18O/16O 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 δ18O values of the kaolinite in these samples. These calculations yielded kaolinite δD values of about -73‰ and δ18O values of about +18.7‰. The δD and δ18O 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 δ18O values indicate a crystallization temperature of 22 (± 5)°C. A nominal paleotemperature of 22°C implies a δ18O value for the corresponding water of -6.3‰. The combination of temperature and meteoric water δ18O 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 ~22°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 CO2 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 ~40°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 kaolinite 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 pisolithic 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 pisolithic material in the argillaceous zone.

Two sample locales are indicated in Fig. 1a. At site A (“Purgatory Creek location”, Fig. 1c), the laterite outcrop is exposed in a roadcut located next to Renville Co Hwy 51 near Purgatory Creek (GPS coordinates: 44°32′01.38″ N; 94°55′41.34″ W; elevation: ~267 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°32′33.84″ N; 95°01′58.1″ W; elevation: ~295 m). At this location, the exposed sequence of the paleosol is finer-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 Fe(CO)₅OH 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 Fe²⁺ minerals such as berthierine (idealized chemical formula is Fe₂Al₅Si₃O₁₀(OH)₂) 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 “tp” 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 µm 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-Kα 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 05MN1 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$_2$O$_2$ to remove organic matter (four consecutive H$_2$O$_2$ 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$_2$O 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$_2$O with a methanol-dry ice bath. H$_2$O 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 Toeppler pump with a precision of ±1 μmol. 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 ±0.1 μmol. The 18O/16O 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, δX = (R_{sample} - 1)×1000‰ (1)

For X = 18O, R = 18O/16O, whereas X = D, for R = D/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 isotope measurements is ±3‰ for δD values and ±0.3‰ for δ18O 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°31’05.16” N; 94°53’05.34” 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°31’18.78” N; 94°53’43.92” W; elevation: ~261 m). 05WMN-3 is water from Crow Creek (GPS: 44°32’27.96” N; 95°1’26.76” 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$_2$O over depleted uranium metal at 760°C and measured for δD values with a precision of about ±1‰. δ18O values were determined with a precision of ±0.1‰ using the CO$_2$-H$_2$O 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$_2$O$_2$-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 some 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$_2$O$_2$) 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 δ18O values measured for the 05WMN water samples are listed in Table 2. δ18O values range from -8.5‰ to -7.9‰, whereas δD values range from -64‰ to -62‰. These δ18O 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 isotopic 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 225°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 δ18O values range from to 10.1‰ to 18.3‰, whereas the oxygen yields range from 12.1 to 16.7 μmol/mg. Among the total of six pairs of replicate analyses in Table 5, four show analytically significant shifts of both δ18O values and oxygen yields. The shifts of δ18O values range from +1.2 to +5.0‰, while the shifts of oxygen yield range from 2.5 to 3.5 μmol/mg.

4. DISCUSSION

4.1. Hydrogen isotopes in gibbsite and kaolinite

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4.1.1 Determination of endmember $\delta D$ 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 $\delta D$ 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 $\delta D$ 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” $\delta D$ 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 $\delta D$ 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 ($\delta D = +450\%$). For the kaolinite in 05MN11-12, the $\delta D$ 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 $\delta D$ is only about 4% of the expected difference of approximately 450 to 500‰ between the $\delta D$ 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 $\delta D$ 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 05MN1 samples of Table 3 which were heated at 220°C and 850°C (after outgassing at 100°C) had an average $\delta D$ value of $-44 \pm 4\%$ for hydrogen evolved at 220°C, and $-76 \pm 6\%$ for hydrogen evolved at 850°C. The 05MN6 samples (Table 4) had similar average $\delta D$ values of $-50 \pm 7\%$ for hydrogen evolved at 220°C (or 225°C) and $-75 \pm 2\%$ for hydrogen evolved at 850°C. The likelihood that these $\delta D$ values correctly represent the $\delta D$ values of the gibbsite ($\sim 220°C$ hydrogen) and kaolinite ($\sim 850°C$ 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 05MN11-5p) gibbsite and kaolinite are the predominant hydrogen-bearing minerals in the treated samples of this study. Thus, to a first approximation, the $\delta D$ values of the total hydrogen ($\delta D_{tot}$) 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:

