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## Goethite, calcite, and organic matter from Permian and Triassic soils: Carbon isotopes and CO<sub>2</sub> concentrations

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**Abstract**—Pedogenic goethites in each of two Early Permian paleosols appear to record mixing of two isotopically distinct CO<sub>2</sub> components—atmospheric CO<sub>2</sub> and CO<sub>2</sub> from in situ oxidation of organic matter. The  $\delta^{13}\text{C}$  values measured for the Fe(CO<sub>3</sub>)OH component in solid solution in these Permian goethites are  $-13.5\text{‰}$  for the Lower Leonardian ( $\sim 283$  Ma BP) paleosol (MCGoeth) and  $-13.9\text{‰}$  for the Upper Leonardian ( $\sim 270$  Ma BP) paleosol (SAP). These goethites contain the most  $^{13}\text{C}$ -rich Fe(CO<sub>3</sub>)OH measured to date for pedogenic goethites crystallized in soils exhibiting mixing of the two aforementioned CO<sub>2</sub> components.  $\delta^{13}\text{C}$  measured for 43 organic matter samples in the Lower Leonardian (Waggoner Ranch Fm.) has an average value of  $-20.3 \pm 1.1\text{‰}$  (1s). The average value yields a calculated Early Permian atmospheric Pco<sub>2</sub> value of about  $1 \times \text{PAL}$ , but the scatter in the measured  $\delta^{13}\text{C}$  values of organic matter permits a calculated maximum Pco<sub>2</sub> of  $11 \times \text{PAL}$  (PAL = present atmospheric level). Measured values of the mole fraction of Fe(CO<sub>3</sub>)OH in MCGoeth and SAP correspond to soil CO<sub>2</sub> concentrations in the Early Permian paleosol profiles of 54,000 and 50,000 ppmV, respectively. Such high soil CO<sub>2</sub> concentrations are similar to modern soils in warm, wet environments.

The average  $\delta^{13}\text{C}$  values of pedogenic calcite from 9 paleosol profiles stratigraphically associated with MCGoeth (Waggoner Ranch Fm.) range from  $-6.5\text{‰}$  to  $-4.4\text{‰}$ , with a mean  $\delta^{13}\text{C}$  value for all profiles of  $-5.4\text{‰}$ . Thus, the value of  $\Delta^{13}\text{C}$  between the pedogenic calcite data set and MCGoeth is  $8.1 (\pm 0.9)\text{‰}$ , which is in reasonable accord with the value of  $7.7\text{‰}$  expected if atmospheric Pco<sub>2</sub> and organic matter  $\delta^{13}\text{C}$  values were the same for both paleosol types. Furthermore, the atmospheric Pco<sub>2</sub> calculated for the Early Permian from the average measured carbon isotopic compositions of the paleosol calcite and organic matter is also analytically indistinguishable from  $1 \times \text{PAL}$ , with a maximum calculated atmospheric Pco<sub>2</sub> (permitted by one standard deviation of the organic matter  $\delta^{13}\text{C}$  value) of  $\sim 5 \times \text{PAL}$ .

If, however, measured average  $\delta^{13}\text{C}$  values of the plant organic matter are more positive than the original soil organic matter as a result of diagenetic loss of  $^{13}\text{C}$ -depleted, labile organic compounds, calculated Permian atmospheric Pco<sub>2</sub> using these  $^{13}\text{C}$ -enriched organic values would underestimate the actual atmospheric Pco<sub>2</sub> using either goethite or calcite. This is the first stratigraphically constrained, intrabasinal study to compare ancient atmospheric CO<sub>2</sub> concentrations calculated from pedogenic goethite and calcite. These results demonstrate that the two different proxies record the same information about atmospheric CO<sub>2</sub>.

The Fe(CO<sub>3</sub>)OH component in pedogenic goethite from a Triassic paleosol in Utah is significantly enriched in  $^{13}\text{C}$  relative to Fe(CO<sub>3</sub>)OH in goethites from soils in which there are mixtures of two isotopic CO<sub>2</sub> components. Field-relationships and the  $\delta^{13}\text{C}$  value ( $-1.9\text{‰}$ ) of the Triassic goethite indicate that this ancient paleosol profile experienced mixing of three isotopically distinct CO<sub>2</sub> components at the time of goethite crystallization. The three components were probably atmospheric CO<sub>2</sub>, CO<sub>2</sub> from in situ oxidation of organic matter and CO<sub>2</sub> from in situ dissolution of preexisting calcite. Although mixing of three isotopically distinct CO<sub>2</sub> components, as recorded by Fe(CO<sub>3</sub>)OH in goethite, has been described in modern soil, this is the first example from a documented paleosol. Its preservation affirms the need for careful, case-by-case assessment of ancient paleosols to establish that goethite in any particular soil is likely to be a valid proxy of atmospheric Pco<sub>2</sub>. Copyright © 2004 Elsevier Ltd

### 1. INTRODUCTION

Carbon dioxide is the dominant atmospheric gas facilitating exchange of carbon among Earth's near-surface carbon reservoirs. Global carbon flux balance models have been developed that identify and attempt to quantify the principal factors influencing the concentration of atmospheric CO<sub>2</sub> in the Phanerozoic (Berner, 1991, 1994, 1997; Berner and Kothavala, 2001; Wallmann, 2001). These models have yielded calculated values of atmospheric CO<sub>2</sub> concentrations that indicate significant

variation of Pco<sub>2</sub> throughout the Phanerozoic and have provided insight into the dynamics of the ancient carbon cycle. However, there is presently a rather limited amount of quantitative paleoenvironmental data based solely on the lithologic record that can be used to test and refine these models. Several recently developed methods have been employed to address this problem (Royer et al., 2001, and references therein). New results that use the following two methods are discussed herein: (1) the concentrations and  $\delta^{13}\text{C}$  values of the Fe(CO<sub>3</sub>)OH component in solid-solution in the common low-temperature mineral goethite [ $\alpha$ -FeOOH] (Yapp, 1987; Yapp and Poths, 1990, 1991, 1992, 1993, 1996) and (2) the  $\delta^{13}\text{C}$  values of pedogenic calcite (e.g., Cerling, 1991; Mora et al., 1996; Ekart

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et al., 1999). Pedogenic calcite typically forms in relatively dry soils, whereas pedogenic goethite is found in wet environments. Despite this obvious difference in the conditions of formation, the two systems exhibit similar overall patterns of temporal variation of  $\delta^{13}\text{C}$  throughout the Phanerozoic, because both types of soils are open to exchange with the atmospheric  $\text{CO}_2$  reservoir (Yapp and Poths, 1996).

The common low-temperature mineral goethite ( $\alpha\text{-FeOOH}$ ) exists in solid solution with small amounts of a ferric carbonate component ( $\text{Fe}(\text{CO}_3)\text{OH}$ ). The concentration and carbon isotopic composition of the ferric carbonate component are a function of the concentration and  $\delta^{13}\text{C}$ , respectively, of the  $\text{CO}_2$  present during crystallization of goethite (Yapp, 1987, 2001; Yapp and Poths, 1991, 1992, 1993, 1996). On the basis of the  $\delta^{13}\text{C}$  values of the  $\text{Fe}(\text{CO}_3)\text{OH}$  and inferred paragenetic pathways of goethite formation, Hsieh and Yapp (1999) and Yapp (2001) concluded that the  $\text{Fe}(\text{CO}_3)\text{OH}$  in goethite commonly records information on mixing of  $\text{CO}_2$  in systems with either two or three isotopically distinct  $\text{CO}_2$  components. Apparent two-component mixing in soils involves  $\text{CO}_2$  from the open atmosphere and  $\text{CO}_2$  from oxidation of organic matter in the soil. Goethites formed in such environments may preserve information on the partial pressure of  $\text{CO}_2$  in the Earth's ancient atmosphere. A mixing system with three isotopically distinct components could include  $\text{CO}_2$  from the oxidation of organic matter in the soil,  $\text{CO}_2$  from the open atmosphere, and  $\text{CO}_2$  from dissolution of pre existing carbonates such as calcite (Hsieh and Yapp, 1999; Yapp, 2001). The addition of  $\text{CO}_2$  from dissolution of carbonate in a soil would preclude calculation of ancient atmospheric  $\text{P}\text{CO}_2$  using the  $\text{Fe}(\text{CO}_3)\text{OH}$  component in goethite (Yapp, 2001).

In this paper, we present analyses of the concentration and  $\delta^{13}\text{C}$  values of the  $\text{Fe}(\text{CO}_3)\text{OH}$  component in pedogenic goethite from Permian and Triassic age strata as well as data from associated pedogenic calcite and organic matter. The data from the goethites are used in combination with field relations to distinguish between mixing of either two or three isotopic components of  $\text{CO}_2$  in the ancient soils. Concentrations of Early Permian atmospheric  $\text{CO}_2$  are estimated from the 2-component systems.

## 2. SAMPLES AND FIELD SETTING

The iron (III) oxide-rich samples analyzed in this work represent (1) an Early Permian (Lower Leonardian,  $\sim 283$  Ma BP) rhizo-structure (MCGoeth), composed largely of goethite, from the Waggoner Ranch Formation of north-central Texas; (2) an Early Permian (Upper Leonardian  $\sim 270$  Ma BP) goethite-replaced fossil plant (SAP) from the Blaine Formation of north-central Texas; and (3) a Triassic ironstone sample (TRIUT#2) from a paleosol that represents at least part of the hiatus between deposition of the Middle Triassic (Anisian) Moenkopi Formation and Late Triassic (Norian) Chinle Formation near Natural Bridges State Park in southeastern Utah. The strata associated with the Triassic-age ironstone are informally named the "mottled beds" (e.g. Lucas and Morales, 1993). The parent materials for MCGoeth and TRIUT#2 are thinly bedded to laminated alluvial mudstones dominated by 2:1 phyllosilicates and quartz (Tabor, 2002). The MCGoeth profile formed upon the eastern Flank of the Midland Basin.

Subsequent diagenesis of the Midland Basin has been mild, with maximum burial temperatures in Early Permian strata along the flanks of the basin never exceeding 40–45°C (Bein and Land, 1983).

The paleosol containing the MCGoeth sample is thin ( $\sim 18$  cm) and noncalcareous (Fig. 1AA). Given that this paleosol has no soil structure or secondary accumulation of pedogenic minerals other than rooting structures that are replaced by goethite, it likely formed under moist to saturated conditions. In addition, the profile exhibits low chroma and high value matrix colors indicative of seasonally poorly drained conditions in modern soils (Type E paleosols in Tabor, 2002; Tabor and Montañez, 2002; aquents in Soil Survey Staff, 1998). The MCGoeth sample was collected 15 cm beneath the surface of the profile. The goethite occurs as stacked "discs" with concentric bands around a central circular cavity (Figs. 1A,B). Nine different calcite-bearing paleosol profiles stratigraphically associated with the MCGoeth profile were also logged and described in the field and calcite samples from each paleosol were collected for isotopic analysis. Care was taken to sample carbonates from the deeper portions of each pedogenic carbonate horizon. Two different paleosol morphologies were recognized: (1) angular blocky, reddish-brown mudstones with horizons bearing discrete micritic calcite nodules ranging in size from a few mm to  $\sim 5$  cm in diameter (Fig. 1C). These paleosols are interpreted as calcisols (Mack et al., 1993) and may have been inceptisol-like soils (Soil Survey Staff, 1998). (2) Reddish-brown to gray clay-rich mudstones with wedge-shaped aggregate structure and slickensides at depth grading upward to angular blocky structure with mud and sand-filled clastic dikes extending downward from the interpreted surface (Fig. 1D). Calcite in this latter morphology occurs as both discrete micritic calcite nodules and as lenses of coalesced and cemented micritic nodules along slicken plane surfaces. These paleosols are interpreted as calcic vertisols (Mack et al., 1993) and may have been xerert soils (Soil Survey Staff, 1998).

