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Juxtaposed Permian and Pleistocene isotopic archives: Surficial environments recorded in calcite and goethite from the Wichita Mountains, Oklahoma

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ABSTRACT

A paleokarst fill deposit from the Wichita Mountains, south-central Oklahoma, United States, consists primarily of sparry calcite, Fe-sulfides, and goethite. Previous cement-stratigraphic studies and paleontological finds suggest that calcite mineralization was initiated during Permian time, whereas goethite and other oxides apparently formed from oxidation of preexisting Fe-sulfides during Pleistocene time. Therefore, these deposits have the potential to offer insight into surficial hydrology and paleoenvironment in an upland setting from two time periods at a single site.

$\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{SMOW}}$ measurements of 17 samples from growth bands in a single karst-fill calcite crystal range from -10.7‰ to -6.6‰ (mean = -8.6‰) and 27.1‰ to 28.3‰ (mean = 28‰), respectively. Large oscillations in the $\delta^{13}\text{C}$ values through the growth series may originate from seasonal changes in the magnitude of biological productivity during Permian time. These $\delta^{13}\text{C}$ oscillations contrast with the relative stability of the $\delta^{18}\text{O}$ values, which are more positive than would be expected for isotopic equilibrium with local modern waters. The $\delta^{18}\text{O}$ values of the calcite may reflect the $\delta^{18}\text{O}$ values of ambient meteoric groundwaters in the Permian that were isotopically similar to waters in modern, seasonally dry, low-latitude coastal regions.

Goethites are not in equilibrium with modern waters or coexisting calcites in the fissure-fill deposit as determined from $\delta^{18}\text{O}$ and δD values of the goethites. Furthermore, the combined $\delta^{18}\text{O}$ and δD values of the goethites are indicative of formation from meteoric waters at a temperature of $\sim 9\text{ °C} \pm 3\text{ °C}$. This inferred temperature is $7\text{ °C} \pm 3\text{ °C}$ cooler than local modern mean annual temperature and corresponds well with independent studies that propose temperatures $\sim 6\text{ °C}$ cooler in this region during Pleistocene time.

The mole fraction and $\delta^{13}\text{C}$ values of the $\text{Fe}(\text{CO}_3)\text{OH}$ component in solid solution in the goethite sample are 0.0103 and -10.1‰ , respectively. In combination, these values suggest that goethite formed in an environment characterized by mixing of three isotopically distinct CO_2 components: (1) oxidized biological carbon, (2) atmospheric CO_2 , and (3) CO_2 from dissolution of carbonate in the karst system. Oxidized biological carbon may have originated either from flora characterized by C3 or mixed C3:C4 photosynthesizers. Mass balance calculations between these three CO_2 end members correspond to an inferred soil CO_2 concentration [CO_2 contributed from (1) and (2) above] ranging from $\sim 8,000\text{ ppmV}$ to $\sim 16,000\text{ ppmV}$ for a local ecosystem dominated by C₃ flora. This inferred range of soil CO_2 concentrations is typical of grasslands characterized by relatively high biological productivity. If C4 flora were a significant

source of oxidizing carbon, the higher calculated ambient CO₂ concentration at the time of goethite crystallization in the cave (~20,000 ppmV) might be interpreted to correspond to an unusually productive C4 soil present at a time of generally cooler and drier conditions across the southern Great Plains of North America.

Keywords: Permian; Pleistocene; P_{CO₂}; oxygen, hydrogen and carbon isotopes, paleoclimate.

INTRODUCTION

The relationship between oxygen and hydrogen isotopes in meteoric waters [the Meteoric Water Line (MWL) of Craig, 1961] has served as a basis for using single-mineral geothermometers in hydroxyl minerals to deduce paleotemperatures (Savin and Epstein, 1970; Yapp, 1987, 1993, 2000; Delgado and Reyes, 1996; Tabor et al., 2004a). Furthermore, isotopic analyses of secondary alteration minerals preserved in nearly continuous stratigraphic successions have been used to infer regional Cretaceous and Late Paleozoic paleoatmospheric circulation patterns (Ludvigson, 1998; Tabor and Montañez, 2002) and to monitor the long-term effects (10⁶ to 10⁸ m.y.) of tectonic uplift (Poage and Chamberlain, 2001) and continental drift (e.g., Bird and Chivas, 1988; Lawrence and Rashkes-Meaux, 1993; Gilg, 2000). In the current study, we present data from juxtaposed Permian and Pleistocene minerals that contain isotopic records of contrasting surficial environments.

The area is centered around the Wichita Mountains of south-central Oklahoma and consists of karsted Ordovician limestones that have been upland (or piedmont) terrain since early Permian time (Donovan et al., 2001). The Ordovician karst hosts two temporally distinct groups of secondary minerals: (1) early Permian calcite and Fe-sulfide and (2) Pleistocene Fe (III) oxides (hydroxides) formed by oxidative dissolution of preexisting sulfides. Hydrogen-, oxygen-, and carbon-isotope analyses of calcites and goethites from a cave-fill deposit in the Wichita Mountains, south-central Oklahoma, United States, are discussed in terms of their implications for ambient Pleistocene and Permian paleoenvironments.

BACKGROUND

The Wichita Mountains region of southern Oklahoma appears to be part of a failed ancient continental rift (aulacogen; Donovan, 1986). Initial heat flux and lithospheric expansion in this region with attendant intrusive igneous activity probably began in late Precambrian–Cambrian time, followed by lithospheric cooling, basin subsidence, and deposition of thousands of meters of carbonate and siliciclastic strata during the Late Cambrian, Ordovician, and Carboniferous (Donovan, 1986). A transpressive-stress regime, related to the assembly of Pangea in the late Carboniferous and early Permian, created several asymmetric basins and uplifts before the aulacogen stabilized and tectonic quiescence ensued in middle Permian time. These uplifts include the Wichita and Arbuckle Mountain chains.

Displacement along the Meers and Mountain View faults, bounding the northern edge of the eastern Wichita Mountains, exhumed and exposed Ordovician-age marine carbonate strata to surficial terrestrial weathering during Late Pennsylvanian and early Permian time. Physical weathering of the Ordovician deposits resulted in fluvial deposition of the Post-Oak Conglomerate, whereas chemical weathering resulted in widespread karstification, as indicated by numerous and small, back-filled cave systems (Donovan et al., 2001). Both the Post-Oak Conglomerate and cave systems are found in the Slick Hills region of southwestern Oklahoma (Fig. 1).

Back-filling of the cave systems in this karsted terrain owes its origins to surface-tied hydrology indicative of a shallow burial history (Donovan et al., 2001). In addition, late Paleozoic vertebrate fossils preserved within authigenic sulfide-bearing calcareous rocks in the fissure-fill deposits indicate a Permian (Leonardian to ~Artinskian) age for these fissure-fill deposits (Olson, 1967). Subsequent erosion of a thin sedimentary overburden in Pleistocene time led to oxidation of Fe-sulfides, dissolution of carbonate, and crystallization of secondary Fe (III) oxides and oxyhydroxides (Donovan et al., 2001; 2003, personal commun.).

METHODS

The karst-fill deposit in this study is exposed along Highway 58, in Blue-Creek Canyon, in Ordovician-age marine limestones of the upper Arbuckle Group. The karst deposit is vertically oriented, with a height of ~6 m and a width of as much as 1 m (Fig. 2A). Internally, the fissure-fill deposit is characterized by two lithologies: (1) a 5–25-cm-thick red-to-brown iron-oxide-rich layer that lines the contact with the karsted Ordovician limestone and (2) sparry calcite veins and “pockets” that range from 10 cm to 35 cm thick (Fig. 2B).

Fissure-Fill Calcite and Ordovician Limestone

A sparry calcite crystal from the fissure fill and a sample of the Ordovician limestone that hosts the fissure fill deposits were sectioned and polished (Fig. 3). Samples from a number of different “growth bands” in the fissure-fill calcite were taken directly from the polished slab using a cleaned hand-held metal probe. The Ordovician limestone was sampled using a hand-held dental drill with faceted burr and 100 μm bit. Approximately 50 μg of carbonate powder were roasted at 375 °C in vacuum for three hours to remove organics. Carbonate samples were then reacted

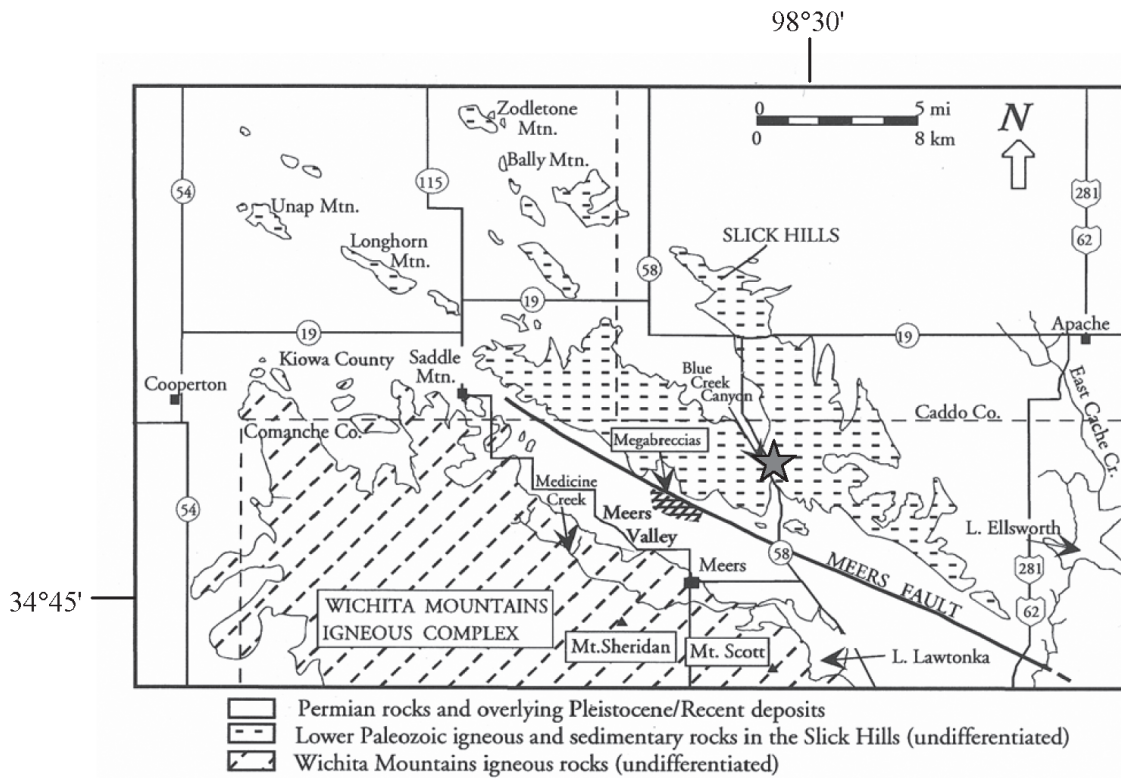


Figure 1. Regional map of south-central Oklahoma (after Donovan et al., 2001). The area denoted by the arrow is the general vicinity of the cave-fill deposit that is the focus of this study.



