# Occurance and stable isotope compositions of soil carbonate and organic matter within a climatic transect of modern Vertisols along the coastal prairie of Texas 

Dana Lynette Miller

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[^0]To the Graduate Council:
I am submitting herewith a thesis written by Dana Lynette Miller entitled "Occurance and stable isotope compositions of soil carbonate and organic matter within a climatic transect of modern Vertisols along the coastal prairie of Texas." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Geology.

Claudia I Mora, Major Professor
We have read this thesis and recommend its acceptance:
Steven G. Driese, Linsa C. Kah
Accepted for the Council:
Carolyn R. Hodges
Vice Provost and Dean of the Graduate School
(Original signatures are on file with official student records.)

## To the Graduate Council.

I am submitting herewith a thesis written by Dana L Miller entitled " Occurrence and Stable Isotope Compositions of Soul Carbonate and Organic Matter Within a Climatic Transect of Modern Vertisols Along the Coastal Prarre of Texas". I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirement for the degree of Master of Science, with a major in Geology


Dr. Claudia I Mora, Major Professor

We have read this thesis
And recommend its acceptance:


Dr Steven G. Dries
Sued C. Yah

## Dr Linda C Kah

Accepted for Council


Dean of The Graduate School

# Occurrence and Stable Isotope Compositions of Soil Carbonate and Organic Matter Within a Climatic Transect of Modern Vertisols Along the Coastal Prairie of Texas 

A Thesis

Presented for the
Master's Degree
The University of Tennessee, Knoxville

## Dana Lynette Miller

August, 2000

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#### Abstract

Stable carbon and oxygen isotopes from pedogenic carbonate and soil organic matter in a modern Vertisol preserve coherent isotopic records that reflect changes in climate and vegetation during pedogenesis. Three sites from Lake Charles series Vertisols, on the Coastal Prairie of Texas showed sımilar and systematic carbon 1sotope inflections with depth. These inflections suggest the following climate/ecosystem changes: base of the profiles record cooler conditions, warmer/drier conditions are recorded at mid-profile, and evidence for cooler/wetter conditions again is present at the top of the profiles which agrees with a historical increase in $C_{3}$ vegetation seen in Texas and Oklahoma. Although both soil organic matter and pedogenic carbonate have similar depth profiles, coexısting organic matter and carbonate are not contemporaneous. Pedogenic carbonates do not show the uppermost, negative shift in isotopic composition, most likely the result of insufficient time to crystallize carbonate with modern signatures. Stable carbon isotopes of soil organic matter and pedogenic carbonate appear to be sensitive to soil horizonation and microtopography. The coherent record of stable carbon isotopes preserved in these Vertisols indicate that these sorls have not expenenced significant "self-mulching" or whole sale pedoturbation. Instead, the systematic soll morphology and isotopic profiles suggest that Vertisols may preserve useful paleoclimate records.


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## I. Introduction

Quaternary soil formation is strongly associated with climatic conditions on both continental as well as a global scales (Mack and James 1994). Climatic conditions are expressed in soil morphology, mineralogy, and chemistry (Smith et al., 1993; Hall and Anderson, 2000). This association has prompted several studies of paleosols in order to reconstruct pre-Quaternary paleoclimates (i.e., McPherson, 1979; Wright, 1982; Retallack, 1983; Cerling and Hay, 1986; Cerlıng et al., 1989; Vanstone, 1991, Mack et al., 1991; Mack, 1992; Driese and Mora, 1993; Mora et al., 1996). Recent studies of modern and ancient soils employ stable isotope analysis of soil-formed minerals and soil organic matter to describe and constrain the soil ecosystems and (paleo)climate (e.g. Amundson et al., 1989; Kelly et al., 1991, 1998; Nordt, 1994; Mora et al., 1996; Boutton, et al., 1998). Unfortunately, clımatic inferences based on paleosol features are often very generaluzed. For example, vertic soil morphology is typically interpreted to sumply indicate "seasonal wet and dry conditions". Few studies on modern soils have systematically characterized climate-sensitive parameters that are likely to be preserved in the rock record. Without a thorough understanding of modern climate indicators, the climate information stored within paleosols may be significantly underinterpreted.

This study contributes to a larger-scale examination of a climate transect or "climosequence" of a modern Vertisol sequence along the Coastal Prairie region of Texas. Typical climosequence studies examine changes in soil morphology and chemistry across a precipitation gradient in which all other soil forming factors, except vegetation, are held constant (e.g. time, parent maternal, topography). This study focuses on three sites within the Texas Vertisol climosequence, examining: (1) pedogenic
carbonate morphology as observed using transmitted light and cathodoluminescence petrography, (2) the stable carbon and oxygen isotope compositions of soil organic matter (SOM) and soil carbonate, and (3) the relationship between those isotopic compositions and depth in the soil profile or characteristic Vertisol features such as microtopography or pedogenic slickensides. These observations are used to constrain the impact of pedogenic processes on the soil isotopic record and utility of the isotope record to determine the climate/ecosystem in effect during pedogenesis.

The three study sites span only a limited precipitation range ( $\sim 17.8 \mathrm{~cm} / \mathrm{yr}$ ) and it is expected that only minor variability from pedon to pedon will be observed. Ultimately, isotopic trends observed in this study may be compared to results of related work along the entire clımosequence to evaluate whether all the soils retain a sımilar isotopic record and which, if any, trends are clımate sensitive.

## II. Study Area

This study is part of a much larger NSF funded project that investigates a modern Vertisol climosequence along the Coast Prairie of Texas. The focus of this study is three sites within the Lake Charles Series soils, near Houston, Texas (Figure 1). The parent material for the Lake Charles Vertisols at each of these sites consists largely of alluvial to deltaic deposits of the Beaumont Formation (Late Pleistocene), which possess a relatıvely uniform and fine-grained texture (Bernard and LeBlanc, 1965; Barton, 1930a \& b; Kunze et al., 1963). The soils developed on an exposed terrace during low sea-level stand (Bernard and LeBlanc, 1965). The maximum age of the Lake Charles series Vertisols is constrained by soil development on the youngest facies of the parent Beaumont Formation which is $\sim 35 \mathrm{~K}$ years old (Birdseye and Aronow, 1991). The three sites examined in this study stretch across a sub-humid climate range that has a precipitation regime from 104 to $122 \mathrm{~cm} / \mathrm{yr}$ and are located, from wettest to driest site, in Harris County (201), Fort Bend County (157), and Wharton County (481) (Figure 1; Table 1).


Figure 1. Precipitation map of study areas.
Table 1. Lake Charles Vertisol sampling site locations and information

| Information | Wharton County | Fort Bend County | Harris County |
| :--- | :---: | :---: | :---: |
| County Number | 481 | 157 | 201 |
| 7.5 minute USGS <br> Quadrangle | Smithers Lake | Hungerford | League City |
| Latitude | 29 N 24 15 | 29 N 2538 | 29 N 35 40 |
| Longitude | 95 W 0114 | 96 W 0435 | 95 W 4338 |
| Average Precipitation | $104 \mathrm{~cm} / \mathrm{yr}$ | $114 \mathrm{~cm} / \mathrm{yr}$ | $122 \mathrm{~cm} / \mathrm{yr}$ |

## III. Summary of Physical Processes During Vertisol Formation

The modern soil order Vertisol accounts for approximately 2.2 to $2.4 \%$ of the Earth's land surface (Dudal and Eswaran, 1988; USDA-SCS, 1994). Although Vertisols are reported to occur in most temperature and moisture regimes, Vertisol occurrence is most abundant in the tropics (60\%) and subtropics (30\%) (Dudal and Eswaran, 1988; Wilding and Coulombe, 1996). Modern Vertisols, such as the Lake Charles series of coastal Texas, are composed predominantly of smectitic clays that possess high shrink/swell potential (Huckabee et al., 1977). Although other mineralogies can be dominant, Vertisol development requres the soil matrix to respond to seasonal morsture changes by shrink/swell phenomena (Coulombe et al., 1996a). Vertisols experience seasonal, and sometimes extreme, wetting and drying periods that intensify the shrink/swell processes of the clays. Shrink/swell of the soll matrix results in mechanical failure and movement of soil materials along shear planes or slickenslides (Figure 2). As a result, topographic microhigh and microlow environments are developed that are expressed on the surface as hummock and swale topography known as gilgai, and in the subsurface as pseudo-anticlinal and pseudo-synclinal features in cross-section (Figure 2, 3,4). The Lake Charles Vertisols examined in this study exhibit this characteristic hummock and swale topography, whuch allows for differentiation into microhigh and mucrolow pedons at each sample site.

Figure 2. Schematic diagram showing structural features of a Vertisol
microlow and adjacent microhigh. Master slickensides are located along the edges of the microlow/microhigh contact.


Figure 3. Field shot of Lake Charles microhigh pedon from Harris Co. (Armond Bayou), Texas shows a depth of $\sim 1.5 \mathrm{~m}$. Slickenside faces are observed concentrating more toward the bottom of the profile and along the edges of the microhigh.


Figure 4. Field shot of Lake Charles microlow pedon from Harris Co. (Armond Bayou, 201), Texas, shows a depth of $\sim 1.5 \mathrm{~m}$. Slickenside faces are observed and are especially concentrated along the edges of the bowl structure.

## IV. Controls on the Isotopic Composition of Pedogenic Carbonate

The formation of soil carbonate has been extensively studied (i.e., Singh and Singh, 1972; Mermut and Dasog, 1986; Cerling, 1984; Cerling and Quade, 1993). Soil carbonates form in arnd to sub-humid conditions or in environments with a significant seasonal moisture defictt (Birkeland, 1984; Jenny, 1980). Atmospheric carbon dioxide $\left(\mathrm{CO}_{2}\right)$ and allochthonous carbonate dust are the likely sources for the calcium and carbonate ions that precipitate as pedogenic carbonate (Ahmad and Mermut, 1996).

Within the vadose zone, most soil environments behave as open systems in which equilibrium is quickly established between the soil solution and gaseous soll $\mathrm{CO}_{2}$ (Bottinga, 1968; Magaritz and Amiel, 1980). Pedogenic carbonate precipitation ( $10^{-7}$ to $\left.10^{-9} \mathrm{moles} / \mathrm{cm} / \mathrm{yr}\right)$ is much slower than the respiration flux of $\mathrm{CO}_{2(\mathrm{~g})}$ in soils $\left(10^{-3}\right.$ to $10^{-5}$ moles $/ \mathrm{cm} / \mathrm{yr}$ ) (Cerling and Quade, 1993). Consequently, soil carbonates precipitating from the bicarbonate solutions will have isotopic compositions reflecting soil $\mathrm{CO}_{2}$ compositions (Cerling, 1984).

Vegetation contributes the vast majority of carbon in most soils. Most temperate region terrestrial plants utilize the $\mathrm{C}_{3}$ metabolic pathway (Calvin cycle) and produce organic matter having $\delta^{13} \mathrm{C}$ values of -24 to $-34 \%$ (mean $\sim-27 \%$ ) (PDB) (Deines, 1980). Many arid region plants, salt marsh plants, and some tropical grasses utilize the HatchSlack metabolic pathway, which discrimunates less aganst isotopically heavy carbon (Deines, 1980). $\mathrm{C}_{4}$-type organic matter has $\delta^{13} \mathrm{C}$ values of -9 to $-16 \%$ (mean $\sim-12 \%$ ) (PDB). Thus, soil ecology plays the predominant role in controlling the isotopic composition of SOM and, ultimately, of soil $\mathrm{CO}_{2(\mathrm{~g})}$ and soil carbonate. Soil-respired $\mathrm{CO}_{2}$ is produced by root respiration and microbial oxidation of organic material in the soll
(Cerling, 1984). These processes combine to create a soil $p \mathrm{CO}_{2}$ that is much greater than atmospheric $p \mathrm{CO}_{2}$. Typical soil $p \mathrm{CO}_{2}$ values are $3000-10,000 \mathrm{ppmV}$ whereas atmospheric $p \mathrm{CO}_{2}$ is about 360 ppm (Cerling, 1984, 1991). As a result, atmospheric $p \mathrm{CO}_{2}$ is considered to have negligible influence on the isotopic measurements of soil carbon, except in the geological past, when atmospheric $\mathrm{CO}_{2}$ levels were significantly elevated (Cerling, 1991; Mora et al., 1996; Ekart, et al. 1999; Mora and Driese, 1999).

Dorr and Munnich (1980) observed that the $\mathrm{CO}_{2(\mathrm{~g})}$ collected in soil pores is $\sim 4.4 \%$ enrıched in ${ }^{13} \mathrm{C}$ compared to soll-respired $\mathrm{CO}_{2(\mathrm{~g})}$. This effect is due to isotopic fractionation resulting from $\mathrm{CO}_{2(\mathrm{~g})}$ diffusion through the soil. In fact, carbon undergoes several fractionation steps as organic matter is converted to carbon dioxide and, ultimately, soll carbonate (Figure 5). First, soil respired $\mathrm{CO}_{2(\mathrm{~g})}$ is fractionated during diffusion through soll resultung in a $4.4 \%$ enrichment. As sorl gas $\mathrm{CO}_{2}$ is converted to bicarbonate $\mathrm{HCO}_{3}{ }^{-}(\mathrm{aq})$, carbon is enriched by $\sim 7.1$ to $9.2 \%$. From bicarbonate in the soil solution, carbon expenences a further 1.9 to $2.0 \%$ enrıchment as soil carbonate is precipitated. Therefore, the resulting $\delta^{13} \mathrm{C}$ value of pedogenic carbonate is approximately 14 to $16 \%$ o heavier than the origunal organic matter (Cerling, 1984).

In addıtion to the composition of soil organic matter, several other factors may affect the isotopic signature of pedogenic carbonate nodules including microbial activity, soil $p \mathrm{CO}_{2}$, and temperature (Cerling and Quade, 1993). For example, studies of soil $\mathrm{CO}_{2(\mathrm{~g})}$ and soil carbonate indicate that $\delta^{13} \mathrm{C}$ values systematıcally decrease with depth in the soil profile until a steady state condition is reached (Cerling, 1984, 1991). Near the soil-atmosphere interface, the influence of isotopically heavy C from atmospheric $\mathrm{CO}_{2(\mathrm{~g})}$ is more prevalent (Cerling, 1984; Quade et al., 1989a). As a result, pedogenic carbonate


Figure 5. Schematıc illustrating the carbon isotopıc fractıonation process as soil organic matter is converted to pedogenic carbonate (after Mora et al., 1993).
precipitated in the upper portions of the profile or within the zone of soil cracking might exhibit an 1sotopically heavier carbon signature due to relatively greater exposure to atmospheric $\mathrm{CO}_{2}$. Conversely, carbonate precipitated at greater depths and often below the zone of soil cracking is likely to record isotopic compositions influenced mainly by soil respiration. These effects are noted in both modern soils (Quade et al., 1989) and ancrent paleosols (Driese and Mora, 1993). Seasonal wet and dry periods may, respectively, increase or lower soil respiration rates, thereby, influencing the isotopic composition of pedogenic carbonate (Cerling, 1984, 1991).