The TRIUT profile is approximately 3.5 m thick with a 1.5 m thick stage III Bkm horizon (*sensu* Machette, 1985) near the base of the profile that is overlain by a one meter thick, medium subangular blocky, noncalcareous horizon composed of kaolinite, quartz and goethite (Fig. 2). The original surface of this soil was likely truncated, given that parts of the existing profile are deeply scoured and the overlying conglomerate contains calcareous and goethite nodules similar to those in the paleosol profile. These superimposed pedogenic horizons likely formed during two distinctly different episodes of pedogenesis resulting from at least two different episodes of climate: (1) an earlier drier climate related to development of the Bk horizon and (2) a subsequent wetter climate related to desilication of 2:1 expandable phyllosilicates and production of Fe-oxyhydroxides and, almost certainly, dissolution of calcite. This paleosol is interpreted to be a calcisol (Mack et al., 1993). The goethite is most concentrated near the top of the profile and occurs as both massive nodular and vermicular concretions and as thick coatings upon paleosol ped structures (ferrans; Brewer, 1976). TRIUT#2 is an example of goethite ferrans collected at a depth between 40 and 60 cm below the truncated surface of the profile (Fig. 2).

SAP is a fossilized goethitic wood fragment from the Leonardian Blaine Formation of north Texas. The material was found

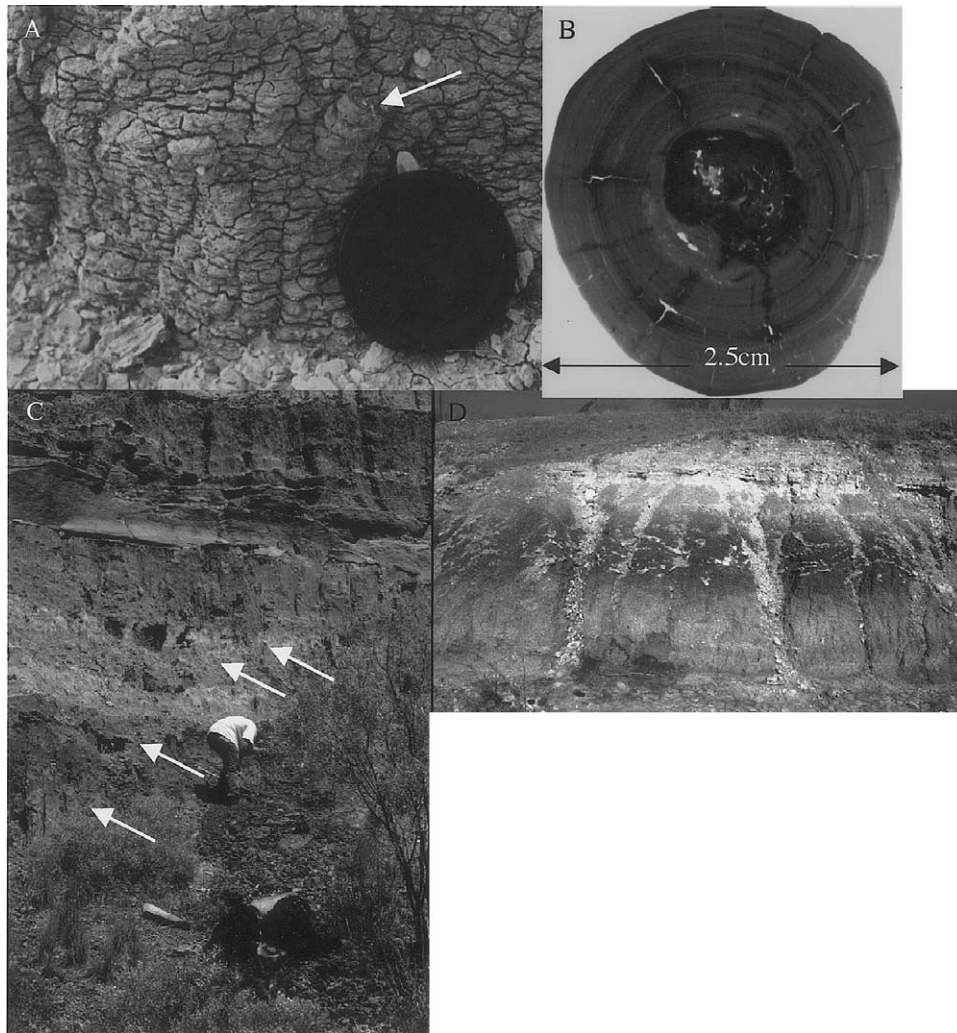


Fig. 1. Field and petrographic photographs of the paleosols and samples associated with MCGoeth. (A) Field photograph of the paleosol from which the MCGoeth sample was collected. Goethite in this sample occurs as vertical to subvertical stacked “discs” (arrow). MCGoeth was sampled near the base of the profile, approximately 15 cm beneath the interpreted profile surface. The 35 mm camera lens cap is for scale. (B) Thin-section photograph of the MCGoeth sample. The sample is dominantly composed of goethite with substituent kaolinite and quartz situated as concentric rings about a central circular cavity or mud-filled axis (see text). (C) Field photograph of the Waggoner Ranch Formation stratigraphy. The base of the outcrop approximately correlates with the stratigraphic position of the MCGoeth profile. Arrows point to clearly observable nodular calcium carbonate-bearing horizons that represent paleosol profiles interpreted to have been inceptionisols (Soil Survey Staff, 1998) or calcisols (Mack et al., 1993) in this work. (D) Field photograph of paleosol profile near the top of the Waggoner Ranch Formation. The white, lenticular subhorizontal features in the darkest horizon near the center of the photograph are interpreted to be pedogenic calcium carbonate. This profile is representative of the two profiles interpreted to have been vertisols, or possibly xererts (Soil Survey Staff, 1998; Mack et al., 1993) in this work. The total thickness of the red-bed sequence in this photograph is ~3.5 m.

near the top of an exposed north-south trending paleochannel that is approximately 2 m deep and 10 m wide (Fig. 3). The sedimentary fill within the channel is composed primarily of gray siltstone and claystone channeled into older red mudstone. The lower 60 cm of the channel contains gently inclined thin carbonate lenses. Petrographic analysis of these lenses indicates structures similar to those observed in algal mats (Scholle, 1978). Furthermore, XRD analysis indicates the carbonate lenses are composed of ankerite  $[\text{Fe}_{0.3}\text{Mg}_{0.7}\text{Ca}(\text{CO}_3)_2]$  ( $\delta^{13}\text{C} = -3.1\text{‰}$ ). A large channel-depth to width ratio and close stratigraphic association with bedded gypsum and marine ammonite-bearing carbonates suggest this struc-

ture is a paleo-tidal channel. SAP was taken from a single log longitudinally oriented along the top of the channel axis.

Field-based observations suggest MCGoeth and TRIUT#2 formed as a result of pedogenesis, and therefore the concentration and the stable isotope composition of the  $\text{Fe}(\text{CO}_3)\text{OH}$  component should provide a record of Early Permian and Early Triassic conditions, respectively. There are no obvious field criteria to indicate that SAP was permineralized in the soil environment. However, recent work by Dunn and others (1997) shows that iron-replacement of plant organic matter is a relatively rapid microbially mediated process that occurs on the

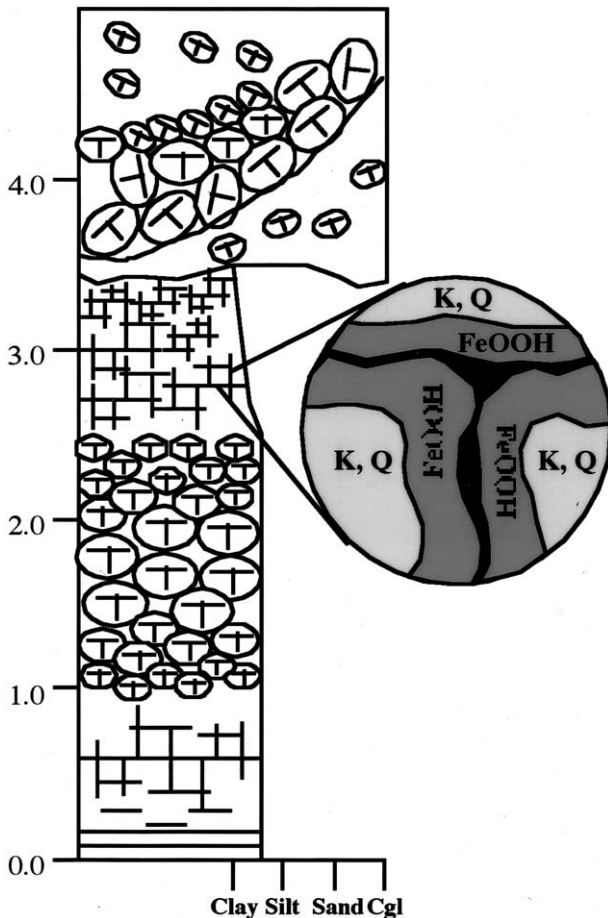


Fig. 2. Field sketch of the Triassic-age paleosol profile associated with TRIUT#2. Subcircular structures represent calcium carbonate nodules. Cross-hatch pattern represents subangular blocky structure interpreted as original soil structure. Magnified (~1.25 cm across) outset portion of sketch illustrates the goethite-enriched ferrans (Brewer, 1976), or coatings, associated with the soil structure representing the TRIUT sample.

order of weeks to years. Furthermore, the fact that this sample appears to preserve the original structure of the woody tissue from the plant suggests that the SAP goethite (a ferric oxyhydroxide) replaced the original organic matter in an aerobic environment soon after burial.

### 3. EXPERIMENTAL METHODS

Prior to analysis, goethite samples were hand-picked from bulk soil matrix material. Analyses were then performed according to published procedures (Yapp, 1998; Yapp and Poths, 1991, 1993; Hsieh and Yapp, 1999). Samples were ground under reagent grade acetone and sized by passage through a brass sieve. Only the size fraction less than 63  $\mu\text{m}$  was used for isotopic analysis. Samples were chemically pretreated with 0.5 M HCl for about 20 h at room temperature to remove calcite that may have been present, then rinsed with deionized water. This was followed by six to eight successive 30%  $\text{H}_2\text{O}_2$  treatments at room temperature to remove organics (cf. Yapp and Poths, 1991, 1993) with subsequent drying under vacuum at room temperature. The mineralogy of the samples was verified by X-ray diffraction (XRD) analysis on a Diano 8500 diffractometer with  $\text{Cu-K}\alpha$  radiation. Measurements were performed with step-scan increments of  $0.01^\circ 2\theta$ , counting times of 12 s per increment, 0.5/1.0 mm for the primary slits and 0.2/0.3 mm for

the receiving slits (Schulze, 1984). Due to the limited amount of sample available for analysis, the same aliquot used in XRD was also used for isotopic analysis.