Figure 2. (A) Outcrop photograph of the cave-fill deposit. Dan Chaney (~155 cm tall) for scale. (B) Close-up photograph showing the Fe-oxide (orange) and calcite dominated (white) areas of the cave-fill deposit. Hammer for scale. See text for discussion of features.

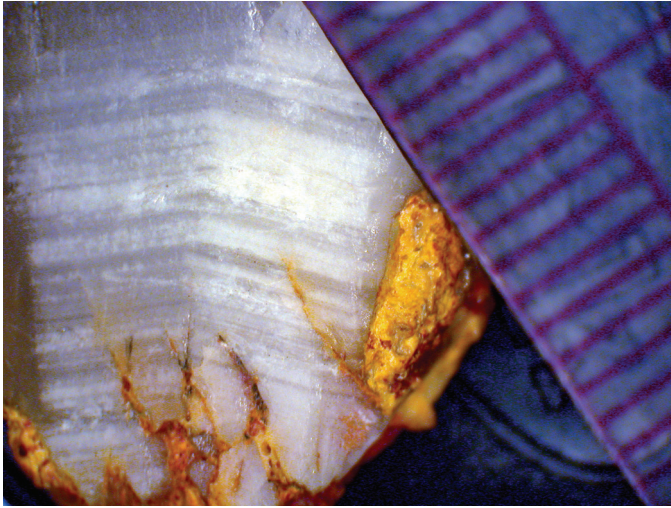


Figure 3. Reflected-light photomicrograph of a sparry calcite sample from the cave-fill deposit. Light-colored bands have a high concentration of fluid inclusions, whereas darker-colored bands do not contain fluid inclusions. Note the occurrence of Fe-oxide coatings on the exterior of the sample and dissolution pitting near the base of the photograph. Demarcations on ruler are 1 mm apart. See text for discussion.

at 90 °C with 100% H_3PO_4 to produce CO_2 . $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses of CO_2 evolved from all calcite samples were carried out on a Fisons-Optima IR gas source mass spectrometer in the Department of Geology at the University of California, Davis.

In this work, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and δD values of CO_2 and H_2 derived from carbonates and goethites are given relative to the Pee Dee belemnite (PDB) standard for carbon (Craig 1957) and the Vienna standard mean ocean water (V-SMOW) standard for hydrogen and oxygen isotopes (Gonfiantini 1984), where

$$\delta^{13}\text{C}, \delta^{18}\text{O}, \delta\text{D} = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000\text{‰} \quad (1)$$

and $R = {}^{13}\text{C}/{}^{12}\text{C}$, ${}^{18}\text{O}/{}^{16}\text{O}$, D/H , respectively. Based on 19 measurements of NBS-19 over the period of analysis, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements of CO_2 evolved from calcite are $\pm 0.1\text{‰}$ and $\pm 0.2\text{‰}$, respectively.

Iron Oxides

After collection from the karst-fill deposit, two iron-oxide-rich samples, labeled OKCave and OKCaveM, were transported to the laboratory wrapped in aluminum foil. The iron-oxide samples were prepared for isotopic analysis using the methods of Yapp (1998). Samples were ground in an aluminum oxide mortar and pestle under reagent-grade acetone and sized by passage through a 63 μm brass sieve. Only powders from the <63 μm particle size fraction were used in this study. Powdered samples were treated overnight with ~40 mL of 0.5N HCl solution to remove admixed carbonates and then rinsed with successive aliquots of deionized H_2O until the pH of the rinse water was equivalent to the initial

pH of the deionized H_2O . Each sample was subsequently treated over a period of 28–35 days with successive 40 mL aliquots of 30% H_2O_2 at room temperature in order to promote oxidation of any admixed organic matter that may have been present within the samples. As the reactivity of the solution diminished and the suspended particles settled, the solution was decanted and replaced by a fresh aliquot of H_2O_2 . After 12–14 H_2O_2 treatments, samples were dried in a vacuum desiccator at room temperature. In this paper, samples subjected only to the foregoing treatments are designated bulk samples.

Mineralogy was determined by X-ray diffraction (XRD) analysis of powdered samples using $\text{Cu-K}\alpha$ radiation on a Diano 8500 X-ray diffractometer in the Department of Land, Air and Water Resources at the University of California, Davis. Powders were backmounted into an aluminum holder and step-scanned from 2 to 70° 2θ with 0.01° steps, a dwell time of 12 s, 40 kV, and 20 mA, 1° divergence and scatter slits, and a 0.2 mm receiving slit. The amount of Al substituted for Fe in goethite was determined by the XRD method of Schulze (1984). This XRD-based calculation for Al^{3+} substitution has an analytical uncertainty of ± 3 mol%.

Chemical Analysis

For chemical analyses, bulk samples of OKCave and OKCaveM were combined with lithium tetraborate to produce a 2:1 mixture on a mass basis. These mixtures were fused in graphite crucibles at temperatures of 1000 °C for one hour and then quenched in deionized water to produce a glass that was subsequently ground to <63 μm . For each sample, ~125 mg of fused glass was sealed in 15 mL Teflon bombs with 10 mL of concentrated HNO_3 and left on a hot plate at 100 °C until all of the solids dissolved. Dissolution of the samples occurred within 2 days. Each 10 mL aliquot was then transferred to 100 mL volumetric flasks, and the solution was diluted to 2%–3% HNO_3 . Chemical analyses of the dilute solutions of HNO_3^+ sample were performed on an inductively coupled plasma–optical emission spectroscopy (ICP-OES) at the DANR Analytical Facility at the University of California, Davis. The relative analytical error of these analyses is no greater than $\pm 2\%$ of the reported value for the oxide component.

In order to assess the isotopic composition of non-iron oxide constituents within the samples, ~200 mg aliquots of bulk samples were subjected to citrate-bicarbonate-dithionite (CBD) digestion solutions to remove iron oxides (Jackson, 1979). The remaining residue was then washed with five to eight successive 50 mL aliquots of deionized H_2O and subsequently treated with three to four successive 40 mL aliquots of 30% H_2O_2 in order to facilitate oxidation of any additional organics that may have become accessible as a result of CBD treatment. After H_2O_2 treatment, the residues were dried at room temperature in a vacuum desiccator. In this paper, these non-iron oxide constituents are designated “residue” samples.

Structural oxygen was extracted from the bulk and residue samples and quantitatively converted to CO_2 with BrF_5 in the

TABLE 1A. DATA FROM INCREMENTAL DEHYDRATION OF OKCAVEMICRO

Time (min)	T (°C)	H ₂ yield (μmol)	CO ₂		X _v (H ₂)	F
			Yield (μmol)	δ ¹³ C		
Initial goethite mass = 305.0mg						
30*	210	468	5.2	-12.9	0.27	0.0111
30	210	746	7.3	-10.1	0.69	0.0098
30	210	200	2.4	-10.0	0.80	0.0120
30	210	63	1.0	-11.6	0.84	0.0159
108	210	41	0.5	-22.1	0.86	0.0122
30*	850	247	10.2	-16.9	1.00	0.0413

*Closed system dehydration in ~0.16 bar of O₂. All other increments open system in vacuum.

TABLE 1B. PLATEAU VALUES FOR OKCAVEMICRO

F	X _m *	1/X _m	δ ¹³ C
0.0103	0.0052	192	-10.1‰

*X = 0.5F for plateau values and X = the mol fraction of Fe(CO₃)OH.

Department of Geological Sciences at the Southern Methodist University using the procedure of Clayton and Mayeda (1963). The oxygen-isotope composition of the resultant CO₂ was measured on a Finnigan MAT 252 isotope ratio mass spectrometer in the Department of Geological Sciences at the Southern Methodist University.

For D/H (deuterium/hydrogen; H²/H¹) analysis, samples were initially outgassed under vacuum at ~120 °C for ~10 h to remove adsorbed water. Mineral-bound hydrogen for δD analysis was extracted as H₂O by heating the samples to ~1100 °C under vacuum in closed-system conditions. The liberated structural water was then converted to H₂ by passage over hot (~750 °C) U-metal (Bigeleisen, 1952) at the Southern Methodist University. The hydrogen yield was determined manometrically, and the δD values of evolved gases were measured with a Finnigan MAT 252 at the Southern Methodist University. Based on the range of values for a single sample, the reported δD values have an analytical uncertainty of about ±3‰.

