992; Park and Epstein, 1960; Smith and Epstein, 1971).

To have speleothem calcium carbonate δ^{13}C values that accurately indicate the type of vegetation growing above a cave at the time of speleogenesis, speleothems need to be deposited under a state of isotopic equilibrium (Hendy, 1971; Swartcz, 1986). This equilibrium occurs away from cave openings in environments where humidity is at or near 100% (Desmarchelier et al., 2000). Cave atmospheres which maintain a high and stable pCO_2 allow for the slow degassing of CO_2 from calcium carbonate supersaturated waters. This maintains equilibrium between the bicarbonate (HCO_3^-), carbonate (CO_3^{-2}), and CO_2 species during speleothem calcite ($CaCO_3$) formation (White and White, 1989). These equilibrium conditions allow the ability to calculate predicted values of calcium carbonate $\delta^{13}C$ for speleothems through geochemical models. Various researchers have used these models to calculate ranges for speleothem calcium carbonate. Hendy (1971) was one of the first to do so. He calculated values of $^{-}13.2$‰ for an open system and $^{-}11.5$‰ to $^{-}10.5$‰ for a closed system. For a speleothem in southern Scotland, calculated speleothem calcium carbonate $\delta^{13}C$ values based on open\closed system behavior were $^{-}13.5$‰ and $^{-}11.5$‰ to $^{-}10.5$‰ respectively (Genty et al., 2001). Baker et al.'s (1997) research of a British cave system calculated predicted values of speleothem calcium carbonate $\delta^{13}C$ that range from $^{-}6$‰ to $^{-}12$‰. Finally, Brook et al. (1990) modeled speleothem calcium carbonate under C_3 dominant vegetation to range from $^{-}12$‰ to $^{-}9$‰ in a more arid environment.

The interpretation of speleothem calcium carbonate $\delta^{13}C$ values as a reliable indicator of changes in paleovegetation has been shown to be problematic (Baker et al., 1997 and Bar-Matthews, et al. 1996). A study of a British Isles cave system by Baker et al. (1997) established three processes leading to variations in speleothem calcium carbonate $\delta^{13}C$ values. The first is degassing of the groundwater in the unsaturated zone causing enrichment in speleothem calcium carbonate $\delta^{13}C$ values (Baker et al., 1997; Genty et al., 2001). Another process leading to enrichment is kinetic fractionation during calcium carbonate precipitation. Finally, disequilibrium with soil carbon dioxide (CO_2) allowing for a more atmospheric supply of carbon available for calcium carbonate precipitation. These sources of variations in speleothem calcium carbonate $\delta^{13}C$ values are hard to differentiate and trying to determine which process is causing the variations may not possible (Baker et al., 1997).

Speleothem calcium carbonate $\delta^{13}C$ values from caves under C_3 surface vegetation have exhibited $\delta^{13}C$ values which are predicted for C_4 vegetation (Baker et al., 1997; Hellstrom et al., 1998; and Tooth and Fairchild, 2003). Elkins (2002) compares the predicted and measured speleothem calcium carbonate $\delta^{13}C$ values under C_3 vegetation (Figure 2). These authors suggest this discrepancy is due to incomplete equilibration of atmospheric CO_2 with shorter residence times of percolating groundwater. At a New Zealand site, speleothem calcium carbonate $\delta^{13}C$ values were indicative of C_4 plants, yet no C_4 plants are close to the area (Hellstrom et al., 1998). This was interpreted to result from inorganic processes interacting on soil $CO_{2,}$ low seepage water flow rates, and low productivity in an arid environment. Fantidis and Ehhaldt (1970) reported isotopic variations in carbon and oxygen within speleothem calcium carbonate which are related to drip rate. Their study indicated higher drip rates yielded lower calcite $\delta^{13}C$ values and lower drip rates yielded higher $\delta^{13}C$ values. Slightly enriched soil $\delta^{13}C$ values from a study of various caves in arid regions have been demonstrated by Brook et al. (1990). The C_3 and C_4 surface vegetation in the study area exhibited $\delta^{13}C$ values of $^-27$‰ and $^-13$‰ respectively. The soil $\delta^{13}C$ values showed a slight enrichment to $^-22$‰ for the C_3 vegetation, and the C_4 vegetation soils were enriched to $^-9$‰. Enrichment of the soil organic matter $\delta^{13}C$ values due to the decomposition of bulk soil mass and lignin factions were observed in a research study involving C_3 grass decomposition (Wedin et al., 1995). Kelly et al. (1998) observed that diagenesis and microbial decomposition could lead to an enrichment of 1-2‰. Overall, soil organic matter $\delta^{13}C$ values within the first 10 cm of the surface and soils up to a meter thick with no paleosols present were observed to be in good agreement with the present vegetation type (Kelly et al., 1993).

SAMPLE SITE LOCATION

The sampling areas are located in the states of Kentucky and Ohio, in the north-central region of the United States of America. A temperate climate is prevalent across the region where mean higher moisture and mean lower temperature are favorable for C_3 vegetation. This is supported by the presence of hardwood and softwood deciduous trees dominating the karstic terrain in which the caves of this study are located (Figures 3 and 4). Average temperatures and rainfall for the period of 1895 to the present are 10.4°C and 96.0 centimeters in Ohio and 13.2°C and 120.3 centimeters in Kentucky (National Climate Data Center, 2005).

The carbonate samples were obtained from seven caves found in Paleozoic carbonate strata. Caves for this research in Kentucky are located along the intersection of the eastern part of the Mississippian Plateau and western part of the Cumberland Plateau within Mississippian age strata. The five caves are developed within the Newman Formation. The Ste. Genevieve Limestone and Upper Member subdivisions are the main cave forming units (Grabowski, 2001). The caves include Hard Baker Cave (Figure 5), Floyd Mullins Cave, Crooked Creek Ice Cave (Figure 6), Great Salt Peter Cave (Figure 7), and Pine Hill Cave (Figure 8) located in Rockcastle Co., KY. Perry's Cave and Seneca Caverns in north central Ohio are located along the eastern limb of the Findlay Arch, a northeast striking anticlinal structure that separates the Michigan and Appalachian basins. The caves occur in the Big Lime Formation which contains the Columbus/Delaware Limestone groups and the Tymochtee, Greenfield, and Lockport Dolomites (Golder and Associates, 1983).

METHODS

Fourteen soil samples were collected directly above caves at five locations to obtain soil organic matter $\delta^{13}C$: Crooked Creek Ice Cave, Hard Baker Cave, Pine Hill Cave, Perry's Cave and Seneca Caverns. Bulk soils were collected, but only soil organic matter was analyzed. As noted by Wedin et al, (1995), there is enrichment of soil ^{13}C as the bulk fraction material decomposes. The bulk fraction material contributing to the $\delta^{13}C$ value includes everything in the soil together with, bedrock pieces, plant matter, and pedogenic carbonates. All of these sources of carbon can lead to a bias of the results by incorporating inorganic sources of carbon. For this research, the soil organic matter $\delta^{13}C$ values are desirable because the majority of soil carbon dioxide comes from decaying plant matter and the carbon dioxide in drip water comes from the soil atmosphere (Dorale et al., 1992; White and White, 1989; Hendy, 1971). A 15 centimeter, small garden shovel was used to collect the soil samples. The soils were collected by removing actively growing plant material (grasses) and shoveling down to the length of the shovel to remove roughly 2 liters of soil. The soils were placed into sealable, one-gallon Ziploc™ plastic bags and stored in a brown, opaque plastic trash bag and refrigerated until analyzed. These samples were sent to the University of Georgia Soil Ecology Laboratory for $\delta^{13}C$ analysis. The volume of material supplied for each sample was sufficiently large to take two sub-samples from each.

All speleothem carbonate samples were sampled from actively growing/ actively dripping speleothems. The Pine Hill Cave samples were taken from soda straw stalactites (Figure 9). These stalactites range from a few centimeters to tens of centimeters in length. The Hard Baker Cave sample is a 6-cm-long stalactite off of a flowstone (Figure 10). The Seneca Caverns samples were stalactites ranging from a few millimeters to a few centimeters in length (Figure

11). All calcium carbonate samples were collected from actively growing speleothems (stalactites, stalagmites and flowstones) using a model 800 Dremel ™ cordless drill. A minimum of 10 mg (milligrams) of sample was collected from each speleothem and placed into brown, opaque 40 ml (milliliter), sealed jar. The samples were sent to the University of Michigan Stable Isotope Lab for $\delta^{13}C$ and $\delta^{18}O$ analysis, where the samples were placed in individual borosilicate reaction vessels and reacted at 77° ± 1°C with 4 drops of anhydrous phosphoric acid for 8 minutes. Samples were roasted at 200° C in a vacuum for one hour to remove volatile contaminants and water in a Finnigan MAT Kiel IV preparation device coupled directly to the inlet of a Finnigan MAT 253 triple collector isotope ratio mass spectrometer. The $\delta^{18}O$ data are corrected for acid fractionation and source mixing by calibration to a best-fit regression line defined by two NBS standards, NBS 18 and NBS 19. Data are reported in per mil (‰) notation relative to VPDB. Precision is maintained at better than ±0.1 ‰ for both carbon and oxygen isotope compositions.

