

$^{18}\text{O}/^{16}\text{O}$ and D/H Ratios of Pedogenic Kaolinite in A North American Cenomanian Laterite: Paleoclimatic Implications

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ABSTRACT

Kaolinite, gibbsite and quartz are the dominant minerals in samples collected from two outcrops of a Cenomanian (~95 Ma) laterite in southwestern Minnesota. A combination of measured yields and isotope ratios permitted mass balance calculations of the δD and $\delta^{18}\text{O}$ values of the kaolinite in these samples. These calculations yielded kaolinite δD values of about -73‰ and $\delta^{18}\text{O}$ values of about +18.7‰. The δD and $\delta^{18}\text{O}$ values appear to preserve information on the ancient weathering system.

If formed in hydrogen and oxygen isotope equilibrium with water characterized by the global meteoric water line (GMWL), the kaolinite δD and $\delta^{18}\text{O}$ values indicate a crystallization temperature of $22 (\pm 5)^\circ\text{C}$. A nominal paleotemperature of 22°C implies a $\delta^{18}\text{O}$ value for the corresponding water of -6.3‰. The combination of temperature and meteoric water $\delta^{18}\text{O}$ values is consistent with relatively intense rainfall at that mid-paleolatitude location (~40°N) on the eastern shore of the North American Western Interior Seaway. The inferred Cenomanian paleosol temperature of $\sim 22^\circ\text{C}$ is in general accord with published mid-Cretaceous continental mean annual temperatures (MAT) estimated from leaf margin analyses of fossil plants.

When compared with results from a published GCM-based Cenomanian climate simulation which specifies a latitudinal sea surface temperature (SST) gradient that was either near modern or smaller-than-modern, the kaolinite paleotemperature of 22°C is closer to the GCM-predicted MAT for a smaller equator-to-pole temperature difference in the mid-Cretaceous. Moreover, the warm, kaolinite-derived, mid-paleolatitude temperature of 22°C is associated with proxy estimates of high concentrations of atmospheric CO_2 in the Cenomanian. The overall similarity of proxy and model results suggests that the general features of Cenomanian continental climate in that North American locale are probably being revealed.

1. INTRODUCTION

The mid-Cretaceous (Cenomanian and Turonian, 100 Ma to 89 Ma) was characterized by a “climatic optimum” (e.g., Huber, et al, 1995; Miller, et al., 2003) that is manifested in 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 sea surface temperature (SST) gradient during the mid-Cretaceous was smaller than the modern value, with high latitude regions warmed up more than low latitude regions (Barron, 1984; Herman and Spicer, 1997; Huber, et al, 1995, 2002). For example, a reported mid-Cretaceous latitudinal SST gradient of 0.25°C per degree of latitude at 100-99 Ma contrasts with the modern value of 0.40°C per degree of latitude (Huber, et al., 2002). However, a case has also been made that the mid-Cretaceous latitudinal SST gradient was similar to modern and that equatorial SST were proportionately higher in the mid-Cretaceous (e.g., Pucéat, et al., 2007; Wagner, et al., 2008). Additional quantitative paleoclimatic information (in particular from continental systems) would be of value in the effort to understand the nature of the mid-Cretaceous “climatic optimum”. In this paper, we present the results of hydrogen and oxygen isotope analyses of kaolinite from a mid-paleolatitude Cenomanian paleosol and discuss their paleoenvironmental significance.

2. Samples and Methods

2.1 Paleosol samples

The outcrops of the paleosol sampled for this study are located in the Minnesota River Valley, Renville County, in southwestern Minnesota. In the Cenomanian, the paleosol was in a coastal locale on the eastern side of the Western Interior Seaway (WIS) at a paleolatitude of $\sim 40^{\circ}\text{N}$ (see Fig. 1 of Feng and Yapp, 2009) 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 ~ 3.4 Ga Morton gneiss (Toth and Fritz, 1997; Schmitz, et al., 2006). The Cretaceous fluvial sediments are subdivided vertically into two parts, a lower arenaceous zone and an upper argillaceous zone, which 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, whereas the argillaceous zone is composed of kaolinitic silt and clay with some thin, fine-sand layers and organic-rich deposits at the bottom. A mid-Cretaceous laterite dominates at the top of the argillaceous zone and forms an extensive pisolitic horizon (Fig. 1c), although Toth and Fritz (1997) noted that laterite layers occur at different intervals in the formation. Toth and Fritz

(1997) also stated that there is no evidence of reworking of pisolitic material in the argillaceous zone.

Two sample locales are indicated in Fig. 1a. At site A (“Purgatory Creek locale”, Fig. 1c), the laterite outcrop is exposed in a roadcut located next to Renville Co Hwy 51, near Purgatory Creek (GPS coordinates: $44^{\circ}32'01.38''\text{N}$; $94^{\circ}55'41.34''\text{W}$; elevation $\sim 267\text{m}$). Site B (Quarry Locale) is about 6 km to the west of site A, on the north side of “Mike’s” quarry (GPS coordinates: $44^{\circ}32'33.84''\text{N}$; $95^{\circ}01'58.1''\text{W}$; elevation: $\sim 295\text{m}$). At this location, the exposed sequence of the paleosol is fined-grained (clay), gray to white-colored and displays no distinct horizonation and only a few scattered pisolites (Fig. 1b).

A stable carbon isotope study of the $\text{Fe}(\text{CO}_3)\text{OH}$ component in pisolitic goethite from the Purgatory Creek outcrop (site A, Fig. 1c) indicated that there might be more than one generation of goethite (Feng and Yapp, 2009). This reinforced the conclusion of Toth and Fritz (1997) that the lateritic paleosol experienced some degree of low temperature reductive diagenesis followed by re-oxidation.

Nine samples were collected from the Purgatory Creek outcrop for hydrogen and oxygen isotopic analysis (Fig. 1c, Table 1; 05MN11 samples). Samples 05MN11-1 to 05MN11-5 and 05MN11-11 contain relatively abundant reddish pisolites, as well as pale green, white, or yellow pisolites. These pisolites are 2mm to 20mm in diameter, and the rims appear to be darker (Feng and Yapp, 2009). The matrix surrounding the pisolites is pale brown, yellow, or sometimes green. Samples 05MN11-7 to 05MN11-10 and 05MN11-12 have fewer pisolites. The green color probably indicates the presence of Fe^{2+} minerals such as berthierine (idealized chemical formula is $\text{Fe}_2\text{Al}_2\text{SiO}_5(\text{OH})_4$) and/or siderite (Toth and Fritz, 1997). Different parts of a sample were physically separated for analysis as indicated by a descriptor added to each sample label. “m” indicates material that is predominantly from the matrix, while “rp” indicates material from the “reddish part of the pisolites” hand-picked from that sample.

The three analyzed samples from the quarry locale (site B, Fig. 1) are 05MN6-8, 05MN6-10, and 05MN6-17 (Fig. 1b, Table 1). These samples contain few observable pisolites, and are mostly white in color.

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 carried out on a Rigaku Ultima III X-ray diffraction instrument with Cu-K α radiation (40KV, 44mA) at Southern Methodist University (SMU). Detailed equipment configurations are the same as in Feng and Yapp (2008).

Prior to isotopic analysis, samples were chemically treated to: 1) remove “impurities” such as organic matter and carbonates (Yapp and Poths, 1991; Yapp, 1998); and 2) simplify the mineral assemblage by removing iron oxides including goethite and hematite (Jackson, 1979; Tabor and Yapp, 2005). Iron (III) oxides were removed from the 05MN11 samples of site A (Fig. 1) by treatment at 22°C with a citrate-dithionite (CD) solution using the same procedure employed by Tabor and Yapp (2005), which is a modification of the method of Jackson (1979). Three iron oxide-free samples (05MN6 samples) from site B (Fig. 1) underwent room temperature treatments only with 0.5 M HCl (~ 12 h) to remove any

admixed calcite, followed by rinsing with deionized (D.I.) water, then treatment with 30% H_2O_2 to remove organic matter (four consecutive H_2O_2 treatments for a total of 1 to 1.5 months).

Nine samples were analyzed for incremental δD values using a three-step procedure: 1) outgassing at 100°C for 60 min in a vacuum chamber; 2) subsequent dehydration in vacuum at 220°C for ~150 min; and 3) dehydration in vacuum at 850°C for ~30 min. For subsequent mass balance calculations, five additional samples were analyzed for δD values using a two-step dehydration method (outgassing in vacuum at 100°C , followed by 850°C dehydroxylation) of Yapp and Pedley (1985).

H_2O and CO_2 were continuously collected in a liquid nitrogen-cooled trap during each dehydration step. The small amounts of CO_2 were cryogenically separated from the H_2O with a methanol-dry ice bath. H_2O was quantitatively converted to H_2 by reaction with depleted uranium metal at 760°C . The H_2 was collected and measured for yield with a Toepler pump with a precision of $\pm 1\ \mu\text{mol}$. The D/H ratio of the H_2 gas was subsequently measured on a Finnigan isotope ratio mass spectrometer in the Stable Isotope Laboratory at SMU.