Ferric Carbonate Analysis

Abundance and δ¹³C values for the iron (III) carbonate (Fe(CO₃)OH) component in solid solution in goethite were measured at the Department of Geological Sciences at the Southern Methodist University on samples treated with 0.5N HCl, followed by deionized H₂O, then 30% H₂O₂, using the published incremental dehydration-decarbonation methods of Yapp and Poths (1991, 1993). The detailed results for each incremental dehydration-decarbonation procedure are given in Table 1. The CO₂ and H₂O collected at each step were separated cryogenically. The evolved water was quantitatively converted to H₂ over U-metal at ~750 °C. Yields of H₂ were measured manometrically with a precision of about ±1 μmol. For CO₂, differences in yield of ~0.1 μmol could be resolved. Amounts of CO₂ as low as 0.1 μmol can be evolved from the Fe(CO₃)OH in a single step during incremental dehydration-decarbonation. Samples of evolved CO₂ were analyzed for δ¹³C values on a Finnigan MAT 252 mass spectrometer at the Southern Methodist University. The analytical uncertainty of the δ¹³C value of Fe(CO₃)OH is about ±0.2‰ (Yapp and Poths, 1993).

RESULTS

Calcite-Rich Fissure Fill

Calcite-spar crystals from the fissure-fill deposit exhibit drusy crystal morphologies (Fig. 3) with ~1-mm-thick laminations of alternating clear and cloudy bands oblique to the crystallographic c-axis. The layers with a cloudy appearance are a result of relatively high concentrations of fluid inclusions. The exterior of this sample, which was taken from the interface between the oxide-rich and calcite-rich parts of the fissure-fill deposit, exhibits dissolution pitting and microkarst fabrics (Fig. 3). In addition, a number of flowstone and stalactite samples from the fissure-fill deposits also locally contain laminations with abundant sulfide minerals intercalated with calcite (Fig. 4).

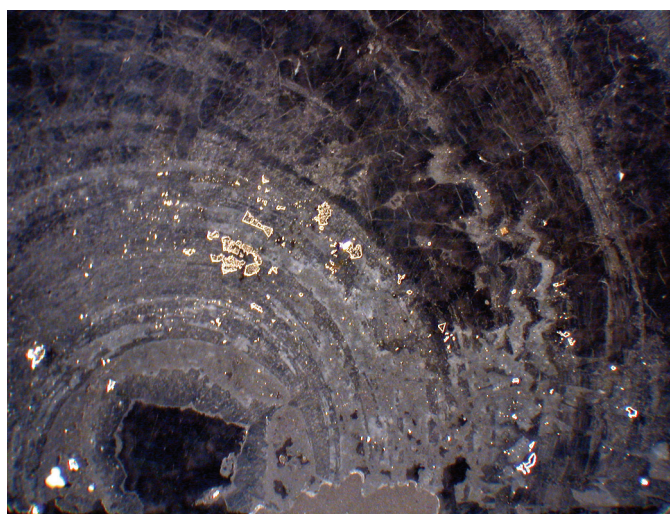


Figure 4. Reflected light photomicrograph of a speleothem from a cave-fill deposit. The speleothem is primarily composed of calcite with subordinate Fe-sulfides (white areas). The long field of view in this figure is 1cm. See text for discussion.

The measured carbon- and oxygen-isotope compositions from a series of cloudy and clear growth bands in the calcite-spar crystal (Fig. 3) are presented in Table 2 and Figure 5. Oxygen-isotope compositions exhibit fairly uniform and positive $\delta^{18}\text{O}_{\text{SMOW}}$ values ranging from 27.1‰ to 28.3‰ ($\delta^{18}\text{O}_{\text{PDB}} = -3.7\text{‰}$ to -2.5‰ , $n = 17$), with a mean isotopic composition of 28.0‰ ($\delta^{18}\text{O}_{\text{PDB}} = -2.8\text{‰} \pm 0.3\text{‰}$, 1s) (Table 2 and Fig. 5). $\delta^{13}\text{C}_{\text{PDB}}$ values are more variable, ranging from -6.6‰ to -10.7‰ , with a mean isotopic composition of $-8.6\text{‰} \pm 1.5\text{‰}$ (1s, $n = 17$). The $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{PDB}}$ values of Ordovician marine limestone associated with the karst are $1.5 \pm 0.1\text{‰}$ and $-1.2 \pm 0.2\text{‰}$ ($n = 2$), respectively.

TABLE 2. CARBON AND OXYGEN ISOTOPE COMPOSITIONS FOR A CALCITE-SPAR CRYSTAL FROM THE FISSURE FILL DEPOSIT

Growth Band #	$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{SMOW}}$
1	-6.6	-3.7	27.1
2	-10.1	-2.7	28.1
3	-10.1	-2.8	28.0
4	-9.1	-2.9	27.9
5	-7.4	-2.7	28.1
6	-6.9	-2.6	28.2
7	-9.0	-3.1	27.7
8	-9.3	-2.7	28.1
9	-9.4	-2.8	28.0
10	-10.7	-2.6	28.2
11	-8.9	-2.7	28.1
12	-7.5	-2.5	28.3
13	-6.7	-2.9	27.9
14	-10.2	-2.8	28.0
15	-6	-2.7	28.1
21	-10.0	-2.8	28.0
41	-9.1	-2.9	27.9
Avg.	-8.6	-2.8	28.0
St. dev. (1 σ)	1.5	0.3	0.3

Iron Oxide-Rich Fissure Fill

XRD analyses of the OKCave and OKCaveM samples are essentially identical, with high and broad peaks at low angle reflections of 5.96° and 12.52° 2θ (Fig. 6). These peaks likely correspond to the basal (001) spacings of 2:1 and 1:1 phyllosilicates, respectively (Moore and Reynolds, 1997). High angle reflections at 17.88° , 21.28° , 33.28° , and 36.72° 2θ correspond to crystallographic $d(hkl)$ spacings of goethite ($\alpha\text{-FeOOH}$). Goethite (111) and (110) d -spacings of 2.448\AA and 4.183\AA for both OKCaveM and OKCave indicate 3 ± 3 mol% Al^{3+} substitution for Fe^{3+} in goethite in both samples (Schulze, 1984).

Results of the chemical analyses for OKCaveM and OKCave are reported in Table 3 as the mole fraction of the oxide components. $X(\text{O})_{\text{Fe}}$ values are the calculated amount of oxygen in stoichiometric goethite as a mole fraction of the total oxygen in the bulk sample. Also reported in Table 3 is the value $X(\text{O})_{\text{Al}}$, which is the amount of oxygen in the goethite crystal lattice associated with Al^{3+} substitution as a mole fraction of the total oxygen in the

goethite. The value of $X(\text{O})_{\text{Al}}$ was determined from X-ray diffraction analysis (Schulze, 1984).

Measured $\delta^{18}\text{O}$ and δD values for the bulk and residue samples are presented in Table 4. In both cases, the residues remaining after complete or partial dissolution of goethite and hematite have more positive $\delta^{18}\text{O}$ and δD values than the bulk (Fe-oxide-rich) fractions. The $X(\text{O})_{\text{Fe}}$ and $X(\text{O})_{\text{Al}}$ values reported in Table 3 were used to calculate the end-member oxygen-isotope compositions of goethite in OKCave and OKCaveM for both samples following the mass-balance approach of Yapp (1998), in which

$$\delta^{18}\text{O}_{\text{bulk}} = X(\text{O})_{\text{Fe}} * \delta^{18}\text{O}_{\text{Fe}} + X(\text{O})_{\text{Al}} * \delta^{18}\text{O}_{\text{Al}} + X(\text{O})_{\text{residue}} * \delta^{18}\text{O}_{\text{residue}} \quad (2a)$$

$$1 = X(\text{O})_{\text{Fe}} + X(\text{O})_{\text{Al}} + X(\text{O})_{\text{residue}} \quad (2b)$$

$\delta^{18}\text{O}_{\text{residue}}$ was measured directly, whereas the value for $X(\text{O})_{\text{residue}}$ was determined from the chemical data presented in Table 3 as the remaining fraction of oxygen after subtraction of $X(\text{O})_{\text{Fe}}$ and $X(\text{O})_{\text{Al}}$ contributed from goethite to the total oxygen.

The hydrogen-isotope compositions of end-member goethite samples were determined by a mass balance calculation similar to that of the oxygen calculations. The D/H calculation considers the differences between the measured wt% H_2O and the δD values of the bulk and residue samples as well as the calculated mole fraction of hydrogen $X(\text{H})_{\text{Fe}}$ in goethite. These end-member oxygen- and hydrogen-isotope compositions of goethite are reported in Table 4.

The results of the incremental vacuum dehydration-decarbonation analyses of OKCaveM goethite are given in Table 1 and depicted as incremental dehydration-decarbonation spectra in Figure 7. The progress variable $X_v(\text{H}_2)$ is the cumulative sum of evolved H_2 as a mole fraction of the total hydrogen in the goethite sample. When $X_v(\text{H}_2) = 0$, there has been no breakdown of goethite. When $X_v(\text{H}_2) = 1$, the goethite has been completely converted to hematite (Yapp and Poths, 1993). The "F" parameter in Figure 7A is defined as follows (Yapp and Poths, 1993): $F = n(\text{CO}_2)/n(\text{H}_2\text{O})$, where $n(\text{CO}_2) = \mu\text{mol}$ of CO_2 evolved in an increment of goethite dehydration-decarbonation and $n(\text{H}_2\text{O}) = \mu\text{mol}$ of H_2O evolved over that same increment.