Bedrock carbonate samples were collected using a rock hammer from four caves: Crooked Creek Ice Cave, Pine Hill, Perry's Cave, and Seneca Caverns. Samples were collected using a model 800 Dremel ™ cordless drill. Again, a minimum of 10 mg of sample was collected from each bedrock carbonate sample and placed into brown, opaque 40 ml, sealed jar. These carbonate samples were also sent to the University of Michigan Stable Isotope Lab. The $\delta^{13}C$ and $\delta^{18}O$ analysis was preformed to determine if there was any bedrock influence on speleothem calcium carbonate $\delta^{13}C$ and $\delta^{18}O$ values.

RESULTS

δ^{13}C values were determined for 14 soil, 19 speleothem, and 3 bedrock samples (Tables 1-4; Figure 12). The results for each sample type are presented separately in the following sections.

Soil δ^{13}C values

The soil organic matter δ^{13}C values from Kentucky are more negative than the approximate dividing line between C_3 and C_4 vegetation, indicating a C_3 vegetation source. The samples from Ohio plot near the dividing line. The soil organic matter δ^{13}C values associated with Crooked Creek Ice Cave, Hard Baker Cave and Pine Hill are consistent with C_3 vegetation dominated environments. The ranges of soil organic matter δ^{13}C values for these caves are $^-$27.3‰ to $^-$26.1‰, $^-$27.1‰ to $^-$26.3‰ and $^-$27.4‰ to $^-$26.5‰. The Perry's Cave and Seneca Caverns soil samples contain soil organic matter δ^{13}C values similar to the predicted range for C_3 vegetation with the exception of two samples which exhibit signs of enrichment relative to C_3 vegetation. The soil organic matter δ^{13}C values associated with Perry's Cave range between $^-$26.6‰ and $^-$17.8‰. For Seneca Caverns, the range is $^-$26.4‰ to $^-$16.0‰.

Speleothem δ^{13}C and δ^{18}O values

The speleothem calcium carbonate δ^{13}C values from Kentucky and Ohio are around the $^-$9‰ to $^-$6‰ disputed range. Four samples are in the range predicted by both authors for C_3 vegetation; five samples plotted in the C_4 vegetation range. The remaining samples plotted within the disputed range. At Hard Baker Cave, the values range from $^-$9.3‰ to $^-$10.8‰. Crooked Creek Ice Cave, Floyd Mullins, and Great Salt Peter Cave speleothem calcium carbonate δ^{13}C values are $^-$8.3‰, $^-$7.5‰, and $^-$7.0‰ respectively. The speleothem calcium carbonate δ^{13}C values from the two caverns in Ohio, Seneca Caverns and Perry's Cave, range from $^{-}$3.0‰ to $^{-}$6.4‰ and $^{-}$7.1‰ to $^{-}$11.3‰ respectively. In contrast, speleothem calcium carbonate δ^{13}C values from the caves in Kentucky vary less than the Ohio caves, except the samples from Pine Hill Cave, Kentucky which range from $^{-}$4.9‰ to $^{-}$8.4‰. The speleothem calcium carbonate δ^{18}O values associated with the Ohio cave samples vary from $^{-}$6.7‰ to $^{-}$7.0‰ for Seneca Caverns and $^{-}$5.9‰ to $^{-}$6.7‰ at Perry's Cave. In Kentucky, the Pine Hill Cave speleothem calcium carbonate δ^{18}O values vary from $^{-}$4.9‰ to $^{-}$5.8‰. Hard Baker Cave speleothem calcium carbonate δ^{18}O values vary between $^{-}$5.2‰ to $^{-}$5.7‰. Finally, Crooked Creek Ice Cave, Floyd Mullins, and Great Salt Peter Cave speleothem calcium carbonate δ^{18}O values are $^{-}$4.7‰, $^{-}$4.7‰, and $^{-}$5.5‰ respectively.

Bedrock δ^{13}C and δ^{18}O values

Three carbonate bedrock samples were analyzed for δ^{13}C and δ^{18}O. The calcium carbonate δ^{13}C values for Seneca Caverns, Crooked Creek Ice Cave and Pine Hill are 1.0‰, 1.1‰ and 1.7‰ respectively. The ratios associated with δ^{18}O are $^{-}$5.9‰, $^{-}$5.2‰ and $^{-}$5.9‰ respectively. These carbonate bedrock δ^{13}C and δ^{18}O values are consistent with Paleozoic bedrocks (Hoefs, 1997).

DISCUSSION

Several of the measured speleothem calcium carbonate δ^{13}C values fall outside of the range predicted by Brook et al. (1990) and Baker et al. (1997). These published values represent the end member ranges for speleothem calcium carbonate δ^{13}C values modeled under C_3 vegetation. The model of Brook et al. (1990) has open-system behavior, and the model of Baker et al. (1997) has closed-system behavior. The predicted δ^{13}C values calculated by Brook et al., (1990) for speleothem calcium carbonate precipitated under 100% C_3 vegetation would be between $^{-}$12‰ to $^{-}$9‰. The results of this study indicate that 80% of the samples from caves overlain by C_3 vegetation do not fall within the predicted range as established by Brook (1990). However, if the predicted range proposed by Baker et al. (1997) of $^{-}$12‰ to $^{-}$6‰ is used, then 20% of samples in this study fall outside the predicted range. Sixty percent of the speleothem samples from caves overlain by C_3 vegetation have δ^{13}C values within the disputed range between $^{-}$6‰ and $^{-}$9‰. Possible processes leading to the variations observed include: changes in atmospheric carbon δ^{13}C values, changes in the type of vegetation(C_3 verses C_4), changes in infiltration rates, soils with thin or no vegetation, open verse closed system behavior, kinetic fractionation due to prior degassing and kinetic fractionation associated with evaporation. These are summarized in Table 5 and further explained below.

Atmospheric δ^{13}C is roughly $^{-}$8.0‰ and is gradually decreasing due to the influx of anthropogenic carbon from industrial activity. Changes in the δ^{13}C values of speleothems associated with changes in atmospheric δ^{13}C are minimal due dominance of soil respired carbon dioxide in temperate climates. At the sample locations in this study, changes in speleothem calcium carbonate δ^{13}C attributed to changes in atmospheric δ^{13}C is not applicable. This study is a modern assessment of the ability of speleothems to reflect surface vegetation. This effect would be relevant when doing $\delta^{13}C$ time-series studies.

The soil organic matter $\delta^{13}C$ values associated with C_3 soils, which are around $^{-}23‰$, are slightly enriched when compared to the plant $\delta^{13}C$ values. This is due to various sources of organic decomposition of dead plant material by microbes, plant root respiration and plant productivity. C_4 photosynthetic plants ($\delta^{13}C \approx {}^{-}12.5‰$), may influence speleothem calcium carbonate $\delta^{13}C$ compositions at the cave locations. This may be a source for the slightly enriched soil organic matter $\delta^{13}C$ values (Tables 1 and 2) at Seneca Caverns, Perry's Cave and the enriched speleothem calcium carbonate $\delta^{13}C$ values at Seneca Caverns. Any C_4 contribution is most likely from agricultural sources because during the period of speleothem growth, the regional climate has not been favorable for C_4 vegetation. Fields contiguous to the Seneca Caverns property are row cropped with wheat, soybeans and corn with corn being planted the year the speleothems were sampled (Richard Bell, personal communication). Slow turnover rates of the soil organic material may lead to an averaging of the C_3/C_4 signal because other agricultural crops such as wheat and soybeans are grown one year after the other. This may lead to soil organic matter that is a mixture of all of these carbon sources leading to an intermediate ^{13}C value. At Seneca Caverns, the enriched $\delta^{13}C$ values of the speleothems appear to be related to the influence of soil organic matter that has a C_4 component.