$$\delta D_{tot} = X(H)_K \delta D_K + X(H)_{Gb} \delta D_{Gb}$$

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

$$\delta D_{tot} = (\delta D_{Gb} - \delta D_K) X(H)_{Gb} + \delta D_K$$

If kaolinite and gibbsite are the only hydrogen-bearing substances in the samples, and if $\delta D_K$ and $\delta D_{Gb}$ each have a constant value among the various samples, Eq. 2b indicates that a plot of $\delta D_{tot}$ against $X(H)_{Gb}$ should yield a straight line whose intercept is $\delta D_K$. The value of $\delta D_{Gb}$ 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 $\delta D$ 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 $\delta D_{tot}$ against $X(H)_{Gb}$ 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 $X(H)_{Gb}$ 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 $X(H)_{Gb}$ 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., $X(H)_{Gb} = 0.00$). Linear regression of the 05MN11 and 05MN6 data of Fig. 3 yields the following equation:

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

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 $\delta D_{Gb}$ value is approximately $-47 (\pm 5)\%$, whereas the kaolinite of these samples has a $\delta D_K$ value of about $-73 (\pm 2)\%$. These two inferred endmember $\delta D$ values are the same (within analytical error) as the overall averages of the $\delta D$ values measured directly for hydrogen evolved by stepwise dehydration at 220°C ($\delta D_{Gb} = -46 \pm 6\%$) and 850°C ($\delta D_K = -$.
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 equation 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 δ18O 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 δ18O 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 ±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 δ18O 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 δ18O value of a laboratory standard routinely run on that BrF5 extraction line. This suggests that, for the samples of this study, δ18O 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 (Al2Si2O5(OH)4), gibbsite (Al(OH)3), and quartz (SiO2), 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 δ18O 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:

\[ \delta^{18}O_{\text{tot}} = X(O)_K \delta^{18}O_K + X(O)_{\text{Gib}} \delta^{18}O_{\text{Gib}} + X(O)_{\text{Q}} \delta^{18}O_{\text{Q}} \]  

(4)

Where \( \delta^{18}O_{\text{tot}} \) is the δ18O value of the bulk sample; \( X(O)_K \) is oxygen in kaolinite as a mole fraction of total sample oxygen, \( X(O)_{\text{Gib}} \) is oxygen in gibbsite as a mole fraction of total sample oxygen, and \( X(O)_{\text{Q}} \) is oxygen in kaolinite as a mole fraction of total sample oxygen. \( \delta^{18}O_K \), \( \delta^{18}O_{\text{Gib}} \), and \( \delta^{18}O_{\text{Q}} \) are the respective δ18O values of endmember kaolinite, gibbsite, and quartz. Because \( X(O)_K + X(O)_{\text{Gib}} + X(O)_{\text{Q}} = 1 \), Eq. 4 can be rewritten as:

\[ \delta^{18}O_{\text{tot}} = m X(O)_K + b \]  

(5)

Where, 

\[ m = (\delta^{18}O_{\text{Q}} - \delta^{18}O_K) \]  

\[ b = (\delta^{18}O_K - \delta^{18}O_G) \]