Previous work has shown that, for $X_v(\text{H}_2)$ values from ~ 0.2 or 0.3 to ~ 0.6 or 0.8 , values of F and $\delta^{13}\text{C}$ commonly exhibit "plateaus" for which there is little change in either $\delta^{13}\text{C}$ or F as a function of $X_v(\text{H}_2)$ (Yapp and Poths, 1991, 1993; Yapp, 1997; Hsieh and Yapp, 1999). Such plateaus are produced by the CO_2 evolved from $\text{Fe}(\text{CO}_3)\text{OH}$ in the goethite structure, because $\text{Fe}(\text{CO}_3)\text{OH}$ only breaks down when the local, confining goethite structure is destroyed (Yapp and Poths, 1991). The 850°C step (and, at times, the longer duration vacuum dehydration steps that immediately precede the 850°C step) commonly does not exhibit these plateau values, because this increment may include CO_2 from oxidation of refractory organic matter (Yapp and Poths, 1991, 1992, 1993). Average plateau $\delta^{13}\text{C}$ and F values represent the weighted mean of CO_2 and H_2O incremental values over the plateau interval

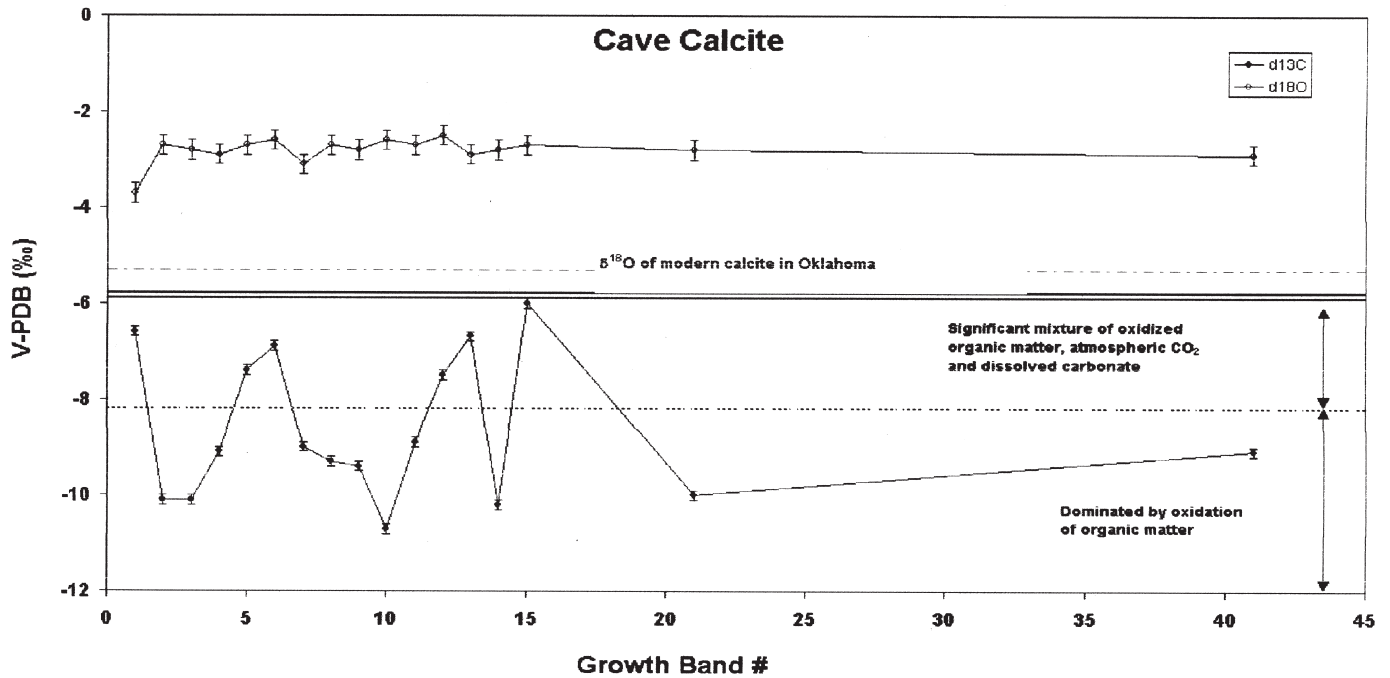


Figure 5. Graph of the measured calcite $\delta^{18}\text{O}_{\text{PDB}}$ (open circles) and $\delta^{13}\text{C}_{\text{PDB}}$ (closed circles) values versus the relative position within the sparry calcite sample (see Fig. 3) taken from cave-fill deposit. Oxygen-isotope values are relatively invariant and $\sim 2\text{‰}$ more positive than the expected $\delta^{18}\text{O}_{\text{PDB}}$ value for calcites that form in equilibrium with modern meteoric water in this region (solid line; -5.4‰). Carbon-isotope values range from -10.7‰ to -6.6‰ , and there appears to be episodic shifts between more positive and negative $\delta^{13}\text{C}_{\text{PDB}}$ values through the growth series. See text for details and discussion.

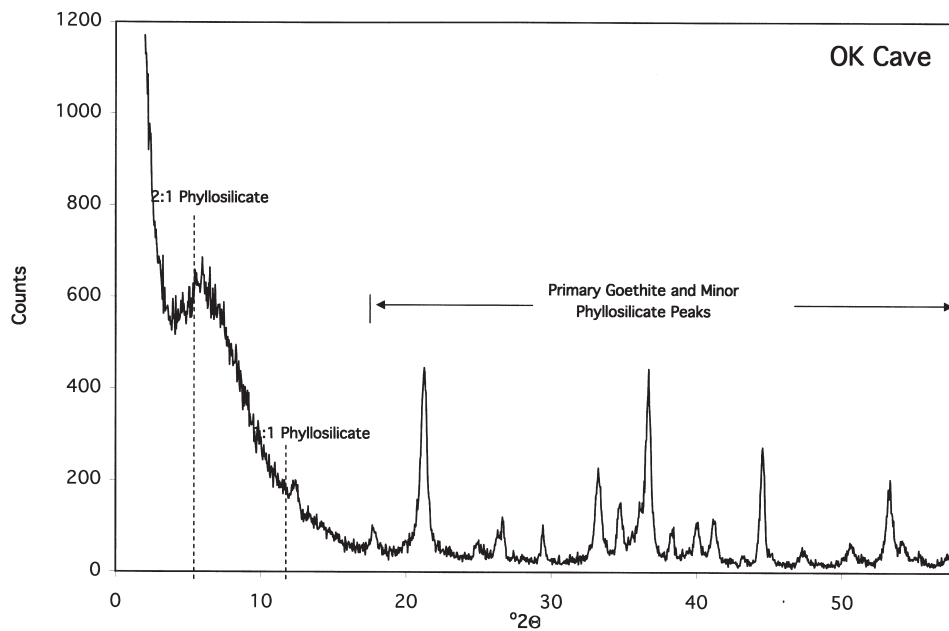


Figure 6. X-ray diffractogram of the OK-Cave sample from the cave-fill deposit. The combination of peaks indicates that this sample dominantly consists of goethite ($\alpha\text{-FeOOH}$) with minor 2:1 and 1:1 phyllosilicate. The d(110) and d(111) peaks of goethite correspond to 3 mol% Al^{3+} substitution for Fe^{3+} in the goethite structure (Schulze, 1984).

TABLE 3. MASS FRACTIONS OF OXYGEN FROM THE VARIOUS OXIDE COMPONENTS IN THE SAMPLES AS WELL AS THE MOLE FRACTION OF OXYGEN ASSOCIATED WITH IRON, $X(O)_{Fe}$, AND ALUMINUM $X(O)_{Al}$, FROM GOETHITE FOR EACH SAMPLE

Sample	P_2O_5	K_2O	CaO	MgO	Na ₂ O	MnO ₂	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	TiO ₂	H ₂ O	$X(O)_{Fe}$	$X(O)_{Al}$
OKCave Micro	B.D.	0.0009	0.0007	0.0010	B.D.	0.0004	0.7083	0.0400	0.0276	0.0008	0.2179	0.9444	0.0417
OKCAVE	B.D.	0.0008	0.0001	0.0001	0.0001	0.0003	0.7334	0.0145	0.0127	0.0005	0.2374	.9779	0.0417

Note: B.D.—below detection limit.

TABLE 4. MEASURED OXYGEN AND HYDROGEN ISOTOPE COMPOSITIONS FOR BULK AND RESIDUE FRACTIONS OF THE OKCAVEMICRO AND OKCAVE SAMPLES

Sample	$\delta^{18}O_b$	δD_b	$\delta^{18}O_r$	δD_r	$\delta^{18}O_{go}$	δD_{go}
OKCaveMicro	3.8‰	-124‰	20.3‰	-65‰	$3.1 \pm 2\%$	$-125 \pm 3\%$
OKCAVE	3.0‰	-121‰	21.0‰	-55‰	$2.7 \pm 2\%$	$-122 \pm 3\%$

Note: Also shown are the calculated oxygen and hydrogen isotope compositions for pure end-member goethite in each sample.

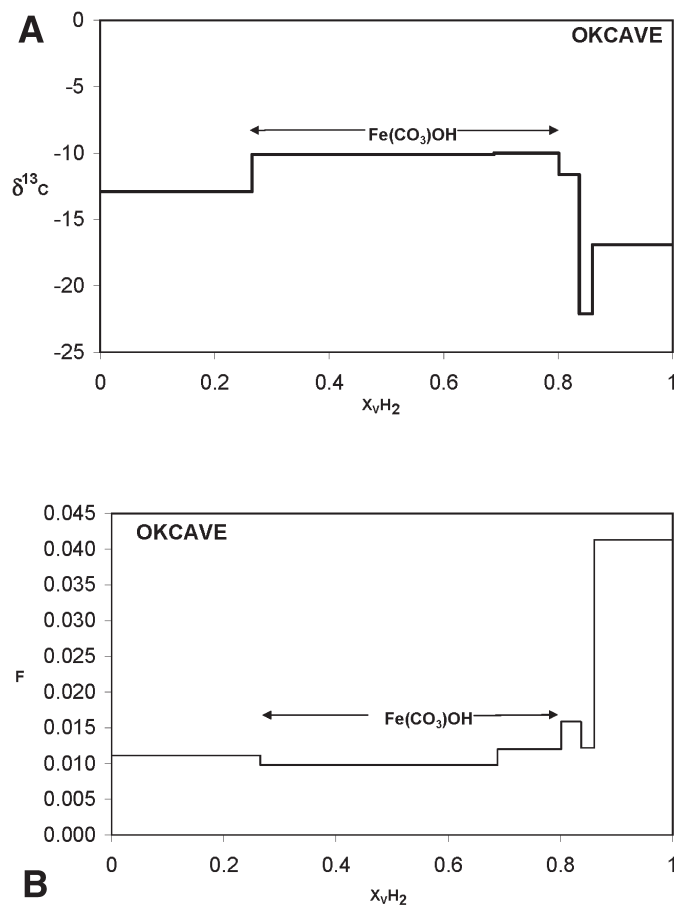


Figure 7. Incremental vacuum dehydration-decarbonation spectra for the $Fe(CO_3)OH$ component in solid solution in OKCave goethite. The graphs present the progress variable $X_v(H_2)$ versus (A) F values (nCO_2/nH_2O) and (B) corresponding $\delta^{13}C$ values of CO_2 evolved during individual increments of sample dehydration. For this sample, there is an apparent plateau in F and $\delta^{13}C$ values over the $X_v(H_2)$ range 0.27–0.80. See text for details and discussion.