Increased infiltration rates of groundwater can affect the $\delta^{13}C$ values of speleothems. The conclusions of Fantidis and Ehhalt (1970) connecting higher drip rates with enriched $\delta^{13}C$ values may shed light on the values obtained in this study. Infiltrating water will have less time to equilibrate within the soil atmosphere, allowing for an increased proportion of carbon incorporated from the atmosphere ($^{-}8‰$) versus from soil organic matter ($^{-}23‰$). Insufficient residence times due to increased infiltration as a result of high rain fall rates or soil cover that is thin are likely causes for enriched $\delta^{13}C$ values. The temperature and precipitation (Figure 13a through Figure 13c) are consistent with temperate climates. There is no indication of monsoonal or Mediterranean climate patterns that have large swings in rainfall amounts during a particular season and very little in another. Thus, for this research, infiltration rates or residence time issues are not likely a cause of variations seen in the speleothem ^{13}C values.

Surfaces with thin or no vegetation can exhibit enriched $\delta^{13}C$ because of the limited biogenic carbon dioxide. The infiltrating carbon dioxide would have more of an atmospheric component and lower partial pressure. However, this is not the case for the Kentucky study area because these caves are located in old growth forests with at least a minimum of 15 centimeters of soil cover (Figure 3 and Figure 4). The soil thickness at Seneca Caverns, Ohio is also greater than 15 centimeters. At Perry's Cave one soil sample indicated poor soil development. The site had been backfilled in some areas, and stones were encountered at one sample location at a depth less than 15 centimeters.

All of the processes mentioned above can change the overall dynamics between open and closed systems relating to the carbon sources. Generally, it is assumed that open system behavior is normal, hence for this study it will be assumed that open system behavior is obtained (McDermott, 2004). In an open system, the soil carbon dioxide reservoir is essentially infinite and equilibration is continuous with the infiltrating water. This drives the ^{13}C signal of the CO_2 in the infiltrating water to be reflective of the soil atmosphere and not the bedrock (Hendy, 1971). In a closed system, the infiltrating water is no longer constrained by the unlimited carbon dioxide reservoir as in the open system. Hence, the soil carbon dioxide no longer dominates the process because it is consumed early in the formation of carbonic acid. Since the infiltrating water no longer has a constant supply of carbon dioxide from the soil atmosphere, the water is no longer saturated with respect to carbon dioxide. These conditions allow for the dissolution of carbonate bedrock which then influences the isotopic signal of the infiltrating water from which speleothems precipitate from (Hendy, 1971).

Another potential source of ^{13}C enrichment is associated with kinetic fractionation due to degassing in voids prior to deposition, as proposed by Baker et al. (1997). Carbon dioxide degassing drives calcium carbonate precipitation. If prior degassing is occurring, the δ^{13}C of the infiltrating water will become enriched as predicted by Rayleigh distillation. Proximity to the cave entrance can cause an increase in carbon dioxide degassing specifically because the humidity and carbon dioxide will be significantly lower. The reduced partial pressure of the carbon dioxide in the cave atmosphere increases the degassing of carbon dioxide from solution. The increased degassing of carbon dioxide causes disequilibrium in calcium carbonate precipitation due to an increase in the rate of precipitation (Mickler et al., 2004). At the locations sampled in this study, this may be a significant source of variation. The caves in this study have multiple levels with differing sizes. The possibility of voids prior to deposition is high. Thus, the possibility of prior degassing in those voids is high

Kinetic fractionation is also associated with the precipitation of calcium carbonate due to evaporation caused by low cave humidity (Hendy, 1971). The humidity in a cave is less near the entrance which would enrich ^{13}C composition of speleothems in relation to temperate climates. In arid climates, an increase in temperature may cause soil respiration rates to go down due to a lack of water. Over time there will be less vegetation allowing greater bedrock influence if soils are thin enough (Mickler et al., 2006). However, this region is not susceptible to the wet/dry cycling (Figures 13a-13c) typical of the Israeli samples of Bar-Matthews et al.(1996) where speleothem calcium carbonate $\delta^{13}C$ values that varied as much as 5‰ were attributed to fluctuations in rainfall amounts.

CONCLUSION

In this study, speleothem samples overlain by C_3 vegetation demonstrate enriched speleothem calcium carbonate $\delta^{13}C$ values compared with the predicted ranges associated with C_3 vegetation-dominant landscapes. This research demonstrates, at a minimum, that 20% of the speleothem calcium carbonate samples do not fall within the predicted values established for speleothems precipitated under C_3 vegetation. This research compliments the works of several others regarding the use of $\delta^{13}C$ as an indicator of vegetation, and ultimately climate by further illustrating the variability of speleothem $\delta^{13}C$ values even under consistent vegetative conditions.

This study was designed to determine if modern actively growing speleothems can indicate the surface vegetation at the time of their formation by determining soil organic matter and speleothem calcium carbonate $\delta^{13}C$ values. The soils organic matter $\delta^{13}C$ values reflect the parent vegetation faithfully. The speleothem calcium carbonate $\delta^{13}C$ values on the other hand did not faithfully reflect $\delta^{13}C$ what was predicted under C_3 environments. The main cause of the enriched speleothem $\delta^{13}C$ values observed in this study is unclear. Kinetic fractionation and inorganic processes may be contributing 1‰ to 5‰ of the variations seen in these samples, but the degree to which $\delta^{13}C$ analysis can identify the source is limited. At Seneca Caverns, the speleothem samples are influenced by the surface C_4 vegetation that is grown multi-seasonally (row cropped fields). Speleothem $\delta^{13}C$ analysis alone is insufficient as a direct proxy for vegetation, as factors independent of vegetation such as drip rate, soil solution chemistry, and soil pCO_2, are impacting the speleothem $\delta^{13}C$ values in these two regions.

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APPENDIX A

Table 1: Soil sample data from Kentucky

Cave	Sample Number		Date Collected	$\delta^{13}C$ (‰)			Comments
	*						
Crooked Creek Ice Cave (CCIC)	1a	CCIC-1S	6/26/2004	-26.5			Deciduous trees, moderately dense coverage with roughly a 2.5cm molic soil layer. Samples collected the day after carbonate collection due to weather. C_3 plants
	1a			-26.5			
	1b			-26.7			
	1b			-26.7			
CCIC	2a	CCIC-2S	6/26/2004	-27.0	x	-26.6	
	2a			-27.2	σ	0.4	
	2b			-27.1	max	-26.1	
	2b			-27.3	min	-27.3	
CCIC	3a	CCIC-3S	6/26/2004	-26.1			
	3a			-26.2			
	3b			-26.1			
	3b			-26.2			
Hard Baker	4a	HB-1S	6/25/2004	-27.1			Deciduous trees, moderately dense coverage with roughly a 2.5cm molic soil layer. C_3 plants
	4a			-27.1			
	4b			-27.1	x	-26.8	
	4b			-27.0	σ	0.3	
Hard Baker	5a	HB-2S	6/25/2004	-26.4	max	-26.3	
	5a			-26.3	min	-27.1	
	5b			-26.7			
	5b			-26.8			
Pine Hill	9a	PH-1S	6/26/2004	-27.0			Deciduous trees, moderately dense coverage with roughly a 2.5cm molic soil layer. C_3 plants
	9a			-27.1			
	9b			-27.3	x	-26.9	
	9b			-27.4	σ	0.4	
Pine Hill	10a	PH-2S	6/26/2004	-26.6	max	-26.4	
	10a			-26.6	min	-27.4	
	10b			-26.5			
	10b			-26.4			

notes:

*a,b - samples were split and replicated

Table 2: Soil sample data from Ohio

Cave	Sample Number		Date Collected	$\delta^{13}C$ (‰)			Comments
	*						
Perry's Cave	6a	PCPB-01S	8/16/2004	-18.0			Deciduous trees, moderate coverage with 2.5cm organic layer. The area had been renovated, the soil may be backfill.
	6a			-17.8			
	6b			-18.9			
	6b			-19.0			
Perry's Cave	7a	PCPB-02S	8/16/2004	-24.3	x	-23.0	
	7a			-24.3	σ	3.6	
	7b			-24.1	max	-17.8	
	7b			-24.2	min	-26.6	
Perry's Cave	8a	PCPB-03S	8/16/2004	-26.4			
	8a			-26.6			
	8b			-26.4			
	8b			-26.5			
Seneca Caverns	11a	SCOH-01S	8/18/2004	-26.3			Samples were taken from the mowed grass area of the property unless noted otherwise. Agricultural fields surround the lot. Sample from field south of property.
	11a			-26.3			
	11b			-26.4			
	11b			-26.4			
Seneca Caverns	12a	SCOH-02S	8/18/2004	-18.3			
	12a			-17.9	x	-21.2	
	12b			-20.7	σ	3.6	
	12b			-20.4	max	-16.0	
Seneca Caverns	13a	SCOH-03S	8/18/2004	-16.0	min	-26.4	
	13a			-16.5			
	13b			-18.9			
	13b			-18.3			
Seneca Caverns	14a	SCOH-04S	7/8/2005	-21.7			
	14a			-22.0			
	14b			-21.7			
	14b			-21.6			

notes:
*a,b - samples were split and replicated

Table 3: Carbonate sample data from Kentucky

Cave	Sample Number		Date Collected	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	Comments
Crooked Creek Ice Cave (CCIC)	15	CCIC-1	6/26/2004	-8.3	-4.7	Stalactite
	0002	CCIC-B	8/20/2005	1.1	-5.2	Bedrock
Floyd Mullins Cave	16	FMC-1	6/25/2004	-7.5	-4.7	Stalactite
Great Salt Peter Cave	17	GSP-1	6/26/2004	-7.0	-5.5	Flowstone
Hard Baker	18	HBC-01	6/25/2004	-10.1	-5.5	Stalactite off of a flowstone
	19	HBC-02	6/25/2004	-9.3	-5.2	Stalagmite
	20	HBC-03	6/25/2004	-10.8	-5.7	Stalactite soda straw
Pine Hill	25	PH-01	6/26/2004	-4.9	-5.5	Stalagmite
	26	PH-02	6/26/2004	-7.2	-5.4	Flowstone
	27	PH-03	6/26/2004	-8.4	-5.0	Stalactite
	28	PH-04	6/26/2004	-5.9	-5.7	Flowstone
	0003	PH-B	8/20/2005	1.7	-5.8	Bedrock
	33	PH-05	8/20/2005	-7.4	-5.8	Stalactite

Table 4: Carbonate sampling data from Ohio

Cave	Sample Number		Date Collected	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	Comments
Perry's Cave	21	PCPB-01	8/16/2004	-8.1	-6.1	Stalagmite
	22	PCPB-02	8/16/2004	-7.1	-5.9	Stalactite soda straw
	23	PCPB-03	8/16/2004	-8.9	-6.5	Stalactite soda straw
	24	PCPB-04	8/16/2004	-11.3	-6.1	Stalactite soda straw
Seneca Caverns	29	SCOH-01	8/18/2004	-6.4	-6.9	Flowstone ribbon
	30	SCOH-02	8/18/2004	-6.5	-6.7	Stalactite soda straw
	31	SCOH-03	8/18/2004	-4.8	-6.8	Stalactite soda straw
	32	SCOH-04	8/18/2004	-3.0	-7.0	Flowstone
	0001	SCOH-B	7/6/2005	1.0	-5.9	Bedrock

Table 5: Processes influencing soil and speleothem calcium carbonate $\delta^{13}C$ values.

1	Process / mechanisms:	*Changes in $\delta^{13}C$ of atmospheric carbon*		
	Effect:	Negligible effect due to the major proportion of CO_2 is from soil respired carbon dioxide. Changes may be seen over longer time frames.		
	+/- ‰ shift:	Not applicable for this study.	Source(s):	Dorale et.al.,1992
	Potential for this stud	No, this study looks at modern speleothems in modern environments.		
2	Process / mechanisms:	*Changes in C_3 and C_4 vegetation dominance*		
	Effect:	If the C_3 vegetation is encroach and taken over by C_4 plants, the $\delta^{13}C$ values of precipitated speleothems will show a gradual enrichment.		
	+/- ‰ shift:	Speleothem $\delta^{13}C$ values become heavier as C_4 plants take over.	Source(s):	Dorale et.al.,1992; Baker et al.., 1997
	Potential for this stud	Yes, at two sites. One site has agricultural plants growing contiguous to the property; the other has backfilled soil		
3	Process / mechanisms:	*Aridity*		
	Effect:	Enrichment as a result of evaporative effects. Increased values associated with dryer periods		
	+/- ‰ shift:	Up to +5‰ has been demonstrated.	Source(s):	Bar-Matthews et al.., 1997
	Potential for this stud	No, temperature and precipitation for the two locations are temperate regions.		
4	Process / mechanisms:	*Changes in plant productivity (can be related to #3)*		
	Effect:	C^{13} ratios are enriched due to the increased dominance of atmospheric and bedrock CO_2 sources verses soil atmosphere.		
	+/- ‰ shift:	As high as 10‰ demonstrated.	Source(s):	Helstrom et al., 1998; Genty et. al., 2003
	Potential for this stud	No, temperature and precipitation for the two locations have not change significantly.		
5	Process / mechanisms:	*Soil-Water Residence time*		
	Effect:	Enrichment due to soil carbon dioxide/ infiltrating water not equilibrated; infiltrating water with more of an atmospheric carbon component.		
	+/- ‰ shift:	3‰ to 4‰ potentially	Source(s):	Denniston et al., 2000; Fanditis and Ehhaldt, 1970
	Potential for this stud	Not a likely source of variation.		
6	Process / mechanisms:	*Prior degassing of carbon dioxide in voids*		
	Effect:	Enrichment due to prior degassing caused by pCO_2 differences between infiltrating water and the cave atmosphere. If this happens in a void above the speleothem, the resulting infiltrating water is enriched in C^{13}		
	+/- ‰ shift:	As high as +10‰ demonstrated.	Source(s):	Baker et al., 1997; Mickler et. al.,2004
	Potential for this stud	Potentially, given that the sample areas are highly karstified.		
7	Process / mechanisms:	*Changes in drip rates (related to #5)*		
	Effect:	Higher drip rates yielded a more depleted $\delta^{13}C$ values; lower drip rates yielded a more enriched $\delta^{13}C$ values		
	+/- ‰ shift:	3‰ to 4‰ potentially	Source(s):	Fanditis and Ehhaldt, 1970; Tooth and Fairchild, 2003
	Potential for this stud	Potentially, depending on the extent of karst features above the cave and the hydrological flow path.		
8	Process / mechanisms:	*Open verses Closed system behavior*		
	Effect:	Open system behavior assumes an unlimited soil CO_2 source driving the ^{13}C signal to be reflective of the soil atmosphere. In a closed system, soil atmosphere is no longer as dominate and the bedrock and atmosphere ^{13}C signals are more		
	+/- ‰ shift:	As much as +/- 3‰	Source(s):	Hendy, 1971; McDermott, 2004; Salomon and Mook, 1986
	Potential for this stud	In this study, it is assumed that open system behavior is taking place.		