If the respective values of \( \delta^{18}O_K \), \( \delta^{18}O_{\text{Gib}} \), and \( \delta^{18}O_{\text{Q}} \) are constant among the samples and if the value of \( X(O)_K \) is constant and/or small in the sample population of interest, Eq. 5 indicates that a plot of \( \delta^{18}O_{\text{tot}} \) against \( X(O)_K \) should yield a linear data array. The \( \delta^{18}O_{\text{tot}} \) data of Table 8 are plotted against corresponding values of \( X(O)_K \) in Fig. 5. Linear regression of the data of Fig. 5 yields the equation \( \delta^{18}O_{\text{tot}} = -14.0(±1.2)X(O)_K + 18.7(±0.2) \) 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 \( X(O)_K \) is small implies that the quantity \( (\delta^{18}O_{\text{Q}} - \delta^{18}O_K)X(O)_K \) in the expression for “b” is small. For example, even if the absolute value \( \delta^{18}O_{\text{Q}} - \delta^{18}O_K \) were as large as 10‰, the small average value of 0.024 for \( X(O)_K \) (Table 8) would imply a value for \( (\delta^{18}O_{\text{Q}} - \delta^{18}O_K)X(O)_K \) of only about 0.2‰. Thus, \( b = \delta^{18}O_K \) with an average additional uncertainty associated with the presence of the small amount of admixed quartz of about ±0.2‰. Similarly, \( m + b = \delta^{18}O_{\text{Gib}} \). The δ18O values of endmember kaolinite and gibbsite in the four samples of Fig. 5 (and Table 8) can be calculated in this manner are: \( \delta^{18}O_K = 18.7(±0.4)‰ \) and \( \delta^{18}O_{\text{Gib}} = 4.7(±1.6)‰ \). 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 δ18O value of kaolinite, subsequent paleoenvironmental interpretations use only the kaolinite data.

4.3. Paleoenvironment

4.3.1 Paleotemperature

The relationship between the δD and δ18O 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):

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

(6)

Where, \( \delta^D_K \) and \( \delta^D_{K-W} \) are the measured δD and δ18O values of the kaolinite, \( \delta^D_{K-W} \) and \( \delta^D_{K-W} \) 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 δ18O for temperatures from 0°C to 40°C (Fig. 6). The data point in Fig. 6 representing the measured δD and δ18O values of the Cenomanian pedogenic kaolinite (δDk = -73‰, and δ18Ok = 18.7‰) indicates a formation temperature of 22 (+±5)°C. The uncertainty of ±5°C is derived from the uncertainty in the δD and δ18O values. For a nominal paleotemperature of 22°C, the value of 18Okw is about 1.0252 (Sheppard and Gilg, 1996). This implies a δ18O 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 Hsielt, 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 (1998) and Eslinger (1971) in combination with the hydrogen isotopic fractionation factor of Sheppard and Gilg (1996). The calculated paleotemperature for this case was about 26 (+±5)°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°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 (~40°N). Linear regression of isotopic data (IAEA/WMO, 2004) for monthly precipitation (years 1961 to 1995) at Genoa yields the following equation: δD = 7.3δ18O + 5 (r² = 0.93). If such a LMWL characterized the ancient environment of the Cenomanian paleosol, the kaolinite δD and δ18O 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 δ18O values of the Cenomanian kaolinite of this study. Moreover, it is observed that the multi-year annual averages of the δ18O (-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 δD – 8δ18O) 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 δ18O 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 δ18O 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 δ18O values. On a plot of the type in Fig. 6, this evaporative effect would 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 18O 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 (+±5)°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 δ18O values of local modern waters (~63‰ and -9.3‰, 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 δ18O value of +20.3‰ (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 was neformed 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 δ18O 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 δ18O 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 palaeolatitudes of 40°N, and >14°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 palaeolatitudes (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 average annual signal of 20 to 21°C for southeastern North America, and a latitudinal temperature gradient of 0.3°C/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 CO2 concentrations. With an atmospheric CO2 concentration of 8 to 12 PAL (PreIndustrial Atmospheric Levels, ~280ppmV), 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 ~15°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 CO2 concentration of 4 PAL. The results of Feng and Yapp (2009) suggest that Cenomanian CO2 concentrations may have been about 7 PAL. Poulsen et al. (2007) suggested that an increase of atmospheric CO2 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-Kacmarkick 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 δ18O values of Cenomanian soil water with those of global modern annual average precipitation may provide some insight into this question.