Abundance and  $\delta^{13}\text{C}$  data for the iron (III) carbonate component in goethite were measured at the Department of Geological Sciences, Southern Methodist University, on 0.5 M HCl +  $\text{H}_2\text{O}_2$ -treated samples 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 Appendix 1. The  $\text{CO}_2$  and  $\text{H}_2\text{O}$  collected at each step were separated cryogenically. The evolved water was quantitatively converted to  $\text{H}_2$  over uranium at about  $800^\circ\text{C}$ . Yields of  $\text{H}_2$  and  $\text{CO}_2$  were measured manometrically.  $\text{H}_2$  yield was measured with a precision of about  $\pm 1 \mu\text{mol}$ . For  $\text{CO}_2$ , differences in yield of about  $0.2 \mu\text{mol}$  could be resolved. Amounts of  $\text{CO}_2$  as low as  $0.2 \mu\text{mol}$  can be evolved from the  $\text{Fe}(\text{CO}_3)\text{OH}$  in a single step during incremental dehydration-decarbonation. Samples of evolved  $\text{CO}_2$  were analyzed for  $\delta^{13}\text{C}$  values on a Finnigan MAT 252 mass spectrometer, where

$$\delta^{13}\text{C} = \left[ \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 1000\text{‰},$$

$R = {}^{13}\text{C}/{}^{12}\text{C}$  and the standard is PDB (Craig, 1957). The analytical uncertainty of the  $\delta^{13}\text{C}$  value of  $\text{Fe}(\text{CO}_3)\text{OH}$  is about  $\pm 0.2\text{‰}$  (Yapp and Poths, 1993).

Calcites from calcitic paleosols stratigraphically associated with the goethite-rich MCGoeth and TRIUT#2 paleosols were also collected. Doubly polished thin sections were analyzed petrographically to differentiate original pedogenic carbonate fabrics from later, diagenetic fabrics (Deutz et al., 2001). Areas in the carbonate nodules and rhizoliths that exhibit pedogenic textures were microsampled in order to avoid calcite microspar or sparry cements. Approximately 50  $\mu\text{g}$  of carbonate powder were roasted at  $375^\circ\text{C}$  in vacuum for three hours to remove organics.  $\delta^{13}\text{C}$  analyses from all calcite samples were carried out on a Fisons-Optima IR gas source mass spectrometer in the Department of Geology at UC Davis. Replicate analysis of NBS-19 yielded  $\delta^{13}\text{C}$  values of  $1.92\text{‰} \pm 0.14$  and  $\delta^{13}\text{C}$  values of  $-2.07\text{‰} \pm 0.15$  ( $n = 39$ ) relative to PDB over the period of analyses.

Organic samples were either collected by the authors or obtained from the Smithsonian Institution of Natural History (with whom we jointly collected samples in the field). Organic samples were hand picked with cleaned metal probe and tweezers and placed into cleaned Pyrex test tubes. The samples were treated with 1 N HCl for ~16 h at room temperature and then rinsed four times with distilled  $\text{H}_2\text{O}$  to remove any carbonate and potentially younger, hydrolysable carbon. All organic samples were dried at room temperature under vacuum desiccation. Approximately 60 to 96  $\mu\text{g}$  of cleaned sample was loaded in tin boats.  $\delta^{13}\text{C}$  analysis was carried out on an Isoprime isotope ratio mass spectrometer interfaced to a Carlo Erba elemental analyzer housed at the University of California, Davis. The concentration of organics in the distilled water is  $<1$  ppm, and therefore should have

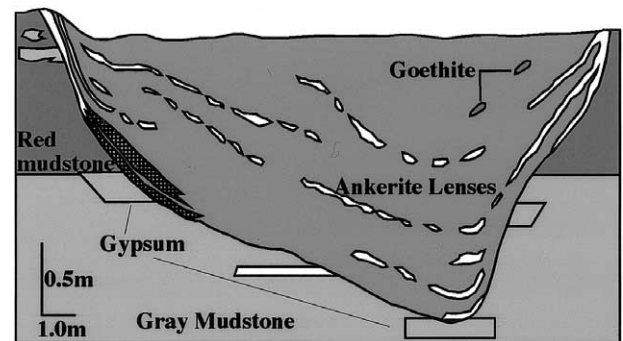


Fig. 3. Field sketch of the Permian-age deposit from which the SAP sample was collected. The SAP sample was taken from a permineralized log near the top of the deposit. See text for details.

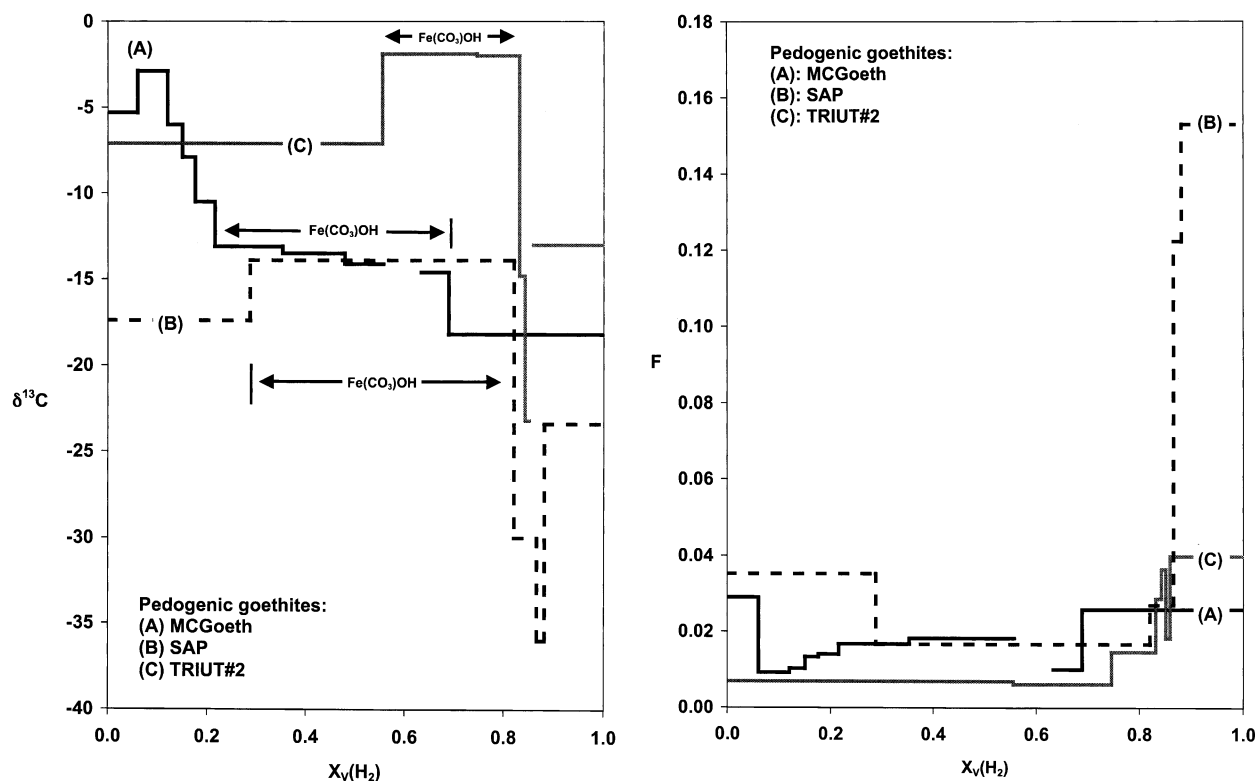


Fig. 4. Incremental dehydration spectra for (A) MCGoeth, (B) SAP and (C) TRIUT#2. The “plateaus” in  $\delta^{13}\text{C}$  and  $F$  values are interpreted as the  $\text{Fe}(\text{CO}_3)\text{OH}$  component of the goethite. See Appendix 1 for tabulated results of dehydration-decarbonation experiments.

had no significant effect on the resulting measured isotopic composition of the samples.

## 4. RESULTS

### 4.1. Pedogenic Goethites

The results of the incremental dehydration-decarbonation analyses of the Permian and Triassic goethite samples are tabulated in Appendix 1 and depicted as incremental dehydration-decarbonation spectra in Figure 4. The progress variable  $X_v(\text{H}_2)$  is the cumulative sum of evolved  $\text{H}_2$  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 4b 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  $\text{CO}_2$  evolved in an increment of goethite dehydration-decarbonation, and  $n(\text{H}_2\text{O}) = \mu\text{mol}$  of  $\text{H}_2\text{O}$  evolved over that same increment.

Previous work has shown that, for  $X_v(\text{H}_2)$  values from about 0.2 or 0.3 to about 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  $\text{CO}_2$  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  $850^\circ\text{C}$  step (and, at times, the longer duration

vacuum dehydration steps that immediately precede the  $850^\circ\text{C}$  step) commonly does not exhibit these plateau values, because this increment may include  $\text{CO}_2$  from oxidation of refractory organic matter (Yapp and Poths, 1991, 1992, 1993). Note that the different goethites of this study have different plateau  $\delta^{13}\text{C}$  and  $F$  values (Fig. 1). Average plateau  $\delta^{13}\text{C}$  values for these samples are  $-1.9\text{‰}$  for TRIUT#2,  $-13.5\text{‰}$  for MCGoeth and  $-13.9\text{‰}$  for SAP with analytical uncertainties of about  $\pm 0.2\text{‰}$  (see Table 1; Appendix 1).

### 4.2. Pedogenic Carbonates and Plant Organic Matter

Twenty-three calcite nodules from nine calcitic paleosol profiles stratigraphically associated with the MCGoeth goe-

Table 1. Pedogenic goethite data.

Sample	Depth (cm) <sup>a</sup>	Location	Age	$X^b$	$1/X$	$\delta^{13}\text{C}_{m(\text{go})}$ (‰)
MCGoeth	15	Texas	Early Permian	0.0090	111	-13.5
SAP	—	Texas	Early Permian	0.0083	120	-13.9
TRIUT#2	40–60	Utah	Early-Late Triassic	0.0030	333	-1.9

<sup>a</sup> Depth below interpreted paleosol surface.

<sup>b</sup> See text for definitions of  $X$  and  $\delta^{13}\text{C}_{m(\text{go})}$ .

Table 2.  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of pedogenic calcites associated with the MCGoeth profile.

Single nodules from different calcitic soils			Average values for different calcitic soils		Average value for Waggoner
Stratigraphic height (m) <sup>a</sup>	$\delta^{13}\text{C}_{\text{ca}}$	$\delta^{18}\text{O}_{\text{ca}}$	Avg. stratigraphic height of soil <sup>b</sup> (m)	Avg. paleosol $\delta^{13}\text{C}_{\text{ca}}$ <sup>c</sup>	Ranch Fm. $\delta^{13}\text{C}_{\text{cc}}$
WRCc soil #9					
18.2	-5.2	1.8	18.2	-5.2 (n = 1)	-5.4 (n = 23)
WRCc soil #8					
15.5	-5.3	0.4	15.5	-5.3 (n = 1)	
WRCc soil #7					
13.7	-4.6	1.1	13.5	-5.3 (n = 5)	
13.6	-4.2	0.7			
13.5	-4.8	1.0			
13.4	-4.8	1.2			
13.3	-7.9	-3.2			
WRCc soil #6					
9.0	-5.7	-0.1	8.5	-5.3 (n = 4)	
8.8	-6.0	0.8			
8.6	-3.7	1.3			
7.6	-5.9	1.2			
WRCc soil #5					
7.0	-5.5	0.8	6.5	-5.4 (n = 2)	
6.0	-5.4	0.2			
WRCcl soil #4					
5.8	-4.6	0.5	5.8	-4.6 (n = 2)	
5.8	-4.6	0.8			
WRCc soil #3					
5.6	-4.8	-0.6	5.6	-4.8 (n = 1)	
WRCc soil #2					
5.4	-7.8	-2.8	5.3	-6.5 (n = 5)	
5.4	-6.2	-3.8			
5.4	-4.8	-0.6			
5.1	-6.9	-2.2			
5.1	-6.7	-2.4			
WRCc soil #1					
3.3	-4.9	0.7	3.3	-4.4 (n = 2)	
3.3	-3.8	1.1			

<sup>a</sup> Height (m) above the LS1 marine limestone of the Permian Waggoner Ranch Formation (Hentz, 1988).