The oxygen isotopic composition of pedogenic carbonate is controlled largely by meteoric water compositions and temperature (Cerling, 1984; Siegenthaler et al., 1984; Cerling and Hay, 1986; Pazdur et al., 1988; Cerling et al., 1989; Quade et al., 1989; Cerling and Quade, 1993). Due to the effects of evaporation, the isotopic composition of soil carbonate is typically slightly heavier than that of local meteoric water (Quade et al., 1989). The isotopic composition of oxygen is much more susceptible to alteration during recrystallization of carbonate during pedogenesis or diagenesis. Recrystallization isotopic exchange of reactive carbonate minerals and water-rich fluids moving through the soil may alter the oxygen isotopic ratio, even at very low water to rock ratios (Banner and Hanson, 1990), without significantly affecting the carbon ratios (Mora et al., 1998). Pedogenic and diagenetic fluids are typically water-rich and, thus, much more abundant in oxygen than carbon.

## V. Previous Isotopic Studies of Texas Soils

Recent isotopic studies on Quaternary Texas soils (i.e., Humphrey and Ferring, 1994; Waters and Nordt, 1995; Nordt et al., 1998, Nordt, 1992) emphasized the importance of carbon and oxygen isotopic ratios in interpreting previous climate regimes, vegetation types, and soil water temperatures, as well as various soll properties that affect the isotopic compositions of these soils. Based on the isotopic compositions of pedogenic carbonate, Humphrey and Ferring (1994) inferred fluctuations in the relative abundance of $\mathrm{C}_{3} / \mathrm{C}_{4}$-type vegetation corresponding to Quaternary climate changes in central Texas. They suggest that the Late Pleistocene climate was relatively cool with cool grassland conditions dominating (i.e., $\mathrm{C}_{3}$-dominated). Other studies (i.e., Gardner, 1984; Bryant and Holloway, 1985; Nordt et al., 1994) also suggest cooler conditions prevailed in the Late Pleistocene. Further, in north-central Texas, the early Holocene is characterized by rapid alluvial sedimentation. Pedogenic carbonate precipitated in the early Holocene also record $\mathrm{C}_{3}$-dominated conditions. This sedimentological evidence, coupled with the ${ }^{13} \mathrm{C}$ depleted isotope values, led Humphrey and Ferring (1994) to conclude that the early Holocene was relatıvely cool, moist and humid. In contrast, slower rates of alluvial deposition and carbon isotope values more typical of $\mathrm{C}_{4}$ vegetation suggest a shift to climatic conditions that were relatively warm and dry during the middle Holocene, around 6000 to 4000 yr B.P. (Humphrey and Ferring, 1994; Nordt et al., 1994). This middle Holocene warming/drying trend appears concurrent with a Southern High Plains drought, identified by Holliday (1989), that occurred between ca. 6500 to 4000 yr B.P. Late Holocene conditions in the Southern Hıgh Plains are considered to be morst overall, with a minor dry event occurring ca. 2000 to 1000 yr B.P. Other studies report very
recent increases in $\mathrm{C}_{3}$ shrubby vegetation in Texas and Oklahoma over the past few hundreds of years (Boutton et al., 1998; Follett et al., 1997).

Studies utilizing pollen data, phytolith analysis, and mammalian faunas further support this Late Pleistocene to Holocene clımate/ecosystem history. Pollen, diatom data, and mammalian faunas show that the Late Pleistocene in Texas was cool, with increased winter precipitation supporting cool grassland vegetation, and exhibited different plant communities than those of the Holocene (Bousman, 1998; Bradbury, 1997; Hall and Valastro, 1995; Toomey et al., 1993). Pollen and phytolith analysis of sediments from north-central Texas suggest during the mid-Holocene increased andity which is characterized by warm season grasses and estimated temperatures that were $3^{\circ} \mathrm{C}$ higher and estimated mean annual precipitation that is 5 cm less than today (Fredlund $e t$ al., 1998; Bousman, 1998; Toomey et al., 1993). Extreme dry intervals in the midHolocene occurred ~ 6500 yr B.P. and 5000yr B.P. (Bousman, 1998). Phytolith analysis also supports the most recent increase in cool season grasses (Fredlund et al., 1998).

## VI. Methodology

## A. Field Work

Soil pits 2 to 3.5 m deep were dug by backhoe to reveal a soil topographic profile that contained both a microhigh and mucrolow for each of the three sites. Bulk soil samples were systematically collected in the field at 10 cm intervals through a microhigh and laterally adjacent microlow. Pedogenic carbonate was collected as part of the bulk soil samples with the exception of a few large nodules that were collected individually. Oriented samples for thin-section analysis were also collected from each soil horizon. Soll descriptions were made using standard field methods including characterization of horizons/subhorizons, soil color, soll texture, and soil structures with respect to soil depth (Soil Survey Staff, 1994). Soll descriptions were made by researchers from the USDANRCS, Baylor University, Texas A\&M University, and the University of Tennessee at Knoxville (Appendix 1).

## B. Laboratory Analysis

Soil samples were allowed to arr dry. Select samples from each horizon were coated in boat resin to ensure cohesiveness during thin section procedures. Soil samples were cut dry on a hand saw, epoxied to a glass slide, and dry ground on sand paper to $\sim 30 \mu \mathrm{~m}$ thickness. Thin sections were made of soll matrix as well as individual carbonate nodules, for microscopic analysis using transmutted light and cathodolummescence.

Stable isotopic analyses were conducted on both soll organic matter and pedogenic carbonate from each possible 10 cm interval. Carbonate material sampled was
representative of the different carbonate morphologies observed; pedogenic morphology is described in detail in a later section.

Pedogenic carbonate was extracted from the soil matrix using a binocular scope equipped with a dentist drill and pick. Carbonate samples were finely ground with a mortar and pestle and placed in a muffle oven and heated at $375^{\circ} \mathrm{C}$ for two hours in order to remove volatile organic matter. Samples were weighed and $\sim 6 \mathrm{mg}$ allquots were placed in a reaction vessel. Carbonate powder was reacted under vacuum with $100 \%$ $\mathrm{H}_{3} \mathrm{PO}_{4}$ at $25^{\circ} \mathrm{C}$ and the gas evolved was cryogencally purified following the method of McCrea (1950). Isotopic ratios were measured on a Finnigan-MAT DELTA plus mass spectrometer at the University of Tennessee and are reported in standard $\delta$-permil notation (Hoefs, 1980) relative to the Pee Dee Belemnite Standard (PDB) according to the expression:

$$
\delta^{13} \mathrm{C}(\%)=\left[\left(\mathrm{R}_{\text {sample }} / \mathrm{R}_{\text {standard }}\right)-1\right] \times 10^{3}
$$

where R is the ${ }^{13} \mathrm{C} /{ }^{12} \mathrm{C}$ ratio of sample or standard $\mathrm{CO}_{2}$, respectively. $\delta^{18} \mathrm{O}$ values are sımılarly reported relatıve to PDB. Analytical precision is $\pm 0.02 \%$ for carbon and $\pm 0.10 \%$ for oxygen.

Carbon 1sotope analysis of soil organic matter was also performed on bulk samples of soil matrix collected at 10 cm intervals. Macroscopic organic matter was handprcked from soil samples prior to analysis. Dried soil samples were crushed with a mortar and pestle and reacted with 1 NHCl to remove any inorganic carbonate (acid pretreatment has no effect on $\delta^{13} \mathrm{C}$ value of soil organic matter; Nordt et al., 1994). Once reaction was complete, samples were washed with deionized (DI) water, centrifuged, and excess water and acid decanted. The DI water wash and centrifuge process was repeated
until the soil samples obtained a pH of 5 to 6 . Washed samples were allowed to air dry and pulverized to a fine powder with a mortar and pestle. Soil samples ( $\sim 60$ to 200 mg sample to yield $\sim 0.1$ to 0.5 mg of C ) were loaded $\mathrm{in} \sim 20 \mathrm{~cm}$ long quartz tubes along with $\sim 600 \mathrm{mg}$ of $\mathrm{CuO}, 600 \mathrm{mg}$ of pure Cu metal beads, and a platınum wire. Quartz tubes were evacuated, sealed, and the samples were combusted in a muffle furnace at $850^{\circ} \mathrm{C}$ for 3 hours. $\mathrm{CO}_{2}$ gas was collected and cryogenically purified. The carbon isotopic composition of the organic matter was measured on a Finnigan-MAT DELTA plus mass spectrometer and reported in $\delta$-permil notation relative to PDB as described above.

## VII. Results and Discussion

## A. Pedogenic Carbonate Morphology and Isotopic Compositions

Pedogenic carbonate is common in the Lake Charles sorl profiles and exhibits a range of morphologies from soft, powdery, diffuse carbonate masses to hard, discrete nodules as large as 4 cm across (Figures 6, 7, 8). Soft carbonate masses are not abundant in the soil profiles and generally occur below 100 cm depth in Bss or Bkss soil horizons.

Hard nodules are the predomunant carbonate morphology in the Lake Charles series. Nodules occur at the following depths: in pedon 157 , microhigh $90-210 \mathrm{~cm}$ and microlow $90-190 \mathrm{~cm}$; in pedon 481 , microhigh $10-220 \mathrm{~cm}$ and microlow $110-220 \mathrm{~cm}$; and in pedon 201 , microhigh $10-218 \mathrm{~cm}$ and microlow $150-270 \mathrm{~cm}$ (Appendix 2). Hard nodules occur in two basic types: (1) red, ferric iron stained nodules 2 to 40 mm in diameter which likely incorporate remnant iron oxides from the soil matrix (Figure 9) and (2) unstained nodules of similar size having a gray calcite matrix (Figure 10). Abundant MnO dendrites occur in both types of nodules but are especially abundant in the gray matrix nodules. Detrital quartz and soil matrix fragments are incorporated into many of the hard nodules.

A few nodules are micrite, but the majority of both hard and soft nodules are microspar (individual crystals up to $40 \mu \mathrm{~m}$ across; Figure 10), suggesting that these nodules have undergone recrystallization from an original micrite precipitate. Under cathodoluminescence, nodules exhibit a dull luminescence with no zonation patterns, except a very small reaction rım around the nodules, which exhıbits a brighter luminesence. This suggests that the environmental conditions of precipitation did not significantly vary during crystallization or recrystallization.


Figure 6. This thin-section from Fort Bend Co. (157), microhigh pedon at the Ak2 horizon, shows soft carbonate disseminated through the soil matrix. Photomicrograph is in cross-nicols.


Figure 7. Soft carbonate masses are the second of two main morphologies of pedogenic carbonate which occur in the Lake Charles Vertisols. These soft masses have a diffusive boundary into the soil matrix. This soft carbonate mass is from the Ft. Bend County (157) microhigh pedon from the Bkss3 horizon at -95 to -129 cm depth. The scale bar at the bottom is divided into centimeter sections.


Figure 8. Hard discrete nodules are one of the two main morphologies of pedogenic carbonate which occur in the Lake Charles Vertisols. These hard nodules have a discrete boundary with the soil matrix. This nodule is from the Ft. Bend County (157) microhigh profile Bkss4 horizon at -129 to -144 cm depth. The scale bar on the right is divided into centimeter sections.


Figure 9. Photomicrograph in cross-nicols of thin-section of a hard $\mathrm{Fe}^{+3}$ stained nodule from the Lake Charles, Ft. Bend (157) site. This nodule is from the Bkss2 horizon of the microhigh and shows iron staining around the exposed surfaces of the nodule.


Figure 10. Photomicrograph in cross-nicols of a gray matrix hard nodule (which appears yellow) from the Lake Charles, Fort Bend county (157) site. This nodule is from the Bkss2 horizon of the microhigh. The coarse carbonate fabric of the nodule reveals recrystallization.

The carbon isotope compositions of both hard and soft carbonate ( $\delta^{13} \mathrm{C}=-11.02$ to $-1.36 \%$ ) (Figures $11,12,13$ ) are significantly different from modern marine carbonate ( $+1 \%$; Hoefs, 1980). The relatively low $\delta^{13} \mathrm{C}$ values reflect the variable input of isotopically light, soll $\mathrm{CO}_{2}$ and, thus, constrains therr pedogenic orgin.

Oxygen isotope values (Figure 14) of most of the pedogenic carbonate fall within the range of modern meteoric waters for Texas: $-2.72 \%$ (Humphrey and Ferring, 1994) and $-3.6 \%$ (IAEA at Waco, TX). The majority of hard nodules have a microspar matrix suggesting recrystallization during pedogenesis. Soft carbonate masses are especially sensitive to recrystallization due to their relatively large surface area. Soft masses show a consistent and narrow range of consistent $\delta^{18} \mathrm{O}$ values (mean $\sim-3.5 \% \mathrm{PDB}$ ). In the Wharton County (481) mucrolow profile (Flgure 13) some hard nodules occurring at lower depths in the profile have significantly more negative $\delta^{18} \mathrm{O}$ values (i.e., $-120 \mathrm{~cm}=$ $-5.0 \%$; and $-200 \mathrm{~cm}=-4.5 \%$ ). Low oxygen isotope values are also observed at depth in the Fort Bend County (157) microhigh pedon (i.e., $-150 \mathrm{~cm}=-6.0 \%$; $-190 \mathrm{~cm}=-5.3 \%$; and $-200 \mathrm{~cm}=-5.5 \%$ ). These values may be more representative of original pedogenic oxygen isotopic compositions (Figure 14). Throughout the Harris County (201) pedons, the oxygen isotope compositions are unform. As the wettest of the sites ( 122 cm MAP), the greatest influxes of meteoric water are expected through the system, increasing the likelihood of recrystallization and exchange.

Isotopic compositions were determined for coexisting hard nodules and bulk matrix carbonate (i.e., soft carbonate) from depths of -100 to -220 cm in the 481 microhigh pedon (Table 2). If the carbonate nodules are derived from, or form at the same time as disseminated matrix carbonate, then the two should have sumilar 1sotopic


Figure 11. Plot of $\delta{ }^{13} \mathrm{C}$ versus depth for both SOM and pedogenic carbonate for microhigh and microlow profiles of Harris Co. (201), showing climate/ecosystem changes with horizonation.

157 MH


Figure 12. Plots for $\delta^{13} \mathrm{C}$ for both SOM and pedogenic carbonate for microhigh and microlow pedons at Fort Bend Co. (157), showing climate/ecosystem trends with soil horizonation.


Figure 13. Plots of $\delta{ }^{13} \mathrm{C}$ versus depth for both SOM and pedogenic carbonate for microhigh and microlow of Wharton County (481) show separate climate/ecosystem changes with horizonation.

Microhigh
$\mathrm{Fe}^{+3}$ hicrolow
nodule

| gray matrix |
| :--- |
| hard nodule |


| soft $\mathrm{CO}_{3}$ |
| :--- |


| masses |
| :--- |



Microhigh | Microlow |
| :--- |
| $\mathrm{Fe}^{+3}$ hard |
| nodule |

Figure 14. Oxygen isotopic signatures of the pedogenic carbonates from the Lake Charles soils. The majority of oxygen has been reset isotopically to modern values denoted by the yellow lines. (-2.7 o/oo PDB Humphrey and Ferring, 1994; -3.5 0/00 PDB IAEA Waco, TX).