The δ18O 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 δ18O values of modern average annual precipitation at elevations of ≤ 100m as presented by Rozanski et al. (1993). The ancient water δ18O value plots toward the lower end of the range of isothermal scatter of the modern δ18O values. At mid-latitudes δ18O values of summer rain are generally more positive than those of average annual precipitation (e.g., Rozanski et al., 1993). Consequently, the negative δ18O 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 δ18O 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 laternites (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.
warm paleotemperature and an inferred $\delta^{18}O$ 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.

6. Acknowledgement

The paper benefited from the constructive comments of Albert Gilg and two anonymous reviewers. We wish to thank Kurt Ferguson and Ian Richards for assistance with hydrogen and/or oxygen isotopic analyses, and Roy Beavers for training W.F. in XRD analysis. We would also like to thank Mike of "Mike's Quarry" for generously allowing access to collect some of the samples. This research was supported by NSF grant EAR-0616627 to C.J. Yapp.

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Published paper (may contain minor typographic differences), doi: [http://dx.doi.org/10.1016/j.gca.2009.07.025](http://dx.doi.org/10.1016/j.gca.2009.07.025)


Table 1. Sample summary

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<tr>
<th>Sample #</th>
<th>Sample site</th>
<th>depth (cm)</th>
<th>Mineral Composition before CD treatment</th>
<th>Mineral Composition after CD treatment</th>
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<td>A</td>
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<td>Q(10); K(2); Gb(2); G(1); Hm(1); Bo(0.5)</td>
<td>Q(10); K(1); Gb(2); Bo(0.1)</td>
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<td>Q(10); K(1); Gb(2); Bo(0.1)</td>
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05MN6- before 0.5 M HCl + H2O2: 0.5 M HCl + H2O2:

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<tr>
<th>Sample #</th>
<th>Sample site</th>
<th>depth (cm)</th>
<th>Mineral Composition before 0.5 M HCl + H2O2</th>
<th>Mineral Composition after 0.5 M HCl + H2O2</th>
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*sample site A is near Purgatory Creek, site B is in "Mike’s Quarry" (see text and Fig. 1)."depth below the top of the existing outcrop. "the term ‘CD treatment’ is used to represent a series of chemical treatments including 0.5 M HCl, 30% H3O; and CD (see text). Q = quartz; K = kaolinite; Gb = gibbsite; G = goethite; Hm = hematite; Bo = boehmite; Bh = Berthierine; L = lepidocrocite. Relative peak heights (in parentheses) as estimated from XRD patterns; 10 = highest. The peaks (d-spacing in Å) used to represent each mineral are Q = 3.34; K = 7.16; Gb = 4.82; G = 4.18; Hm = 3.68; Bo = 6.10; L = 6.26; Bh = 7.08. A double peak in the vicinity of 7.10 Å on the XRD pattern indicates the co-existence of berthierine and kaolinite in sample 05MN11-7rp.
## Table 2. Water samples (collected May, 2005)

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Table 3. Results of hydrogen isotopic analyses of 05MN11 samples

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<th>H₂ μmol</th>
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<td>2</td>
<td>850</td>
<td>35</td>
<td>308</td>
<td>-72</td>
<td>ND</td>
<td>-72</td>
</tr>
<tr>
<td>11rp</td>
<td>CD</td>
<td>2560</td>
<td>69.7</td>
<td>2</td>
<td>220</td>
<td>157</td>
<td>427</td>
<td>-44</td>
<td>0.66</td>
<td>-57</td>
</tr>
<tr>
<td>3</td>
<td>850</td>
<td>30</td>
<td>218</td>
<td>-83</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>CD</td>
<td>2548</td>
<td>92.6</td>
<td>2</td>
<td>850</td>
<td>35</td>
<td>612</td>
<td>-71</td>
<td>0</td>
<td>-71</td>
</tr>
</tbody>
</table>

aSample mass after outgassing at 100°C in vacuum (60 minutes). bFr# indicates which step is represented in the sequential steps of dehydration experiments (see text). cX(H)Gb = the hydrogen recovered at 220°C as a mole fraction of the total hydrogen in the sample. The values of X(H)Gb for 1rp-2, 2rp-2, and 7rp were determined from hydrogen yields in multi-step (≥ 3 steps) dehydrations performed for another study (in progress) on CO₂ in gibbsite. dδDtot is the δD value of the total hydrogen in the bulk sample (after the samples were first outgassed at 100°C in vacuum). For samples that underwent stepwise dehydration, δDtot represents the weighted average of the 220°C and 850°C steps. ND = not determined.
Table 4. Results of hydrogen isotopic analyses of 05MN6 samples