APPENDIX B

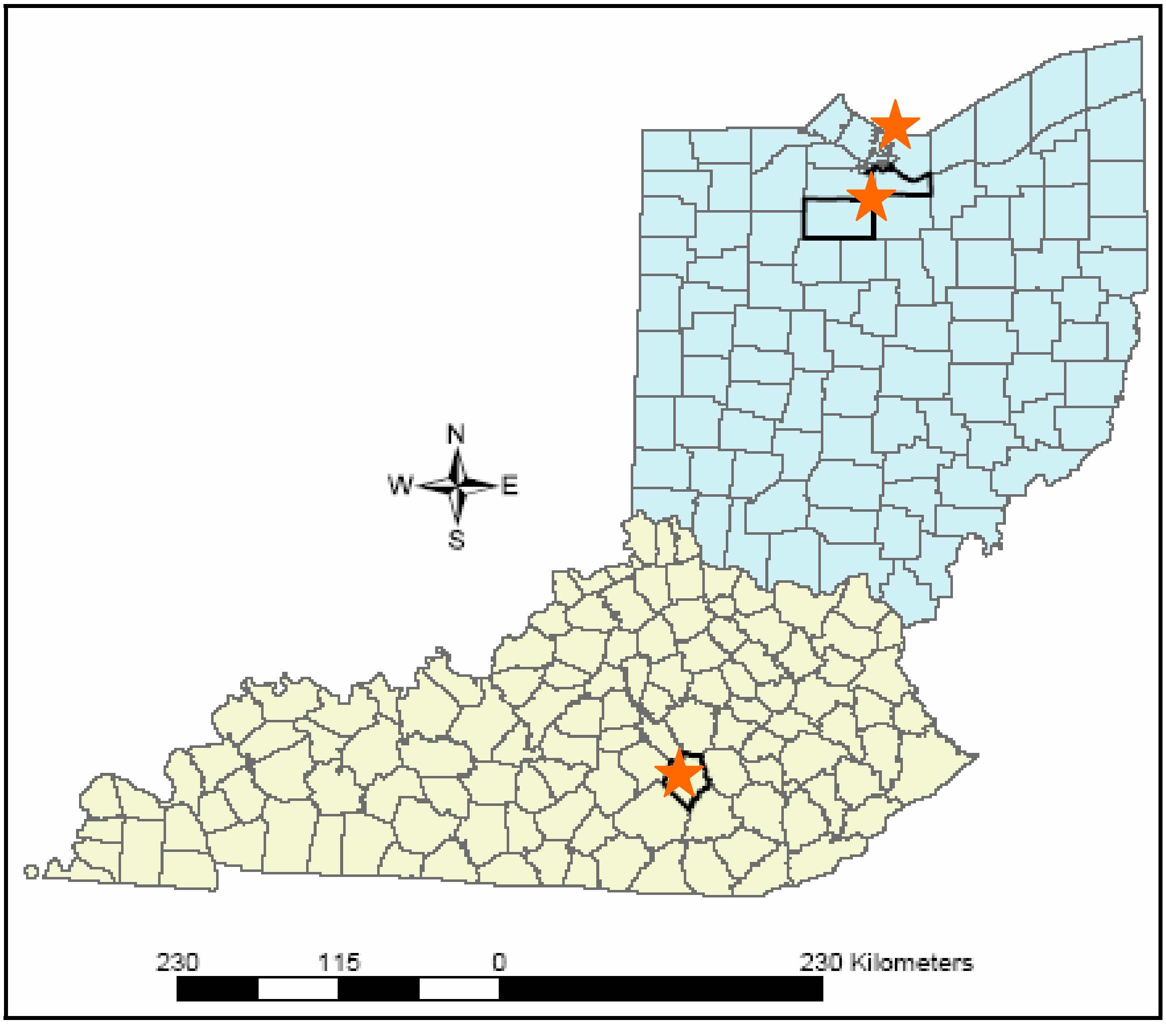

Figure 1: Study area map. Caves are located in the outlined counties.

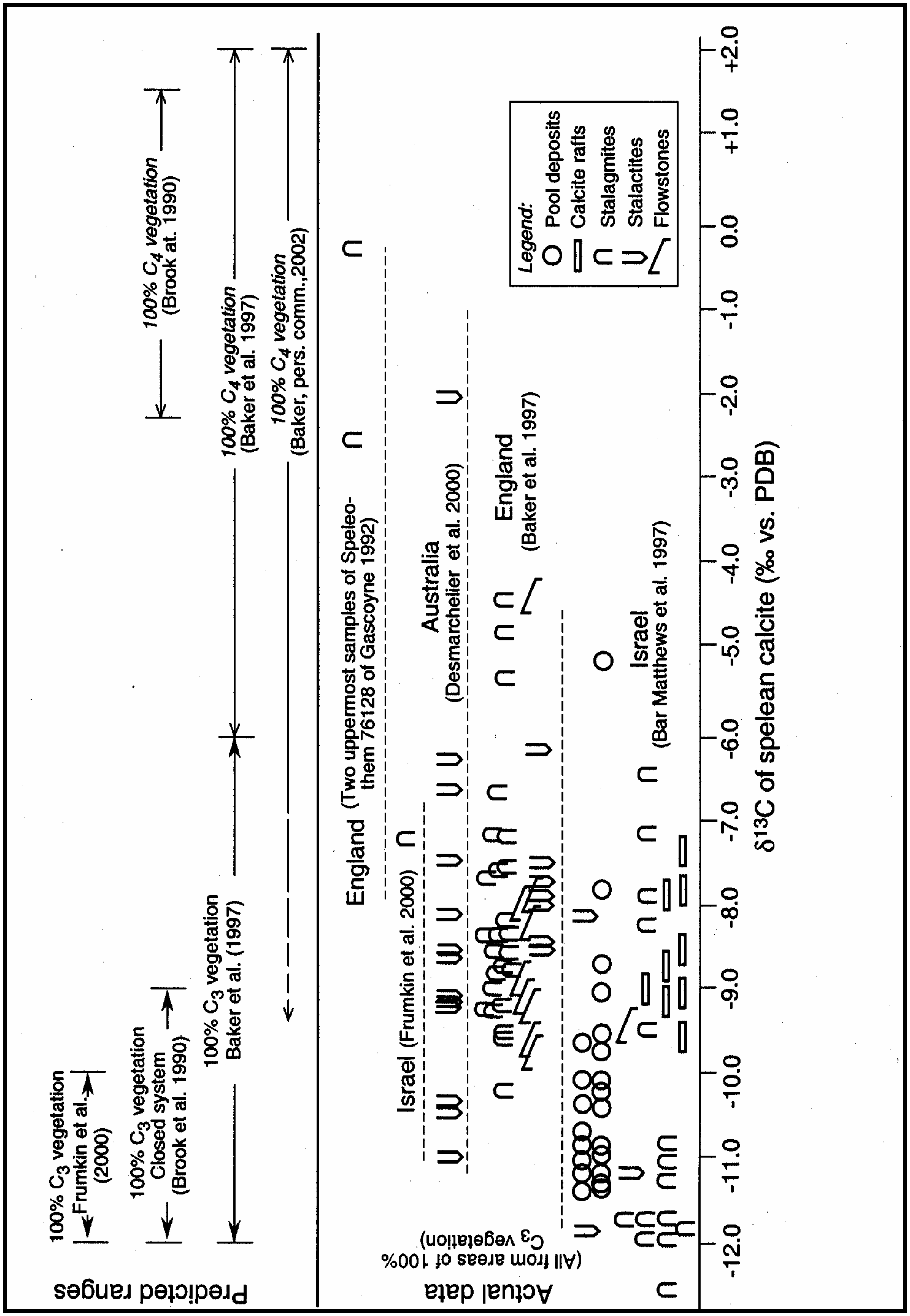

Figure 2: Predicted verses actual speleothem calcium carbonate $\delta^{13}C$ values under C_3 vegetation (Elkins, 2002 - reprinted with permission)

