

## Paleoenvironmental Implications Of Concentration And $^{13}\text{C}/^{12}\text{C}$ Ratios Of $\text{Fe}(\text{CO}_3)\text{OH}$ In Goethite From A Mid-Latitude Cenomanian Laterite In Southwestern Minnesota

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### ABSTRACT

A mid-Cretaceous (~95 Ma) laterite in southwestern Minnesota contains pisolites that consist primarily of gibbsite, quartz, and kaolinite with smaller amounts of goethite ( $\alpha\text{-FeOOH}$ ) and hematite. The presence of minor berthierine (an Fe (II) sheet silicate) suggests that this Cenomanian laterite experienced some degree of low temperature reductive diagenesis during its burial history. The prospects for extracting useful paleoenvironmental information from the pisolitic goethite were explored by studying measured mole fraction ( $X_m$ ) and  $\delta^{13}\text{C}_m$  values of the  $\text{Fe}(\text{CO}_3)\text{OH}$  component in solid solution in the goethite using the method of incremental vacuum dehydration-decarbonation.

Data arrays that occupy distinctly different domains in plots of  $\delta^{13}\text{C}_m$  vs.  $1/X_m$  suggest the existence of two generations of goethite in the pisolites. The apparently younger generation of goethite ("generation 2") evolves  $\text{CO}_2$  at  $170^\circ\text{C}$ , while the older generation ("generation 1") evolves  $\text{CO}_2$  at  $220^\circ\text{C}$ . The distribution of the data suggests that generation 2 goethite is a proxy for mixing of  $\text{CO}_2$  from three distinct  $\text{CO}_2$  sources in an oxidative environment which post-dated the reductive diagenesis. The small amount of generation 1 goethite seems to have persisted through the reductive diagenesis, and nine of the generation 1 goethite data appear to define a proxy, two-endmember, soil  $\text{CO}_2$  mixing line. Such two-component mixing is consistent with expectations for a highly evolved, carbonate-free laterite (i.e., the pre-diagenetic Cenomanian weathering system). The  $\delta^{13}\text{C}_m$  values of these nine data points range from -23.1‰ to -13.7‰, whereas  $X_m$  values range from 0.0007 to 0.0222. Linear regression of these nine data yields a slope of 0.0064, which corresponds to an ancient tropospheric  $\text{CO}_2$  concentration of about 1900 ppmv.

Isotopic data from pisolitic kaolinite indicate a paleotemperature of about  $24^\circ\text{C}$  at a paleolatitude of  $\sim 40^\circ\text{N}$ . This is substantially warmer than modern continental temperatures at such latitudes and is consistent with published indications of a generally warmer mid-Cretaceous climate. Moreover, the correspondence of a warmer mid-Cretaceous climate with the inferred, relatively high concentration of Cenomanian tropospheric  $\text{CO}_2$  ( $\sim 1900$  ppmV) is consistent with the idea that variations of atmospheric  $\text{CO}_2$  have a relation to climate change. The results of this study emphasize the importance of careful evaluation of incremental dehydration-decarbonation data from natural goethites to assess the possibility that more than one generation of goethite is present in a sample. However, the results also indicate that the carbon isotope information recorded in admixed goethite generations may be sorted out and used in paleoenvironmental interpretations.

## 1. INTRODUCTION

Earth's mid-Cretaceous (100-90 Ma) climate was generally warmer than present with a thermal maximum at the end of the Cenomanian and beginning of the Turonian (e.g., Huber, et al, 1995; Miller, et al., 2003). The existence of a warmer climate in the mid-Cretaceous is supported by such paleoecological evidence as: 1) poleward habitat expansion of thermophilic marine organisms (e.g., larger foraminifera and rudistid bivalves, Kauffman, 1973; Lloyd, 1982); 2) the occurrence of dinosaurs of presumed warm weather affinity in the Arctic (Colbert, 1973) and Antarctic (Olivero, et al., 1991); and 3) poleward expansion of biogeographic provinces of flora (Barnard, 1973). Some authors also suggest that the latitudinal temperature gradient during the mid-Cretaceous was smaller than the modern value--i.e. higher latitude regions were warmed up more than lower latitude regions (Barron, 1984; Herman and Spicer, 1997; Huber, et al, 1995, 2002). For example, a reported mid-Cretaceous (100 to 99 Ma) sea surface latitudinal temperature gradient of about  $0.25^\circ\text{C}$  per degree of latitude, is significantly lower than the modern value of  $0.40^\circ\text{C}$  per degree of latitude (Huber, et al., 2002). However, an alternative case is made for a mid-Cretaceous latitudinal temperature gradient that was similar to modern and that the equatorial Sea Surface Temperature (SST) was higher in the mid-Cretaceous (e.g., Puc at, et al., 2007; Wagner, et al., 2008).

Warmer mid-Cretaceous temperatures at mid- to high latitude may have been related to several factors: 1) paleogeography as shown in Fig. 1 (e.g., Barron, et al., 1995); 2) ocean circulation (e.g., Barron, et al., 1985, Schneider, et al., 1985); 3) increased latent heat transfer through enhanced precipitation (e.g., Ufnar, et al., 2002, 2004a, 2004b); and 4) increased  $\text{CO}_2$  concentration in the atmosphere (e.g., Barron and Washington, 1985; Royer, et al., 2004; Royer, 2006). "Proxies" developed for estimation of ancient atmospheric  $\text{CO}_2$  concentrations include: 1) the  $\delta^{13}\text{C}$  of phytoplankton (e.g., Pagani, et al., 1999); 2) the  $\delta^{11}\text{B}$  of planktonic foraminifera from oceanic regions (Pearson and Palmer, 2000); 3) stomatal indices (e.g., Van der Burgh, et al., 1993; Retallack, 2001; Haworth, et al., 2005); 4)  $\delta^{13}\text{C}$  of pedogenic calcite in paleosols (e.g., Cerling, 1991; Ekart, et al., 1999); 5) concentration and  $\delta^{13}\text{C}$  of  $\text{CO}_2$  occluded in the structure of pedogenic goethite (Yapp, 1987, 2001, 2002, 2004; Yapp and Poths, 1992, 1993, 1996; Tabor, et al., 2004); and 6) possibly pedogenic gibbsite (Schroeder and Melear, 1999; Tabor and Yapp, 2005a). Bice and Norris (2002) summarized variations of Cretaceous atmospheric  $\text{CO}_2$  concentrations based on some of these  $\text{CO}_2$  proxies. The composite estimates of mid-Cretaceous atmospheric  $\text{CO}_2$  concentrations range from 900 to 5500 ppmv. Bice and Norris (2002) used GCM based calculations to suggest that the range of  $\text{CO}_2$  concentrations indicated by the mid-Cretaceous proxies might be credible and could reflect significant variability of mid-Cretaceous atmospheric  $\text{CO}_2$ . This suggestion motivates a search for more proxy  $\text{CO}_2$  data from that seminal interval in Earth's climatic

history. In this paper, we report analyses of concentrations and  $^{13}\text{C}/^{12}\text{C}$  ratios of  $\text{CO}_2$  occluded in pedogenic goethite from a Cenomanian laterite in North America. The results are discussed in the context of low temperature redox diagenesis of the paleosol, two generations of goethite, and a possible determination of the concentration of Cenomanian tropospheric  $\text{CO}_2$ .