<sup>b</sup> Average height of a soil profile (average for individual calcite nodules from the same paleosol profile).

<sup>c</sup> Average  $\delta^{13}\text{C}_{\text{m(cc)}}$  value of a soil profile (average of individual calcite nodules from the same paleosol profile).

thite-rich profile have an average  $\delta^{13}\text{C}$  of  $-5.4 \pm 1.1\%$  and an average  $\delta^{18}\text{O}$  value of  $-0.10 \pm 1.6\%$  (Table 2), where the uncertainty of the mean represents one standard deviation (1s). The lower seven paleosol profiles are interpreted as calcisols and the upper two paleosol profiles are calcic vertisols (Mack et al., 1993). There is no significant change in average  $\delta^{13}\text{C}$  or  $\delta^{18}\text{O}$  values of calcite nodules in individual soil profiles through the stratigraphic section with the exception of paleosol #2 (Table 2), a calcisol at  $\sim 5$  m in Figure 5. The range of  $\delta^{13}\text{C}$  values exhibited by individual soil nodules within a single soil profile is greater than the range exhibited by the average values among the different paleosol profiles. Four calcite nodules from the Bk horizon beneath the goethite-rich horizon in the TRIUT paleosol have an average  $\delta^{13}\text{C}$  value of  $-5.5 \pm 0.3\%$  and an average  $\delta^{18}\text{O}$  of  $-4.8 \pm 0.5\%$  (Table 3). The observed scatter in the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  compositions of the paleopedogenic calcites from the Permian and Triassic age profiles are well within the limits of the observed scatter in modern pedogenic calcites (e.g. Cerling and Quade, 1993; Deutz et al., 2001).

Carbon isotope analyses of the organic matter in 43 fossilized vascular plants from six stratigraphic horizons in the Waggoner Ranch Formation have an average  $\delta^{13}\text{C}$  of  $-20.3 \pm 1.1\%$  (Table 4, Fig. 5). This  $\delta^{13}\text{C}$  value is significantly more

positive than the  $\delta^{13}\text{C}$  values observed in modern  $\text{C}_3$  plants (e.g., Arens et al., 2000). Similar relatively positive  $\delta^{13}\text{C}$  values were measured for 10 fossilized vascular plant fossils within 20 m stratigraphically of the SAP horizon (average  $\delta^{13}\text{C} = -20.6 \pm 0.9\%$ , Table 4).

There were no organic matter samples found in the TRIUT paleosol or the associated strata. However, the 850°C increment from the TRIUT#2 goethite has a carbon isotope composition of  $-13.0 \pm 0.2\%$ , suggesting the contribution of  $\text{CO}_2$  from oxidation of some small amount of refractory organic carbon in this goethite.

## 5. DISCUSSION

### 5.1. Soil $\text{CO}_2$ Mixing Models

On the basis of geological arguments and the measured mole fraction (X) and  $\delta^{13}\text{C}$  values of the  $\text{Fe}(\text{CO}_3)\text{OH}$  in pedogenic goethites, Hsieh and Yapp (1999) and Yapp (2001) concluded that either two-component or three-component  $\text{CO}_2$  mixing relationships can exist in various wet soils. The two-component mixing concept assumes that the only two sources contributing to soil  $\text{CO}_2$  are  $\text{CO}_2$  from the open atmosphere and  $\text{CO}_2$  from

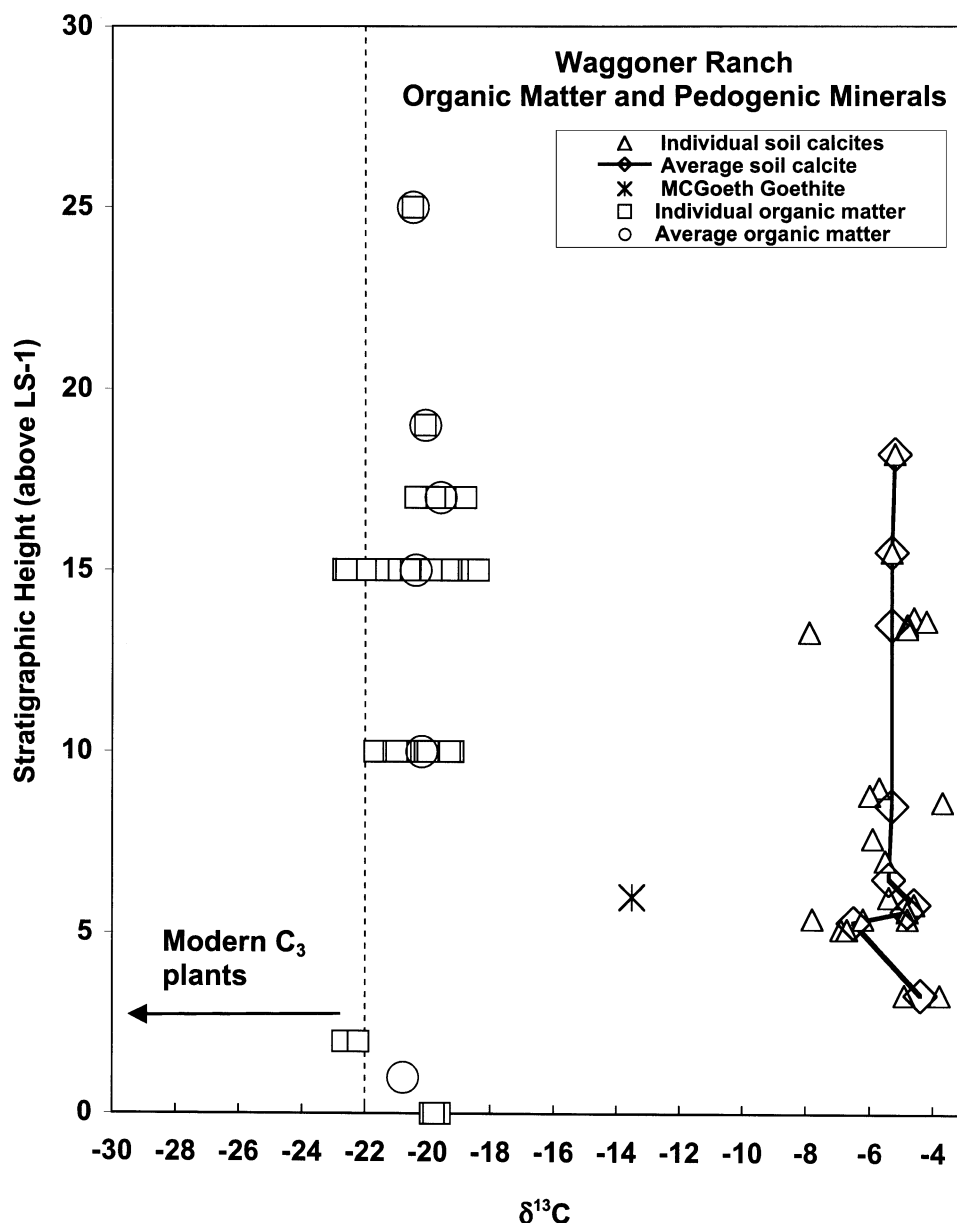


Fig. 5. A plot of  $\delta^{13}\text{C}$  vs. stratigraphic height (m) above LS-1 (Hentz, 1988) for pedogenic calcite nodules (triangles) and plant organic matter (squares). The mean  $\delta^{13}\text{C}$  values of pedogenic calcite nodules for individual paleosol profiles are plotted as diamonds, whereas the mean  $\delta^{13}\text{C}$  values of plant organic matter are plotted as circles. The dashed line at  $-22\text{‰}$  denotes the approximate upper limit of  $\delta^{13}\text{C}$  values measured for modern  $\text{C}_3$  plants (see text), while the arrow indicates the approximate range of  $\delta^{13}\text{C}$  values of modern  $\text{C}_3$  plants. The cross represents the MCGoeth sample.

in situ oxidation of biological carbon in the soil. The concept of 3-component mixing assumes an additional source of  $\text{CO}_2$  that is derived from the in situ dissolution of preexisting carbonates such as calcite. Carbon dioxide that is produced from dissolution of carbonate generally is enriched in  $^{13}\text{C}$  relative to atmospheric  $\text{CO}_2$  or  $\text{CO}_2$  from oxidation of biological material in the soil (e.g., Hoefs, 1997). The practical ramification of these mixing relationships is that  $\delta^{13}\text{C}$  values for  $\text{Fe}(\text{CO}_3)\text{OH}$  in goethites formed in three-component systems are typically much more positive than those for goethites from two-component systems (Yapp, 2001).

#### 5.1.1. Mixing in soils with two $\text{CO}_2$ components (MCGoeth and SAP)

Although younger and older paleosol profiles stratigraphically above and below the MCGoeth profile contain pedogenic calcite, the MCGoeth profile itself is noncalcareous. In addition, the local sedimentary fill from which SAP was collected is noncalcareous, although, as noted, there are ankerite lenses  $\sim 1.5$  m beneath the position of the goethitic wood fragment. This ankerite contains ferrous [Fe(II)] iron and represents formation in a reducing environment in contrast to the oxidizing

environment that would have characterized goethite crystallization. It is unlikely that the absence of carbonate in MCGoeth and SAP represents carbonate leaching during burial diagenesis, because most formational waters are saturated with respect to calcite (Choquette and James, 1990). On the basis of these lines of evidence, it seems probable that the sediments associated with MCGoeth and SAP were noncalcareous at the time of goethite crystallization. Therefore, it is most likely that MCGoeth and SAP formed in soils with mixing of two isotopically distinct endmembers (CO<sub>2</sub> from oxidation of biological carbon and atmospheric CO<sub>2</sub>).