Oxygen was extracted from the treated samples for isotopic analysis at SMU using the BrF_5 method of Clayton and Mayeda (1963). Oxygen yields (determined for the resultant CO_2 gas) were measured manometrically with a precision of about $\pm 0.1\ \mu\text{mol}$. The $^{18}\text{O}/^{16}\text{O}$ ratios of the product CO_2 were measured on a Finnigan isotope ratio mass spectrometer.

Oxygen and hydrogen isotopic compositions are reported with the usual “ δ ” notation, where, $\delta\text{X} = (\text{R}_{\text{sample}} / \text{R}_{\text{standard}} - 1) \times 1000\ \text{‰}$ (1)

For $\text{X} = ^{18}\text{O}$, $\text{R} = ^{18}\text{O}/^{16}\text{O}$, whereas $\text{X} = \text{D}$, for $\text{R} = \text{D}/\text{H}$. The standard for both hydrogen and oxygen is V-SMOW (Gonfiantini, 1978). In the following sections, the standard is referred to as “SMOW” for convenience. Overall analytical precision of the isotopic measurements is $\pm 3\ \text{‰}$ for δD values and $\pm 0.3\ \text{‰}$ for $\delta^{18}\text{O}$ values.

2.2 Water samples

Three modern water samples (Table 2) were collected from the locale of the studied paleosol for hydrogen and oxygen isotopic analyses. 05WMN-1 is water from the Minnesota River collected from the north bank near the bridge on Renville Co Hwy 5 (GPS: $44^\circ 31' 05.16''\ \text{N}$; $94^\circ 53' 05.34''\ \text{W}$; elevation: ~257 m). About 200 to 300 ml of water were collected 10 cm below surface of the river. 05WMN-2 is water collected from a small first-order stream on the north side of Renville Co Hwy 51 (GPS: $44^\circ 31' 18.78''\ \text{N}$; $94^\circ 53' 43.92''\ \text{W}$; elevation: ~261 m). 05WMN-3 is water from Crow Creek (GPS: $44^\circ 32' 27.96''\ \text{N}$; $95^\circ 1' 26.76''\ \text{W}$; elevation: ~253 m), a tributary of the Minnesota River. This sample was collected about 20 cm below the water surface.

Water samples were quantitatively converted to H_2 over depleted uranium metal at 760°C and measured for δD values with a precision of about $\pm 1\ \text{‰}$. $\delta^{18}\text{O}$ values were determined with a precision of $\pm 0.1\ \text{‰}$ using the CO_2 - H_2O equilibration method of Epstein and Mayeda (1953).

3. RESULTS

3.1 XRD results

The XRD spectra for untreated 05MN11-5rp (site A) and 05MN6-8 (site B) are shown in Fig. 2 and represent the

typical mineral compositions of samples from these sites. Also shown in Fig. 2 is the XRD pattern of CD-treated 05MN11-5rp and 0.5 M HCl and 30% H_2O_2 -treated 05MN6-8.

05MN11 samples (site A, Fig. 1a, c) consist primarily of quartz, kaolinite, and gibbsite, with significant, but less abundant goethite and hematite, minor boehmite, and in two samples, berthierine or lepidocrocite (Table 1). A notable exception is untreated 05MN11-12, which has a relatively simple mineral assemblage of kaolinite, quartz and goethite. Also, except for 05MN11-7rp, XRD spectra of samples after CD treatment show no XRD-detectable goethite and hematite (e.g., Table 1, Fig. 2). The removal of iron oxides (goethite, hematite) is accompanied by a change in the color of the powdered samples from reddish before the CD treatment to mostly white afterwards.

XRD spectra for 05MN6 samples from the quarry locale (site B) indicate that only kaolinite, gibbsite, and quartz are present (Fig. 2, Table 1). Chemical treatments applied to these three samples (0.5M HCl + 30% H_2O_2) were intended to remove trace amounts of carbonates and easily oxidizable organic matter (cf. Yapp and Poths, 1991). There were no detectable changes in the XRD spectra after treatment of the 05MN6 samples (Table 1, Fig. 2).

3.2 Isotopic results

3.2.1 Water isotopic results

The δD and $\delta^{18}\text{O}$ values measured for the 05WMN water samples are listed in Table 2. $\delta^{18}\text{O}$ values range from -8.5‰ to -7.9‰, while δD values range from -64‰ to -62‰. These $\delta^{18}\text{O}$ and δD values are within the range of values reported by Coplen and Kendall (2000) for Minnesota River samples near Jordon, Minnesota, and will be used in the following discussion as representative of local modern meteoric water.

3.2.2 Mineral hydrogen isotopic results

Results of the hydrogen isotope analyses are listed in Tables 3 and 4. The δD values of hydrogen evolved at 220°C from six of the outgassed 05MN11 samples range from -49‰ to -38‰, whereas δD values of the corresponding 850°C hydrogen range from -83‰ to -70‰ (Table 3). The δD values of hydrogen evolved from five 05MN11 samples at 850°C using the two-step procedure (outgassing at 100°C , followed by 850°C dehydroxylation) range from -72‰ to -53‰ (Table 3). For the 05MN6 samples, δD values of H_2 from the 220°C to 225°C dehydration steps range from -59‰ to -42‰, while the δD values for the 850°C steps range from -78‰ to -73‰ (Table 4).

3.2.3 Mineral oxygen isotopic results

Results of oxygen isotopic analyses of nine samples are listed in Table 5. Repetitive analyses were carried out for five samples with higher proportions of gibbsite (as indicated by XRD spectra and hydrogen yields from stepwise dehydrations, Tables 1, 3 and 4) and for CD-treated 05MN11-12, which has no XRD-detectable gibbsite (Table 1). The $\delta^{18}\text{O}$ values range from +10.1‰ to 18.3‰, whereas the oxygen yields range from 12.1 to 16.7 $\mu\text{mol}/\text{mg}$. Among the total of six pairs of replicate analyses in Table 5, four show analytically significant shifts of both $\delta^{18}\text{O}$ values and oxygen yields. The shifts of $\delta^{18}\text{O}$ values range from +1.2 to +5.0‰, while the shifts of oxygen yield range from 2.5 to 3.5 $\mu\text{mol}/\text{mg}$.

4. DISCUSSION

4.1. Hydrogen isotopes in gibbsite and kaolinite

4.1.1 Determination of endmember δD values

Except for 05MN11-12, the treated 05MN11 and 05MN6 samples contain significant amounts of quartz, gibbsite, and kaolinite (Table 1). However, for 05MN11-12, only quartz and kaolinite were detectable by XRD. Determination of accurate δD values of the endmember kaolinite and gibbsite required knowledge of the extent to which pre-treatment of these mixtures with 0.5 M HCl might alter δD values. This was tested using the extreme case of treatment with 15 M HCl at room temperature (22°C).

To test mixtures of kaolinite and gibbsite, an aliquot of CD-treated 05MN11-5m (Table 1) was treated for 5 days with 15 M HCl of “normal” δD value (i.e., deuterium at natural abundance levels). The results are listed in Table 6. Comparison of the results for 05MN11-5m before and after the 15 M HCl treatment (Table 6) indicates no significant change (within experimental error) in the δD values for either the 220°C or 850°C increments of evolved hydrogen.

To isolate the possible hydrogen isotope effects on kaolinite, an aliquot of CD-treated 05MN11-12 (Table 1) was treated for 5 days at 22°C with deuterium-enriched 15 M HCl ($\delta\text{D} = +450\text{‰}$). For the kaolinite in 05MN11-12, the δD value after treatment with deuterium-enriched 15 M HCl (Table 6) is 18‰ more positive than before treatment. Yet, this positive shift in the kaolinite δD is only about 4% of the expected difference of approximately 450 to 500‰ between the δD values of the “normal” and deuterium-enriched 15 M HCl. Such a small relative shift and the results for 05MN11-5m (treated with isotopically “normal” 15 M HCl; Table 6) suggest that, for the samples of this study, treatment with 0.5 M HCl solutions at room temperature will have no analytically significant effect on the mineral δD values (and by inference, no effect on the even less exchangeable oxygen isotopes; e.g., Bird and Chivas, 1988).

Girard and Savin (1996) indicated that kaolinite will not break down at a temperature of ~220°C. However, gibbsite does dehydroxylate at 220°C (Schroeder and Melear, 1999; Tabor and Yapp, 2005). Thus, the hydrogen evolved at ~220°C from the samples of the current study is overwhelmingly from gibbsite, and the hydrogen evolved at 850°C should be predominantly from kaolinite (Girard and Savin, 1996).

The six 05MN11 samples of Table 3 which were heated at 220°C and 850°C (after outgassing at 100°C) had an average δD value of $-44 \pm 4 \text{‰}$ for hydrogen evolved at 220°C, and $-76 \pm 6 \text{‰}$ for hydrogen evolved at 850°C. The 05MN6 samples (Table 4) had similar average δD values of $-50 \pm 7 \text{‰}$ for hydrogen evolved at 220°C (or 225°C) and $-75 \pm 2 \text{‰}$ for hydrogen evolved at 850°C. The likelihood that these δD values correctly represent the δD values of the gibbsite (~220°C hydrogen) and kaolinite (850°C hydrogen), and thus may represent a useful analytical technique, was evaluated using a mass balance approach as well as some D/H exchange experiments.