## 2. SAMPLES AND METHODS

The studied paleosol is located in the Minnesota River Valley, Renville County, in southwestern Minnesota. In the Cenomanian, this location was on the eastern coast of the Western Interior Seaway (WIS) at a paleo-latitude of  $\sim 40^\circ\text{N}$  (Fig. 1), and was part of a fluvial system that drained into the WIS (Toth and Fritz, 1997). The fluvial sediments are associated with the Greenhorn cyclothem of the WIS (Toth and Fritz, 1997). The Cenomanian age saprolite-derived fluvial sediments consist of unconsolidated kaolinitic sand, silt, and clay and are correlative with the Nishnabotna Member of the Dakota Formation (Toth and Fritz, 1997). The precursor saprolite, in turn, appears to have formed earlier in the Cretaceous by weathering of the  $\sim 3.4\text{Ga}$  Morton gneiss (Toth and Fritz, 1997; Schmitz, et al., 2006). The Cretaceous fluvial sediments are subdivided into a lower arenaceous zone and an upper argillaceous zone. They represent changes in the fluvial system associated, respectively, with a minor regression and transgression of the WIS (Toth and Fritz, 1997). The arenaceous zone is characterized by conglomeratic kaolin at its base and fines upward. The argillaceous zone is characterized by kaolinitic silt and clay with some thin, fine-sand layers and organic-rich deposits at the bottom and a mid-Cretaceous laterite at the top that forms an extensive pisolitic horizon (Fig. 2). Pisolites are inorganic spheroidal structures with diameters large than 2mm (Palache, et al., 1951). This laterite represents the Cenomanian weathering of the saprolite-derived fluvial sediments (Toth and Fritz, 1997). These authors reported that this laterite consists of indurated kaolinitic, goethitic, and gibbsitic pisoids that increase in quantity upwards from a few scattered pisoids within silt and clay to a pisolite-dominated horizon at the top that lacks any primary sedimentary bedding structures. No evidence of reworking of pisolitic material in the argillaceous zone was observed. Other minerals reported by Toth and Fritz (1997) to be in these sediments are quartz, berthierine (idealized chemical formula is  $\text{Fe}_2\text{Al}_2\text{SiO}_5(\text{OH})_4$ ) and siderite. The latter two minerals contain iron as  $\text{Fe}(\text{II})$  and indicate some degree of low temperature reductive diagenesis of the system (Landuydt, 1990; Toth and Fritz, 1997) that could complicate interpretation of goethite isotopic data.

Eleven samples were collected from different depths in an outcrop of laterite exposed in a roadcut located next to Renville County highway 51, near Purgatory Creek (GPS coordinates:  $44^\circ 32' 01.38'' \text{N}$ ;  $94^\circ 55' 41.34'' \text{W}$ ; elevation  $\sim 267 \text{ m}$ ). Specific sampling positions in the outcrop are shown in the photo in Fig. 2. The samples are labeled, from top to bottom, 05MN11-1 to 05MN11-11. Ten of these eleven samples have been

analyzed and will be discussed in this report. Samples 05MN11-1 to 05MN11-5 and 05MN11-11 contain relatively abundant reddish pisolites, as well as pale green, white, or yellow pisolites. In hand samples, these pisolites are ~2 mm to 20 mm in diameter, and the rims appear to be darker than the interiors. The matrix surrounding the pisolites is pale brown, yellow, or sometimes green. Samples 05MN11-7 to 05MN11-10 have more greenish matrix and fewer pisolites. The green color might indicate the presence of Fe (II) minerals such as berthierine and/or siderite (Toth and Fritz, 1997).

Photomicrographs of some of these pisolitic samples are shown in Fig. 3. Some pisolites (e.g., the large pisolite shown in Fig. 3b) are characterized by a reddish brown to yellow interior filling with two or three concentric bands in a zone about 1 to 2 mm thick around the rims. These bands are generally reddish in color, suggesting proportionally higher amounts of iron oxides. However, opaque minerals (iron oxides) are found in both the matrix, and the pisolites (Fig. 3). Irregular fractures with translucent to yellow colored filling are present in all samples. The fractures are generally 10 to 50  $\mu\text{m}$  in width and crosscut the pisolites and matrix. Quartz grains are 20 to 800  $\mu\text{m}$  in diameter, and comprise ~5 to 20% of the thin sections. Quartz is present in both pisolites and matrix, but appears to be more abundant in the latter. Quartz grains are subangular to rounded and exhibit evidence of partial dissolution.

Pisolites were hand-picked from each sample with emphasis on the reddish part of the pisolites (mostly outer rims) in an effort to pre-concentrate goethite. A descriptor of “rp” is included as part of the label of samples prepared in this manner to indicate that they are from “reddish pisolites”. We also prepared a matrix sample from 05MN11-2, which is indicated with a descriptor of “m”. All samples were powdered to <63 $\mu\text{m}$  grain size. The grinding process was carried out in reagent-grade acetone (Yapp, 1987).

Minerals were identified by XRD (X-Ray Diffraction) analyses of these powdered samples. Analyses were carried out on a Rigaku Ultima III X-ray diffraction instrument with  $\text{Cu-K}\alpha$  radiation at Southern Methodist University (SMU). The extent of substitution of Al for Fe in the goethite samples was determined using the XRD method of Schulze (1984) with an uncertainty of  $\pm 3$  mole %. Detailed configurations of the instrument are the same as in Feng and Yapp (2008).

Prior to the extraction and analysis of  $\text{CO}_2$  from goethite, samples were chemically treated to: 1) further concentrate the goethite by selectively dissolving other minerals; and 2) remove other potential sources of  $\text{CO}_2$  such as organic matter, gibbsite, and carbonates (Yapp and Poths, 1991; Yapp, 1998; Schroeder and Melear, 1999; Tabor and Yapp, 2005a, 2005b; Schroeder, et al., 2006). The procedure is summarized briefly here. Previously powdered samples were first treated at room temperature with 0.5 M reagent-grade HCl in pyrex beakers over night (~12 h) to remove carbonates such as calcite, then rinsed with successive aliquots of deionized (D.I.) water until the rinse water remained at the original pH after at least 10 minutes of contact with the sample.

Aliquots of these HCl-treated samples were subsequently treated up to four times with 5M reagent-grade NaOH in closed Teflon tubes immersed in a 100°C water bath to dissolve minerals such as gibbsite, kaolinite, and berthierine (Yapp, 1991). This NaOH treatment is followed by rinsing with successive aliquots of D.I. water. These NaOH-treated samples were treated with 0.5 M HCl at room temperature for at least 3 h before further rinsing with D.I. water. After rinsing, samples were treated with four successive aliquots of reagent-grade 30%  $\text{H}_2\text{O}_2$  at room temperature over a period of 1 to 1.5 months to remove easily oxidizable organic matter (Yapp and Poths, 1991; 1993). The samples were subsequently dried in vacuum at room temperature. For convenience in subsequent discussion, “5M NaOH treatment” will be used to represent this series of chemical treatments.

The mole fraction (i.e. concentration) and carbon isotopic composition of the  $\text{Fe}(\text{CO}_3)\text{OH}$  component of the goethite in these samples were measured using the modified (Hsieh and Yapp, 1999; Tabor and Yapp, 2005a) incremental dehydration-decarbonation method of Yapp (1983). The particulars of the method as used in the current work are summarized below.