Steady-state solutions to the one-dimensional Fickian diffusion equation provide good representation of depth-dependent CO<sub>2</sub> concentrations in modern soils (Cerling, 1984). In these models, the Earth's atmosphere is the upper boundary condition, and there is a depth-dependent CO<sub>2</sub> production term that describes the oxidation of organic carbon in the soil. Thus, the CO<sub>2</sub> in soil gas can generally be regarded as a mixture of two isotopically distinct end members *in a two-component soil*: atmospheric CO<sub>2</sub> and CO<sub>2</sub> derived from the oxidation of biological material. It is known from previous studies that the concentration and δ<sup>13</sup>C value of the Fe(CO<sub>3</sub>)OH component in goethite reflect the partial pressure and δ<sup>13</sup>C value of CO<sub>2</sub> present during goethite formation (Yapp, 1987; Yapp and Poths, 1991, 1992, 1993, 1996; Hsieh and Yapp, 1999). For the Fe(CO<sub>3</sub>)OH component in pedogenic goethite as a proxy of soil CO<sub>2</sub>, the steady-state two-end-member mixing equation can be expressed as follows (Yapp and Poths, 1992, 1993):

$$\delta^{13}\text{C}_m = [(\delta^{13}\text{C}_A - \delta^{13}\text{C}_O)X_A] \left[ \frac{1}{X_m} \right] + \delta^{13}\text{C}_O \quad (1a)$$

$$\delta^{13}\text{C}_O = [\alpha_k \delta^{13}\text{C}_B + 1000(\alpha_k - 1)]. \quad (1b)$$

δ<sup>13</sup>C<sub>O</sub> arises from the derivation of Eqn 1 (Yapp and Poths, 1993; Yapp, 2001) and represents the isotopic effects of CO<sub>2</sub> diffusion in the soils. In other words, δ<sup>13</sup>C<sub>O</sub> accounts for the diffusive modification of δ<sup>13</sup>C<sub>B</sub>. α<sub>k</sub> is the ratio of the soil diffusion coefficients of the CO<sub>2</sub> molecules with mass numbers 44 and 45 (<sup>44</sup>D/<sup>45</sup>D). The value of α<sub>k</sub> is 1.0044 (Cerling et al., 1991). δ<sup>13</sup>C<sub>B</sub> is the δ<sup>13</sup>C value of the Fe(CO<sub>3</sub>)OH if it were in equilibrium with gaseous CO<sub>2</sub> which had the same carbon isotope ratio as the biological carbon being oxidized in the soil profile (Yapp, 2001). The carbon isotope fractionation factor between Fe(CO<sub>3</sub>)OH in goethite and gaseous CO<sub>2</sub> is about 1.0025 at 25°C (Yapp and Poths, 1993). δ<sup>13</sup>C<sub>m</sub> is the measured δ<sup>13</sup>C value of the Fe(CO<sub>3</sub>)OH component in goethite; δ<sup>13</sup>C<sub>A</sub> would be the δ<sup>13</sup>C value of the Fe(CO<sub>3</sub>)OH component if atmospheric CO<sub>2</sub> were the only CO<sub>2</sub> in the soil; X<sub>m</sub> is the measured value of X for the Fe(CO<sub>3</sub>)OH component in goe-

Table 3. Pedogenic calcite δ<sup>13</sup>C and δ<sup>18</sup>O values from the TRIUT profile.

Depth (cm) <sup>a</sup>	δ <sup>13</sup> C <sub>ca</sub>	δ <sup>18</sup> O <sub>ca</sub>
100	-5.1	-5.4
120	-5.7	-4.2
120	-5.7	-4.7
120	-5.4	-5.1

<sup>a</sup> Centimeters beneath interpreted paleosol surface.

Table 4. Plant organic matter δ<sup>13</sup>C values (Early Permian strata of north Texas).

Formation <sup>a</sup>	δ <sup>13</sup> C	Meters above LS-1 <sup>b</sup>
Waggoner Ranch	-19.6	0
Waggoner Ranch	-19.9	0
Waggoner Ranch	-19.8	0
Waggoner Ranch	-22.7	2
Waggoner Ranch	-22.2	2
Waggoner Ranch	-20.5	10
Waggoner Ranch	-20.4	10
Waggoner Ranch	-20.2	10
Waggoner Ranch	-19.3	10
Waggoner Ranch	-19.7	10
Waggoner Ranch	-19.7	10
Waggoner Ranch	-20.1	10
Waggoner Ranch	-20	10
Waggoner Ranch	-21.7	10
Waggoner Ranch	-21.1	10
Waggoner Ranch	-21	10
Waggoner Ranch	-19.2	10
Waggoner Ranch	-19.3	10
Waggoner Ranch	-19.5	15
Waggoner Ranch	-19.5	15
Waggoner Ranch	-19.3	15
Waggoner Ranch	-20.2	15
Waggoner Ranch	-20.2	15
Waggoner Ranch	-19.3	15
Waggoner Ranch	-18.7	15
Waggoner Ranch	-20.6	15
Waggoner Ranch	-18.6	15
Waggoner Ranch	-18.4	15
Waggoner Ranch	-21.2	15
Waggoner Ranch	-21.6	15
Waggoner Ranch	-22	15
Waggoner Ranch	-22	15
Waggoner Ranch	-22.7	15
Waggoner Ranch	-22.6	15
Waggoner Ranch	-19.9	15
Waggoner Ranch	-19.9	15
Waggoner Ranch	-19.4	17
Waggoner Ranch	-18.8	17
Waggoner Ranch	-19.8	17
Waggoner Ranch	-20.4	17
Waggoner Ranch	-20.1	19
Waggoner Ranch	-20.5	25
Waggoner Ranch	Average = -20.3‰ (±1.1)	
Blaine	-22	
Blaine	-22	
Blaine	-21.1	
Blaine	-20.5	
Blaine	-21.4	
Blaine	-19.5	
Blaine	-19.7	
Blaine	-19.7	
Blaine	-20.2	
Blaine	-20.2	
Blaine	Average = -20.6‰ (±0.9)	

<sup>a</sup> Samples from the Waggoner Ranch Formation are used for calculation of δ<sup>13</sup>C<sub>O</sub> values associated with the ferric carbonate component of MCGoeth, whereas samples from the Blaine Formation are used for calculation of δ<sup>13</sup>C<sub>O</sub> values associated with the ferric carbonate component of SAP.

<sup>b</sup> LS-1 is a regionally traceable fusulinid-bearing limestone on the Eastern Shelf of the Midland Basin (Hentz, 1988).

thite; X<sub>A</sub> is the value of X for the Fe(CO<sub>3</sub>)OH component if atmospheric CO<sub>2</sub> were the only CO<sub>2</sub> in the soil. Equation 1 indicates that, in a plot of δ<sup>13</sup>C<sub>m</sub> vs. 1/X<sub>m</sub>, goethite samples



from the shallower portions of any particular soil will yield a linear array with a positive slope from which an apparent  $P_{CO_2}$  for Earth's ancient atmosphere can be calculated (Yapp and Poths, 1992, 1993, 1994, 1996; Yapp, 2001).

Moreover, combination of the  $X_m$  values with the Henry's Law Equation of Yapp and Poths (1992) for pedogenic goethites yields calculated soil  $CO_2$  concentrations. For the MCGoeth and SAP paleosols, these concentrations are  $\sim 54,000$  and  $50,000$  ppmV, respectively. Such soil  $CO_2$  concentrations are well within the expected range for wet soils (Yapp and Poths, 1996).

### 5.1.2. Constraints on atmospheric $P_{CO_2}$ from MCGoeth and SAP

The value of  $(\delta^{13}C_A - \delta^{13}C_O)$  in Eqn. 1, is assumed to be the same at all times in the Phanerozoic for  $C_3$  photosynthesis. A value of  $+16\text{‰}$  was adopted by Yapp and Poths (1996), because it represents the approximate difference between the estimated  $\delta^{13}C$  values of pre-industrial atmospheric  $CO_2$  ( $-6.5\text{‰}$ ) and recent  $C_3$  continental biota ( $-27\text{‰}$ ), after the latter value is adjusted for the diffusive  $4.4\text{‰}$  enrichment in  $\delta^{13}C$  in the biologically derived  $CO_2$  of the soil. Although, as discussed later, the measured  $\delta^{13}C$  values of the fossilized plants presented in Table 4 are very positive for the  $C_3$  photosynthetic pathway, there is, thus far, no evidence to suggest that  $C_4$  or CAM photosynthetic pathways were present in pre-Cenozoic time (e.g., Cerling, 1991). Therefore, a value of  $+16\text{‰}$  for  $\delta^{13}C_A - \delta^{13}C_O$  is also used in calculations in the current work. It should be pointed out that errors in the selection of a value for  $\delta^{13}C_A - \delta^{13}C_O$  should not have a large effect on the calculated values of atmospheric  $CO_2$ . For example, if the uncertainty in the value of  $\delta^{13}C_A - \delta^{13}C_O$  were as large as  $4\text{‰}$ , the relative error in the calculated partial pressure of atmospheric  $CO_2$  would be 25%. Such an uncertainty would have little effect on the general conclusions about long term temporal variations of atmospheric  $CO_2$  concentrations that range from a few hundred to several thousand ppmV (e.g., Royer et al., 2001).

Preliminary temperatures of crystallization of  $26 \pm 3^\circ C$  and  $22 \pm 3^\circ C$  have been calculated for SAP and TRIUT#2, respectively, from oxygen and hydrogen isotopic compositions of the goethites (Tabor, 2002). Given that the calculated temperatures of these two samples are identical within analytical uncertainty, a temperature of  $25^\circ C$  will be adopted as their approximate temperature of formation, and this same temperature will be assumed to apply to the goethite from the MCGoeth paleosol (cf. Yapp and Poths, 1996).

$\delta^{13}C_O$  values were calculated from the measured  $\delta^{13}C$  values of the organic matter reported in Table 4 (cf. Yapp and Poths, 1996). These  $\delta^{13}C_O$  values were used, in turn, to calculate two-component mixing lines for the MCGoeth and SAP goethites (Fig. 6). With the uncertainties in appropriate choices for the values of  $\delta^{13}C_O$ , atmospheric  $CO_2$  pressures calculated from the MCGoeth and SAP goethites cannot be analytically distinguished from modern. However, the similar values of  $X$  and  $\delta^{13}C$  for MCGoeth and SAP (Fig. 6, Table 1) suggest that atmospheric  $P_{CO_2}$  values were similar at the times represented by the lower Leonardian ( $\sim 283$  Ma BP) and upper Leonardian ( $\sim 270$  Ma BP). For reference, the smallest slopes in the two

component mixing lines of Figure 6 correspond to an atmospheric  $CO_2$  concentration of  $\sim 300$  ppmV. Mixing lines for MCGoeth and SAP were also calculated using  $\delta^{13}C_O$  values that were, in turn, calculated from the most negative organic matter  $\delta^{13}C$  values defined for each population by the standard deviations of the respective means (Table 4). These probable "most negative" values of  $\delta^{13}C_O$  were  $-14.5\text{‰}$  for MCGoeth and  $-14.6\text{‰}$  for SAP. The atmospheric  $CO_2$  pressures determined from the resulting "maximum probable" slopes are  $11 \times$  PAL for MCGoeth and  $7 \times$  PAL for SAP, where "PAL" = "Present Atmospheric Level" ( $\sim 300$  ppmV). These estimates of maximum probable atmospheric  $P_{CO_2}$  values emphasize the point that, in the absence of an internal proxy soil  $CO_2$  mixing line (e.g., Yapp and Poths, 1992), values of ancient atmospheric  $CO_2$  pressures calculated from  $\delta^{13}C$  values of pedogenic goethite or calcite are highly sensitive to the value assumed for the soil organic matter. For a comparison of Permian atmospheric  $CO_2$  estimates, see Mora et al. (1996), Ekart et al. (1999) and Ghosh et al. (2001).

Some of the  $\delta^{13}C_O$  values in the range of values represented by the standard deviations of  $\delta^{13}C_O$  for MCGoeth and SAP yield negative calculated slopes for the mixing lines. However, no such lines were drawn in Figure 6, because they would imply physically meaningless negative values for the partial pressure of  $CO_2$  in the Earth's atmosphere.