Table 2. Disseminated carbonate matrix from 481 microhigh compared with coexisting hard nodules

| Soil Depth (cm) | Sample- <br> Matrix | Hard Nodule |  | Type |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\delta^{13} \mathrm{C}$ | $\delta^{18} \mathrm{O}$ | $\delta^{13} \mathrm{C}$ | $\delta^{18} \mathrm{O}$ |  |
| -100 | -4.18 | -3.35 | -3.8 | -2.48 | B |
| -140 | -4.75 | -3.46 | -4.56 | -2.85 | A |
| -160 | -4.28 | -3.05 | -5.54 | -3 | A |
| -180 | -4.01 | -3.13 | -8.99 | -2.844 | A |
| -220 | -3.16 | -3.17 | -10.37 | -3.47 | A |

Type $A=\mathrm{Fe}^{+2}$ stained nodule
Type $B=$ gray matrix
sıgnatures. Diffuse carbonate has relatively constant $\delta^{18} \mathrm{O}(-3.1$ to $-3.5 \%)$ and $\delta^{13} \mathrm{C}(-3.2$ to $-4.8 \%$ ) values. By comparison, hard nodules have a significantly wider range of $\delta^{13} \mathrm{C}$ values $(-38$ to $-10.4 \%)$ and consistent but different, $\delta^{18} \mathrm{O}$ values $(-2.5$ to $-3.5 \%)$. The greatest discrepancy between the isotopic compositions of matrix carbonate and coexistung hard nodules occurs at the base of the profile. This might be explained if the nodules analyzed at a particular depth have experienced episodic accretion through their formation. In this scenario, the isotopic signatures of nodules reflect time-averaged conditions of the soil temperature and soll solutions. Because of its greater surface area, matrix carbonate is likely to be recrystallized relatıve to hard nodules and reflect more recent soil conditions.

The ongin of diverse pedogenic carbonate morphologies, including hard nodules, disseminated carbonate, and soft carbonate masses, is not well understood. Numerous parageneses can be argued, on the basis of petrography, including (1) continual dissolution and reprecipitation of disseminated or soft carbonate, (2) preciptation and accretion of soft carbonate to form hard nodules, (3) dissolution of hard nodules to soft masses, and (4) carbonate coalescence and mechanical fracturing (c.f., Mermut and Dasog, 1986; Drees and Wilding, 1987). Most mportant, however, is that the results of these previous studies, as well as the petrographic and isotopic results of this study, indicate that all forms are pedogenic in orngin. In most samples examined for this study, the carbonate morphologies are isotopically indstinguishable. The few exceptions (i.e., the few carbonates with distinct oxygen isotope compositions) provide insıght into the complex, long term pedogenic record.

## B. An Isotopic Proxy Record of Climate and Ecosystem

Stable isotopes of soil carbonate and soil organic matter have been utılized in various studies to assess climate and ecosystem changes (i.e. Cerling, 1984, 1991; Salomons and Mook, 1986; Nordt, 1992; Humphrey and Ferring, 1994; Mora et al., 1996; Boutton et al., 1998; Mora and Driese, 1999). These studies infer climate and ecosystem changes, trends, or relative proportions of $C_{3}$ and $C_{4}$ vegetation contributing to the soil biomass either directly, by measuring soil organic matter, or indurectly, by analysis of pedogenic carbonate. Oxygen isotope compositions, where preserved, reflect temperature and ariduty conditions.

Determinıng the absolute age of climate/ecosystem changes can be challenging. Measured ${ }^{14} \mathrm{C}$ ages of bulk soil organic matter are always younger than true ages of soils due to continuous input of organic matter into soils and can be affected by soil carbon dynamics (Wang et al., 1996a). Allphatic hydrocarbons chemically extracted and analyzed by accelerator mass spectrometry, appear to preserve the most accurate ${ }^{14} \mathrm{C}$ ages due to their low biodegradability (Huang, et al. 1999). Radiocarbon age dating of soil carbonate requires constraints on production/diffusion behavior of soil ${ }^{14} \mathrm{CO}_{2}$ (Amundson et al., 1998) and the relative proportion of carbon in soil $\mathrm{CO}_{2(\mathrm{~g})}$ originating from: (1) respiration from living plant roots, and (2) microbial respiration from the decay of soil humus (Wang et al.1996a; Amundson et al., 1994). As pedogenic nodules accumulate, younger ${ }^{14} \mathrm{C}$ is incorporated into the nodule, resulting in younger outer carbonate coatings surrounding older ${ }^{14} \mathrm{C}$ carbonate in the center of the nodule (Amundson, et al., 1994). Cultivation and logging disturb the $C$ pools and can affect the ${ }^{14} \mathrm{C}$ ages, particularly at shallow depths (Wang et al., 1999).

Despite these challenges, recent ${ }^{14} \mathrm{C}$ studies of Texan soils indicate a gross equivalence of time and depth in the soils (i.e., age of soil carbon increases with depth) (Nordt, 1992; Humphrey and Ferring, 1994; Boutton et al., 1998). For the purpose of this study, we infer a similar age-depth relationship. As will be demonstrated below, the coherence of the isotopic record across three different sites, and in comparison with those nearby soil/climate records, indicate that this is a reasonable assumption.

Isotopic profiles through Vertisol microhighs and microlows at each site are shown in Figures 11-13. Similar patterns are observed in $\delta^{13} \mathrm{C}$ values of soil organic matter and pedogenic carbonate in all three sites. From the bottom of the profiles, $\sim 300 \mathrm{~cm}$ to $\sim 180 \mathrm{~cm}$ depth in the microlow and to $\sim 160 \mathrm{~cm}$ in the microhigh, relatively low $\delta^{13} \mathrm{C}$ values are noted ( $\sim-19$ to $-28 \%$ SOM; $\sim-11$ to $-6 \%$ o pedogenic carbonate). Above this, there is a transition to more enriched isotopic values ( $\sim-13$ to $-20 \%$ o SOM; $\sim-2$ to $-5 \%$ pedogenic carbonate). The top 20 to 50 cm of most of the pedons show a decrease in $\delta^{13} \mathrm{C}$ values of soil organic matter to $\sim-17$ to $-22 \%$ SOM; no similar inflection is seen at the top of the profiles in pedogenic carbonate compositions.

The relative proportions of $C_{3}$ versus $C_{4}$ vegetation can be calculated from soil organic matter $\delta^{13} \mathrm{C}$ values (Figure 15) and a likely clımate history can be inferred. The bases of the profiles indicate predominantly $\mathrm{C}_{3}$-type vegetation expressing cooler/wetter climate conditions typical of the Late Pleistocene (Figure 15) (Gardner, 1984; Humphrey and Ferring, 1994, Nordt et al., 1998). The middle of the isotopic profiles indicate a change from $\mathrm{C}_{3}$ - dominated cooler/wetter clımate typical of the Late Pleistocene/early Holocene condations to $\mathrm{C}_{4}$-dominated warmer/drier conditions characteristic of the middle Holocene. Towards the top of the soil profiles ( $>70 \mathrm{~cm}$ in the microhigh; $>50 \mathrm{~cm}$ in

\%C3 vegetation

Figure 15. Soil ecology as \%C3-type vegetation for all 6 Lake Charles pedons. The data suggests that the Late Pleistocene was mostly $\mathrm{C}_{3}$ with a dramatic increase in $\mathrm{C}_{4}$ vegetation in the mid-Holocene. The modern trend of vegetation toward greater $\mathrm{C}_{3}$ grasses is observed in the very top portions of the profiles. Values greater than $100 \%$ are obtained due to some $\mathrm{C}_{3}$ vegetation having a signature lighter than -26 o/00 (PDB). \%C3 is calculated by: $X(-26)+(1-X)(-12)=\delta^{13} \mathrm{C}$ of soil organic matter where $X$ is the proportion of $\mathrm{C}_{3}$-vegetation (i.e. $\mathrm{C}_{3} / \mathrm{C}_{3}+\mathrm{C}_{4}$ ).
the microlow), soil organic matter shifts again to more negative compositions, from a $>85 \% \mathrm{C}_{4}$-dominated ecosystem to a $40-60 \% \mathrm{C}_{3}$-dominated ecosystem through the late Holocene (Figure 15), consistent with a cooler/wetter late Holocene climate. Thus, all three Lake Charles senes sites record a similar climate/ecosystem history that is consistent with conditions inferred in other types of soils in central and south Texas (1.e., Nordt, 1992; Humphrey and Ferring, 1994). The history is recorded in both the microhigh and microlow postions, although isotopic inflections occur at different depths in these microtopographic positions.

## C. Concordance of Soil Organic Matter and Pedogenic Carbonate Record

In the Lake Charles series, the difference in isotopic composition ( $\Delta$ ) between pedogenic carbonates and soil organic matter varies significantly between and within each site (Figure 16). Assuming equilibrium isotopic fractionation between soil $\mathrm{CO}_{2}$ and calcite at soil temperatures between 0 and $25^{\circ} \mathrm{C}$ and a steady state $\mathrm{CO}_{2}$ diffusional fractionation of $4.4 \%$, pedogenic carbonates precipitated should be $\sim 14 \%$ o $\left(25^{\circ} \mathrm{C}\right)$ to $17 \%\left(0^{\circ} \mathrm{C}\right)$ enriched in ${ }^{13} \mathrm{C}$ relatıve to coexistıng soil organic matter (Figure 5) (Deines et al., 1974; Cerling et al., 1989). At the Fort Bend County site (157), $\Delta_{\text {ped }}$ Co3-org in the mucrohigh is 7.70 to $17.05 \%$, with the majority of samples showing $\sim 12 \%$ difference (Figure 16). A tighter range is measured in the microlow, from 9.86 to $12.94 \%$, with the majority $\sim 11.5-12 \%$. At the Wharton County site (481), $\Delta_{\text {ped CO3-org }}$ is 13.14 to $23.78 \%$, with most values 17.5 to $18 \%$ (Figure 16) in the microhigh and markedly variable $\Delta_{\text {ped CO3-org }}$ values in the microlow ( $\Delta=9.01$ to $19.89 \%$, most 11-12\%). The isotopic fractionation is greatest at the Harris County site (201) with microhigh values of 13.87 to


Figure 16. $\triangle$ pedogenic $\mathrm{CO}_{3}$-organic matter show that the majority of values do not fall within the14-16 o/oo expected if soil carbonate precipitated in equilibrium with SOM found at the same depth in the porfile. The lack of correlation suggests that the solution precipitating carbonate derived a portion of its carbon from elsewhere in the soil profile. This discrepency suggests that soil organic matter and soil carbonate at the same depth are not contemporaneous.
$24.15 \%$ (most $14-16 \%$ ); the larger values occur towards the bottom of the profile (Figure 16). The few data measured in the adjacent microlow suggests $\Delta=11.91$ to $23.35 \%$.

The wide range of $\Delta_{\text {ped CO3-org }}$ values is not well understood but likely reflects different sources of carbon in soil $\mathrm{CO}_{2}$ and soil solutions and possibly the impact of seasonal fluctuations in soil respiration rates or soil hydrology. The wide range of $\Delta_{\text {ped CO3-org }}$ values suggests that soil organic matter and pedogenic carbonate are not quite contemporaneous, but, rather, soil organic matter reflects a more recent signature (Wang et al., 1996a). This is not surprising, given the relatively rapid rate of soil carbon turnover ( $10^{1}$ to $10^{2} \mathrm{yr}$ ) and its impact on soil $\mathrm{CO}_{2}$ composition compared to the much slower rate at which pedogenic carbonate is precipitated ( $10^{2}$ to $10^{3} \mathrm{yr}$ ) (Wang et al., 1996b; Amundson et al., 1994; Cerling, 1991).

## D. Organic Preservation Potential for Paleoclimate Analysis

Soil organic matter preserves the most coherent and complete climate/ecosystem record in these Vertisols. What is the preservation potential of the organic compounds for surviving to the rock record? In Vertisols, most organic matter is found in the claysize fraction (Leınweber, 1999; Skjemstad and Dalal, 1987; Skjemstad et al., 1986). Organic matter stability is greatly enhanced by strong organic-mineral bonds to swelling clays (Coulombe et al., 1996a). Also, in two separate studies (Arai et al., 1996; Gehring et al., 1997), ${ }^{13} \mathrm{C}$-NMR spectra on humic extracts from solls revealed a predominance of aromatic carbon molecules as well as alkyl carbon molecules, both of which have good preservation potential. These organic compounds have low extractability from Vertisols due to the large surface area of clays and, therefore, may have good preservation potential
for the geologic record (Leinweber, 1999). In addition, these Vertisols are basic soils, and organic carbon exhibits low extractability (7-30\%) in alkalıne solutions (Arai et al., 1996; Ristori et al., 1992; Gehring, et al., 1997). Therefore, organic carbon holds good preservation potential for studies of paleo-climate/ecosystem in paleoVertisols, provided that the depths of burial are moderate.

## E. Constraints on Vertisol Pedogenic Processes

Several previous models of Vertisol mechanics have portrayed these soils as "self-mulching" soils (i.e., Buol et al., 1980; Knight, 1980; Duchaufour, 1983) in which material is continually re-mixed and homogenized by mechanical processes. In contrast, the coherent isotopic profiles revealed in the microlow and microhigh of the Lake Charles series Vertisols demonstrate that these soils are not chaotic, pedoturbated mixtures. The chimneys of the microhighs do not serve as wholesale mixing pipes resultung from mechanical translocations. Results of this study support earlier work (i.e. Coulombe et al., 1996b; Wilding and Tessier, 1988; Yaalon and Kalmar, 1978) that suggests that horizonation can be preserved in Vertisols.

Despite the gross smilarity of isotopic trends in the Vertisol microhigh and microlow, some differences persist. In general, isotopic inflections occur at slightly higher soil levels in the microhigh compared to the corresponding microlow (Figure 11, 12, 13). For example, in the Fort Bend County (157) profile, inflection of soil organic matter $\delta^{13} \mathrm{C}$ values is observed at $\sim 80 \mathrm{~cm}$ depth in the microhigh and at $\sim 90 \mathrm{~cm}$ depth in the microlow. Apparent climate shifts appear to coincide with soil horizonation. Climate/ecosystem isotopic inflections interpreted to reflect a change from warmer/drier
conditions towards cooler/wetter conditions occurs within the pedological boundary Bkss1 and/or Bkss2 in both microhigh and mucrolow profiles (Figures 11, 12, 13). These observations suggest not only that clımate exerts a strong control on Vertisol formation, but also that the microhigh and microlow environments are systematically related.