After outgassing at 100°C in vacuum for one hour, samples were heated at 180°C to 195°C in 0.16 bar of oxygen under closed system conditions for 30 minutes to remove organic matter that was not removed by the aforementioned  $\text{H}_2\text{O}_2$  treatments (Yapp and Poths, 1991). After this closed system step, samples underwent “low temperature” open system incremental vacuum dehydration-decarbonations at various temperatures from 170°C to 190°C with most increments carried out at 170°C (see Appendix). These low temperature steps are henceforth characterized as the “170°C” steps for convenience. Co-evolved  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were collected in several consecutive timed increments whose processing is facilitated by the moderate rate of dehydroxylation at 170°C. After completion of the sequence of 170°C steps, samples were heated to ~230°C in 0.16 bar of oxygen under closed system conditions for 30 minutes. This was followed by “high temperature” open system incremental vacuum dehydration-decarbonations at various temperatures from 205°C to 245°C with most at 220°C (see Appendix). These high temperature vacuum increments are henceforth referred to as “220°C” steps. The choice of both low and high temperature intervals of incremental vacuum dehydration-decarbonations for each sample was based on experimental tests of 05MN11-1rp, 2rp, and 11rp at different vacuum dehydration temperatures ranging from 185°C to 245°C. After the 220°C steps, the samples were heated to 850°C in closed system in 0.16 bar oxygen for ~30 minutes.

The  $\text{CO}_2$  and  $\text{H}_2\text{O}$  evolved in aforementioned closed and open system steps were separated by a cryogenic method (Yapp, 1983, Yapp and Poths, 1991). The  $\text{H}_2\text{O}$  was quantitatively converted to  $\text{H}_2$  by reaction with depleted uranium metal at 760°C. The  $\text{H}_2$  was collected and measured for yield with a Toepler pump with a precision of  $\pm 1\mu\text{mol}$ . The yield of  $\text{CO}_2$  was measured with a mercury manometer having a precision of  $\pm 0.1\mu\text{mol}$ . The  $\delta^{13}\text{C}$  values of the  $\text{CO}_2$  were measured

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on a Finnigan MAT 252 mass spectrometer in the stable isotope laboratory at SMU. The overall analytical precision for  $\delta^{13}\text{C}$  was  $\pm 0.3\%$  or better.  $\delta^{13}\text{C}$  is defined by:

$$\delta^{13}\text{C} = (\text{R}_{\text{sample}} / \text{R}_{\text{standard}} - 1)1000 \text{ ‰} \quad (3)$$

Where,  $\text{R} = ^{13}\text{C}/^{12}\text{C}$ . The standard is PDB (Pee Dee Belemnite, Craig, 1957)

### 3. RESULTS

#### 3.1 Mineral Identification

The XRD spectra indicate the presence of kaolinite, gibbsite, goethite, quartz, and hematite in nearly all bulk samples. Minor boehmite, berthierine, and lepidocrocite are also present in some of the samples (Table 1 and Fig. 4a). Kaolinite, gibbsite, and quartz are the dominant minerals, while goethite is a less abundant, but significant phase in all samples. Siderite, although observed by Toth and Fritz (1997), was not detected in our samples by the XRD method. The hierarchy of mineral abundances does not appear to vary systematically with sample depth.

The concentration of Al substituted for Fe in these goethites ranges from ~10 to 28 mole % (Table 1). This degree of Al substitution is consistent with pedogenic formation of the goethites in an Al-rich (i.e., gibbsite and kaolinite) soil environment (e.g., Siehl and Thein, 1989).

XRD analyses indicated no detectable gibbsite in any of the 5M NaOH-treated samples (Table 1, Fig. 4a). Also, kaolinite was not detected in 5M NaOH-treated samples of 05MN11-1rp, 05MN11-2rp, 05MN11-2m, 05MN11-4rp and 05MN11-5rp, but did persist at lower relative abundances in samples 05MN11-3rp, 05MN11-7rp, 05MN11-8rp, 05MN11-9rp, 05MN11-10rp and 05MN11-11rp (Fig. 4a, Table 1). As a test, this 5M NaOH-treatment was applied to a natural berthierine and siderite-rich sample, DRR-P4-2, from the Eocene Weches Fm. of Eastern Texas. Comparison of “before-and-after” XRD spectra in Fig. 4b indicates that there is no XRD-detectable formation of goethite upon treatment of berthierine and siderite with hot 5M NaOH.

#### 3.2 Incremental Dehydration

Incremental dehydration-decarbonation data for ten 5M NaOH-treated goethite-bearing paleosol samples (Fourteen dehydration experiments) of this study are listed in the Appendix. A maximum value of the weight % of goethite in these samples can be calculated, if it is assumed that the hydrogen (as  $\text{H}_2\text{O}$ ) from the 170°C and 220°C dehydration increments is solely structural, stoichiometric hydrogen from goethite. By this method, goethites comprise about 2 to 7 weight percent of these samples (Table 1). During incremental dehydration, 67 to 88% of the goethite breaks down in the 170°C step (Table 1). It should be kept in mind that the preceding values are subject to uncertainties associated with one or more of the following factors: 1) possible presence of HTN hydrogen in goethite (Yapp and Poths, 1995); 2) Al substitution for Fe in the goethite structure; and 3) possible contributions of hydrogen from oxidation of trace amounts of residual refractory organic matter. Notwithstanding the possible sources of error, it is evident that goethite is not a dominant mineral in these samples.

Fig. 5 and Fig. 6 depict typical incremental dehydration-decarbonation results of this study. Plots are presented with incremental values of F and  $\delta^{13}\text{C}_m$  (subscript “m” indicates the *measured* value for each increment) as a function of the progress variable  $X_v(\text{H}_2)$ . F is defined as  $n\text{CO}_2/n\text{H}_2$  ( $n$  = micromoles of the indicated substance).  $X_v(\text{H}_2)$  is the cumulative hydrogen evolved from the sample as a mole fraction of the total hydrogen in the sample. At  $X_v(\text{H}_2) = 1.0$ , all the hydrogen-bearing minerals in the sample are completely dehydrated. Values of F for individual 170°C vacuum increments range from 0.0002 to 0.0127, and  $\delta^{13}\text{C}_m$  values range from -19.4‰ to -5.4‰ (see Appendix). For the 220°C vacuum increments, values of F range from 0.0010 to 0.0444, and  $\delta^{13}\text{C}_m$  values range from -25.1‰ to -11.3‰ (see Appendix). The  $\delta^{13}\text{C}_m$  values of  $\text{CO}_2$  from 220°C increments are generally more negative than those of  $\text{CO}_2$  released from the same sample at 170°C, with limited overlap of the two populations (Fig. 7).

For some samples, as exemplified by 05MN11-2rp-2 and 8rp, in Fig. 5a and 5b, the dehydration-decarbonation pattern of a single sample indicates an approach to plateau values of both F (values within  $\pm 0.005$  for two or more consecutive vacuum increments) and  $\delta^{13}\text{C}_m$  (values within  $\pm 0.5\%$  for two or more consecutive vacuum increments) for incremental dehydrations at 170°C. Other samples, as shown in Fig. 6a and 6b, do not seem to achieve credible plateau values of either F or  $\delta^{13}\text{C}_m$ , especially  $\delta^{13}\text{C}_m$ . Possible implications of these results are discussed in a following section.