### 5.1.3. Constraints on atmospheric $P_{CO_2}$ from pedogenic calcite

The mean of the measured isotopic compositions ( $\delta^{13}C_{Ca}$ ) of the calcite samples from the calcitic paleosols in the Waggoner Ranch Formation is  $-5.4\text{‰}$  (Table 2), whereas the measured  $\delta^{13}C$  value of the  $Fe(CO_3)OH$  in the MCGoeth goethite ( $\delta^{13}C_{Go}$ ) is  $-13.5\text{‰}$  (Table 1). Thus,  $\Delta^{13}C_{Ca-Go} = +8.1 (\pm 0.9)\text{‰}$  ( $\Delta^{13}C_{Ca-Go} = \delta^{13}C_{Ca} - \delta^{13}C_{Go}$ ). This  $\Delta^{13}C_{Ca-Go}$  value is in reasonable accord with the value of  $+7.7\text{‰}$  expected if these two minerals formed in different soils, but under conditions of local isotopic equilibrium at the same temperatures and soil  $CO_2$   $\delta^{13}C$  values (Yapp and Poths, 1996). Additional information may be obtained from these pedogenic calcite samples.

Yapp and Poths (1996) presented the following two-component mixing equation for calcite-bearing soils:

$$\delta^{13}C_{m(cc)} = (\delta^{13}C_{A(cc)} - \delta^{13}C_{O(cc)})(C_A/C_S)_{cc} + \delta^{13}C_{O(cc)}. \quad (2)$$

$\delta^{13}C_{m(cc)}$  is the measured  $\delta^{13}C$  value of pedogenic calcite ( $\delta^{13}C_{Ca}$  in this work; Tables 2 and 3). The  $\delta^{13}C$  values subscripted with "A," and "O" are defined in the manner discussed for Eqn. 1. The subscript "(cc)" indicates calcite.  $C_A$  refers to the concentration of  $CO_2$  gas in the soil if the only contribution to the soil  $CO_2$  were from the atmosphere.  $C_S$  is the actual concentration of  $CO_2$  that was present in the soil.

Following the discussion in an earlier section, the value for  $(\delta^{13}C_{A(cc)} - \delta^{13}C_{O(cc)})$  is assumed to be  $+16\text{‰}$ .  $\delta^{13}C_{O(cc)}$  was calculated in a manner analogous to the calculation of  $\delta^{13}C_O$  for goethite (see Eqn. 1b), using the mean  $\delta^{13}C$  value of the Waggoner Ranch Formation organic matter reported in Table 4

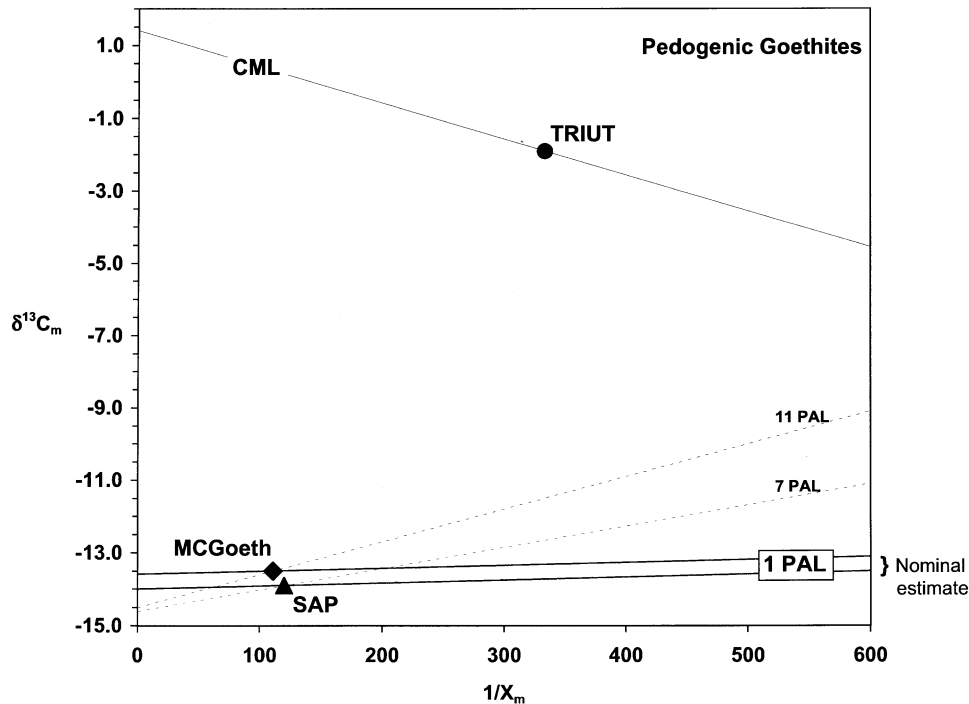


Fig. 6. A plot of  $\delta^{13}\text{C}$  vs.  $1/X$  for MCGoeth, SAP and TRIUT#2. The analytical uncertainties for  $\delta^{13}\text{C}$  and  $1/X$  for the ferric carbonate component lie within the dimensions of the filled symbols representing each data point. The uncertainties in the  $\delta^{13}\text{C}_\text{O}$  values are partially represented by the different y-intercepts for the MCGoeth and SAP samples. See text for details. The straight lines constructed for the MCGoeth and SAP goethites may represent mixing in Early Permian age soils between two isotopically distinct  $\text{CO}_2$  endmembers ( $\text{CO}_2$  from oxidation of organic matter and  $\text{CO}_2$  from the Earth's atmosphere). The labels (1 PAL, 7 PAL, 11 PAL) on the SAP and MCGoeth lines indicate calculated atmospheric  $\text{CO}_2$  pressures (see text). TRIUT#2 may have recorded the mixing of three isotopically distinct soil  $\text{CO}_2$  components (see text). The straight line drawn through the TRIUT#2 data point is the "carbonate mixing line" (CML; Yapp, 2001, 2002) for that sample.

( $-20.3\text{‰}$ ). However, the fractionation between calcite and  $\text{CO}_2$  at  $25^\circ\text{C}$  ( $10.2\text{‰}$ ) was used for the case of  $\delta^{13}\text{C}_{\text{O}(\text{cc})}$ . To be consistent with our treatment of MCGoeth, we also calculated a  $\delta^{13}\text{C}_{\text{O}(\text{cc})}$  value from an organic matter  $\delta^{13}\text{C}$  value of  $-21.4\text{‰}$ , the most negative value permitted by one standard deviation of the average.

Because the activity of  $\text{CO}_3^{2-}$  in calcite is fixed at unity, pedogenic calcite does not, by itself, contain a proxy record of the partial pressure of soil  $\text{CO}_2$ . Therefore, the concentration of soil  $\text{CO}_2$  ( $C_s$ ) must be assumed. From available in situ measurements of soil  $\text{CO}_2$  in modern calcite-producing soils (Solomon and Cerling, 1987; Quade et al., 1989), it has been assumed that  $C_s$  values in ancient calcitic paleosol profiles commonly range from 5,000 to 10,000 ppmV (Cerling, 1991; Mora et al., 1996; Ekart et al., 1999).

Concentrations ( $C_A$ ) of Early Permian atmospheric  $\text{CO}_2$  calculated with Eqn. 2 and the foregoing assumptions are shown in Figure 7 relative to stratigraphic height above the Waggoner Ranch LS1 horizon (Hentz, 1988). When the  $\delta^{13}\text{C}$  value of more than one nodule was measured per soil profile, the  $C_A$  values were calculated from the averages of those measured  $\delta^{13}\text{C}$  values to mitigate the effects of spatial heterogeneities. The circles in Figure 7 represent values of  $C_A$  calculated for  $C_s = 7500$  ppmV and an organic matter  $\delta^{13}\text{C}$  value of  $-20.3\text{‰}$  (i.e.,  $\delta^{13}\text{C}_{\text{O}(\text{cc})} = -5.4\text{‰}$ ). The diamonds represent the value of  $C_A$  calculated with an assumed  $C_s$  of 7500 ppmV and an

organic matter  $\delta^{13}\text{C}$  of  $-21.4\text{‰}$ . Error bars correspond to the atmospheric  $\text{CO}_2$  values calculated from the assumed extremes (5000 and 10,000 ppmV) of soil  $\text{CO}_2$  ( $C_s$ ) values. With one exception, the calculated concentrations of atmospheric  $\text{CO}_2$  range from  $\sim 1 \times \text{PAL}$  to  $5 \times \text{PAL}$  (Fig. 7). The single exception yields negative  $P_{\text{CO}_2}$  when values are calculated for an organic matter  $\delta^{13}\text{C}$  value of  $-20.3\text{‰}$  (paleosol #2, Table 2). Such values have no physical meaning, and, therefore, were not plotted in Figure 7.

With the uncertainties in the value of  $C_s$  and the  $\delta^{13}\text{C}$  value of the organic matter, Early Permian atmospheric  $\text{CO}_2$  concentrations calculated from these calcitic paleosols cannot be distinguished from that of modern atmospheric  $\text{CO}_2$  ( $1 \times \text{PAL}$ ). These low atmospheric  $\text{CO}_2$  values are in accord with the low atmospheric carbon dioxide values calculated from the MCGoeth and SAP goethite samples. As noted, these results contrast with atmospheric  $\text{CO}_2$  estimates of  $\sim 7 \times \text{PAL}$  (Ekart et al., 1999) calculated from an average  $\delta^{13}\text{C}$  value determined for Waggoner Ranch pedogenic calcite. In the absence of available terrestrial organic matter, Ekart et al. (1999) assumed a  $\delta^{13}\text{C}$  value for plant organic matter of  $-22.4\text{‰}$ , which contrasts with the measured value of about  $-20.3\text{‰}$  used in the current work. This difference in organic matter  $\delta^{13}\text{C}$  values is primarily responsible for the difference in the calculated values of atmospheric  $\text{CO}_2$ . It is possible that the measured  $\delta^{13}\text{C}$  values of the plant organic matter from the Waggoner Ranch Formation are

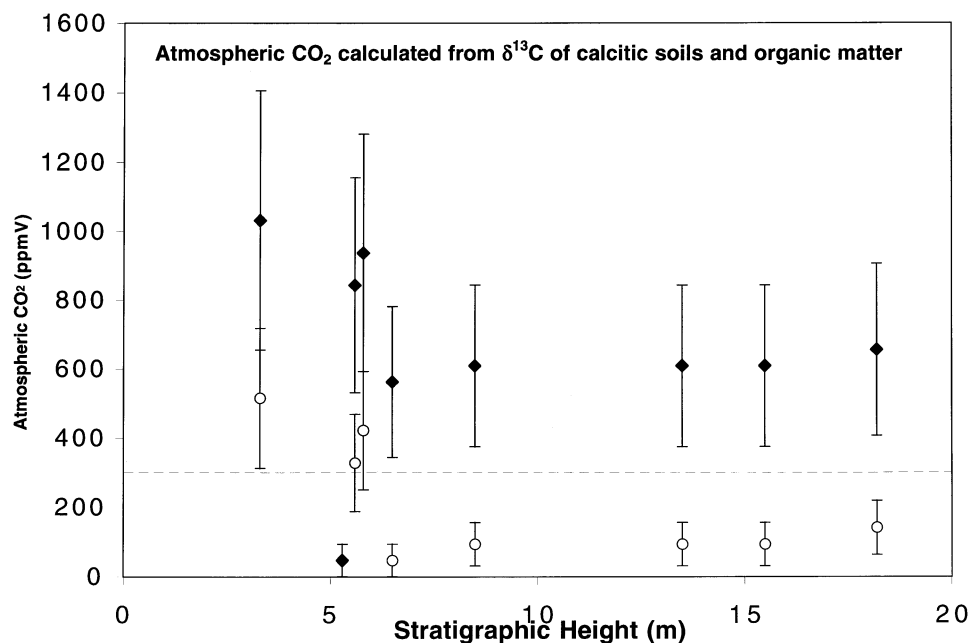


Fig. 7. Atmospheric CO<sub>2</sub> concentrations calculated from the  $\delta^{13}\text{C}$  values of Waggoner Ranch Fm. pedogenic calcites and organic matter in associated fossil plants (see text). Circles represent atmospheric CO<sub>2</sub> values ( $C_A$ ) calculated with the assumption that soil CO<sub>2</sub> concentrations ( $C_S$ ) were 7500 ppmV, while organic matter  $\delta^{13}\text{C}$  values were  $-20.3\text{‰}$ . The diamonds represent the value of  $C_A$  calculated with an assumed  $C_S$  of 7500 ppmV and an organic matter  $\delta^{13}\text{C}$  of  $-21.4\text{‰}$ . Error bars correspond to the atmospheric CO<sub>2</sub> values calculated from the assumed extremes (5000 and 10,000 ppmV) of soil CO<sub>2</sub> ( $C_S$ ) values (see text).

more positive than the original Permian values as a result of degradation of more labile organic compounds during diagenesis. If so, measured  $\delta^{13}\text{C}$  values of the plant organic matter may be more positive than original Permian values by about 1‰ to 2‰ (Goh et al., 1976, 1977). For this case, calculated atmospheric CO<sub>2</sub> concentrations would be about 5×PAL to 9×PAL. This same argument applies to any study that utilizes ancient organic matter to calculate  $P_{\text{CO}_2}$  values.