There is a small proportion of boehmite in several of the treated samples of Table 1, but (with the possible exception of 05MN11-5rp) gibbsite and kaolinite are the predominant hydrogen-bearing minerals in the treated samples of this study. Thus, to a first approximation, the δD values of the total

hydrogen ($\delta\text{D}_{\text{tot}}$) in these samples (after outgassing at 100°C) can be considered a mixture of two endmembers. The simple material balance equation for the hydrogen isotopes at natural abundance levels in these systems is:

$$\delta\text{D}_{\text{tot}} = X(\text{H})_{\text{K}} \delta\text{D}_{\text{K}} + X(\text{H})_{\text{Gb}} \delta\text{D}_{\text{Gb}} \quad (2a)$$

where $\delta\text{D}_{\text{tot}}$ is the δD value of the total hydrogen in the sample (after first outgassing at 100°C), $\delta\text{D}_{\text{K}}$ and $\delta\text{D}_{\text{Gb}}$ are the δD values of the kaolinite and gibbsite endmembers, respectively. $X(\text{H})_{\text{K}}$ and $X(\text{H})_{\text{Gb}}$ are, respectively, the mole fractions of hydrogen contributed to the mixture by kaolinite and gibbsite. $X(\text{H})_{\text{K}} + X(\text{H})_{\text{Gb}} = 1$. Eq. 2a can be rewritten as:

$$\delta\text{D}_{\text{tot}} = (\delta\text{D}_{\text{Gb}} - \delta\text{D}_{\text{K}}) X(\text{H})_{\text{Gb}} + \delta\text{D}_{\text{K}} \quad (2b)$$

If kaolinite and gibbsite are the only hydrogen-bearing substances in the samples, and if $\delta\text{D}_{\text{K}}$ and $\delta\text{D}_{\text{Gb}}$ each have a constant value among the various samples, Eq. 2b indicates that a plot of $\delta\text{D}_{\text{tot}}$ against $X(\text{H})_{\text{Gb}}$ should yield a straight line whose intercept is $\delta\text{D}_{\text{K}}$. The value of $\delta\text{D}_{\text{Gb}}$ can be calculated from addition of the slope and intercept of the best-fit line (Eq. 2b). Note that this type of calculation depends on knowledge of the δD value of the *total* hydrogen in the respective samples as well as the hydrogen in each of the minerals as a fraction of the total sample hydrogen. It requires *no* assumptions about mineral-vapor isotopic exchange (or lack thereof) during the measurement.

Fig. 3 is a plot of $\delta\text{D}_{\text{tot}}$ against $X(\text{H})_{\text{Gb}}$ for the hydrogen data of this study (Tables 3 and 4). After outgassing at 100°C, ten of the fifteen dehydration analyses of Tables 3 and 4 were performed in two successive steps – at 220°C (or 225°C), then at 850°C. Values of $X(\text{H})_{\text{Gb}}$ for these samples were assumed to be equal to the mole fraction of hydrogen recovered at ~220°C. For three of the remaining five samples, the $X(\text{H})_{\text{Gb}}$ values were calculated from hydrogen yields derived from multiple-step (> 3 steps) incremental vacuum dehydration experiments performed as part of a different ongoing study of CO_2 evolved from gibbsite (see Table 3, footnote “c”). The latter experimental procedure followed the approach of Tabor and Yapp (2005). A fourth of these five samples, 05MN11-12, contains no XRD-detectable gibbsite (i.e., $X(\text{H})_{\text{Gb}} = 0.00$). Linear regression of the 05MN11 and 05MN6 data of Fig. 3 yields the following equation:

$$\delta\text{D}_{\text{tot}} = 26 (\pm 3) X(\text{H})_{\text{Gb}} - 73 (\pm 2); \quad r^2 = 0.88 \quad (3)$$

The standard errors of the slope and intercept in Eq. 3 represent only the scatter of the nominal values of the data points plotted in Fig. 3. Some unknown amount of the scatter may be a consequence of varying proportions of small amounts of boehmite (AlOOH; Table 1). However, the indications of linearity in the data array of Fig. 3, in conjunction with the standard error of the regression (Eq. 3), imply that the gibbsite $\delta\text{D}_{\text{Gb}}$ value is approximately $-47 (\pm 5)\text{‰}$, whereas the kaolinite of these samples has a $\delta\text{D}_{\text{K}}$ value of about $-73 (\pm 2)\text{‰}$. These two inferred endmember δD values are the same (within analytical error) as the overall averages of the δD values measured directly for hydrogen evolved by stepwise dehydration at 220°C ($\delta\text{D}_{\text{Gb}} = -46 \pm 6 \text{‰}$) and 850°C ($\delta\text{D}_{\text{K}} = -$

76 ± 5 ‰) from the 05MN6 and 05MN11 samples. The agreement of the endmember gibbsite and kaolinite δD values determined from the mixing array of Fig. 3 with the corresponding δD values determined by the incremental dehydration method of Tables 3 and 4 suggests that the latter method may be a useful way to estimate gibbsite and kaolinite δD values in mixtures in which they are the only hydrogen-bearing minerals.

To get some idea of the magnitude of possible D/H exchange between kaolinite and the water vapor evolved during the dehydration of gibbsite, two exchange experiments were carried out on a CD-treated sample of 05MN11-12 in which kaolinite is the only XRD-detectable hydrogen-bearing mineral (Table 1). The partial equilibration (interpolation) method of Northrop and Clayton (1966) and Suzuoki and Epstein (1976) as adapted by Yapp and Pedley (1985) was used for these experiments. Mineral-vapor exchange experiments were run for approximately 5 hrs at a temperature of 220°C. Experimental conditions are listed in Table 7, and results are plotted in Fig. 4a. The results in Fig. 4a imply about 62% exchange of the hydrogen isotopes in kaolinite after ~5 hrs at 220°C. The interpolated value of the equilibrium kaolinite-vapor D/H fractionation factor at 220°C is 0.982 (Fig. 4a), which corresponds to a kaolinite-liquid H_2O D/H fractionation factor ($^{D}\alpha_{\text{eq}}$) of 0.981 (Friedman and O'Neil, 1977). This value compares favorably with the value of 0.983 at 220°C indicated by the D/H fractionation equation of Sheppard and Gilg (1996).

Cole and Ohmoto (1986) reviewed the kinetics of isotopic exchange in minerals and noted that, for many systems, exchange rates can be usefully represented as pseudo-first or second order processes. There are insufficient data in Fig. 4a to deduce the order of the reaction rate. However, to facilitate discussion, the results were evaluated in terms of both the first and second order cases. Expressing the degree of exchange (f) as a decimal fraction and the rate of exchange in terms of $[1 - f]$ (see Cole and Ohmoto, 1986), the rate constant at 220°C would be 0.19 (hr^{-1}) for a pseudo-first order rate. For a second order rate, expressed in terms of $[1 - f]$, the rate constant for the data of Fig. 4a would be 0.31 (hr^{-1}). The corresponding model curves for the first and second order processes are presented in Fig. 4b in coordinates of $\ln(1 - f)$ vs. time (t).

It should be emphasized that the water vapor evolved from gibbsite during incremental dehydration of gibbsite-kaolinite mixtures under vacuum at 220°C is continuously removed by freezing in a liquid nitrogen-cooled trap. Consequently, increments of H_2O vapor evolved from gibbsite at ~220°C do not remain in contact with the residual kaolinite for more than a few seconds. Thus, the curves of Fig. 4b suggest that even for the case of a second order exchange rate, the extent of kaolinite-vapor D/H exchange will only be about 0.09% at 220°C for a mineral-vapor contact time as long as 10 seconds. This model-derived result reinforces the implications of the mass balance and incremental results—i.e., that the δD values of H_2O evolved in vacuum at 220°C from mixtures containing kaolinite and gibbsite as the only hydrogen-bearing minerals appear to be useful estimates of the gibbsite δD value, and that the δD values of the H_2O evolved in the subsequent step at 850°C are those of kaolinite.

4.1.2 Preservation of δD values of kaolinite

Some published work has suggested that there is significant post-crystallization hydrogen isotope exchange in kaolinite over geological time scales at sedimentary to early diagenetic temperatures (Bird and Chivas, 1988; Lawrence and Rashkes-Meaux, 1993). Others studies support preservation of original kaolinite δD values in the absence of dissolution and recrystallization (e.g., Savin and Hsieh, 1998; Gilg et al., 1999; Gilg, 2000; Girard et al., 2000; Tabor and Montañez, 2005). The preservation of δD values seems to depend on the specific diagenetic processes and history the minerals might have experienced. It has been suggested that burial temperatures above 50°C might cause alteration of δD values of pedogenic kaolinite (Lawrence and Rashkes-Meaux, 1993). Thus, some discussion of the burial history of the paleosol is warranted.