### 4. DISCUSSION

#### 4.1 Values of F and $\delta^{13}\text{C}_m$ for Incrementally Evolved $\text{CO}_2$

If stoichiometric goethites were the only mineral to break down during vacuum dehydration, stepwise increments of  $\text{CO}_2$  evolved from a uniformly distributed  $\text{Fe}(\text{CO}_3)\text{OH}$  component in solid solution should exhibit plateau values of concentration and  $\delta^{13}\text{C}_m$  (Yapp and Poths, 1991). In previous studies, such plateaus have been observed (Yapp and Poths, 1993; Yapp, 1997, 2001, 2002, 2004; Hsieh and Yapp, 1999). However, in this study, some samples do not exhibit plateaus for either the 170°C or 220°C vacuum dehydration-decarbonation increments. This implies a more complex scenario with respect to the release of  $\text{CO}_2$  and raises questions about the possible sources of  $\text{CO}_2$  in these samples.

##### 4.1.1 Evaluation of sources of $\text{CO}_2$ extracted from 5M NaOH-treated samples.

XRD analyses of samples after the 5M NaOH treatments indicate that, in most samples, only goethite, kaolinite, quartz, and hematite are present. Quartz and hematite are not known to contain and/or release  $\text{CO}_2$  at the temperatures of 170 to 245°C employed in this study. Oxidation of trace amounts of organic matter that was *not* removed by  $\text{H}_2\text{O}_2$  treatment might be a source of some additional  $\text{CO}_2$ . However, the closed system step in 0.16 bar  $\text{O}_2$  that precedes (at ~10°C higher temperature) the vacuum dehydration-decarbonation steps should minimize this possibility without significant breakdown of goethite (Yapp, 1983; Yapp and Poths, 1991).

There is no measurable loss of water from



kaolinite at temperatures of 170°C to 245°C (e.g., Girard and Savin, 1996). There was also no detectable release of  $\text{CO}_2$  from  $\text{H}_2\text{O}_2$ -treated kaolinite at any of the dehydration temperatures used in this study. Therefore, admixed kaolinite does *not* appear to be a factor in the lack of plateau values in many of the samples of this study.

Gibbsite can be a source of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  during vacuum dehydration at 170°C to 245°C (Schroeder and Melear, 1999; Tabor and Yapp, 2005a, 2005b; Schroeder, et al., 2006). However, gibbsite is not detectable by XRD in the samples treated with hot 5M NaOH.

Siderite was described by Toth and Fritz (1997) as a significant component in parts of the laterite. For the Purgatory Creek locale, they measured a siderite  $\delta^{13}\text{C}$  value of -6.2‰. However, our XRD analyses found no evidence of siderite in any of the samples of this study. Moreover, siderite does not break down at vacuum dehydration temperatures of 170 to 245°C (Yapp, 2007).

In summary, the weight of the experimental evidence suggests that goethite is the only (or overwhelming) source of  $\text{CO}_2$  recovered during the 170°C to 245°C incremental vacuum dehydration of the 5M NaOH-treated samples.

#### 4.1.2 Possible perturbations of plateau values

The existence of two apparently different isotopic populations of  $\text{CO}_2$ , distinguished by their particular dehydration temperatures (170°C and 220°C; Fig. 7), may indicate more than one generation of goethite in a single hand sample (e.g., Tabor and Yapp, 2005b).

Intimate mixtures of more than one generation of goethite could arise from: 1) preservation of small volumes of goethite formed successively at different depths in a soil as erosion progressively removed surface materials and the depth of a sample below the surface diminished; 2) later reductive burial diagenesis and mineralogical reaction of much (but *not* all) of the original goethite to berthierine and/or siderite (Toth and Fritz, 1997), followed by 3) one or more subsequent oxidative weathering events that partially converted diagenetic minerals back to high-Al goethite before reburial. If at least two such generations of goethite with different rates of breakdown and different  $\text{Fe}(\text{CO}_3)\text{OH}$  concentrations (F) and  $\delta^{13}\text{C}_m$  values coexist in these samples, the vacuum dehydration-decarbonation procedure might be used to sort out the  $\text{CO}_2$  evolved from each generation. This assumption is adopted as a working hypothesis.

A set of criteria was employed to permit consistent presentation of data from the complex incremental dehydration-decarbonation spectra of the goethites of this study. The intent was to establish criteria that would minimize consideration of data from increments that may have been influenced by  $\text{CO}_2$  or  $\text{H}_2\text{O}$  sources other than  $\text{Fe}(\text{CO}_3)\text{OH}$  and structural hydrogen in the goethite. Data from individual increments which fit into any of the following five categories were eliminated from discussion of the  $\text{Fe}(\text{CO}_3)\text{OH}$  component. "Robust" incremental data (with respect to paleoenvironmental interpretation) were those which did *not* fit into any of the five following discriminator categories:

1. Results are not discussed for any individual increment of  $\text{CO}_2$  gas whose measured  $\delta^{13}\text{C}_m$  value had a

standard deviation of  $\geq 0.2\%$  during measurement on the mass spectrometer. Such a standard deviation reflects poor mass spectrometer counting statistics, which (if present) were generally associated with smaller samples (0.1 to 0.2  $\mu\text{mol}$ ) and/or suggested some degree of contamination of unknown origin in the gas sample.

2. Any individual increment of  $\text{CO}_2$  gas whose yield is *less than* 0.2  $\mu\text{mol}$  was not included in subsequent discussion. Because of the analytical uncertainty of  $\pm 0.1$   $\mu\text{mol}$  in the measured yield,  $\text{CO}_2$  increments of less than 0.2  $\mu\text{mol}$  have an unacceptably high relative error. Thus, any physical interpretation of values of  $X_m$  calculated for such small samples is highly problematic.

3. The increment of  $\text{CO}_2$  in the first 170°C vacuum dehydration step after a closed system dehydration step in 0.16 bar  $\text{O}_2$  is not considered. This is because HTN hydrogen appears to contribute substantial  $\text{H}_2\text{O}$  in this step and thus lowers the value of F (Yapp and Poths, 1991). HTN water does not appear to be a factor in the initial vacuum increments at 220°C.

4. If, after a closed system dehydration step in 0.16 bar  $\text{O}_2$  at 230°C, the  $\delta^{13}\text{C}_m$  value of the  $\text{CO}_2$  from the subsequent 220°C open system step was within  $\pm 0.5\%$  of the closed system value, the value for that first 220°C vacuum increment was not included in the discussion. The idea in this instance was to reduce the possibility of using increments from a vacuum dehydration that may have retained some "memory" of  $\text{CO}_2$  generated by oxidation of organic matter in the preceding closed system step.

5. The final vacuum increments for both 170°C and 220°C dehydration in any sample were not considered, *if* the yield of  $\text{CO}_2$  was *less than or equal to* 0.2  $\mu\text{mol}$  and the measured  $\delta^{13}\text{C}_m$  value for the  $\text{CO}_2$  from these increments differed by more than  $\pm 0.5\%$  from the preceding vacuum increment. These final vacuum increments were of considerable duration (normally ~120 minutes), and the amount of  $\text{CO}_2$  recovered in these increments is generally small (~0.1  $\mu\text{mol}$ ). Such small amounts are particularly susceptible to possible contamination of  $\text{CO}_2$  from sources such as oxidation by the  $\text{Fe}(\text{III})$  oxide of trace amounts of relatively refractory organic matter.