(Yapp and Poths, 1991, 1992, 1993; Tabor et al., 2004b). The average plateau $\delta^{13}\text{C}$ and F values for OKCaveM are $-10.1 \pm 0.2\text{‰}$ and 0.0103 ± 0.0016 , respectively (Table 1).

DISCUSSION

Numerous studies have documented a close correspondence between $\alpha^{18}\text{O}$ and αD values of goethite, the isotopic composition of ambient waters, and the temperature of goethite crystallization (Yapp, 1987, 1990, 1993, 1997, 2000; Bao and Koch, 1999; Bao et al., 2000; Bird et al., 1992, 1993; Girard et al., 1997, 2000). This relationship may, in turn, be used to reconstruct paleoenvironmental conditions from the $\delta^{18}\text{O}$ and δD values of ancient goethite if mineral-water isotope fractionation factors are well known. Partial equilibration and synthesis experiments over the range 25 °C to 145 °C presented in Yapp and Pedley (1985) and Yapp (1987) offer the only available goethite-water hydrogen-isotope fractionation factor [$\text{D}\alpha = (\text{D}/\text{H})_{\text{goethite}}/(\text{D}/\text{H})_{\text{water}}$]. Within analytical uncertainty, goethite-water hydrogen-isotope fractionation is:

$$\text{D}\alpha = 0.905 \pm 0.004, \quad (3)$$

and there appears to be no temperature-dependent hydrogen-isotope fractionation. However, several goethite-water oxygen-isotope fractionation factors [$^{18}\alpha_{\text{g}} = (^{18}\text{O}/^{16}\text{O})_{\text{goethite}}/(^{18}\text{O}/^{16}\text{O})_{\text{water}}$] have been proposed (Yapp, 1990; Müller, 1995; Zheng, 1998; Bao and Koch, 1999). Yapp (2000, 2001) concluded that the

goethite-water oxygen-isotope fractionation factor presented in Yapp (1990) appears to provide the closest approximation to goethite-water oxygen-isotope fractionation observed in most natural environments to date. This is illustrated by the plot of $\text{D}\alpha$ versus $^{18}\alpha_{\text{g}}$ in Figure 8. There are two pairs of goethite isotherms depicted in Figure 8. One pair was calculated using the goethite-water oxygen-isotope fractionation factor of Yapp (1990) for temperatures of 0 °C and 30 °C . The other pair was calculated using the oxygen-isotope fractionation factors of Bao and Koch (1999):

$$10^3 \ln^{18}\alpha_{\text{g}} = (1.63 \cdot 10^6 / T_{\text{k}}^2) - 12.3 \quad (\text{Yapp, 1990}), \quad (4)$$

$$10^3 \ln^{18}\alpha_{\text{g}} = (1.97 \cdot 10^3 / T_{\text{k}}) - 8.004 \quad (\text{Bao and Koch, 1999}), \quad (5)$$

where T_{k} is temperature in degrees Kelvin. Both pairs of isotherms in Figure 8 were calculated with the assumption that the goethite formed in the presence of meteoric water as described by the equation of Craig (1961). This global meteoric water line is shown in Figure 8 for reference. The freezing point of pure H_2O at one atm (0 °C) was chosen as the lower temperature limit (cf., Yapp, 2000). The higher temperature of 30 °C was selected because it appears to represent an approximate upper limit to modern mean annual Earth surface air temperatures (e.g., Rozanski et al., 1993). The δD and $\delta^{18}\text{O}$ values measured for the OKCave goethite samples are plotted in Figure 8 and lie within the range of values permitted by the Yapp (1987, 1990) fractionation equations. However, these measured data are well outside the range of

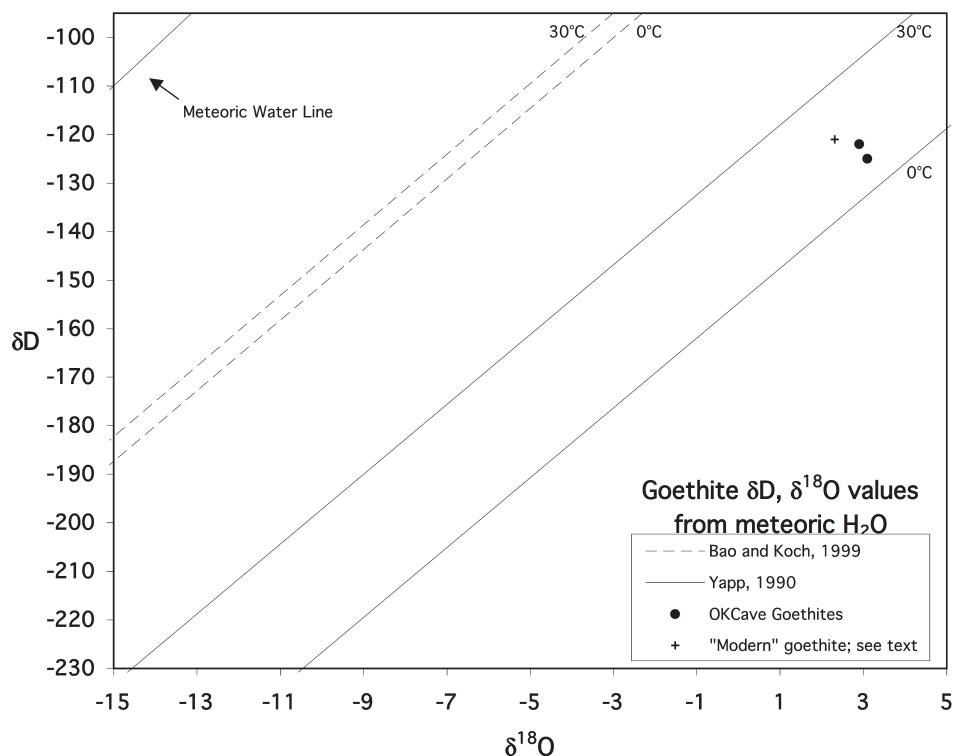


Figure 8. Plot of δD against $\delta^{18}\text{O}$ for waters of the meteoric waters (MWL) of Craig (1961). Also, "goethite lines" calculated using the goethite-water hydrogen-isotope fractionation equation of Yapp (1987) and two different goethite-water oxygen-isotope fractionation equations: one proposed by Bao and Koch (1999), the other by Yapp (1990). Also shown are the measured hydrogen- and oxygen-isotope values for OKCave and OKCaveM goethite samples (filled black circles) and a hypothetical "modern" goethite in equilibrium with local meteoric water at mean annual surface air temperature in Oklahoma (cross). The hypothetical goethite δD and $\delta^{18}\text{O}$ values were calculated using the oxygen- and hydrogen-isotope fractionation factors of Yapp (1987, 1990). See text for discussion.

values represented by the oxygen-isotope fractionation equation of Bao and Koch (1999) in combination with the goethite-water D/H fractionation equation of Yapp (1987). Further discussion of the data in this work will utilize the goethite-water hydrogen- and oxygen-isotope fractionation equations determined in studies by Yapp (1987, 1990).

SIGNIFICANCE OF GOETHITE D/H AND $^{18}\text{O}/^{16}\text{O}$ RATIOS

Figure 8 presents the measured oxygen- and hydrogen-isotope compositions of the OKCave and OKCaveM goethites in this study (filled circles). Figure 8 depicts the oxygen- and hydrogen-isotope values expected for goethites in isotopic equilibrium with modern local meteoric waters of southern Oklahoma at present mean annual temperatures (crosses in Fig. 8). Modern meteoric water oxygen- ($\delta^{18}\text{O} = -4.8\text{‰}$) and hydrogen- ($\delta\text{D} = -28\text{‰}$) isotope values were taken from the data presented in Kendall and Coplen (2001), whereas the value for mean annual surface air temperature ($T = 16.3\text{ °C}$) was taken from local weather stations in nearby Lawton, Oklahoma, as reported in the National Oceanic and Atmospheric Administration database. The oxygen- and hydrogen-isotope compositions calculated for hypothetical modern goethites at this locale are $\delta^{18}\text{O} = 2.3\text{‰}$ and $\delta\text{D} = -121\text{‰}$ (Fig. 9). Within analytical uncertainty, hydrogen-isotope compositions of the OKCave and OKCaveM samples are indistinguishable from values expected for modern goethites forming in southern Oklahoma. The goethite-water hydrogen-isotope fractionation is essentially independent of temperature in the range of temperatures encountered in surface environments (equation 3 above; Yapp, 1987). Therefore, OKCave goethite samples appear to have formed in the presence of waters that were not significantly

different in their hydrogen- or oxygen-isotope values from modern meteoric water. However, the measured oxygen-isotope compositions of the OKCave goethites ($\delta^{18}\text{O} = 2.9\text{‰}$, 3.1‰) are more positive than the value expected for modern goethite ($\delta^{18}\text{O} = 2.3\text{‰}$). Goethite-water oxygen-isotope fractionation is temperature-dependent (Yapp, 1990), suggesting that these goethites may have formed at temperatures that are different from modern surface air temperatures in southern Oklahoma. Yapp (1987, 1993, 2000) proposed that the oxygen- and hydrogen-isotope composition of goethites might serve as a single-mineral paleothermometer. For the current calculation, it is assumed that the goethite formed in isotopic equilibrium with meteoric waters and the isotopic composition of the samples has not changed since their formation.