The difference in depth to the Bkss1 honzon between the microhigh and microlow of each pedon increases as the mean annual precipitation (MAP; cm/yr) increases (Figure 17). The depth difference between the occurrence of the Bkss1 of the microhugh and mucrolow at site 201 soll is 141 cm (MAP $122 \mathrm{~cm} / \mathrm{yr}$ ); site 157 soil is 114 cm (MAP $114 \mathrm{~cm} / \mathrm{yr}$ ); site 481 soil is 107 cm (MAP $104 \mathrm{~cm} / \mathrm{yr}$ ). The wettest soll (201) shows the greatest difference between sımilar horizons in adjacent microhigh and microlow environments. This phenomenon suggests climatic control on soil microtoography. It also suggests a direct correlation between depth to pedogenic carbonate precipitation and mean annual precipıtation (MAP), a correlation that has been championed in recent literature (Retallack, 1994).

Comparison of the ecosystem changes inferred from carbon isotopes (Figure 15) across the study sites reveals several systematic results. The present relative precipitation relationship among the three sites (Table 1) appears to have remaned consistent throughout the accumulation of these soils. The presently wettest site, 201, records the greatest proportion of $\mathrm{C}_{3}$ vegetation throughout the profile suggesting it has consistently been wettest over the past 35,000 years. For example, in site 201 mid-profile ( $\sim-80$ to -175 cm ) interpreted to record the warmest/driest period during Vertisol formation, the inferred ecosystem was $60-70 \% \mathrm{C}_{3}$ vegetation. At the other sites, the proportion at the same depth/time was at most $15-25 \% \mathrm{C}_{3}$ vegetation. Sites with greater moisture stress


Figure 17. Depth variation between the microhigh and microlow
occurrence of the Bkss1 horizon across the precipitation gradient.
(i.e., 157) show the greatest proportion of $\mathrm{C}_{4}$ throughout the profile as well as more abrupt shifts from a $\mathrm{C}_{3}$-dominated ecosystem in the base of the profiles to a $\mathrm{C}_{4}$-dominated ecosystem at mid-profile, compared to the wetter site 201 (Figure 15). The inferred soil ecosystem appears not only influenced by precipitation but microtopography as well.

Site 481 shows the greatest difference in vegetation type between microhigh and mucrolow environments. For example, at -130 cm depth in the microlow, site 481 , records a $\sim 25 \% \mathrm{C}_{3}$ environment. The adjacent microhigh shows a $\sim 70 \% \mathrm{C}_{3}$ ecosystem at this same depth. This observation seems counter-intutuve to the general observation that wetter microenvironments (i.e., ponding of water) occurs in Vertisol mirolows. Only site 481 shows a large discrepancy between the microlow and microhigh vegetation. A possible explanation is that site 481 , as the driest site, may be less affected by ponding or experienced more extensive soil cracking which allowed greater infiltration of water along fracture flow paths.

Several recent studies of Texas Vertisol chemistry indicate significant differences in the moisture content, shrinkage and exchangeable bases/cations chemistry in gilgai mucrohighs and mucrolows (Wilding et al., 1991; Driese et al., 2000). Unlike these geochemical trends, however, most isotopic profiles of the Lake Charles series do not record the significantly different histories. Soil organic matter and pedogenic carbonate may be more resilient to the changes induced by the sorl water fluxes or Eh changes compared to soluble soil cations and redox-sensitive trace elements. The rate of fluid flow can be quite rapid in Vertisols (Bouma and Loveday, 1988; Coen and Wang, 1989; Lin et al., 1997). Slickensides, cracks, and matrix macropores act as major transport ártenes for mass, water, and soluble species through these Vertisols; fluid movement by-
passes most of the soil clay matrix (Bouma and Wosten, 1979; Lin et al., 1996, 1998). Much of the soil water may simply miss the carbonates.

Accretionary growth of large carbonate nodules also has implications concerning Vertisol formation. Two large carbonate nodules were taken from the microhigh of the 481 series (Fort Bend County) at 140 cm ( 4 cm diameter) and one from $180 \mathrm{~cm}(2.7 \mathrm{~cm}$ diameter) depth. Despite the lack of zonation under cathodoluminescence, these hard nodules appear in isotopic analysis to show an accretionary growth pattern similar to concentric rings. Each nodule was dissected and carbonate samples were drilled and taken every 5 mm across the interior of the nodule. Both nodules show isotopic zonation, with ${ }^{13} \mathrm{C}$-enriched compositions in the nodule center and progressively lighter signatures somewhat concentrically out from the center (Figure 18 and 19); the total variation in each nodule is $\sim-3 \%$ (PDB). By comparison, $\delta^{18} \mathrm{O}$ values do not vary showing values of $-3.9 \pm 1 \%$ (PDB) in the nodule from 140 cm depth and $-3.0 \pm 0.5 \%$ (PDB) in the 180 cm depth nodule.

The progression of heavier isotopes toward the centers of the nodules can be explained in a number of ways. One possibility is that the carbonate nodule has remaned at the same depth throughout the duration of its growth, and the soil environment at that depth has changed over time precipitating $\delta^{13} \mathrm{C}$ values representative of the changing environment. Another possibility is that the nodule has moved upward in the soil profile and, therefore, accreted different $\delta^{13} \mathrm{C}$ values as it has moved through changing soil environments. If this is the case, then the nodule may be traced downward in the microhigh to its possible origin. Figure 20 depicts a possible scenario for the origin of the nodule at $\sim 180 \mathrm{~cm}$, moved to its present depth of 140 cm . Accretionary growth pattern


Figure 18. Microsample isotopic transect across 4 cm diameter hard nodule from 481 microhigh pedon at 140 cm . The carbon isotopes suggest that this nodule has an accretionary growth pattern representing several climate/ecosytem changes. The oxygen isotopes do not show a variation expected from several climate/ecosystem changes but instead show a pattern suggesting these values_were reset to $-4+0.5 \mathrm{o} / 00$, with the exception of one analysis.


Figure 19. Microsample isotopic transect across hard nodule from 481 microhigh at 180 cm depth. The $\delta{ }^{13} \mathrm{C}$ values suggest that this nodule has existed in different climate/ecosystem environments.

## 481 Microhigh



Figure 20. Carbon isotope compositions of the core (open crossed symbol) and rim (closed cross symbol) of a large nodule from 140 cm depth in the microhigh of site 481 . The center of the nodule ( $\delta^{13} \mathrm{C}=-1.50 / 00$ ) closely matches other nodules found at 180 cm depth. The edge of the nodule ( -4.1 $0 / 00$ ) matches other nodules found at 140 cm . It is hypothesized that the large, zoned nodule originated at a depth of $\sim 180 \mathrm{~cm}$ and moved to its present depth of 140 cm , accreting isotopically distinct material as it rose.
of the hard carbonate nodules compounds implications for using pedogenic carbonates for paleoclimate/paleoecology reconstruction. Larger nodules ( $>10 \mathrm{~mm}$ diameter) will likely preserve a mıxed "tıme- averaged" composition that is petrographically cryptic. Small pedogenic carbonate nodules ( $<10 \mathrm{~mm}$ diameter) should be used in these analyses in efforts to avoid "averaged" carbonate sıgnatures at a particular depth.

## VIII. Conclusion

All three sites investigated in the Lake Charles series contained soil organic matter as well as pedogenic hard nodules and soft carbonate, which showed similar and systematic inflections with depth. If increasing soil depth is consistent with increasing age in $\delta^{13} \mathrm{C}$ values, as indicated by other studies of central and eastern Texas, then the stable carbon isotopes of pedogenic carbonate and soil organic matter appear to preserve a climate/ecosystem record. Systematic isotopic inflections suggest climate/ecosystem change from cooler/wetter conditions at the base of the profiles, to warmer/drier conditions at mid-profile, and then shiftıng back to a historical cooler/wetter ecosystem at the top of the profiles. This interpretation is consistent with other age-dated Texas soils. Although both soil organic matter and pedogenic carbonate show similar climate/ecosystem shifts, soil organic matter preserves the most coherent and complete record. Lack of isotopic equilibrium between coexisting soil organic matter and pedogenic carbonate suggests that the two carbon pools are not exactly contemporaneous, especially at the top of the profiles in the most recent soil accumulations. Still, the two pools record a significantly simular record of climate/ecosystem change. Horizonation appears to be sensitive to climate as observed in the depth to the Bkss1 horizon in the microhigh and the microlow as well as changes in depth of the Bkss1 horizon between consecutive microhigh and microlow environments. Finally, the similar and apparently coherent records of soll organic matter and pedogenic carbonate preserved in all three Lake Charles sites does not support the "self-mulching" concept for these Vertisols.

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## Appendices

Appendix 1: Soıl Profile Descriptions
Fort Bend County- 157 Microhigh
Sample Date: 6/22/99
Soll Series: Lake Charles
Site Identification \#: 99TX157001A (microhigh)
Described by: Wes Miller and Larry Wilding
Recorded by: Mary Dunn
Location Information
Soil Survey Area Name: Fort Bend CO.
Classification: Fine, smectitic, hyperthermic Typic Hapludert
Ak1--0 to 10 cm ; very dark gray (10YR 3/1) clay; weak fine granular structure; firm; many fine roots; common fine and few medium interstitial pores; common medium rounded white ( $2.5 \mathrm{Y} 8 / 1$ ) nodules of calcium carbonate and few calcium carbonate nodules are coated with yellowish brown (10YR 5/6) iron; clear smooth boundary.

Ak2--10 to 28 cm ; very dark gray (10YR 3/1) clay; weak medium subangular blocky structure parting to moderate fine and medium granular; firm; common fine roots; few fine interstitial and few fine tubular pores; common fine and medium rounded white ( $2.5 \mathrm{Y} 8 / 1$ ) nodules of calcuum carbonate and few calcium carbonate nodules are coated with yellowish brown (10YR 5/6) iron; slightly effervescent; clear wavy boundary.

Bkss1--28 to 70 cm ; dark gray (10YR 4/1) clay; moderate fine and medium angular blocky structure; firm; common fine roots; few fine tubular pores; common distinct intersecting slickensides that are tilted 55 to 60 degrees to the horizontal; common fine and medium rounded white ( $10 \mathrm{YR} 8 / 1$ ) nodules of calcium carbonate and few calcium carbonate nodules are coated with yellowish brown (10YR 5/6) iron; slightly effervescent; clear smooth boundary.

Bkss2--70 to 95 cm ; dark grayish brown (2.5Y 4/2) clay; moderate fine and medium angular blocky structure; firm; common fine roots; few fine tubular pores; common intersecting slickensides that are tilted 40 to 50 degrees to the horizontal; few distinct pressure surfaces; common fine and medium white (10YR 8/1) nodules of calcium carbonate; 5 percent fine and medium yellowish brown (10YR 5/6) masses of iron with sharp boundaries; slightly effervescent; gradual wavy boundary.

Bkss3--95 to 129 cm ; dark grayish brown (2.5Y 4/2) clay; moderate fine and medium angular blocky structure; firm; common fine roots; few fine tubular pores; common intersectung slickensides that are tilted 40 to 50 degrees to the horizontal; few distinct pressure surfaces; common fine and medium white (10YR 8/1) nodules of calcium
carbonate; 5 percent fine and medium yellowish brown (10YR 5/6) masses of iron with sharp boundaries; slightly effervescent; gradual wavy boundary.

Bkss4--129 to 144 cm ; 60 percent olive brown ( $2.5 \mathrm{Y} 4 / 3$ ), 20 percent dark gray (10YR $4 / 1$ ), 20 percent yellowish brown (10YR 5/6) clay; strong medium and coarse angular blocky structure; very firm; common fine roots; common intersecting slickensides that are tilted 35 to 45 degrees to the horizontal; dark gray (10YR 4/1) matrix material are filled cracks 5 mm to 2.5 cm wide mixed within the olive brown ( $2.5 \mathrm{Y} 4 / 3$ ) matrix material; yellowish brown (10YR 5/6) matrix material is an oval mass about 10 cm wide and 8 cm thick and is bounded by the olive brown ( $2.5 \mathrm{Y} 4 / 3$ ) material; common fine to coarse rounded light brownish gray (10YR 6/2) and whrte (10YR 8/1) nodules of calcium carbonate; slightly effervescent; clear wavy boundary.

Bkss5-144 to 176 cm ; dark yellowish brown (10YR 4/4), dark gray (10YR 4/1), strong brown (7.5YR 5/8) clay; strong medium and coarse angular blocky structure; very firm; common fine roots; common intersecting slickensides that are tilted 30 to 40 degrees to the horizontal; dark gray (10YR 4/1) matrix material are filled cracks 5 mm to 2 cm wide throughout the honzon; strong brown (7.5YR 5/8) matrix material dominates the lower 5 cm of the horizon; common fine to coarse rounded light brownish gray (10YR 6/2) and white (10YR 8/1) nodules and masses of calcium carbonate that are concentrated near the contact with the Bss1 horizon; strongly effervescent; clear wavy boundary.

Bss1-176 to 210 cm ; strong brown (7.5YR 4/6) clay; moderate medium and coarse angular blocky structure; very firm; common fine roots; common distinct intersecting slickensides that are tilted 30 to 40 degrees to the horizontal; 6 percent fine and medium prominent greenish gray ( $5 \mathrm{G} 6 / 1$ ) iron depletions with clear boundaries on surfaces of slickensides and on root pore linings; few fine rounded white (10YR 8/1) nodules of calcuum carbonate; strongly effervescent; gradual wavy boundary.

Bss2--210 to 240 cm ; yellowish red (5YR 4/6) clay; moderate medium and coarse angular blocky structure; extremely firm; common fine roots; many prominent intersectung slickensides that are tilted 20 to 30 degrees to the horizontal; 8 percent fine prominent light greensh gray (5GY 7/1) iron depletions with clear boundaries on surfaces of slickensides; few fine dendritic black (10YR 2/1) masses of iron-manganese on surfaces of slickensides within the light greenish gray (5GY 7/1) iron depletions; strongly effervescent gradual wavy boundary.

## Fort Bend County- 157 Microlow

Sample Date: 6/22/99
Soil Series: Lake Charles
Site Identification \#: 99TX157001 (Microlow)
Location Information
Soil Survey Area Name: Fort Bend CO.

# Described by: Edward Griffin and Jon Wiedenfeld 

Classification: Fine, smectitic, hyperthermic Typic Hapludert

A1--0 to 10 cm ; black ( $2.5 \mathrm{Y} 2 / 1$ ) clay; moderate fine and medum subangular blocky structure parting to moderate medium granular; very hard, very firm, moderate, very sticky and very plastic; common very fine and fine roots; common fine interstitial pores; few faint pressure surfaces; abrupt smooth boundary.

A2--10 to 29 cm ; black ( $2.5 \mathrm{Y} 2 / 1$ ) clay; moderate fine and medium subangular blocky structure; very hard, very firm, very sticky and very plastic; common fine and medium roots; common fine tubular pores; common distinct pressure surfaces; clear smooth boundary.

Bss1--29 to 61 cm ; black ( $2.5 \mathrm{Y} 2 / 1$ ) clay; weak medium wedge-shaped structure parting to moderate medium subangular blocky; very hard, very firm, very sticky and very plastic; common fine roots; common fine tubular pores; common distinct intersecting slickensides that are tilted at 50 to 65 degrees to the horizontal; clear wavy boundary.