These criteria for rejection of certain  $\text{CO}_2$  increments in a discussion of the possible paleoenvironmental implications of the data may not be definitive, but they do provide a consistently applied protocol in this study. Fifty-three robust data from the 170°C vacuum increments are listed in Table 2, and nineteen robust data from the 220°C vacuum increments are listed in Table 3.

#### 4.1.3 Relationship between $\delta^{13}\text{C}_m$ and $1/X_m$

The carbon isotopic fractionation factor between  $\text{Fe}(\text{CO}_3)\text{OH}$  goethite and  $\text{CO}_2$  gas is about 1.0025 (Yapp and Poths, 1993). Thus,  $(\delta^{13}\text{C}_{\text{Fe}(\text{CO}_3)\text{OH}} - \delta^{13}\text{C}_{\text{CO}_2})$  is about +2.5‰. Atmospheric  $\text{PCO}_2$  can be determined from a mixing line defined by values of  $X_m$  ( $X_m = F/2$ ) and  $\delta^{13}\text{C}_m$  from  $\text{Fe}(\text{CO}_3)\text{OH}$  in ancient pedogenic goethites formed at different depths in soils in which the local soil  $\text{CO}_2$  was a mixture of two components. The two components are: 1) atmospheric  $\text{CO}_2$  and 2)  $\text{CO}_2$  from *in situ* oxidation of soil organic matter (Yapp and Poths,

1992). For pedogenic goethite as a proxy for soil  $\text{CO}_2$ , the upper 50 cm of the soil profile are preferable, because the variations of concentration and  $\delta^{13}\text{C}$  values of soil  $\text{CO}_2$  are significant at shallow depths (Cerling and Quade, 1993). The two-component model for pedogenic goethite as a proxy for soil  $\text{CO}_2$  can be expressed as follows (Yapp and Poths, 1992, 1993; Yapp, 2004):

$$\delta^{13}\text{C}_m = (\delta^{13}\text{C}_A - \delta^{13}\text{C}_O)X_A(1/X_m) + \delta^{13}\text{C}_O \quad (4)$$

$$\text{where, } \delta^{13}\text{C}_O = \alpha_k \delta^{13}\text{C}_B + 1000(\alpha_k - 1). \quad (5)$$

$\delta^{13}\text{C}_m$  is the measured  $\delta^{13}\text{C}$  value of the  $\text{Fe}(\text{CO}_3)\text{OH}$  component in goethite.  $\delta^{13}\text{C}_A$  is the  $\delta^{13}\text{C}$  value of the  $\text{Fe}(\text{CO}_3)\text{OH}$  component if atmospheric  $\text{CO}_2$  were the only source of the  $\text{CO}_2$  occluded in the goethite structure. Thus, for an assumed atmospheric  $\text{CO}_2$   $\delta^{13}\text{C}$  value of -6.5‰, the value of  $\delta^{13}\text{C}_A$  would be about -4‰.  $\delta^{13}\text{C}_B$  is the  $\delta^{13}\text{C}$  value expected for the  $\text{Fe}(\text{CO}_3)\text{OH}$  if it were in equilibrium only with gaseous  $\text{CO}_2$  of the same  $\delta^{13}\text{C}$  value as  $\text{CO}_2$  introduced into the soil from oxidizing biological carbon (irrespective of the biologic source or sources--i.e., respiring roots, microbially mediated oxidation of soil organic matter, etc). Thus,  $\delta^{13}\text{C}_B = \delta^{13}\text{C}_{(\text{Organic matter})} + 2.5\text{‰}$ . The kinetic carbon isotopic fractionation factor ( $\alpha_k$ ) arises from diffusive transport of  $\text{CO}_2$  through a soil. The value of  $\alpha_k$  is taken to be 1.0044 (Cerling, et al., 1991).  $X_m$  is the measured mole fraction of  $\text{Fe}(\text{CO}_3)\text{OH}$  in pedogenic goethite.  $X_A$  is the mole fraction of  $\text{Fe}(\text{CO}_3)\text{OH}$  if it were in equilibrium only with  $\text{CO}_2$  from Earth's atmosphere. Eq. 4 predicts that a plot of  $\delta^{13}\text{C}_m$  against  $1/X_m$  should be linear for goethites from any particular two-component soil, and the slope of Eq. 4 is generally expected to be positive. The value of  $X_A$  can be extracted from the slope (Eq. 4). In general, values of  $X$  in goethite are related to  $\text{PCO}_2$  by the following expression (Yapp and Poths, 1992):

$$\log_{10}\text{PCO}_2 = \log_{10}X + 6.04 - (1570/T) \quad (6)$$

Previous studies (Hsieh and Yapp, 1999; Yapp, 2001, 2002) also revealed more complex soil  $\text{CO}_2$  mixing scenarios when goethites form at low pH (<5.5) under the influence of three isotopically distinct sources of  $\text{CO}_2$ . The relationship of  $\delta^{13}\text{C}_m$  and  $1/X_m$  values for goethite as a proxy of such mixing systems in near-surface oxidizing environments can be described by the following equation (Yapp, 2002):

$$\delta^{13}\text{C}_m = [(\delta^{13}\text{C}_A - \delta^{13}\text{C}_O)X_A + (\delta^{13}\text{C}_O - \delta^{13}\text{C}_C)X_S](1/X_m) + \delta^{13}\text{C}_C \quad (7)$$

$\delta^{13}\text{C}_C$  is the theoretical  $\delta^{13}\text{C}$  value of  $\text{Fe}(\text{CO}_3)\text{OH}$  in goethite if the only source of  $\text{CO}_2$  were dissolution of an ambient carbonate source.  $X_S$  is the mole fraction of  $\text{Fe}(\text{CO}_3)\text{OH}$  in goethite if it were in equilibrium only with the  $\text{CO}_2$  gas in a two-component soil  $\text{CO}_2$  mixture (i.e., a presumptive two-component soil  $\text{CO}_2$  system if there were no carbonate dissolution). Other terms are as defined for Eq. 4 (see Yapp, 2001, 2002 for details).

A hypothetical case is illustrated in Fig. 8 (after Yapp, 2001, 2002). To calculate the illustrative mixing lines in Fig. 8, it was assumed that there were three possible sources for gaseous  $\text{CO}_2$  in a soil profile. (1) Atmospheric  $\text{CO}_2$  with a  $\delta^{13}\text{C}$  value of -6.5‰, yielding a

$\delta^{13}\text{C}_A$  value of -4.0‰. (2)  $\text{CO}_2$  from oxidation of soil organic matter. Three different organic matter  $\delta^{13}\text{C}$  values (-25.4‰, -29.4‰, -33.4‰) were specified for Fig. 8, yielding corresponding  $\delta^{13}\text{C}_O$  values of -18.5‰, -22.5‰, and -26.5‰. (3)  $\text{CO}_2$  from dissolution of a carbonate mineral with a  $\delta^{13}\text{C}$  value of -6.2‰, yielding a  $\delta^{13}\text{C}_C$  value of +0.7‰ ( $\delta^{13}\text{C}_C = -6.2\text{‰} + 4.4\text{‰} + 2.5\text{‰}$ ). This selection of the third  $\text{CO}_2$  source will be discussed in the following section.