Figure 3: Vegetation above Crooked Creek Ice Cave, Kentucky

Figure 4: Vegetation above Pine Hill Cave, Kentucky

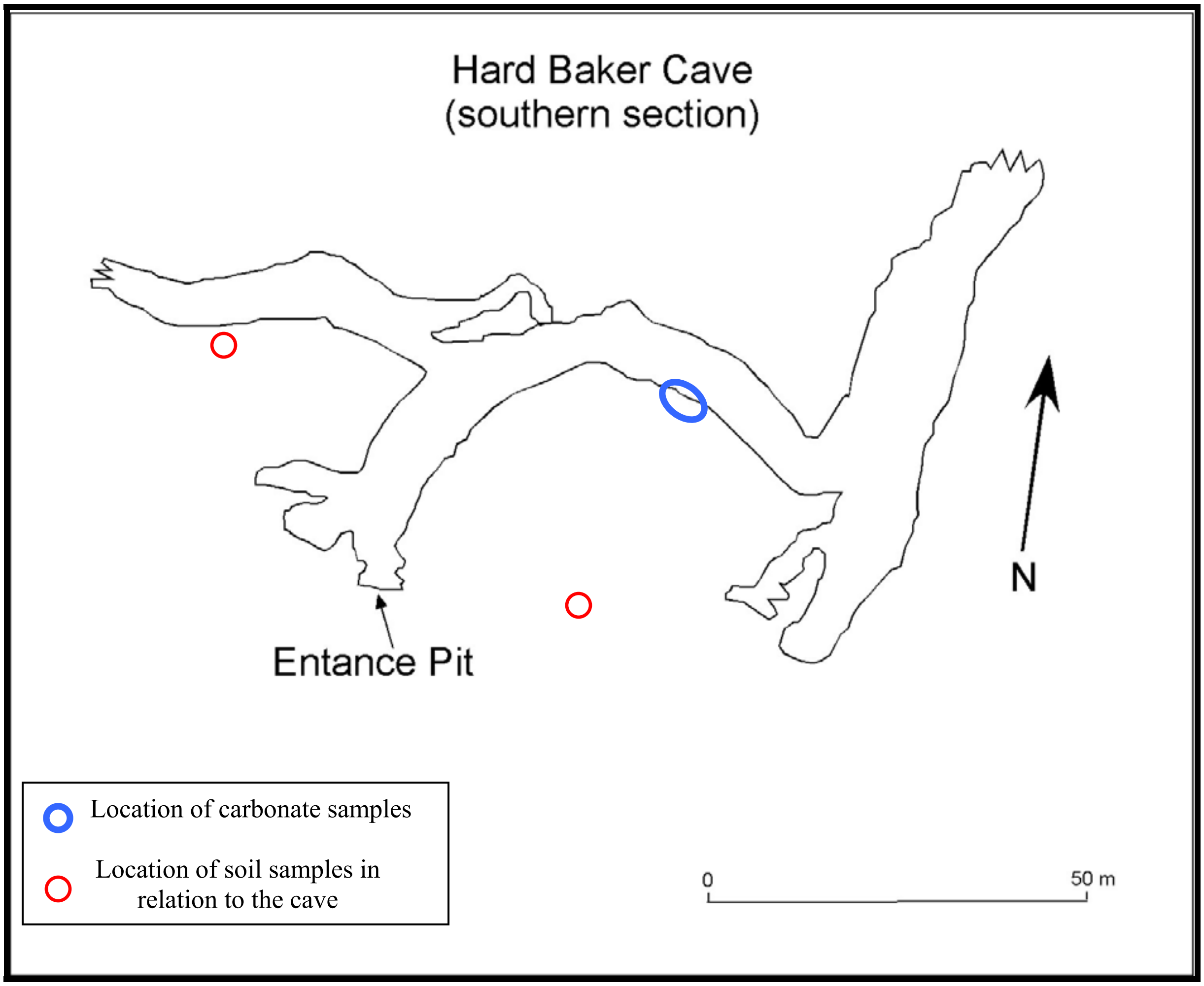

Figure 5: Map of Hard Baker Cave, Kentucky (Karst-O-Rama Guidebook, 2004)

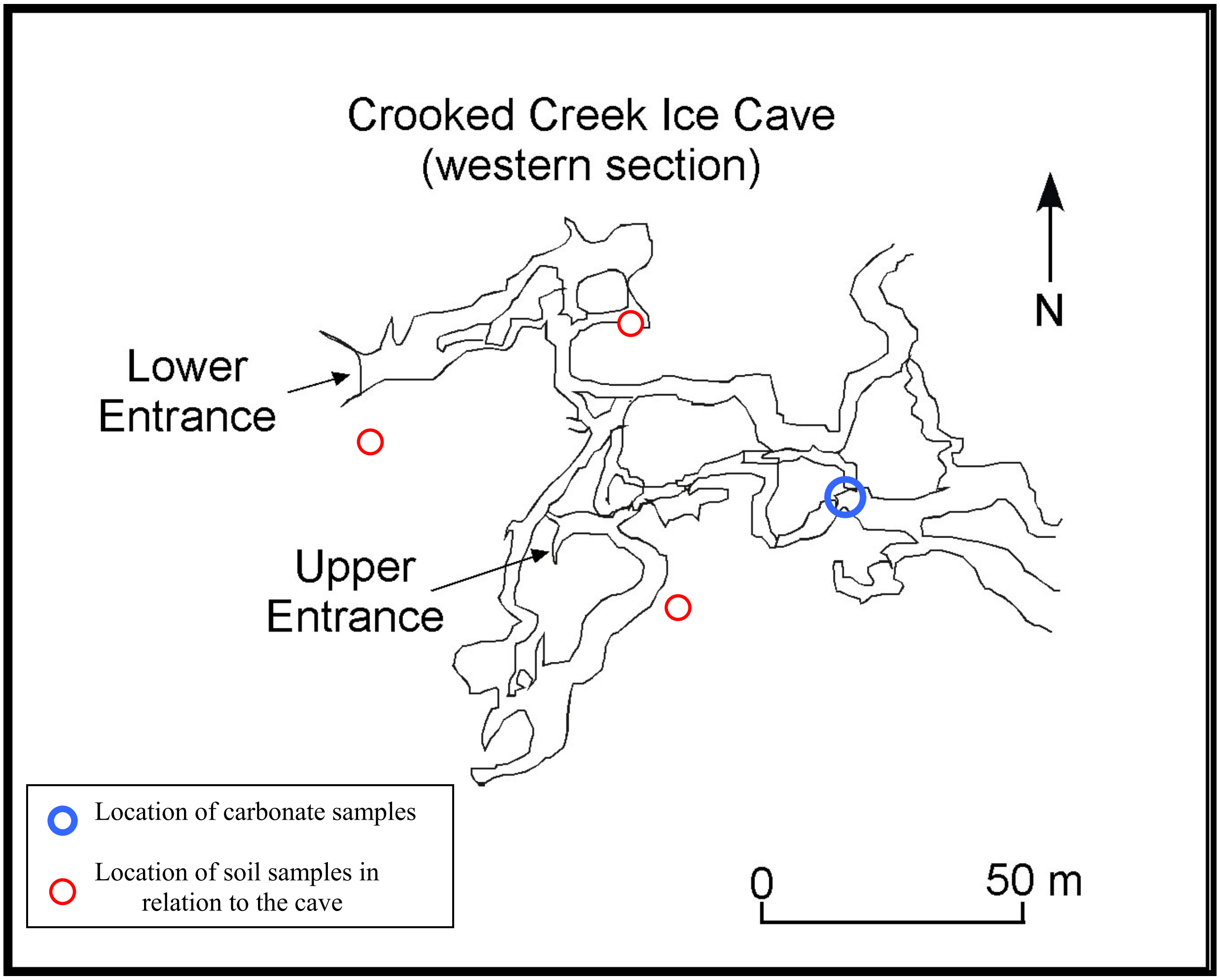

Figure 6: Map of Crooked Creek Ice Cave, Kentucky (Karst-O-Rama Guidebook, 2004)

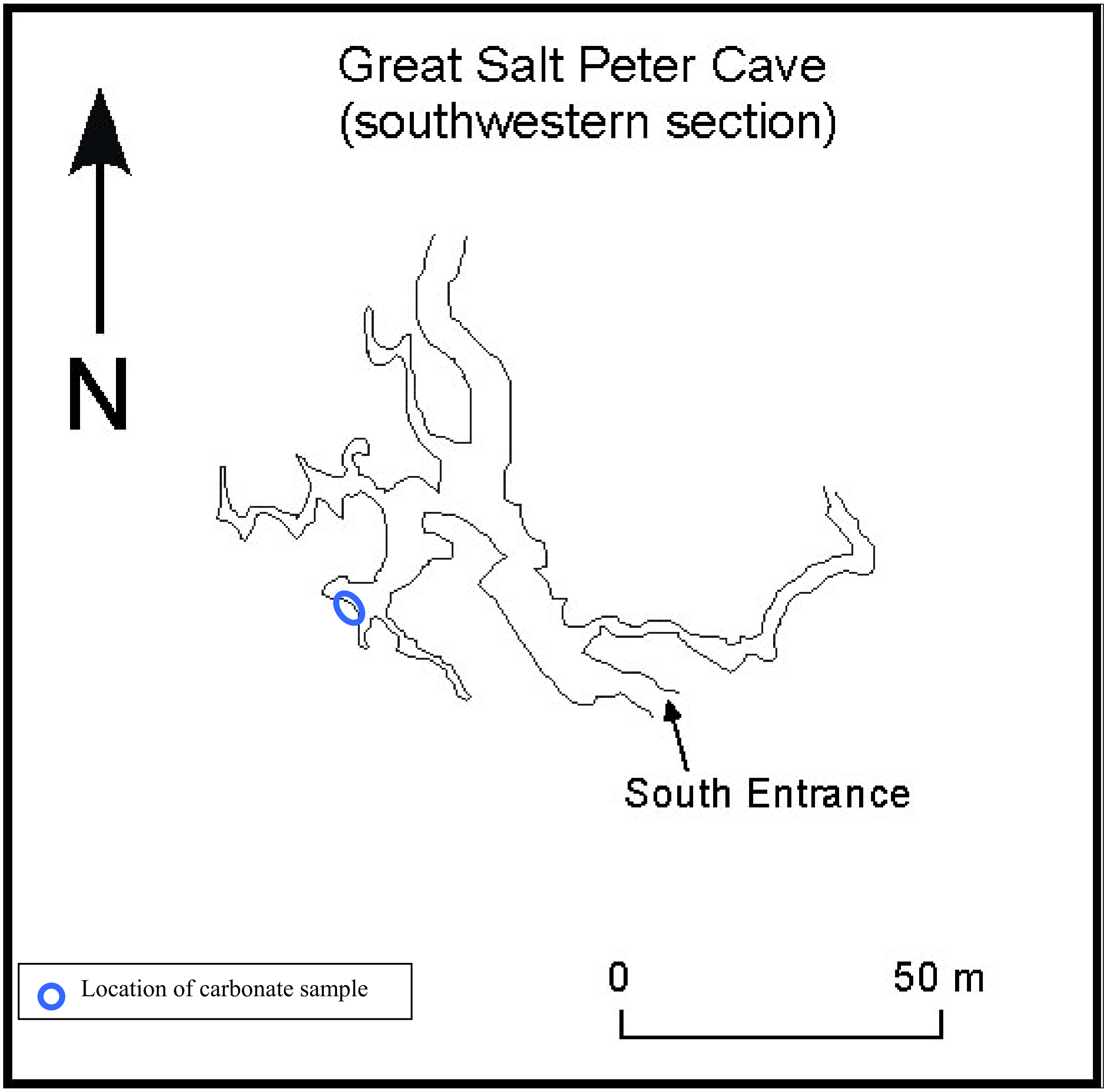

Figure 7: Map of Great Salt Peter Cave, Kentucky (Karst-O-Rama Guidebook, 2004)