<table>
<thead>
<tr>
<th>sample #&lt;br&gt;05MN6-</th>
<th>Chem. Treatment</th>
<th>MHD#</th>
<th>Mass mg&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Fr#&lt;sup&gt;b&lt;/sup&gt;</th>
<th>T °C</th>
<th>time min</th>
<th>H&lt;sub&gt;2&lt;/sub&gt; μmol</th>
<th>δD ‰</th>
<th>X(H)&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
<th>δD&lt;sub&gt;tot&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt; ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>HCl+H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2606</td>
<td>78.4</td>
<td>2</td>
<td>220</td>
<td>150</td>
<td>62</td>
<td>-59</td>
<td>0.10</td>
<td>-72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>850</td>
<td>38</td>
<td>570</td>
<td>-73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>HCl+H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2611</td>
<td>79.8</td>
<td>2</td>
<td>225</td>
<td>151</td>
<td>60</td>
<td>-51</td>
<td>0.10</td>
<td>-72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>850</td>
<td>36</td>
<td>563</td>
<td>-74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>HCl+H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2612</td>
<td>84.7</td>
<td>2</td>
<td>220</td>
<td>150</td>
<td>109</td>
<td>-50</td>
<td>0.15</td>
<td>-70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>850</td>
<td>31</td>
<td>595</td>
<td>-74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>HCl+H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2582</td>
<td>58.5</td>
<td>2</td>
<td>220</td>
<td>150</td>
<td>333</td>
<td>-42</td>
<td>0.51</td>
<td>-60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>850</td>
<td>30</td>
<td>318</td>
<td>-78</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Sample mass after outgassing at 100°C in vacuum (60 minutes).  
<sup>b</sup>Fr# indicates which step is represented in the sequential steps of dehydration experiments (see text).  
<sup>c</sup>X(H)<sub>2</sub> = the hydrogen recovered at 220°C (or 225°C) as a mole fraction of the total hydrogen in the sample.  
<sup>d</sup>δD<sub>tot</sub> is the δD value of the total hydrogen in the bulk sample (after the samples were first outgassed at 100°C in vacuum).  
δD<sub>tot</sub> values represent the weighted average of the 220°C and 850°C steps.
Table 5. Results of oxygen isotopic analyses of chemically treated 05MN samples (see Tables 1, 3, and 4 for information about chemical treatments).

<table>
<thead>
<tr>
<th>Sample #</th>
<th>aliquot #1</th>
<th>aliquot #2</th>
<th>aliquot #1</th>
<th>aliquot #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>05MN11-2m</td>
<td>16.2</td>
<td></td>
<td>15.4 (87%)</td>
<td></td>
</tr>
<tr>
<td>05MN11-4rp</td>
<td>11.2</td>
<td>13.6</td>
<td>12.2 (68%)</td>
<td>14.9 (83%)</td>
</tr>
<tr>
<td>05MN11-5m</td>
<td>11.2</td>
<td>16.2</td>
<td>13.0 (73%)</td>
<td>16.5 (93%)</td>
</tr>
<tr>
<td>05MN11-7rp</td>
<td>14.4</td>
<td></td>
<td>12.1 (68%)</td>
<td></td>
</tr>
<tr>
<td>05MN11-10rp</td>
<td>13.6</td>
<td>14.8</td>
<td>13.1 (ND)</td>
<td>15.6 (ND)</td>
</tr>
<tr>
<td>05MN11-12</td>
<td>18.1</td>
<td>18.3</td>
<td>14.5 (84%)</td>
<td>14.9 (86%)</td>
</tr>
<tr>
<td>05MN6-8</td>
<td>17.5</td>
<td>18.2</td>
<td>16.3 (93%)</td>
<td>16.3 (93%)</td>
</tr>
<tr>
<td>05MN6-10</td>
<td>18.0</td>
<td></td>
<td>16.7 (95%)</td>
<td></td>
</tr>
<tr>
<td>05MN6-17</td>
<td>10.1</td>
<td>14.3</td>
<td>14.4 (80%)</td>
<td>16.4 (91%)</td>
</tr>
</tbody>
</table>