Two sets of two-endmember mixing arrays in Fig. 8 (with positive slopes) indicate two different specified atmospheric  $\text{CO}_2$  concentrations (IPAL and 16PAL, "PAL" stands for "Pre-Industrial Atmospheric Level", i.e., 280 ppmV). If there were contributions from an *in situ* third  $\text{CO}_2$  endmember with a relatively high  $\delta^{13}\text{C}$  value (i.e., *in situ* dissolution and oxidation of siderite), it would cause proxy goethite data to depart from the two-endmember mixing lines in ways indicated by the three-component mixing lines (the dashed lines in Fig. 8 with negative slopes).

In the following section, the relationships of  $\delta^{13}\text{C}_m$  and  $1/X_m$  for the previously proposed generations of goethite are discussed in the context of the concepts represented by Fig. 8. For purposes of this discussion, the  $\text{CO}_2$  evolved at 220°C is presumed to originate from an older "generation 1" goethite, whereas the  $\text{CO}_2$  evolved at 170°C is considered to derive from a younger goethite of "generation 2". This interpretation of relative ages is generally consistent with similar evidence for two generations of goethite in a Paleocene laterite in Northern Ireland (Tabor and Yapp, 2005b).

#### 4.2 The 170°C (Generation 2) Data

Fig. 9 contains a plot of  $\delta^{13}\text{C}_m$  against  $1/X_m$  for the robust 170°C (generation 2) data of Table 2. The scatter of the data is enclosed within a hypothesized three endmember mixing field of the sort depicted in Fig. 8. Two questions arise from the postulate that the generation 2 goethite formed in a soil environment with three distinct  $\text{CO}_2$  sources.

First, what was the source of the third  $\text{CO}_2$  endmember in this mixing environment? Toth and Fritz (1997) reported a  $\delta^{13}\text{C}$  value of -6.2‰ for a diagenetic siderite from the Purgatory Creek locale. Dissolution and oxidation of this siderite at lower values of pH during "post-diagenetic" weathering would have provided an *in situ*  $\text{CO}_2$  source with a relatively positive  $\delta^{13}\text{C}$  value as well as iron for formation of generation 2 goethite. To facilitate further discussion, the following conditions were assumed: a) this siderite-derived  $\text{CO}_2$  was dominantly in the soil gas phase; b) there was a 4.4‰ steady-state enrichment in  $^{13}\text{C}$  of siderite-derived soil  $\text{CO}_2$  relative to the input  $\text{CO}_2$  from siderite (Cerling, et al., 1991); and c) the carbon isotopic fractionation between  $\text{CO}_2$  occluded in goethite and gaseous  $\text{CO}_2$  is 2.5‰ (Yapp and Poths, 1993). With these assumptions, it was calculated that a hypothetical goethite formed in equilibrium only with siderite-derived soil  $\text{CO}_2$  would have a  $\delta^{13}\text{C}_C$  value of +0.7‰. This latter value is the presumed third endmember (see Eq. 7) for the proposed three component mixing and would account for the positive shifts of  $\delta^{13}\text{C}_m$  values

Second, is the generation 2 goethite represented by the  $170^\circ\text{C}$  vacuum steps actually younger than the generation 1 goethite presumed to correspond to the  $220^\circ\text{C}$  steps? As indicated by the data array of Fig. 9, a younger age for the generation 2 goethite is consistent with the idea of its formation by oxidative dissolution of diagenetic siderite in a younger weathering environment. This could imply that the small amount of isotopically distinct goethite which breaks down at  $220^\circ\text{C}$  (generation 1) is a relic from an earlier oxidizing soil environment, and that this older goethite may have persisted through the reductive diagenetic event that produced the siderite and berthierine. If so, the younger and older generations of pedogenic goethite preserve information on different soil  $\text{CO}_2$  mixing systems. In addition, a lower temperature ( $170^\circ\text{C}$ ) of breakdown probably indicates that these goethite crystals are smaller and perhaps less well organized than the goethite which breaks down at  $220^\circ\text{C}$ . If so, this would be consistent with a younger age for the generation 2 goethite.

#### 4.3 The $220^\circ\text{C}$ (Generation 1) Data

Based on the pattern of hydrogen yield from the incremental dehydration of each sample (e.g., Fig. 5 and Fig. 6), goethite that broke down at  $220^\circ\text{C}$  (generation 1) comprises ~12 to 33 wt % of the total goethite in each sample. The “robust” (as previously defined)  $\delta^{13}\text{C}_m$  and  $1/X_m$  values from nineteen vacuum dehydration increments at  $220^\circ\text{C}$  (generation 1 goethite) are listed in Table 3 and plotted in Fig. 10a. The hypothesized three-endmember mixing domain representing generation 2 goethite is also plotted for comparison. There is scatter in the data from generation 1. The range of  $1/X_m$  is comparable to the range for generation 2 goethite. However, as previously noted (Fig. 7), the  $\delta^{13}\text{C}_m$  values of  $\text{CO}_2$  from the increments of generation 1 are generally more negative. As noted, this difference in  $\delta^{13}\text{C}_m$  values suggests that the generation 1 goethite preserves information about an environment different from the post-diagenetic environment of generation 2. Because this small amount of generation 1 goethite seems to have persisted through the reductive diagenesis that produced the siderite and berthierine, generation 1 goethite is a plausible source of information on the pre-diagenetic, intense Cenomanian weathering (Toth and Fritz, 1997) near the eastern shore of the WIS. Two-component mixing of soil  $\text{CO}_2$  might be expected in such an intensely weathered, highly evolved system.

Here we propose a model-derived criterion to assess the existence or absence of a coherent, proxy, two-endmember mixing relationship among a significant fraction of the  $220^\circ\text{C}$  goethite data. The model to be used is represented by Eq. 4. Rearrangement of that equation yields:

$$(\delta^{13}\text{C}_m - \delta^{13}\text{C}_O) X_m = (\delta^{13}\text{C}_A - \delta^{13}\text{C}_O) X_A \quad (8)$$

The right-hand side of Eq. 8 represents the slope of a two-component mixing line in a plot of  $\delta^{13}\text{C}_m$  vs.  $1/X_m$  (see Eq. 4). As shown in Eq. 8, this slope is equal to the combination of two *measured* parameters ( $\delta^{13}\text{C}_m$  and  $X_m$ ; Table 3) and one *specified* parameter ( $\delta^{13}\text{C}_O$ ). In principle,

if  $\delta^{13}\text{C}_O$  is known, it can be paired with any other measured goethite data point (represented by  $\delta^{13}\text{C}_m$  and  $X_m$ ) in that soil to calculate the slope of a hypothetical proxy mixing line for soil  $\text{CO}_2$ . If the specified value of  $\delta^{13}\text{C}_O$  is paired with *each* measured data point in succession to calculate a two-point line, the resulting values for those slopes can be plotted on a histogram to depict the degree of scatter in the data set. This model-based procedure for calculating separate two-point slopes is analogous to an approach used by Clark-Thorne and Yapp (2003) in a study of  $\text{CO}_2$  mixing in an urban atmosphere.