Most Cretaceous rocks in Minnesota are found in the western part of the state. The Cretaceous deposits are unconformably overlain by Pleistocene till that makes up the present day surface of portions of southwestern Minnesota. These Cretaceous strata, including sandstone and some limestone, have a maximum thickness of only about 200 m. Moreover, there was likely no significant deposition throughout the Tertiary (Ojakangas and Matsch, 1982; Sims and Morey 1982). Therefore, even with addition of Pleistocene till, it seems likely that the maximum burial temperatures of the paleosol were probably no more than ~30 to 35°C. If so, this would seem to favor preservation of a kaolinite hydrogen isotopic signal that could reflect the Cretaceous environment.

Low temperature reductive diagenesis has affected iron-bearing minerals in the Cenomanian laterite of this study (Toth and Fritz, 1997; Feng and Yapp, 2009). However, it is hypothesized that low temperature oxidation-reduction (redox) processes, per se, would have a minimal impact on redox-insensitive minerals such as kaolinite.

If measured δD values of the pedogenic kaolinite differ from those expected for hydrogen isotope exchange with local modern waters, it would enhance the possibility that there has been preservation of the original Cretaceous δD value of the kaolinite. The δD value of -63 ‰ measured for modern local waters (Table 2) and a modern average annual temperature of 7°C (Baker et al., 1985) combine with the kaolinite-water D/H fractionation factor of Sheppard and Gilg (1996) to predict a modern kaolinite δD value of about -96 ‰. This latter value contrasts with the measured δD value of about -73 ‰ and is consistent with formation of the kaolinite under different environmental conditions.

Lawrence and Rashkes-Meaux (1993) suggested that significant variability of δD values for kaolinites that would otherwise be expected to have the same δD values (if they had preserved their original D/H ratios) was an indication of post-crystallization kaolinite-water hydrogen isotope exchange. The high degree of linearity in the data array of Fig. 3 implies that the δD values of the kaolinites from the two sampled paleosol locations are relatively uniform. Such uniformity might be expected in the coastal Cenomanian weathering environment in which this laterite formed. Thus, this uniformity appears to reinforce the possibility that the kaolinite δD values reflect Cenomanian conditions. Interestingly, a similar argument could be made for the gibbsite δD data from the array in Fig. 3,

because the difference of about 26‰ between its nominal, inferred δD value (-47‰) and the δD value of the kaolinite (-73‰) is approximately that expected for an equilibrium hydrogen isotope difference of about 30‰ at sedimentary temperatures of 0 to 30°C (Sheppard and Gilg, 1996; Vitali et al., 2001). As a working hypothesis, we assume that the measured kaolinite δD value preserves information about the water that was in the paleosol during the Cenomanian.

4.2. Oxygen isotopes in kaolinite

The high degree of linearity in the δD data of Fig. 3 also suggests that the respective $\delta^{18}\text{O}$ values of kaolinite and gibbsite could be relatively constant among different samples. However, the presence of quartz in varying proportions in these treated samples means that the total $\delta^{18}\text{O}$ values of most of the treated samples represent mixing of three principal endmembers (quartz, kaolinite, and gibbsite).

The nominal percent yields of oxygen (Table 5) have an analytical error of $\pm 3\%$. However, even allowing for analytical uncertainty, some of the analyses of Table 5 exhibit oxygen yields that are significantly less than expected from the proportions of the minerals in the samples (as determined from the mineral stoichiometries, sample masses, and hydrogen yields of the vacuum dehydration experiments of Tables 3 and 4). These low yields are commonly associated with poor reproducibility of corresponding $\delta^{18}\text{O}$ values. The reason for the comparatively low oxygen yields in some of the analyses of Table 5 is not known at this time.

However, a number of the analyses of Table 5 had nominal oxygen yields of at least 91(± 3)%. Such yields overlap the range of yields associated with the correct $\delta^{18}\text{O}$ value of a laboratory standard routinely run on that BrF_5 extraction line. This suggests that, for the samples of this study, $\delta^{18}\text{O}$ values from analyses with nominal yields of at least 91% of expected oxygen can be taken seriously. The following samples of Table 5 satisfy this criterion of a nominal oxygen yield of at least 91%: 05MN11-5m (aliquot #2), 05MN6-8 (aliquots #1 and #2), 05MN6-10 (aliquot #1), and 05MN6-17 (aliquot #2).

XRD spectra indicate that treated samples of 05MN6-8, 05MN6-10, 05MN6-17, and 05MN11-5m consist of kaolinite, gibbsite, and minor quartz (Table 1). The sample masses and incremental yields of hydrogen (Tables 3 and 4), together with the stoichiometric formulas for kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), gibbsite (AlOOH), and quartz (SiO_2), provide sufficient information to calculate the oxygen in any one of these minerals as a mole fraction of the total oxygen in the sample of interest. These calculated oxygen mole fractions are listed in Table 8 along with the measured $\delta^{18}\text{O}$ values of the total oxygen in the respective samples.

The oxygen isotope composition of a three-endmember mixture of kaolinite, gibbsite, and quartz can be expressed as:

$$\delta^{18}\text{O}_{\text{tot}} = \text{X}(\text{O})_{\text{K}} \delta^{18}\text{O}_{\text{K}} + \text{X}(\text{O})_{\text{Gb}} \delta^{18}\text{O}_{\text{Gb}} + \text{X}(\text{O})_{\text{Q}} \delta^{18}\text{O}_{\text{Q}} \quad (4)$$

Where $\delta^{18}\text{O}_{\text{tot}}$ is the $\delta^{18}\text{O}$ value of the bulk sample; $\text{X}(\text{O})_{\text{Gb}}$ is oxygen in gibbsite as a mole fraction of total oxygen, $\text{X}(\text{O})_{\text{Q}}$ is oxygen in quartz as a mole fraction of total sample oxygen, and $\text{X}(\text{O})_{\text{K}}$ is oxygen in kaolinite as a mole

fraction of total sample oxygen. $\delta^{18}\text{O}_{\text{K}}$, $\delta^{18}\text{O}_{\text{Gb}}$, and $\delta^{18}\text{O}_{\text{Q}}$ are the respective $\delta^{18}\text{O}$ values of endmember kaolinite, gibbsite, and quartz. Because $\text{X}(\text{O})_{\text{K}} + \text{X}(\text{O})_{\text{Gb}} + \text{X}(\text{O})_{\text{Q}} = 1$, Eq. 4 can be rewritten as

$$\delta^{18}\text{O}_{\text{tot}} = m \text{X}(\text{O})_{\text{Gb}} + b \quad (5)$$

Where, $m = (\delta^{18}\text{O}_{\text{Gb}} - \delta^{18}\text{O}_{\text{K}})$

$$b = (\delta^{18}\text{O}_{\text{Q}} - \delta^{18}\text{O}_{\text{K}})\text{X}(\text{O})_{\text{Q}} + \delta^{18}\text{O}_{\text{K}}$$

If the respective values of $\delta^{18}\text{O}_{\text{K}}$, $\delta^{18}\text{O}_{\text{Gb}}$, and $\delta^{18}\text{O}_{\text{Q}}$ are constant among the samples and if the value of $\text{X}(\text{O})_{\text{Q}}$ is constant and/or small in the sample population of interest, Eq. 5 indicates that a plot of $\delta^{18}\text{O}_{\text{tot}}$ against $\text{X}(\text{O})_{\text{Gb}}$ should yield a linear data array. The $\delta^{18}\text{O}_{\text{tot}}$ data of Table 8 are plotted against corresponding values of $\text{X}(\text{O})_{\text{Gb}}$ in Fig. 5. Linear regression of the data of Fig. 5 yields the equation $\delta^{18}\text{O}_{\text{tot}} = -14.0(\pm 1.2)\text{X}(\text{O})_{\text{Gb}} + 18.7(\pm 0.2)$ with $r^2 = 0.99$. The apparently linear data array of Fig. 5 supports the assumptions of the foregoing mixing model. Moreover, the fact that $\text{X}(\text{O})_{\text{Q}}$ is small implies that the quantity $(\delta^{18}\text{O}_{\text{Q}} - \delta^{18}\text{O}_{\text{K}})\text{X}(\text{O})_{\text{Q}}$ in the expression for "b" is small. For example, even if the absolute value $|\delta^{18}\text{O}_{\text{Q}} - \delta^{18}\text{O}_{\text{K}}|$ were as large as 10‰, the small average value of 0.024 for $\text{X}(\text{O})_{\text{Q}}$ (Table 8) would imply a value for $(\delta^{18}\text{O}_{\text{Q}} - \delta^{18}\text{O}_{\text{K}})\text{X}(\text{O})_{\text{Q}}$ of only about 0.2‰. Thus, $b \approx \delta^{18}\text{O}_{\text{K}}$ with an average additional uncertainty associated with the presence of the small amount of admixed quartz of only about $\pm 0.2\%$. Similarly, $m + b \approx \delta^{18}\text{O}_{\text{Gb}}$. The $\delta^{18}\text{O}$ values of endmember kaolinite and gibbsite in the four samples of Fig. 5 (and Table 8) as calculated in this manner are: $\delta^{18}\text{O}_{\text{K}} = 18.7(\pm 0.4)\%$ and $\delta^{18}\text{O}_{\text{Gb}} = 4.7(\pm 1.6)\%$. The uncertainties in these values represent the standard errors of the regression as well as the aforementioned presence of quartz. Because of the higher precision associated with the $\delta^{18}\text{O}$ value of kaolinite, subsequent paleoenvironmental interpretations use only the kaolinite data.