*The three-digit values for yield are in units of μmoles/mg. The values in parentheses represent the oxygen extracted from a sample as a mole percentage of the expected oxygen (calculated from ideal stoichiometries and the proportions of oxygen in each of the minerals as calculated from data in Tables 3 and 4). The analytical error of the percentage yields is about ±3%. Bold values highlight analyses that have nominal percent oxygen yields of at least 91%. Within analytical uncertainty, nominal yields of at least 91(±3)% are in the range of yields associated with the correct δ¹⁸O value of a laboratory standard routinely run on that BrF₅ extraction line. Values shown in italics represent analyses with low oxygen yields. ND = no determination of % yield because of lack quantitative information on the proportions of gibbsite and kaolinite in 05MN11-10rp (see Table 3).
Table 6. Hydrogen isotopic analyses of samples treated as indicated at 22°C.

<table>
<thead>
<tr>
<th>sample #</th>
<th>Chemical Treatment</th>
<th>Mass mg</th>
<th>Fr#</th>
<th>T °C</th>
<th>time min</th>
<th>H₂ μmol</th>
<th>δD ‰</th>
<th>X(H₂) ‰</th>
<th>δDox ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>05MN11-5m</td>
<td>CD+15M HCl</td>
<td>2567</td>
<td>2</td>
<td>220</td>
<td>147</td>
<td>146</td>
<td>-44</td>
<td>0.33</td>
<td>-61</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>850</td>
<td>33</td>
<td>299</td>
<td>-70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>05MN11-5m</td>
<td>CD</td>
<td>2555</td>
<td>2</td>
<td>220</td>
<td>150</td>
<td>148</td>
<td>-49</td>
<td>0.34</td>
<td>-63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>850</td>
<td>44</td>
<td>293</td>
<td>-70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>05MN11-12</td>
<td>CD+15M HCl (δD = +450‰)</td>
<td>2584</td>
<td>2</td>
<td>850</td>
<td>33</td>
<td>209</td>
<td>-53</td>
<td>0</td>
<td>-53</td>
</tr>
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<td></td>
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<td>2</td>
<td>850</td>
<td>35</td>
<td>612</td>
<td>-71</td>
<td>0</td>
<td>-71</td>
</tr>
</tbody>
</table>

* Sample mass after outgassing in vacuum at room temperature (up to 120 minutes) followed by 100°C in vacuum (60 minutes).

* Fr# indicates which increment is represented in the sequential steps of dehydration experiments (see text).
Citation: Feng, W., and Yapp, C.J. \( ^{18}\text{O}/^{16}\text{O} \) and \( D/H \) ratios of pedogenic kaolinite in a North American Cenomanian laterite: Paleoclimatic implications, Geochim, Cosmochim.Acta, Vol 73, 6249-6263

Table 7. Results of kaolinite-water vapor hydrogen isotope exchange experiments at 220°C for CD-treated sample 05MN11-12

<table>
<thead>
<tr>
<th>MHD#</th>
<th>Mass (mg)</th>
<th>Exchange time (min)</th>
<th>Amount (µmol)</th>
<th>( \delta D_k ) (%)</th>
<th>( H_2 ) yield (µmol)</th>
<th>Kaolinite ( \delta D_k ) after exchange (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2563</td>
<td>45.4</td>
<td>328</td>
<td>217</td>
<td>+114</td>
<td>290</td>
<td>-33</td>
</tr>
<tr>
<td>2566</td>
<td>46.9</td>
<td>300</td>
<td>200</td>
<td>-252</td>
<td>300</td>
<td>-111</td>
</tr>
</tbody>
</table>

*\( \delta D \) value of the kaolinite before exchange is -73‰ (see text).
Table 8. δ¹⁸O of the total oxygen in a sample, and oxygen in the indicated mineral as a mole fraction of the total sample oxygen.