The systematic relationship between hydrogen and oxygen isotopes in global meteoric waters (Craig, 1961) is:

$$\delta\text{D}_w = 8\delta^{18}\text{O}_w + 10, \quad (6)$$

where the subscript “w” represents meteoric water. Measured δD and $\delta^{18}\text{O}$ values of a goethite may be used in combination with equations 2, 3, 4, and 6 to calculate the temperature of goethite crystallization:

$$T = \left(\frac{1.63 \times 10^6}{\Delta^{18}\text{O}_{g-w} + 12.3} \right)^{\frac{1}{2}} \quad (7a)$$

$$10^3 \ln^{18}\alpha \approx \delta^{18}\text{O}_g - \delta^{18}\text{O}_w = \Delta^{18}\text{O}_{g-w}; \quad \delta^{18}\text{O}_w = \left[\frac{\left[\frac{1000 + \delta D_g}{D\alpha} \right] - 1010}{8} \right]$$

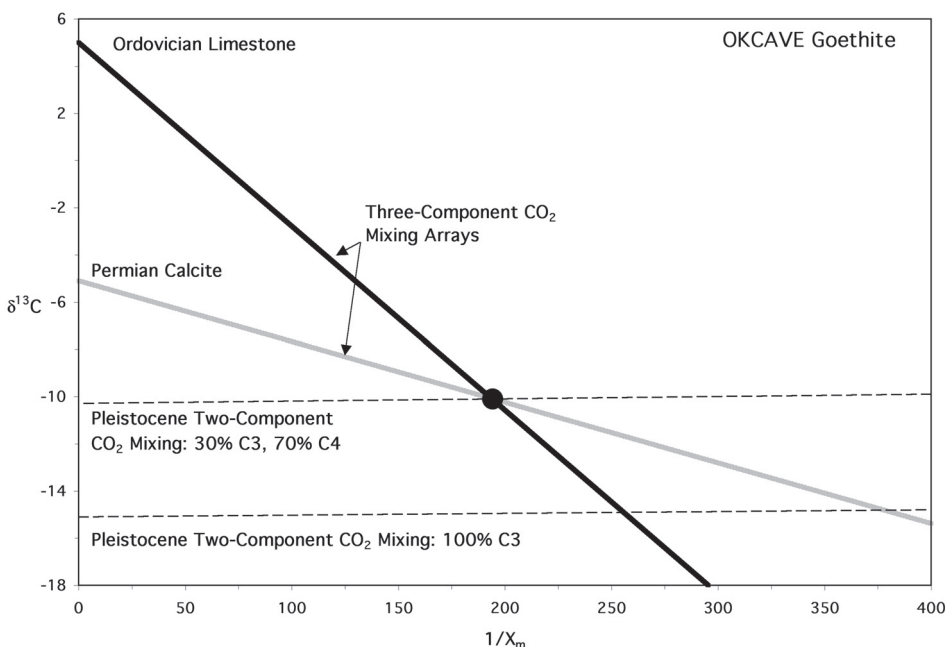


Figure 9. Plot of $\delta^{13}\text{C}$ versus $1/X_m$ for the $\text{Fe}(\text{CO}_3)\text{OH}$ component in solid solution in goethite. The measured $1/X_m$ and $\delta^{13}\text{C}$ values for the sample OKCaveM (closed circle) lie above expected values for two-component mixing of CO_2 (lower dashed line) in a soil dominated by oxidation of C3 organic matter. Therefore, the $\text{Fe}(\text{CO}_3)\text{OH}$ data probably represent formation of goethite in a system of three-component mixing of CO_2 . Possible sources of the third component in this CO_2 -mixing system are dissolving Ordovician marine limestone (solid black line) and/or Permian calcite within the cave-fill deposit (solid gray line), or oxidizing organic matter with a significant C4 component (upper dashed line). See text.

where

$$\delta D_g \text{ and } \delta^{18}O_g \quad (7b)$$

are the measured hydrogen- and oxygen-isotope composition, respectively, of goethite, and ^{18}O is the stable hydrogen-isotope fractionation factor between goethite and water (0.905). The measured δD_g and $\delta^{18}O_g$ values for OKCave and OKCaveM result in calculated temperatures of $7^\circ \pm 3^\circ \text{C}$ and $11^\circ \pm 3^\circ \text{C}$, respectively, for goethite crystallization. Considering that shallow subterranean and soil-forming environments typically remain within $\pm 2^\circ \text{C}$ of mean annual surface temperatures (Buol et al., 1997), it is likely that a calculated temperature of $\sim 9^\circ \text{C} \pm 3^\circ \text{C}$ (average of OKCave and OKCaveM goethites) represents mean annual surface temperatures over the period of goethite crystallization. Note that the calculated temperatures of goethite formation for OKCave and OKCaveM are $\sim 7^\circ \text{C}$ lower than the current reported mean annual surface air temperature for nearby Lawton, Oklahoma. This suggests that the isotopic composition of the OKCave and OKCaveM goethites records cooler climatic conditions at some time in the geological past. Southern Oklahoma currently resides near its highest latitude for the entire Phanerozoic eon (Scotese and Golonka, 1992). Thus, the low temperatures calculated from the Oklahoma goethites suggest cooler conditions of goethite crystallization either in its current, or more equatorial, geographic position. Lithostratigraphic proxy records around this region indicate a generally warm climate from late Paleozoic through Eocene time (e.g., McGowen et al., 1979; Tabor et al., 2002; Tabor and Moñtanez, 2004; Tabor et al., 2004a). Cenozoic $\delta^{18}O$ records of benthic foraminifera indicate a general Neogene cooling, culminating in globally low temperatures during the Pleistocene glacial maxima (e.g., Zachos et al., 2001). Furthermore, noble gas concentrations of groundwater systems in the Carrizo Aquifer of the northern Gulf coastal plain, Texas, United States (~ 300 km south of Wichita Mountains), indicate that surface temperatures were 5°C to 7°C lower than modern surface temperatures during the last glacial maximum, ~ 20 ka– 10 ka (Stute et al., 1992; Stute and Schlosser, 1993). Notably, cement stratigraphic relationships point to a Pleistocene age of goethite crystallization in these karst-fill deposits of the Wichita Mountains (Donovan et al., 2001). There are no other contemporaneous geochemical proxies of paleoenvironment in this region to compare with this data set. However, palynological, paleobotanical, geomorphic, and paleolake level records around this region do indicate that Pleistocene climate became quite cool and dry (Wells and Stewart, 1987; Fredlund and Jauman, 1987). This cooling was most pronounced during the Pleistocene glacial maximum (Fredlund, 1995). Furthermore, global circulation models suggest that during the Pleistocene glacial maximum the Great Plains region was drier, windier, and 6°C cooler than current conditions (Kutzbach and Wright, 1985). Therefore, unless the agreement is accidental, the paleotemperature of $\sim 9^\circ \text{C}$ (i.e., $\sim 7^\circ \text{C}$ cooler than modern) that was calculated from goethite δD and $\delta^{18}O$ values suggests that these goethites crystallized during one or more glacial stages in the Pleistocene.

SIGNIFICANCE OF CALCITE $\delta^{18}O$ AND $\delta^{13}C$ VALUES

Oxygen Isotopes

The $\delta^{18}O$ value of “fictive” calcite in isotopic equilibrium with modern local meteoric waters at current mean annual temperatures of southern Oklahoma is depicted by the horizontal reference line in Figure 5. This fictive calcite value was calculated using the calcite-water oxygen-isotope fractionation equation of O’Neil et al. (1969). The equation of O’Neil et al. (1969) is

$$10^3 \ln^{18}\alpha_{cc} = (2.78 * 10^6 / T_k^2) - 2.89. \quad (8)$$

The mean measured $\delta^{18}O$ value for the cave calcite is 28.0‰, which is 2.6‰ more positive than the value expected for modern calcite forming in this region (Fig. 5). This indicates that the cave calcites preserve an isotopic record different from the modern. Using a combination of the oxygen-isotope fractionation equations for goethite and calcite (equations 4 and 8) to calculate calcite-goethite mineral pair temperatures yields values of -1°C and -4°C . Therefore, the measured oxygen-isotope values of the goethite and calcite do not appear to represent equilibrium crystallization conditions in the presence of the same waters at a common temperature, because the implied temperature would correspond to frozen fresh water in which mineral crystallization and growth of the sort indicated by the calcite and goethite of this study would not occur (cf., Yapp, 2001).

If the calcite did not crystallize in the same environment as goethite, but did form in equilibrium with its own ancient environment, the $\delta^{18}O$ value of the calcite must be considered in terms of two controlling variables of unknown magnitude (temperature and $\delta^{18}O$ of the ambient water, equation 8). As mentioned, there is no geologic evidence to indicate that this region of the world experienced annual temperatures as cool as, or cooler than, Pleistocene glacial stage temperatures at earlier times in the Phanerozoic eon (e.g., Scotese and Golonka, 1992). In addition, cooler mean annual temperatures generally result in more negative isotopic compositions of meteoric precipitation (e.g., Rozanski et al., 1993), which could result in a more negative oxygen-isotope composition of calcite, despite a larger oxygen-isotope fractionation at lower temperatures. Therefore, crystallization of the cave calcite at temperatures significantly cooler than modern is not likely responsible for the measured $\delta^{18}O$ values. As mentioned, the karst-fill sequences of Ordovician limestone have never been deeply buried, and all of the karst-fill calcite cements owe their origin to surface-tied hydrology (Donovan, 1986; Donovan et al., 2001). Furthermore, preservation of Permian vertebrate assemblages and stratigraphic relationships (Olson, 1967) within these karst deposits strongly indicate a Permian age of calcite formation. Based on the oxygen- and hydrogen-isotope compositions of phyllosilicates and goethites from paleosols of the southwestern United States, Permian paleotemperatures of this region ranged from 25°C to 30°C (Tabor, 2002). If these temperatures also apply to mineralization of the karst-fill calcites, then the oxy-

gen-isotope composition of the water in equilibrium with these calcites ranged from -0.4% to 0.6% . There are only five modern sites that report such isotopically heavy precipitation (Rozanski et al., 1993). These sites may serve as modern analogs for the environmental conditions associated with calcite precipitation within this fissure-fill deposit. Four out of these five modern sites occur at low latitudes with relatively low mean annual precipitation (<500 mm/yr) and mean annual temperatures ranging from 25.5 °C to 29 °C. These modern analogs correspond well with the paleoequatorial position, calculated paleotemperatures, and inferred paleoprecipitation for this region during early Permian time (Tabor, 2002).