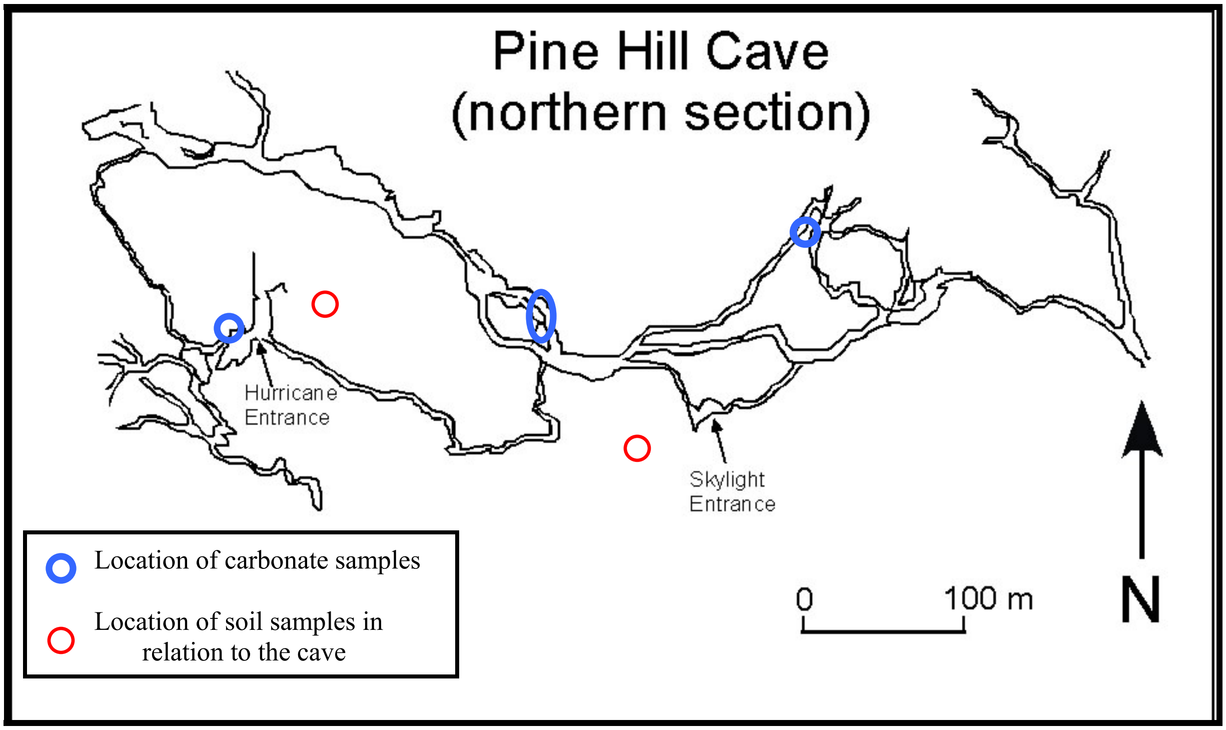

Figure 8: Map of Pine Hill Cave, Kentucky (Karst-O-Rama Guidebook, 2004)