Bss2--61 to 103 cm ; very dark gray ( $2.5 \mathrm{Y} 3 / 1$ ) clay; strong medium and coarse wedgeshaped structure parting to moderate medium angular blocky; very hard, very firm, very sticky and very plastic; common fine roots; common fine tubular pores; very few crayfish krotovina filled with yellowish red (5YR $5 / 6$ ) and very dark gray ( $2.5 \mathrm{Y} 3 / 1$ ) clay; many prominent intersecting slickensides that are tilted 30 to 40 degrees to the horizontal; very slightly effervescent; gradual wavy boundary.

Bss3--103 to 135 cm ; very dark gray ( $2.5 \mathrm{Y} 3 / 1$ ) clay; strong medium and coarse wedgeshaped structure parting to moderate medium angular blocky; very hard, very firm, very sticky and very plastic; common fine roots; very few crayfish krotovina filled with yellowish red (5YR 5/6) and very dark gray ( $2.5 \mathrm{Y} 3 / 1$ ) clay; many prominent intersecting slickensides that are tilted at 45 to 60 degrees to the horizontal; few fine black (10YR $2 / 1$ ) nodules of iron-manganese; very slightly effervescent; gradual wavy boundary.

Bkss1--135 to 158 cm ; dark gray ( $2.5 \mathrm{Y} 4 / 1$ ) clay; moderate medium and coarse wedgeshaped structure parting to moderate medium and coarse angular blocky; very hard, very firm, very sticky and very plastic; common very fine and fine roots; very few crayfish krotovina filled with yellowish red (5YR 5/6) and very dark gray ( $2.5 \mathrm{Y} 3 / 1$ ) clay; common prominent intersecting slickensides that are tilted 35 to 45 degrees to the horizontal; 1 percent fine uncoated nodules of calcium carbonate; 2 percent nodules of calcium carbonate coated with strong brown (7.5YR 5/6) iron; very slightly effervescent; gradual wavy boundary.

Bkss2-158 to 175 cm ; 60 percent gray ( $2.5 \mathrm{Y} 5 / 1$ ), 20 percent light olive brown ( 2.5 Y $5 / 3$ ), 20 percent light yellowish brown ( $2.5 \mathrm{Y} 6 / 3$ ) clay; weak coarse wedge-shaped structure parting to moderate medium and coarse angular blocky; very hard, very firm,
very sticky and very plastic; common very fine and fine roots; common prominent intersecting slickensides that are tilted at 30 to 45 degrees to the horizontal; 3 percent fine and medium nodules of calcium carbonate coated with brown (10YR 4/3) iron; 2 percent uncoated nodules of calcium carbonate; strongly effervescent; gradual smooth boundary.

Bkss3--175 to 193 cm ; yellowish red (5YR 5/6) clay; moderate coarse prismatic structure parting to moderate medium and coarse subangular blocky; extremely hard, extremely firm, very sticky and very plastic; common very fine and fine roots; 5 percent crayfish krotovinas filled with yellowish red (5YR 5/6) and very dark gray (10YR 3/1) clay and few fine nodules of calcium carbonate; common distinct intersecting slickensides that are tilted at 35 to 40 degrees to the horizontal on horizontal faces of peds; 1 percent fine prominent light greenish gray ( 5 GY 7/1) iron depletions with clear boundaries on surfaces of slickensides; strongly effervescent; clear wavy boundary.

B'ss1--193 to 216 cm ; yellowish red (5YR 5/6) clay; weak coarse wedge-shaped structure parting to weak medium and coarse subangular blocky; extremely hard, extremely firm, very sticky and very plastic; common distinct dark gray (10YR 4/1) intersecting slickensides that are tilted 30 to 35 degrees to the horizontal; 7 percent fine and medium prominent light greenish gray ( 5 GY 7/1) iron depletions with sharp boundaries on surfaces of slickensides; few fine rounded concretions of calcium carbonate coated with yellow (10YR 7/8) iron; strongly effervescent; gradual smooth boundary.

B'ss2--216 to 240 cm ; yellowish red (5YR 4/6) clay; moderate coarse wedge-shaped structure parting to moderate medum and coarse subangular blocky; extremely hard, extremely firm, very sticky and very plastic; very few very fine roots between peds; common prominent intersecting slickensides that are tilted 25 to 35 degrees to the horizontal; 10 percent fine prominent light greenish gray (10GY 7/1,8/1) ron depletions with sharp boundanes on the surfaces of slickensides; strongly effervescent; gradual smooth boundary.

B'ss3--240 to 272 cm ; yellowish red (5YR 5/6) clay; weak coarse angular blocky structure parting to weak medium angular blocky; extremely hard, extremely firm, very sticky and very plastic; very few very fine roots between peds; few faint intersecting slickensides that are tilted 15 to 25 percent to the horizontal; 4 percent fine prominent light olive gray ( $5 \mathrm{Y} 6 / 2$ ) iron depletions with sharp boundaries on root traces in interiors of peds and on surfaces of slickensides; few fine and medium black (10YR $2 / 1$ ) masses of iron manganese on root traces; strongly effervescent; gradual smooth boundary.

B'ss4--272 to 300 cm ; yellowish red (5YR 5/6) clay extremely hard, extremely firm, very sticky and very plastic; very few very fine roots between peds; few prominent intersecting slickensides that are tilted 15 to 25 percent to the horizontal; 6 percent fine and medium light gray ( $5 \mathrm{Y} 7 / 2$ ) iron depletions with sharp boundaries on root traces in interiors of peds and on surfaces of slickensides; strongly effervescent.

# Wharton County- 481 Microhigh 

Sample Date: 6/23/99
Soil Senıes: Lake Charles
Site Identufication \#: 99TX481001A (microhıgh)
Described by: Wes Miller and Larry Wilding
Recorded by: Mary Dunn
Location Information
Soil Survey Area Name: Wharton Co.
Classification: Fine, smectitic, hyperthermic Typic Hapludert
Ak1--0 to 15 cm ; very dark gray (10YR 3/1) clay; weak medium subangular blocky structure parting to moderate fine and medium granular; friable; many fine roots; common fine and few medium interstitial pores; few fine masses of grayish brown (2.5Y $5 / 2$ ) clay throughout; 3 percent subrounded nodules of calcium carbonates 2 to 4 mm in size; matrix is noncalcareous; clear smooth boundary.

Ak2--15 to 33 cm ; very dark gray ( $2.5 \mathrm{Y} 3 / 1$ ) clay; moderate fine and medium angular blocky structure; friable; common fine roots; few fine tubular and interstitial pores; common distinct pressure surfaces; few distinct intersectıng slickensides; 20 percent light yellowish brown ( $2.5 \mathrm{Y} 6 / 3$ ) masses and nodules of calcium carbonates along surfaces of slickensides; slightly effervescent; clear smooth boundary.

Bkss1--33 to 78 cm ; dark gray ( $2.5 \mathrm{Y} 4 / 1$ ) clay; strong fine and medium angular blocky structure; friable; common fine roots; few fine tubular pores; common distinct intersecting slickensides that are tilted 40 to 50 degrees to the horizontal; 30 percent fine and medium rounded nodules of calcium carbonate and 1 percent nodules of calcium carbonate coated with brownish yellow (10YR 6/8) iron; strongly effervescent; abrupt wavy boundary.

Bkss2--78 to 104 cm ; weak red (7.5R 4/4) clay; moderate fine and medium angular blocky structure; firm; common fine roots; few very fine tubular pores; many distinct intersecting slickensides that are tilted 30 to 45 degrees to the horizontal; 5 percent of matrix are cracks filled with very dark gray ( $2.5 \mathrm{Y} 3 / 1$ ) clay 1 cm to 3 cm wide; 5 percent subrounded nodules of calcium carbonate 2 to 4 mm in size; 10 percent masses of olive brown ( $2.5 \mathrm{Y} 4 / 3$ ) clay 1 to 3 cm in size mixed within the weak red ( $7.5 \mathrm{YR} 4 / 4$ ) matrix material; 5 percent of the horizon is a reddish yellow (7.5YR 6/6) strongly effervescent clay intrusion 4 to 8 cm wide that arcs from the upper part of the Bkss3 horizon and extends to the lower part of the Bkss1 horizon; strongly effervescent; abrupt wavy boundary.

Bkss3--104 to 157 cm ; dark grayish brown (2.5Y 4/2) clay; strong medium and coarse angular blocky structure; firm; common fine roots; very few very fine tubular pores; common distinct intersecting slickensides that are tilted 30 to 50 degrees to the
horizontal; 5 percent fine and medium subrounded nodules of calcium carbonate; 5 percent of the horizon is a strong brown (7.5YR 5/6) strongly effervescent clay intrusion 4 to 8 cm wide that arcs from the upper part of the Bkss 4 horizon and extends to the lower part of the Bkss2 horizon; strongly effervescent; abrupt wavy boundary.'

Bkss4--157 to 181 cm ; light olive brown (2.5Y 5/4) clay; strong medium and coarse angular blocky structure; firm; common fine roots; very few very fine pores; common distinct coarsely grooved intersecting slickensides tilted 30 to 60 degrees to the horizontal; 10 percent fien and medium nodules of calcium carbonate concentrated near contact with Bss1 horizon; 10 percent of the horizon is a strong brown (7.5YR 4/6) strongly effervescent clay intrusion 4 to 10 cm wide that arcs from the Bss1 horizon and extends to the lower part of the Bkss3 horizon; 4 percent fine rounded black (10YR 2/1) iron-manganese nodules and masses; strongly effervescent; clear wavy boundary.

Bss1--181 to 260 cm ; yellowish red (5YR 5/6) clay; strong medium to very coarse angular blocky structure; firm; common fine roots; common distınct intersecting slickensides that are tilted 20 to 60 degrees to the horizontal; 2 percent fine and medium prominent light brownish gray ( $2.5 \mathrm{Y} 6 / 2$ ) iron depletions on surfaces of slickensides; 10 percent fine rounded black (10YR 2/1) iron-manganese nodules and masses; 2 percent fine nodules of calcium carbonate; 10 percent of the horizon is reddish yellow (7.5YR 7/6) clay mixed with the yellowish red (5YR 5/6) matrix material; strongly effervescent; abrupt wavy boundary.

Bss2--260 to 300 cm ; yellowish red (5YR 5/6) clay; strong very coarse angular blocky structure; very firm; very few very fine roots; common prominent intersecting slickensides that are tilted 20 to 40 degrees to the horizontal; 8 percent fine and medium light brownish gray ( $2.5 \mathrm{Y} 6 / 2$ ) iron depletions on surfaces of slickensides; 1 percent fine masses of black (10YR 2/1) dendritic masses of iron-manganese on surfaces of slickensides; less than 1 percent fine nodules of calcium carbonate; strongly effervescent.

## Wharton County- 481 Microlow

Sample Date: 6/23/99
Soil Series: Lake Charles
Site Identification \#: 99TX481001microlow
Described by: Edward Griffin and Jon Wiedenfeld
Recorded by: J. David Wagner
Location Information
Soil Survey Area Name: Wharton CO.
Classification: Fine, smectutic, hyperthermıc Typic Hapluderts
A1--0 to 12 cm ; black ( $2.5 \mathrm{Y} 2 / 1$ ) clay; moderate fine and medium subangular blocky structure; hard, firm, very sticky and very plastic; common fine roots; common fine
tubular pores; less than 1 percent vey fine and fien rounded nodules of iron-manganese; less than 1 percent fine rounded nodules of calcium carbonate coated with brownish yellow (10YR 6/8) iron; clear smooth boundary.

A2--12 to 28 cm ; black ( $2.5 \mathrm{Y} 2 / 1$ ) clay; moderate fine and medium subangular blocky structure; hard, firm, very sticky and very plastic; common fine roots; common fine tubular pores; very few distinct pressure surfaces; clear smooth boundary.

Bss1--28 to 59 cm ; black ( $2.5 \mathrm{Y} 2 / 1$ ) clay; moderate medium and coarse subangular blocky structure; very hard, firm; common fine roots; many fine tubular pores; common distinct intersecting slickensides that are tilted 60 to 70 degrees to the horizontal; few fine rounded nodules of calcium carbonate coated with brownish yellow (10YR 6/8) iron; clear smooth boundary.

Bss2--59 to 83 cm ; black ( $2.5 \mathrm{Y} 2 / 1$ ) clay; moderate medium and coarse subangular blocky structure; very hard, very firm; common fine roots; common fine and medium tubular pores; common distinct intersecting slickensides that are tilted 60 to 70 degrees to the horizontal; less than 1 percent fine rounded nodules of calcium carbonate coated with brownish yellow (10YR 6/8) iron; less than 1 percent very fine and fine rounded nodules of iron-manganese; gradual wavy boundary.

Bss3--83 to 123 cm ; very dark gray ( $2.5 \mathrm{Y} 3 / 1$ ) clay; moderate medium wedge-shaped structure parting to moderate fine and medium angular blocky; very hard, very firm; common fine roots along surfaces of slickensides; common fine and medium tubular pores; many promunent intersecting slickensides that are tilted 50 to 60 degrees to the horizontal; gradual wavy boundary.

Bss4--123 to 147 cm ; dark gray ( $2.5 \mathrm{Y} 4 / 1$ ) clay; moderate medium wedge-shaped structure parting to moderate fine and medium angular blocky; very hard, very firm; common fine roots along surfaces of slickensides; many prominent intersecting slickensides that are tilted 40 to 50 degrees to the horizontal; few crawfish krotovinas 3 to 4 cm in dıameter filled with a muxture of grayish brown (2.5Y 5/2), dark gray ( $2.5 \mathrm{Y} 4 / 1$ ), and yellowish red (5YR 5/6) clay; less than 1 percent fine faint light olive brown (2.5Y $5 / 3$ ) iron concentrations with diffuse boundaries along surfaces of slickensides; very slightly effervescent; clear smooth boundary.

Bkss1--147 to 165 cm ; dark gray ( $2.5 \mathrm{Y} 4 / 1$ ) clay; moderate medium and coarse wedgeshaped structure parting to moderate fine and medium angular blocky; very hard, very firm; common fine roots on surfaces of slickensides; many prominent intersecting slickensides that are tilted 30 to 40 degrees to the horizontal; few crawfish krotovinas 3 to 4 cm wide and filled with a mixture of grayish brown (2.5Y 5/2), dark gray ( $2.5 \mathrm{Y} 4 / 1$ ), and yellowish red (5YR 5/6) clay; few fine rounded uncoated nodules of calcium carbonate; very slightly effervescent; clear smooth boundary.