In addition, although cave environments typically have a relative humidity near 100% (Gascoyne, 1992), it is possible that this calcite formed from cave waters that were isotopically modified by evaporation. Furthermore, the effect of diagenetic modification cannot be ignored, in spite of the shallow and low temperature burial history associated with these deposits. Future studies of the hydrogen-isotope composition of fluid inclusion waters in these calcites may help to resolve these issues.

Carbon Isotopes

The cave-calcite sample shows large shifts in $\delta^{13}\text{C}$ values through the growth series (Fig. 5) that may be related to temporal changes in mixing of different carbon reservoirs during crystallization (cf., Gascoyne, 1992). In general, there are three primary carbon reservoirs in terrestrial environments that may contribute to the $\delta^{13}\text{C}$ composition of newly formed calcite: (1) oxidized biological carbon characterized by relatively negative $\delta^{13}\text{C}$ values, (2) inorganic marine and terrestrial carbonate characterized by relatively positive $\delta^{13}\text{C}$ values, and (3) atmospheric CO_2 with $\delta^{13}\text{C}$ values between biological and inorganic carbonate (e.g., Hoefs, 1997).

There is currently no evidence to suggest that any photosynthetic pathway other than C3 was utilized by terrestrial flora prior to Miocene time (e.g., Cerling, 1991). Biological carbon resulting from C3 photosynthesis has $\delta^{13}\text{C}$ values that generally range from $\sim -29\%$ to -23% (Cerling and Quade, 1993). The corresponding range of $\delta^{13}\text{C}$ values of CO_2 derived from oxidation of C3-biological carbon in soils will range from $\sim -24.6\%$ to -18.6% , after a 4.4% diffusive enrichment (Cerling et al., 1991). At 25 °C, the isotopic composition of calcite will be 10.4% more positive than coexisting CO_2 (Bottinga, 1968). This results in a possible range of calcite $\delta^{13}\text{C}$ values from -14.2% to -8.2% in a system dominated by CO_2 gas derived from oxidation of biological material.

The $\delta^{13}\text{C}$ value of the ancient atmosphere may be estimated from the carbon-isotope composition of contemporaneous marine calcite (Cerling, 1991). This approach has been used to estimate a range of Permian atmospheric $\delta^{13}\text{C}$ values from -4.9% to -4.0% (Ekart et al., 1999). Thus, in a freshwater system in equilibrium with atmospheric CO_2 , $\delta^{13}\text{C}$ values of calcite could range from $+5.5\%$ to $+6.4\%$.

There is no isotopic fractionation associated with congruent dissolution of carbonate (Wigley et al., 1978). Thus the $\delta^{13}\text{C}$ value of HCO_3^- (at pH ~ 8) derived from dissolution of the host Ordovician limestone in this karst system was likely near the limestone value of $+1.5\%$. However, equilibrium reprecipitation of calcite at 25 °C from this bicarbonate solution would be 0.9% more positive than the dissolved component (Mook et al., 1974), resulting in a $\delta^{13}\text{C}$ of $+2.4\%$ for a newly formed calcite in the fissure-fill deposit derived solely from dissolution of Ordovician carbonate.

Based on the preceding discussion, cave calcite $\delta^{13}\text{C}$ values $\leq -8.2\%$ likely record a system dominated by high, but variable, proportions of CO_2 from oxidation of biological carbon, whereas $\delta^{13}\text{C}$ values $> -8.2\%$ likely record a system with a significant addition of CO_2 from atmospheric CO_2 and/or dissolved limestone (Fig. 5). The $\delta^{13}\text{C}$ variation of the cave calcite sample is typical of modern subterranean environments characterized by seasonal changes in rainfall and biological productivity (i.e., in xeric or monsoonal climates; Gascoyne, 1992 and examples therein). Although the exact mechanism for variable $\delta^{13}\text{C}$ values in the calcite crystal is not known, changes in the $\delta^{13}\text{C}$ value may be related to episodic changes in productivity of the Permian soil mantle above the karst system as a result of seasonal climate variability and changing CO_2 concentrations in the cave atmosphere. This inferred climate system is consistent with paleoclimate reconstructions based on the morphological character of Permian-age paleosols that formed in this region (Tabor and Montañez, 2002).

$\delta^{13}\text{C}$ VALUES OF $\text{Fe}(\text{CO}_3)\text{OH}$ IN GOETHITE AND CO_2 MIXING MODELS

Yapp and Poths (1992) presented the following Henry's Law expression for the ferric carbonate component in goethite:

$$\log_{10} P_{\text{CO}_2} = \log_{10} X_m + 6.04 - 1570/T(\text{°K}). \quad (9)$$

The X_m value of ferric carbonate in OKCaveM goethite is 0.0052 (Table 1). If goethite in the OKCaveM precipitated at ~ 9 °C, the ambient partial pressure of CO_2 in the cave would have been $\sim 20,000$ ppmV. Such high CO_2 concentrations are typical of cave atmospheres in modern-day cool temperate zones as a result of CO_2 diffusion from high-productivity soils overlying the cave space (Ek and Gewalt, 1985). Therefore, the X_m and $\delta^{13}\text{C}$ value of ferric carbonate in the OKCaveM goethite may provide some insight into the productivity of soils overlying the cave atmosphere during Pleistocene time.

On the basis of geological arguments and the measured mole fraction (X_m) and $\delta^{13}\text{C}$ values of the $\text{Fe}(\text{CO}_3)\text{OH}$ in goethites of various origins, several studies have concluded that either two-component or three-component CO_2 mixing relations can exist in wet subsurface environments (Hsieh and Yapp, 1999; Yapp, 2001; Tabor et al., 2004b). Two-component mixing assumes that the only two sources contributing to soil CO_2 are CO_2 from the

open atmosphere and CO₂ from in situ oxidation of biological carbon. Three-component mixing incorporates an additional source of CO₂ derived from in situ dissolution of preexisting carbonates such as calcite, which is generally enriched in ¹³C compared to atmospheric CO₂ or CO₂ from oxidation of biological material in the soil (e.g., Hoefs, 1997). These two- and three-component CO₂ mixing models have been used to conceptualize mixing of different CO₂ sources in soils. However, these mixing relations may also apply to CO₂ in caves because these subterranean environments are comprised of CO₂ from the open atmosphere and oxidized organic matter from overlying and juxtaposed soils through diffusive transport (e.g., Gascoyne, 1992). Furthermore, many cave systems will also include some component of CO₂ from the dissolution of host limestones and dolomites as most karst systems form by carbonate dissolution.

Yapp and Poths (1992, 1993) derived the following general equation, expressed in terms of mole fraction (X) and δ¹³C value of the Fe(CO₃)OH component in goethite, for mixing of CO₂ derived from the atmosphere and oxidation of organic matter.

$$\delta^{13}C_m = (\delta^{13}C_A - \delta^{13}C_O)X_A/X_m + \delta^{13}C_O, \quad (10a)$$

and

$$\delta^{13}C_O = [\alpha_k \delta^{13}C_B + 1000(\alpha_k - 1)]. \quad (10b)$$

δ¹³C_m is the measured δ¹³C value of the Fe(CO₃)OH in goethite; δ¹³C_A would be the δ¹³C value of the Fe(CO₃)OH component if atmospheric CO₂ were the only CO₂ in the soil; X_m is the measured value of X for the Fe(CO₃)OH component in goethite; X_A is the value of X for the Fe(CO₃)OH component if atmospheric CO₂ were the only CO₂ in the soil; δ¹³C_O is the value that accounts for the diffusive modification of δ¹³C_B (Yapp and Poths, 1993). δ¹³C_B is the δ¹³C value of the Fe(CO₃)OH if it were in equilibrium with gaseous CO₂ of the same carbon-isotope ratio as the biological carbon being oxidized in the profile (Yapp, 2001). The carbon-isotope fractionation factor between the Fe(CO₃)OH in goethite and CO₂ gas is 1.0025 at 25 °C (Yapp and Poths, 1993). The value α_k is the ratio of the diffusion coefficients (D) of the CO₂ molecules with mass numbers 44 and 45 (α_k = ⁴⁴D/⁴⁵D). The α_k value in soils is ~1.0044 (Cerling et al., 1991). However, many cave atmospheres appear to circulate through advective flow (Ek and Gewalt, 1985), which could result in α_k values of ~1.0000 for organic matter that is directly oxidized in the cave (i.e., δ¹³C_O = δ¹³C_B; Yapp, 2001). These extreme values of α_k result in two δ¹³C_O values for a given value of δ¹³C_B.

The magnitude of (δ¹³C_A - δ¹³C_O) in equation 7a is assumed to be about the same at all times in the Phanerozoic for soils dominated by C3 photosynthesis, which is the dominant photosynthetic pathway of plants in the humid climates that favor the formation of goethite (e.g., Hsieh and Yapp, 1999). Yapp and Poths (1996) adopted a value of +16‰ because it represents the approximate difference between preindustrial CO₂ (-6.5‰) and recent C3 continental biota (-27‰), after including a 4.4‰ dif-

fusive ¹³C enrichment in the biologically derived CO₂ (Cerling et al., 1991). However, as stated earlier, if α_k values for oxidizing organic matter in a cave atmosphere approach ~1.0000, the quantity (δ¹³C_A - δ¹³C_O) will be 20.4‰. Furthermore, if soil organic matter was characterized by a mixture of 30% C3 and 70% C4 photosynthesizers as suggested by other studies (Fox and Koch, 2004; Koch et al., 2004), then (δ¹³C_A - δ¹³C_O) would have been a smaller value than for C3 photosynthesis alone. However, an OKCave goethite Fe(CO₃)OH δ¹³C value of -10.1‰ constrains (δ¹³C_A - δ¹³C_O) to be 10.7‰ for a C3-C4 mix with a δ¹³C value of -14.7‰ and atmospheric CO₂ concentrations of 180 ppmV. It should be pointed out that error in the selection of a value for δ¹³C_A - δ¹³C_O has a marginal effect on the concentration of tropospheric CO₂ calculated with equation 10. For example, if the uncertainty in the value of δ¹³C_A - δ¹³C_O were as large as 4‰, the relative error in the calculated partial pressure of atmospheric CO₂ would be 25%.