For the robust data from the  $\sim 220^\circ\text{C}$  increments (Table 3), the increment with the most negative value of  $\delta^{13}\text{C}_m$  (-23.1‰) also had the highest value for  $X_m$  (0.0222). Therefore, this  $\delta^{13}\text{C}_m$  value (-23.1‰) was taken as an approximation of  $\delta^{13}\text{C}_O$  in the ancient soil. Pairing of this  $\delta^{13}\text{C}_O$  value with each of the other eighteen measured  $\delta^{13}\text{C}_m$  values in succession generated calculated values for the slopes of eighteen, two-point, hypothetical, proxy mixing lines. The values of these slopes are plotted in the histogram of Fig. 10b. About 44% (eight of the eighteen) of the values in Fig. 10b appear to cluster (diagonal fill) and exhibit an approximate peak around a slope of about 0.006. Moreover, these eight values are distinctly separate from the remaining ten, rather widely scattered values (stippled fill) in Fig. 10b. This “cluster” of the slopes suggests the possibility that the data of these eight increments represent the same soil  $\text{CO}_2$  mixing conditions. The fact that this grouping of eight calculated values in Fig. 10b is at the lower end of the scatter of two-point slopes reinforces the visual impression from Fig. 10a that some of the  $220^\circ\text{C}$  data are arrayed in an approximately linear lower bound to the  $220^\circ\text{C}$  data. Positive deviations from such a lower bound (Fig. 10a) might be attributed to contamination during vacuum dehydration at  $220^\circ\text{C}$  by  $\text{CO}_2$  from small amounts of generation 2 goethite that persisted after the  $170^\circ\text{C}$  steps (the possibility of such persistence is suggested by the kinetic results of Yapp, 1983).

A linear regression of  $\delta^{13}\text{C}_m$  against  $1/X_m$  for the eight clustered points of Fig. 10b, together with the point used to define  $\delta^{13}\text{C}_O$ , yields the following equation:

$$\delta^{13}\text{C}_m = 0.0064 (1/X_m) - 23.2 \quad (9)$$

$$r^2 = 0.98$$

The large value for  $r^2$  (0.98) is simply a reflection of the selection criterion (Fig. 10b) applied to decide which data points to include in the regression. The fact that different increments of a particular sample aliquot, or increments from different aliquots of a sample, exhibit different values of  $\delta^{13}\text{C}_m$  and  $X_m$  (Table 3) is illustrative of the previously mentioned lack of plateaus in the incremental dehydration spectra. One speculation is that such differences might indicate that different volumes in the putative generation 1 goethite formed at different times (depths) in the Cenomanian soil. Differences in the timing of breakdown of these volumes during incremental vacuum dehydration at  $220^\circ\text{C}$  could explain the differences in  $\delta^{13}\text{C}_m$  and  $X_m$  of  $\text{CO}_2$  recovered from these steps.

There is also the possibility that there is more than



one paleosol in the outcrop. This is suggested by a plot of  $\delta^{13}\text{C}_m$  as a function of depth below the top of the outcrop (Fig. 11) for the nine goethite data points (filled diamonds) of the apparent linear array of Fig. 10a. The most negative “two-component”  $\delta^{13}\text{C}_m$  values are near the top of the outcrop, while the most positive value is near the bottom (Fig. 11). This pattern is the opposite of that expected in a single soil exhibiting the usual mixing of two  $\text{CO}_2$  endmembers (e.g., Cerling and Quade, 1993; Yapp and Poths, 1992). Such a “reversed” pattern has been observed in a young soil in eastern Texas, which exhibits mixing of three  $\text{CO}_2$  endmembers (i.e., addition of  $\text{CO}_2$  from dissolving calcite; Hsieh and Yapp, 1999). However, in that Texas soil, the plot of  $\delta^{13}\text{C}_m$  vs.  $1/X_m$  for the pedogenic goethite has a negative slope (Yapp, 2001, 2002). The slope of the apparent two-component Cenomanian data array in the current study (Fig. 10a) is positive.

Thus, the pattern of data in Fig. 11 might indicate the presence of more than one paleosol in the outcrop of Fig. 2. One speculation is that different portions of the original paleosols (corresponding to different soil productivities and/or different original depths beneath the ancient surfaces) have been preserved, or sampled, leading fortuitously to the pattern seen in Fig. 11. The existence of more than one pisolite-rich layer in the outcrop (Fig. 2) might support this idea. However, if the  $\delta^{13}\text{C}$  values of atmospheric  $\text{CO}_2$  and oxidizing organic matter, as well as atmospheric  $\text{CO}_2$  concentration, remained relatively constant over the intervals of soil formation, the various individual increments of  $\text{CO}_2$  recovered from goethite would still lie on a proxy mixing line common to all of those soils in a plot of  $\delta^{13}\text{C}_m$  against  $1/X_m$  (Fig. 10a and Eq. 4).

The partial pressure of atmospheric  $\text{CO}_2$  can be determined from the value of  $X_A$  and knowledge of the temperature of goethite formation (Eq. 6). The temperature was determined from measurements of the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values of the pisolitic kaolinite in the samples. This determination assumed that ancient soil waters would have plotted on the meteoric water line (MWL) of Craig (1961). There is some support for this assumption in results from other ancient lateritic systems (e.g., Yapp, 2008). The temperature calculated from kaolinite data was  $24^\circ\text{C}$  (details will be presented in separate paper).

A value of  $+19\text{‰}$  was assumed for  $(\delta^{13}\text{C}_A - \delta^{13}\text{C}_O)$  and was derived from the intercept of Eq. 9 (i.e.,  $\delta^{13}\text{C}_O = -23.2\text{‰}$ ) and the previously discussed  $\delta^{13}\text{C}_A$  value of  $-4.0\text{‰}$ . Division of the slope (0.0064, Eq. 9) by 19 yields a value of 0.00034 for  $X_A$  (Eqs. 4 and 9). From Eq. 6, this  $X_A$  corresponds to an atmospheric  $\text{CO}_2$  partial pressure of 0.0019 atm at a temperature of  $24^\circ\text{C}$ . For a total gas pressure of one atm, this corresponds to an atmospheric  $\text{CO}_2$  concentration of  $1900(\pm 100)$  ppmV. The uncertainty of  $\pm 100$  ppmV is simply a reflection of the scatter of the nine data points and does not carry significant overall analytical or physical meaning.

#### 4.4 Paleoenvironmental and Paleoclimatic Implications

There are comparatively few proxy determinations of atmospheric  $\text{CO}_2$  concentrations in the

Cenomanian and Turonian, one of the warmest intervals of geological history. For the interval from 100 to 90 Ma, Retallack (2001) obtained atmospheric  $\text{CO}_2$  concentrations of about 4000-5500 ppmV using the stomatal indices of fossil plants related to present-day *Ginkgo*. Freeman and Hayes (1992) estimated values of 830-1100 ppmV at about 94 Ma from the carbon isotopic composition of marine organic compounds, whereas Ekart, et al. (1999) obtained  $\text{CO}_2$  concentrations of about 1200-2600 ppmV at 80Ma, 108Ma and 115Ma using  $\delta^{13}\text{C}$  values of paleosol pedogenic calcite. Berner and Kothavala (2001) used a global carbon flux balance model to estimate a range of about 500-2000 ppmV at  $\sim 94$ Ma. The tropospheric  $\text{CO}_2$  concentration of about 1900 ppmV presented here for the Cenomanian ( $\sim 95$ Ma B.P.) is near the middle of the range determined by Ekart, et al. (1999) for the mid-Cretaceous and is in accord with the implications of the published results that Cenomanian atmospheric  $\text{CO}_2$  levels were high.