Figure 8 depicts  $\delta^{13}\text{C}$  data for the  $\text{Fe}(\text{CO}_3)\text{OH}$  component in goethites from the two Early Permian soils of this study (filled diamonds) as well as previously published data (open triangles) for  $\text{Fe}(\text{CO}_3)\text{OH}$  in goethite from Phanerozoic soils that exhibited two-component mixing of CO<sub>2</sub> (Yapp and Poths, 1996; Yapp, 2001). The MCGoeth and SAP samples of the current study have the most positive  $\delta^{13}\text{C}$  values measured thus far for pedogenic goethites that record two-component mixing in soil CO<sub>2</sub> (Yapp and Poths, 1996; Yapp, 2001). Also shown in Fig. 8 is a three-point moving average of  $\delta^{13}\text{C}$  values (averages of values with the same age) of pedogenic calcites ranging in age from Late Ordovician to Pliocene (Retallack, 1993; Mora et al., 1996; Ekart et al., 1999). There is an overall similarity of the temporal variations of the  $\delta^{13}\text{C}$  values of the pedogenic goethite and calcite. As discussed by Yapp and Poths (1996), this similarity of long-term variations of  $\delta^{13}\text{C}$  values of two different minerals from distinctly different soil environments suggests that both are recording the same global scale trends in the carbon cycle. Thus, estimates of atmospheric CO<sub>2</sub> could be expected to concur when the pedogenic goethite and calcite are the same age irrespective of location.

#### 5.1.4. Mixing in the soil with three CO<sub>2</sub> components (TRIUT)

At equilibrium and 25°C, the  $\delta^{13}\text{C}$  of calcite ( $\delta^{13}\text{C}_{\text{Ca}}$ ) is 10.2‰ more positive than gaseous CO<sub>2</sub> (Bottinga, 1968), whereas the  $\delta^{13}\text{C}$  of  $\text{Fe}(\text{CO}_3)\text{OH}$  ( $\delta^{13}\text{C}_{\text{Go}}$ ) is 2.5‰ more positive (Yapp and Poths, 1993). As mentioned, if calcite and goethite form at the same temperature (25°C) in equilibrium with soil CO<sub>2</sub> gases which have the same  $\delta^{13}\text{C}$  values, a value of +7.7‰ is expected for  $\Delta^{13}\text{C}_{\text{Ca-Go}}$  (Yapp and Poths, 1996). The  $\Delta^{13}\text{C}_{(\text{Ca-Go})}$  value for the TRIUT paleosol is about  $-3.6\text{‰}$ . This value contrasts significantly with the expected equilibrium value of +7.7‰.

It is assumed, as previously stated, that TRIUT#2 goethite formed at approximately 25°C, and that  $\Delta^{13}\text{C}_{\text{Go-CO}_2}$  between  $\text{Fe}(\text{CO}_3)\text{OH}$  and gaseous CO<sub>2</sub> is +2.5‰ (Yapp and Poths, 1993). The equilibrium carbon isotope fractionation between calcite and gaseous CO<sub>2</sub> ( $\Delta^{13}\text{C}_{\text{CC-CO}_2}$ ) is +9.0‰ at 35°C and +14.4 at 0°C (Bottinga, 1968). The range of values indicates that even if the TRIUT pedogenic calcite formed between 0°C and 35°C, the  $\Delta^{13}\text{C}_{(\text{Ca-Go})}$  between pedogenic calcite of the TRIUT profile and  $\text{Fe}(\text{CO}_3)\text{OH}$  in TRIUT#2 goethite should be no less than +6.5‰. Therefore, formation of the pedogenic calcite and goethite at different temperatures in the TRIUT paleosol can probably be ruled out as a cause for the disequilibrium value of  $\Delta^{13}\text{C}_{(\text{Ca-Go})}$ .

The average  $\delta^{13}\text{C}$  value of pedogenic calcite from the TRIUT paleosol is  $-5.5\text{‰}$ , which corresponds to a calculated soil CO<sub>2</sub>  $\delta^{13}\text{C}$  value of approximately  $-15.7\text{‰}$  (implying a  $\delta^{13}\text{C}$  value of about  $-20\text{‰}$  for soil organic matter if atmo-

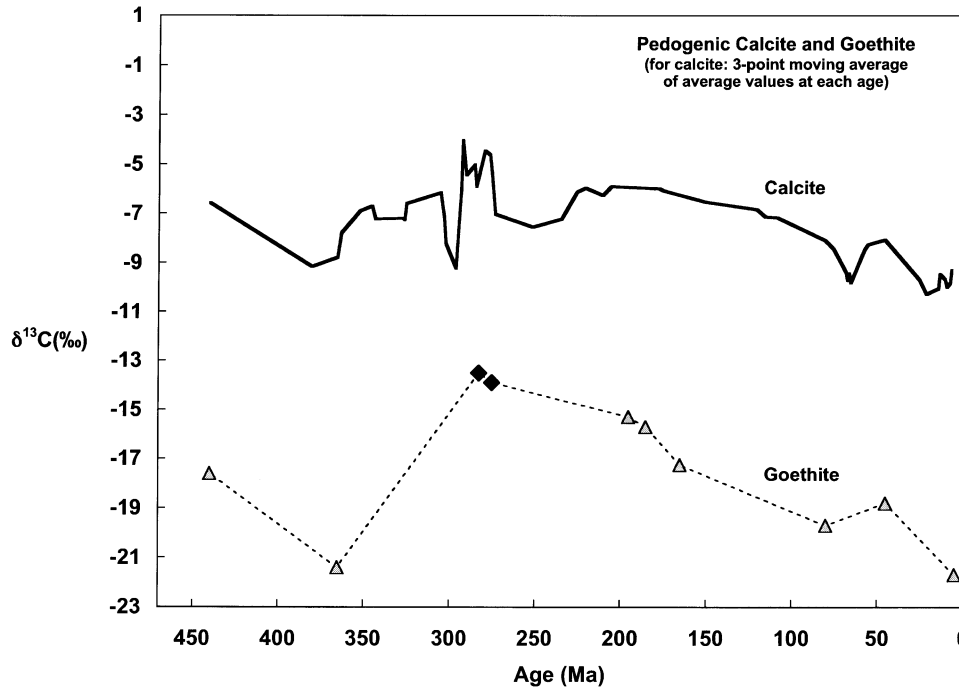


Fig. 8. A plot of measured  $\delta^{13}\text{C}$  values of the  $\text{Fe}(\text{CO}_3)\text{OH}$  component from Early Permian pedogenic goethites (filled diamonds) and previously published  $\delta^{13}\text{C}$  values of the  $\text{Fe}(\text{CO}_3)\text{OH}$  component from goethites of various ages (triangles; Yapp and Poths, 1996; Yapp, 2001) versus approximate age of each geological formation. Ma B.P. = millions of years before the present. The thick solid line represents a three-point moving average of the average  $\delta^{13}\text{C}$  values (at each age) of 77 Phanerozoic pedogenic calcite samples (Retallack, 1993; Mora et al., 1996; Ekart et al., 1999). There is an overall similarity in the temporal variations of  $\delta^{13}\text{C}$  in these pedogenic calcite and goethite samples (see text).

spheric  $\text{CO}_2$  pressures were very low). As stated, for equilibrium at  $25^\circ\text{C}$ , the  $\Delta^{13}\text{C}$  between  $\text{Fe}(\text{CO}_3)\text{OH}$  in goethite and  $\text{CO}_2$  is about  $2.5\text{‰}$  (Yapp and Poths, 1996; Hsieh and Yapp, 1999). With the additional consideration of a  $4.4\text{‰}$   $^{13}\text{C}$  enrichment of soil  $\text{CO}_2$  because of steady-state diffusive transport, the measured  $\delta^{13}\text{C}$  of  $-1.9\text{‰}$  for  $\text{Fe}(\text{CO}_3)\text{OH}$  in TRIUT#2 implies a  $\delta^{13}\text{C}$  value of approximately  $-9\text{‰}$  for organic matter in that soil (assuming two-component mixing with low atmospheric  $P_{\text{CO}_2}$ ). A soil organic matter  $\delta^{13}\text{C}$  value of  $-9\text{‰}$  would appear to correspond to a soil ecosystem dominated by plants that utilized a  $\text{C}_4$  photosynthetic pathway (Cerling and Quade, 1993). However, there is no evidence to suggest that  $\text{C}_4$  plants existed during Triassic time (e.g., Cerling, 1991). Moreover, in modern ecosystems,  $\text{C}_4$  plants are associated with dry, water-stressed environments typical of calcite precipitation, not the wet environments of goethite precipitation (Teeri and Stowe, 1976; Tieszen et al., 1979; Cerling and Quade, 1993). Therefore, it is concluded that contrasting  $\delta^{13}\text{C}$  values of soil organic matter at the times of calcite and goethite crystallization do not explain the negative  $\Delta^{13}\text{C}_{(\text{cc-go})}$  values in the TRIUT soil.

The upper 1m of the TRIUT paleosol is presently noncalcareous. If calcite had been distributed throughout the upper meter of the TRIUT profile prior to onset of wetter conditions, and then actively underwent dissolution concomitant with goethite precipitation, a significant amount of  $\text{CO}_2$  from the dissolved calcite may have contributed to the carbon isotope budget of the soil  $\text{CO}_2$  and affected the  $\delta^{13}\text{C}$  value of the  $\text{Fe}(\text{CO}_3)\text{OH}$  in the goethite. A similar scenario has been documented for the  $\text{Fe}(\text{CO}_3)\text{OH}$  component in goethite in a mod-

ern, wet soil in eastern Texas that is actively undergoing precipitation of goethite while simultaneously dissolving marine calcite (Hsieh and Yapp, 1999; Yapp, 2001). Based on these arguments, it is thought that the goethite in the TRIUT profile formed when the system represented mixing of three isotopically distinct  $\text{CO}_2$  components (atmospheric  $\text{CO}_2$ ,  $\text{CO}_2$  from dissolution of pre-existing pedogenic carbonate, and  $\text{CO}_2$  from oxidation of organic matter). If such mixing occurred under conditions of low soil pH ( $\leq 5$ ), further calculations relevant to the soil  $\text{CO}_2$  system can be performed.