4.3. Paleoenvironment

4.3.1 Paleotemperature

The relationship between the δD and $\delta^{18}\text{O}$ values of kaolinite formed at equilibrium in the presence of waters which correspond to the Global Meteoric Water Line (GMWL) of Craig (1961) is predicted by the equation of Savin and Epstein (1970):

$$\delta D_K = 8 \left(\frac{D}{18} \alpha_{K-W} \right) \delta^{18} O_K + 1000 \left[8 \left(\frac{D}{18} \alpha_{K-W} \right) - 1 \right] - 6990^D \alpha_{K-W} \quad (6)$$

Where, δD_K and $\delta^{18} O_K$ are the measured δD and $\delta^{18}\text{O}$ values of the kaolinite. $^D \alpha_{K-W}$ and $^{18} \alpha_{K-W}$ are the hydrogen and oxygen isotopic fractionation factors, respectively, between kaolinite and ambient liquid water at the time of incorporation in the mineral.

Equations of the type represented by Eq. 6 have been used with apparent success to calculate paleotemperatures and the isotopic composition of ancient waters using various hydroxyl-bearing minerals in

paleosols of Late Ordovician, Permo-Pennsylvanian, and Early Eocene ages (e.g., Yapp, 1993, 2008; Tabor and Montañez, 2005; Tabor, 2007). In those studies, evidence of the success of the approach using Eq. 6 derived from confirmation of calculated temperatures using either oxygen isotope fractionations measured for coexisting mineral pairs (Yapp, 1993; Tabor, 2007) or associated non-isotopic proxies (Yapp, 2008).

In the current paper, the temperature dependent kaolinite-water fractionation factors of Sheppard and Gilg (1996) were used in combination with Eq. 6 to calculate isotherms in a plot of δD against $\delta^{18}\text{O}$ for temperatures from 0°C to 40°C (Fig. 6). The data point in Fig. 6 representing the measured δD and $\delta^{18}\text{O}$ values of the Cenomanian pedogenic kaolinite ($\delta\text{D}_K = -73\text{‰}$, and $\delta^{18}\text{O}_K = 18.7\text{‰}$) indicates a formation temperature of $22 (\pm 5)^\circ\text{C}$. The uncertainty of $\pm 5^\circ\text{C}$ is derived from the uncertainty in the δD and $\delta^{18}\text{O}$ values. For a nominal paleotemperature of 22°C , the value of $^{18}\alpha_{K-W}$ is about 1.0252 (Sheppard and Gilg, 1996). This implies a $\delta^{18}\text{O}$ value of -6.3‰ for the corresponding water.

There have been other published studies suggesting different kaolinite-water oxygen isotopic fractionation factors (see the discussion in Savin and Hsieh, 1998). As an example of the effect of a different fractionation factor, calculations were carried out for Eq. 6 using kaolinite-water oxygen isotopic fractionation factors estimated by Savin and Lee (1988) and Eslinger (1971) in combination with the hydrogen isotope fractionation factor of Sheppard and Gilg (1996). The calculated paleotemperature for this case was about $26 (\pm 5)^\circ\text{C}$.

Although the aforementioned studies of Yapp (1993, 2008), Tabor and Montañez (2005), and Tabor (2007) support the assumption that the GMWL can represent ancient waters present at the time of crystallization, they might not be representative. If the ancient waters in some systems were characterized by a "Local Meteoric Water Line" (LMWL) which differed from the GMWL, use of Eq. 6 could yield calculations of spurious temperatures.

As an example, the effect of a LMWL was examined using the LMWL for Genoa, Italy (elevation = 2 m [s.l.d.]; annual precipitation = 1117 mm; annual $T = 14.5^\circ\text{C}$). Genoa, on the coast of the Mediterranean Sea (i.e., an "interior seaway"), is situated at a latitude of about 44°N , which is similar to the paleolatitude of the Cenomanian paleosol ($\sim 40^\circ\text{N}$). Linear regression of isotopic data (IAEA/WMO, 2004) for monthly precipitation (years 1961 to 1995) at Genoa yields the following equation: $\delta\text{D} = 7.3\delta^{18}\text{O} + 5$ ($r^2 = 0.93$). If such a LMWL characterized the ancient environment of the Cenomanian paleosol, the kaolinite δD and $\delta^{18}\text{O}$ values of this study when combined with that LMWL would yield a nominal temperature of 22°C – i.e., the same as that determined using the GMWL. Therefore, unless an ancient LMWL differed even more significantly from the GMWL than does that of Genoa, it would have little effect on the temperature calculated from the particular δD and $\delta^{18}\text{O}$ values of the Cenomanian kaolinite of this study. Moreover, it is observed that the multi-year annual

averages of the $\delta^{18}\text{O}$ (-5.8‰) and δD (-35‰) values of the modern precipitation at Genoa plot, within analytical uncertainty, on the GMWL (Rozanski et al., 1993).

More generally, examination of amount-weighted, average annual isotopic data for precipitation from 205 IAEA stations (Rozanski et al., 1993) indicates that, for about 73% of those stations, the calculated "deuterium excess" values (defined as $\delta\text{D} - 8\delta^{18}\text{O}$) differ by 4‰ or less from the GMWL deuterium excess value of 10‰. Thus, proximity to the GMWL seems to be a relatively common characteristic of average annual precipitation (Rozanski et al., 1993). Since soils form on long time scales, this characteristic of average annual precipitation might explain, in part, why the GMWL seems to be a reasonable representation of water δD and $\delta^{18}\text{O}$ values in the wet, ancient, continental weathering environments studied thus far.

However, there may be situations in which the applicability of the GMWL assumption to studies of δD and $\delta^{18}\text{O}$ values of minerals in paleosols would be severely compromised. One situation would be significant evaporation of ancient soil waters. Such evaporation would shift the soil waters off and to the right of the GMWL along an evaporative trajectory with a slope of about 4 (e.g., Barnes and Allison, 1988). If pedogenic kaolinite formed from these evaporated waters, it would exhibit a corresponding shift of δD and $\delta^{18}\text{O}$ values. On a plot of the type in Fig. 6, this evaporative effect would yield lower calculated apparent temperatures. Yet, the nominal paleotemperature calculated for the kaolinite of the Cenomanian laterite (using the GMWL assumption) is a relatively warm 22°C , and this warmer inferred temperature seems to be consistent with a condition of little, or no, evaporative enrichment of ^{18}O or D in the soil water at the time of kaolinite crystallization.

4.3.2. Comparison of hypothetical modern kaolinite with ancient kaolinite

The temperature of $22 (\pm 5)^\circ\text{C}$ calculated for the Cenomanian pedogenic kaolinite contrasts with the local modern mean annual temperature (MAT) of 7°C (Baker et al., 1985). The measured δD and $\delta^{18}\text{O}$ values of local modern waters (-63‰ and -8.3‰ , respectively; Table 2), a temperature of 7°C , and the fractionation factors of Sheppard and Gilg (1996) imply that modern kaolinite would have a δD value of -96‰ and a $\delta^{18}\text{O}$ value of $+20.3\text{‰}$ (Fig. 6, shaded triangle). As seen in Fig. 6, the ancient pedogenic and hypothetical modern kaolinites are distinctly different.

Although the modern MAT (7°C) of the studied locale is significantly cooler than the temperature determined from the kaolinite (22°C), modern summer temperatures at Morton, Minnesota, average about 21°C (Baker et al., 1985). The similarity of the latter two temperatures requires some consideration. If the kaolinite in the paleosol were neofomed in "modern" summer months, the ambient temperature of the microenvironments at the shallower modern depths of collection (Table 1) could be expected to reflect somewhat attenuated modern summer air temperatures (e.g., Hillel, 1982). Chicago (Midway) is the IAEA/GNIP station closest to Morton, Minnesota. Amount-weighted average δD and $\delta^{18}\text{O}$ values for the summer months of June, July, and August at

Chicago are -24‰ and -3.1‰ , respectively (IAEA/WMO, 2004). Kaolinite formed from this water at 21°C would have δD and $\delta^{18}\text{O}$ values of, respectively, -56‰ and 22.3‰ (shaded circle, Fig. 6). These hypothetical modern summer kaolinite values are distinctly different from (more positive than) the actual values determined for the kaolinites in the paleosol (Fig. 6), suggesting that the kaolinite in the paleosol did *not* form in Holocene-like summer conditions. Note that the isotopic composition of average Chicago summer precipitation plots off (to the right of) the GMWL. Thus, the hypothetical, summer kaolinite point in Fig. 6 plots to the right of a GMWL-derived 21°C isotherm.