Bkss2--165 to 176 cm ; grayısh brown ( $2.5 \mathrm{Y} 5 / 2$ ) clay; weak medium and coarse wedgeshaped structure parting to moderate medium and coarse angular blocky; very hard, very
firm, very sticky and very plastic; common very fine and fine roots along surfaces of slickensides; common distinct intersecting slickensides that are tilted 30 to 40 degrees to the horizontal; few crawfish krotovinas 3 to 4 cm in diameter and filled with a mixture of grayish brown ( $2.5 \mathrm{Y} 5 / 2$ ), dark gray ( $2.5 \mathrm{Y} 4 / 1$ ), and yellowish red (5YR 5/6) clay; 5 percent fine and meduum rounded nodules of calcium carbonate and 1 percent of the nodules are coated with brownish yellow (10YR 6/8) iron; strongly effervescent; abrupt smooth boundary.

Bkss3--176 to 200 cm ; reddish brown (5YR 5/4); weak medium and coarse subangular blocky structure; extremely hard, extremely firm, slightly sticky and slightly plastic; very few very fine and fine roots; few crawfish krotovinas 3 to 4 cm in diameter and filled with a mixture of grayish brown (2.5Y 5/2), dark gray ( $2.5 \mathrm{Y} 4 / 1$ ), yellowish red ( 5 YR $5 / 6$ ) clay, and few fine rounded masses and nodules of calcium carbonate; common distinct intersecting slickensides that are tilted 15 to 25 degrees to the horizontal; 7 percent fine and medıum grayish green ( $5 \mathrm{G} 5 / 2$ ) iron depletions with sharp boundaries on surfaces of slickensides; 1 percent fine and medium rounded nodules of calcium carbonate in matrix; strongly effervescent; gradual wavy boundary.

Bkss4--200 to 250 cm ; yellowish red (5YR 5/6) clay; moderate medium and coarse wedge-shaped structure parting to moderate medium and coarse subangular blocky; extremely hard, extremely firm, slightly sticky and slightly plastic; very few very fine roots; common prominent intersecting slickensides that are tilted 10 to 20 degrees to the horizontal; 5 percent fine and medium grayish green ( $5 \mathrm{G} 5 / 2$ ) and 2 percent fine gray ( $2.5 \mathrm{Y} 5 / 1$ ) iron depletions with sharp boundanes on surfaces of slickensides; 1 percent fine and medium rounded nodules of calcium carbonate; strongly effervescent.

## Harris County- 201 Microhigh

Sample Date: 6/24/99
Soil Series: Lake Charles (microhigh)
Site Identification \#: 99TX201001A
Location Information
Soil Survey Area Name: Armand Bayou, Harrıs County, Texas
Described by: Wes Miller and Larry Wilding
Recorded by: Ricky Lambert
Classıfication: Fine, smectitic, hyperthermic Aquic Hapludert (This would be a Calciudert if provided in Taxonomy)

Ak--0 to 10 cm ; dark gray ( $2.5 \mathrm{Y} 4 / 1$ ) clay; weak coarse angular blocky structure parting to moderate medium granular; firm, very sticky and very plastic; many fine roots;
common fine interstitial pores; very few faint intersecting slickensides; 2 percent fine prominent strong brown (7.5YR 4/6) iron concentrations along root pore linings; few fine uncoated nodules of calcium carbonate; matrix is noncalcareous; clear smooth boundary.


#### Abstract

Bkssg1--10 to 27 cm ; grayish brown ( $2.5 \mathrm{Y} 5 / 2$ ) clay; moderate medum angular blocky structure; firm, very sticky and very plastic; common fine roots; few fine interstitial pores; common faint intersecting slickensides; few rounded 2 to 4 mm black (10YR 2/1) nodules of iron-manganese; 2 percent fine prominent yellowish red (5YR 5/8) iron concentrations with clear boundaries on surfaces of peds and on root pore linings; few 2 to 10 mm weakly indurated nodules of calcium carbonate coated with olive yellow ( 2.5 Y $6 / 6$ ) iron; few masses of calcareous red ( $2.5 \mathrm{YR} 5 / 8$ ) clay 5 mm to 1 cm in size mixed with calcium carbonate nodules; matrix is noncalcareous; clear wavy boundary.


Bkssg2--27 to 49 cm ; grayish brown (2.5Y 5/2) clay; moderate fine and medum angular blocky structure; firm, very sticky and very plastic; common fine roots; few fine tubular pores; common distinct weakly grooved interesecting slickensides that are tilted 20 to 40 degrees from the horizontal; 1 percent fine prominent strong brown (7.5YR 5/6) iron concentrations with clear boundaries on root pore linings; few rounded 2 to 4 mm black (10YR 2/1) nodules of iron-manganese; common weakly indurated nodules of calcium carbonate coated with olive yellow ( $2.5 \mathrm{Y} 6 / 6$ ) iron; few masses of calcareous red (2.5YR $5 / 8$ ) clay 5 mm to 1 cm in size mixed with calcium carbonate nodules; matrix is noncalcareous; clear wavy boundary.

Bkssg3-49 to 67 cm ; grayish brown (2.5Y 5/2) clay; moderate fine and medium angular blocky structure; firm, very sticky and very plastic; common fine roots; few fine tubular pores; many weakly grooved distmet intersecting slickensides that are tilted at 30 to 40 degrees from the honzontal; 5 percent fine distinct dark grayish brown (2.5Y 4/2) iron depletions on surfaces of slickensides; few rounded 2 to 10 mm black (10YR 2/1) nodules of iron-manganese; common weakly indurated nodules of calcium carbonate coated with olive yellow ( $2.5 \mathrm{Y} 6 / 6$ ) iron; common masses of calcareous red ( $2.5 \mathrm{YR} 5 / 8$ ) clay 5 mm to 2 cm in size mixed with calcıum carbonate nodules; slightly effervescent; abrupt wavy boundary.

Bkssg4--67 to 105 cm ; grayish brown (2.5Y 5/2) clay; moderate medium and coarse angular blocky structure; firm, very sticky and very plastic; common fine roots; few fine tubular pores; many weakly grooved distinct intersecting slickensides that are tilted at 15 to 30 degrees from the horizontal; 15 percent medium faint olive brown (2.5Y4/4)iron concentrations with diffuse boundaries on surfaces of slickensides; 10 percent medium faint dark gray ( $2.5 \mathrm{Y} 4 / 1$ ) iron depletıons with diffuse boundaries on surfaces of slickensides; common uncoated rounded nodules of calcium carbonate 2 to 5 mm in size; few rounded nodules of black (10YR 2/1) of iron-manganese 4 to 8 mm in size; strongly effervescent; clear wavy boundary.

Bkssg5--105 to 148 cm ; gray ( $2.5 \mathrm{Y} 5 / 1$ ) clay; moderate medium and coarse angular blocky structure; firm, very sticky and very plastic; common fine roots between peds; few
very fine tubular pores; many prominent coarsely grooved intersecting slickensides; 35 percent fine and medıum distinct light yellowish brown (2.5Y 6/4) iron concentrations with diffuse boundaries on surfaces of slickensides; 10 percent fine prominent dark gray ( $2.5 \mathrm{Y} 4 / 1$ ) iron depletions with clear boundaries on surfaces of slickensides; common rounded black ( $10 \mathrm{YR} 2 / 1$ ) nodules of iron-manganese 2 to 8 mm in size; common rounded uncoated nodules of calcium carbonate 2 to 15 mm in size; slightly effervescent; clear wavy boundary.

Bkssg6--148 to 177 cm ; gray (5Y 6/1) clay; moderate medium and coarse angular blocky structure; firm, very sticky and very plastic; common fine roots; few fine tubular pores; common distinct finely grooved intersecting slickensides that are tilted at 30 to 35 degrees to the horizontal; 40 percent coarse prominent light yellowish brown ( $2.5 \mathrm{Y} 6 / 3$ ) iron concentrations with diffuse boundaries on surfaces of slickensides; common rounded black (10YR 2/1) iron-manganese concretions; few rounded uncoated strongly indurated nodules of calcium carbonate 2 to 3 mm in size; slightly effervescent; clear wavy boundary.

B kss1--177 to 202 cm ; yellowish red (5YR 5/6) clay; weak coarse angular blocky structure; firm, very sticky and very plastic; common fine roots between peds; common distinct finely grooved intersecting slickensides that are tilted 35 to 50 degrees to the horizontal; 5 percent fine distinct pale brown (10YR 6/3) iron concentrations with diffuse boundaries; 2 percent fine prominent gray ( $5 \mathrm{Y} 5 / 1$ ) iron depletions with clear boundaries throughout; few fine dendritic black (10YR 2/1) iron-manganese concentrations in gray (5Y 5/1) iron depletions; common rounded nodules of black (10YR 2/1) iron-manganese 1 to 2 mm in size; few rounded uncoated strongly indurated nodules of calcium carbonate 2 to 3 mm in size; strongly effervescent; clear wavy boundary.

B'ss1--202 to 235 cm ; yellowish red (5YR 4/6) clay; weak coarse angular blocky structure; firm, very sticky and very plastic; common very fine and fine roots; few distinct finely grooved intersecting slickensides that are tulted at 20 to 40 degrees to the horizontal; 5 percent medium prominent light yellowish brown ( $2.5 \mathrm{Y} 6 / 3$ ) iron concentrations with clear boundaries on surfaces of peds; common rounded nodules of black (10YR 2/1) iron-manganese 1 to 2 mm in size; few medium masses of ron manganese on surfaces of slickensides; few masses of calcium carbonate 3 to 5 mm in size; strongly effervescent; clear wavy boundary.
B'ss2--235 to 270 cm ; red ( $2.5 \mathrm{YR} 4 / 6$ ) clay; strong coarse angular blocky structure parting to moderate medium angular blocky; very firm, very sticky and very plastic; common very fine and fine roots; common prominent coarsely grooved intersecting slickensides that are tilted 35 to 45 degrees to the horizontal; 5 percent fine and medium promınent light greenish gray (10Y 7/1) iron depletions with clear boundaries on surfaces of slickensides; 1 percent fine prominent light yellowish brown ( $2.5 \mathrm{Y} 6 / 3$ ) iron depletions on surfaces of slickensides; common rounded black nodules of (10YR $2 / 1$ ) ironmanganese 1 to 2 mm in size; common fine masses of black (10YR $2 / 1$ ) iron-manganese on surfaces of slickensides; strongly effervescent.

# Harris County- 201 Microlow 

Sample Date: 6/24/99
Soil Series: Lake Charles
Site Identification \#: 99TX201001 (microlow)
Described by: Lee Nordt and Jon Wiedenfeld
Recorded by: J. David Wagner
Location Information
Soil Survey Area Name: Armand Bayou, Harris County, Texas

## Classification: Fine, smectitic, hyperthermic Aquic Hapludert

A--0 to 16 cm ; very dark gray ( $10 \mathrm{YR} 3 / 1$ ) clay; weak fine and medium subangular blocky structure; firm, very sticky and very plastic; many very fine and fine roots; common very fine and fine interstitial pores; few fine pores filled with coarse material; few actıve unfilled krotovinas 1 to 5 cm wide; 3 percent fine distinct brown (7.5YR 4/4) iron concentrations with sharp boundaries along root pores linings; few fine ironmanganese nodules; clear smooth boundary.

Bw-16 to 44 cm ; black ( $2.5 \mathrm{Y} 2 / 1$ ) clay; weak medium prismatic structure parting to moderate medium and coarse angular blocky; firm, very sticky and very plastic; common very fine and fine roots; common fine tubular pores; very few faint intersecting slickensides; very few distinct pressure faces; 1 percent fine prominent strong brown (7.5YR 5/6) iron concentrations with clear boundaries along root pore linings; 1 percent fine faint gray ( $2.5 \mathrm{Y} 5 / 1$ ) iron depletions with clear boundaries on surfaces of peds; few fine and medium iron-manganese nodules; gradual smooth boundary.

Bss1--44 to 65 cm ; dark gray ( $2.5 \mathrm{Y} 4 / 1$ ) clay; moderate medium prismatic structure partıng to moderate medium angular blocky; firm, very sticky and very plastic; common very fine and fine roots; common fine tubular pores; common distinct intersecting slickensides that tilt 30 to 45 degrees from the horizontal; 3 percent fine prominent yellowish red (5YR 5/6) iron concentrations with sharp boundaries along root pore linings; few medium iron-manganese nodules; gradual wavy boundary.

Bss2--65 to 88 cm ; dark gray ( $2.5 \mathrm{Y} 4 / 1$ ) clay; weak coarse prismatic structure partıng to moderate medium angular blocky; firm, very sticky and very plastic; common very fine and fine roots; common very fine and fine tubular pores; common distinct intersecting slickensides that tilt 35 to 55 degree from the horizontal; 10 percent fine faint light yellowish brown ( $2.5 \mathrm{Y} 6 / 3$ ) iron concentrations with diffuse boundaries on surfaces of slickensides and peds; 3 percent fine faint gray ( $2.5 \mathrm{Y} 5 / 1$ ) ron depletions with clear boundaries on surfaces of slickensides and peds; few medium iron-manganese nodules; gradual wavy boundary.

Bss3--88 to 117 cm ; gray ( $2.5 \mathrm{Y} 5 / 1$ ) clay; moderate medium angular blocky structure; very firm, very sticky and very plastic; common fine roots; very fine and fine tubular
pores; few crawfish krotovina 1 to 5 cm wide filled with grayish brown ( $2.5 \mathrm{Y} 5 / 2$ ) and very dark gray ( $2.5 \mathrm{Y} 3 / 1$ ) material; few active unfilled krotovinas; common distinct intersecting slickensides that tilt 40 to 55 degrees from the horizontal; 15 percent fine faint light yellowish brown ( $2.5 \mathrm{Y} 6 / 3$ ) and 3 percent fine and medium distinct light yellowish brown ( $2.5 \mathrm{Y} 6 / 4$ ) iron concentrations with diffuse boundaries on surfaces and interiors of peds; few fine and medium iron-manganese nodules; clear wavy boundary.

Bss4--117 to 151 cm ; light brownish gray ( 2.5 Y 6/2) clay; moderate medium angular blocky structure; very firm, very sticky and very plastic; common fine roots; very fine and fine tubular pores; few crawfish krotovinas 1 to 5 cm wide filled with grayish brown ( $2.5 \mathrm{Y} 5 / 2$ ) and very dark gray ( $2.5 \mathrm{Y} 3 / 1$ ) material; common distinct intersecting slickensides that tilt 30 to 40 degrees from the horizontal; 15 percent fine and medium faint light yellowish brown (2.5Y 6/4) iron concentrations with diffuse boundaries on surfaces of slickensides and on interiors of peds; 1 percent fine distinct greenish gray (5BG 6/1) iron depletions with diffuse boundaries on surfaces of slickensides and on interiors of peds; few fine and medium iron-manganese nodules; clear wavy boundary.