Yapp (2001, 2002) presented a three-component, low-pH mixing equation which contains a term,  $X_s$ , that is of interest here.  $X_s$  is the mole fraction of  $\text{Fe}(\text{CO}_3)\text{OH}$  in goethite if that  $\text{Fe}(\text{CO}_3)\text{OH}$  were in equilibrium with soil  $\text{CO}_2$  which represented only a two-component mixture of atmospheric  $\text{CO}_2$  and  $\text{CO}_2$  from oxidation of organic matter. The equation shown in Yapp (2001) for that three-component mixing contains a printer's error. The corrected three-component equation is presented in Yapp (2002) and is reproduced below:

$$\delta^{13}\text{C} = [X_A(\delta^{13}\text{C}_A - \delta^{13}\text{C}_O) + X_S(\delta^{13}\text{C}_O - \delta^{13}\text{C}_{\text{CC}})]/[1/X_m] + \delta^{13}\text{C}_{\text{CC}} \quad (3)$$

$X_A$ ,  $\delta^{13}\text{C}_A$ ,  $\delta^{13}\text{C}_O$ , and  $X_m$  are the same as in Eqn. 1.  $\delta^{13}\text{C}_{\text{CC}}$  is the calculated value of the  $\text{Fe}(\text{CO}_3)\text{OH}$  if it were in equilibrium with steady-state soil  $\text{CO}_2$  derived only from dissolving calcite. It is assumed that there is no carbon isotopic fractionation accompanying irreversible dissolution of calcite, but that the resulting hypothetical endmember soil  $\text{CO}_2$  gas is diffu-

sively enriched in  $^{13}\text{C}$  by 4.4‰ relative to the calcite (Cerling et al., 1991).  $\delta^{13}\text{C}_{\text{CC}}$  is calculated from the measured  $\delta^{13}\text{C}$  value of calcite ( $\delta^{13}\text{C}_{\text{Ca}}$  as used in this work), adjusted by 6.9‰ (i.e.,  $\delta^{13}\text{C}_{\text{CC}} = \delta^{13}\text{C}_{\text{Ca}} + 6.9\text{‰}$ ; see Yapp, 2001). For TRIUT#2,  $\delta^{13}\text{C}_{\text{CC}} = +1.4\text{‰}$ .

The extent of the contribution of atmospheric  $\text{CO}_2$  to the carbon isotopic composition of the  $\text{Fe}(\text{CO}_3)\text{OH}$  component in TRIUT#2 is unknown. Other studies have suggested that Triassic atmospheric  $\text{P}_{\text{CO}_2}$  may have ranged from 2×PAL to 10×PAL (see Ekart et al., 1999, and references therein). However, for the purposes of this calculation it was assumed that TRIUT formed at 25°C under possible atmospheric  $\text{P}_{\text{CO}_2}$  values that ranged from no lower than the Holocene pre-industrial value (1×PAL  $\approx 10^{-3.547}$  bar) to 16×PAL. This upper limit of 16×PAL was chosen based on evidence for such high values at certain times in the Phanerozoic (cf. Yapp, 2001). Furthermore, it was assumed that the TRIUT profile was dominated by organic matter from plants which utilize the  $\text{C}_3$  photosynthetic pathway and that organic matter  $\delta^{13}\text{C}$  values may have had values anywhere between -29‰ and -22‰ (cf. O'Leary, 1988; Holmes, 1995; Arens et al., 2000). This range of atmospheric  $\text{CO}_2$  pressures and organic matter  $\delta^{13}\text{C}$  values together with the  $\delta^{13}\text{C}_{\text{CC}}$  value of +1.4‰, a ( $\delta^{13}\text{C}_{\text{A}} - \delta^{13}\text{C}_{\text{O}}$ ) value of +16‰, and the measured values of  $X_{\text{m}}$  (0.0030) and  $\delta^{13}\text{C}_{\text{m}}$  (-1.9‰) for TRIUT#2 allow the use of Eqn. 3 to calculate a corresponding range of  $X_{\text{s}}$  values.

From this range of  $X_{\text{s}}$  values, a range of hypothetical two-component soil  $\text{CO}_2$  pressures can be calculated using the Henry's Law equation of Yapp and Poths (1992). These calculated, hypothetical two-component soil  $\text{CO}_2$  pressures (mixtures of atmospheric  $\text{CO}_2$  and  $\text{CO}_2$  from oxidation of biological material) range from about 0.004 to 0.011 bar. Such calculated soil  $\text{CO}_2$  pressures are within the large range of pressures observed in modern soils exhibiting mixing of only those two  $\text{CO}_2$  components (Boynton and Reuther, 1938; Yamaguchi et al., 1967; Cerling and Quade, 1993). Interestingly, these values of hypothetical, two-component soil  $\text{CO}_2$  pressures calculated for the TRIUT#2 soil are substantially smaller than the soil  $\text{CO}_2$  pressures of about 0.053 and 0.050 bar calculated from the measured values of  $X$  in the goethites from the MCGoeth and SAP soils, respectively. The lower hypothetical two-component soil  $\text{CO}_2$  pressures calculated for TRIUT#2 could imply lower levels of biological productivity in that soil.

## 6. SUMMARY AND CONCLUSIONS

Comparison of published  $\delta^{13}\text{C}$  values of pedogenic calcites (dry soils) with the  $\delta^{13}\text{C}$  values of pedogenic goethites (wet soils) from this and published studies emphasizes a previously observed similarity of the temporal  $\delta^{13}\text{C}$  variations of these two distinctly different soil types throughout the Phanerozoic and reinforces the earlier assertion that the carbon isotope variations of both soil types have responded to global scale changes in the carbon cycle.

This paper reports the first example of three-component mixing of  $\text{CO}_2$  in a documented ancient soil (TRIUT#2). Although this three component mixing precludes determination of ancient atmospheric  $\text{CO}_2$  pressures, the TRIUT#2 paleosol

indicates that information about ancient soil  $\text{CO}_2$  carbon isotope budgets and soil development is preserved in the  $\text{Fe}(\text{CO}_3)\text{OH}$  in goethite from such soils.

Data from two Early Permian terrestrial goethites formed in soils in which only two  $\text{CO}_2$  components mixed imply values for atmospheric  $\text{P}_{\text{CO}_2}$  that are analytically indistinguishable from modern (1×PAL), although uncertainty in the  $\delta^{13}\text{C}$  value of organic carbon permits a calculated atmospheric  $\text{P}_{\text{CO}_2}$  of 11×PAL. Essentially the same values for atmospheric  $\text{CO}_2$  pressure were deduced from  $\delta^{13}\text{C}$  values of associated Early Permian Waggoner Ranch pedogenic calcite. The  $\delta^{13}\text{C}$  values of  $\text{Fe}(\text{CO}_3)\text{OH}$  in goethites from Early Permian terrestrial strata of north Texas are the most positive values (-13.5‰ and -13.9‰) reported to date for wet soils that preserve information on mixing of two isotopic  $\text{CO}_2$  components. These Early Permian goethite  $\delta^{13}\text{C}$  values appear to reflect the higher  $\delta^{13}\text{C}$  values measured for associated organic matter.

To the best of our knowledge, the  $\delta^{13}\text{C}$  values of  $-20.3 \pm 1.1\text{‰}$  and  $-20.6 \pm 0.9\text{‰}$  reported here for the organic matter in Early Permian plant fossils are among the most positive  $\delta^{13}\text{C}$  values observed thus far (Gröcke et al., 1999) for well-preserved plant material that predates the presumed first appearance of  $\text{C}_4$  plants in the Miocene (e.g., Cerling, 1991). If these Early Permian plant  $\delta^{13}\text{C}$  values reflect  $\text{C}_3$  photosynthesis at that time, they may provide insight into the carbon isotopic composition of atmospheric  $\text{CO}_2$  and/or the water stress experienced by plants at that time and place in Earth's history (e.g., Arens et al., 2000).

The relatively positive  $\delta^{13}\text{C}$  values measured here for Early Permian fossil plants, pedogenic calcite, and SAP and MCGoeth pedogenic goethites may be a continental manifestation of the positive  $\delta^{13}\text{C}$  values observed in Permian marine carbonates (e.g., Veizer et al., 1999). If so, this correspondence emphasizes the critical role of atmospheric  $\text{CO}_2$  as a medium of global carbon exchange throughout the Phanerozoic.

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## APPENDIX 1

MCGoeth (MHD-2031)				Sample mass = 240.6 mg			
CO <sub>2</sub>							
Time (min)	T (°C)	μmoles	δ <sup>13</sup> C	H <sub>2</sub> μmoles	X <sub>v</sub> (H <sub>2</sub> )	F	
35	205*	2.2	-5.3	77	0.06	0.0286	
30	190	0.7	-2.9	76	0.12	0.0092	
30	190	0.4	-6.0	39	0.15	0.0103	
30	190	0.4	-7.9	30	0.18	0.0133	
30	190	0.7	-10.5	50	0.22	0.0140	
55	212	2.9	-13.1	173	0.35	0.0168	
60	212	2.9	-13.5	159	0.48	0.0182	
35	212	1.8	-14.1	99	0.56	0.0182	
35	212	—	—	96	0.63	—	
50	212	0.7	-14.6	70	0.69	0.0100	
30	850*	10.1	-18.2	392	1.00	0.0258	
SAP (MHD-2029)				Sample mass = 97.3 mg			
CO <sub>2</sub>							
Time (min)	T (°C)	μmoles	δ <sup>13</sup> C	H <sub>2</sub> μmoles	X <sub>v</sub> (H <sub>2</sub> )	F	
33	205*	5.8	-17.4	165	0.29	0.0352	
30	205	5.1	-13.9	306	0.82	0.0167	
34	205	0.7	-30.0 <sup>1</sup>	26	0.87	0.0269	
74	205	1.1	-36.0 <sup>1</sup>	9	0.88	0.1222	
30	850*	10.4	-23.4 <sup>1</sup>	68	1.00	0.1529	
TRIUT#2 (MHD-2033)				Sample mass = 356.1 mg			
CO <sub>2</sub>							
Time (min)	T (°C)	μmoles	δ <sup>13</sup> C	H <sub>2</sub> μmoles	X <sub>v</sub> (H <sub>2</sub> )	F	
36	210*	4.9	-7.1	716	0.56	0.0068	
30	195	1.5	-1.9	246	0.75	0.0061	
102	185–210	1.6	-2.0	110	0.83	0.0146	
33	210	0.4	-14.8	14	0.84	0.0286	
60	210	0.4	-23.2	11	0.85	0.0364	
60	210	0.2	—	11	0.86	0.0182	
30	850*	7.2	-13.0	181	1.00	0.0398	

<sup>1</sup>CO<sub>2</sub> samples may have been contaminated with SO<sub>2</sub>. Partial removal of SO<sub>2</sub> was effected with a n-pentane slush. Evolved gas was passed through a Cu-CuO furnace (300°C). δ<sup>13</sup>C values are problematic for these three aliquots.

\*Closed system in O<sub>2</sub>. All other increments open system in vacuum. Sample masses are after 100°C outgassing.