4.3.3. Comparison with published estimates of Cenomanian climatic temperatures

Most isotopic determinations of Cretaceous temperatures were made on marine deposits (e.g., Huber et al., 1995; Norris et al., 2002; Wilson et al., 2002; Bice et al., 2006; Pucéat et al., 2007). These various studies suggested values of up to 36°C for equatorial sea surface temperatures (SST), 19 to 29°C for the SST at paleolatitudes of 40°N , and $>14^\circ\text{C}$ for the SST in polar regions. These results, taken together, suggest that the equator-to-pole temperature gradient in the Cenomanian was smaller than the modern value. However, some studies, also using results from marine proxies of paleotemperature, deduced that the latitudinal SST gradient of the warm mid-Cretaceous had a near-modern value (e.g., Pucéat, et al., 2007; Wagner, et al., 2008).

There are some paleobotanical estimates of Cretaceous continental temperatures (Wolfe and Upchurch, 1987; Herman and Spicer, 1997; Spicer and Corfield, 1992; Spicer et al., 1993). These studies indicate a temperature of about 10°C at high paleolatitudes (Siberia, Alaska, and the Antarctic Peninsula). Wolfe and Upchurch (1987) assessed North American continental climate from the Cenomanian to Maastrichtian using leaf margin analysis. Their compilation includes Cenomanian data from southeastern North America, Texas, New Mexico, Colorado, Kansas, the Pacific Coast, and Alaska. Wolfe and Upchurch (1987) estimated a Cenomanian MAT of approximately 23°C at 30°N for southeastern North America, and a latitudinal temperature gradient of $0.3^\circ\text{C}/\text{degree}$ of latitude.

GCM (general circulation model)-based studies also indicate significant warmth in the mid-Cretaceous (e.g., Bice et al., 2002; Fluteau et al., 2007; Poulsen et al., 2007). Poulsen et al (2007) estimated mean annual zonal surface temperatures at different paleolatitudes and different atmospheric CO_2 concentrations. With an atmospheric CO_2 concentration of 8 to 12 PAL (Preindustrial Atmospheric Levels, $\sim 280\text{ppmV}$), the MAT at 40°N , was estimated to be 18 to 20°C . Fluteau et al (2007) examined the possible impact of changes in latitudinal SST gradients as well as geographic features such as the Western Interior Seaway (WIS) in North America. Their GCM-derived results suggested that seasonal fluctuations of Cenomanian air temperature over the North American continent were mitigated by the WIS and that such seasonal fluctuations would also be smaller if the global latitudinal SST gradient were smaller than the modern SST gradient.

The paleosol of the current study was in a coastal location at 40°N on the eastern shore of the WIS during the Cenomanian (see Fig. 1 in Feng and Yapp, 2009). The nominal paleotemperature of 22°C determined from the isotopic composition of the pedogenic kaolinite differs significantly

from the local Cenomanian MAT of $\sim 15^\circ\text{C}$ calculated by Fluteau et al. (2007) using a near-modern latitudinal SST gradient. For a smaller than modern latitudinal SST gradient, the GCM results of Fluteau et al. (2007) indicate a MAT of about 17°C – i.e., somewhat closer to the kaolinite isotopic temperature.

Some of the difference between the paleotemperature of 22°C inferred from the kaolinite of this study and the temperature of 17°C inferred from the GCM-derived results of Fluteau et al. (2007) may be related to the fact that their calculations used an atmospheric CO_2 concentration of 4 PAL. The results of Feng and Yapp (2009) suggest that Cenomanian CO_2 concentrations may have been about 7 PAL. Poulsen et al. (2007) suggested that an increase of atmospheric CO_2 concentrations from 4 PAL to 7 or 8 PAL would result in a modeled zonal temperature increase of 3 to 4°C at 40°N . If a temperature which was 3 or 4°C higher were applied to the results of Fluteau et al. (2007), it would imply a MAT in the locale of the Cenomanian paleosol of ~ 20 to 21°C (i.e., comparable to the nominal value of 22°C inferred from the kaolinite). Thus, within the uncertainties of the methods, there is enough similarity of proxy and model results to suggest that the general features of Cenomanian continental climate in that North American locale are probably being revealed.

There is also the possibility that the pedogenic kaolinite formed in the summer months in the Cenomanian. The results of Giral-Kacmarkcik et al. (1998) for a young tropical soil suggest the possibility of such a seasonal bias, but those same authors indicate that an average annual signal is commonly to be expected. At present, we have no results which allow an unequivocal assessment of the annual vs. summer character of the Cenomanian signal preserved in the studied kaolinite. However, comparison of inferred $\delta^{18}\text{O}$ values of Cenomanian soil water with those of global modern average annual precipitation may provide some insight into this question.

The $\delta^{18}\text{O}$ value of -6.3‰ inferred for the waters present at the time of kaolinite crystallization is plotted against the inferred temperature of 22°C in Fig. 7. Also plotted in Fig. 7 are the $\delta^{18}\text{O}$ values of modern average annual precipitation at elevations of $\leq 100\text{m}$ as presented by Rozanski et al. (1993). The ancient water $\delta^{18}\text{O}$ value plots toward the lower end of the range of isothermal scatter of the modern $\delta^{18}\text{O}$ values. At mid-latitudes $\delta^{18}\text{O}$ values of summer rain are generally more *positive* than those of average annual precipitation (e.g., Rozanski et al., 1993). Consequently, the negative $\delta^{18}\text{O}$ bias of the inferred Cenomanian water seems to favor an interpretation of an isotopic signal that is dominantly annual.

In addition, a negative bias for the $\delta^{18}\text{O}$ values of the ancient waters (Fig. 7) could be consistent with more intense rainfall (Dansgaard, 1964) and the warm, wet climatic conditions which favor formation of laterites (Aleva, 1994). This inference is also consistent with the Ufnar et al. (2002, 2004) conclusion that the isotopic results from North American Aptian-age sphaerosiderites imply enhanced precipitation at mid to high paleolatitudes in the warm mid-Cretaceous.

5. CONCLUSIONS

Stable hydrogen and oxygen isotopic results from pedogenic kaolinite in a Cenomanian paleosol from southwestern Minnesota imply a temperature of $22 \pm 5^\circ\text{C}$. This Cenomanian temperature of 22°C contrasts with a local modern average annual air temperature of 7°C . The

warm paleotemperature and an inferred $\delta^{18}\text{O}$ value of about -6.3‰ for the ancient water are generally consistent with models that favor a smaller equator-to-pole temperature gradient in the mid-Cretaceous and a high concentration of atmospheric CO_2 . Results of this study also support the use of pedogenic kaolinite stable hydrogen and oxygen isotope data in paleoclimatic studies when the paleosol has experienced only relatively low temperatures during its burial history.

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6. REFERENCES CITED

- Aleva, G.J.J. (1994): *Laterites. Concepts, Geology, Morphology and Chemistry*. ISRIC, Wageningen, The Netherlands.
- Baker, D. G., Kuehnast, E. L., and Zandle, J. A. (1985) Climate of Minnesota, Part XV-Normal Temperatures (1951-1980) and their Application. *University of Minnesota Agricultural Experiment Station Technical Bulletin AD-SB-2777*.
- Barnard, P. (1973) Mesozoic floras, in Hughes, N., ed., *Organisms and continents through time. Palaeontological Assoc. London Spec. Pap. Paleontol.*, 12, 175-188.
- Barnes C.J. and Allison G.B. (1988) Tracing of water movement in the unsaturated zone using stable isotopes of hydrogen and oxygen. *J. Hydrol.* 100: 143-76.
- Barron, E. J. (1984) Climatic implications of the variable obliquity explanation of Cretaceous-Paleogene high-latitude floras. *Geology*, 12, 595-598.
- Bice, K. L. and Norris, R. D. (2002) Possible atmospheric CO_2 extremes of the middle Cretaceous (late Albian-Turonian). *Paleoceanography*, 17, 1070-1087.
- Bice, K.L., Birgel, D., Meyers, P.A., Dahl, K.A., Hinrichs, K.-U., and Norris, R.D. (2006) A multiple proxy and model study of Cretaceous upper ocean temperatures and atmospheric CO_2 concentrations. *Paleoceanography*, 21, PA2002
- Bird, M.I. and Chivas, A.R., (1988) Stable-isotope evidence for low temperature kaolinitic weathering and post-formational hydrogen-isotope exchange in Permian kaolinites. *Chem. Geol.* 72, 249-265.
- Clayton, R.N. and Mayeda, T.K. (1963) The use of bromine penta-fluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochim. Cosmochim. Acta* 27, 43-52.
- Colbert, E.H. (1973) Continental drift and the distribution of fossil reptiles. In: Tarling DH and Runcorn SK(ed.) *Implications of continental drift to the Earth sciences*. Academic Press, New York, 395-412.
- Cole, D.R. and Ohmoto, H. (1986) Kinetics of isotopic exchange at elevated temperatures and pressures. In: *Stable Isotopes in High Temperature Geological Processes* (editors: Valley, J.W., Taylor Jr, H.P., and O'Neil, J.R.) *Rev. Min.* 16, 41 – 90.
- Coplen, T. B., and Kendall, C. (2000) Stable Hydrogen and Oxygen Isotope Ratios for Selected Sites of the U.S. Geological Survey's NASQAN and Benchmark Surface-water Networks. *U.S. Geological Survey Open-File Report 00-160*, 174
- Craig, H. (1961) Isotopic variations in meteoric waters. *Science* 133, 1702-1703.
- Dansgaard, W. (1964) Stable isotopes in precipitation. *Tellus*, 16, 436-68
- Epstein, S. and Mayeda, T. (1953) Variation of O^{18} content of waters from natural sources. *Geochim. Cosmochim. Acta.* 4, 213-224
- Eslinger, E. V. (1971) Mineralogy and Oxygen Isotope Ratios of Hydrothermal and Low-Grade Metamorphic Argillaceous Rocks. PhD Thesis. Case Western Reserve University, Cleveland, Ohio.
- Feng, W. and Yapp, C.J. (2008) Experimental Tests of the Effects of Al Substitution on the Goethite-Water D/H Fractionation Factor. *Geochim. Cosmochim. Acta.* 72, 1295-1311
- Feng, W. and Yapp, C. J. (2009) 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. *Geochim. Cosmochim. Acta.* 73, 2559-2580.
- Fluteau, F., Ramstein, G., Besse, J., Guiraud, R., and Masse, J. P. (2007) Impacts of palaeogeography and sea level changes on Mid-Cretaceous climate. *Palaeogeog., Palaeoclim., Palaeoecol.* 247, 357-381.
- Friedman, I. and O'Neil, J. R. (1977) Compilation of stable isotope fractionation factors of geochemical interest. *USGS Prof. Paper* 440-KK
- Gilg, H.A., Hülmeier, S., Miller, H., and Sheppard, S.M.F. (1999) Supergene origin of the Lastarria kaolin deposit, south-central Chile, and paleoclimatic implications. *Clays Clay Min.* 47, 201-211.
- Gilg, H.A. (2000) D-H evidence for the timing of kaolinization in Northeast Bavaria, Germany. *Chem. Geol.* 170, 5 – 18.
- Giral-Kacmarkcik S., Savin S. M., Nahon D., Girard J.-P., Lucas Y., and Abel L. (1998) Oxygen isotope geochemistry of kaolinite in laterite-forming processes, Manaus, Amazonas, Brazil. *Geochim. Cosmochim. Acta* 62, 1865-1879.
- Girard, J. P. and Savin, S. M. (1996) Intracrystalline fractionation of oxygen isotopes between hydroxyl and non-hydroxyl sites in kaolinite measured by thermal dehydroxylation and partial fluorination. *Geochim. Cosmochim. Acta.* 60, 469-487.
- Girard, J.P., Freyssinet, P., and Chazot, G. (2000) Unraveling climatic changes from intra-profile variation in oxygen and hydrogen isotopic composition of goethite and kaolinite in laterites: an integrated study from Yaou, French Guiana. *Geochim. Cosmochim. Acta* 64, 409-426.