Under these proposed conditions, there are two possible end-member two-component mixing equations:

$$\delta^{13}C_m = 10.7 * X_A/X_m + \delta^{13}C_O, \quad (11a)$$

(all oxidation of C3-C4 mix in the soil),

$$\delta^{13}C_m = 20.4 * X_A/X_m + \delta^{13}C_B \quad (11b)$$

(all oxidation of pure C3 material in the cave atmosphere).

The δ¹³C of naturally occurring modern C3 plants ranges from -29‰ to -23‰ (e.g., Cerling and Quade, 1993). There is no evidence to suggest that Pleistocene atmospheric CO₂ concentrations were much more than preindustrial Holocene values (~300 ppmV) but may be as low as 180 ppmV (e.g., Jouzel et al., 1993; Schlessinger, 1997). As mentioned, the concentration of OKCave ferric carbonate (X_m) is 0.0052, and this sample crystallized at ~9 °C. Therefore, with the values assumed for δ¹³C_B, α_k, and X_m, equations 11a and 11b indicate that the δ¹³C_m value of Pleistocene ferric carbonate in the cave goethite would be no more positive than -14.8‰ for a two-component CO₂ mixing system characterized by oxidation of organic matter derived from C3 photosynthesis (Fig. 9). Therefore, the ferric carbonate δ¹³C_m value of -10.1‰ for OKCave indicates this mineral either formed (1) in the presence of oxidizing organic matter derived from mixed C3 and C4 photosynthesizers, (2) in a three-component CO₂ mixing system, regardless of the α_k and the δ¹³C value of oxidizing organic matter at the time of goethite crystallization, or (3) a combination of (1) and (2).

On the basis of Pleistocene-age herbivore teeth δ¹³C values from northern Texas, United States, Fox and Koch (2004) and Koch et al. (2004) assert that Pleistocene grasslands of the southern Great Plains were occupied by a mixture of ~30% C3 and ~70% C4 grasses. C4 grass δ¹³C values typically range from about -9‰ to -15‰ (Teeri and Stowe, 1976). However, considering that OKCave goethite Fe(CO₃)OH has a δ¹³C value of -10.1‰ and formed in the presence of Pleistocene atmospheric CO₂ concentrations ≤300 ppmV, and assuming α_k was 1.0044

(i.e., oxidation of organic matter in the soil), the $\delta^{13}\text{C}$ value of oxidizing organic matter was probably no greater than -17.2‰ at the time of goethite crystallization (i.e., $\delta^{13}\text{C}_\text{O} = -10.3\text{‰}$). If the ratio of C3 to C4 plants determined in Koch et al. (2004) is applicable to the OKCave deposit and C3 plants had a relatively heavy $\delta^{13}\text{C}$ value (-23‰), then C4 plant $\delta^{13}\text{C}$ values would have been about -14.7‰ in the vicinity of this deposit in order to facilitate two component soil CO_2 mixing, yielding a $\delta^{13}\text{C}_\text{O}$ value of -10.3‰ .

The goethite layers in this karst system are situated between Ordovician marine limestone and sparry calcites. The latter likely formed in the phreatic zone. A probable third CO_2 component in OKCave ferric carbonate could have been derived from dissolution of one or both of these potential sources. Fe-sulfides are occluded within some of the sparry cave-calcite deposits (Fig. 4). This suggests that pore waters were sufficiently anoxic for Eh conditions to favor precipitation of Fe^{2+} minerals while also having a pH (~ 8.3) that favored precipitation of carbonate. However, if these ferrous minerals were subsequently exposed to oxygenated waters and transformed to ferric minerals such as goethite, pore waters within the vicinity of this reaction boundary would become quite acidic and promote carbonate dissolution:



and



Yapp (2001, 2002) presented the following three-component CO_2 mixing equation for the ferric carbonate component in goethite that forms at low pH:

$$\delta^{13}\text{C} = \left[\frac{X_A(\delta^{13}\text{C}_A - \delta^{13}\text{C}_\text{O}) + X_S(\delta^{13}\text{C}_\text{O} - \delta^{13}\text{C}_\text{CC})}{[1/X_m] + \delta^{13}\text{C}_\text{CC}} \right] \quad (13)$$

X_A , $\delta^{13}\text{C}_A$, $\delta^{13}\text{C}_\text{O}$, and X_m are the same as in equation 1. X_S is the mole fraction of $\text{Fe}(\text{CO}_3)\text{OH}$ in goethite if it were in equilibrium only with the CO_2 gas in a two-component soil CO_2 mixture (i.e., oxidized biological material and atmospheric CO_2). $\delta^{13}\text{C}_\text{CC}$ is the calculated value of the $\text{Fe}(\text{CO}_3)\text{OH}$ if it were in equilibrium with aqueous CO_2 solely derived from dissolving calcite. The value of $\delta^{13}\text{C}_\text{CC}$ in ferric carbonate will be $\sim 3.5\text{‰}$ more positive than the $\delta^{13}\text{C}$ value of aqueous CO_2 (Yapp, 2001). The potential sources of dissolving carbonate in the presence of OKCave goethite precipitation are Ordovician marine limestone ($\delta^{13}\text{C}$ value = $+1.5\text{‰}$) and sparry cave calcite ($\delta^{13}\text{C}$ value = -8.6‰), corresponding to $\delta^{13}\text{C}_\text{CC}$ values of 5.0‰ and -5.1‰ , respectively (Fig. 9). With low pH three-component mixing involving this range of $\delta^{13}\text{C}_\text{CC}$ values and with the hypothetical two-component mixing lines (equations 11a and 11b), it is possible to calculate values for X_S (equation 13), which provides limits upon the CO_2 concentra-

tions in "upstream" two-component systems representing mixing of CO_2 from Earth's atmosphere and CO_2 from oxidation of organic matter at the time of goethite crystallization. With certain assumed values for $\delta^{13}\text{C}_A$, $\delta^{13}\text{C}_\text{CC}$, $\delta^{13}\text{C}_\text{O}$, and atmospheric P_{CO_2} , CO_2 concentrations in the soils in the vicinity of OKCave goethite would have been between 8,000 ppmV and 16,000 ppmV. This calculated range of soil CO_2 values reflects, in part, variable contributions of CO_2 from assumed endmembers such as dissolving Ordovician- and Permian-age calcite, oxidizing of plant organic matter derived solely from C3 organic matter (i.e., $\delta^{13}\text{C}_\text{O} = -23\text{‰}$; Fig. 9) or oxidizing mixed C3:C4 organic matter (i.e., $\delta^{13}\text{C}_\text{O} = -17.2\text{‰}$; Fig. 9) and α_k values from 1.0044. Such two-component CO_2 concentrations are similar to those found in modern grassland soils of the southern Great Plains (e.g., Wood and Petraitis, 1984). Notably, higher proportions of C4 organic matter result in the higher estimates of CO_2 concentrations contributed from oxidation of organic matter during OKCave goethite crystallization. The isotopic results of the OKCave and OKCaveM goethites are intriguing, as these data imply a relatively high-productivity soil in the southern plains at a time of significantly cooler Pleistocene climate.

CONCLUSIONS

δD , $\delta^{18}\text{O}$, and $\delta^{13}\text{C}$ values of secondary calcites and goethites preserved within a karst-fill deposit in the Wichita Mountains, south-central Oklahoma, are suggestive of formation under two distinctly different environmental conditions. Prior studies have suggested that calcites in the fissure fill formed during early Permian time, whereas the goethites formed from dissolution and oxidation of Fe-sulfides and reprecipitation of iron oxyhydroxides during Pleistocene time. Calcite from a cave-fill deposit has relatively invariant oxygen-isotope compositions suggestive of formation in a warm and dry, seasonal, coastal environment. Furthermore, large, episodic shifts in the carbon-isotope composition of calcite in this deposit may record seasonal changes in biological productivity of the overlying soil mantle in a Permian monsoonal or xeric climate. These conclusions are consistent with other Permian paleoclimate reconstructions inferred from lithologic and isotopic proxy data in this region.

Goethites from the cave-fill deposit are not in isotopic equilibrium with modern waters of south-central Oklahoma nor with coexisting calcites. The combined $\delta^{18}\text{O}$ and δD values of the goethites indicate that crystallization occurred at $\sim 9^\circ\text{C}$, which is $\sim 7^\circ\text{C}$ cooler than modern temperatures in this region. This lower temperature is in reasonable accord with a late Pleistocene glacial stage temperature $\sim 6^\circ\text{C}$ cooler than modern, which was determined from groundwater noble gas concentrations in the United States Gulf Coastal Plain (Stute et al., 1992; Stute and Schlosser, 1993), and also with a glacial maximum temperature that was $\sim 6^\circ\text{C}$ cooler in the Pleistocene in the southern Great Plains, as predicted from general circulation models (Kutzbach and Wright, 1985).

The carbon-isotope composition of the $\text{Fe}(\text{CO}_3)\text{OH}$ component in solid solution in goethite was probably acquired in a system in which three distinct CO_2 components were mixing. The combination of CO_2 derived from atmospheric CO_2 and oxidation of biological material likely totaled no less than 8,000 ppmV and no greater than 16,000 ppmV in this system.

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