Bkss1--151 to 177 cm ; light yellowish brown (2.5Y 6/3) clay; weak medium and coarse subangular blocky structure; very firm, very sticky and very plastic; common fine roots; very fine and fine tubular pores; few crawfish krotovinas 1 to 5 cm wide filled with yellowish red (5YR 5/6) and very dark gray (2.5YR 3/1) material; common distınct intersecting slickensides that tilt 30 degrees from the horizontal; 5 cm wide arcing yellowish red (5YR 5/6) clay intrusion from Bkss2 horizon; 3 percent fine faint gray (2.5Y 5/1) iron depletions with clear boundaries on surfaces of slickensides; less than 1 percent fine prominent strong brown (7.5YR 5/6)iron concentrations with diffuse boundaries along surfaces of slickensides and as a halo around manganese nodules; 1 percent fine faint greenish gray (5BG 6/1) ron depletions with sharp boundaries along root pore linings; common fine rounded strong brown (7.5YR 5/6) iron-manganese concretions; few fine nodules of calcium carbonate; slightly effervescent; gradual smooth boundary.

Bkss2--177 to 212 cm ; reddish brown (5YR 5/4) clay; weak coarse subangular blocky structure; very firm, very sticky and very plastic; very few very fine and fine roots; very fine and fine tubular pores; few crawfish krotovinas filled with dark gray (10YR 4/1) and reddish brown (5YR 5/4) matenal; common faint intersecting slickensides that tilt 20 degrees from the horizontal; 7 percent fine prominent gray ( $2.5 \mathrm{Y} 6 / 1$ ) iron depletions with clear boundaries on surfaces of slickensides; 1 percent fine prominent greenish gray (5BG 6/1) iron depletions along root pore linings; 1 percent fine prominent light yellowish brown (10YR 6/4) iron concentrations with diffuse boundaries between peds; common fine nodules of calcium carbonate; strongly effervescent; gradual wavy boundary.

B'ss1--212 to 242 cm ; red ( $2.5 \mathrm{YR} 5 / 6$ ) clay; weak medium and coarse prismatic structure; very firm, very sticky and very plastic; very few very fine and fine roots; very few very fine and fine tubular pores; few crawfish krotovinas 0.5 to 1.5 cm wide filled with dark gray ( $2.5 \mathrm{Y} 4 / 1$ ) and red (2.5YR 4/8) material; common faint intersecting
slickensides that tilt 20 degrees from the horizontal; 5 percent fine and medium prominent yellow (2.5Y 7/6) iron concentrations with diffuse boundaries on surfaces of peds; 3 percent fine prominent greenish gray ( 5 BG 6/1)iron depletıons with clear boundaries on root pore linings; few fine and medium nodules of calcium carbonate; strongly effervescent; clear smooth boundary.

B'ss2--242 to 261 cm ; red (2.5YR 5/6) clay; moderate fine and medrum platy structure parting to moderate fine angular blocky; very firm, very sticky and very plastic; very fine and fine roots; very fine and fine tubular pores; few crawfish krotovinas 1 to 2 cm wide filled with gray ( $2.5 \mathrm{Y} 6 / 1$ ), red ( $2.5 \mathrm{YR} 5 / 6$ ) clay and few fine very pale brown ( 10 YR 8/2) nodules of calcium carbonate; common faint intersecting slickensides that tilt 15 to 20 degrees from the horizontal; common fine and medium prominent light greenish gray ( $10 \mathrm{Y} 7 / 1$ ) iron depletions with clear boundaries on root pore linings; common fine nodules of iron-manganese at top of horizon; strongly effervescent.

B'ss3--261 to 279 cm ; red (2.5YR 4/6) clay; moderate fine and medium platy structure parting to moderate fine angular blocky; very firm, very sticky and very plastic; very few very fine and fine roots; very few very fine and fine tubular pores; 10 percent of horizon are red (2.5YR 4/8) fractured conchoidal blocks; common faint intersecting slickensides that tilt 15 to 20 degrees from the horizontal; 10 percent fine and medium prominent light greenish gray ( $10 \mathrm{Y} 7 / 1$ ) iron depletıons with clear boundaries along root pore linings; strongly effervescent.

B'ss4--279 to 300 cm ; red ( $2.5 \mathrm{YR} 5 / 6$ ) clay; moderate fine and medium platy structure parting to moderate fine angular blocky; very firm, very sticky and very plastic; very fine and fine roots; very fine and fine tubular pores; 15 percent of horizon are red (2.5YR 4/8) fractured conchoidal blocks; 10 percent lenses 1 to 2 cm thick of light yellowish brown (10YR 6/4) silt loam; few faint intersecting slickensides; common fine and medium prominent light greenish gray (10Y 7/1) iron depletions with clear boundaries along root pore linings; strongly effervescent.
Appendix 2. Carbon and Oxygen Isotope Compositions of Soil Organic Matter and Pedogenic Carbonate in Lake Charles Series Vertisols
Key LAC= Lake Charles Serres and site no, MH=Mcrohigh pedon and ML=Microlow pedon

## SOM=Sorl Organic Matter

$\mathrm{PC}=$ Pedogentc Carbonate (Types- $\mathrm{HN}=$ Hard Nodule $\mathrm{SC}=$ Soft Carbonate )
Types of Hard Nodules Type $\mathrm{A}=\mathrm{Fe}+2$ stanned and Type $\mathrm{B}=$ gray matrix
COMP $=$ Composite of both types of hard nodules ( A and B )
STD = Laboratory Standard,
Spec-no =Mass spectrometer run number

| Pedon and Site | Sample Type | Depth (cm) and Type of Carbonate |
| :---: | :---: | :---: |
| LAC-MH-157 | PC | $70-\mathrm{HN}-\mathrm{A}$ |
| LAC-MH-157 | PC | $50-\mathrm{HN}-\mathrm{B}$ |
| LAC-MH-157 | PC | $40-\mathrm{HN}-\mathrm{B}$ |
| LAC-MH-157 | PC | $60-\mathrm{HN}-\mathrm{B}$ |
| LAC-MH-157 | PC | $60-\mathrm{HN}-\mathrm{A}$ |
| LAC-MH-157 | PC | $180-\mathrm{SC}$ |
| LAC-MH-157 | PC | $20-\mathrm{HN}-\mathrm{A}$ |
| LAC-MH-157 | PC | $70-\mathrm{HN}-\mathrm{B}$ |
| LAC-MH-157 | PC | $80-\mathrm{HN}-\mathrm{B}$ |
| LAC-MH-157 | PC | $30-\mathrm{HN}-\mathrm{A}$ |
| LAC-MH-157 | PC | $20-\mathrm{HN}-\mathrm{B}$ |
| LAC-MH-157 | PC | $120-\mathrm{HN}-\mathrm{A}$ |
| LAC-MH-157 | PC | $110-\mathrm{HN}-\mathrm{A}$ |
| LAC-MH-157 | PC | $120-\mathrm{HN}-\mathrm{B}$ |
| LAC-MH-157 | PC | $100-\mathrm{COMP}$ |



| LAC-MH-157 | SOM | 110 | 6323 | -2068 | N/A |
| :---: | :---: | :---: | :---: | :---: | :---: |
| LAC-MH-157 | SOM | 150 | 6324 | -2426 | - N/A |
| LAC-MH-157 | SOM | 210 | 6325 | -2183 | N/A |
| LAC-MH-157 | SOM | 160 | 6326 | -1545 | N/A |
| LAC-MH-157 | SOM | 120 | 6327 | -1582 | N/A |
| LAC-MH-157 | SOM | 10 | 6328 | -1993 | N/A |
| USGS GRAPHHTE-STD | SOM | USGS GRAPHITE | 6329 | -1645 | N/A |
| LAC-MH-157 | SOM | 70 | 6330 | -17.65 | N/A |
| LAC-MH-157 | SOM | 40 | 6331 | -1988 | N/A |
| LAC-MH-157 | SOM | 190 | 6332 | -2568 | N/A |
| LAC-MH-157 | SOM | 130 | 6333 | -1498 | N/A |
| LAC-MH-157 | SOM | 50 | 6334 | -1483 | N/A |
| LAC-MH-157 | SOM | 140 | 6335 | -1512 | N/A |
| LAC-MH-157 | SOM | 200 | 6336 | -2025 | N/A |
| LAC-MH-157 | SOM | 170 | 6337 | -1650 | N/A |
| LAC-MH-157 | SOM | 180 | 6338 | -1803 | N/A |
| CHCC (D)-STD | PC | CHCC (D) | 6339 | -1065 | -920 |
| LAC-MH-481 | PC | HN150A | 6340 | -451 | -339 |
| LAC-MH-481 | PC | HN50A | 6341 | -443 | -371 |
| LAC-MH-481 | PC | SC210 | 6342 | -410 | -312 |
| LAC-MH-481 | PC | SC200 | 6343 | -393 | -263 |
| LAC-MH-481 | PC | HN190A | 6345 | -284 | -213 |
| LAC-MH-481 | PC | HN180A | 6346 | -899 | -284 |
| LAC-MH-481 | PC | HN120A | 6347 | -407 | -276 |
| LAC-MH-481 | PC | HN80B | 6348 | -290 | -341 |
| LAC-MH-481 | PC | HNN200A | 6349 | -497 | -289 |
| LAC-MH-481 | PC | HN210A | 6350 | -988 | -326 |
| LAC-MH-481 | PC | HN20AB | 6351 | -423 | -306 |


| CHCC (D) STD | PC | CHCC (D) STD | 6352 | -1068 | -936 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| LAC-MH-481 | PC | HN140A | 6353 | -456 | --285 |
| LAC-MH-481 | PC | HN90A | 6354 | -394 | -336 |
| LAC-MH-481 | PC | HN110A | 6355 | -458 | -264 |
| LAC-MH-481 | PC | HN70B | 6356 | -298 | -356 |
| LAC-MH-481 | PC | HN130A | 6357 | -310 | -329 |
| LAC-MH-481 | PC | HN220A | 6358 | -1037 | -347 |
| LAC-MH-481 | PC | HN100B | 6359 | -380 | -248 |
| LAC-MH-481 | PC | HN10A | 6360 | -708 | -327 |
| LAC-MH-481 | PC | HN80A | 6361 | -255 | -349 |
| LAC-MH-481 | PC | HN170A | 6362 | -409 | -265 |
| LAC-MH-481 | PC | HN160A | 6363 | -554 | -300 |
| USGS GRAPHITE24 | SOM | USGS GRAPHITE24 | 6364 | -1646 | N/A |
| LAC-MH-481 | SOM | 60 | 6365 | -1443 | N/A |
| LAC-MH-481 | SOM | 20 | 6366 | -1775 | N/A |
| LAC-MH-481 | SOM | 30 | 6367 | -1489 | N/A |
| LAC-MH-481 | SOM | 10 | 6368 | -2205 | N/A |
| LAC-MH-481 | SOM | 220 | 6369 | -2436 | N/A |
| LAC-MH-481 | SOM | 19 | 6370 | -3277 | N/A |
| LAC-MH-481 | SOM | 100 | 6371 | -3432 | N/A |
| LAC-MH-481 | SOM | 70 | 6372 | -21.58 | N/A |
| LAC-MH-481 | SOM | 80 | 6373 | -1616 | N/A |
| LAC-MH-481 | SOM | 40 | 6374 | -1575 | N/A |
| LAC-MH-481 | SOM | 120 | 6375 | -1417 | N/A |
| LAC-MH-481 | SOM | 180 | 6376 | -1893 | N/A |
| LAC-MH-481 | SOM | 150 | 6377 | -2047 | N/A |
| LAC-MH-481 | SOM | 140 | 6378 | -1817 | N/A |
| LAC-MH-481 | SOM |  | 6379 | -2050 | N/A |


| LAC-MH-481 | SOM | 90 | 6380 | -1651 | N/A |
| :---: | :---: | :---: | :---: | :---: | :---: |
| LAC-MH-481 | SOM | 170 | 6381 | -20 55 | - N/A |
| LAC-MH-481 | SOM | 160 | 6382 | -2243 | N/A |
| LAC-MH-481 | SOM | 110 | 6383 | -2194 | N/A |
| LAC-MH-481 | SOM | 130 | 6384 | -2035 | N/A |
| LAC-MH-481 | SOM | 200 | 6385 | -38 55 | N/A |
| LAC-MH-481 | SOM | 50 | 6386 | -1456 | N/A |
| CHCC(D) - STD | PC | STD CHCC(D) | 6387 | -1065 | -940 |
| LAC-ML-481 | PC | 120 HN -B | 6389 | -363 | -357 |
| LAC-ML-481 | PC | $220-\mathrm{HN}$-A | 6390 | -4 46 | -280 |
| LAC-ML-481 | PC | 150-HN-B | 6391 | -394 | -338 |
| LAC-ML-481 | PC | $120-\mathrm{HN}$-B | 6392 | -278 | -501 |
| LAC-ML-481 | PC | $190-\mathrm{HN}$-A | 6393 | -572 | -327 |
| LAC-ML-481 | PC | $160-\mathrm{HN}$-B | 6394 | -618 | -332 |
| LAC-ML-481 | PC | 210-HN-A | 6395 | -536 | -365 |
| LAC-ML-481 | PC | $180-\mathrm{HN}-\mathrm{A}$ | 6396 | -375 | -344 |
| LAC-ML-481 | PC | 110-HN-B | 6397 | -264 | -351 |
| LAC-ML-481 | PC | 170-HNB-A | 6398 | -521 | -338 |
| LAC-ML-481 | PC | 90 SC | 6399 | -082 | -376 |
| LAC-ML-481 | PC | 240-HN-A-B | 6400 | -700 | -321 |
| LAC-ML-481 | PC | $110-\mathrm{HN}$-B | 6401 | -277 | -336 |
| LAC-ML-481 | PC | $130-\mathrm{HN}$-B | 6402 | -315 | -369 |
| LAC-ML-481 | PC | 200-HN-A | 6403 | -563 | -447 |
| LAC-ML-481 | PC | 210-HNSC | 6404 | -396 | -342 |
| LAC-ML-481 | PC | $140-\mathrm{HN}-\mathrm{B}$ | 6405 | -296 | -331 |
| LAC-ML-481 | SOM | 100 | 6406 | -1301 | N/A |
| LAC-ML-481 | SOM | 160 | 6407 | -1515 | N/A |
| LAC-ML-481 | SOM | 90 | 6408 | -1304 | N/A |