Variations of atmospheric  $\text{CO}_2$  concentrations have been proposed as a significant factor in Phanerozoic climate change (e.g., Barron and Washington, 1985; Berner and Kothavala, 2001, Royer, et al., 2004). Royer (2006) further summarized model and proxy studies to point out the striking covariance of atmospheric  $\text{CO}_2$  concentrations and Earth's global climate through Phanerozoic time. The tropospheric  $\text{CO}_2$  concentration of 1900 ppmV obtained from the generation 1 pisolitic goethite of the current study, combined with the warm, mid-paleolatitude ( $\sim 40^\circ\text{N}$ ), coastal continental temperature of  $24^\circ\text{C}$  obtained from the pisolitic kaolinite, is consistent with the expectation of a positive relationship between Earth surface temperatures and atmospheric  $\text{CO}_2$  concentrations. However, the question of whether or not there was a smaller latitudinal temperature gradient on the warm Cenomanian continents awaits data from other surficial systems of the same age, but a wide range of paleolatitudes.

## 5. CONCLUSIONS

This carbon isotope study of goethite in a Cenomanian paleosol from southwestern Minnesota suggests that the characteristics of a dehydration data array in a plot of  $\delta^{13}\text{C}_m$  vs.  $1/X_m$  may permit one (in some circumstances) to “see through” a low temperature diagenetic event to an earlier environment of lateritic soil formation. The data from the original pedogenic goethite appear to preserve information on the concentration of atmospheric  $\text{CO}_2$  in the Cenomanian ( $\sim 95$ Ma). The inferred Cenomanian tropospheric  $\text{CO}_2$  concentration of  $\sim 1900$  ppmV is generally consistent with published values from studies of other proxies as well as a global carbon flux balance model. Thus, diagenesis does not necessarily completely erase the original paleoenvironmental information recorded in pedogenic goethite, and careful incremental dehydration-decarbonation analyses may reveal the presence of the ancient material.

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#### FIGURE CAPTIONS

- Fig. 1. Paleogeographic map of North America during the Cenomanian, redrawn from Scotese (1997). Filled star indicates the location of the Cretaceous laterite discussed in this report.
- Fig. 2. Photograph of the roadcut from which the samples were collected. Squares indicate the positions of samples. Densities of the empty circles filling the squares indicate the relative abundance of pisolites in each sample. Samples from 05MN11-1 to 05MN11-5, as well as 05MN11-11 have more abundant pisolites, while the abundance of pisolites diminishes gradually from 05MN11-7 to 05MN11-10.
- Fig. 3. Thin sections. a) 05MN11-2, b) 05MN11-4, c) 05MN11-8, and d) 05MN11-11. Black scale bars are 2.0 mm.
- Fig. 4. XRD patterns of some of 05MN11 samples of this study. a) XRD patterns for 05MN11-11rp. Lower pattern (2) is the sample before any chemical treatment, while upper pattern (1) is the same sample after hot 5 M NaOH treatment (see text for procedure of this treatment). The prominent difference is the disappearance of the gibbsite peaks. b) XRD patterns for sample DRR-P4-2 used to test of the effect of hot 5 M NaOH treatments on berthierine and siderite. Lower pattern (2) is the sample before the treatment, while upper pattern (1) is the same sample after 5 M NaOH treatments, the berthierine and siderite peaks have been removed while no significant change for the goethite peak can be observed. K=kaolinite; Bh=berthierine; Q=quartz; Hm=hematite; G=goethite; Gb=gibbsite; S=siderite. "NCT" = not chemically treated.
- Fig. 5. Isothermal dehydration-decarbonation patterns of samples 05MN11-2rp-2 and 05MN11-8rp. F is defined as the  $n\text{CO}_2/n\text{H}_2$  ratio of each increment.  $X_v(\text{H}_2)$  is the progress variable which ranges from 0.0 to 1.0, indicating the fraction of the total hydrogen that has been removed from the sample (see text). Asterisks indicate steps performed under closed system conditions in  $\sim 0.16$  bar of  $\text{O}_2$ .
- Fig. 6. Isothermal dehydration-decarbonation patterns of samples 05MN11-5rp and 05MN11-11rp. F,  $X_v(\text{H}_2)$ , and asterisks have the same meaning as in Fig. 5.
- Fig. 7. Histogram of "robust" (see text and Table 2, Table 3)  $\delta^{13}\text{C}_m$  values of  $\text{CO}_2$  extracted from 170°C and 220°C increments of 05MN11 goethite samples.
- Fig. 8. Model simulation of  $\delta^{13}\text{C}_m$  vs.  $1/X_m$  for goethites formed under the influence of two and three distinct sources of  $\text{CO}_2$  (after Yapp, 2001, 2002). The solid lines (positive slopes) are mixing lines calculated for mixing of two  $\text{CO}_2$  components in soils according to Eqs. 4 and 6 with different specified values of  $\delta^{13}\text{C}_O$  (-18.5‰, -22.5‰ and -26.5‰). Atmospheric  $\text{CO}_2$  concentrations for the two-component lines are expressed in units of PAL (Pre-industrial Atmospheric Level, i.e., 280ppmV). Steeper slopes represent higher concentrations of atmospheric  $\text{CO}_2$  levels. The dashed lines with the negative slopes were calculated for simple three-component mixing of  $\text{CO}_2$  in accord with Eqs. 6 and 7. The three components were assumed to be atmospheric  $\text{CO}_2$ , oxidized soil organic matter and  $\text{CO}_2$  derived from dissolution and oxidation of siderite with a  $\delta^{13}\text{C}$  value of -6.2‰. The arrows indicate the directions that two-component goethite would shift, if it were to be dissolved and reprecipitated under the influence of the aforementioned third component (see text).
- Fig. 9.  $\delta^{13}\text{C}_m$  vs.  $1/X_m$  for vacuum dehydration-decarbonation increments at 170°C. Only "robust" data are plotted (see text). Dashed lines enclosing the shaded triangular area are the boundaries that represent the proposed mixing domain of three  $\text{CO}_2$  sources for these generation 2 goethites (see text).
- Fig. 10. Results from "robust" data for the 220°C vacuum steps. a)  $\delta^{13}\text{C}_m$  vs.  $1/X_m$  for 220°C increments. Dashed lines enclosing the shaded triangular area are the boundaries that represent mixing domain of three  $\text{CO}_2$  sources for generation 2 goethites. Shaded squares are increments whose  $1/X_m$  and/or  $\delta^{13}\text{C}_m$  values might be influenced by cross-contamination of generation 2 goethites. Filled circles are nine data selected using the pattern of distributions in Fig. 10b (see text). The solid line represents the linear regression of these nine data points and has a slope of  $\sim 0.0064$  (see text). b) Histogram of the slopes of two-point regressions between each of the 220°C vacuum data points and an assumed  $\delta^{13}\text{C}_O$  value (see text).
- Fig. 11.  $\delta^{13}\text{C}_m$  values of the nine data from the 220°C dehydrations of generation 1 goethites that appear to represent two-component mixing of soil  $\text{CO}_2$  (see text) are plotted against their respective depths below the top of the outcrop. The apparent "reverse" relationship between the  $\delta^{13}\text{C}_m$  values and depths might be a result of the presence of more than one paleosol in the outcrop (see text).