<table>
<thead>
<tr>
<th>Sample# 05MN</th>
<th>treatment</th>
<th>mole fraction of oxygen</th>
<th>total sample measured δ¹⁸O(‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11-5m</td>
<td>CD</td>
<td>0.787 0.177 0.036</td>
<td>16.2</td>
</tr>
<tr>
<td>6-8</td>
<td>HCl + H₂O₂</td>
<td>0.922 0.044c 0.034c</td>
<td>17.9d</td>
</tr>
<tr>
<td>6-10</td>
<td>HCl + H₂O₂</td>
<td>0.902 0.073 0.025</td>
<td>18.0</td>
</tr>
<tr>
<td>6-17</td>
<td>HCl + H₂O₂</td>
<td>0.681 0.317 0.002</td>
<td>14.3</td>
</tr>
</tbody>
</table>

aSee text for details. bMole fractions are oxygen in the indicated mineral as a mole fraction of the total oxygen in the sample of interest. Mole fractions were calculated from data in Tables 3 and 4 (see text). cAverage mole fraction values as determined from the two dehydration analyses of Table 4. dAverage δ¹⁸O of aliquots #1 and #2 in Table 5.
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. δDtot vs. X(H)tot for all 05MN11 and 05MN6 samples (after first outgassing at 100°C). X(H)tot 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(αig - 1) against 1000(αig - 1). The straight line is the two-point regression whose equation is: 1000(αig - 1) = -1600(αig - 1) - 20. αig = (D/H)vap/(D/H)spec after exchange. αig 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 correspond to the interpolated equilibrium kaolinite-vapor D/H fractionation expressed as 1000(αio - 1). From the data in the figure, the inferred value of αio is 0.982. The extent of isotopic exchange (f) is calculated as (αig - αio)/(αio - αig). (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 δ18O values of the total oxygen (δ18Ototal) in a sample plotted against the oxygen in gibbsite as a mole fraction, X(O18Ogb), of the total oxygen in that sample. The values of δ18Ototal 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 δ18Ototal against X(O18Ogb) 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 δ18O 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 δ18O 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 δ18O 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 δ18O 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).
Fig. 2

(1) 05MN11-5r, NCT
(2) 05MN11-5r, CD
(3) 05MN6-8, NCT
(4) 05MN6-8, 0.5M HCl + H₂O₂
\[ y = 26(\pm 3)x - 73(\pm 2) \]

\[ r^2 = 0.88 \]
Fig. 4

(1) Kaolinite-water vapor D/H Exchange
CD-treated 05MN11-12

(2) 

\[ 1000 (\alpha_f - \alpha_i) \]

\[ \ln (1 - f) \]

\( f \): degree of exchange (as a decimal fraction)

~62% exchanged

0 100 200 300

0 0 0 0

0 0 0 0

0 0 0 0

-1.2 -0.8 -0.4 0 0 0 0
$\delta^{18}O_{\text{tot}} = -14.0(\pm 1.2)X(O)_{\text{Gb}} + 18.7(\pm 0.2)$

$r^2 = 0.99$

inferred $\delta^{18}O_K = 18.7 (\pm 0.4)\%$

inferred $\delta^{18}O_{Gb} = 4.7 (\pm 1.6)\%$
Fig. 6

Kaolinite

- hypothetical modern - annual
- measured Cenomanian
- hypothetical modern - summer

δD(‰)SMOW

GMWL (Craig, 1961)

δ18O(‰)SMOW

0°C
10°C
20°C
30°C
40°C
Average annual surface air T (°C)

Water δ¹⁸O(%o)SMOW

-20
-16
-12
-8
-4
0

0
5
10
15
20
25
30

△ modern Earth amount-weighted average annual precipitation
■ water inferred from Cenomanian pedogenic kaolinite