| LAC-ML-481 | SOM | 30 | 6409 | -1429 | N/A |
| :---: | :---: | :---: | :---: | :---: | :---: |
| LAC-ML-481 | SOM | 20 | 6410 | -1508 | N/A |
| LAC-ML-481 | SOM | 130 | 6411 | -1457 | N/A |
| LAC-ML-481 | SOM | 10 | 6412 | -1639 | N/A |
| USGS GRAPHITE-STD | SOM | USGS GRAPHITE24 | 6413 | -1595 | N/A |
| LAC-ML-481 | SOM | 200 | 6414 | -2656 | N/A |
| LAC-ML-481 | SOM | 60 | 6415 | -1326 | N/A |
| LAC-ML-481 | SOM | 50 | 6416 | -1344 | N/A |
| LAC-ML-481 | SOM | 70 | 6417 | -1334 | N/A |
| LAC-ML-481 | SOM | 80 | 6418 | -1340 | N/A |
| LAC-ML-481 | SOM | 110 | 6419 | -1389 | N/A |
| LAC-MH-481 | PC | 140-MICROSAMPLE-A | 6420 | -420 | -383 |
| LAC-MH-481 | PC' | 140-MICROSAMPLE-B | 6421 | -287 | -411 |
| LAC-MH-481 | PC | 140-MICROSAMPLE-D | 6422 | -222 | -499 |
| LAC-MH-481 | PC | 140-MICROSAMPLE-E | 6423 | -155 | -390 |
| LAC-MH-481 | PC | 140-MICROSAMPLE-H | 6424 | -387 | -384 |
| LAC-MH-481 | PC | 140-MICROSAMPLE-C | 6425 | -269 | -392 |
| LAC-MH-481 | PC | 140-MICROSAMPLE-F | 6426 | -240 | -369 |
| LAC-MH-481 | PC | 140-MICROSAMPLE-G | 6427 | -269 | -4.15 |
| CHCC(D) STD | PC | CHCC(D) STD | 6428 | -1065 | -924 |
| LAC-ML-481 | SOM | 120 | 6429 | -1883 | N/A |
| LAC-ML-481 | SOM | 140 | 6430 | -1772 | N/A |
| LAC-ML-481 | SOM | 40 | 6431 | -16.47 | N/A |
| LAC-ML-481 | SOM | 180 | 6432 | -25 55 | N/A |
| LAC-ML-481 | SOM | 150 | 6433 | -2546 | N/A |
| LAC-ML-481 | SOM | 170 | 6434 | -2648 | N/A |
| LAC-ML-481 | SOM | 210 | 6435 | -30 52 | N/A |
| LAC-ML-481 | PC | 160-HN-B | 6436 | -5 52 | -3.30 |


| LAC-ML-201 | PC | 150-HN-B | 6437 | -4 63 | -321 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| LAC-ML-201 | PC | $170-\mathrm{HN}-\mathrm{B}$ | 6438 | -659 | --303 |
| LAC-ML-201 | PC | $160-\mathrm{HN}$-A | 6439 | -5 54 | -345 |
| LAC-ML-201 | PC | SC177-212 | 6440 | -533 | -3 34 |
| CHCC (D) STD | PC | CHCC (D) STD | 6441 | -1067 | -915 |
| LAC-ML-201 | PC | 300-SC | 6442 | -4 05 | -274 |
| LAC-ML-201 | PC | $180-$ SC | 6443 | -5 43 | -327 |
| LAC-ML-201 | PC | 261-279-HN -A | 6444 | -601 | -311 |
| LAC-ML-201 | PC | 242-261-HN-A\&B | 6447 | -692 | -321 |
| LAC-ML-201 | PC | $180-\mathrm{HN}$-A | 6448 | -532 | -323 |
| LAC-ML-201 | PC | 177-212-HN-A | 6449 | -544 | -3.24 |
| LAC-ML-481 | SOM | 140 | 6450 | -2496 | N/A |
| LAC-ML-481 | SOM | 150 | 6451 | -2859 | N/A |
| LAC-ML-481 | SOM | 230 | 6452 | -3146 | N/A |
| LAC-ML-481 | SOM | 190 | 6453 | -2698 | N/A |
| LAC-ML-481 | SOM | 220 | 6454 | -3137 | N/A |
| LAC-ML-481 | SOM | 240 | 6455 | -3147 | N/A |
| LAC-ML-481 | SOM | 250 | 6456 | -3248 | N/A |
| LAC-MH-201 | PC | $10-\mathrm{HN}-\mathrm{B}$ | 6464 | -423 | -346 |
| LAC-MH-201 | PC | 20-HN--B | 6465 | -433 | -396 |
| LAC-MH-201 | PC | 40-HN-B | 6466 | -401 | -326 |
| LAC-MH-201 | PC | 30-HN-B | 6467 | -390 | -343 |
| LAC-MH-201 | PC | $50-\mathrm{HN}-\mathrm{B}$ | 6468 | -422 | -316 |
| LAC-MH-201 | PC | $60 \mathrm{HN}-\mathrm{B}$ | 6469 | -395 | -3.34 |
| CHCC (D) STD | PC | CHCC (D) STD | 6470 | -1064 | -945 |
| LAC-MH-201 | PC | 80-HN-B | 6471 | -406 | -321 |
| LAC-MH-201 | PC | 70-HN-B | 6472 | -515 | -353 |
| LAC-MH-201 | PC | 100-HN-B | 6473 | -496 | -345 |


| LAC-MH-201 | PC | 167 5-HN | 6477 | -575 | -326 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| LAC-MH-201 | PC | 175 5-HN | 6478 | -4 64 | - 333 |
| LAC-MH-201 | PC | 1895 -HN | 6479 | -382 | -292 |
| LAC-MH-201 | PC | 2185 -HN | 6480 | -427 | -249 |
| LAC-MH-201 | PC | $60-\mathrm{HN}-\mathrm{A}$ | 6481 | -495 | -293 |
| LAC-MH-201 | PC | $90-\mathrm{HN}$-B | 6482 | -370 | -314 |
| LAC-MH-201 | PC | 189-HN | 6483 | -4 63 | -297 |
| LAC-MH-201 | PC | 218-HN-B | 6484 | -391 | -232 |
| LAC-MH-481 | PC | 180MICROSAMPLE-D | 6545 | -2 40 | -310 |
| LAC-MH-481 | PC | 180MICROSAMPLE-C | 6546 | -225 | -3 33 |
| LAC-MH-481 | PC | 180MICROSAMPLE-B | 6547 | -142 | -325 |
| LAC-MH-481 | PC | 180MICROSAMPLE-A | 6548 | -222 | -305 |
| LAC-MH-481 | PC | 180 MICROSAMPLE-E | 6549 | -322 | -326 |
| LAC-MH-481 | PC | 180 MICROSAMPLE-F | 6550 | -301 | -359 |
| CHCC(D) STD | PC | CHCC(D) STD | 6551 | -1062 | -932 |
| LAC-MH-481 | SOM | 120 | 6664 | -2152 | N/A |
| LAC-MH-481 | SOM | 170 | 6665 | -2389 | N/A |
| LAC-MH-481 | SOM | 160 | 6666 | -2509 | N/A |
| LAC-MH-481 | SOM | 180 | 6667 | -23 39 | N/A |
| LAC-MH-481 | SOM | 130 | 6668 | -2310 | N/A |
| LAC-MH-481 | SOM | 190 | 6669 | -2624 | N/A |
| LAC-MH-481 | SOM | 200 | 6670 | -2876 | N/A |
| LAC-MH-481 | SOM | 150 | 6671 | -22 52 | N/A |
| LAC-MH-481 | SOM | 210 | 6672 | -2842 | N/A |
| LAC-MH-481 | SOM | 220 | 6673 | -2791 | N/A |
| LAC-MH-481 | SOM | 110 | 6674 | -22.75 | N/A |
| LAC-MH-481 | SOM | 100 | 6675 | -2188 | N/A |
| LAC-MH-201 | SOM | 50 | 6676 | -1823 | N/A |


| LAC-MH-201 | SOM | 70 | 6677 | -1908 | N/A |
| :---: | :---: | :---: | :---: | :---: | :---: |
| LAC-MH-201 | SOM | 30 | 6678 | -1906 | - N/A |
| LAC-MH-201 | SOM | 90 | 6679 | -1935 | N/A |
| LAC-MH-201 | SOM | 40 | 6680 | -1969 | N/A |
| LAC-MH-201 | SOM | 202-235 | 6681 | -25.62 | N/A |
| LAC-MH-201 | SOM | 60 | 6682 | -1829 | N/A |
| LAC-MH-201 | SOM | 20 | 6684 | -1820 | N/A |
| LAC-MH-201 | SOM | 10 | 6685 | -1849 | N/A |
| LAC-MH-201 | SOM | 100 | 6686 | -1919 | N/A |
| LAC-MH-201 | SOM | 80 | 6687 | -1995 | N/A |
| LAC-MH-201 | SOM | 105-148 | 6688 | -1793 | N/A |
| LAC-MH-481 | SOM | 70 | 6707 | -1782 | N/A |
| LAC-MH-481 | SOM | 80 | 6708 | -1692 | N/A |
| LAC-MH-481 | SOM | 60 | 6709 | -1813 | N/A |
| LAC-MH-481 | SOM | 10 | 6710 | -2022 | N/A |
| LAC-ML-201 | SOM | 170 | 6711 | -1849 | N/A |
| LAC-ML-201 | SOM | 20 | 6712 | -1620 | N/A |
| LAC-ML-201 | SOM | 30 | 6713 | -1479 | N/A |
| LAC-ML-201 | SOM | 80 | 6714 | -2251 | N/A |
| LAC-ML-201 | SOM | 90 | 6715 | -1590 | N/A |
| LAC-ML-201 | SOM | 40 | 6716 | -1443 | N/A |
| LAC-ML-201 | SOM | 70 | 6717 | -1463 | N/A |
| LAC-ML-201 | SOM | 130 | 6718 | -16.38 | N/A |
| LAC-ML-201 | SOM | 110 | 6719 | -2377 | N/A |
| LAC-ML-201 | SOM | 60 | 6720 | -2061 | N/A |
| LAC-ML-201 | SOM | 10 | 6721 | -1840 | N/A |
| LAC-ML-201 | SOM | 177-212 | 6729 | -2722 | N/A |
| LAC-MH-201 | SOM | 177-202 | 6730 | -2322 | N/A |


| LAC-ML-201 | SOM | 300 | 6731 | -2740 | N/A |
| :---: | :---: | :---: | :---: | :---: | :---: |
| LAC-MH-201 | SOM | 148-177 | 6732 | -2066 | - N/A |
| LAC-MH-157 | SOM | 20 | 6738 | -1668 | N/A |
| LAC-MH-157 | SOM | 130 | 6739 | -1495 | N/A |
| LAC-MH-157 | SOM | 120 | 6740 | -1923 | N/A |
| LAC-MH-157 | SOM | 200 | 6741 | -2368 | N/A |
| LAC-MH-157 | SOM | 210 | 6742 | -1872 | N/A |
| LAC-MH-157 | SOM | 80 | 6743 | -1488 | N/A |
| LAC-MH-157 | SOM | 50 | 6744 | -1736 | N/A |
| LAC-MH-157 | SOM | 180 | 6745 | -20 03 | N/A |
| LAC-MH-157 | SOM | 140 | 6746 | -1652 | N/A |
| LAC-MH-157 | SOM | 60 | 6747 | -1428 | N/A |
| LAC-MH-157 | SOM | 170 | 6748 | -2073 | N/A |
| LAC-MH-157 | SOM | 100 | 6749 | -15 62 | N/A |
| LAC-ML-201 | SOM | 50 | 6750 | -1661 | N/A |
| LAC-ML-201 | SOM | 100 | 6751 | -1889 | N/A |
| LAC-ML-201 | SOM | 212-242 | 6752 | -2737 | N/A |
| USGS GRAPHITE-STD | SOM | USGS GRAPHITE24 | 6753 | -1596 | N/A |
| USGS GRAPHITE-STD | SOM | USGS GRAPHITE24 | 6754 | -1600 | N/A |
| LAC-MH-157 | SOM | 150 | 6755 | -1427 | N/A |
| LAC-MH-157 | SOM | 30 | 6756 | -1730 | N/A |
| LAC-MH-157 | SOM | 160 | 6757 | -1477 | N/A |
| LAC-MH-157 | SOM | 70 | 6758 | -1477 | N/A |
| LAC-MH-157 | SOM | 10 | 6759 | -1968 | N/A |
| LAC-MH-157 | SOM | 260 | 6760 | -2277 | N/A |
| LAC-MH-157 | SOM | 220 | 6761 | -1701 | N/A |
| LAC-MH-157 | SOM | 190 | 6762 | -1675 | N/A |
| LAC-MH-157 | SOM | 210 | 6763 | -1444 | N/A |


| LAC-ML-157 | SOM | 100 | 6764 | -1421 | N/A |
| :---: | :---: | :---: | :---: | :---: | :---: |
| LAC-ML-157 | SOM | 280 | 6765 | -2182 | N/A |
| LAC-ML-157 | SOM | 70 | 6766 | -1554 | N/A |
| LAC-ML-157 | SOM | 160 | 6767 | -1505 | N/A |
| LAC-ML-157 | SOM | 50 | 6771 | -1446 | N/A |
| LAC-ML-157 | SOM | 120 | 6772 | -14.41 | N/A |
| LAC-ML-157 | SOM | 40 | 6773 | -1434 | N/A |
| LAC-ML-157 | SOM | 150 | 6774 | -1415 | N/A |
| LAC-ML-157 | SOM | 130 | 6775 | -1414 | N/A |
| LAC-ML-157 | SOM | 140 | 6777 | -1429 | N/A |
| LAC-ML-157 | SOM | 90 | 6778 | -1466 | N/A |
| LAC-ML-157 | SOM | 170 | 6785 | -1437 | N/A |
| LAC-ML-157 | SOM | 110 | 6786 | -1394 | N/A |
| LAC-ML-157 | SOM | 200 | 6787 | -1875 | N/A |
| LAC-ML-157 | SOM | 190 | 6788 | -1773 | N/A |
| LAC-ML-157 | SOM | 230 | 6789 | -2164 | N/A |
| LAC-ML-157 | SOM | 240 | 6790 | -2144 | N/A |
| LAC-ML-157 | SOM | 220 | 6791 | -2149 | N/A |
| CHCC (C) STD | SOM | CHCC (C) STD | 6844 | -1066 | N/A |
| LAC-MH-481 | PC | 100 BULK CO3 SAMPLE | 6845 | -418 | -3.35 |
| LAC-MH-481 | PC | 220 BULK CO3 SAMPLE | 6846 | -316 | -317 |
| LAC-MH-481 | PC | 160 BULK CO3 SAMPLE | 6847 | -428 | -305 |
| LAC-MH-481 | PC | 140 BULK CO3 SAMPLE | 6848 | -475 | -346 |
| LAC-MH-481 | PC | 180 BULK CO3 SAMPLE | 6849 | -401 | -313 |

Vita
Dana Lynette Miller was born on February 5, 1974 in Chattanooga, Tennessee. She is the youngest of three chuldren and the only daughter of Dan and Martha Miller. She graduated from Manchester Central High School in May of 1992. She attended college at Middle Tennessee State University (MTSU) in Murfreesboro, Tennessee on a full four-year academic scholarship. Despite the entucement of a full tuition waver, she left after two long years and transferred to Tennessee Technological University (TTU) in Cookeville, Tennessee. While miserably perusing a chemical engineerıng degree, she stumbled into a geology major who introduced her to the Geology Department and the Upper Cumberland Grotto. She spent the next three years finishing a B.S. degree in geology and treading through caves. While finushing her B.S. degree and before beginning graduate school, she worked for a year as a mine geologist at the Savage Zinc sphalente mines in Carthage, Tennessee. Although mining was quite a characterbulding experience, she decided to pursue a graduate degree and attended the University of Tennessee at Knoxville in August of 1998. In July of 2000, she competed her Master's degree in geology.


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