- Gonfiantini, R. (1978) Standards for stable isotope measurements in natural compounds. *Nature* 271, 534-536.
- Herman, A. B. and Spicer, R. A. (1997) New Quantitative palaeoclimate data for the Late Cretaceous Arctic: evidence for a warm polar ocean. *Palaeogeog., Palaeoclim., Palaeoecol.*, 128, 227-251.
- Hillel, D. (1982) *Introduction to Soil Physics*. Academic Press, San Diego, CA, 364 pp.
- Huber, B.T., Hodell, D.A., and Hamilton, C.P. (1995) Middle-Late Cretaceous climate of the southern high latitudes: Stable isotope evidence for minimal equator-to-pole thermal gradient. *GSA Bulletin*, 107, 1164-1191.
- Huber, B. T., Norris, R. D., and MacLeod, K. G. (2002) Deep-sea paleotemperature record of extreme warmth during the Cretaceous. *Geology*, 30, 123-126.
- IAEA/WMO (2004). Global Network of Isotopes in Precipitation. The GNP Database. Accessible at: <http://isohis.iaea.org>
- Jackson, M.L. (1979) *Soil chemical analysis-advanced course 2nd ed.*, 11th Printing. Published by the author, Madison, WI.
- Kauffman, E. G. (1973) Cretaceous Bivalvia. In: Hallam A(ed.) *Atlas of Paleobiogeography*. Elsevier, Amsterdam, 353-383.
- Lambert, S. J. and Epstein, S. (1980) Stable isotope investigations of an active geothermal system in Valles Caldera, Jemez Mountains. New Mexico. *J. Volcan. Geotherm. Res.* 8, 111-129.
- Lawrence, J.R. and Rashkes-Meaux, J.R., (1993) The stable isotopic composition of ancient kaolinites of North America. In: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S. (Eds.), *Climate Change in Continental Isotopic Records. Geophysical Monogr.*, 78, 249-261.
- Lloyd, C. R. (1982) The Mid-Cretaceous Earth: paleogeography, ocean circulation and temperature, atmospheric circulation. *J. Geol.* 90, 393-413
- Miller, K. G., Sugarman, P. J., Browning, J. V., Kominz, M. A., Hernandez, J. C., Olsson, R. K., Wright, J. D., Feigenson, M. D., and Sickel, W. V. (2003) Late Cretaceous chronology of large, rapid sea-level changes: Glacioeustasy during the greenhouse world. *Geology* 31, 585-588
- Norris, R.D., Bice, K.L., Magno, E.A., and Wilson, P.A. (2002) Jiggling the tropical thermostat in the Cretaceous hothouse. *Geology* 30, 299-302
- Northrop, D. A. and Clayton, R. N. (1966) Oxygen isotope fractionations in systems containing dolomite. *J. Geol.* 74, 174-196.
- Olivero, E. B., Gasparini, Z., Rinaldi, C. A., and Scasso, R., (1991) First record of dinosaurs in Antarctica (Upper Cretaceous, James Ross Island): Palaeogeographic implications. In: Thomson, M. R. A., Crame, J. A., and Thomson, J. W., eds., *Geological Evolution of Antarctica*, London, United Kingdom, Cambridge University Press, 617-622.
- O'Neil, J. R., and Kharaka, Y. K. (1976) Hydrogen and oxygen isotope exchange reactions between clay minerals and water. *Geochim. Cosmochim. Acta*, 40, 241-246.
- Ojakangas, R. W. and Matsch, C. L. (1982) *Minnesota's Geology*. University of Minnesota Press. Minneapolis.
- Poulsen, C. J., Pollard, D., and White, T. S. (2007) General circulation model simulation of the $\delta^{18}\text{O}$ content of continental precipitation in the middle Cretaceous: A model-proxy comparison. *Geology* 37, 199-202
- Pucéat, E., Lécuyer, C., Donnadieu, Y., Naveau, P., Ramstein, G., Huber, B.T., and Kriwet, J. (2007) Fish tooth $\delta^{18}\text{O}$ revising Late Cretaceous meridional upper ocean water temperature gradients. *Geology* 35, 107-110.
- Rozanski, K., Araguas-Araguas, L., and Gonfiantini, R. (1993) Isotopic Patterns in Modern Global Precipitation, In: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S. (Eds.), *Climate Change in Continental Isotopic Records. Geophysical Monogr.*, 78, 1-36
- Savin S. and Epstein S. (1970) The oxygen and hydrogen isotope geochemistry of clay minerals. *Geochim. Cosmochim. Acta* 34, 25-42.
- Savin, S.M. and Hsieh, J.C.C., (1998) The hydrogen and oxygen isotope geochemistry of pedogenic clay minerals: principles and theoretical background. *Geoderma* 82, 227-253.
- Savin, S. M. and Lee, M. (1988) Isotopic studies of phyllosilicates. In Bailey, S. W. (Ed.), *Hydrous Phyllosilicates (exclusive of micas)*. *Rev. Mineral.* 19, 189-219.
- Schmitz, M. D., Bowring, S. A., Southwick, D. L., Boerboom, T. J., and Wirth, K. R., (2006) High-precision U-Pb geochronology in the Minnesota River Valley subprovince and its bearing on the Neoproterozoic to Paleoproterozoic evolution of the southern Superior Province. *GSA Bull.* 118, 82-93.
- Schroeder, P. A. and Melear, N. D. (1999) Stable carbon isotope signatures preserved in authigenic gibbsite from a forested granitic regolith: Panola Mt., Georgia, USA. *Geoderma* 91, 261-279.
- Sheppard, S. M. F. and Gilg, H. A. (1996) Stable isotope geochemistry of clay minerals. *Clay Min.* 31, 1-24.
- Sims, P. K. and Morey, G. B., Ed. (1972) *Geology of Minnesota: A Centennial Volume in honor of George M. Schwartz*. Minnesota Geological Survey, St. Paul.
- Spicer, R.A. and Corfield, R.M. (1992) A review of terrestrial and marine climates in the Cretaceous with implications for modeling the greenhouse Earth. *Geol. Mag.* 129, 169-180.
- Spicer, R.A., McRees, P., and Chapman, J.L. (1993) Cretaceous phytogeography and climate signals. In: Allen, J.R.L., Sellwood, B.W., Spicer, R.A., Valdes, P.J. (Eds.), *Palaeoclimates and their modeling*. Chapman and Hall, London, 69-77.
- Suzuoki, T. and Epstein, S. (1976) Hydrogen isotope fractionation between OH-bearing minerals and water. *Geochim. Cosmochim. Acta* 40, 1229-1240.
- Tabor, N.J. (2007) Permo-Pennsylvanian palaeotemperatures from Fe-oxide and phyllosilicate $\delta^{18}\text{O}$ values. *Earth Plan. Sci. Lett.* 253, 159-171.
- Tabor, N.J. and Montañez, I. P. (2005) Oxygen and hydrogen isotope compositions of Permian pedogenic phyllosilicates: Development of modern surface domain arrays and implications for paleotemperature reconstructions. *Palaeogeog., Palaeoclim., Palaeoecol.* 223, 127-146.
- Tabor, N.J. and Yapp, C.J. (2005) Incremental vacuum deglydration-decarbonation experiments on a natural