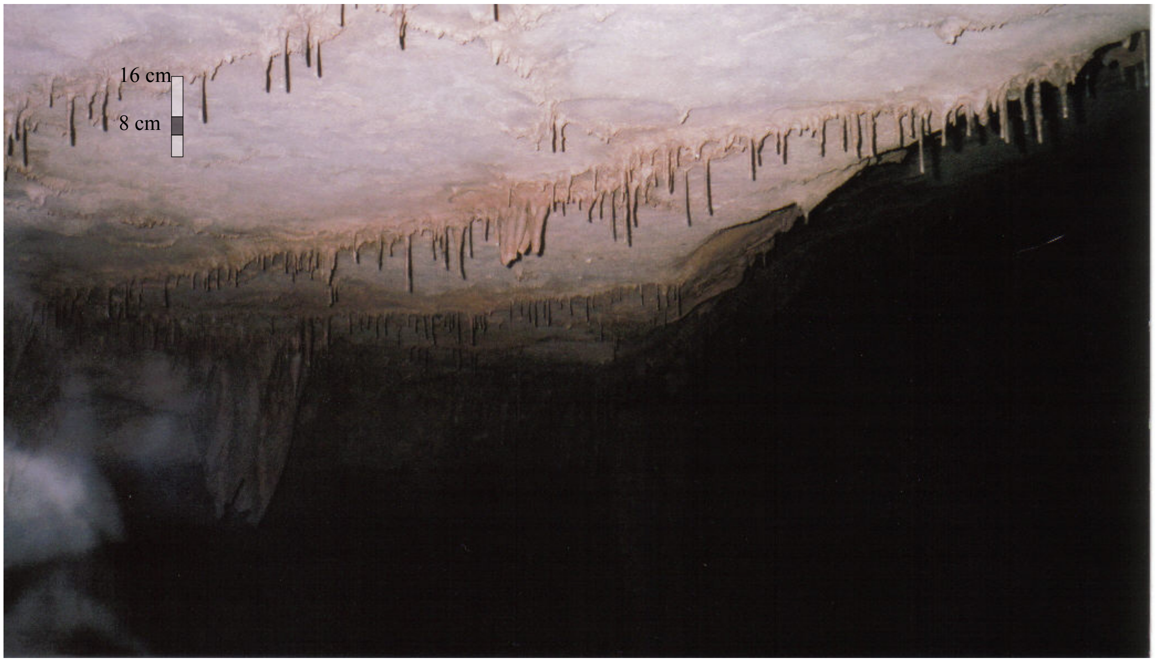

Figure 9: Soda Straw Stalactites in Pine Hill Cave, Kentucky

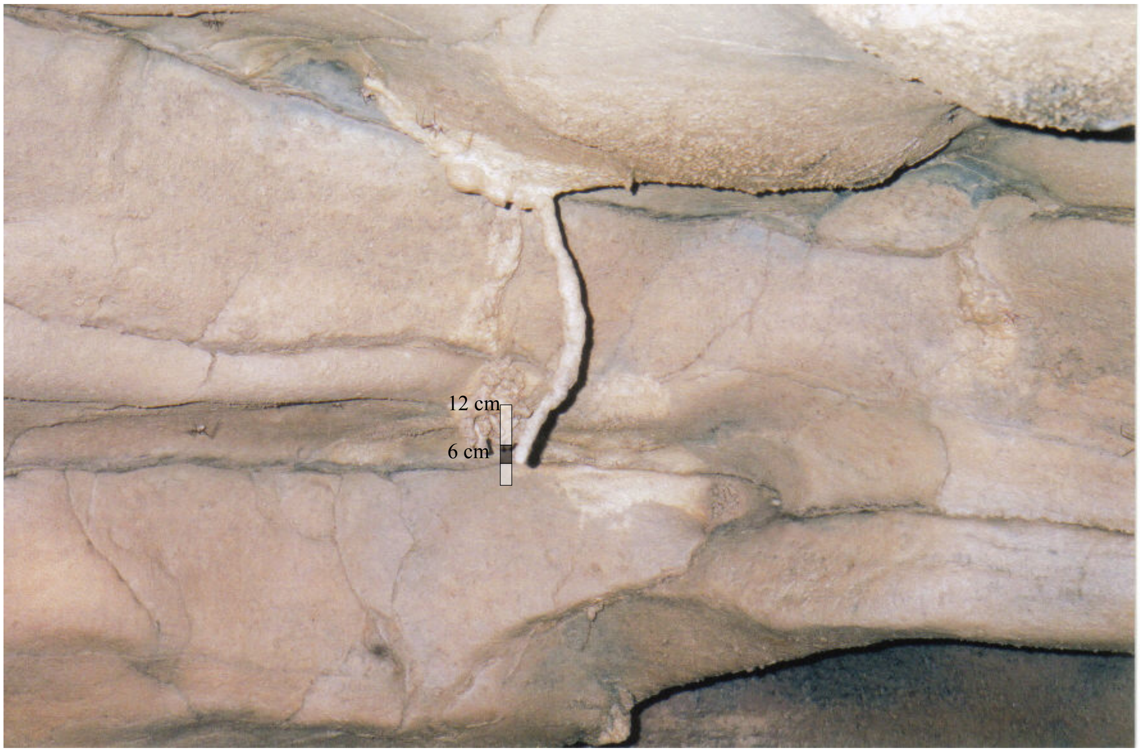

Figure 10: Stalactite off of a flowstone in Hard Baker Cave, Kentucky

Figure 11: Stalactites in Seneca Caverns, Ohio

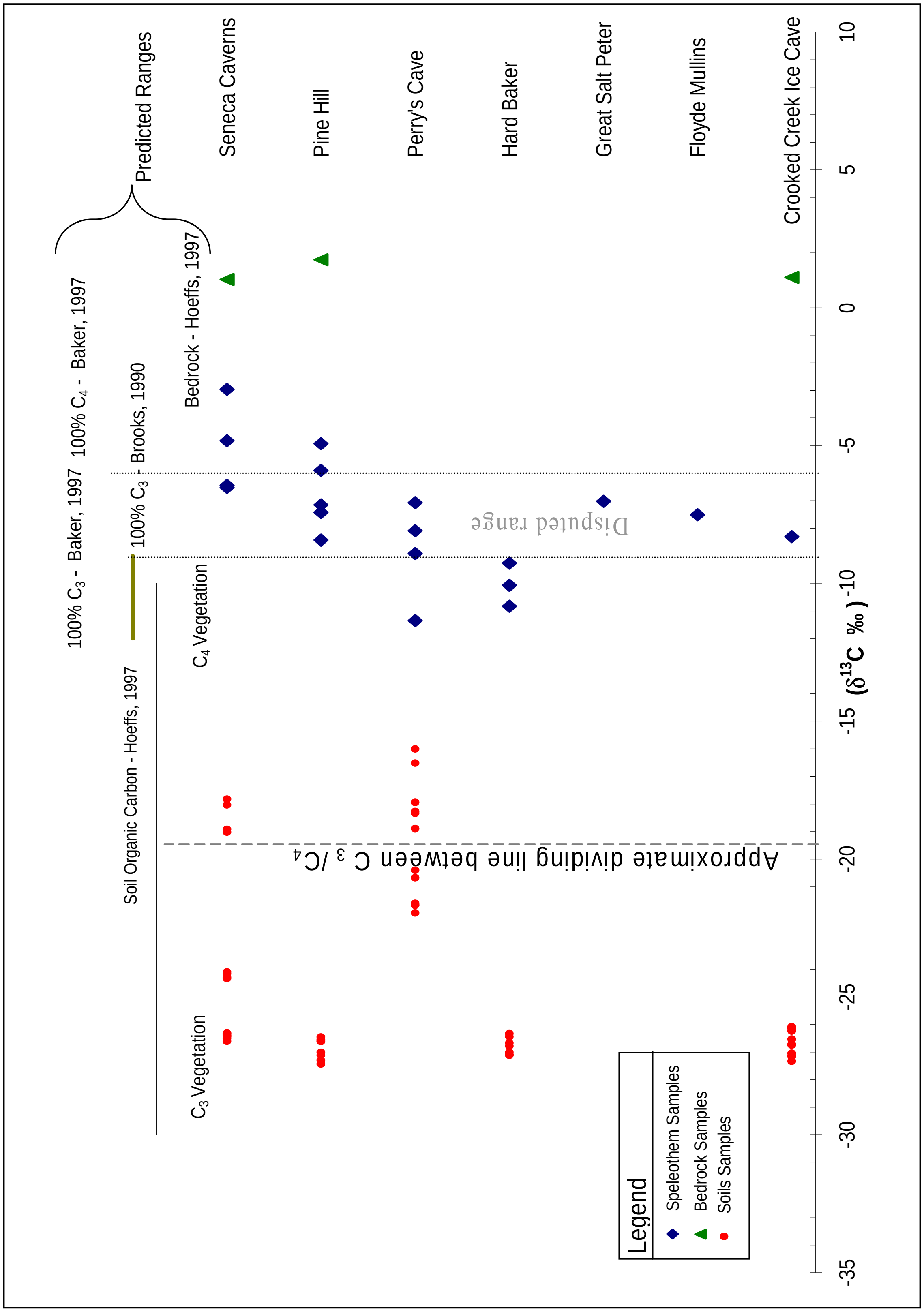

Figure 12: Soil, speleothem, and bedrock $\delta^{13}C$ isotopic values associated with caves located in Kentucky and Ohio.

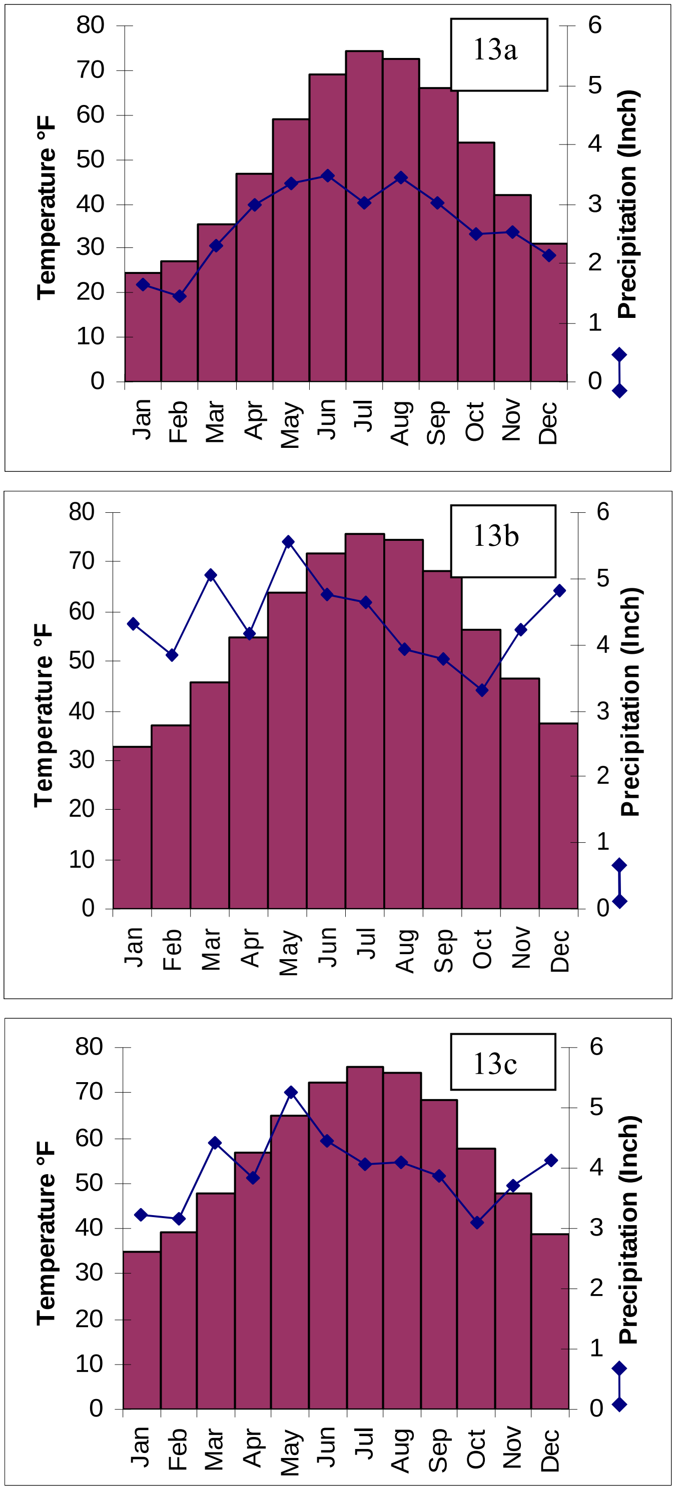

Figure 13a-c: Precipitation and Temperature graphs of Mt. Vernon, Rockcastle County Kentucky(a), Put-In-Bay, Erie County Ohio (b) and Fremont, Sandusky County Ohio (c) (NCDC, 2005)