- gibbsite ($\alpha\text{-Al}(\text{OH})_3$): CO_2 abundance and $\delta^{13}\text{C}$ values. *Geochim. Cosmochim. Acta*, **69**, 519-527.
- Toth, T. A. and Fritz, S. J. (1997) An Fe-berthierine from a Cretaceous Laterite: Part 1. Characterization. *Clay & Clay Min.* **45**, 564-579.
- Ufnar, D.F., González, L.A., Ludvigson, G.A., Brenner, R.L., and Witzke, B.J., (2002) The mid-Cretaceous water bearer: Isotope mass balance quantification of the Albian hydrologic cycle. *Palaeogeog. Palaeoclim. Palaeoecol.* **188**, 51-71.
- Ufnar, D. F., González, L. A., Ludvigson, G. A., Brenner, R.L. and Witzke, B. J. (2004) Evidence for increased latent heat transport during the Cretaceous (Albian) greenhouse warming. *Geology*, **32**, 1049-1052.
- Vitali, F., Longstaffe, F.J., Bird, M.I., and Caldwell, G.E. (2000) Oxygen-isotope fractionation between aluminum-hydroxide phases and water at $<60^\circ\text{C}$: Results from decade-long synthesis experiments. *Clay and Clay Min.* **48**, 230-237
- Vitali, F., Longstaffe, F.J., Bird, M.I., Gage, K.L., and Caldwell, G.E. (2001) Hydrogen-isotope fractionation in aluminum hydroxides: Synthesis products versus natural samples from bauxites. *Geochim. Cosmochim. Acta*, **65**, 1391-1398
- Wagner, T., Herrle, J. O., Damsté, J. S. S., Schouten, S., Stüsser, I., and Hofmann, P. (2008) Rapid warming and salinity changes of Cretaceous surface waters in the subtropical North Atlantic. *Geology* **36**, 203-206.
- Wilson, P.A., Norris, R.D., and Cooper, M.J. (2002) Testing the Cretaceous greenhouse hypothesis using glassy foraminiferal calcite from the core of Turonian tropics on Demerara Rise. *Geology* **30**, 607-610
- Wolfe, J. A. and Upchurch, G. R. Jr. (1987) North American nonmarine climates and vegetation during the late Cretaceous. *Palaeogeog., Palaeoclim., Palaeoecol.* **61**, 33-77.
- Yapp, C. J. (1987) A possible goethite-iron(III) carbonate solid solution and the determination of CO_2 partial pressure in low-temperature geologic systems. *Chem. Geol.* **64**, 259-268.
- Yapp, C.J. (1993) The stable isotope geochemistry of low temperature Fe(III) and Al "oxides" with implications for continental paleoclimates. In: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S. (eds.) *Climate Change in Continental Isotopic Records. Geophysical Monogr.*, **78**, 285-294.
- Yapp, C. J. (1998) Paleoenvironmental interpretation of oxygen isotope ratios in oolitic ironstones. *Geochim. Cosmochim. Acta* **62**, 2409-2420.
- Yapp, C.J. and Pedley, M.D. (1985) Stable hydrogen isotopes in iron oxides: II. D/H variations among natural goethites. *Geochim. Cosmochim. Acta* **49**, 487-495.
- Yapp, C. J. and Poths, H. (1991) $^{13}\text{C}/^{12}\text{C}$ ratios of the Fe(III) carbonate component in natural goethites. In: *Stable isotope geochemistry: A tribute to Samuel Epstein*, Special Publication 3 (ed. H. P. Taylor, Jr. et al.), 257-270, Geochemical Society.

8. FIGURE CAPTIONS

- Fig. 1. Sample locales and field photos of the outcrops. a) Sketch map of the Redwood Falls area; filled squares show the sample sites: A (near Purgatory creek) and B (Mike's quarry); b) Field photo of site B outcrop; c) Field photo of site A outcrop. Sample positions are illustrated in the photos.
- Fig. 2. Illustrative XRD spectra of 05MN6-8 and 05MN11-5rp before and after respective chemical treatments from this study. "NCT" means "not chemically treated". "CD" refers to a sample treated with citrate-dithionite. K = kaolinite, Gb = gibbsite, Qz = quartz, G = goethite, Hm = Hematite, Bo = Boehmite.
- Fig. 3. $\delta\text{D}_{\text{tot}}$ vs. $\text{X}(\text{H})_{\text{Gb}}$ for all 05MN11 and 05MN6 samples (after first outgassing at 100°C). $\text{X}(\text{H})_{\text{Gb}}$ is the hydrogen recovered at 220°C as a mole fraction of the total hydrogen in a treated and outgassed sample (see text and Tables 3 and 4). The regression line is for all data from the 05MN11 and 05MN6 samples. The uncertainties for the slope and intercept represent the standard errors.
- Fig. 4. (a) Results of kaolinite-water vapor hydrogen isotope exchange experiments on sample 05MN11-12 at 220°C are plotted as $1000(\alpha_i - 1)$ against $1000(\alpha_f - \alpha_i)$. The straight line is the two-point regression whose equation is: $1000(\alpha_i - 1) = -1600(\alpha_f - \alpha_i) - 20$. $\alpha_f = (\text{D}/\text{H})_{\text{K}}/(\text{D}/\text{H})_{\text{Vapor}}$ after exchange. α_i is the apparent initial (i.e., before exchange) mineral-vapor fractionation factor. The experimental method is that of Yapp and Pedley (1985) as modified from Northrop and Clayton (1966) and Suzuoki and Epstein (1976). As shown by Northrop and Clayton (1966), the intercept of the line corresponds to the interpolated equilibrium kaolinite-vapor D/H fractionation expressed as $1000(\alpha_{\text{eq}} - 1)$. From the data in the figure, the inferred value of α_{eq} is 0.982. The extent of isotopic exchange (f) is calculated as $(\alpha_f - \alpha_i)/(\alpha_{\text{eq}} - \alpha_i)$. (b) $\ln(1 - f)$ is plotted against the elapsed time of the exchange. The straight line (curve 1) in the figure is based on an assumption of the applicability of a pseudo-first order exchange rate, while curve (2) is based on an assumption of a simple second order exchange rate (e.g., Cole and Ohmoto, 1986, and references therein). The second order curve is non-linear because it is plotted in coordinates of $\ln(1 - f)$ vs. time.
- Fig. 5. Measured $\delta^{18}\text{O}$ values of the total oxygen ($\delta^{18}\text{O}_{\text{total}}$) in a sample plotted against the oxygen in gibbsite as a mole fraction, $\text{X}(\text{O})_{\text{Gb}}$, of the total oxygen in that sample. The values of $\text{X}(\text{O})_{\text{Gb}}$ were calculated from data in Tables 3 and 4 (see text) and are listed in Table 8. The four data points (filled triangles) represent treated samples that were mixtures of three minerals: kaolinite, gibbsite, and quartz (Tables 1 and 8). In these four samples quartz was a consistently minor contributor to the total oxygen in a sample (Table 8). If certain other conditions are satisfied (see text), a plot of $\delta^{18}\text{O}_{\text{total}}$ against $\text{X}(\text{O})_{\text{Gb}}$ should be a nearly linear array for the four samples of Table 8. The data in the figure seem to define such a linear trend. The straight line and equation represent the linear regression of the data. The $\delta^{18}\text{O}$ values of the kaolinite and gibbsite shown in the figure were determined from the slope and intercept of the regression line (see text).
- Fig. 6. Dashed lines are isotherms expected for kaolinite in equilibrium with GMWL waters (Craig, 1961) at temperatures from 0°C to 40°C . The isotherms were calculated using the kaolinite-water hydrogen and oxygen isotopic fractionation factors of Sheppard and Gilg (1996). The filled square represents the measured $\delta^{18}\text{O}$ and δD values of the pedogenic kaolinite from the Cenomanian paleosol of this study. The shaded triangle and shaded circle represent hypothetical modern kaolinites formed, respectively, under modern average annual and summer conditions in that locale (see text).
- Fig. 7. Meteoric water $\delta^{18}\text{O}$ values plotted against the MAT of collection sites with elevations ≤ 100 m (sea level datum - s.l.d.). Modern data are from Rozanski et al. (1993). The $\delta^{18}\text{O}$ value of -6.3‰ inferred for the waters present at the time of formation of the Cenomanian kaolinite at a temperature of 22°C is represented by the filled square (see text).